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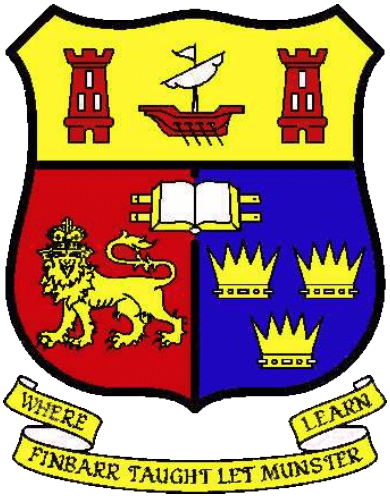
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THE NATIONAL UNIVERSITY OF IRELAND

Coláiste nahOllscoile, Corcaigh

UNIVERSITY COLLEGE CORK

SCHOOL OF FOOD AND NUTRITIONAL SCIENCES



STUDIES ON PHYSICAL, MECHANICAL, AND INDUSTRIALLY RELEVANT PROPERTIES OF SPRAY-DRIED DAIRY SYSTEMS

Thesis presented by

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For the degree of

Doctor of Philosophy

(PhD in Food Science and Technology)

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January 2017

DEDICATION

To my parents with love, respect,

and gratitude

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There are always issues, challenges and mysterious mishaps at each step when you are pursuing a PhD. But once you face them, head on and accept them, then the ride is more predictable and enjoyable. Many people have been part of this journey of my life and I would like to thank each one of them.

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Runjing Li

ABSTRACT

Engineering properties of food solids are highly dependent on their physical state, i.e. amorphous, crystalline, or liquid. Variations of food material properties and state may occur as a result of changes in external thermodynamic conditions and internally in materials because of changes in plasticiser or solvent contents. Understanding glass transition-related relaxations and their coupling with engineering properties of food materials is highly essential.

The present study investigated the physical and mechanical properties of two model dairy solids systems: (i) lactose/milk protein isolate (MPI) solids systems produced by a laboratory scale spray dryer and a pilot scale spray dryer, respectively; (ii) lactose/whey protein isolate (WPI) (4:1) mixtures pre-crystallised before spray drying. The water sorption behaviour, glass transition, and mechanical properties of these two systems were studied. For lactose/MPI solids systems, powders with smaller size particles sorbed larger amount of water with equilibration at water activities 0.11-0.44 a_w, which might be due to higher specific surface area (SSA), and they also showed higher steady water content after lactose crystallization. As a result, dairy solids with smaller size particles showed lower glass transition temperatures (T_g) after equilibration at 0.11-0.33 a_w. For lactose/WPI (4:1) mixtures with different crystallinity, the presence of less than 46.8% crystalline lactose in lactose/WPI mixtures had only a minor impact on water sorption behaviour at 0.11-0.44 a_w, whereas samples with higher crystallinity had higher stable water content after lactose crystallization. Moreover, samples with lower crystallinity had higher initial sorption rates. Increasing the amount of crystalline lactose had no significant influence on the glass transition temperatures and the initial crystallization

temperatures at 0.11-0.44 a_w. Furthermore, dairy powders with higher crystallinity had higher stiffness. Additionally, water plasticisation had a stronger effect on the structural relaxation of dairy powders with lower crystallinity.

The present study also investigated the flow properties of two dairy-based solids systems: (i) lactose/MPI solids systems; (ii) lactose/WPI solids systems pre-crystallized before spray drying. For lactose/MPI solids systems, mechanical property study showed that the higher the lactose content in dairy solids systems, the more significant change in their modulus at the glass transition region. Lactose/MPI mixtures with higher lactose contents showed better flowability at 0 and 44% relative humidity (RH), but they gave bigger friction angles after storage at 44% RH. For pre-crystallization systems, flow function tests indicated that dairy solid with 11.2% crystallinity was more easy-flowing than lactose/WPI mixtures with 1.0, 29.2 and 46.8% crystallintiy after storage at 0 and 44% RH storage conditions. Furthermore, dairy solids with higher amount of crystalline lactose showed better resistance to develop cohesiveness at high RH storage conditions. The friction angle of dairy solid with 1.0% crystallinity increased with increasing water content, while friction angles of lactose/WPI mixtures with higher crystallinity decreased with increasing water content.

At last, the effect of formulation on encapsulation properties and flavor release of amorphous matrix was studied. Firstly, lactose/WPI (4:1, 1:1, and 1:4) mixtures, or WPI were used as wall systems. Wall material consisting of lactose/WPI (4:1) mixture had significantly ($P < 0.05$) higher encapsulation efficiency. However, powders with wall materials consisting of higher amount of lactose showed significant decrease in their flavor retention with equilibration at 0.54 a_w and 0.65 a_w, which was as a result of lactose crystallization. Therefore, increasing lactose content

could increase the encapsulation efficiency of wall materials during spray drying. However, this also resulted in a higher rate of flavor release with storage at high water activity. Then, the encapsulation properties of dairy solids using lactose/WPI (4:1) or lactose/maltodextrin (MD)/WPI (3:1:1 or 1:3:1) mixtures as wall systems were determined. Wall material consisting of lactose/WPI (4:1) mixtures had the highest encapsulation efficiency for ethyl butyrate (EB) during spray drying, while wall materials consisting of lactose/MD/WPI (1:3:1) mixtures had higher encapsulation efficiency compared to wall materials consisting of lactose/MD/WPI (3:1:1) mixtures. The addition of MD could increase stiffness and thus, reduce molecular mobility of encapsulation systems. Wall systems consisting with lactose/MD (13-17)/WPI (1:3:1) mixtures and lactose/MD (23-27)/WPI mixtures had higher flavor retention than other wall systems after equilibration at high water activity (≥ 0.54 a_w).

The results of current study provide information on the physical, mechanical and industrially relevant properties of model dairy solids systems. The data can be used for improving processing, product development and modification of existing process and products, as well as to understand food properties beyond consumption release properties and bioavailability.

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DECLARATION

I hereby declare that the work submitted is entirely my own and has not been submitted to any other university or higher education institute, or for any other academic award in this university.

_____ Date _____

Runjing Li

ABBREVIATIONS

a_w Water Activity

d_{50} Medium Particle Size

$D_{arching}$ Minimum outlet diameter to prevent arching

DTEA Dielectric Thermal Analysis

DE Dextrose Equivalent

DMA Dynamic Mechanical Analyser

DSC Differential Scanning Calorimeter or Differential scanning calorimetry

EB Ethyl Butyrate

FT-IR Fourier Transform Infra-Red

GCA Gas Cooling Accessory

MPI Milk Protein Isolate

MD Maltodextrin

NMR Nuclear Magnetic Resonance

PALS Positron Annihilation Lifetime Spectroscopy

PFT Powder Flow Tester

RH Relative Humidity

SSA Specific Surface Area

TMA	Thermal Mechanical Analysis
T_m	Melting Temperature
T_g	Glass Transition Temperature
T_β	Beta Transition
T_α	α-Relaxation Temperature
T_γ	Gamma Transition
VTF	Vogel-Tammann-Fulcher
WLF	Williams-Landel-Ferry
WPI	Whey Protein Isolate
ρ_{tapped}	Tapped Bulk Density
ρ_p	Particle Density
ε	Porosity
δ_J	Effective Angle of Internal Friction

LIST OF PUBLICATIONS

Journal Publications

1. **Li, R.,** Roos, Y. H., & Miao, S. (2016a). The effect of water plasticization and lactose content on flow properties of dairy model solids. *Journal of Food Engineering, 170*, 50-57.
2. **Li, R.,** Roos, Y. H., & Miao, S. (2016b). Roles of particle size on physical and mechanical properties of dairy model solids. *Journal of Food Engineering, 173*, 69-75.
3. **Li, R.,** Roos, Y. H., & Miao, S. (2016c). Physical and mechanical properties of lactose/WPI mixtures: effect of pre-crystallization. *International Dairy Journal, 56*, 55-63.
4. **Li, R.,** Roos, Y. H., & Miao, S. (2016d). Influence of pre-crystallization and water plasticization on flow properties of lactose/WPI solids systems. *Powder Technology, 294*, 365-372.
5. **Li, R.,** Roos, Y. H., & Miao, S. (2016e). Flavor release from spray-dried amorphous matrix: Effect of lactose content and water plasticization. *Food Research International, 86*, 147-155.
6. **Li, R.**, Roos, Y. H., & Miao, S. (2017). Characterization of mechanical and encapsulation properties of lactose/maltodextrin/WPI matrix. *Food Hydrocolloids*, 63, 149-159.

Conference Presentations

1. **Li, R.,** Roos, Y. H., Fenelon, M., & Miao, S. The effects of solids composition on water sorption and fluidness properties of spray-dried dairy powders. *8th International Conference on Water In Food*, May 25-27, 2014, Timisoara, Romania (**Oral presentation**).
2. **Li, R.,** Roos, Y. H., Fenelon, M., & Miao, S. Influence of composition on physical and mechanical properties of dairy model solids based on lactose/MPI mixtures. *43rd Annual Food Research Conference*, December 10-11, 2014, Dublin, Ireland (**Oral presentation**).
3. **Li, R.,** Roos, Y. H., Fenelon, M., & Miao, S. Influence of pre-crystallization and composition on the physical characteristics and flow properties of model dairy solids. *12th International Congress on Engineering and Food*, June 14-18, 2015, Québec, Canada (**Poster presentation**).
4. **Li, R.,** Roos, Y. H., Fenelon, M., & Miao, S. Physical and mechanical properties of lactose/MPI solids systems: the effect of particle size. *44th Annual Food Research Conference*, December 14, 2015, Fermoy, Ireland (**Poster presentation**).
5. **Li, R.,** Roos, Y. H., & Miao, S. Roles of water plasticization and amorphous lactose content on flow properties of lactose/milk protein isolate systems. *IDF Parallel Symposia*, April 11-13, 2016, Dublin, Ireland (**Poster presentation**).
6. **Li, R.,** Roos, Y. H., & Miao, S. Roles of milk protein on the flow properties of model dairy powders. *20th International Drying Symposium*, August 7-10, 2016, Gifu, Japan (**Oral presentation**).
7. **Li, R.,** Roos, Y. H., & Miao, S. Flavor release from Flavor release from spray-dried amorphous matrix: Effect of lactose content and water plasticization. *18th*

World Congress of Food Science and Technology, August 21-25, 2016, Dublin, Ireland (**Poster presentation**).

INTRODUCTION

The main carbohydrate in dairy powders is lactose (Arellano et al., 2004), which can exist in various crystalline and non-crystalline forms in dairy systems. These forms affect lactose behaviour, particularly in processing and storage of low-water contents dairy foods. When milk or whey is spray-dried, any lactose which has not been pre-crystallised forms an amorphous solid. Amorphous solids are characterized by the lack of long-range order symmetry operators (translational, orientational, and conformational order) found in crystalline solids (Shah et al., 2014) and they have played an essential role in food and pharmaceutical industries for several decades (Bandyopadhyay et al., 1987; Aguilar & Ziegler, 1994; Buckton & Darcy, 1996; Chiou et al., 2008; Gänzle et al., 2008; Bashaiwoldu et al., 2011). In these applications, the glass transition temperature of amorphous materials has been used as the central physical parameter for the optimization of processing conditions and storage stability (Soottitantawat et al., 2004; Townrow et al., 2010). When the temperature increases from below to above the glass transition temperature (T_g), many of the physical properties of amorphous materials show a rapid change, including increases in the free volume, molecular mobility, and dielectric coefficient. Large changes in viscoelastic properties of amorphous powders also occur above the glass transition temperatures (Jones, 1999; Kasapis, 2001; Royall et al., 2005).

Glass transition is a kinetic and relaxation process associated with the primary relaxation of the material (Champion et al., 2000). Changes in physical properties of amorphous materials occurring around glass transition often result in an α-relaxation (Champion et al., 2000; Roudaut et al., 2004; Silalai & Roos, 2011a), which is related to molecular mobility. The physical properties and stability of dairy solids are

dependent on the molecular mobility of the amorphous region (Hancock et al., 1995). Zhou et al. (2001) indicated that the free volume of amorphous systems is mainly dependent on water content and temperature. Increasing temperature or water content of amorphous solids could increase molecular mobility and free volume, which result in instability of amorphous solids. Many studies have reported the effects of glass transition on physical properties, such as stickiness (Boonyai et al., 2004; Murti et al., 2009;; Silalai & Roos, 2010a, 2011a; O'Callaghan & Hogan, 2013), and caking (Aguilera et al., 1995; Foster et al., 2006; Fitzpatrick et al., 2007b) of amorphous food powders. Powders with larger amounts of amorphous components, such as amorphous lactose, were more sensitive to absorbing moisture, giving rise to lumping and caking problems (Le Meste et al., 2002; Liu et al., 2006; Fitzpatrick et al., 2007a, 2007b; Silalai & Roos, 2010a). In addition, Levi and Karel (1995) stated that flavor retention was found to depend on temperature, moisture content and the degree of matrix collapse. Zhou and Roos (2012) indicated that the amorphous structure protected the entrapped vitamin at low a_w, and glass transition and critical water activity of solids and crystallization of component sugars should be considered in the stabilization of sensitive components.

Previous studies have indicated that the composition and structure formation of lactose/protein systems affected the physical properties, glass transition, and structural relaxation of amorphous solids (Haque & Roos, 2004a; Silalai & Roos, 2011b; Potes et al., 2012), which may influence their functionality and stability (Rosenberg & Sheu, 1996; Fitzpatrick et al., 2007b; Hogan & O'Callaghan, 2010). However, there is no further study about the effects of formulation on physical and mechanical properties of dairy solids and the roles of these properties on the flow properties and encapsulation properties of dairy powders.

In the present study, the physical and mechanical properties of carbohydrate/protein systems, pre-crystallised systems, and encapsulation systems were investigated, and the effects of composition and mechanical properties on flow properties and encapsulation properties of amorphous solids were also studied. The overall objectives of this study were to have a better understanding of the relationship between mechanical properties and industrially relevant properties of spray-dried dairy solids. The specific objectives were:

(1) To prepare lactose/milk protein isolate (MPI) solids systems with different particle size, and study the role of particle size on physical and mechanical properties of lactose/MPI solids systems.
(2) To prepare lactose/whey protein isolate (WPI) mixtures with different crystallinity, and characterize the physical, mechanical and flow properties of lactose/WPI mixtures with different crystallinity.
(3) To investigate the influence of amorphous lactose content and water plasticization on flow properties of lactose/MPI solids systems.
(4) To prepare encapsulation systems using wall materials consisting of lactose/WPI mixtures and ethyl butyrate as core material, to determine the effect of wall materials' composition on encapsulation properties, and flavor release from amorphous matrix during storage.
(5) To prepare encapsulation systems using wall materials consisting of different types and ratios of maltodextrins, to study the effect of high molecular weight carbohydrate on encapsulation properties and flavor release of amorphous matrix.

CHAPTER ONE

Literature Review

Abstract

Many food products exist in a partly or fully amorphous state. This review discusses the concept of amorphous state and its molecular arrangement. Two main factors affecting the stability of amorphous food solids are discussed. Molecular mobility and free volume show significant change at and above the glass transition temperatures (T_g). As water plasticises the material and the T_g approaches storage temperature (T), the material will clearly start to change structure, which results in a collapse and densification prior to crystallization. Moreover, increasing molecular mobility of amorphous solids could result in serious problems, such as crystallization, caking, and sticking, which cause poor flowability and solubility, and destroy the encapsulation matrix. This chapter provides an overview of the current understanding of amorphous food solids, the stability of amorphous systems, and the applications of amorphous matrix.

Keywords: Amorphous solids; Glass transition; Molecular mobility; Flow properties; Encapsulation properties

1. Introduction

Amorphous materials have been known for several decades, and scientific understanding of these systems has evolved (Rahman, 2006). The important role played by amorphous solids has been increasingly recognised within food and pharmaceutical industries during the past decades (Downton et al., 1982; Angell, 1991; Roos, 1993, 2013; Aguilera et al., 1995; Brent Jr et al., 1997; Bhandari & Howes, 1999; Chung & Lim, 2003; Aguilera, 2005; Haque et al., 2006; Abbas et al., 2010; Huppertz & Gazi, 2015). An amorphous solid is characterized by the lack of long-range order symmetry operators (translational, orientational, and conformational order) found in crystalline solid (Shah et al., 2014). The molecular pattern of an amorphous solid is often depicted as that of a frozen liquid with the viscosity of a solid having internal degrees of freedom and conformational diversities (disorder). Hancock and Zofrafi (1997) stated that an amorphous solid has a liquid-like structure with a viscosity > 10^{12} Pa·s. At the molecular level, it has properties similar to liquids; but at the macroscopic level, it has properties of solids (Shah et al., 2014).

The internal molecular arrangement of a solid can be projected as a continuum between well-ordered crystalline state and completely disordered amorphous state (Figure 1-1). Amorphous solids are considered as glasses, which have rheological properties of solids and molecular properties of liquids (Kittel, 2005). The behaviour of amorphous glasses can be explained by enthalpy or molar volume changes with the changes of temperature. When enthalpy or molar volume of a sample is plotted against the temperature, these variables change smoothly until it comes to the region known as glass transition temperature, where the variables change abruptly. The temperature region below the glass transition temperature is known as “glassy state”

and above the glass transition temperature is known as "rubbery state". The physicochemical and mechanical properties of the materials are significantly different between these two regions.

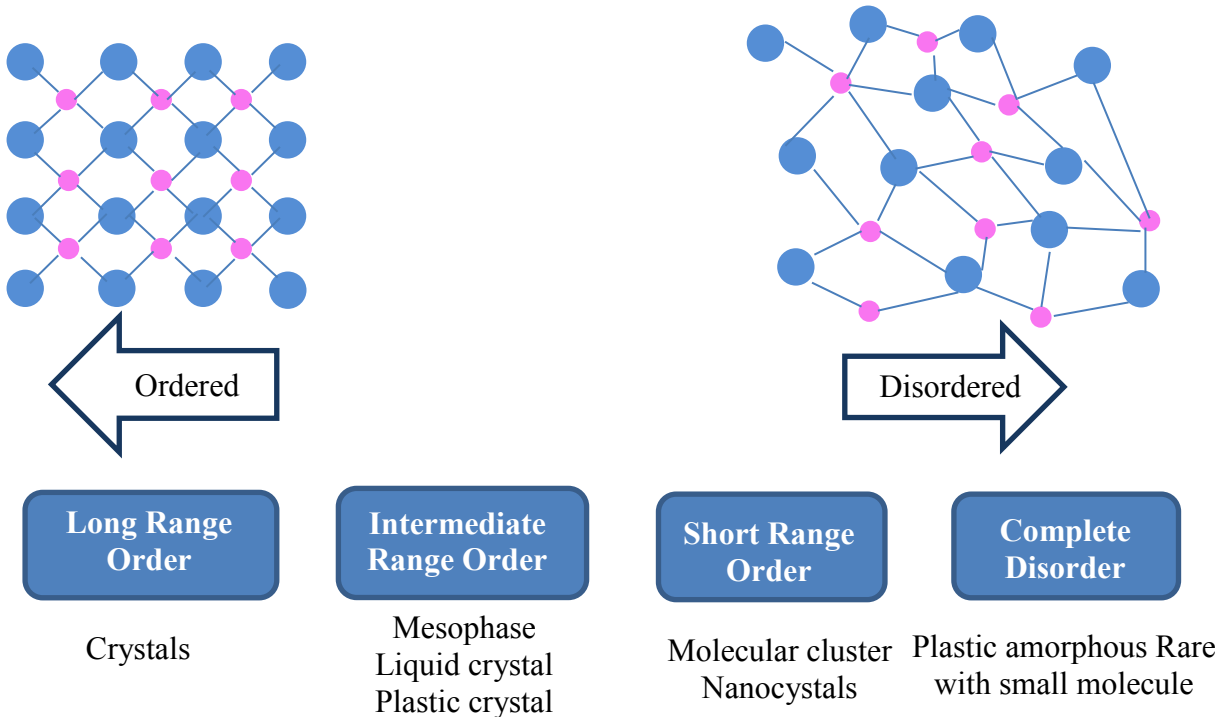


Figure 1-1 Solid form system illustration with long-range ordered (translational, orientational, and conformational) crystals on one end and completely disordered amorphous material on the other end. Solid forms can assume various length scale of order (long range, medium range, short range and/or mesomorphic states) (Shah et al., 2014).

Many food solids exist in a completely or partially amorphous state due to food processing (Pouplin et al., 1999; Kim et al., 2001; Foster et al., 2006; Liu et al., 2006; Rogers et al., 2006; Gharsallaoui et al., 2007; Abbas et al., 2010; Fazaeli et al., 2012;). The physical state and molecular mobility of amorphous food solids are affected by temperature and also by composition of food solids. Glass transition is one of the most important physicochemical characteristics of amorphous food solids.

Glass transition is perhaps also the most important state transition responsible for processing, stability, and quality characteristics of food materials (Roos, 2010). Rapid changes in the physical, mechanical, electrical, thermal, and other properties of amorphous food solids can be observed through the glass transition region (Rahman, 2007). Cornacchia and Roos (2012) indicated that sugar crystallization appeared above the glass transition temperature in protein-stabilized emulsions, which led to emulsion breakdown. Fitzpatrick et al. (2007a) stated that exposing milk powder to over 10-20 ºC above the lactose glass transition made milk powder more sticky, rendering it a lot more cohesive and also increased its adhesion to a stainless steel surface. Moreover, according to Huang (1999), the rheological properties of amorphous food polymers can change as large as 1000 times during the glass transition range. The study of Labuza et al. (1985) showed that caking and crystallization of cotton candy, whole milk powder and soft cookies occurred in real time at or near the T_g values. Furthermore, Whorton (1995) stated that the rates of deteriorative reactions and diffusion of flavor from amorphous matrix increased when an encapsulated matrix went through the glass transition.

The objective of present study is to give an update overview of recent researches in amorphous food solids. A brief summary is firstly made on how to produce amorphous food solids, while emphasis is given on the factors affecting the stability of amorphous food solids, inducing the increase of molecular mobility of amorphous food solids, and causing mechanical properties changes. In the last section, the flowability and functionality of amorphous food solids are discussed, and encapsulation properties of an amorphous matrix are also introduced.

2. Preparation and characterization of amorphous food solids

2.1 Amorphous food solids

Amorphous products have been used from ancient times not only in our daily life but also in some laboratory experiments (Šesták et al., 2010). Many processed food materials exist in an amorphous state, such as hard candy and many food powders: dairy, instant coffee and tea, protein, spice, cocoa, etc. Several delivery systems for sensitive food components and pharmaceuticals also use non-crystalline solids as protective matrices, or the active components need to remain non-crystalline for rapid release and uptake. The amorphous food structure could result from melting, denaturation, glass transition, gelatinization, mechanical shear, rapid removal of dispersing solvent, and depolymerisation of large structure (Liu et al., 2006). Familiar food-processing techniques to form an amorphous state include drying, such as spray-drying (Haque & Roos, 2004a, 2004b; Paterson et al., 2005; Chiou et al., 2008; Kurozawa et al., 2009; Hogan & O'Callaghan, 2010) and hot air-drying (Bhandari & Hartel, 2005); freezing, such as rapid cooling (Hancock & Zografi, 1997) and freeze drying (Miao & Roos, 2004, 2005; Barham et al., 2006; Zhou & Roos, 2012); grinding, such as ball-milling (Kim et al., 2001); extrusion (Le Meste et al., 2002), etc. In the present review, the amorphous food solids produced by spray drying are mainly discussed.

2.2 Characterisation of amorphous food solids

An amorphous state of a material refers to its random, disordered molecular structure, i.e., no exact position for any of the constituent molecules at a given time can be defined (Roos, 2010). Compared to tightly packed molecules in crystalline state, molecules in amorphous state are in anarchy, tangled, more open and porous, which can be seen in Figure 1-1. Food solids in amorphous state can absorb water

easily, which means they have high hygroscopicity. Therefore, rehydration properties of food powders, such as dispersibility and rate of dispersion, can be affected by the present of amorphous components. Amorphous food materials rehydrate rapidly, because the bonding between the molecules is weaker, and the solvent can be easily reintroduced (Hancock & Parks, 2000). However, high hygroscopicity also makes amorphous materials easily lumping and caking during production and storage (Aguilera et al., 1995; Bhandari & Howes, 1999; Boonyai et al., 2004; Hogan & O'Callaghan, 2010), which resulted in the deterioration of powder flowability (Fitzpatrick et al., 2004; Juliano & Barbosa-Cánovas, 2010). Furthermore, amorphous food powders show good compressibility, low density, and high internal porosity. As a result, powders with amorphous components deform and compact easily, and tend to cake under stress. In addition, the mechanical strength of amorphous solids is brittle or fragile, while that of crystalline solids is strong. Typically most crystalline materials tend to exhibit high levels of elasticity upon exposure to an external stress. By contrast, molecules in the amorphous state tend to exhibit varying degrees of viscoelasticity, depending on their temperature relative to T_g (Hancock & Zografi, 1997). Hancock and Zografi (1997) stated that a fragile material has a stronger temperature dependence of the molecular mobility, which cause high chemical reactivity at or above glass transition temperature. Many physico-chemical changes are observed to take place rapidly around glass transition temperatures of amorphous food systems, such as stickiness (Paterson et al., 2005), caking (Aguilera et al., 1995), Maillard reaction (Miao & Roos, 2004), crystallization (Bronlund & Paterson, 2004; Haque & Roos, 2004a), etc.

3. Factors related to the stability of amorphous food solids

The changes in external thermodynamic conditions, such as pressure and temperature, and changes in plasticiser or solvent (water) contents can result in variations of food material properties and states (Roos, 2013). Two key factors, temperature and water content, related to the changes of properties and states of amorphous food solids will be mainly discussed in this review.

3.1 Glass transition temperature

In food materials the physical state and stability are related to both first-order phase transitions such as crystallization and melting, and second-order phase change that occurs at the glass transition of an amorphous material. Le Meste et al. (2002) stated that glass transition is the name given to the phenomena observed when a glass is changed into a supercooled melt during heating, or to the reverse transformations during cooling. Glass transition is an important keyword for amorphous food science and technology. It has been used as indicator of food stability and to predict the behaviour of food solids for many decades (Aguilera et al., 1995; Buckton & Darcy, 1996; Bai et al., 2001; Fitzpatrick et al., 2007a; Foster et al., 2006; Silalai & Roos, 2011b).

3.1.1 Changes over glass transition temperatures

3.1.1.1 Free volume and structural relaxation

It is recognised that the molecular mobility of the amorphous region of solids will be important in determining its physical stability (Hancock et al., 1995) and that the nature of the amorphous solid will change depending upon the difference between the temperature (T) and the glass transition temperature (T_g). Well below the glass transition, molecules are immobilized in their positions, and their molecular motions

are limited to rotations and vibrations, which results in the solid-like characteristics of the material (Sperling, 2006). When a glass is heated to above the glass transition, molecules gain translational mobility and enter the supercooled, liquid-like state with a concomitant appearance of viscosity (Sperling, 2006). Molecular mobility within amorphous structures can be expressed as free volume, v_f, available for the motion of molecules (Doolittle, 1951). In the glassy state, major differences in free volume structure of amorphous materials are observed depending on the molecular weight of the carbohydrates: the lower molecular weight, the smaller the free volume holes at any given temperature (Ubbink, 2012). Palzer (2010) indicated that a critical free volume is accumulated near a molecule with increasing temperature, and the molecule can leave its fixed position.

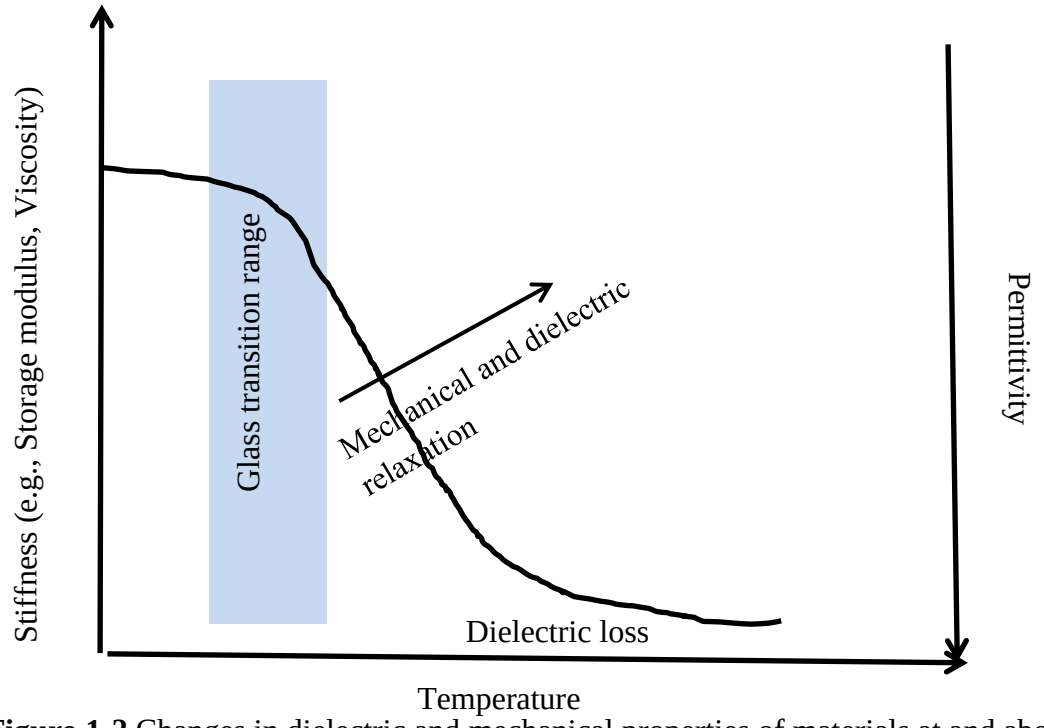


Figure 1-2 Changes in dielectric and mechanical properties of materials at and above the glass transition. The rapid increase in molecular mobility around the glass transition in heating of a material can be observed in an exponential decrease in modulus and viscosity (storage modulus) (Roos, 2010).

Amorphous food components have been studied for glass transitions, dielectric relaxations, mechanical relaxations, spectroscopic properties and various other characteristics showing changes in molecular mobility at and around the glass transition (Roos, 2013). There are also other properties of materials changing dramatically around the glass transition, including stiffness, free volume and thermal expansion, and dielectric properties (Figure 1-2) (Roos, 2010).

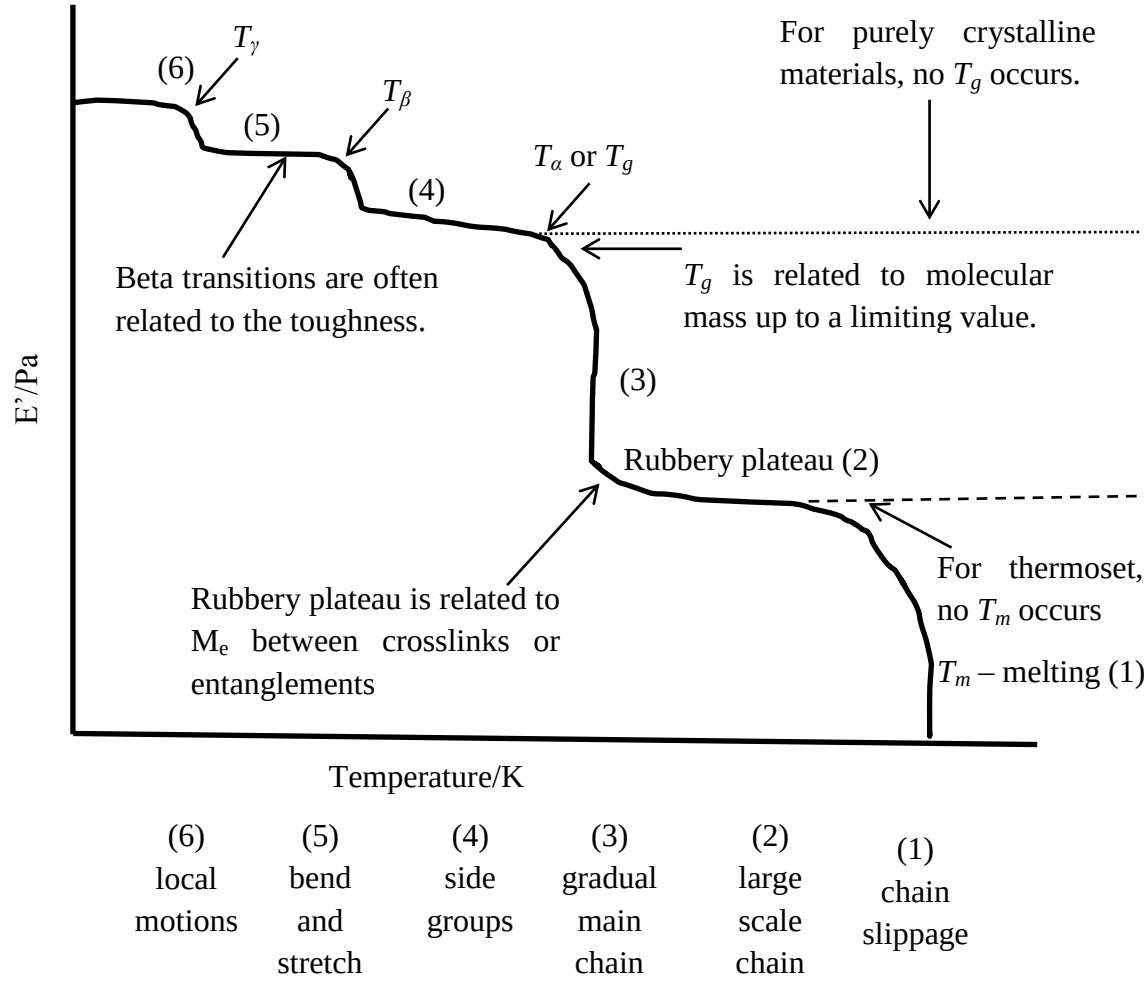


Figure 1-3 Idealized DMA scan. An idealized scan showing the effects of various molecular relaxations of the storage modulus, E', curve (Menard, 2008).

Glass transition is a kinetic process associated with the primary relaxation of the material (Champion et al., 2000). The relaxation time (characteristic time of mobility) is the time that is necessary for the recovery of equilibrium conditions after perturbation of a property of the material. The viscosity of amorphous systems is

strongly related to timeframes for relaxations. In particular, systems that respond quickly to deviations from equilibrium, such as an applied stress, are characterized by short relaxation times and low viscosities, while systems that respond slowly are characterized by long relaxation times and high viscosities (Shah et al., 2014).

In previous studies (Silalai & Roos, 2010b, 2011a; Potes et al., 2012), mechanical α-relaxation of amorphous systems was often observed from a decrease in storage modulus and a peak in the loss modulus. An idealized scan of various transitions determined using a dynamic mechanical analyser (DMA) is shown in Figure 1-3 (Menard, 2008), along with the molecular motions associated with the transitions.

At very low temperature, the molecule is tightly compressed. This process is shown in Figure 1-3 (6). As the material warms and expands, the free volume increases so that localized bond movements (bending and stretching) and side chain movements can occur. This is the gamma transition, T_γ, which may also involve associations with water. As the temperature and the free volume continue to increase, the whole side chains and localized groups of four to eight backbone atoms begin to have enough space to move and the material starts to develop some toughness. This transition is called the beta transition T_β. As heating continues, it reaches the T_g, where the chains in the amorphous regions begin to coordinate large-scale motions (Figure 1-3 (4)). Continued heating bring it to the T_α (Figure 1-3 (3)). This is a movement of coordinated segments in the amorphous phase that relates to reduced viscosity. Finally, it reaches the melt (Figure 1-3 (2)) where large-scale chain slippage occurs and the material flows. This is the melting temperature, T_m. For a cured thermoset, nothing happens after the T_g until the sample begins to burn and degrade because the cross-links prevent the chains from slipping past each other.

The temperature dependence of the relaxation times of mechanical properties are often predicted by the Vogel-Tammann-Fulcher (VTF) (1-1) and the Williams-Landel-Ferry (WLF) (1-2) expressions:

$$\eta_T=\eta_0 \exp(B/(T-T_0)) \quad (1\text{-}1)$$

$$\log(\eta/\eta_{Tg})=-C_1(T-T_g)/(C_2+(T-T_g)) \quad (1\text{-}2)$$

where η and η_{Tg} are viscosities at T and T_g respectively; η_0, B, T_0, C_1, and C_2 are phenomenological coefficients. Both expressions can be inter-converted according to the following relationships between the coefficients (B'=B/ln 10) (Liu et al., 2006):

$$C_1=B'/(T_g-T_0)=B/((T_g-T_0)\ln 10)$$

$$C_2=T_g-T_0$$

C_1 and C_2 in the WLF equation can fluctuate slightly around the "universal" values given by Williams et al. (1955) (C_1=17.4 and C_2=51.6) as a function of the considered material. According to Angell et al. (1994), this is probably true for C_1, but not for C_2. The variation of C_2 corresponds to the classification proposed by Angell (1995) to strong/fragile materials according to the variation of their dynamic properties through the glass transition.

The fragility parameter *m* was introduced to differentiate fragile systems from strong ones. It can be calculated from the VTF and WLF coefficients (1-3):

$$m=C_1+C_1^2 T_0 \ln 10/B \text{ or } m=(C_1/C_2)T_g \quad (1\text{-}3)$$

A strong liquid ($16 < m < 100$) typically exhibits Arrhenius-like behaviour or weak temperature dependence of the molecular mobility, but a fragile liquid ($100 <$

m < 200) has a stronger temperature dependence of the molecular mobility near T_g (Hancock & Zografi, 1997).

3.1.1.2 Physical properties changes

Glass transition theory from the study of polymer science could help to understand textural properties of food systems and explain changes which occur during food processing and storage, such as stickiness, caking, softening and hardening (Abbas et al., 2010). Glass transition reflects the molecular mobility in formulations with miscible components, and it can be measured from changes in material characteristics (Kalichevsky & Blanshard, 1992, 1993; Roudaut et al., 2004). When the temperature is around or above T_g, various changes such as increase of free volume and specific heat, as well as decrease of viscosity, are noticed. These factors control various time-dependent structural transformations (Tonon et al., 2009). A number of studies have reported the effects of glass transition on physical properties, such as stickiness (Boonyai et al., 2004; Murti et al., 2009; Silalai & Roos, 2010a, 2011a; O'Callaghan & Hogan, 2013), and caking (Aguilera et al., 1995; Foster et al., 2006; Fitzpatrick et al., 2007a) of amorphous food powders.

Foster et al. (2006) indicated that the mechanism for sticking and caking of amorphous sugars is through the phase change of the amorphous sugar from a glass to a rubber at temperatures above the glass transition temperature, and also the rate of cohesiveness development is proportional to the T-T_g values, that is, the greater the temperature above the T_g, the quicker the powders will develop liquid bridges, which may result in caking. In addition, the oxidative stability of encapsulated oil was influenced by the state of wall materials (Drusch et al., 2006). Drusch et al. (2006) indicated that at low relative humidity, fish oil oxidation was decreased in

trehalose containing samples indicating that in the amorphous state trehalose is a more suitable wall material for microencapsulation than glucose syrup, while at 54% relative humidity, a rapid oxidation of the microencapsulated oil was observed upon crystallization of trehalose. Zhou and Roos (2012) indicated that glass transition of solids and crystallization of component sugars should be considered in the stabilization of sensitive components. In addition, the influence of T_g on the translational diffusivity or the diffusion of molecules has an important impact on the diffusion-controlled physical and chemical processes, which limit the shelf life of food products. Moreover, phase transitions with physical aspects of matrix are factors affecting the rates of nonenzymatic browning reactions. Karmas et al. (1992) indicated that the rate of reaction is low at temperatures below glass and increases with increase in T-T_g.

3.1.2 Determination of glass transition

The measurement of glass transition and observation of molecular mobility in amorphous food systems is done using thermal, mechanical techniques, dielectric, or spectroscopic techniques. Differential scanning calorimetry (DSC) is the most popular method to determine glass transition (Kalichevsky et al., 1993; Jouppila & Roos, 1994; Le Meste et al., 2002; Haque et al., 2006; Fitzpatrick et al., 2007a; Hogan & O'Callaghan, 2013). In DSC, T_g is characterised by measurable discontinuity in specific heat capacity (Hogan et al., 2010). In addition, Hogan et al. (2010) provided a novel technique for observing glass-rubber transition. They used standard rheological equipment to determine the glass-rubber transitions of a range of both non-fat and fat-containing dairy powders. Furthermore, DMA is the most sensitive technique for monitoring relaxation events, such as glass transitions, as the mechanical properties change dramatically when relaxation behaviour is observed

(Huang, 1999; Mahlin et al., 2009; Gearing et al., 2010; Gracia-Fernández et al., 2010; Hu et al., 2013; Silalai & Roos, 2010b). DMA applies a sinusoidal force to the material and the resultant changes in storage and loss moduli, as a function of temperature, allow determination of glass transition. Moreover, thermal mechanical analysis (TMA) could also find glass transition. TMA measures dimensional changes in materials as a function of temperature and defines glass transition in terms of the change in the coefficient of expansion as the material changes from glass to rubber. Dielectric thermal analysis (DTEA) also provides analogous relaxation information to DMA data on dielectric relaxations in amorphous food systems (Arbe et al., 1996; Noel et al., 1996; Silalai & Roos, 2010b, 2011a). Several spectroscopic techniques can also be used to observe molecular mobility in amorphous materials, including infra-red and Fourier transform infra-red (IR/FTIR) (Carpenter & Crowe, 1989; Hogan & Buckton, 2001), Raman (Yi & Jonas, 1996), various Nuclear Magnetic Resonance (NMR) (Hills et al., 1990, 1996), and Positron Annihilation Lifetime Spectroscopy (PALS) (Townrow et al., 2007). In addition, according to Le Meste et al. (2002), the glass transition temperature is strongly dependent on molecular weight.

The Gordon-Taylor equation (1-4) has been used to predict the T_g of a binary mixture (Roos & Karel, 1991; Roos, 1995b; Fan & Roos, 2015).

$$T_g = (w_1 T_{g1} + k w_2 T_{g2})/(w_1 + k w_2) \qquad (1\text{-}4)$$

Where w_1 and w_2 are weight fractions of component compounds; T_{g1} and T_{g2} are glass transition temperatures of the component compounds; and k is constant.

3.2 Water content

As water strongly affects the structures of amorphous food solids, it is an important factor determining their chemical and physical stability (Angell, 1993, 2002; Haque & Roos, 2004a, 2004b; Fitzpatrick et al., 2007a; Hogan & O'Callaghan, 2013). Previous studies have shown that changes in water content of an amorphous carbohydrate matrix have profound effect on the local structure and dynamics of a carbohydrate matrix even in the glassy state (Figure 1-4) (van den Dries et al., 2000; Cicerone & Soles, 2004; Kilburn et al., 2004).

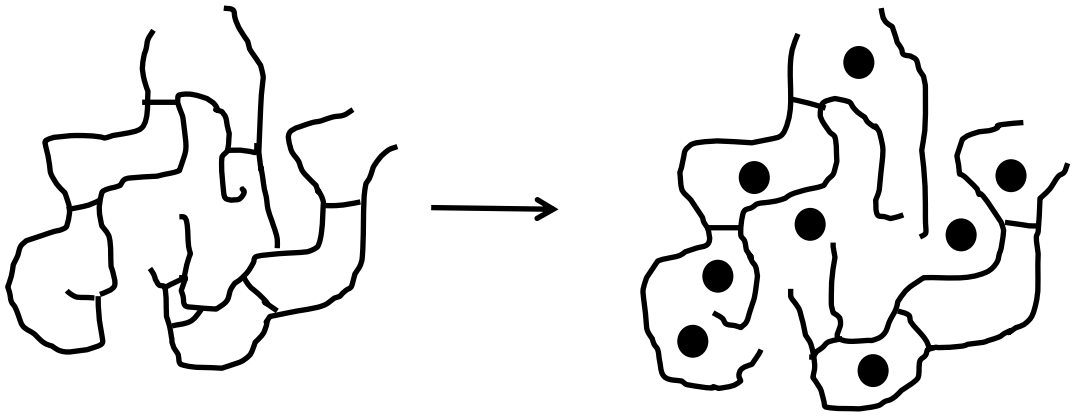


Figure 1-4 A molecular interpretation of the interaction of water with amorphous carbohydrates. In dry state, the hydroxyl groups on the sugar residues form hydrogen bonds (left diagram). Water absorbed into the system leads to plasticization both by interference with hydrogen bonding between the carbohydrate chains and by creation of additional free volume (right diagram) (Ubbink & Krüger, 2006).

3.2.1 Changes with increasing water content

3.2.1.1 Free volume and structural relaxation

Water is a 'mobility enhancer', in that its low molecular weight leads to a large increase in mobility, due to increased free volume and decreased local viscosity (Ferry, 1980). It is a well-known plasticizer in amorphous systems. Positron annihilation studies showed that the addition of a plasticizer can have several effects

on the free volume between the matrix molecules (van den Dries et al., 2000). On one hand, plasticizer molecules can fill up voids between the matrix molecules and thereby they can lower the free volume. On the other hand, addition of plasticizers can also lead to an increase in free volume by decreasing the molecular packing of the matrix molecules. Therefore, the free volume of amorphous food solids is dependent on both temperature and water content. Kilburn et al. (2006) used positron annihilation lifetime spectroscopy (PALS) to probe the free volume of trehalose matrices, and developed a molecular picture of the organization and mobility of water in both amorphous and crystalline states. They found that in amorphous matrices, water increases the average intermolecular hole size, while in the crystalline dehydrate it is organized as a confined one-dimensional fluid in channels of fixed diameter that allow activated diffusion of water in and out of the crystallites. In addition, water acting as a plasticiser in amorphous food materials has an effect on lowering T_g values, which may be due to shielding of attractive, inter- and intra-molecular interactions and by decreasing the activation energy of molecular motion (Matveev et al., 2000). T_g values decrease with increasing water content showing significant water plasticization (Haque & Roos, 2004a; Liu et al., 2007; Omar & Roos, 2007; Roussenova et al., 2010; Potes et al., 2012).

3.2.1.2 Physical changes with increasing water content

Water entrapped in an amorphous structure may well give rise to problems of instability (Buckton & Darcy, 1996). As water plasticises the material and the T_g approaches *T*, the material will clearly start to change structure, which results in a collapse and densification prior to crystallization. Depressing T_g of amorphous food solids with increasing water content results in rearrangement of molecules to the crystalline state (Jouppila & Roos, 1994; Jouppila et al., 1997; Bronlund & Paterson,

2004; Haque & Roos, 2004a). Crystallization causes the most drastic changes to the physical properties of amorphous food systems. It may affect food stability and impair the rehydration properties of food powders. Moreover, increasing water content of food powders induces the formation of liquid bridges between particles, which results in caking and sticking problems of food powders. Furthermore, Soottitantawat et al. (2004) indicated that the release rate and the oxidation rate of encapsulated D-limonene by spray drying increased with increasing water content

Zhou et al. (2001) indicated that the free volume of amorphous systems is dependent on water content and temperature. As water plasticization depresses T_g significantly, the glass transition dependence on water content has been taken into account in the prediction of amorphous food stability at various water activities and water contents.

4. Stability and applications of amorphous solids

4.1 Flow properties

The flow of a powder is the relative movement of a bulk of particles among neighbouring particles or along the container wall surface (Peleg, 1977). The forces that are involved are gravitational forces, friction, cohesion (interparticle attraction) and adhesion (particle-wall attraction) (Peleg, 1977). From a rheological point of view, powder flow has been studied from several different perspectives: as a fluid, as a solid body undergoing elastic/plastic deformation (Sutton, 1976), and as the mechanical failure of a solid structure (Jenike, 1964). Elastic/plastic deformation and mechanical failure can describe powder flow more accurately and therefore have been widely adopted to explain powder flow (Juliano & Barbosa-Cánovas, 2010). Furthermore, wall friction is the friction between a bulk solid and a solid surface.

The wall friction angle is important for silo design for flow and for silo design for strength, but also for the design of chutes and other equipment, where the bulk solid will flow across a solid surface (Schulze, 2007). Flowability depends on the powder's bulk properties (moisture content, density, composition, shape, and particle size distribution), some of which can change as a result of impact during handling, air relative humidity, temperature, and storage time conditions (Ilari, 2002; Fitzpatrick et al., 2004, 2007a; Emery et al., 2009; Crowley et al., 2014a). Powder particles can stick together and form a stable caking structure, which would prevent flow. Physico-chemical changes occur during glass transition allowing the flow of liquids, which contributes to the formation of liquid bridges. This could result in poor flowability. Pre-crystallizing the amorphous components in food solids during processing may help to resolve the problem of product stickiness and stability during subsequent storage (Das & Langrish, 2012).

Flow properties of spray-dried food solids are very important in handling and processing operations (Knowlton et al., 1994; Fitzpatrick et al., 2007a;). Previous studies have indicated that flow properties depend on the composition and physical properties of powders, such as particle size and shape, surface structure, amorphous lactose content, and water content (Kim et al., 2005; Fitzpatrick et al., 2007a; Schulze, 2007; Janjatović et al., 2012; Crowley et al., 2014a). Stickiness and caking of powders usually result from formation of liquid bridges between individual particles, and they are responsible for impaired flow properties (Lazar et al., 1956; Peleg, 1977). Many studies have shown that powders with larger amounts of amorphous components were more sensitive to absorbing moisture, giving rise to lumping and caking problems (Le Meste et al., 2002; Liu et al., 2006; Fitzpatrick et al., 2007a, 2007b; Silalai & Roos, 2010a).

The importance of sticky behaviour of amorphous food solids has been recognized over many decades in the food industry due to its influence on process and handling abilities and quality of the powders (Boonyai et al., 2004). Stickiness of amorphous food powders due to viscous flow mechanism is governed by temperature and water content (Boonyai et al., 2004; Silalai & Roos, 2011b).

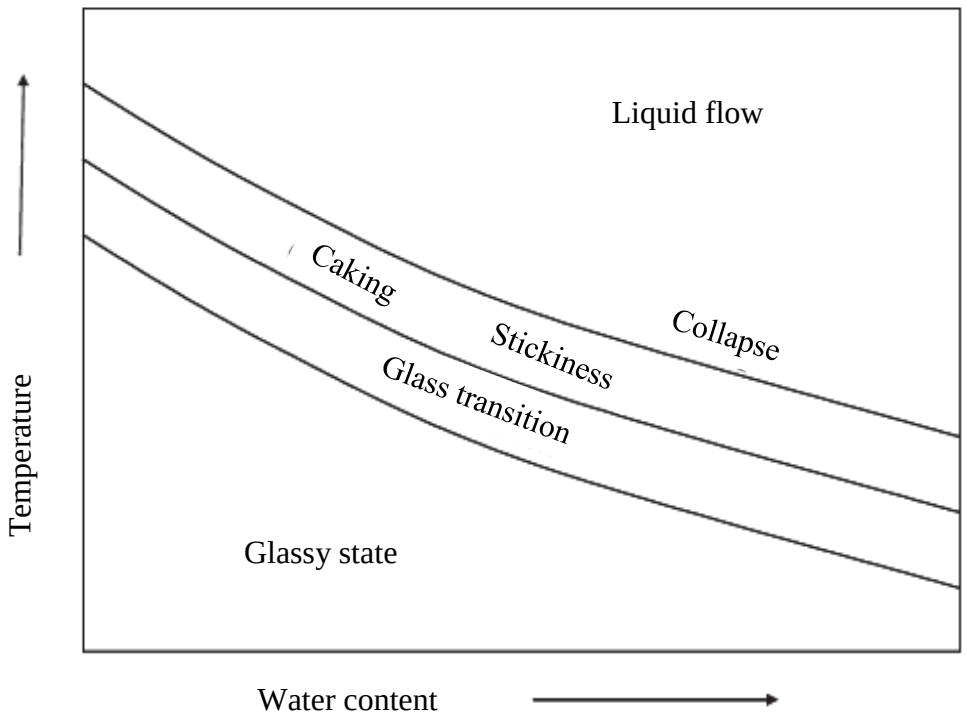


Figure 1-5 Consequences of glass transition on physical phenomena. (Roos, 1995a)

Figure 1-5 shows the consequence of glass transition on stickiness, caking and collapse phenomena as influenced by water content and temperature (Roos, 1995a). Above the T_g, the molecules are able to rearrange themselves from the disordered structure of amorphous solids in the "glassy" state to a very viscous "liquid" state, allowing viscous flow and sticking to occur under suitable conditions. Ultimately, the molecules will rearrange themselves to form structured crystalline arrays and solid bridges, resulting in a hard caked material (Murti et al., 2009). Silalai and Roos (2010a) stated that physical properties of amorphous lactose governed the stickiness

of milk powders, and increasing protein content improved flow characteristics and contributed to decrease stickiness of milk powders around glass transition. They also showed that the mechanical α-relaxation behaviour was governed by the solids system composition and was related to the development of stickiness (Silalai & Roos, 2011b). Moreover, the sticky point was governed by the glass transition of the carbohydrate phase (Silalai & Roos, 2011b). According to the study of Hogan and O'Callaghan (2013), powders containing hydrolysed whey proteins were more susceptible to stickiness compared to intact proteins. Hydrolysis of whey protein affected the relaxation behaviour of whey protein/ lactose powders and altered the rate at which lactose underwent viscous flow behaviour.

4.2 Rehydration properties

Food powders are intended for rehydration with water or in an aqueous system. For consumers, the powder dissolution property is an important benchmark of a particular product's feature. Therefore, various efforts have been made to improve food powder rehydration properties in both industry and research setting (Bhandari et al., 2013). Rehydration of food powder generally includes the following steps: wetting of particles (wettability), sinking (sinkability), dispersing (dispersibility), and particles dissolving into solution (solubility) (Fang et al., 2007). As food solids in the amorphous state have high hygroscopicity, rehydration properties of food powders can be affected by the presence of amorphous components. Amorphous food materials rehydrate rapidly, because the bonding between the molecules is weaker, and the solvent can be easily reintroduced (Hancock & Parks, 2000). However, increasing temperature or water content of amorphous food solids results in rearrangement of molecules to the crystalline state. Crystallization causes the most drastic changes to the physical properties of food solids, which may impair the

rehydration properties of food powders. Furthermore, as lactose crystallization in milk powders leads to increased free surface fat, the increase of surface fat could induce slow wetting of powders. Moreover, caking in dairy powders causes serious problems in terms of storage and product quality, and stickiness/caking problem by expelling free fat onto the particle surface that forms liquid bridges (Foster et al., 2005). These problems impair the solubility of amorphous powders.

4.3 Encapsulation properties

Encapsulation requires entrapment of food components or dispersed particles in a continuous phase. This continuous phase is often a solid matrix formed by glass-forming food components, particularly sugars and other carbohydrates (Roos, 2010). Amorphous carbohydrates in the glassy state are widely used as matrices for the encapsulation and stabilization of nutrients, pharmaceutics, and other bioactive compounds. Numerous recent studies have discussed the glass formation of amorphous matrices in encapsulation processes (Vega & Roos, 2006) and emphasized the importance of the glass-forming ability of the encapsulant in protecting sensitive components (Ubbink & Krüger, 2006). Ubbink and Krüger (2006) announced that encapsulation systems based on amorphous carbohydrates in the glassy state have been very effective in reducing the rate of release of the flavor during storage, and in minimizing the rate of oxidation of oxygen-sensitive flavors by environmental oxygen. Zhou and Roos (2012) studied the stability of water-soluble vitamins protected by lactose and trehalose amorphous system. They suggested that the amorphous structure protected the entrapped vitamins. In these applications, the glass transition temperature and water content of the amorphous matrix have been used as the central physical parameters for the optimization of processing conditions and storage stability (Townrow et al., 2010).

The main issue in the design of encapsulation matrices with optimal barrier properties is the molecular mobility in the matrix (Roussenova et al., 2014). However, increased molecular mobility and structural changes resulting from water plasticization of amorphous solids may lead to loss of the entrapped compounds from encapsulant systems. Rosenberg and Sheu (1996) indicated that incorporation of lactose into WPI-based wall systems enhanced volatile retention during drying and limited the core extractability. Moreover, the incorporation of lactose in the whey protein-based wall system can limit the diffusion of apolar substances through this wall. Lactose in its amorphous state acts as a hydrophilic sealant that significantly limits diffusion of the hydrophobic core through the wall and thus leads to high microencapsulation efficiency values. In amorphous encapsulant systems, the release and stability of core materials is related to the molecular mobility of wall materials. According to Goubet et al. (1998), the glassy state is characterized by a very low mobility of the carrier molecules. Due to this low mobility, release of the encapsulated materials is primarily via Fickian diffusion through the pores in the matrix. The amount of volatile released will also depend on the composition of the matrix, pore size, particle size, and the thickness and area of wall around the entrapped volatiles. When the plasticizer content, for example water content, increases, a transition occurs from the solid glassy to a liquid-like rubbery state. The hydrogen bonds which are responsible for the main structural forces in dried amorphous products are weakened. Molecular mobility and diffusion increase. With increasing water content, collapse may occur when plasticization of the carrier decrease the viscosity to the extent that the polymer matrix is unable to support itself against gravity. When it happens, porosity is lost, reducing diffusion through the

matrix. Therefore, it is essential to understand the relationship between the molecular structure of amorphous matrices and the barrier properties.

5. Conclusions

Through processing, many food products and materials exist in partly and fully amorphous state. Understanding glass-transition-related relaxations and molecular mobility with stability and functionality of amorphous food solids is essential for the design of complex food and nutrient delivery systems. Extensive studies have been performed to understand the stability of amorphous food solids and food processing has benefited from understanding the glass transitions of food components and their impact on food characteristics. When an amorphous solid is heated to above the glass transition, its molecules gain translational mobility and enter the supercooled, liquid-like state with a concomitant appearance of viscous flow. Relaxation times of mechanical properties and free volume are related to molecular mobility. Increasing molecular mobility of amorphous solids could result in stickiness and caking, impair the flowability of food solids, decrease solubility, and destroy the encapsulation matrix.

CHAPTER TWO

Roles of particle size on physical and mechanical properties of dairy powders

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Abstract

Lactose/milk protein isolate (MPI) solids systems were prepared by a laboratory-scale spray dryer (defined as S-lactose/MPI solids systems) and a pilot-scale spray dryer (defined as L-lactose/MPI solids systems). Particles of L-lactose/MPI solids systems had more rounded shape and smoother surface compared to S-lactose/MPI solids systems. Water sorption studies showed that S-lactose/MPI solids systems sorbed 5-30% larger amount of water than L-lactose/MPI solids systems after equilibration at water activities 0.11-0.44 a_w. Compared to the samples with same composition, dairy solids with smaller size particles showed higher steady water content at the end of lactose crystallization. Moreover, S-lactose/MPI solids systems showed lower glass transition temperature (T_g) values than L-lactose/MPI solids systems after equilibration at 0.11 a_w, 0.23 a_w and 0.33 a_w, which might be due to the higher water content of S-lactose/MPI solids systems. The study of mechanical properties indicated that the stiffness of S-lactose/MPI solids systems was higher compared to L-lactose/MPI solids systems at 0.23 a_w and 0.33 a_w when temperature was below T_g values. Water plasticization had stronger effect on the structural relaxation of dairy solids with smaller size particles.

Keywords: Particle size; Water sorption; Glass transition; Mechanical properties; Relaxation times

1. Introduction

Several single particle characteristics are important to powder properties. These include particle size, shape, surface, density, hardness, adsorption properties, and so on (Bronlund & Paterson, 2004; Fitzpatrick et al., 2004, 2007b; Fu et al., 2012). Of these features, particle size is the most essential and important. Particle size of powders is primarily determined by physical properties of the infeed emulsion (such as viscosity and solids concentration) and the atomization operating parameters, such as the rotational speed and wheel diameter in the case of centrifugal atomization and the orifice size and pressure in the case of nozzle atomization (Finney et al., 2002; Fang et al., 2005). According to Langrish et al. (2006), the dryer type and settings can also be used to control the morphology of the powder particles and the functional properties of the powders. They stated that the powders produced by the laboratory- and pilot-scale dryers were significantly different from the commercially dried powders in both surface composition and morphology.

Although the role of particle size is not clear, it is often desirable to produce large particles to facilitate rehydration (Ji et al., 2015). Small particles tend to disperse very poorly, especially in cold water, and instead form lumps on liquid surface. Large particles can be obtained through appropriate choice of spray dryer operating conditions or the use of agglomeration techniques (Ji et al., 2015). Powders in small particle size give a large surface area per unit volume, which is related to hygroscopicity (e.g., high degree of moisture absorption). The stability of a powder, in terms of physical and chemical properties, is usually impaired by increased water sorption (Bhandari & Hartel, 2005). The study of Haque and Roos (2004b) showed that fine powders sorbed more water than coarse powders at relative humidity (RH) $\leq$ 33.2%. Additionally, powder particle size could also influence the encapsulation

efficiency of oils during spray drying (Jafari et al., 2007). Jafari et al. (2007) revealed that larger particles (> 63 μm) retained more volatiles than smaller particles (< 38 μm), but at the same time there was more unencapsulated oil at the surface of larger particles.

In addition, the bulk density, compressibility, and flowability of a food powder are highly dependent on particle size and its distribution. According to Schulze (2007), the flow properties of a fine-grained bulk solid are mainly influenced by adhesive forces due to liquid bridges (if water is present) and van de Waals forces (dominating force for dry, fine-grained bulk solids). Both forces are proportional to particle size. Moreover, for quality control or system property description, it becomes paramount to present the particle size distribution of food powders.

The objective of this study was to study the effect of particle size on physical and mechanical properties of lactose/milk protein isolate (MPI) solids systems. In this study two kinds of spray dryers were used to produce dairy solids with different size particles. The aim was to build a better understanding of the roles of particle size on physical properties and mechanical properties of spray-dried dairy solids.

2. Materials and methods

2.1 Materials

α-lactose monohydrate (> 99% purity) and MPI were donated by Arla Foods Ingredients (Sønderhøj 10-12, 8260 Viby J, Denmark) and Kerry Ingredients & Flavours (Kerry Group, Tralee, Co. Kerry, Ireland), respectively. MPI contained ≥ 89% protein and ≤ 0.35% lactose. Aluminum oxide calcined powder (≥ 99% purity) was purchased from Sigma−Aldrich (St. Louis, MO, USA).

2.2 Preparation of lactose/MPI solids systems

Aqueous solution (15 %, w/w) of lactose, and lactose/MPI (4:1, 1:1, and 1:4) mixtures were spray-dried using a laboratory-scale spray dryer, BÜCHI Mini Spray dryer B-191 (BÜCHI Laboratoriums-Technik, Flawil, Switzerland) (defined as S-lactose/MPI solids systems) and a pilot-scale spray dryer, ANHYDRO single stage spray dryer with a centrifugal atomizer (Copenhagen, Denmark) (defined as L-lactose/MPI solids systems), respectively, at the Teagasc Food Research Centre, Moorepark, Fermoy, Co. Cork, Ireland. The inlet air temperature was around 170 ± 2 °C and the outlet temperature was around 90 ± 2 °C. Spray-dried solids were kept immediately in evacuated desiccators over P_2O_5 at room temperature. Each analysis was carried out within 3 months after spray drying.

2.3 Powder characterisation

Protein content was determined using a FP 628 Nitrogen Determinator (LECO Corporation, Lakeview Avenue, St. Joseph, Michigan, USA). Lactose content was determined using an Automatic Polarimeter (Autopol 1, Rudolph Research Analytical, Hackettstown, NJ, USA). Chemical analysis of powders was carried out immediately after manufacture. Powder particle size distribution and specific surface area (SSA) were determined by laser light scattering using a Malvern Mastersizer 3000 (Malvern Instruments Ltd., Worcestershire, UK). Powder sample was added to the standard venturi disperser with a hopper gap of 2.5 mm and then fed into the dispersion system. Compressed air at 0.75 bar was used to transport and suspend the powder particles through the optical cell. A measurement time of 10 s was used, and background measurements were made using air for 20 s. The laser obscuration level was at 2-10%.

2.4 Morphological characteristics

Morphological characteristics were determined using a Malvern Morphologi G3 S (Malvern Instruments Ltd., Worcestershire, UK). 5 mm^3 volume powder samples were dispersed on the glass plate. 2.5× objective was used for the measurement in this study. Circularity, elongation and convexity are three commonly used shape factors (Ji et al., 2015). One way to measure shape is to quantify how close the shape is to a perfect circle. Circularity is the ratio of perimeter of a circle with the same area as the particle divided by the perimeter of the actual particle image. Several definitions of circularity could be used but for accuracy the software reports HS Circularity (HS for high sensitivity) in addition to circularity. Circularity has values in the range of 0-1. A perfect circle has a circularity of 1 while a 'spiky' or irregular object has a circularity value closer to 0. Circularity is sensitive to both overall form and surface roughness. Elongation is defined as [1-aspect ratio] or [1- width/length]. As the name suggests, it is a measure of elongation and again has values in the range 0-1. A shape symmetrical in all axes, such as a circle or square, has an elongation value of 0; shapes with large aspect ratios have an elongation closer to 1. Convexity is a measurement of the surface roughness of a particle. It is calculated by dividing the convex hull perimeter by the actual particle perimeter. A smooth shape has a convexity of 1 while a very 'spiky' or irregular object has a convexity closer to 0. In this study, each sample was measured in triplicate to get the average values for circularity, elongation and convexity.

2.5 Water sorption and lactose crystallization

Water sorption for each solid was measured using the static gravimetric method. Approximately 1 g powder was weighed into small glass vials (25 mL). Triplicate

samples of spray-dried lactose/MPI solids systems were dried in a vacuum oven (OV-12, Medline Industries, Inc., Mundelein, Illinois, USA) at 50 °C for 48 h to remove residual water. All powders were then equilibrated for 168 h in evacuated desiccators over saturated salt solutions of LiCl, CH_3COOK, $MgCl_2$, K_2CO_3, $Mg(NO_3)_2$, and $NaNO_2$, giving RH of 11%, 23%, 33%, 44%, 54%, and 65%, respectively. All desiccators were kept in incubators with temperature of 25 °C during equilibration. The samples were weighed at 0, 3, 6, 9, 12 and 24 h, and then at 24-h intervals. All vials were kept closed with caps after the vacuum was released in the desiccators before weighing. Water content of each powder was measured as a function of time and the mean weight of triplicate samples was calculated.

2.6 Differential scanning calorimetry

Glass transition temperatures, T_g (onset), of L- and S-lactose/MPI solids systems were determined using a differential scanning calorimeter (DSC Q2000, TA Instruments, Crawley, UK). To determine the T_g values, spray-dried dairy solids (1 g) were transferred to glass vials and dried in a vacuum oven at 50 °C for 48 h. The dehydrated powders were equilibrated in evacuated desiccators over P_2O_5 and saturated salt solutions of LiCl, CH_3COOK, $MgCl_2$, and K_2CO_3 for 168 h. Then 10 to 15 mg of equilibrated powders was transferred to Tzero pans. The DSC pans were hermetically sealed with Tzero hermetic lids and samples were analysed. An empty pan was used as a reference. At the first scan, the samples were heated over the glass transition temperatures region at 5 °C/min and then cooled at 10 °C/min to below glass transition, a 2nd heating scan was then run to far above the glass transition temperature at 5 °C/min. Anhydrous samples were scanned using pans with punctured lids to allow evaporation of residual water during the measurements

(Silalai & Roos, 2010a). At the first scan, the samples were heated at 5 °C/min to 100 °C and then cooled at 10 °C/min to below glass transition, a 2nd heating scan was then run to far above the glass transition temperature at 5 °C/min. The first scan was to evaporate the residual water, while the "anhydrous" state of powders during the subsequent heating scans was expected. All measurements were carried out in duplicate.

2.7 Dynamic mechanical analysis

A Dynamic Mechanical Analyser (DMA Q800, TA Instruments, Crawley, UK) was used, in conjunction with a gas cooling accessory (GCA) tank, to determine dynamic mechanical properties of L- and S-lactose/WPI solids systems. A rectangular stainless steel powder pocket was designed to generate a defined geometry to contain powder with inner dimensions of 60 mm × 11 mm × 1 mm. A pre-weighed mass of powder mixed with aluminum oxide calcined powder at the ratio 4:1 was evenly spread within this shallow container, and the upper lid was then placed onto the top surface of the powder (Mahlin et al., 2009). As aluminum oxide calcined showed no influence on the mechanical results of dairy solids in the temperature range, it was added to protect dairy powder from sticking on the powder pocket during the heating test. The sample pocket was mounted in the instrument in a dual cantilever clamp during measurement. For anhydrous samples and samples equilibrated at 0.11 a_w, the measurements were made at a heating rate of 2 °C/min from 0 to 150 °C. For samples equilibrated at 0.23 a_w, 0.33 a_w and 0.44 a_w, the measurements were made at a heating rate of 2 °C/min from 0 to 120 °C. DMA was operated by a sinusoidal deformation applied to the powder sample pocket at a fixed strain. The amplitude was 15 µm. During dynamic heating, the samples were

analysed for storage modulus (E') and loss modulus (E'') using single frequency 1 Hz. Frequency of deformation (oscillating frequency) was changed in multiple frequencies of 0.5, 1, 3, 5, 10, and 20 Hz. The α-relaxation times were determined directly from the frequencies (f) using the relationship $\tau_\alpha=1/(2\pi f)$ (Noel et al., 2000). The temperature dependence of α-relaxation time was modelled using the Vogel-Tamman-Fulcher (VTF) relationship of Eq. (2-1) (Angell, 2008; Silalai & Roos, 2011a).

$$\tau_\alpha=A\exp[DT_0/(T-T_0)], \qquad (2\text{-}1)$$

where A, D and T_0 are constants.

2.8 Statistical analysis

Measurement of protein content, glass transition, and dynamic mechanical analysis were performed in duplicate, with all other analysis performed in triplicate. Results were expressed as mean ± standard deviations (SD). One-way analysis of variance (ANOVA) was used to determine the significant differences between the mean values of each test (Microsoft Office Excel 2010, Microsoft, Inc., WA, USA). A significance level of $P < 0.05$ was used throughout the study.

3. Results and discussion

3.1 Powder characterisation

Two kinds of lactose/MPI solids systems with different size particles were prepared by spray drying (Table 2-1). Particles of S-lactose/MPI solids systems spray-dried by a BÜCHI Mini Spray dryer B-191 had small particle size (d_{50}: 6-7 μm), while those of L-lactose/MPI solids systems spray-dried by an ANHYDRO

single stage spray dryer had large particle size (d_{50}: lactose: 24.95 μm; lactose/MPI mixtures: 40-50 μm).

Table 2-1 Physical characteristics of L- and S-lactose/MPI solids systems

Systems	Protein Content (%)	Lactose Content (%)	d_{50} (μm)	$(d_{90}-d_{10})/d_{50}$	SSA (m^2/kg)
L-Lactose	0	100	24.95±0.25	1.89±0.21	678.25±2.25
L-Lactose/MPI 4:1	20.48±0.63	78.95±0.12	40.90±0.01	1.68±0.15	234.85±0.95
L-Lactose/MPI 1:1	46.54±0.36	51.79±0.42	44.85±0.15	1.50±0.24	196.65±0.04
L-Lactose/MPI 1:4	74.59±0.11	20.52±0.29	49.20±0.50	1.56±0.35	182.75±2.75
S-Lactose	0	100	6.73±0.09	7.06±0.78	2389±2.00
S-Lactose/MPI 4:1	20.32±0.37	79.21±0.26	7.41±0.02	2.25±0.04	2131±36.00
S-Lactose/MPI 1:1	46.97±0.17	52.03±0.52	7.11±0.10	2.04±0.18	2047±25.00
S-Lactose/MPI 1:4	73.98±0.38	20.96±0.15	6.70±0.02	2.46±0.17	2220±17.00

[1] Values are mean ± standard deviation (protein content: n = 2; for the other values, n = 3).
[2 a-g] Values within columns with different superscripts are significantly different ($P < 0.05$).

As SSA values are typically inferred from particle size data (Crowley et al., 2014a), SSA is increased as the particle size becomes small. L-lactose/MPI solids systems had much smaller SSA values than S-lactose/MPI solids systems. The ratios of SSA values for L-lactose/MPI solids systems and S-lactose solids systems were only between 8.2-28.3%. The ratio decreased with decreasing lactose content. The difference in their SSA values might affect their water sorption behaviour.

3.2 Particle shape

The particle shape of L- and S-lactose/MPI solids systems was also investigated. Three morphological characteristics (circularity, elongation and convexity) were used to identify the particle shape of L- and S-lactose/MPI solids systems (Table 2-2).

Table 2-2 Particle shape parameters of L- and S-lactose/MPI solids systems

Systems	Circularity	Elongation	Convexity
L-lactose	$0.8810^{c} \pm 0.0050$	$0.1970^{e} \pm 0.0085$	$0.9923^{b} \pm 0.0005$
L-lactose/MPI 4:1	$0.9050^{b} \pm 0.0022$	$0.1773^{f} \pm 0.0039$	$0.9933^{b} \pm 0.0005$
L-lactose/MPI 1:1	$0.9340^{a} \pm 0.0057$	$0.1300^{g} \pm 0.0059$	$0.9960^{a} \pm 0.0008$
L-lactose/MPI 1:4	$0.9393^{a} \pm 0.0086$	$0.1177^{g} \pm 0.0106$	$0.9960^{a} \pm 0.0008$
S-Lactose	$0.7815^{f} \pm 0.0055$	$0.3140^{a} \pm 0.0010$	$0.9865^{c} \pm 0.0015$
S-lactose/MPI 4:1	$0.8120^{d} \pm 0.0040$	$0.2840^{b} \pm 0.0050$	$0.9865^{c} \pm 0.0005$
S-lactose/MPI 1:1	$0.8090^{d} \pm 0.0020$	$0.2715^{d} \pm 0.0005$	$0.9815^{d} \pm 0.0035$
S-lactose/MPI 1:4	$0.7900^{e} \pm 0.0010$	$0.2740^{c} \pm 0.0000$	$0.9825^{d} \pm 0.0005$

[1] Values are mean ± standard deviation (n = 3).
[2 a-g] Values within columns with different superscripts are significantly different ($P < 0.05$).

The circularity and convexity of L-lactose/MPI solids systems increased with decreasing lactose content, while the elongation decreased with decreasing lactose content. However, S-lactose/MPI solids systems did not show the similar results. Lactose and lactose/MPI mixtures with small size particles showed similar circularity and convexity, while the elongation decreased with decreasing lactose content. Moreover, compared to dairy solids with same composition, dairy solids with small size particles showed 11-16% smaller circularity values and 13-18% larger elongation values than dairy solids with large size particles (Table 2-2). These results indicated that particles of L-lactose/MPI solids systems had more rounded shape and smoother surface compared to S-lactose/MPI solids systems with small size particles. Previous studies have indicated that particle shape often influences the final product performance, such as flowability, abrasive efficiency, and bio-availability (Bumiller et al., 2002; Fu, et al., 2012). According to their studies, powders consisting of regularly shaped particles flow better than those consisting of irregular shaped particles. Moreover, the more the particles are in a powder resemble spheres, the better the powder flows. Coarse powders in general have better flow properties than fine powders.

3.3 Water sorption and lactose crystallization

Water content of L- and S-lactose/MPI solids systems after equilibration at different water activities are given in Table 2-3. S-lactose/MPI solids systems sorbed 5-30% larger amount of water than S-lactose/MPI solids systems after equilibration at the same storage conditions.

Table 2-3 Water content (g/100 g of dry solids) of L- and S-lactose/MPI solids systems equilibration over saturated salt solutions at room temperature (25 ºC) for 168 h.

Systems	0.11 a_w	0.23 a_w	0.33 a_w	0.44 a_w
L-lactose	$2.00^{e} \pm 0.08$	$3.88^{e} \pm 0.06$	$6.16^{d} \pm 0.12$	$9.25^{b} \pm 0.10$
L-lactose/MPI 4:1	$1.99^{e} \pm 0.02$	$3.43^{f} \pm 0.03$	$5.23^{f} \pm 0.03$	$7.42^{f} \pm 0.70$
L-lactose/MPI 1:1	$2.60^{d} \pm 0.02$	$4.09^{e} \pm 0.03$	$5.76^{e} \pm 0.06$	$7.82^{e} \pm 0.05$
L-lactose/MPI 1:4	$3.47^{ab} \pm 0.08$	$5.15^{b} \pm 0.07$	$6.70^{c} \pm 0.00$	$8.20^{d} \pm 0.11$
S-lactose	$2.75^{c} \pm 0.05$	$4.49^{d} \pm 0.02$	$6.79^{bc} \pm 0.02$	$10.21^{a} \pm 0.09$
S-lactose/MPI 4:1	$3.30^{b} \pm 0.01$	$5.07^{c} \pm 0.05$	$6.92^{b} \pm 0.05$	$9.43^{a} \pm 0.10$
S-lactose/MPI 1:1	$3.39^{b} \pm 0.09$	$5.06^{c} \pm 0.21$	$6.68^{c} \pm 0.30$	$8.78^{c} \pm 0.26$
S-lactose/MPI 1:4	$3.75^{a} \pm 0.04$	$5.59^{a} \pm 0.19$	$7.05^{a} \pm 0.26$	$8.71^{c} \pm 0.27$

[1] Values are mean ± standard deviation (n = 3).
[2 a-f] Values within columns with different superscripts are significantly different ($P < 0.05$).

Similar result was also stated by Haque and Roos (2004b). They showed that fine powders sorbed more water than coarse powders at RH ≤ 33%. The large SSA values of S-lactose/MPI solids systems might be one of the reasons that S-lactose/MPI solids sorbed larger amount of water during equilibration. Larger surface area of particles meant more area for water molecular. It is also possible that hydrogen bonding between molecules varies, depending on particle size and affects water sorption (Haque & Roos, 2004b). The other possible reason might be the difference in their particle shapes. Particles of S-lactose/MPI solids systems had rougher surface (Table 2-2), which might be easier for water sorption. In addition, L-

lactose/MPI (4:1) mixture sorbed lower amount of water than L-lactose at 0.11 a_w and 0.23 a_w, while S-lactose/MPI (4:1) mixture showed the opposite result. These results indicated that particle size of dairy solids was one of the factors which could affect water sorption properties.

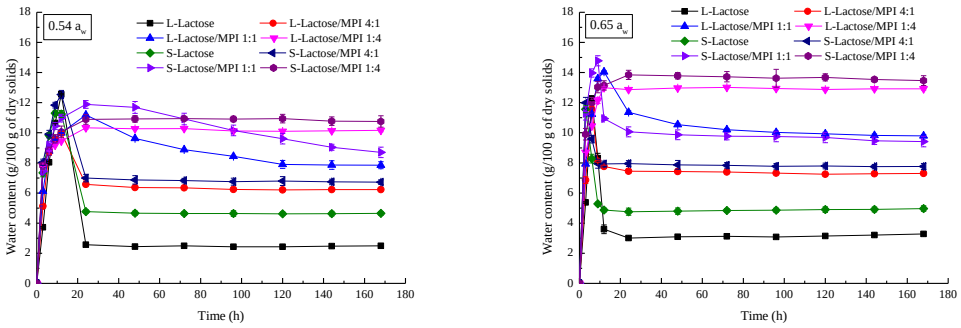


Figure 2-1 Lactose crystallization of L- and S-lactose/MPI solids systems equilibration at 0.54 a_w and 0.65 a_w at 25 °C for 168 h.

Sorbed water of L- and S-lactose/MPI solids systems decreased within 24 h at water activities > 0.44 as a result of lactose crystallization (Figure 2-1). The steady state water contents of L- and S-lactose/MPI solids systems at the end of lactose crystallization all increased with increasing protein content. Loss of sorbed water in pure L- and S-lactose, and L- and S-lactose/MPI (4:1) mixture occurred rapidly at 0.54 a_w, while the amount of sorbed water for L- and S-lactose/MPI mixtures at ratio 1:1 and 1:4 only showed minor decreases after equilibration at 0.54 a_w. These results indicated that milk protein retarded lactose crystallization of dairy solids, regardless of their particle size. Furthermore, compared to the samples with same ratios of lactose/MPI, dairy solids with small size particles showed higher steady water content at the end of lactose crystallization than those with large size particles. As a result, L-lactose showed the lowest steady water content (2.49 g/100 g of dry solids)

after equilibration, while S-lactose/MPI (1:4) mixture showed the highest steady water content (10.75 g/100 g of dry solids) after equilibration.

3.4 Glass transition

The glass transition temperatures for anhydrous and water plasticized L- and S-lactose/MPI solids systems were determined using a DSC (Table 2-4).

Table 2-4 Glass transition temperatures, T_g, and α-relaxation temperatures, T_α, for L- and S-lactose/MPI solids systems equilibration over saturated salt solutions at room temperature (25 ºC) for 168 h.

Systems		0 a_w	0.11 a_w	0.23 a_w	0.33 a_w	0.44 a_w
L-lactose	T_g	111 ± 0.0	73 ± 0.5	54 ± 0.0	35 ± 0.0	18 ± 0.5
	T_α	123 ± 0.5	122 ± 0.0	77 ± 0.0	51 ± 0.0	N/O
L-lactose/MPI 4:1	T_g	109 ± 0.0	72 ± 0.0	54 ± 0.0	36 ± 1.0	20 ± 0.5
	T_α	124 ± 1.0	124 ± 0.5	77 ± 0.0	52 ± 1.0	40 ± 0.5
L-lactose/MPI 1:1	T_g	110 ± 0.5	67 ± 0.0	51 ± 0.5	38 ± 0.0	21 ± 0.0
	T_α	129 ± 0.0	130 ± 1.0	73 ± 1.5	67 ± 0.5	45 ± 0.0
L-lactose/MPI 1:4	T_g	N/O	67 ± 0.5	50 ± 0.0	43 ± 0.0	33 ± 0.0
	T_α	N/O	N/O	69 ± 0.5	65 ± 1.0	61 ± 0.0
S-lactose	T_g	112 ± 0.5	68 ± 0.0	52 ± 0.5	34 ± 0.0	18 ± 0.0
	T_α	121 ± 1.0	121 ± 1.0	80 ± 0.5	57 ± 0.5	N/O
S-lactose/MPI 4:1	T_g	111 ± 1.0	63 ± 0.0	50 ± 0.5	35 ± 1.0	20 ± 0.5
	T_α	126 ± 1.0	122 ± 0.5	78 ± 0.5	60 ± 1.0	38 ± 0.5
S-lactose/MPI 1:1	T_g	115 ± 0.5	59 ± 1.0	49 ± 0.0	37 ± 0.5	22 ± 0.0
	T_α	130 ± 0.5	130 ± 1.0	78 ± 0.5	71 ± 0.5	49 ± 0.5
S-lactose/MPI 1:4	T_g	N/O	63 ± 0.5	50 ± 0.0	45 ± 1.0	37 ± 0.5
	T_α	N/O	N/O	73 ± 0.5	66 ± 0.5	66 ± 0.0

[1] Values are mean ± standard deviation (n = 2).

[2] N/O: Not observed.

For anhydrous lactose/MPI solids systems, the T_g values of S-lactose/MPI solids systems showed 1-5 ºC higher than those of L-lactose/MPI solids systems. However, the T_g values of S-lactose/MPI solids systems showed 2-9 ºC lower than those of L-

lactose/MPI solids systems after equilibration at 0.11 a_w, 0.23 a_w and 0.33 a_w (Table 2-4), which might be due to the higher water content of S-lactose/MPI solids systems (Table 2-3). But at 0.44 a_w, pure lactose and lactose/MPI mixtures at ratio 4:1 and 1:1 with different size particles showed similar T_g values, while S-lactose/MPI (1:4) mixture had a higher T_g value than L-lactose/MPI (1:4) mixture. These results indicated that particle size affected water sorption behaviour of dairy solids, which might result in the difference in their T_g values. Additionally, all T_g values of L- and S-lactose/MPI solids systems decreased with increasing water content, which showed typical water plasticization of dairy solids with amorphous lactose (Jouppila & Roos, 1994; Haque & Roos, 2004b; Schuck et al., 2005; Silalai & Roos, 2010a).

3.5 Mechanical properties

3.5.1 Modulus changes

Changes in physical properties of materials often occur around the glass transition, which also results in an α-relaxation (Roudaut et al., 2004; Silalai & Roos, 2011a, 2011b). Mechanical properties changes at and around glass transition are key factors in governing the functionality and stability of materials (Peleg, 1993). DMA is the most sensitive technique for monitoring relaxation events, such as glass transitions, as the mechanical properties change dramatically when relaxation behaviour is observed (Menard, 2008). The mechanical properties of L- and S-lactose/MPI solids systems were studied using a DMA (Figure 2-2). In this study, mechanical α-relaxation of L- and S-lactose/MPI solids systems occurred above the glass transition and was observed from a decrease in storage modulus and a peak in the loss modulus. At temperatures above the glass transition, large changes in viscoelastic properties were expected (Kasapis, 2001; Royall et al., 2005; Silalai & Roos, 2011b). The

storage modulus of L- and S-lactose/MPI solids systems decreased significantly in agreement with increasing loss modulus as a result of increasing molecular mobility at the glass transition region (Figure 2-2).

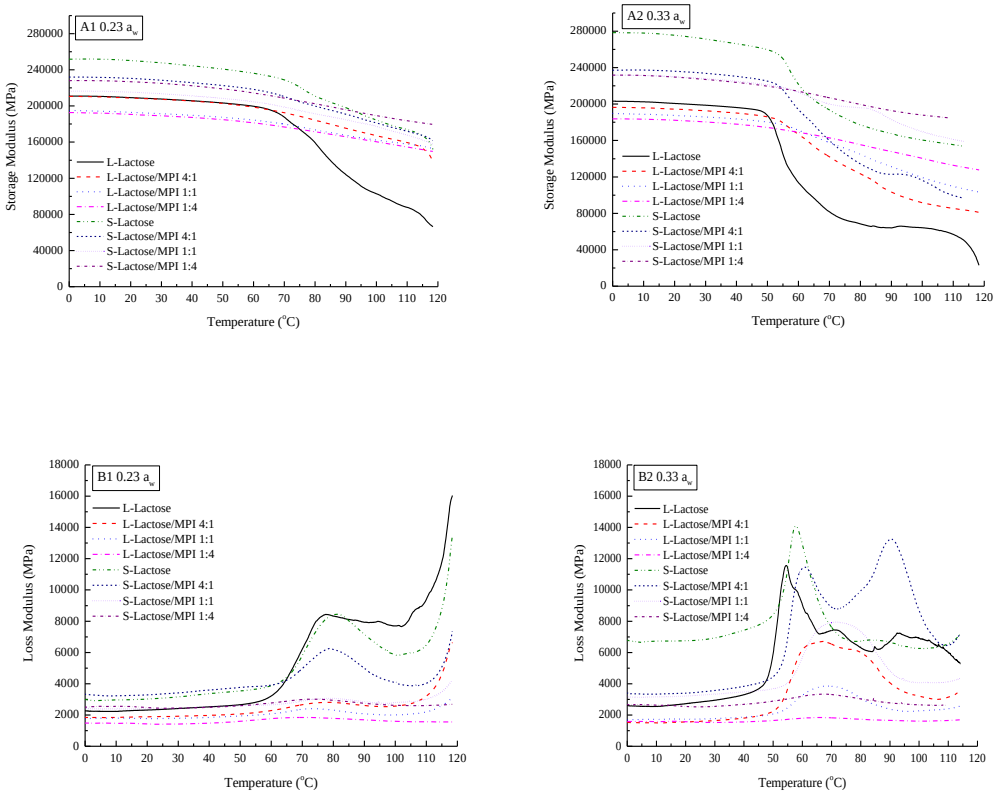


Figure 2-2 Storage modulus and loss modulus of L- and S-lactose/WPI solids systems after equilibration at 0.23 a_w and 0.33 a_w at 25 °C for 168 h.

The storage modulus of S-lactose/MPI solids systems was higher than that of L-lactose/MPI solids systems at 0.23 a_w and 0.33 a_w when temperature was below the glass transition temperatures (Figure 2-2 A1 and A2). The storage modulus for S-lactose/MPI solids systems at the glassy state increased when water content increased (Figure 2-2 A1 and A2). However, the storage modulus for L-lactose/MPI solids systems at the glassy state decreased with increasing water content. For the special case of unconstrained uniaxial tension or compression, Young's modulus can be as a measure of the stiffness of a material. In this study, the results of storage

modulus could reflect the changes of stiffness of L- and S-lactose/WPI solids systems. The results of storage modulus indicated that S-lactose/MPI solids systems had higher stiffness than those systems with larger size particles. Furthermore, the stiffness of S-lactose/MPI solids systems increased with increasing water content, while that of L-lactose/MPI solids systems decreased with increasing water content. Dairy solids, spray-dried by different spray dryers, might have different microstructure and hydrogen bonding between molecules, which resulted in the difference in their stiffness.

In addition, the magnitude of storage modulus change for L-lactose was around 30% and 20% higher than those for S-lactose from the glassy state to the rubbery state at 0.23 a_w and 0.33 a_w, respectively. According to Silalai and Roos (2010b), the magnitudes of modulus changes indicated mechanical α-relaxations which were relative to molecular mobility. Therefore, those results showed that L-lactose had higher molecular mobility than S-lactose at and above the glass transition temperatures. However, the storage modulus of L-lactose/MPI (1:4) mixture showed smaller change compared to S-lactose/MPI (1:4) mixture above the glass transition temperature at 0.23 a_w, while the opposite result occurred at 0.33 a_w. In addition, the magnitudes of storage modulus changes of S-lactose/MPI solids systems and L-lactose/MPI systems all increased with increasing water content, which meant water plasticization could increase molecular mobility of solids systems.

The loss modulus changes from the glassy state to the rubbery state for L- and S-lactose/MPI solids systems were also monitored using a DMA (Figure 2-2 B1 and B2). The loss modulus of L-lactose/MPI solids systems and S-lactose/MPI solids systems showed minor changes in the glassy state and the rubbery state, while they

showed dramatically change in the glass transition regions. The magnitudes of loss modulus changes for L-lactose/MPI solids systems and S-lactose/MPI solids systems were different. For pure lactose, the magnitude of loss modulus change of L-lactose was around 10-20% higher than that of S-lactose at 0.23 a_w and 0.33 a_w. However, for lactose/MPI mixtures, solids with larger size particles showed smaller magnitudes of loss modulus changes than solids with smaller size particles at 0.23 a_w and 0.33 a_w. Moreover, dairy solids with higher lactose content showed higher magnitudes of loss modulus change. Furthermore, increasing water content of L- and S-lactose/MPI solids systems could also result in a higher magnitude of loss modulus (Figure 2-2 B1 and B2). This was similar with the results of Silalai and Roos (2011b). They stated that the magnitudes of the drop in storage modulus and loss modulus peaks increased dramatically with increasing a_w. As higher magnitudes indicated a higher molecular mobility, particle size as well as amorphous lactose content and water content could affect the molecular mobility of solids systems.

3.5.2 Structural relaxation

The appearance of transitional mobility of molecular around the glass transition results in the frequency-dependent α-relaxation (Roudaut et al., 2004; Royall et al., 2005, Silalai & Roos, 2011b). In this study, the α-relaxation temperatures, T_α, were taken from the temperatures of loss modulus peak values determined at different frequencies. T_α values of L- and S-lactose/MPI solids systems at 0.23 a_w and 0.33 a_w are also shown in Table 2-4. Those T_α values were measured using a DMA at 1 Hz. L-lactose/MPI solids systems and S-lactose/MPI solids systems showed similar T_α values at 0 and 0.11 a_w. However, S-lactose/MPI solids systems showed higher T_α values at 0.23 a_w, 0.33 a_w and 0.44 a_w than L-lactose/MPI solids systems. Moreover,

T_α values of L- and S-lactose/MPI solids systems were also affected by water plasticization. Increasing water content made T_α shift to lower values.

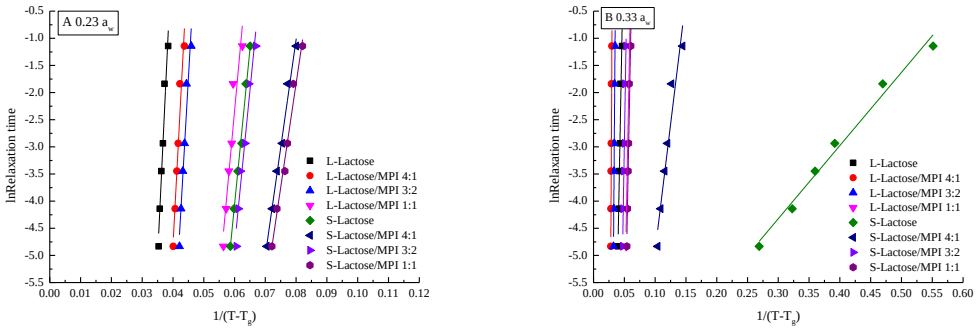


Figure 2-3 Plots of ln (relaxation time) against temperature difference 1/(T-T_g) for L- and S-lactose/MPI solids systems after equilibration at 0.23 a_w and 0.33 a_w at 25 °C for 168 h.

The temperature dependence of α-relaxation times of amorphous materials above the glass transition temperature can be described using the VTF relationship (Angell, 1991, 1997, 2002, 2008). The mechanical α-relaxations for L- and S-lactose/WPI solids systems at 0.23 a_w and 0.33 a_w were measured by multi-frequency mode using a DMA. The magnitude of mechanical α-relaxations and T_α values for L- and S-lactose/WPI solids systems decreased with increasing frequency (data not shown). Plots of ln (relaxation time) against 1/(T-T_g) gave a linear relationship with regression coefficients of 0.90-0.99. At 0.23 a_w, L-lactose/MPI solids showed higher (T_α-T_g) values than S-lactose/MPI solids for the corresponding relaxation, which meant the α-relaxation occurred at higher temperatures above the glass transition temperatures with increasing particle size (Figure 2-3 A). For pure lactose, S-lactose showed more significant change on (T_α-T_g) values than L-lactose, when water content increased (Figure 2-3 A and B). These results indicated that the viscosity and molecular mobility of dairy solids with smaller size particles had stronger

temperature dependence, and water plasticization had stronger effect on the structural relaxation of dairy solids with smaller size particles.

4. Conclusions

The particle size of lactose/MPI solids systems spray-dried by laboratory- and pilot-scale spray dryers was different. Morphological study indicated that particles of L-lactose/MPI solids systems had more rounded shape and smoother surface than those of S-lactose/MPI solids systems. Water sorption properties of dairy solids were not only governed by the composition of non-fat solids, but also influenced by particle size distribution. Moreover, compared to the samples with the same composition, dairy solids with small size particles showed higher steady water content at the end of lactose crystallization than those with large size particles. As particle size affected water sorption behaviour of dairy solids, different water contents of dairy solids resulted in difference in their T_g values. In addition, the storage modulus of S-lactose/MPI solids systems was higher than that of L-lactose/MPI solids systems at 0.23 a_w and 0.33 a_w when temperature was below the glass transition temperatures. Thus, the stiffness of S-lactose/MPI solids systems was higher compared to solids systems with large size particles at the amorphous state. Furthermore, the stiffness of S-lactose/MPI solids systems increased with increasing water content, while that of L-lactose/MPI solids systems decreased with increasing water content. L-lactose/MPI solids systems and S-lactose/MPI solids systems had similar T_α values at 0 and 0.11 a_w, while S-lactose/MPI solids systems had higher T_α values at 0.23 a_w, 0.33 a_w and 0.44 a_w than L-lactose/MPI solids systems. The molecular mobility of dairy solids with small size particles showed stronger

temperature dependence, and water plasticization had stronger effect on structural relaxation of dairy solids with smaller size particles.

CHAPTER THREE

Physical and mechanical properties of lactose/WPI mixtures: Effect of pre-crystallization

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Abstract

This study investigated the physical and mechanical properties of spray-dried lactose/whey protein isolate (WPI) (4:1) mixtures with different contents of α-lactose monohydrate (1.0%, 11.2%, 29.2%, and 46.8%, w/w). Particle size of samples with 11.2%, 29.2%, and 46.8% crystallinity was significantly ($P < 0.05$) larger compared to the sample with 1.0% crystallinity. The presence of less than 46.8% crystalline lactose in lactose/WPI mixtures had only a minor effect on water sorption behaviour at 0.11-0.44 a_w, whereas samples with higher crystallinity had higher stable water content after showing lactose crystallization. Moreover, samples with lower crystallinity showed higher initial sorption rates. Increasing the amount of crystalline lactose had no significant influence on the glass transition temperatures and the initial crystallization temperatures at 0.11-0.44 a_w. Furthermore, dairy powders with higher crystallinity had higher stiffness. Additionally, water plasticisation had a stronger effect on the structural relaxation of dairy powders with lower crystallinity.

Keywords: Pre-crystallization; Crystalline lactose; Glass transition; Mechanical properties; Structural relaxation

1. Introduction

The main carbohydrate in dairy powders is lactose (Arellano et al., 2004), which can exist in various crystalline and non-crystalline forms. The crystalline state is a solid state having molecules well arranged in regular lattice. According to Haque and Roos (2005), the main types of crystallised lactose are α-lactose monohydrate, anhydrous β-lactose, and anhydrous forms of α- and β-lactose in molar ratios of 5:3 and 4:1. Compared to lactose in the crystalline state, the molecular arrangement of lactose in the amorphous state is disordered. Moreover, amorphous lactose is thermodynamically unstable and hygroscopic, easily absorbing moisture from the surroundings and then plasticizing, while the crystalline lactose is thermodynamically stable and much less hygroscopic. These different state forms affect the behaviour of lactose and materials containing lactose, such as dairy powders (McSweeney & Fox, 2009). There has been considerable interest in amorphous components in dairy and pharmaceuticals industries. The presence of even small amounts of amorphous components can have a significant impact on the physico-chemical properties of materials, and subsequently alter product performance (Buckton & Darcy, 1996).

According to Bronlund and Paterson (2004) and Ibach and Kind (2007), the amorphous form of lactose has a much higher water content at a given humidity than the crystalline form and Hogan and Buckton (2001) stated that water sorption can be used to quantify the amorphous content of predominantly crystalline materials. In addition, Bronlund and Paterson (2004) indicated that the amount of water sorbed by crystalline powders at high water activity was dependent on the packing density of the powder particles, and small quantities of amorphous lactose present on crystalline powders caused significant changes to the water sorption behaviour.

In dairy powders, amorphous solids have a liquid-like structure with an extremely high viscosity. The amorphous residue will be changed to a nonequilibrium liquid state when temperature increases. Under the same thermodynamic conditions amorphous solids display higher molecular mobility than crystalline solids (Liu et al., 2006). The molecular mobility of the amorphous components is of great importance in determining the physical stability of food materials (Hancock et al., 1995). When the temperature increases from below to above the glass transition temperature (T_g), many of the physical properties of the amorphous materials show a rapid change, including increases in the free volume, molecular mobility, and dielectric coefficient. Additionally, large changes in viscoelastic properties of amorphous powders were expected above T_g (Jones, 1999; Kasapis, 2001; Royall et al., 2005). Crystallization of amorphous components in food products may enhance both physical and chemical stability (Berlin et al., 1968a, 1968b; Roos & Karel, 1991; Miao & Roos, 2004), and changing the crystallinity of lactose in dairy powders often affects product quality (Aguilar & Ziegler, 1994; Roos et al., 1999).

Water sorption behaviour, crystallization and glass transitions of amorphous lactose, amorphous lactose/protein systems and amorphous lactose/salts mixtures after freeze drying or spray drying have been widely studied (Berlin et al., 1968a, 1968b, 1970; Hermansson, 1977; Bandyopadhyay et al., 1987; Kaminaski & Al-Bezweni, 1994; Jouppila et al., 1997; Hogan & Buckton, 2001; Haque & Roos, 2004a, 2004b, 2005, 2006; Foster et al., 2005; Haque et al., 2006; Shrestha et al., 2007; Potes et al., 2012). Moreover, the amounts of crystalline lactose can affect the sorption behaviour of lactose powders significantly (Bronlund & Paterson, 2004). However, there has been no further study about the effects of crystalline lactose content on mechanical properties of dairy powders, which is essential for dairy

research and industry. The objectives of this study were to determine the influence of crystalline lactose content on physical and mechanical properties of lactose/whey protein isolate (WPI) mixtures.

2. Materials and methods

2.1 Materials

Powdered α-lactose monohydrate (> 99% purity) was offered by Arla Foods Ingredients (Sønderhøj 10-12, 8260 Viby J, Denmark). WPI, containing 71% β-lactoglobulin and 12% α-lactalbumin, was obtained from Davisco Food International (Le Sueur, MN, USA). Aluminum oxide calcined powder was purchased from Sigma−Aldrich (St. Louis, MO, USA).

2.2 Sample preparation

Lactose/WPI (4:1) mixtures at 40% (w/w) dry matter were prepared in de-ionized water at 65 °C in a water bath for 2 h with a stirring speed of 500 rpm. These solutions were kept at room temperature (20-22 °C) with a stirring speed of 150 rpm for 0, 3, 15 and 20 h pre-crystallization; these lactose/WPI mixtures were defined as S1, S2, S3 and S4, respectively, according to the pre-crystallization time. After pre-crystallization, samples were spray-dried using an ANHYDRO single stage spray dryer with a centrifugal atomizer (Copenhagen, Denmark). The inlet air temperature was around 170 °C, and the outlet temperature was around 90 °C. Spray-dried solids were immediately placed in evacuated desiccators over P_2O_5 at room temperature. Each analysis was carried out within 3 months after spray-drying.

2.3 Powder characterisation

2.3.1 Determination of α-lactose monohydrate content in spray-dried lactose/WPI mixtures

The content of α-lactose monohydrate (%Cº) in spray-dried lactose/WPI mixtures was determined according to the method of Schuck and Dolivet (2002) based on the difference between total water, determined using a Karl Fischer Titration (Mettler Toledo International Inc., Im Langacher Greifensee, Switzerland), and unbound water, determined by weight loss following 6 h drying of 1 g powder at 87 ºC. In this study, the content of α-lactose monohydrate (%Cº) was used to represent the crystallinity of lactose/WPI mixtures. It was assumed that there was no bound water in amorphous lactose. Each analysis was carried out in triplicate.

2.3.2 Light microscopy

Lactose crystals were observed with a polarized light microscope fitted with a ProgRes® camera system (JENOPTIK I Optical Systems, Jena, Germany). The lactose/WPI mixtures were spread on slides and one drop of sunflower oil was used to blend with the samples. Coverslips were then placed on the sample, which was observed with a 10× objective. Images were acquired using an Olympus BX51 light microscope (Olympus Optical Co. Ltd., Tokyo, Japan) with polarizer filters.

2.3.3 Powder characteristics

Protein content was determined using a FP 628 Nitrogen Determinator (LECO Corporation, Lakeview Avenue, St. Joseph, MI, USA). Lactose content was determined using an Automatic Polarimeter (Autopol 1, Rudolph Research Analytical, Hackettstown, NJ, USA). Water content was determined using an HR83 Halogen Moisture Analyzer (Mettler Toledo International Inc., Im Langacher Greifensee, Switzerland). All chemical analysis of powders was carried out

immediately after manufacture. Powder particle size distribution and specific surface area (SSA) were determined by laser light scattering using a Malvern Mastersizer 3000 (Malvern Instruments Ltd., Worcestershire, UK).

2.4 Water sorption and lactose crystallization

Water sorption for each powder was measured using the static gravimetric method and performed in triplicate. Approximately 1 g of spray-dried lactose/WPI mixtures was weighed into small glass vials (25 mL) and dried in a vacuum oven (OV-12, Medline Industries, Inc., Mundelein, IL, USA) at 45 °C for 48 h to remove residual water. After drying, all samples were equilibrated for 240 h in evacuated desiccators over different saturated salt solutions. These saturated salt solutions were LiCl, CH_3COOK, $MgCl_2$, K_2CO_3, $Mg(NO_3)_2$, and $NaNO_2$, which gave relative humidity (RH) of 11%, 23%, 33%, 44%, 54%, and 65%, respectively. All desiccators were placed at incubators with temperature of 25 °C during equilibration. The samples were weighed at 0, 3, 6, 9, 12 and 24 h, and then at 24-h intervals. Water content of each powder was measured as a function of time and the mean weight of triplicate samples was calculated.

The water sorption of lactose/WPI mixtures at 24 h was also monitored using a Multisample Dynamic Moisture Sorption SPS11-10μ (ProUmid GmbH & Co. KG, August-Nagel-Str. 23, Ulm, Germany). The measurement cycles were started at 11%, 23%, 33%, 44%, 54%, and 65% RH, respectively, and ended at 11%, 23%, 33%, 44%, 54%, and 65% RH, respectively. The time for one cycle was 24 h. The measurement temperature was 25 ± 0.1 °C. Sorption rate of spray-dried lactose/WPI mixtures was calculated according to the water sorption results:

Sorption rate = dw/dt (3-1)

Where *w* is water content, and *t* is time.

2.5 Differential scanning calorimetry

T_g (onset), and initial crystallization temperatures, (T_{ic}) of lactose/WPI mixtures were determined using a differential scanning calorimeter (DSC Q2000, TA Instruments, Crawley, UK). To determine the T_g values, dairy powders (1 g) were transferred to glass vials and dried in the vacuum oven at 45 °C for 48 h. The dehydrated powders were equilibrated in evacuated desiccators over P_2O_5 and saturated salt solutions of LiCl, CH_3COOK, $MgCl_2$, and K_2CO_3 for 168 h. Then 10 to 15 mg of equilibrated powders was transferred to Tzero pans (TA Instruments). The DSC pans were hermetically sealed with Tzero hermetic lids and samples were analysed. An empty pan was used as a reference. At the first scan, the samples were heated to at least 20 °C higher than the glass transition temperature region at 5 °C/min and then cooled at 10 °C/min to 0 °C; a second heating scan was then run to at least 100 °C higher than the glass transition temperature at 5 °C/min. Anhydrous samples were scanned using pans with punctured lids to allow evaporation of residual water during the measurements (Silalai & Roos, 2010a). At the first scan, the samples were heated at 5°C/min to 100 °C to evaporate residual water and then cooled at 10 °C/min to below glass transition. A second heating scan was then performed on the anhydrous powders to far above the glass transition temperature at 5 °C/min. All measurements were carried out in duplicate. T_g values were taken as the onset-point of the endothermic baseline shift. The T_g and T_{ic} values were determined using TA Universal analysis software, version 5.1.2 (TA Instruments).

2.6 Dynamic mechanical analysis

A Dynamic Mechanical Analyser (DMA Q800, TA Instruments) was used, in conjunction with a gas cooling accessory (GCA) tank, to determine the dynamic mechanical properties of lactose/WPI mixtures. A rectangular stainless steel powder holder was designed to generate a defined geometry to contain powder with inner dimensions of 60 mm × 11 mm × 1 mm. A pre-weighed mass of powder mixed with aluminum oxide calcined powder at the ratio 4:1 was evenly spread within this shallow container, and the upper lid was then placed onto the top surface of the powder (Mahlin et al., 2009). As aluminum oxide calcined powder had no influence on mechanical property results of dairy powders in the temperature range, it was added to protect dairy powder from sticking on the powder holder during the heating test. The sample holder was mounted in the instrument in a dual cantilever clamp during measurement. For anhydrous samples and samples equilibrated at 0.11 a_w, the measurements were made at a heating rate of 2 °C/min from 0 to 150 °C. For samples equilibrated at 0.23 a_w, 0.33 a_w and 0.44 a_w, the measurements were made at a heating rate of 2 °C/min from 0 to 120 °C. DMA was operated by a sinusoidal deformation applied to the powder sample holder at a fixed strain. The amplitude was 15 μm. During dynamic heating, the samples were analysed for storage modulus (E') and loss modulus (E'') using single frequency 1 Hz. Frequency of deformation (oscillating frequency) was changed in multiple frequencies of 0.5, 1, 3, 5, 10, and 20 Hz. The α-relaxation times were determined directly from the frequencies (f) using the relationship of Eq. (3-2) (Noel et al., 2000).

$$\tau_\alpha = 1/(2\pi f) \quad (3\text{-}2)$$

The temperature dependence of α-relaxation time was modelled using the Vogel-Tamman-Fulcher (VTF) relationship of Eq. (3-3) (Angell, 2008; Silalai & Roos, 2011a).

$\tau_\alpha = A\exp[DT_0/(T-T_0)]$, (3-3)

where A, D and T_0 are constants.

2.7 Statistical analysis

Measurement of protein content, glass transition, and dynamic mechanical analysis were performed in duplicate, with all other analyses performed in triplicate. Results were expressed as mean ± standard deviations (SD). One-way analysis of variance (ANOVA), followed by Tukey's test, was used to determine the significant differences between the mean values of each test (Microsoft Office Excel 2010, Microsoft, Inc., Redmond, WA, USA). A significance level of $P < 0.05$ was used throughout the study.

3. Results and discussion

3.1 Powder characterisation

The characteristics of lactose/WPI mixtures are shown in Table 3-1. Crystalline lactose content increased as the pre-crystallization time was increased (Table 3-1), yielding samples containing 1.0% (S1), 11.2% (S2), 29.2% (S3) and 46.8% (S4) crystalline lactose. The amount of crystalline lactose is defined as crystallinity of the samples in this study. The physical appearance of samples is shown in Figure 3-1. It was obvious that the amount of crystalline lactose increased from S1 to S4 with increasing pre-crystallised time, which further confirmed that the crystallinity of S1, S2, S3 and S4 was different. Lactose crystals were very hard and brittle and its

particle shape was different from that of amorphous lactose, which might affect the physical properties and flow properties of dairy powders.

Table 3-1 Powder characteristics of lactose/WPI (4:1) mixtures.

Systems	Crystallinity (%)	Protein content (%)	Lactose content (%)	Water content (%)	d_{50} (µm)	SSA (m^2 kg^{-1})
S1	1.0 ± 0.58	19.94 ±0.07	78.91 ± 0.02	2.47 ± 0.04	22.85^{c} ± 0.25	714.75^{a} ± 7.45
S2	11.2 ± 0.97	19.55 ± 0.04	79.03 ± 0.11	2.93 ± 0.16	25.35^{a} ± 0.05	629.95^{c} ± 0.85
S3	29.2 ± 0.92	19.45 ± 0.02	78.99 ± 0.06	2.45 ± 0.09	25.20^{ab} ± 1.20	682.10^{b} ± 9.30
S4	46.8 ± 1.11	19.66 ± 0.02	79.45 ± 0.09	2.53 ± 0.15	23.85^{b} ± 0.05	695.05^{b} ± 1.05

[1] [a-c] Values within columns with different superscripts are significantly different at $P < 0.05$.

[2] Values are mean ± standard deviation (protein content: n = 2; for the other values, n = 3).

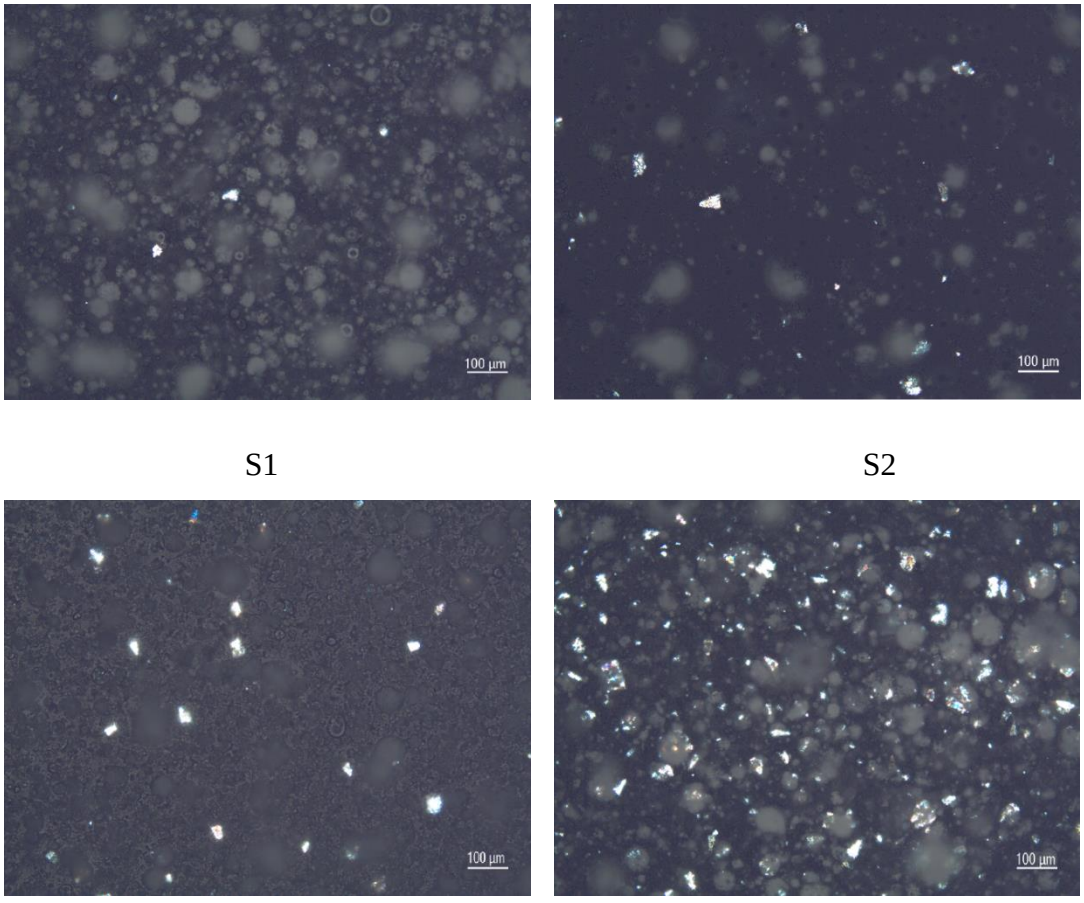


Figure 3-1 Images obtained by polarized light microscope for lactose/WPI (4:1) mixtures with 1.0 (S1), 11.2 (S2), 29.2 (S3) and 46.8 (S4) % crystallinity.

Protein and lactose contents for lactose/WPI mixtures were around 20% and 80%, respectively (Table 3-1). The particle size of S2, S3, and S4 was significantly larger than S1. However, there were only minor differences in the particle size between samples S2, S3, and S4. As specific surface area (SSA) values are typically inferred from particle size data, S1 with the smallest particle size had the largest SSA value. These results indicated that pre-crystallization before spray drying could increase the particle size of dairy powders. But the amount of crystalline lactose had only a minor effect on the particle size of powders. These differences in particle size and SSA values of dairy powders might affect their physical properties and functionality.

3.2 Water sorption and lactose crystallization

3.2.1 Water sorption

The experimental water contents of lactose/WPI mixtures with different crystallinity equilibration at various RH are shown in Table 3-2. In lactose/WPI mixtures, the water may be sorbed by proteins, amorphous lactose, crystalline lactose, with some bound as the water of crystallization 5% of mass of crystals. The amount of water sorbed by S2 with 11.2% crystallinity was significantly higher ($P < 0.05$) than those of S1 (1.0% crystallinity), S3 (29.2% crystallinity), and S4 (46.8% crystallinity) at water activity range of 0.11- 0.33 a_w, while S3 sorbed the highest amount of water at 0.44 a_w. S1, with the lowest crystallinity, did not sorb the highest amount of water at water activity range of 0.11- 0.44 a_w, but did sorb the highest amount of water at 0.54 a_w and 0.65 a_w before showing loss of sorbed water.

According to Bronlund and Paterson (2004), crystalline lactose sorbed very little water over the water activity range (0-0.85 a_w). However, the presence of crystalline lactose in lactose/WPI mixtures did not show significant effect on their water

sorption behaviour during equilibration (Table 3-2). It was assumed that the presence of WPI in dairy powders weakened the effect of crystalline lactose on water sorption behaviour of lactose/WPI mixtures. Previous studies also indicated that water contents sorbed by lactose/WPI mixtures were determined by water sorption behaviour of non-crystalline lactose and protein (Fan & Roos, 2015).

Table 3-2 Water content (g/100 g of dry solids) of lactose/WPI (4:1) mixtures with 1.0 (S1), 11.2 (S2), 29.2 (S3) and 46.8 (S4) % crystallinity after equilibration at 0.11-0.65 a_w at 25 °C for 240 h.

a_w	S1	S2	S3	S4
0.11	$2.48^{b} \pm 0.00$	$2.77^{a} \pm 0.03$	$2.54^{b} \pm 0.09$	$2.45^{b} \pm 0.03$
0.23	$4.13^{b} \pm 0.11$	$4.33^{a} \pm 0.05$	$4.26^{a} \pm 0.04$	$4.00^{c} \pm 0.04$
0.33	$5.94^{b} \pm 0.11$	$6.05^{a} \pm 0.05$	$6.04^{a} \pm 0.07$	$5.71^{c} \pm 0.05$
0.44	$8.69^{b} \pm 0.07$	$8.52^{c} \pm 0.02$	$8.76^{a} \pm 0.11$	$8.43^{d} \pm 0.05$
0.54	$5.68^{b} \pm 0.04$	$6.78^{a} \pm 0.32$	$6.85^{a} \pm 0.07$	$6.90^{a} \pm 0.06$
0.65	$7.17^{c} \pm 0.08$	$7.78^{b} \pm 0.13$	$7.85^{b} \pm 0.06$	$8.51^{a} \pm 0.05$

[1] [a-c] Values within rows with different superscripts are significantly different at $P < 0.05$.
[2] Values are mean ± standard deviation (n=3).

Sorbed water of lactose/WPI mixtures decreased within 24 h at $a_w > 0.44$ as a result of lactose crystallization (Figure 3-2). Loss of sorbed water occurred more rapidly at 0.65 a_w as compared to at 0.54 a_w, which was in agreement with the study of Haque and Roos (2004b). Since loss of sorbed water does not occur in crystalline lactose, S2, S3, and S4 showed higher amount of stable water after lactose crystallization than those of S1 without pre-crystallization at 0.54 a_w and 0.65 a_w (Figure 3-2). These results indicated that the crystallinity had minor influence on the water sorption behaviour of dairy powders containing protein at 0.11-0.44 a_w. However, dairy powders with higher crystallinity showed higher stable water content after lactose crystallization.

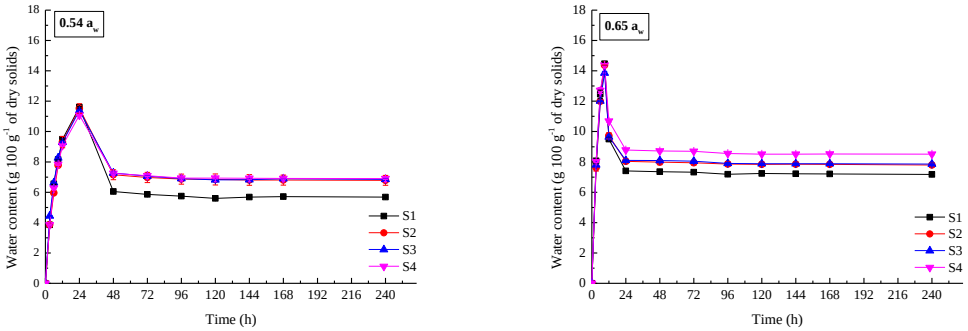


Figure 3-2 Lactose crystallization of at 0.54 a_w and 0.65 a_w at 25 °C lactose/WPI (4:1) mixtures with 1.0% (S1), 11.2% (S2), 29.2% (S3) and 46.8% (S4) crystallinity.

3.2.2 Sorption rate

Water sorption behaviour of lactose/WPI mixtures with different crystallinity was also measured using a Multisample Dynamic Moisture Sorption SPS11-10μ. Water sorption of lactose/WPI mixtures were near equilibrium within 24 h (raw data not shown). Using the water sorption results, sorption rates in the first hour of equilibration were calculated (Figure 3-3).

The sorption rates of lactose/WPI mixtures increased with increasing storage relative humidity (Figure 3-3 A-F). The sorption rates of lactose/WPI mixtures decreased and then arrived at constant values at 1 h (Figure 3-3), and the final constant sorption rates of S1, S2, S3 and S4 were not significantly different at 0.11 a_w (Figure 3-3 A). The sorption rates of S2 with 11.2% crystallinity were higher than those of S1, S3, and S4 at 0.23-0.65 a_w.

In addition, the initial sorption rates of lactose/WPI mixtures were divided into two groups, higher initial sorption rate group for S1 and S2 with lower crystallinity, and lower initial sorption rate group for S3 and S4 with higher crystallinity (Figure 3-3). It was obvious that the difference between two groups increased with increasing storage relative humidity. Therefore, the crystallinity affected the initial

sorption rate of the lactose/WPI mixtures significantly; samples with higher crystallinity had lower sorption rates.

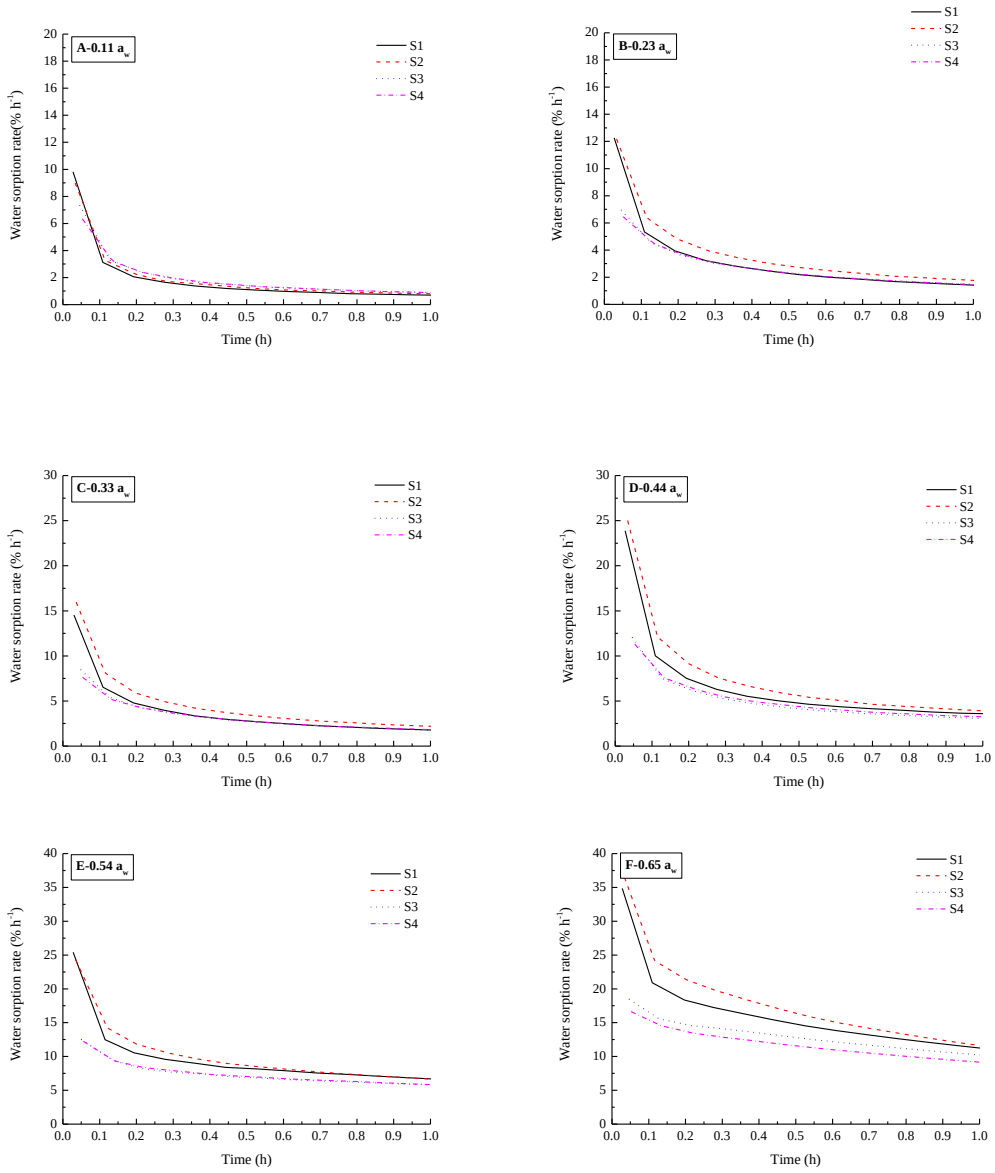


Figure 3-3 Sorption rate of lactose/WPI (4:1) mixtures with 1.0% (S1), 11.2% (S2), 29.2% (S3) and 46.8% (S4) crystallinity during equilibration at 0.11-0.65 a_w for 24 h at 25 °C.

3.3 Glass transition

The T_g and T_{ic} values for anhydrous and equilibrated lactose/WPI mixtures are shown in Table 3-3. It was obvious that the T_g values of lactose/WPI mixtures

decreased with increasing water content, which showed typical water plasticization of dairy powders containing amorphous lactose (Jouppila et al., 1997; Haque et al., 2006; Potes et al., 2012).

Table 3-3 Glass transition temperatures (T_g), initial crystallization temperatures (T_{ic}), and α-relaxation temperatures (T_α) of lactose/WPI (4:1) mixtures with 1.0 (S1), 11.2 (S2), 29.2 (S3) and 46.8 (S4) % crystallinity equilibrated at 0-0.44 a_w at 25 °C for 168 h.

Systems		**0 a_w**	**0.11 a_w**	**0.23 a_w**	**0.33 a_w**	**0.44 a_w**
S1	T_g	105 ± 0.5	71 ± 0.0	58 ± 0.5	40 ± 0.0	21 ± 0.5
	T_{ic}	N/O	127 ± 1.0	115 ± 0.5	94 ± 0.5	72 ± 0.0
	T_α	126.5 ± 0.4	126.6 ± 0.4	80.0 ± 0.3	70.6 ± 0.9	44.4 ± 1.1
S2	T_g	105 ± 0.0	70 ± 0.0	58 ± 0.5	40 ± 0.5	22 ± 0.0
	T_{ic}	N/O	125 ± 0.5	112 ± 0.0	92 ± 0.5	73 ± 0.5
	T_α	125.8 ± 0.1	125.1 ± 0.3	77.8 ± 0.7	66.4 ± 0.9	37.4 ± 0.9
S3	T_g	104 ± 0.5	70 ± 0.0	58 ± 1.0	39 ± 0.0	21 ± 0.0
	T_{ic}	N/O	126 ± 1.0	114 ± 0.5	93 ± 0.0	73 ± 0.5
	T_α	127.0 ± 0.3	127.0 ± 0.3	78.9 ± 0.3	61.0 ± 0.6	38.0 ± 0.9
S4	T_g	105 ± 0.0	70 ± 0.5	58 ± 0.0	38 ± 0.5	21 ± 0.5
	T_{ic}	N/O	127 ± 0.5	113 ± 0.5	93 ± 0.5	72 ± 0.0
	T_α	127.0 ± 0.4	126.3 ± 0.2	77.9 ± 0.5	62.0 ± 0.8	41.0 ± 0.9

[1] Values are mean ± standard deviation (n = 2).

[2] N/O: Not observed.

There was no significant difference in the T_g values of lactose/WPI mixtures with different levels of crystallinity at the same water activities. Therefore, the T_g values of lactose/WPI mixtures with different amount of crystalline lactose was primarily dependent on the amorphous lactose, which was in agreement with previous studies. According to previous studies (Silalai & Roos, 2010a; Potes et al., 2012; Fan & Roos, 2015), lactose-protein systems showed phase separation and their T_g values were dependent on amorphous lactose. The T_g values of lactose/WPI mixtures in this study were higher than those reported by Haque and Roos (2004a) and Fan and Roos

(2015) for lactose/WPI mixtures at corresponding water activities. As water content significantly affected T_g values of dairy powders, the differences in the T_g values between our study and other studies were probably a result of different water contents with equilibration at 0.11-0.44 a_w. Haque and Roos (2004b) have indicated that drying methods, storage time, and storage temperature could result in the differences in final water content of lactose/protein mixtures. In addition, the T_{ic} values of lactose/WPI mixtures also decreased with increasing water content (Table 3-3). Since lactose crystallization could be delayed by the presence of protein, the T_{ic} values of lactose/WPI mixtures was higher than that of pure lactose (Haque & Roos, 2004a; Zhou & Roos, 2012). Lactose/WPI mixtures with different amount of crystalline lactose showed similar T_{ic} values in the range of 0.11-0.44 a_w. Therefore, the amount of crystalline lactose showed no significant influence on the T_{ic} values of the lactose/WPI mixtures.

3.4 Mechanical properties

3.4.1 Modulus and stiffness

The physical properties of amorphous materials often change around the glass transition temperatures, which may result in an α-relaxation (Roudaut et al., 2004; Silalai & Roos, 2011a, 2011b). The mechanical properties of lactose/WPI mixtures with different amount of crystalline lactose were measured using a DMA. A loss of water occurred during dynamic measurements for dairy powders with lower water activities (a_w < 0.23), which was also reported by Silalai and Roos (2011b). Moreover, lactose/WPI mixtures showed lactose crystallization during storage at 0.54 a_w and 0.65 a_w. Therefore, the results of mechanical properties of lactose/WPI mixtures at 0.11 a_w, 0.54 a_w and 0.65 a_w are not shown.

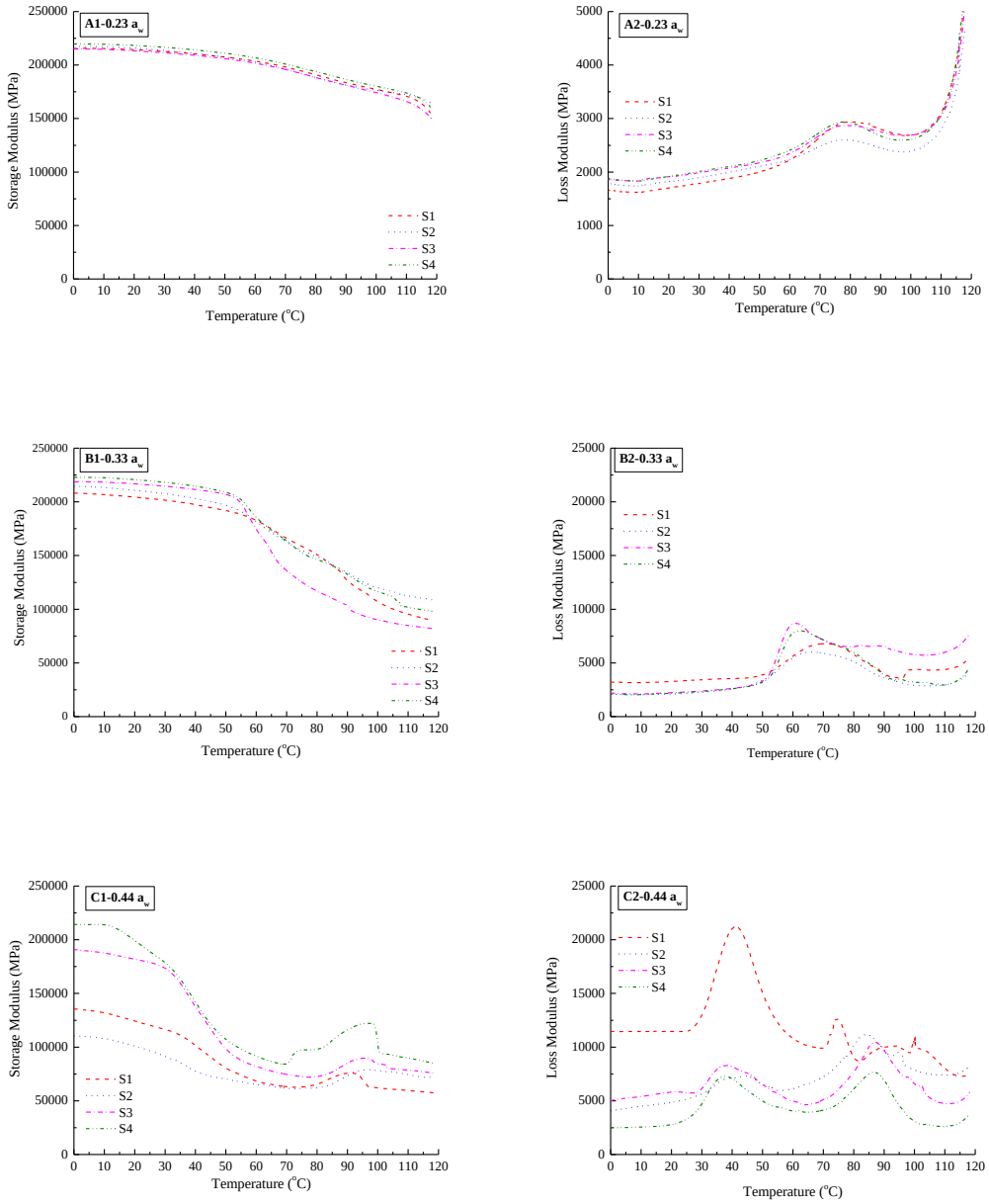


Figure 3-4 Storage modulus and loss modulus of lactose/WPI (4:1) mixtures with 1.0% (S1), 11.2% (S2), 29.2% (S3) and 46.8% (S4) crystallinity with equilibration at 0.23 a_w, 0.33 a_w, and 0.44 a_w at 25 °C for 168 h.

Mechanical α-relaxation of lactose/WPI mixtures occurred above T_g and was observed from a sharp decrease in their storage modulus and a peak in their loss modulus (Figure 3-4). The storage modulus shows the amount of energy that the material stores (Edward et al., 2014). Furthermore, the magnitudes of storage modulus and loss modulus changes are relative to molecular mobility (Roudaut et al.,

2004; Silalai & Roos, 2010a, 2011b). Sample S4, with the highest crystallinity, showed higher storage modulus than samples S1, S2, and S3 at the glassy state at 0.23-0.44 a_w (Figure 3-4 A1, B1, and C1). Additionally, the difference in storage modulus of lactose/WPI mixtures increased with increasing storage RH (Figure 3-4 A1, B1 and C1). At the glassy state, the storage modulus of lactose/WPI mixtures with lower crystallinity (S1 and S2) decreased significantly from 0.33 a_w to 0.44 a_w (Figure 3-4 B1 and C1). The storage modulus of S4 with 46.8% crystallinity showed the smallest change at the glassy state with increasing water content. These results indicated that the addition of crystalline lactose could maintain the stiffness of dairy powders when water content increased. This might be due to the different molecular mobility and free volume of amorphous and crystalline state lactose. According to Kilburn et al. (2004), the effect of water plasticization in carbohydrates solids is related to hydrogen bond formation and disruption, and also involves to the changes in free volume. Unlike amorphous structure, the crystalline state has molecules well arranged, which is in the favourable low energy state. Water plasticization had no significant effect on molecular mobility of crystalline lactose, and only exhibited a minor effect on the storage modulus of dairy powders with higher crystallinity. At the glass transition region, the storage modulus of lactose/WPI mixtures decreased significantly at 0.23 a_w, 0.33 a_w and 0.44 a_w as a result of increasing molecular mobility (Figure 3-4 A1, B1 and C1). A greater change in the storage modulus was experienced with lactose/WPI mixtures at 0.33 a_w and 0.44 a_w compared to at 0.23 a_w, which indicated that lactose/WPI mixtures with higher water content showed higher molecular mobility at the glass transition region. Therefore, the magnitude of the storage modulus changes of lactose/WPI mixtures were affected by the amount of

crystalline lactose and water. Dairy powders with higher crystallinity showed lower molecular mobility with increasing temperature.

Stiffness of materials refers to the ability to carry stress without changing dimension (Ebewele, 2000). For the measurement of unconstrained uniaxial tension or compression, Young's modulus can be used as a measure of the stiffness of a material. In this study, the change of storage modulus could reflect the change of stiffness of lactose/WPI mixtures. The changes of stiffness for lactose/WPI mixtures were directly related to the storage modulus when temperature increased from 0 to 120 °C at 1 Hz (the stiffness results were not shown). S4 with the highest crystallinity gave the largest storage modulus at 0.23 a_w, 0.33 a_w and 0.44 a_w (Figure 3-4 A1, B1 and C1), which meant S4 had the highest stiffness at 0.23 to 0.44 a_w. However, S1 and S2 with lower crystallinity showed lower stiffness at 0.33 a_w and 0.44 a_w. These results indicated that dairy powders with higher amount of crystalline lactose had higher stiffness, which might be due to the physical properties of crystalline lactose. As crystallinity is the result of a highly ordered arrangement of the lactose molecules, lactose crystals are very hard and stiff.

The changes of loss modulus for lactose/WPI mixtures with different crystallinity were also determined using a DMA. The loss modulus, E'', of lactose/WPI mixtures showed minor changes at the glassy state and the rubbery state, while they increased dramatically and arrived at the peak values in the glass transition region (Figure 3-4 A2, B2 and C2). This result could be explained from the point of mechanical internal friction (Guo et al., 2013). According to Guo et al. (2013), the chain segment motion of lactose and proteins molecules is in a frozen state when in the glassy state, and is in a free moving state when in the rubbery state. The chain segment motion changes from a frozen state to a free moving state during

the glass transition region. This change of motion leads to large internal loss. The internal friction loss approaches maximum as the temperature reaches glass transition temperature, which is reflected from the peak of loss modulus. Since the physical state of amorphous powders is strongly affected by the concentration of water, the peak values of loss modulus for lactose/WPI mixtures increased as water content was increased (Figure 3-4 A2, B2, and C2). Moreover, the loss modulus of lactose/WPI mixtures in the glassy state also increased with increasing water content, especially for S1 with the lowest crystallinity. Since the magnitude of loss modulus changes is also related to the molecular mobility, dairy powders with lower crystallinity showed higher molecular mobility as water content was increased.

3.4.2 Mechanical structural relaxation

In this study, the α-relaxation temperatures, T_α, were taken from the temperatures of loss modulus peak values at 1 Hz. T_α values of dairy powders shifted to lower temperatures with increasing water content (Table 3-3), which was in agreement with previous studies (Silalai & Roos, 2011b; Potes et al., 2012). Lactose/WPI mixtures with different crystallinity showed similar T_α values at 0 a_w and 0.11 a_w, while S1 with the lowest amount of crystalline lactose showed the highest T_α values at 0.23-0.44 a_w.

Furthermore, the mechanical α-relaxations for lactose/WPI mixtures at 0.23, 0.33, and 0.44 a_w were determined by multi-frequency mode using a DMA. The magnitude of mechanical α-relaxations for lactose/WPI mixtures decreased when frequency was increased (data not shown). Many studies have indicated that the Vogel-Tammann-Fulcher (VTF) relationship can be used to describe the temperature dependence of relaxation times for amorphous materials at temperatures above glass

transition (Angell, 1995, 2008; Angell et al., 2000; Silalai & Roos, 2011b; Potes et al., 2012).

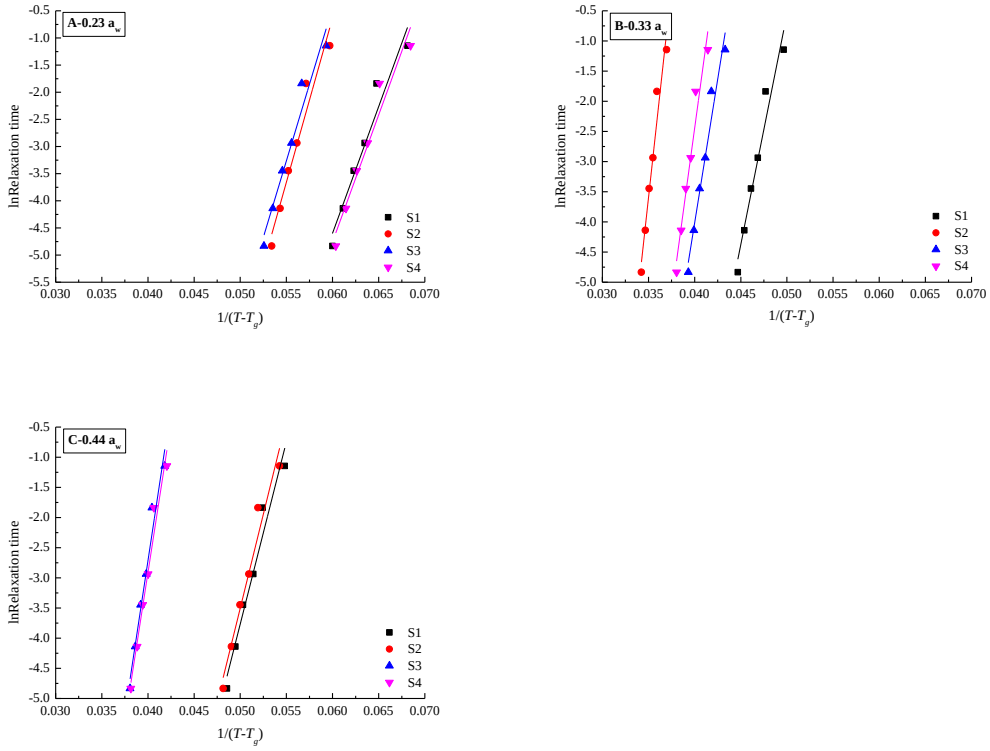


Figure 3-5 Plots of ln (relaxation time) against temperature difference $1/(T\text{-}T_g)$ for lactose/WPI (4:1) mixtures with 1.0% (S1), 11.2% (S2), 29.2% (S3) and 46.8% (S4) crystallinity during equilibration at 0.23 a_w, 0.33 a_w and 0.44 a_w at 25 °C for 168 h.

The VTF plots indicated that the T_α values of lactose/WPI mixtures at various frequencies were at higher temperatures with increasing frequency (Figure 3-5). Moreover, lower $T\text{-}T_g$ values were shown by S1 for the corresponding relaxation at 0.23-0.44 a_w, which meant α-relaxation of S1 occurred at lower temperatures above T_g values than those of S2, S3, and S4. Compared with the VTF plots at 0.23 a_w and 0.33 a_w (Figure 3-5 A and B), the α-relaxations of lactose/WPI mixtures occurred at higher $T\text{-}T_g$ values with increasing water content. Then the $T\text{-}T_g$ values of S1 and S2 decreased when a_w was increased from 0.33 to 0.44 (Figure 3-5 B and C), while those of S3 and S4 showed only minor changes. According to Liu et al. (2006), the

viscosity and molecular mobility of S1 and S2 with lower crystallinity might have strong temperature dependence. Thus, they exhibit larger changes on relaxation time in the vicinity of the glass transition than dairy powders with higher crystallinity. Therefore, water plasticisation had a stronger effect on the structural relaxation of dairy powders with lower crystallinity.

4. Conclusions

As crystalline lactose and amorphous lactose have different molecular arrangement, they show different behaviour in physical properties and functionality. Lactose/WPI mixtures with different amount of crystalline lactose were prepared by pre-crystallization. Particle size of dairy powders with 11.2%, 29.2%, and 46.8% crystallinity was significantly ($P < 0.05$) larger compared to dairy powder with 1.0% cyrstallinity. As physical properties, flowability and functionality of dairy powders are highly dependent on the particle size of powders, pre-crystallization could have a significant impact on the final properties of dairy powers. The presence of less than 46.8% crystalline lactose in dairy powders had only a minor effect on water sorption behaviour of dairy powder at 0.11-0.44 a_w. Dairy powders with higher crystallinity had higher stable water content after lactose crystallization. Furthermore, dairy powders with lower amount of crystalline lactose showed higher sorption rates at the beginning of water sorption. Increasing the amount of crystalline lactose in dairy powders did not have significant influence on the T_g and T_{ic} values. The mechanical property study indicated that lactose/WPI mixtures with higher amount of crystalline lactose had higher stiffness, and the addition of crystalline lactose could maintain the stiffness of dairy powders when water content is increased. In addition, water plasticisation had a stronger effect on the structural relaxation of dairy powders with lower amount of crystalline lactose. Since pre-crystallization of lactose is widely

used in the production of dairy powders, the findings of this study could be very useful in the dairy industry.

CHAPTER FOUR

Effects of water plasticization and lactose content on flow properties of model dairy solids

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Abstract

The flow properties of spray-dried solids depend on their composition and physical characteristics. This study investigated the influence of water plasticization and lactose content on flow properties of lactose/milk protein isolate (MPI) solids systems. Particle size (d_{50}) of lactose/MPI solids systems increased with decreasing lactose content, while pure lactose had the largest specific surface area (SSA). Particles of dairy solids with higher lactose content had less rounded shape and rougher surface. The T_g values of lactose/MPI mixtures (protein content $\leq$ 60%) showed only minor differences compared to the T_g values of pure lactose in this study. Mechanical study showed that the higher was the lactose content in dairy solids, the more significant was the change in their modulus at the glass transition region. Lactose/MPI mixtures with higher lactose contents showed better flowability at 0% and 44% relative humidity (RH), but they gave bigger friction angles after storage at 44% RH.

Keywords: Water plasticization; Lactose content; Glass transition; Mechanical properties; Flow properties

1. Introduction

Spray-dried dairy solids are very important ingredients in many food and dairy products. There is a need for information about handling and processing characteristics of spray-dried dairy solids. Flow properties of spray-dried dairy solids are very important in handling and processing operations (Knowlton et al., 1994; Fitzpatrick et al., 2007a). Food powders are commonly stored in bulk silos before packaging, dry-mixing with other powders or dehydration (Crowley et al., 2014b). Flow problems in hoppers, silos and transport containers are severe problems for engineers and process operatives (Marinelli & Carson, 1992; Fitzpatrick et al., 2007a).

The flow properties of powders depend on their composition and physical characteristics, such as particle size distribution, particle shape, surface structure, particle density, bulk density, water content and chemical composition (Kim et al., 2005; Schulze, 2007; Janjatović et al., 2012; Crowley et al., 2014b). Many food powders and food ingredient mixes are rendered complicated by the fact that they contain many different components, and this makes it difficult to predict their flow behaviour (Fitzpatrick et al., 2007a). Crowley et al. (2014a, 2014b) demonstrated that the composition and processing of milk protein concentrates across a range of protein concentrations resulted in powders with different physical characteristics, which, in turn, affected their flow properties. Previous study also indicated that the presence of free-fat on the powder surface was critical to the deterioration of dairy powder flowability (Kim et al., 2005). Fitzpatrick et al. (2007b) stated that the dominant compositional factors affecting the cohesiveness of dairy powders were moisture, amorphous lactose and state transitions.

In addition, stickiness of powder particles is responsible for impaired flow properties (Lazar et al., 1956). Stickiness and caking of powders result from formation of liquid bridges between individual particles (Peleg, 1977). Many studies have shown that powders with larger amounts of amorphous components are more sensitive to absorbing moisture (Le Meste et al., 2002; Liu et al., 2006; Fitzpatrick et al., 2007a, 2007b; Silalai & Roos, 2010a). High moisture levels affect flowability negatively, due to increased liquid bridging and capillary interactions between particles, which would result in lumping and caking problems for powders. Moreover, since amorphous solid has a kinetically frozen liquid-like structure and is not in a thermodynamic equilibrium state, amorphous materials exhibit increasing molecular mobility and rapidly decreasing viscosity above the glass transition (Roos & Karel, 1991; Champion et al., 2000; Roudaut et al., 2004). Several studies have confirmed that stickiness was controlled by the glass transition (Hennigs et al., 2001; Ozmen & Langrish, 2002; Silalai & Roos, 2011a). Furthermore, changes in mechanical α-relaxations of milk solids/maltodextrin systems are also associated with powder stickiness, which is also as a result of increasing molecular mobility above the glass transition of powder components (Silalai & Roos, 2011b). Thus, the content of amorphous lactose of dairy solids might affect their flow properties, as lactose causes caking and stickiness during storage and transportation.

However, there are only a few studies about the relationship between amorphous lactose content and flow function of dairy solids. The objectives of this study were to investigate the glass transition, mechanical properties and flow properties of lactose/milk protein isolate (MPI) solids systems, to have further study about the effect of water plasticization and amorphous lactose content on the flow properties of model dairy solids.

2. Materials and methods

2.1 Materials

α-lactose monohydrate (> 99% purity) and MPI were donated by Arla Foods Ingredients (Sønderhøj 10-12, 8260 Viby J, Denmark) and Kerry Ingredients & Flavours (Kerry Group, Tralee, Co. Kerry, Ireland), respectively. MPI contained ≥ 89% protein and ≤ 0.35% lactose. Aluminum oxide calcined powder (≥ 99% purity) was purchased from Sigma−Aldrich (St. Louis, MO, USA).

2.2 Preparation of lactose/MPI solids systems

Solution of lactose/MPI mixtures was prepared at room temperature while the solid concentration was 15% (w/w). They were lactose, lactose/MPI (4:1, 3:2, 1:1, 2:3, and 1:4) mixtures, and MPI. All sample solutions were spray-dried by an ANHYDRO spray dryer with a centrifugal atomizer (Copenhagen, Denmark) at the Teagasc Food Research Centre, Moorepark, Fermoy, Co. Cork, Ireland. The inlet air temperature was around 170 °C and the outlet temperature around 90 °C. Spray-dried dairy solids were kept immediately in evacuated desiccators over P_2O_5 at room temperature. Each analysis was carried out within 3 months after spray drying.

2.3 Powder characterisation

Protein content was determined using a FP 628 Nitrogen Determinator (LECO Corporation, Lakeview Avenue, St. Joseph, MI, USA). Lactose content was determined using an Automatic Polarimeter (Autopol 1, Rudolph Research Analytical, Hackettstown, NJ, USA). Water content was determined using an HR83 Halogen Moisture Analyser (Mettler Toledo International Inc., Im Langacher Greifensee, Switzerland). Ash content was determined after overnight incineration at

550 °C furnace. All chemical analysis of powders was carried out immediately after manufacture. Particle size distribution and specific surface area (SSA) of dairy solids systems were determined by laser light scattering using a Malvern Mastersizer 3000 (Malvern Instruments Ltd., Worcestershire, UK). Powder sample was added to the standard venturi disperser with a hopper gap of 2.5 mm and then fed into the dispersion system. Compressed air at 0.75 bar was used to transport and suspend the powder particles through the optical cell. A measurement time of 10 s was used, and background measurements were made using air for 20 s. The laser obscuration level was at 2-10%. Particle density was determined using a Gas Pycnometer (Accupyc II 1340 Gas Pycnometer, Micromeritics Instrument Corporation, Norcross, GA, USA).

2.4 Morphological characteristics

Morphological characteristics were determined using a Malvern Morphologi G3 S (Malvern Instruments Ltd., Worcestershire, UK). 5 mm^3 volume powder samples were dispersed on the glass plate. 2.5× objective was used for the measurement in this study. Circularity, convexity and elongation are three commonly used shape factors. One way to measure shape is to quantify how close the shape is to a perfect circle. Circularity is the ratio of perimeter of a circle with the same area as the particle divided by the perimeter of the actual particle image. Several definitions of circularity could be used but for accuracy the software reports HS Circularity (HS for high sensitivity) in addition to circularity. Circularity has values in the range 0-1. A perfect circle has a circularity of 1 while a ‘spiky’ or irregular object has a circularity value closer to 0. Circularity is sensitive to both overall form and surface roughness. Convexity is a measurement of the surface roughness of a particle. It is calculated by dividing the convex hull perimeter by the actual particle perimeter. A smooth shape has a convexity of 1 while a very ‘spiky’ or irregular object has a

convexity closer to 0. Elongation is defined as [1-aspect ratio] or [1- width/length]. As the name suggests, it is a measure of elongation and again has values in the range 0-1. A shape symmetrical in all axes, such as a circle or square, has an elongation value of 0; shapes with large aspect ratios have an elongation closer to 1. In this study, each sample was measured in triplicate to get the average value for circularity, convexity and elongation.

2.5 Powder preparation for flow function test

In order to study the flow properties of dairy solids with different water contents, two moisture levels of spray-dried dairy solids were prepared in a vacuum oven (OV-12, Meline Industries, Inc., Mundelein, Illinois, USA). For dairy solids with low moisture (LM) content, the powders were placed in a vacuum oven at 45 °C for 36 h. For dairy solids with high moisture (HM) content, spray-dried dairy solids were firstly dried at 45 °C in a vacuum oven for 36 h, and then equilibrated over saturated K_2CO_3 solution, giving 44% relative humidity, at 25 °C for 5 days in a vacuum oven. During equilibration, all powders were put in petri dishes with thickness around 10 mm. The final water content was measured in triplicate using an HR83 Halogen Moisture Analyser before measuring the flow properties.

2.6 Differential scanning calorimetry

Glass transition temperatures, T_g (onset), of spray-dried dairy solids were determined using a differential scanning calorimeter (DSC Q2000, TA Instruments, Crawley, UK). To determine the T_g, spray-dried solids (1 g) were transferred to glass vials and dried in a vacuum oven at 45 °C for 48 h. The dehydrated powders were equilibrated in evacuated desiccators over P_2O_5 and saturated salt solutions of LiCl, CH_3COOK, $MgCl_2$, and K_2CO_3 for 144 h. Then 10 to 15 mg of equilibrated powders

was transferred to DSC aluminium pans. The DSC pans were hermitically sealed and samples were analysed. An empty pan was used as a reference. At the first scan, the samples were heated over the glass transition temperature region at 5 °C/min and then cooled at 10 °C/min to below glass transition, a 2nd heating scan was then run to far above the glass transition temperature at 5 °C/min. Anhydrous samples were scanned using pans with punctured lids to allow evaporation of residual water during the measurements (Silalai & Roos, 2010a). At the first scan, the samples were heated at 5 °C/min to 100 °C and then cooled at 10 °C/min to below glass transition, a 2nd heating scan was then run to far above the glass transition temperature at 5 °C/min. The first scan was to evaporate the residual water, while the "anhydrous" state of powders during the rest heating scans was expected. T_g values of spray-dried solids with different moisture contents were determined using a DSC before flow function test. All measurements were carried out in duplicate.

2.7 Dynamic mechanical analysis

A Dynamic Mechanical Analyser (DMA Q800, TA Instruments, Crawley, UK) was used, in conjunction with a gas cooling accessory (GCA) tank, to determine dynamic mechanical properties of spray-dried dairy solids. A rectangular stainless steel powder holder was designed to generate a defined geometry to contain powder with inner dimensions of 60 mm × 11 mm × 1 mm. A pre-weighed mass of powder mixed with aluminum oxide calcined powder (4:1, w/w) was evenly spread within this shallow container, and the upper lid was then placed onto the top surface of the powder (Mahlin et al., 2009). As aluminum oxide calcined showed no influence on the mechanical results of dairy solids in the temperature range, it was added to protect dairy powder from sticking on the powder holder during the heating test. The

sample holder was mounted in the instrument in a dual cantilever clamp so that during measurement, the DMA oscillated the sample perpendicularly to the base plane of the sample holder by a vertical motion of the middle clamp. For anhydrous samples and samples equilibrated at 0.11 a_w, the measurements were made at a heating rate of 2 °C/min from 0 to 150 °C. For samples equilibrated at 0.23 a_w, 0.33 a_w and 0.44 a_w, the measurements were made at a heating rate of 2 °C/min from 0 to 120 °C. DMA was operated by a sinusoidal deformation applied to the powder sample holder at a fixed strain. The amplitude was 15 µm. During dynamic heating, the samples were analysed for storage modulus (E') and loss modulus (E'') using single frequency 1 Hz. All measurements were carried out in duplicate.

2.8 Powder flow testing

The flow properties of lactose/MPI solids systems were determined using a Powder Flow Tester (PFT) (Brookfield Engineering Laboratories, Inc., Middleboro, MA, USA). The axial and torsional speeds for the PFT were 1.0 mm/s and 1 rev/h, respectively. Samples were filled into the aluminium trough of the annular shear cell at room temperature (22-25 °C). Curved- or flat-profiled shaping blades were used to level the powder surface in the trough for flow- or wall fiction-testing, respectively. The mass of the powder was recorded before testing, with axial distance between the lid and the powder used to calculate changes in the volume of powder during testing. Vane- or flat-profiled lids were attached to compression plate of the PFT for flow- or wall friction-testing. Flowability, cohesion and bulk density were measured using standard flow function test. Friction angle was determined using standard wall friction test. For standard flow function test, the involved uniaxial normal stresses

were between 0.2 and 4.8 kPa. For standard wall friction test, ten normal stresses, between 0.4 and 4.8 kPa, were applied to measure the wall friction angles.

2.9 Statistical analysis

Measurement of protein content, glass transition, dynamic mechanical analysis, standard flow function test and wall friction test were performed in duplicate, with all other analyses performed in triplicate. Results were expressed as mean ± standard deviations (SD). One-way analysis of variance (ANOVA) was used to determine the significant differences between the mean values of each test (Microsoft Office Excel 2010, Microsoft, Inc., WA, USA). A significance level of $P < 0.05$ was used throughout the study.

3. Results and discussion

3.1 Powder characterisation

Protein contents ranged from 0 to 89.91%, and lactose contents were from 100 to 1.29% for lactose/MPI solids systems. The median particle size (d_{50}) of lactose/MPI solids systems increased with decreasing lactose content (Table 4-1). As specific surface area (SSA) values are typically inferred from particle size data, pure lactose gave the largest SSA value (Table 4-1). However, lactose/MPI (2:3) mixture had the lowest SSA while its median particle size (d_{50}) was not the largest one, which indicated that the difference in SSA values might not be only due to the difference in particle size alone, suggesting that alterations to surface morphology might have been a contributing factor (Crowley et al., 2014b).

Table 4-1 Physical properties of lactose/MPI solids systems

Systems	Protein Content (%)	Lactose Content (%)	Water content (%)	Ash Content (%)	d_{50} (μm)	SSA (m^2/kg)	ρ_p (g/cm^3)
lactose	0 ± 0.00	100 ± 0.00	3.47 ± 0.07	0.12 ± 0.01	24.95 ± 0.25	678.25 ± 2.25	1.22 ± 0.00
lactose/MPI 4:1	20.48 ± 0.50	78.95 ± 0.92	2.63 ± 0.13	1.56 ± 0.01	40.90 ± 0.10	234.85 ± 0.95	1.05 ± 0.02
lactose/MPI 3:2	36.92 ± 0.42	62.04 ± 0.23	3.25 ± 0.12	2.55 ± 0.02	40.70 ± 0.10	224.55 ± 0.45	1.05 ± 0.02
lactose/MPI 1:1	46.54 ± 0.51	51.79 ± 0.60	3.13 ± 0.10	3.28 ± 0.07	44.85 ± 0.15	196.65 ± 0.35	1.14 ± 0.04
lactose/MPI 2:3	56.95 ± 0.36	40.61 ± 0.52	2.35 ± 0.16	3.87 ± 0.02	49.50 ± 0.00	160.25 ± 0.65	1.21 ± 0.04
lactose/MPI 1:4	74.59 ± 0.48	20.52 ± 0.34	3.76 ± 0.09	5.05 ± 0.05	49.20 ± 0.50	182.75 ± 2.75	1.25 ± 0.05
MPI	89.91 ± 0.61	1.29 ± 0.00	4.53 ± 0.16	6.01 ± 0.04	50.90 ± 0.30	182.60 ± 0.50	1.28 ± 0.02

[1] Values are mean ± standard deviation (protein content: n = 2; for the other values, n = 3).

Particle size distribution has a major influence on the flow properties of dairy solids (Fitzpatrick et al., 2004). Fitzpatrick et al.(2004) stated that a significant disimprovement in flowability would be expected if the powder is reduced in size by an order of magnitude. According to Fitzpatrick et al. (2004), this reduction in flowability at smaller particle size was due to the increased surface area per unit mass of powder. More surface area is available for cohesive forces, in particular, and frictional forces to resist flow. Thus, the difference in particle size distribution and SSA values of spray-dried lactose/MPI solids systems might affect their flowability. For lactose/MPI mixtures, particle density increased with decreasing lactose content. This might be due to the decrease in the volume of occluded air with increasing protein content in lactose/MPI mixtures and MPI (Crowley et al., 2014b).

3.2 Particle shape

Three morphological characteristics (circularity, convexity, and elongation) were used to identify the particle shape of lactose/MPI solids systems. The circularity and convexity of lactose/MPI solids systems increased with decreasing lactose content, while the elongation decreased with decreasing lactose content (Table 4-2).

Table 4-2 Morphological characteristics of lactose/MPI solids systems

Systems	Circularity	Elongation	Convexity
Lactose	0.8810 ± 0.0050	0.1970 ± 0.0085	0.9923 ± 0.0005
Lactose/MPI 4:1	0.9050 ± 0.0022	0.1773 ± 0.0039	0.9933 ± 0.0005
Lactose/MPI 3:2	0.9283 ± 0.0045	0.1403 ± 0.0068	0.9950 ± 0.0000
Lactose/MPI 1:1	0.9340 ± 0.0057	0.1300 ± 0.0059	0.9960 ± 0.0008
Lactose/MPI 2:3	0.9347 ± 0.0062	0.1300 ± 0.0051	0.9960 ± 0.0008
Lactose/MPI 1:4	0.9393 ± 0.0086	0.1177 ± 0.0106	0.9960 ± 0.0008
MPI	0.9420 ± 0.0042	0.1213 ± 0.0090	0.9970 ± 0.0000

[1] Values are mean ± standard deviation (n = 3).

These results indicated that particle shape of lactose/MPI solids systems with higher amount of lactose had less rounded shape and rougher surface. Particle shape often has a significant influence on final product performance parameters such as flowability, abrasive efficiency, bio-availability, etc. Powders consisting of regularly shaped particles flow better than those consisting of irregular shaped particles. Moreover, the more the particles in a powder resemble spheres, the better the powder flows. Coarse powders in general have better flow properties than fine powders. Consequently, the difference in particle shape of lactose/MPI solids systems might be linked to the flow properties of spray-dried dairy solids.

3.3 Glass transition

Glass transitions for anhydrous and water plasticized lactose and lactose/MPI mixtures were determined using a DSC. Lactose/MPI mixtures showed slightly lower T_g values than pure lactose at 0.11 a_w and 0.23 a_w (Table 4-3). However, at 0.33 a_w and 0.44 a_w, lactose/MPI mixtures showed slightly higher T_g values than pure lactose. The lower T_g values of lactose/MPI mixtures might be related to the change in water sorption properties.

Pure lactose sorbed less water during storage at $a_w \leq 0.23$ and more water at 0.33 a_w and 0.44 a_w. Haque and Roos (2004b) also showed similar results. They stated that T_g of lactose/protein mixtures were lower than T_g of pure lactose in humidified samples at a_w 0.23 and below, but slightly higher at 0.33 a_w and above (Haque & Roos, 2004b). In addition, T_g values of lactose and lactose/MPI mixtures decreased with increasing water content as shown in Table 4-3, which showed typical water plasticization of amorphous materials (Jouppila & Roos, 1994; Haque & Roos, 2004b; Schuck et al., 2005; Silalai & Roos, 2010a).

Table 4-3 Water content, *m*, glass transition temperatures, T_g, and α-relaxation temperatures, T_α, for spray-dried lactose and lactose/MPI mixtures with equilibration over saturated salt solutions at room temperature (25 °C) for 144 h.

Systems		0 a_w	0.11 a_w	0.23 a_w	0.33 a_w	0.44 a_w
Lactose	*m*	0 ± 0	2.00 ± 0.08	3.88 ± 0.06	6.16 ± 0.12	9.25 ± 0.10
	T_g	108 ± 0.0	73 ± 0.5	54 ± 0.0	35 ± 0.0	18 ± 0.5
	T_α	123 ± 0.5	122 ± 0.0	77 ± 0.0	51 ± 0.0	N/O
Lactose/MPI 4:1	*m*	0 ± 0	1.99 ± 0.02	3.43 ± 0.03	5.23 ± 0.03	7.42 ± 0.70
	T_g	109 ± 0.0	72 ± 0.0	54 ± 0.0	36 ± 1.0	20 ± 0.5
	T_α	124 ± 1.0	124 ± 0.5	77 ± 0.0	52 ± 1.0	40 ± 0.5
Lactose/MPI 3:2	*m*	0 ± 0	2.50 ± 0.02	4.04 ± 0.09	5.81 ± 0.06	8.14 ± 0.07
	T_g	109 ± 0.5	70 ± 0.0	51 ± 0.0	36 ± 0.5	20 ± 1.0
	T_α	128 ± 1.0	126 ± 0.5	76 ± 0.0	68 ± 1.5	38 ± 0.5
Lactose/MPI 1:1	*m*	0 ± 0	2.60 ± 0.02	4.09 ± 0.03	5.76 ± 0.06	7.82 ± 0.05
	T_g	110 ± 0.5	67 ± 0.0	51 ± 0.5	38 ± 0.0	21 ± 0.0
	T_α	129 ± 0.0	130 ± 1.0	73 ± 1.5	67 ± 0.5	45 ± 0.0
Lactose/MPI 2:3	*m*	0 ± 0	2.68 ± 0.06	4.31 ± 0.02	5.99 ± 0.01	7.65 ± 0.02
	T_g	109 ± 0.5	67 ± 0.0	51 ± 0.0	37 ± 0.0	22 ± 0.0
	T_α	N/O	N/O	70 ± 0.5	64 ± 0.0	64 ± 0.5
Lactose/MPI 1:4	*m*	0 ± 0	3.47 ± 0.08	5.15 ± 0.07	6.70 ± 0.00	8.20 ± 0.11
	T_g	N/O	67 ± 0.5	50 ± 0.0	43 ± 0.0	33 ± 0.0
	T_α	N/O	N/O	69 ± 0.5	65 ± 1.0	61 ± 0.0
MPI	*m*	0 ± 0	3.91 ± 0.04	5.83 ± 0.12	7.59 ± 0.23	9.20 ± 0.12
	T_g	N/O	N/O	N/O	N/O	N/O
	T_α	N/O	N/O	66 ± 0.5	59 ± 0.0	65 ± 0.0

[1] *m*= water content (g/100g dry solids).
[2] T_g= onset temperature (°C).
[3] Values are mean ± standard deviation (*m* values: n = 3; T_g and T_α values: n = 2).
[4] N/O: Not observed.

Lactose/MPI solids systems showed difference in the glass transition temperatures after storage at 0% and 44% RH (Table 4-4). Water plasticization depressed the glass transition temperatures of lactose and lactose/MPI mixtures. Fitzpatrick et al. (2007b) stated that glass transition of lactose had a major influence on the development of cake strength and it was influencing the initial development of cake strength.

3.4 Dynamic mechanical properties

The mechanical properties of dairy solids storage at 0% and 44% RH were investigated using a DMA. The changes of mechanical properties at and around their glass transition are key factors in their functionality and stability (Peleg, 1993). DMA is the most sensitive technique for monitoring relaxation events, such as glass transitions, as the mechanical properties change dramatically when relaxation behaviour is observed (Menard, 2008). In the present study, mechanical α-relaxation of lactose/MPI solids systems occurred above the glass transition and was observed from a decrease in storage modulus and a peak in the loss modulus (Figure 4-1).

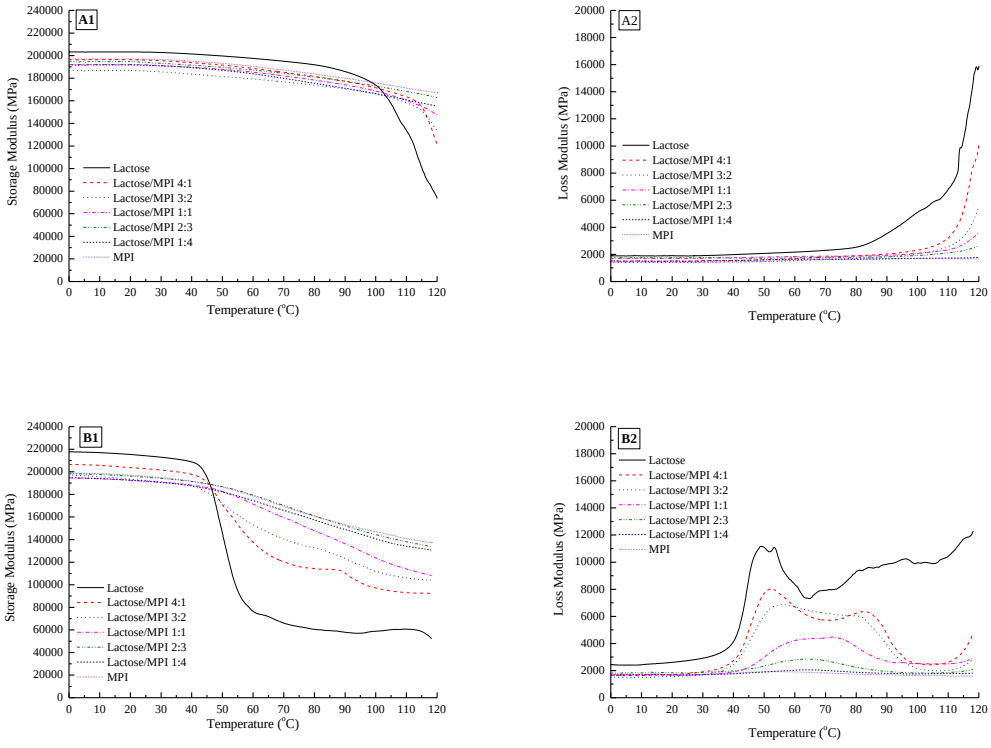


Figure 4-1 Storage modulus and loss modulus for lactose/MPI solids systems with low moisture (LM) content (A1 and A2) and high moisture (HM) content (B1 and B2).

Table 4-4 Water content, *m*, glass transition temperature, T_g, α-relaxation temperature, T_α and flow index values of lactose/MPI solids systems storage at 0% RH and 44% RH.

System	***m* (%)**		**T_g (ºC)**		**T_α(ºC)**		**Flow index**	
	LM	HM	LM	HM	LM	HM	LM	HM
lactose	1.50 ± 0.05	5.29 ± 0.31	73 ± 0.0	32 ± 0.0	121 ± 0.5	46 ± 0.0	5.88 ± 0.12	4.55 ± 0.05
lactose/MPI 4:1	1.89 ± 0.34	5.86 ± 0.09	74 ± 0.0	31 ± 0.5	125 ± 1.0	52 ± 0.0	9.09 ± 0.10	6.67 ± 0.13
lactose/MPI 3:2	1.96 ± 0.15	6.43 ± 0.06	73 ± 0.5	29 ± 0.0	125 ± 0.5	55 ± 0.0	9.09 ± 0.09	6.25 ± 0.00
lactose/MPI 1:1	2.24 ± 0.16	5.93 ± 0.12	75 ± 0.5	31 ± 0.5	130 ± 0.0	64 ± 0.5	5.88 ± 0.13	5.00 ± 0.05
lactose/MPI 2:3	2.19 ± 0.14	5.91 ± 0.07	76 ± 0.5	31 ± 0.0	N/O	64 ± 0.5	5.26 ± 0.04	4.55 ± 0.03
lactose/MPI 1:4	2.22 ± 0.13	6.37 ± 0.09	73 ± 0.0	44 ± 0.5	N/O	64 ± 0.0	4.35 ± 0.21	4.17 ± 0.03
MPI	3.06 ± 0.01	7.53 ± 0.19	N/O	N/O	N/O	51 ± 0.0	4.00 ± 0.00	4.17 ± 0.05

[1] Values are mean ± standard deviation (Water content: n = 3; T_g, T_α, and flow index values: n = 2).

[2] N/O: Not observed.

At temperatures above the glass transition, large changes in viscoelastic properties were expected (Royall et al., 2005; Silalai & Roos, 2011b; Roos, 2013). The storage modulus of spray-dried dairy solids decreased slowly in the amorphous state at the beginning of heating (Figure 4-1 A1 and B1). However, in the glass transition region, the storage modulus dropped sharply from the original value at the glassy state to the value at the rubbery state (Figure 4-1 A1 and B1). The magnitudes of modulus changes indicated mechanical α-relaxations which were relative to molecular mobility (Roudaut et al., 2004; Silalai & Roos, 2011b). The magnitudes of storage modulus for lactose/MPI solids systems with higher lactose content showed more significant change at the glass transition region (Figure 4-1 A1 and B1). However, the storage modulus of dairy solids with lower lactose contents showed a smaller decrease and remained at a higher level at the rubbery plateau. These results indicated that the magnitude of the modulus change of lactose/MPI solids systems was relative to the ratio of lactose/MPI mixtures. In addition, all dairy solids sorbed much water from air during storage at 44% RH (Table 4-4). Water, acting as a plasticizer in lactose/MPI solids systems, could increase the free volume between the molecules and decrease the T_g values (Figure 4-1 A1 and B1). The plasticization effect of water in carbohydrates is via a complex mechanism involving both hydrogen bond formation and disruption and changes in the matric free volume (Kilbrum et al., 2004).

Stiffness refers to the ability to carry stress without changing dimension (Ebewele, 2000). For the special case of unconstrained uniaxial tension or compression, Young's modulus can be as a measure of the stiffness of a material. In this study, the change of storage modulus could reflect the change of stiffness for dairy solids. The stiffness of spray-dried dairy solids showed the same trend as the change of storage

modulus when temperature increased from 0 to 120 °C. Pure lactose showed the highest stiffness at the glassy state after equilibration at 0 and 44% RH, while dairy solids with lower lactose content had higher stiffness at and above the glass transition temperatures. Silalai and Roos (2011b) indicated the similar results. They stated that the addition of high molecular weight compounds, such as maltodextrins, could increase stiffness, and thus, reduce the molecular mobility of lactose molecules due to a high degree of association as observed from the small magnitudes of modulus changes.

The results of loss modulus are also shown in Figure 4-1 A2 and B2. The values of loss modulus for lactose/MPI solids systems with different water contents were small and had minor changes when they were in the amorphous state (Figure 4-1 A2 and B2). However, when they were in the glass transition region, the loss modulus of spray-dried dairy solids increased dramatically and reached the peak values. This result could be explained from the theory of mechanical internal friction (Guo et al., 2013). According to Guo et al. (2013), in the glassy state, the chain segment motion of lactose and proteins molecules is frozen. No relative slipping can occur between different chain segments, so the internal loss is very small, which was reflected in the minor change of loss modulus. In the rubbery state, the chain segment could move freely, so the internal loss is also small when the chain segment relatively slipped. In the glass transition region, the chain segment changes from the frozen state to the free moving state. The motion needs to overcome the larger friction leading to larger internal loss. The loss will approach maximum when the temperature reaches the glass transition region. Thus, the values of loss modulus are related to molecular mobility. In our study, the peak values of loss modulus for lactose/MPI solids systems decreased with decreasing lactose content (Figure 4-1 A2 and B2). Since the

magnitudes of modulus changes indicated mechanical α-relaxations which were relative to molecular mobility (Roudaut et al., 2004; Silalai & Roos, 2011b), lactose/MPI solids systems with larger amount of lactose showed higher molecular mobility when temperature was near T_g.

Moreover, in this study, the α-relaxation temperatures, T_α, were taken from the temperatures of loss modulus peak (Table 4-3). The T_α values of the systems were found to decrease when a_w increased. Dairy solids with higher lactose content had lower T_α values at 0.23 a_w and below, while they gave slightly higher T_α values at 0.33 a_w and above (Table 4-4). The lower T_α values of lactose/MPI mixtures might also be related to the change in water sorption properties. Pure lactose sorbed less water during storage at $a_w \leq 0.23$ and more water at 0.33 a_w and 0.44 a_w. Additionally, according to Hancock and Zografi (1977), the molecular mobility in lower molecular weight solids changes more rapidly near T_g. Therefore, its molecular arrangement or its configuration structure is broken down more rapidly as well at higher a_w (Hancock & Zografi, 1997).

3.5 Flow properties

Standard flow function test and wall friction test of lactose/MPI solids systems was conducted using a Powder Flow Tester. The flowability of powders is usually stress-dependent (Schulze, 2007). Flow function results showed that lactose/MPI solids systems were easy-flowing or cohesive depending on the major principle consolidating stress applied (< 12.5 kPa) (Figure 4-2). After storage at 0% RH, lactose/MPI mixtures at ratios 1:1 and 2:3, which were easy flowing at major principle consolidating stress > 2.7 kPa, were cohesive at major principle consolidating stress ≤ 2.7 kPa (Figure 4-2 A). For lactose/MPI (1:4) mixture and

MPI powders, major principle consolidating stress should be above 6 kPa to make them easy-flowing (Figure 4-2 A). Increasing moisture content of dairy solids impaired their flowability, especially for pure lactose (Figure 4-2 B). Lactose fell into cohesive region after placed at 44% RH at 25 °C for 5 days even when major principle consolidating stress was over 9 kPa. MPI powders without amorphous lactose showed no significant change in its flowability with increasing moisture content (Figure 4-2), which could also be seen from its flow index values (Table 4-4).

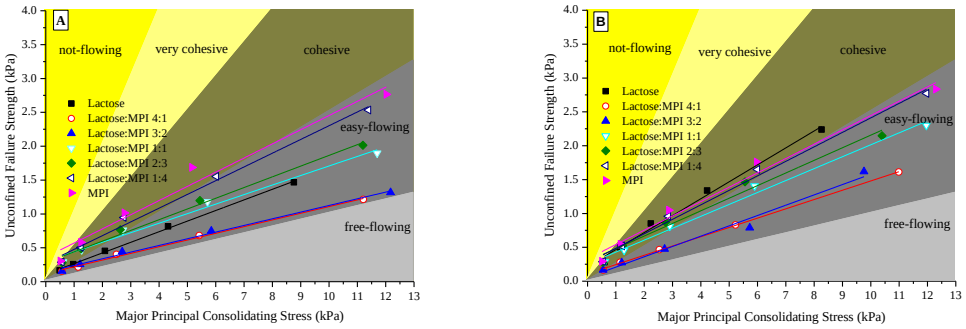


Figure 4-2 Flow function curves showing unconfined strength as a function of major principal consolidating stress for lactose/MPI solids systems with low moisture (LM) content (A) and high moisture (HM) content (B).

Dairy solids with higher amount of lactose showed more significant change in their flowability when moisture content increased. For lactose/MPI mixtures storage at 0% and 44% RH, powders with higher amount of lactose showed better flowability (Figure 4-2), while the particle size of those solids with higher lactose content was smaller. Moreover, particle shape of those solids with higher content of lactose had less rounded shape. These results indicated that particle size and particle shape did not show significant influence on the flowability of lactose/MPI mixtures.

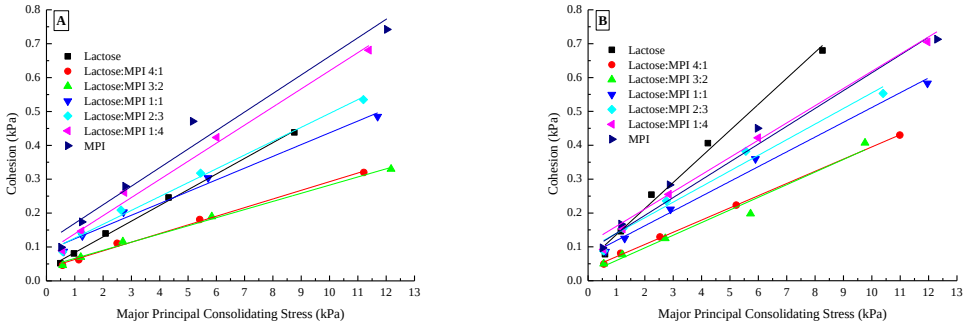


Figure 4-3 Cohesions as a function of major principal consolidating stress for lactose/MPI solids systems with low moisture (LM) content (A) and high moisture (HM) content (B).

Cohesion of lactose/MPI solids systems showed the same tendency as their flowability after storage at 0% and 44% RH (Figure 4-3 A and B). Lactose showed the most significant change in cohesion with increasing moisture content. Cohesion of MPI powder after storage at 44% RH showed the same as it was stored at 0% RH. According to Peleg (1977), interparticle forces play a significant role in free flowing and cohesive powders. Higher cohesion means worse flow behaviour at the same major principle consolidating stress.

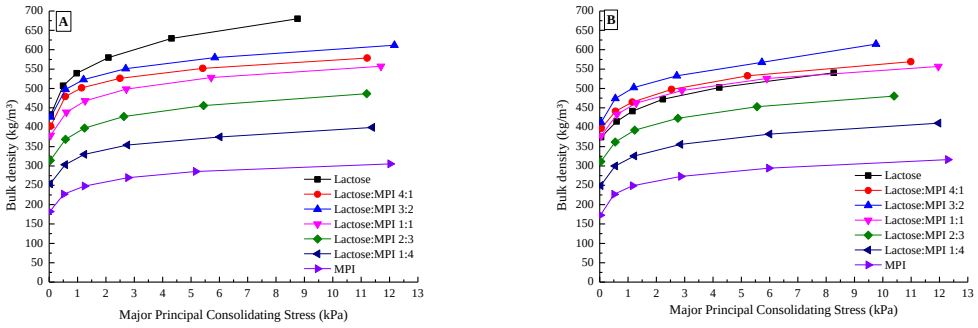


Figure 4-4 Bulk density as a function of major principal consolidating stress for lactose/MPI solids systems with low moisture (LM) content (A) and high moisture (HM) content (B).

The bulk density of lactose/MPI solids systems increased with increasing major principle consolidating stress (Figure 4-4). All dairy solids became compressed on the application of increasing major principle consolidating stress. Spray-dried lactose/MPI mixtures showed difference in loose bulk density. Dairy solids with higher lactose content had higher loose bulk density after storage at 0% RH (Figure 4-4 A). When moisture content increased, the loose bulk density of lactose showed the most significant change while lactose/MPI mixtures and MPI powders showed minor changes, especially lactose/MPI (1:1) mixture (Figure 4-4).

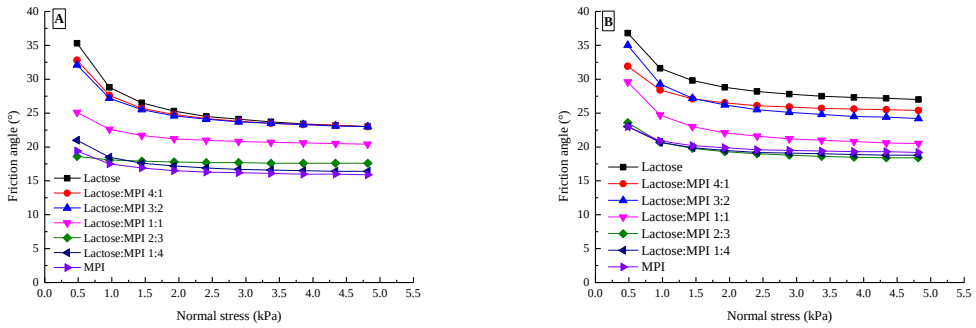


Figure 4-5 Fiction angle as a function of normal stress for lactose/MPI solids systems with low moisture (LM) content (A) and high moisture (HM) content (B).

The wall friction angles of lactose/MPI solids systems were measured at different normal stress by standard wall friction test (Figure 4-5). At the same normal stress, wall friction angles of lactose/MPI solids systems decreased with decreasing lactose content. All lactose/MPI solids systems sorbed moisture when exposed to air with relative humidity 44% (Table 4-4). As a result, friction angles of lactose/MPI solids systems increased with increasing moisture content (Figure 4-5 A and B). The wall friction angle, φ_{χ}, quantifies the effort required to move a bulk solid across the surface of a specific wall material. The larger the wall friction angle, the greater is wall friction, which can result in deposition or segregation of powder (Iqbal &

Fitzpatrick, 2006). In addition, Iqbal and Fitzpatrick (2006) stated that the composition, moisture content and particle size distribution of bulk solids will influence their wall friction characteristics. Powders with smaller particle sizes tend to increase wall friction, as there is greater contact surface area between smaller particles and the wall surface. This might be one reason that friction angles of lactose/MPI solids systems decreased with decreasing lactose content (Figure 4-5).

4. Conclusions

Dairy powders with amorphous components, such as amorphous lactose, could become sticky and caked, as a result of poor flowability, when temperature is at or above the glass transition temperatures or sorb certain amount of water from the environment. The increase in moisture content could increase adhesive forces between individual particles. Adhesive forces are the source of poor flowability or caking of powders (Schulze, 2007). In addition, water plasticization also reduces the T_g values of lactose while the temperature difference between the powder and the glass transition represents a driver for greater molecular mobility, powder stickiness and caking (Fitzpatrick et al., 2007b). This study investigated the influence of water plasticization and lactose content on the flow properties of model dairy solids. Median particle size (d_{50}) of lactose/MPI solids systems increased with decreasing lactose content. Pure lactose showed the largest SSA values, while there is only slightly difference in the SSA values of lactose/MPI mixtures and MPI powders. Moreover, morphological study showed that lactose/MPI solids systems with higher amount of lactose had less regular particle shape. According to previous studies, those powder characteristics might affect the flow properties of lactose/MPI solids systems. However, flow function study showed that for lactose/MPI mixtures storage

at 0% and 44% RH, powders with higher amount of lactose showed better flowability, while pure lactose also showed easy-flowing after storage at 0% RH. Smaller particle size and less rounded particle shape of lactose and lactose/MPI mixtures with higher lactose content did not show significant influence on their flowability.

As amorphous lactose is hygroscopic and readily sorbs water from air, pure lactose sorbed less water during storage at $a_w \leq 0.23$ and more water at 0.33 a_w and 0.44 a_w. Water plasticization depressed the glass transition temperatures of lactose and lactose/MPI mixtures after storage at 44% RH. Lactose/MPI (1:4) mixture showed the largest T_g value compared to lactose and other lactose/MPI mixtures. Mechanical property study indicated that magnitudes of storage modulus and loss modulus for lactose/MPI solids systems with higher lactose content showed more significant change at the glass transition region, which meant dairy solids with higher lactose content had higher molecular mobility with increasing water content. This might cause the highest cohesion of pure lactose after storage at 44% RH. Additionally, at the same normal stress, wall friction angles of lactose/MPI solids systems decreased with decreasing lactose content, while their friction angles all increased with increasing water content.

CHAPTER FIVE

Influence of pre-crystallization and water plasticization on flow properties of lactose/WPI solids systems

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Abstract

This study investigated the influence of pre-crystallization and water plasticization on flow properties of lactose/whey protein isolate (WPI) solids systems. Powder characteristics of lactose/WPI mixtures with different amounts of α-lactose monohydrate (1.0%, 11.2%, 29.2%, and 46.8%, w/w) were studied. Dairy powders with higher amounts of crystalline lactose had larger tapped bulk density and particle density. Morphological characteristics study indicated that the crystallinity of dairy powders had a minor effect on the particle shape. Increasing protein content or crystalline lactose content could decrease the molecular mobility of dairy solids. Flow function tests indicated that dairy solid with 11.2% crystallinity was more easy-flowing than lactose/WPI mixtures with 1.0%, 29.2% and 46.8% crystallintiy after storage at 0% and 44% relative humidity (RH) storage conditions. Furthermore, dairy solids with higher amount of crystalline lactose showed better resistance to develop cohesive at high RH storage conditions. The friction angle of dairy solid with 1.0% crystallinity increased with increasing water content, while friction angles of lactose/WPI mixtures with higher crystallinity decreased with increasing water content.

Keywords: Pre-crystallization; Crystallinity; Mechanical properties; Flow properties

1. Introduction

Flow properties of spray-dried dairy solids are very important in handling and processing operations (Knowlton et al., 1994; Fitzpatrick et al., 2007b). Previous studies have indicated that the flow properties depend on the composition and physical properties of powders, such as particle size and shape, surface structure, amorphous lactose content, and water content (Kim et al., 2005; Fitzpatrick et al., 2007a; Schulze, 2007; Janjatović et al., 2012; Crowley et al., 2014a). Stickiness and caking of powders usually result from formation of liquid bridges between individual particles (Peleg, 1977), and they are responsible for impaired flow properties (Lazar et al., 1956). Many studies showed that powders with larger amounts of amorphous components, such as amorphous lactose, were more sensitive to absorbing moisture, giving rise to lumping and caking problems (Le Meste et al., 2002; Liu et al., 2006; Fitzpatrick et al., 2007a, 2007b; Silalai & Roos, 2010a).

Lactose in dairy systems can exist in various crystalline and non-crystalline forms. The crystalline state is a solid state having molecules well arranged in regular lattice. For lactose in amorphous state, the molecular arrangement is disordered. Amorphous lactose is thermodynamically unstable and hygroscopic, absorbing moisture from the surroundings and subsequently plasticizing, while the crystalline lactose is thermodynamically stable and significantly less hygroscopic. Reducing stickiness in materials can be achieved through partial or complete crystallization of sticky components (Chiou et al., 2008). Bronlund and Paterson (2004) stated that crystalline lactose absorbed approximately 100 times less water than amorphous lactose in the same conditions. Therefore, pre-crystallizing those amorphous materials during processing may help to resolve the problem of product stickiness and stability during subsequent storage (Das & Langrish, 2012).

Since lactose is around 70% of the dry matter in whey powder, the hygroscopicity of lactose makes whey powder become sticky and adhere to the chamber walls during spray drying (Lorenzen, 1997). Pre-crystallization of lactose in whey concentrates before drying is a successful remedial measure in manufacturing process, and is widely used in the production of whey powder in dairy industry (Roetman, 1979). Powder hygroscopicity and caking are brought under control by lowering the level of amorphous lactose.

Moreover, previous studies indicated that particle shape affected the bulk behaviour and flow properties of dairy solids (Fu et al., 2012). According to the study of Thomas et al. (2004), morphological changes, such as surface deformation, occurred due to the build-up of lactose crystals in dairy powders. This difference in the particle shape of crystalline lactose and amorphous lactose may influence the flow properties of dairy powders and subsequently affect the handling and processing operations. Thus, compared to amorphous lactose, crystalline lactose shows different physical properties and water sorption behaviour during processes of production and storage (Bronlund & Paterson, 2004; Fu et al., 2012), which may finally influence the flow properties of dairy solids.

However, how pre-crystallization and crystalline components content, such as α-lactose monohydrate, affect the flow properties of dairy solids has not been reported so far. The objectives of this study were to investigate the effect of crystalline lactose content on the flow properties of lactose/whey protein isolate (WPI) solids systems. Pre-crystallization of lactose before spray drying was used to prepare dairy solids with different amounts of crystalline lactose in this study.

2. Materials and methods

2.1 Materials

α-lactose monohydrate (> 99% purity) was kindly donated by Arla Foods Ingredients (Sønderhøj 10-12, 8260 Viby J, Denmark). WPI, containing 71% β-lactoglobulin and 12% α-lactalbumin, was obtained from Davisco Food International (Le Sueur, MN, USA). Aluminum oxide calcined powder and α-lactose (≥ 99% purity) were purchased from Sigma−Aldrich (St. Louis, MO, USA).

2.2 Powder preparation

Solution of lactose and lactose/WPI mixtures at the ratio 4:1 were prepared in de-ionized water at 65 °C in a water bath for 2 h with a stirring speed of 500 rpm. The total solid concentration of lactose and lactose/WPI mixtures solution was 40% (w/w). Then the solution of lactose/WPI mixtures was cooled to room temperature (20-22 °C) and kept at room temperature (20-22 °C) for different hours to pre-crystallise. The stirring speed was 150 rpm during pre-crystallization. The pre-crystallization time for lactose/WPI mixtures was 0, 3, 15 and 20 h, respectively. They were defined as S2 (0 h), S3 (3 h), S4 (15 h) and S5 (20 h) according to the pre-crystallization time. Pure lactose without pre-crystallization and WPI were defined as S1 and S6, respectively. They were all spray-dried by an ANHYDRO single stage spray dryer with a centrifugal atomizer (Copenhagen, Denmark) at the Teagasc Food Research Centre, Moorepark, Fermoy, Co. Cork, Ireland. The inlet air temperature was around 170 ± 2 °C and the outlet temperature around 90 ± 2 °C. Spray-dried solids were kept immediately in evacuated desiccators over P_2O_5 at room temperature. Each analysis was carried out within three months after spray drying.

2.3 Powder characterisation

2.3.1 Determination of α-lactose monohydrate content in spray-dried lactose/WPI mixtures

The content of α-lactose monohydrate (%Cº) in spray-dried lactose/WPI mixtures was determined according to the method of Schuck and Dolivet (2002) based on the difference between total water, determined using a Karl Fischer Titration (Mettler Toledo International Inc., Im Langacher Greifensee, Switzerland), and unbound water, determined by weight loss following 6 h drying of 1 g powder at 87 ºC. In this study, the content of α-lactose monohydrate (%Cº) was used to represent the crystallinity of lactose/WPI mixtures. It was assumed that there was no bound water in amorphous lactose. Each analysis was carried out in triplicate.

2.3.2 Powder characteristics

Water content was determined using an HR83 Halogen Moisture Analyser (Mettler Toledo International Inc., Im Langacher Greifensee, Switzerland). Powder particle size distribution and specific surface area (SSA) were determined by laser light scattering using a Malvern Mastersizer 3000 (Malvern Instruments Ltd., Worcestershire, UK). Powder sample was added to the standard venturi disperser with a hopper gap of 2.5 mm and then fed into the dispersion system. Compressed air at 0.75 bar was used to transport and suspend the powder particles through the optical cell. A measurement time of 10 s was used, and background measurements were made using air for 20 s. The laser obscuration level was at 2-10%.

2.4 Bulk density, particle density and porosity

Loose and tapped (100 taps) bulk densities (ρ_{tapped}) of lactose/WPI solids systems was measured as per GEA Niro (2006b), using a Jolting volumeter (Funke Gerber,

Berlin, Gerrmany). Particle density (ρ_p) was measured as per GEA Niro (2006c), using a Gas Pycnometer (Accupyc II 1340 Gas Pycnometer, Micromeritics Instrument Corporation, Norcross, GA, USA). Since the definition of porosity of a porous media corresponds to extra particle void space, the corresponding porosity of dairy solids was calculated as Eq. (5-1):

$$\varepsilon = 1 - \rho_{tapped} / \rho_p \qquad (5\text{-}1)$$

2.5 Morphological characteristics

Morphological characteristics were determined using a Malvern Morphologi G3 S (Malvern Instruments Ltd., Worcestershire, UK). 5 mm^3 volume powder samples were dispersed on the glass plate. 2.5× objective was used for the measurement in this study. Circularity, convexity and elongation are three commonly used shape factors. One way to measure shape is to quantify how close the shape is to a perfect circle. Circularity is the ratio of perimeter of a circle with the same area as the particle divided by the perimeter of the actual particle image. Several definitions of circularity could be used but for accuracy the software reports HS Circularity (HS for high sensitivity) in addition to circularity. Circularity has values in the range 0-1. A perfect circle has a circularity of 1 while a 'spiky' or irregular object has a circularity value closer to 0. Circularity is sensitive to both overall form and surface roughness. Elongation is defined as [1-aspect ratio] or [1- width/length]. As the name suggests, it is a measure of elongation and again has values in the range 0-1. A shape symmetrical in all axes, such as a circle or square, has an elongation value of 0; shapes with large aspect ratios have an elongation closer to 1. Convexity is a measurement of the surface roughness of a particle. It is calculated by dividing the convex hull perimeter by the actual particle perimeter. A smooth shape has a

convexity of 1 while a very ‘spiky’ or irregular object has a convexity closer to 0. In this study, each sample was measured in triplicate to get the average value.

2.6 Powder preparation for flow function test

Two moisture levels of lactose/WPI solids systems were prepared in a vacuum oven (OV-12, Medline Industries, Inc., Mundelein, Illinois, USA). For dairy solids with low moisture (LM) content, the powders were placed in a vacuum oven at 45 °C for 36 h. For dairy solids with high moisture (HM) content, spray-dried dairy solids were firstly dried at 45 °C in a vacuum oven for 36 h, and then equilibrated over saturated K_2CO_3 solution, giving 44% relative humidity, at 25 °C for 48 h in a vacuum oven. During equilibration, all powders were put in petri dishes with thickness around 8 mm. The final water content was measured in triplicate using an HR83 Halogen Moisture Analyser (Mettler Toledo International Inc., Im Langacher Greifensee, Switzerland) before measuring the flow properties.

2.7 Glass transition

Glass transition temperatures, T_g (onset), of lactose and lactose/WPI mixtures were determined using a differential scanning calorimeter (DSC Q2000, TA Instruments, Crawley, UK). 10-15 mg of dairy solids was transferred to DSC aluminium pans (Tzero pan and lid, Switzerland). Then DSC pans were hermetically sealed and samples were analysed. An empty pan was used as a reference. At the first scan, the samples were heated over the glass transition temperature region at 5 °C/min and then cooled at 10 °C/min to below glass transition, a 2nd heating scan was then run to above the glass transition temperature at 5 °C/min. All measurements were carried out in duplicate. Glass transition temperatures were

determined using TA universal analysis software, version 5.1.2 (TA Instruments, Crawley, UK).

2.8 Dynamic mechanical analysis

A dynamic mechanical analyser (DMA Q800, TA Instruments, Crawley, UK) was used, in conjunction with a gas cooling accessory (GCA) tank, to determine dynamic mechanical properties of spray-dried dairy solids. A rectangular stainless steel powder holder was designed to generate a defined geometry to contain powder with inner dimensions of 60 mm × 11 mm × 1 mm. A pre-weighed mass of dairy solids mixed with aluminum oxide calcined powder at the ratio of 4:1 (dairy solids/aluminum oxide calcined), was evenly spread within this shallow container, and the upper lid was then placed onto the top surface of the powder (Mahlin et al., 2009). As aluminum oxide calcined showed no effect on mechanical property results of dairy solids, it was added to protect dairy powder from sticking on the powder holder during the heating test. The sample holder was mounted in the instrument in a dual cantilever clamp so that during measurement, the DMA oscillated the sample perpendicularly to the base plane of the sample holder by a vertical motion of the middle clamp. The measurements were made at a heating rate of 2 °C/min from 0 to 140 °C for dairy solids with low moisture content and from 0 to 120 °C for dairy solids with high moisture content. DMA was operated by a sinusoidal deformation applied to the powder sample holder at a fixed strain. The amplitude was 15 µm. During dynamic heating, the samples were analysed for storage modulus (E') and loss modulus (E'') using single frequency 1 Hz.

2.9 Powder flow testing

The flow function of lactose/WPI solids systems was determined using a Powder Flow Tester (PFT) (Brookfield Engineering Laboratories, Inc., Middleboro, MA, USA). The axial and torsional speeds for the PFT were 1.0 mm/s and 1 rev/h, respectively. Samples were filled into the aluminium trough of the annular shear cell at room temperature (22-25 °C). Curved- or flat-profiled shaping blades were used to level the powder surface in the trough for flow- or wall fiction-testing, respectively. The mass of the powder was recorded before testing, with axial distance between the lid and the powder used to calculate changes in the volume of powder during testing. Vane- or flat-profiled lids were attached to compression plate of the PFT for flow- or wall friction-testing. Flowability, cohesion and bulk density were measured using standard flow function test. Friction angle was determined using standard wall friction test. For standard flow function test, the involved uniaxial normal stresses were between 0.2 and 4.8 kPa. For standard wall friction test, ten normal stresses, between 0.4 and 4.8 kPa, were applied to measure the wall friction angles.

2.10 Statistical analysis

Measurement of glass transition, and dynamic mechanical analysis were performed in duplicate, with all other analysis performed in triplicate. Results were expressed as mean ± standard deviations (SD). One-way analysis of variance (ANOVA) was used to determine the significant differences between the mean values of each test (Microsoft Office Excel 2010, Microsoft, Inc., WA, USA). A significance level of $P < 0.05$ was used throughout the study.

3. Results and discussion

3.1 Powder characterisation

The powder characteristics of lactose/WPI solids systems are shown in Table 5-1. The amount of crystalline lactose for lactose/WPI mixtures (S2-S5) increased with increasing the pre-crystallised time (Table 5-1). After pre-crystallization, four kinds of lactose/WPI mixtures with different amounts of α-lactose monohydrate were ready for analysis. As the amount of crystalline lactose was defined as the crystallinity of dairy solids in this study, the crystallinity of lactose/WPI mixtures (S2-S5) were 1.0%, 11.2%, 29.2% and 46.8%, respectively. Lactose (S1) was spray-dried without pre-crystallization and was assumed to be in the amorphous form. Particle size study showed that the particle size of S3, S4, and S5 was higher than S2 (Table 5-1), which indicated that pre-crystallization increased the particle size of dairy solids. As specific surface area (SSA) values are typically inferred from particle size data, S2 with 1.0% crystallinity showed the largest SSA value, while WPI powder gave the smallest SSA value.

It is well known that particle size influences flowability (Fitzpatrick et al., 2004; Schulze, 2007). For example, fine particles tend to be more cohesive and therefore less free-flowing, whereas larger particles tend to be free flowing. Moreover, according to Fitzpatrick et al. (2004), the increased surface area per unit mass of powder means more surface area is available for cohesive forces and frictional forces to resist flow. Therefore, the difference in particle size and SSA values of lactose/WPI mixtures with different crystalline lactose content might affect their flowability.

Table 5-1 Physical characteristics of lactose/WPI solids systems

Systems	Crystallinity (%)	d_{50} (μm)	SSA (m^2/kg)	Loose bulk density (g/cm^3)	Tapped bulk density (g/cm^3)	Particle density (g/cm^3)	Porosity
S1	0.00	$29.25^{a} \pm 0.25$	$620.50^{c} \pm 6.50$	$0.5458^{a} \pm 0.0138$	$0.7110^{a} \pm 0.0096$	$1.2900^{a} \pm 0.0055$	$0.4488^{e} \pm 0.0074$
S2	1.0 ± 0.6	$22.85^{d} \pm 0.25$	$714.75^{a} \pm 7.45$	$0.3282^{d} \pm 0.0027$	$0.3807^{d} \pm 0.0027$	$1.2168^{e} \pm 0.0019$	$0.6871^{b} \pm 0.0023$
S3	11.2 ± 1.0	$25.35^{b} \pm 0.05$	$629.95^{c} \pm 0.85$	$0.3297^{d} \pm 0.0037$	$0.3731^{e} \pm 0.0023$	$1.2182^{e} \pm 0.0016$	$0.6778^{c} \pm 0.0020$
S4	29.2 ± 0.9	$25.20^{b} \pm 1.20$	$682.10^{b} \pm 9.30$	$0.3418^{c} \pm 0.0030$	$0.4022^{c} \pm 0.0044$	$1.2443^{d} \pm 0.0014$	$0.6768^{c} \pm 0.0012$
S5	46.8 ± 1.1	$23.85^{c} \pm 0.05$	$695.05^{b} \pm 1.05$	$0.3614^{b} \pm 0.0070$	$0.4226^{b} \pm 0.0036$	$1.2485^{c} \pm 0.0021$	$0.6615^{d} \pm 0.0031$
S6	0.00	$26.10^{b} \pm 0.50$	$536.00^{d} \pm 6.60$	$0.1916^{e} \pm 0.0007$	$0.2381^{f} \pm 0.0015$	$1.2814^{b} \pm 0.0019$	$0.8142^{a} \pm 0.0018$

[1] S1-S6: S1: amorphous lactose; S2-S5: lactose/WPI mixtures at ratio 4:1 with 1.0%, 11.2%, 29.2% and 46.8% crystallinity, respectively; S6: WPI.

[2] Values are mean ± standard deviation (n = 3).

[3] [a-f] Values within columns with different superscripts are significantly different at $P < 0.05$.

Powder density is an important characteristic for calculating the capacity of packaging materials, containers, hoppers, bins, silos, and also for filling of the die of tableting machines and for capsule filling. Pure lactose (S1) had the largest bulk density and particle density, and the smallest porosity, while WPI powder (S6) gave the opposite results (Table 5-1). For lactose/WPI mixtures (S2-S5), dairy solids with higher amount of crystalline lactose had larger loose bulk density, tapped bulk density and particle density (Table 5-1). Furthermore, dairy solids with higher crystallinity showed lower porosity (Table 5-1). Porosity is defined as the ratio of void volume to total volume of the powder and void volume is the difference between the total volume and particle volume (Turchiuli & Castillo‐Castaneda, 2009). Higher porosity means higher void volume between particles, which might result in dairy solids compress under self-weight during storage.

3.2 Morphological characteristics

The particle shapes of lactose/WPI solids systems were investigated using a Morphologi G3 S. The Morphologi G3 S reports a number of particle shape factors. In this study, three morphological characteristics (circularity, elongation and convexity) were used to identify the particle shape of lactose/WPI solids systems.

Table 5-2 Morphological characteristics of lactose/WPI solids systems

Systems	Circularity	Elongation	Convexity
S1	$0.9120^{a} \pm 0.0010$	$0.1590^{c} \pm 0.0010$	$0.9940^{a} \pm 0.0000$
S2	$0.8593^{b} \pm 0.0074$	$0.2477^{b} \pm 0.0082$	$0.9920^{b} \pm 0.0008$
S3	$0.8430^{bc} \pm 0.0123$	$0.2533^{b} \pm 0.0109$	$0.9900^{bc} \pm 0.0008$
S4	$0.8473^{bc} \pm 0.0012$	$0.2507^{ab} \pm 0.0009$	$0.9903^{bc} \pm 0.0005$
S5	$0.8350^{c} \pm 0.0071$	$0.2630^{a} \pm 0.0050$	$0.9890^{c} \pm 0.0008$
S6	$0.8355^{c} \pm 0.0055$	$0.2570^{a} \pm 0.0030$	$0.9890^{c} \pm 0.0010$

[1] S1-S6: Table 5-1.

[2] Values are mean ± standard deviation (n = 3).

[3] $^{a-c}$ Values within columns with different superscripts are significantly different at $P < 0.05$.

The results in Table 5-2 showed that particles of pure lactose (S1) were more circular than those of lactose/WPI mixtures and WPI. The circularity of particle shape of lactose/WPI mixtures decreased with increasing the crystallinity. Moreover, particle shape of S5 with the highest amount of crystalline lactose had the lowest ratio of width/length and the roughest surface. Those results indicated dairy solids with higher amount of crystalline lactose had less rounded shape and rougher surface. Fu et al. (2012) stated that particle shape significantly affected the flow characteristics of powder over a wide range of stress conditions. Powders consisting of regularly shaped particles flow better than those consisting of irregular shaped particles. Thus, different particle shape of lactose/WPI solids systems may link to their flow behaviours in this study.

3.3 Glass transition

After storage at different humidity conditions, lactose/WPI solids systems with different moisture content were prepared (Table 5-3). There was no trend for the water content of lactose/WPI mixtures with different crystallinity after storage at 44% RH, which might be due to the presence of WPI in dairy powders weakening the effect of crystalline lactose on water sorption behaviour of lactose/WPI mixtures. Water activities of lactose/WPI solids systems with low moisture (LM) content and high moisture (HM) content was around 0.11 a_w and 0.33 a_w, respectively (Table 5-3).

Table 5-3 Water content, *m*, water activity, a_w, glass transition temperatures, T_g, and α-relaxation temperatures, T_α of lactose/WPI solids systems storage at 0% RH and 44% RH.

Systems	*m*		a_w		T_g (°C)		T_α (°C)	
	LM	**HM**	**LM**	**HM**	**LM**	**HM**	**LM**	**HM**
S1	1.35 ± 0.01	4.67 ± 0.02	0.16 ± 0.001	0.34 ± 0.002	72.0 ± 0.1	50.0 ± 0.2	122.1 ± 0.04	69.6 ± 0.02
S2	2.21 ± 0.25	4.80 ± 0.21	0.09 ± 0.001	0.32 ± 0.001	68.9 ± 0.2	47.8 ± 0.0	126.6 ± 0.03	69.7 ± 0.03
S3	2.34 ± 0.15	6.14 ± 0.08	0.09 ± 0.002	0.35 ± 0.003	66.1 ± 0.1	35.9 ± 0.2	125.1 ± 0..05	63.2 ± 0.04
S4	2.40 ± 0.04	6.22 ± 0.11	0.11 ± 0.001	0.34 ± 0.000	67.3 ± 0.3	37.0 ± 0.1	127.0 ± 0.02	58.6 ± 0.04
S5	2.11 ± 0.04	4.78 ± 0.12	0.09 ± 0.003	0.33 ± 0.003	71.4 ± 0.2	48.8 ± 0.4	126.3 ± 0.02	73.2 ± 0.05
S6	3.49 ± 0.01	7.87 ± 0.06	0.09 ± 0.001	0.33 ± 0.000	/	/	/	/

[1] S1-S6: Table 5-1.

[2] Values are mean ± standard deviation (water content: n = 3; T_g and T_α: n = 2).

Lactose and lactose/WPI mixtures showed significant difference in their glass transition temperatures after storage at different RH conditions (Table 5-3). Water plasticization depressed the glass transition temperatures of lactose and lactose/WPI mixtures. For lactose/WPI mixtures (S2-S5), S5 showed the lowest water content after storage at 44% RH, which resulted in the highest T_g value of S5. This might be due to the different water sorption behaviour of amorphous lactose and crystalline lactose. Similar results were also stated by Fitzpatrick et al. (2007a). According to their study, the powders with larger amount of amorphous lactose were more sensitive to absorbing moisture when in intimate contact with air. According to Fitzpatrick et al. (2007b), powders with amorphous components, such as amorphous lactose, may become sticky if the powder temperature is elevated above the components glass transition temperature and into the sticky temperature region. This can lead to the powder becoming much more cohesive and eventually caking, and can also cause a powder to adhere more to a surface. These indicated dairy solids with 46.8% crystallinity sorbed less water during storage, which might give higher T_g values and protect them from stickiness and caking.

3.4 Mechanical properties

The mechanical properties of lactose/WPI solids systems storage at 0% and 44% RH were measured using a DMA. Mechanical α-relaxation of lactose/WPI solids systems occurred above the glass transition and was observed from a decrease in storage modulus and a peak in the loss modulus (Figure 5-1). At temperatures above the glass transition, large changes in viscoelastic properties were expected (Royall et al., 2005; Silalai & Roos, 2011b).

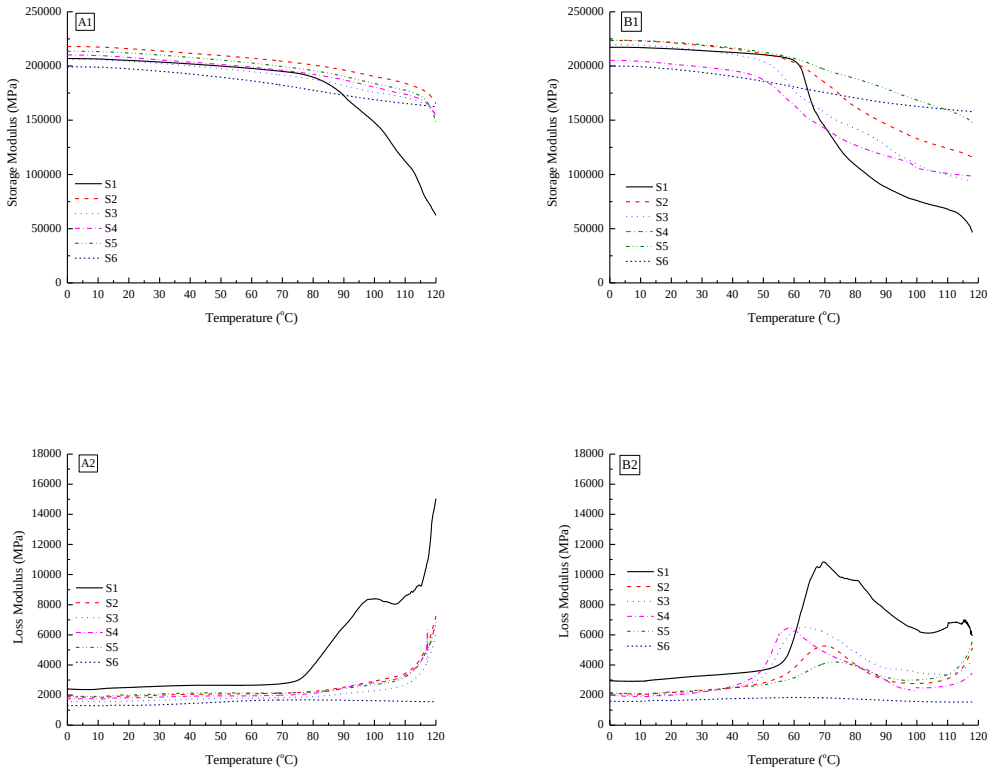


Figure 5-1 Storage modulus and loss modulus of lactose/WPI solids systems with low moisture (LM) content (A1 and A2) and high moisture (HM) content (B1 and B2). S1-S6: S1: amorphous lactose; S2-S5: lactose/WPI mixtures at ratio 4:1 with 1.0%, 11.2%, 29.2% and 46.8% crystallinity, respectively; S6: WPI.

The storage modulus of lactose/WPI solids systems decreased slowly in the amorphous state, while it dropped sharply from the original value at the glassy state to the value at the rubbery state in the glass transition region (Figure 5-1 A1 and B1). There were minor differences in the magnitude of storage modulus change for lactose/WPI mixtures with low moisture content, while pure lactose (S1) with low moisture content showed the most significant change in its storage modulus at glass transition region (Figure 5-1 A1). All dairy solids sorbed much water from air during storage at 44% RH (Table 5-3), which resulted in lactose/WPI solids systems showed more significant change in their storage modulus at the glass transition region. The storage modulus of pure lactose still showed the most significant change

after storage at 44% RH (Figure 5-1 B1). However, for lactose/WPI mixtures, S5 with the highest crystallinity showed the smallest change of storage modulus during the glass transition region (Figure 5-1 B1), while S3 (HM) with lower crystallinity and the largest water content showed the most significant change in its storage modulus. S2 with lower crystallinity showed higher magnitude of storage modulus change than S5. The magnitudes of modulus changes indicated mechanical α-relaxations which were relative to molecular mobility (Roudaut et al., 2004; Silalai & Roos, 2011b). Higher molecular mobility could contribute to the formation of inter-particle bridges and stickiness (Peleg, 1977; Silalai & Roos, 2011b). Consequently, water plasticization could increase molecular mobility of dairy solids, while increasing protein content or crystalline lactose content of dairy solids could decrease the molecular mobility of dairy solids. In other words, increasing protein content or crystalline lactose content might help dairy solids to delay the formation of stickiness and caking and keep them free-flowing.

Stiffness of materials refers to the ability to carry stress without changing dimension (Ebewele, 2000). For the measurement of unconstrained uniaxial tension or compression, Young's modulus can be as a measure of the stiffness of a material. In this study, the change of storage modulus could reflect the change of stiffness for dairy solids. The stiffness of spray-dried dairy solids showed the same trend as the change of storage modulus when temperature increased from 0 to 120 °C. The results of storage modulus indicated that dairy solids with higher crystallinity were stiffer at high moisture content, which might help dairy solids to maintain their flowability after storage at high relative humidity environment.

The changes of loss modulus for lactose/WPI solids systems are shown in Figure 5-1 A2 and B2. Loss modulus of lactose/WPI solids systems showed minor changes in the amorphous state and the rubbery state, while they increased dramatically and reached the peak values in the glass transition region (Figure 5-1 B1 and B2). The magnitudes of loss modulus for lactose/WPI solids systems increased with increasing water content. Although S2 and S5 showed similar water content after storage at 44% RH, S5 with the highest amount of crystalline lactose showed smaller magnitude of loss modulus change. In addition, in this study, the α-relaxation temperatures, T_α, were taken from the temperatures of loss modulus peak (Table 5-3). T_α values of lactose and lactose/WPI mixtures decreased with increasing moisture content. S5 showed the highest T_α values, which might be due to its highest crystallinity and lower moisture content. Those results of storage modulus and loss modulus indicated that the crystallinity of dairy solids affected the mechanical properties of dairy solids.

3.5 Flow properties

Standard flow function test and standard wall friction test of lactose/WPI solids systems were conducted using a Powder Flow Tester. The flowability results are shown in Figure 5-2. According to Schulze (2007), the flowability of powders is usually stress-dependent. For lactose/WPI solids systems with low moisture content, they were easy-flowing or cohesive when the major principle consolidating stress was below 3 kPa, while they were all easy-flowing at major principle consolidating stress > 3 kPa (Figure 5-2 A). However, for dairy solids with high moisture content, lactose/WPI mixtures with 1.0%, 29.2% and 46.8% amount of crystalline lactose fell into cohesive area even when major principle consolidating stress was over 8 kPa.

Therefore, increasing water content decreased flowability of dairy solids, which might be due to the increase in liquid bridges and capillary forces acting between the powder particles. For lactose/WPI mixtures (S2-S5), S3 with 11.2% crystallinity showed more easy-flowing than S2, S4 and S5 after storage at 0% and 44% RH. This could also be derived from the flow index results (Table 5-4). S3 gave higher flow index values than other lactose/WPI mixtures. S4 and S5 with higher amount of crystalline lactose did not show better flowability than S3.

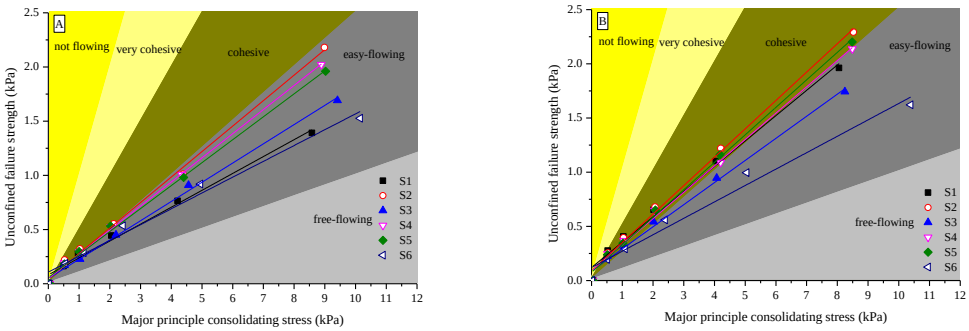


Figure 5-2 Flow function curves showing unconfined strength as a function of major principal consolidating stress for lactose/WPI solids systems with low moisture (LM) content (A) and high moisture (HM) content (B). S1-S6: S1: amorphous lactose; S2-S5: lactose/WPI mixtures at ratio 4:1 with 1.0%, 11.2%, 29.2% and 46.8% crystallinity, respectively; S6: WPI.

According to Fitzpatrick et al. (2007a), this might be due to the high amount of crystalline lactose for S4 and S5, which gave rise to greater frictional resistance between the particles or the differences in surface moisture contents of crystalline and amorphous lactose producing differences in cohesion due to liquid bridging.

Table 5-4 Values relating to flow properties of lactose/WPI solids systems derived from standard flow function test by Powder Flow Tester ($D_{arching}$: minimum outlet diameter to prevent arching; δ_J: effective angle of internal friction).

Systems	Critical stress		$D_{arching}$ (m)		Flow index		δ_J	
	LM	HM	LM	HM	LM	HM	LM	HM
S1	$0.154^{b} \pm 0.001$	$0.264^{a} \pm 0.001$	$0.060^{bc} \pm 0.001$	$0.113^{b} \pm 0.001$	$6.25^{c} \pm 0.01$	$4.17^{bc} \pm 0.01$	$36.3^{d} \pm 0.1$	$44.4^{b} \pm 0.1$
S2	$0.099^{e} \pm 0.000$	$0.210^{b} \pm 0.003$	$0.056^{c} \pm 0.000$	$0.120^{c} \pm 0.002$	$4.17^{a} \pm 0.01$	$3.70^{a} \pm 0.00$	$40.7^{b} \pm 0.1$	$45.2^{a} \pm 0.0$
S3	$0.096^{e} \pm 0.001$	$0.181^{d} \pm 0.001$	$0.056^{c} \pm 0.001$	$0.108^{d} \pm 0.002$	$5.56^{b} \pm 0.20$	$4.76^{c} \pm 0.00$	$39.4^{c} \pm 0.1$	$43.4^{c} \pm 0.0$
S4	$0.106^{d} \pm 0.001$	$0.192^{c} \pm 0.001$	$0.056^{c} \pm 0.001$	$0.101^{d} \pm 0.001$	$4.35^{a} \pm 0.00$	$4.00^{b} \pm 0.01$	$40.1^{c} \pm 0.1$	$45.2^{a} \pm 0.0$
S5	$0.122^{c} \pm 0.000$	$0.175^{d} \pm 0.001$	$0.064^{b} \pm 0.001$	$0.097^{e} \pm 0.001$	$4.55^{a} \pm 0.00$	$3.85^{ab} \pm 0.01$	$40.7^{b} \pm 0.1$	$44.0^{b} \pm 0.1$
S6	$0.193^{a} \pm 0.001$	$0.216^{b} \pm 0.001$	$0.179^{a} \pm 0.001$	$0.199^{a} \pm 0.000$	$6.67^{c} \pm 0.00$	$6.25^{d} \pm 0.00$	$41.1^{a} \pm 0.1$	$40.7^{e} \pm 0.1$

[1] S1-S6: Table 5-1.

[2] Values are mean ± standard deviation (n = 3).

[3] [a-e] Values within columns with different superscripts are significantly different at $P < 0.05$.

Moreover, S4 and S5 had smaller particle size and larger SSA values than S3 (Table 5-1), which meant they had more surface area for cohesive forces and frictional forces to resist flow. Furthermore, morphological study showed that dairy solids with lower crystallinity had more rounded shape, and smoother surface (Table 5-2), which might result that S3 was more easy-flowing than S4 and S5.

In addition, for lactose/WPI mixtures with low moisture content, S5 had a significant higher ($P < 0.05$) critical stress value than other lactose/WPI mixtures (S2, S3, and S4) (Table 5-4), indicating that it had a tendency to develop cohesive arches which required greater stress to collapse (Schulze, 2007; Crowley et al., 2014a). However, after storage at 44% RH, S5 gave a significant lower critical stress value than other lactose/WPI mixtures (S2, S3, and S4). Moreover, $D_{arching}$ value of S5 with low moisture content was significant higher than other lactose/WPI mixtures (S2, S3, and S4), while S5 gave the opposite result after storage at 44% RH. As a result, S5 with the highest crystallinity showed the smallest change in its critical stress and $D_{arching}$ value with increasing water content. It was clear from these results that dairy solids with higher crystallinity showed better resistance to develop cohesive when storage at high relative humidity conditions.

The bulk densities of lactose/WPI solids systems increased as major principle consolidating stress increased (Figure 5-3). All dairy solids became compressed on the application of increasing major principle consolidating stress. There was only a minor difference in the bulk density of lactose/WPI mixtures with different crystallinity. Increasing water content decreased the bulk density of lactose (S1) significantly, while the bulk densities of lactose/WPI mixtures and WPI solids only showed minor decrease.

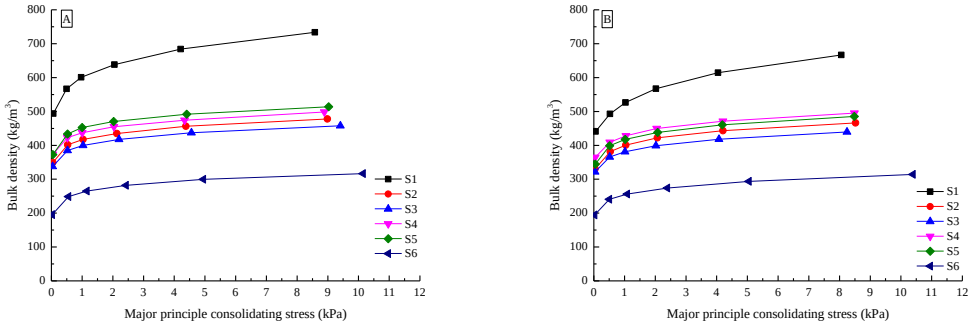


Figure 5-3 Bulk density as a function of major principal consolidating stress for lactose/WPI solids systems with low moisture (LM) content (A) and high moisture (HM) content (B). S1-S6: S1: amorphous lactose; S2-S5: lactose/WPI mixtures at ratio 4:1 with 1.0%, 11.2%, 29.2% and 46.8% crystallinity, respectively; S6: WPI.

Wall friction is the dominant parameter in determining the minimum hopper angle (between the hopper wall and the horizontal) required to ensure mass flow. In this study, the wall friction angles of lactose/WPI solids systems were also determined at different normal stresses using standard wall friction test (Figure 5-4). For lactose/WPI mixtures with low moisture content, friction angles increased as crystallinity was increased at 0.483 kPa (Figure 5-4 A). However, for lactose/WPI mixtures with high moisture content, the friction angles decreased with increasing crystallinity at 0.483 kPa (Figure 5-4 B). Comparing the friction angles of dairy solids with different water content (Figure 5-4 A and B), the friction angles of S2 increased with increasing water content, and the friction angles of S3, S4, and S5 decreased with increasing water content. This might be due to amorphous powders (S2) were more cohesive with increasing water content. However, for S3, S4, and S5, the increased moisture might act as a lubricant and decreased friction angles for partially crystallised powders (Fitzpatrick et al., 2007a).

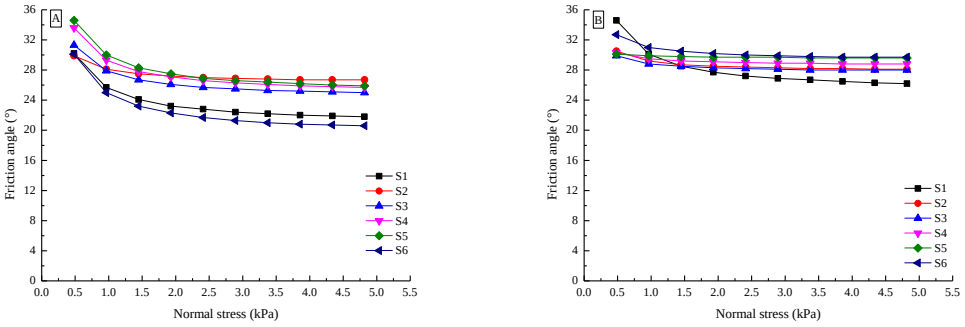


Figure 5-4 Fiction angle as a function of normal stress for lactose/WPI solids systems with low moisture (LM) content (A) and high moisture (HM) content (B). S1-S6: S1: amorphous lactose; S2-S5: lactose/WPI mixtures at ratio 4:1 with 1.0%, 11.2%, 29.2% and 46.8% crystallinity, respectively; S6: WPI.

Additionally, the effective angles of internal friction (δ_J) for lactose/WPI solids systems are also shown in Table 5-4. δ_J values of lactose/WPI solids systems increased with increasing water content. For lactose/WPI solids systems (S1-S6) with low water content, pure lactose (S1) showed the smallest δ_J and WPI (S6) showed the largest δ_J, while the opposite result was shown as water content increasing (Table 5-4). This result indicated increasing protein content decreased the effect of water plasticization on the internal friction of dairy solids.

4. Conclusions

As amorphous lactose and crystalline lactose show different physical and mechanical properties, this study investigated the influence of crystalline lactose content and water plasticization on the flow properties of lactose/WPI solids systems. Particle size study indicated that pre-crystallization increased the particle size of dairy powders. SSA values results showed that S2 with 1.0% crystallinity gave the largest SSA value, while WPI powder showed the smallest SSA value. For lactose/WPI mixtures (S2-S5), dairy solids with higher crystallinity had larger loose

bulk density, tapped bulk density and particle density, whereas they gave lower porosity. Moreover, the crystallinity of dairy powders had a minor effect on the particle shape. Those differences in particle size, SSA, bulk density, particle density and particle shape resulting from the crystallinity might affect their flow properties.

The results of mechanical property study indicated that water plasticization could increase molecular mobility of dairy solids, while increasing protein content or crystalline lactose content of dairy solids might decrease the molecular mobility of dairy solids and maintain their stiffness. Therefore, the presence of protein or crystalline lactose might protect dairy solids from stickiness and caking at high relative humidity conditions. Flow function test showed that for lactose/WPI mixtures with different crystallinity, S3 with 11.2% crystallinity was more easy-flowing than S2 (1.0% crystallinity), S4 (29.2% crystallinity) and S5 (46.8% crystallinity) at 0% and 44% RH storage conditions. Increasing water content reduced the flowability of dairy solids with different levels of crystalline lactose. Moreover, dairy solids with higher crystallinity showed better resistance to develop cohesive when they were at high relative humidity conditions. The friction angles of dairy solids with higher crystallinity (S3, S4, and S5) decreased with increasing water content, while the friction angles of S2 increased with increasing water content. Since pre-crystallization of lactose is widely used in the production of dairy powders, the findings in this study will be very useful in handling and processing of dairy powders.

CHAPTER SIX

Flavor release from spray-dried amorphous matrix: Effect of lactose content and water plasticization

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Abstract

Glass-forming carbohydrates are widely used as matrices for encapsulation and stabilization of nutrients, and bioactive compounds. In this study, powders with lactose/whey protein isolate (WPI) mixtures (4:1, 1:1, and 1:4), or WPI as wall materials and ethyl butyrate as core material were prepared by spray drying. The effects of lactose content and water plasticization on encapsulation efficiency and flavor release were studied. The particle size of powders with higher amount of lactose was smaller. Wall material consisting of lactose/WPI (4:1) mixture had significantly ($P < 0.05$) higher encapsulation efficiency. The flavor retention in powders did not have significant decrease with equilibration at 0.33 a_w, while it was dramatically decreased at 0.54 a_w and 0.65 a_w as a result of lactose crystallization. Mechanical properties study showed that increasing water content of powders with higher lactose content increased molecular mobility and free volume of matrix, which accelerated diffusion of flavor molecules. These results may be used in the assessment of protection and release characteristics of flavor components in formulated systems.

Keywords: Flavor encapsulation; Glass transition; Mechanical properties; Amorphous matrix; Spray drying

1. Introduction

In the food industry there is a growing interest for encapsulation technologies, which are designed to protect the encapsulated materials and to allow controlled release. Many volatile compounds are encapsulated in solid carriers to increase their protection, reduce evaporation, and promote easier handling (Beristain et al., 1996; Goubet et al., 1998; Baranauskiene et al., 2007; Jafari et al., 2007; Kaushik & Roos, 2007; Bae & Lee, 2008; Chin et al., 2010). Since flavoring components are prone to loss by evaporation, oxidation or ingredient interactions, the encapsulation of flavor ingredients is among the most important applications in the food industry (Baranauskiene et al., 2007). The encapsulation matrix for flavor compounds can be selected from a wide variety of polymers, depending on the core material and desired characteristics of the microcapsule. Typical wall materials include proteins (sodium caseinate, whey proteins, soy proteins and gelatin) and hydrocolloids (modified starch and gum arabic). Among proteins, whey proteins have been shown to be an excellent encapsulating agent for microencapsulation of oils/fats and volatiles (Sheu & Rosenberg, 1995; Moreau & Rosenberg, 1996; Rosenberg & Sheu, 1996; Bae & Lee, 2008; Charve & Reineccius, 2009; Rodea-González et al., 2012). Moreover, although a variety of methods have been proposed to encapsulate flavors, spray-drying and extrusion are still the most common techniques. It has been shown that wall systems of spray-dried microcapsules consisting of whey proteins provide effective protection against core oxidation (Kim & Morr, 1996; Bylaitë et al., 2001).

Previous studies have indicated that the addition of small quantities of specific low molecular weight compounds to matrices can improve the storage stability of bioactive (Roussenova et al., 2010). These low molecular weight compounds act as packing enhancer, leading to a reduction of the molecular hole size in the glassy state,

which could explain the improved glassy-state barrier properties and encapsulation performance. According to Rosenberg and Sheu (1996), the addition of lactose into WPI-based wall systems improves the volatile retention during spray drying and limits the core extractability. This is due to lactose in its amorphous state acting as a hydrophilic sealant that significantly limits diffusion of the hydrophobic core through the wall and thus leads to high microencapsulation efficiency values. Furthermore, amorphous carbohydrates in the glassy state are widely used as matrices for the encapsulation and stabilization of nutrients, pharmaceutics, and other bioactive compounds (Levi & Karel, 1995; Fäldt & Bergenståhl, 1996a, 1996b; Drusch et al., 2006; Kaushik & Roos, 2008; Naknean & Meenune, 2010; Zhou & Roos, 2012; Lim et al., 2014; Lim & Roos, 2015). In these applications, the glass transition temperature of amorphous matrix has been used as the central physical parameter for the optimization of processing conditions and storage stability (Soottitantawat et al., 2004; Townrow et al., 2010). When the temperature increases from below to above the glass transition temperature, many of the physical properties of the amorphous matrix show a rapid change, including increases in the free volume, molecular mobility, and dielectric coefficient. Large changes in viscoelastic properties of amorphous powders also occur above the glass transition temperatures (Jones, 1999; Kasapis, 2001; Royall et al., 2005). Once an encapsulation matrix has gone through the glass transition and entered the metastable rubbery state, the rates of deteriorative reactions and diffusion of the flavor from the particle matrix increase dramatically (Risch & Reineccius, 1995; Whorton, 1995).

In addition, since the presence of high molecular weight protein or carbohydrate in the amorphous lactose-based systems could increase diffusion distance (Silalai & Roos, 2010a, 2011b; Potes et al., 2012), the ratios of low molecular weight

compounds in encapsulation systems may affect the properties of whey protein-based systems. Moreover, water is a highly efficient plasticizer of carbohydrates and the glass transition temperature of an amorphous carbohydrate matrix decreases strongly with increasing water content (Jouppila & Roos, 1994; Jouppila et al., 1997; Partanen et al., 2008; Velasco et al., 2009; Zhou & Roos, 2012). According to Kilburn et al. (2004), the diffusional mobility of small molecules such as water, gases, or volatile organic compounds increases rapidly with increasing water content in both the glassy and rubbery states. The water content and water activity of the encapsulation matrix are key parameters for understanding the physical behavior and barrier properties of amorphous carbohydrates (Ubbink, 2003). Levi and Karel (1995) stated that water resulted in a lowering of T_g and acceleration of relaxation processes, which increased the release of 1-n-propanol in amorphous carbohydrate glasses. However, there is no further study about the roles of lactose content and water plasticization on the encapsulation properties of wall systems, and especially the relationship between the mechanical properties of amorphous matrix and their barrier properties.

Therefore, the aim of present study was to investigate the effect of amorphous lactose content and water plasticization on encapsulation properties and flavor release in dairy-based powders. How the physical and mechanical properties of wall systems affect flavor release was also investigated.

2. Materials and methods

2.1 Materials

α-lactose monohydrate (> 99% purity) was donated by Arla Foods Ingredients (Sønderhøj 10-12, 8260 Viby J, Denmark). WPI, containing 71% β-lactoglobulin

and 12% α-lactalbumin, was obtained from Davisco Food International (Le Sueur, MN, USA). Ethyl butyrate (EB), hydroxylamine hydrochloride, *n*-hexane and aluminum oxide calcined powder (≥ 99% purity) were purchased from Sigma−Aldrich (St. Louis, MO, USA).

2.2 Emulsion preparation

Wall material solutions were prepared in deionized water at 40 ºC for 2 h and then kept overnight on the magnetic stirrers to ensure complete hydration at room temperature (23-25 ºC). Total solids concentration of wall materials was 25% (w/w), which composed of lactose/WPI mixtures or WPI. The mass ratios of 4:1, 1:1, and 1:4 for lactose/WPI mixtures were used in this study. They were defined as S1 (lactose/WPI (4:1) mixture), S2 (lactose/WPI (1:1) mixture), S3 (lactose/WPI (1:4) mixture), and S4 (WPI) according to the wall materials. Then ethyl butyrate was emulsified into the wall solutions at a proportion of 20% (w/w of wall solids). All emulsions (oil in water) were prepared in two stages. Coarse emulsion was prepared using an ULTRA-TURRAX (IKA, Staufen, Germany) operated at 10000 rpm for 1 min. Then the coarse emulsion was further homogenized using a M110-EH Microfluidizer with a 75 μm Y-type ceramic interaction chamber (Microfluidics International Corp., Newton, MA, USA) at 50 MPa for three successive homogenization steps. The homogenization process by microfluidizer was performed at room temperature with running cold water.

2.3 Spray drying

All emulsions were spray-dried by an ANHYDRO single stage spray dryer with a centrifugal atomizer (Copenhagen, Denmark) at the Teagasc Food Research Centre, Moorepark, Fermoy, Co. Cork, Ireland. The inlet air temperature was around 170 ±

2 °C and the outlet temperature around 90 ± 2 °C. Spray-dried solids were kept immediately in desiccators over P_2O_5 at room temperature. Each analysis was carried out within 2 months after spray drying.

2.4 Physical properties

Loose bulk density of powders was measured using a Jolting volumeter (Funke Gerber, Berlin, Germany). Particle density (ρ_p) was measured using a Gas Pycnometer (Accupyc II 1340 Gas Pycnometer, Micromeritics Instrument Corporation, USA). Particle size distribution and specific surface area (SSA) of powder particles were determined by laser light scattering using a Malvern Mastersizer 3000 (Malvern Instruments Ltd., Worcestershire, UK). Powder sample was added to the standard venturi disperser with a hopper gap of 2.5 mm and then fed into the dispersion system. Compressed air at 0.75 bar was used to transport and suspend the powder particles through the optical cell. A measurement time of 10 s was used, and background measurements were made using air for 20 s. The laser obscuration level was at 2-10%.

2.5 Chemical analysis

Protein content in powders was determined using a FP 628 Nitrogen Determinator (LECO Corporation, Lakeview Avenue, St. Joseph, Michigan, USA). Lactose content was determined using an Automatic Polarimeter (Autopol 1, Rudolph Research Analytical, Hackettstown, NJ, USA). Water content was determined using a HR83 Halogen Moisture Analyzer (Mettler Toledo International Inc., Im Langacher Greifensee, Switzerland). Water activity was measured using a water activity meter (Novasina LabMaster AW, Novatron Scientific Ltd., West Susses, UK).

In order to determine encapsulated EB content in powders, EB was extracted from encapsulated powders according to the method of Kaushik and Roos (2007). 1 g of powder was dissolved in 20 mL of deionized water in glass bottles and 10 mL of hexane was added, followed by mixing with a rota mixer for 1 min. Encapsulated EB was extracted with hexane by heating the samples in glass bottles at 45 ºC in a water bath for 15 min with intermittent mixing. All glass bottles were kept closed with caps and sealed with sealing film during extraction. Then the bottles were cooled to room temperature and hexane was separated from aqueous phase by centrifugation at 4000 r/min for 20 min. The amount of EB present in hexane was quantified by the method of Sheu and Rosenberg (1995). 0.5 mL of centrifuged hexane was mixed with 4.5 mL 50% ethanol solution. Then 4 mL of a fresh reagent mixture consisting of a 1:1 ratio of 3 mol/L sodium hydroxide and 13.9% (w/w) hydroxylamine hydrochloride was added. The mixture was thoroughly mixed by vortex mixer for 30 sec, and incubated for 10 min at 25 ºC. 2 mL of 3 mol/L hydrochloric acid was then added to stop the reaction. The colour was developed after an addition of 2 mL 10% (w/w) ferric chloride solution in 0.1 mol/L hydrochloric acid and then measured absorbance using a spectrophotometer at 525 nm. The amount of EB was determined from calibration standard curves. The EB content of each sample was carried out in triplicate.

The ratio of encapsulated EB in powders after spray drying to initial EB added in the emulsion was defined as encapsulation efficiency (%). The ratio of encapsulated EB in encapsulated powders during equilibration at different relative humidity (RH) to encapsulated EB in encapsulated powders after spray drying was defined as flavor retention (%).

2.6 Water sorption and flavor release from powders at different RHs

Approximately 1 g of powders was weighed into small glass vials (25 mL). All vials with powders were equilibrated for 216 h in evacuated desiccators over saturated salt solutions of $MgCl_2$, K_2CO_3, $Mg(NO_3)_2$, and $NaNO_2$, giving RH of 33%, 44%, 54%, and 65%, respectively. All desiccators were placed at incubators with temperature of 25 °C during equilibration. 24 vials were prepared for each powder at every RH. Three vials of each powder were taken out from every desiccator at 0, 6, 12, 24, 48, 72, 120, 168 and 216 h, respectively and the weight of samples was measured. Then water content of each powder was determined as a function of time. The residual amount of EB in the powder was determined by the method described above. The flavor retention in powders was calculated as a function of time.

2.7 Glass transition determination

The powders were equilibrated at different RHs for 0, 6, 12, 24, 48, 72, 120, 168 and 216 h, respectively. Then the glass transition temperatures, T_g (onset), of encapsulated powders were determined using a differential scanning calorimeter (DSC Q2000, TA Instruments, Crawley, UK). To determine T_g values, 10-15 mg of equilibrated powders was transferred to Tzero pans. The DSC pans were hermetically sealed with Tzero hermetic lids and samples were analysed. An empty pan was used as a reference. The temperature range of the scans was varied between -10 ºC and 180 ºC depending on the water content of powders. The heating rate was 5 °C/min and the cooling rate was 10 °C/min during scanning. All measurements were carried out in duplicate. T_g values were determined using TA universal analysis software, version 5.1.2 (TA Instruments, Crawley, UK) and were taken as the onset-point of the endothermic baseline shift.

2.8 Dynamic mechanical analysis

The powders were equilibrated at different RHs for 0, 6, 12, 24, 48, 72, 120, 168 and 216 h, respectively. Then a dynamic mechanical analyser (DMA Q800, TA Instruments, Crawley, UK) was used, in conjunction with a gas cooling accessory (GCA) tank, to determine the dynamic mechanical properties of powders. A rectangular stainless steel powder holder was designed to generate a defined geometry to contain powder with inner dimensions of 60 mm × 11 mm × 1 mm. A pre-weighed mass of powder mixed with aluminum oxide calcined powder at the ratio 4:1 was evenly spread within this shallow container, and the upper lid was then placed onto the top surface of the powder (Mahlin et al., 2009). As aluminum oxide calcined powder showed no effect on mechanical property results of dairy solids, it was added to protect dairy powder from sticking on the powder holder during the heating test. The measurements were made at a heating rate of 2 °C /min from 0 to 120 °C. DMA was operated by a sinusoidal deformation applied to the powder sample holder at a fixed strain. The amplitude was 15 μm. During dynamic heating, the samples were analysed for storage modulus (E') and loss modulus (E'') using single frequency 1 Hz. The α-relaxation temperatures, T_α, were determined using TA universal analysis software, version 5.1.2 (TA Instruments, Crawley, UK).

2.9 Statistical analysis

Measurement of protein content, glass transition, and dynamic mechanical analysis were performed in duplicate, with all other analyses performed in triplicate. Results were expressed as mean ± standard deviations (SD). One-way analysis of variance (ANOVA) was used to determine the significant differences between the

mean values of each test (Microsoft Office Excel 2010, Microsoft, Inc., Redmond, WA, USA). A significance level of $P < 0.05$ was used throughout the study.

3. Results and discussion

3.1 Powder characteristics

The powder characteristics of encapsulation systems after spray drying are shown in Table 6-1. The EB content in the encapsulated powder with wall material consisting of lactose/WPI (4:1) mixture was significantly ($P < 0.05$) higher than those in the encapsulated powders with wall materials consisting of lactose/WPI mixtures at ratio 1:1 and 1:4, and WPI. As a result, the wall material consisting of lactose/WPI (4:1) mixture showed significantly ($P < 0.05$) higher encapsulation efficiency than S2, S3 and S4. This might be due to the highest lactose content in S1, which could form a large extent of amorphous structure to entrap EB during spray drying. Roussenova et al. (2010) also observed that the density of the amorphous matrix increased when the molecular weight of a glassy carbohydrate matrix is decreased.

Therefore, the glass structure and increase in density of amorphous matrix might improve the barrier properties of wall materials with higher amount of lactose, and resulted in the higher encapsulation efficiency of wall materials with lactose/WPI (4:1) mixture. However, when lactose content was lower than 50% in the wall materials, the present of lactose did not have significant impact on encapsulation efficiency of wall materials during spray drying (Table 6-1).

Table 6-1 Powder characteristics of encapsulation systems

Systems	Water content (%)	Water activity	d_{50} (μm)	SSA (m^2/kg)	Particle density (g/cm^3)	Loose bulk density (g/cm^3)	Ester content (mg/g of dry solids)	Encapsulation efficiency (%)
S1 lactose/WPI 4:1	$2.52^{d} \pm 0.03$	$0.17^{ab} \pm 0.00$	$26.20^{c} \pm 0.00$	$646.73^{a} \pm 3.27$	$1.0986^{c} \pm 0.0031$	$0.4117^{a} \pm 0.0002$	$71.04^{a} \pm 0.85$	$42.62^{a} \pm 0.51$
S2 lactose/WPI 1:1	$2.69^{c} \pm 0.02$	$0.16^{b} \pm 0.00$	$24.30^{d} \pm 0.43$	$672.93^{a} \pm 5.32$	$1.0949^{c} \pm 0.0093$	$0.3189^{b} \pm 0.0051$	$61.48^{b} \pm 3.65$	$36.89^{b} \pm 2.19$
S3 lactose/WPI 1:4	$4.07^{b} \pm 0.06$	$0.18^{a} \pm 0.00$	$27.20^{b} \pm 0.08$	$608.27^{b} \pm 5.94$	$1.1342^{a} \pm 0.0043$	$0.2763^{c} \pm 0.0010$	$60.44^{b} \pm 1.54$	$36.26^{b} \pm 0.92$
S4 WPI	$4.26^{a} \pm 0.05$	$0.16^{ab} \pm 0.01$	$30.37^{a} \pm 0.09$	$506.53^{c} \pm 3.85$	$1.1232^{b} \pm 0.0001$	$0.2466^{d} \pm 0.0011$	$62.52^{b} \pm 3.55$	$37.51^{b} \pm 2.13$

[1] Values are mean ± standard deviation (n = 3).
[2 a-d] Values within columns with different superscripts are significantly different at $P < 0.05$.

Rosenberg and Sheu (1996) also showed similar results. According to their study (Rosenberg & Sheu, 1996), the retention of EB in wall system consisting of a 1:1 mixture of WPI and lactose was not higher than that in wall system consisting of WPI when the initial core material load was lower than 30% (w/w), which was in agreement with our study. Therefore, the addition of lactose in WPI-based wall systems did not have significant improvement in the barrier properties when the lactose content was lower than 50%. Additionally, the water content of powders with lower ratios of lactose was significantly ($P < 0.05$) higher, while all powders had similar water activities. Moreover, the particle size of powders with higher amount of lactose was smaller, and the SSA values of them were larger. Furthermore, the powders with higher amount of lactose showed smaller particle density, but they showed higher loose bulk density.

3.2 Water sorption

Water sorption of powders over various water activities as a function of time was plotted, as shown in Figure 6-1. Since EB in powders kept releasing during storage period, the water contents of powders shown in Figure 6-1 were not only according to the mass changes of powders during storage, but they were modified according to the mass change of flavor release during storage. The initial water contents of powders before equilibration are shown in Table 6-1.

The wall system consisting of only WPI (S4) sorbed the highest amount of water in the range of 0.33-0.65 a_w. S2 with wall material consisting of lactose/WPI (1:1) mixture sorbed the lowest amount of water at 0.33 a_w and 0.44 a_w. At 0.54 a_w, loss of sorbed water was found in S1 with wall material consisting of lactose/WPI (4:1) mixture after 48 h of storage, while a minor of loss of sorbed water was observed in

S2 with wall material consisting of lactose/WPI (1:1) mixture after 72 h of storage. The rates of water sorption and lactose crystallization for powders at 0.65 a_w were higher than those at 0.54 a_w. The loss of sorbed water was observed in powders with wall materials consisting of lactose/WPI mixtures at ratio 4:1, 1:1, and 1:4 after 12 h, 24 h, and 24 h of storage at 0.65 a_w, respectively. However, there was only a minor loss of sorbed water in S3 with wall material consisting of lactose/WPI (1:4) mixture.

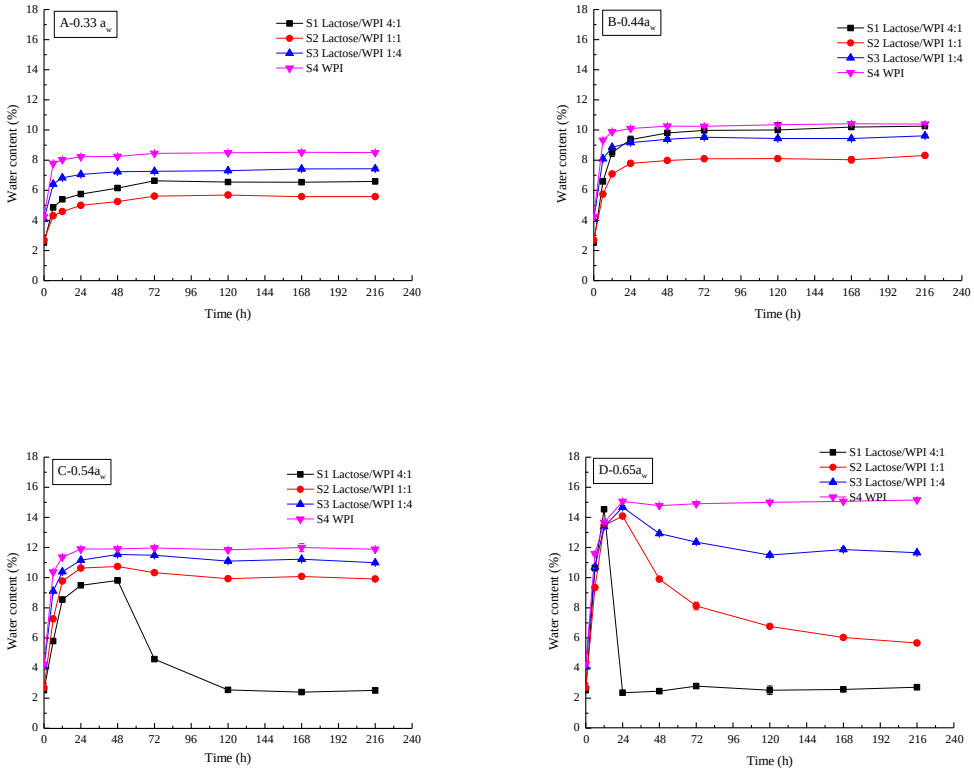


Figure 6-1 Water sorption of powders at 0.33 a_w (A), 0.44 a_w (B), 0.54 a_w (C), and 0.65 a_w (D) at 25 ºC. Loss of sorbed water at 0.54 a_w and 0.65 a_w indicates lactose crystallization.

In the present study, the presence of high molecular weight protein delayed lactose crystallization at 0.54 a_w and 0.65 a_w, which agreed with the previous studies (Haque & Roos, 2004a, 2004b; Fan & Roos, 2015). The presence of protein might

result in the physical blocking or steric hindrance, which could reduce molecular diffusion and delay lactose crystallization (Fan & Roos, 2015).

Since the increase of water can lead to an increase in free volume by decreasing the molecular packing of the matrix molecules (van den Dries et al., 2000), the difference in water content of encapsulated powders (S1-S4) during storage at various water activities might result in different rates of flavor release in the amorphous matrix. Furthermore, the structure of encapsulated matrix was destroyed as lactose crystallization occurred when water content increased at 0.54 a_w and 0.65 a_w, which might result in a quick release of flavor from encapsulated powders. In addition, the collapse of amorphous matrix might also reduce flavor molecular diffusion through the matrix and result in re-encapsulation of flavour compound when lactose crystallised (Goubet et al., 1998).

3.3 Glass transition

The glass transition temperatures of powders (S1-S3) equilibration at various RHs during water sorption were measured using a DSC and are shown in Table 6-2. The T_g values decreased with increasing storage time in the range of 0.33-0.65 a_w before showing lactose crystallization (Table 6-2), which showed typical water plasticization of amorphous materials (Jouppila et al., 1997; Haque & Roos, 2004a, 2004b; Potes et al., 2012; Zhou & Roos, 2011). Moreover, the T_g values of lactose decreased when the storage RH increased. Powder with wall material of lactose/WPI (1:4) mixture showed significantly higher T_g values than those with wall materials of lactose/WPI mixtures at ratio 4:1 and 1:1 at 0.44-0.65 a_w. This was in agreement with the results of Fan and Roos (2016). They indicated the T_g value of lactose/WPI mixture at ratio 3:7 was higher than those of lactose/WPI mixtures at ratios 7:3 and

1:1 at 0.33 a_w. The increasing effect of T_g values in powder with lactose/WPI (1:4) mixture might be due to the presence of high amount of protein with high molecular weight.

Table 6-2 Glass transition temperatures (ºC), T_g, of powders with wall materials consisting of lactose/WPI mixtures storage at 0.33 a_w, 0.44 a_w, 0.54 a_w, and 0.65 a_w at 25 ºC for different hours.

Water activity	Time (h)	Systems		
		S1 lactose/WPI 4:1	S2 lactose/WPI 1:1	S3 lactose/WPI 1:4
Initial powders	**0**	64 ± 0.5	57 ± 0.0	65 ± 0.0
0.33	**6**	55 ± 1.0	56 ± 1.0	63 ± 1.0
	12	46 ± 0.5	46 ± 0.5	45 ± 1.0
	24	46 ± 0.5	47 ± 0.0	47 ± 0.5
	48	45 ± 0.0	46 ± 0.5	49 ± 0.0
	72	41 ± 0.0	44 ± 0.5	45 ± 0.5
	120	40 ± 0.0	42 ± 0.0	42 ± 0.0
	168	39 ± 0.5	42 ± 0.0	43 ± 0.5
	216	40 ± 0.0	41 ± 0.5	43 ± 0.0
0.44	**6**	40 ± 0.0	41 ± 0.0	40 ± 0.0
	12	30 ± 0.0	31 ± 0.0	41 ± 0.0
	24	24 ± 0.5	28 ± 0.5	41 ± 1.0
	48	22 ± 0.0	25 ± 0.5	41 ± 0.0
	72	22 ± 0.0	25 ± 0.0	39 ± 0.0
	120	22 ± 0.5	25 ± 0.5	39 ± 0.5
	168	21 ± 0.5	25 ± 0.0	39 ± 0.0
	216	21 ± 0.0	25 ± 0.5	39 ± 0.5
0.54	**6**	33 ± 0.5	33 ± 0.5	38 ± 0.5
	12	13 ± 0.5	16 ± 0.0	35 ± 0.0
0.65	**6**	15 ± 0.5	16 ± 0.0	34 ± 1.0

[1] Values are mean ± standard deviation (n = 2).

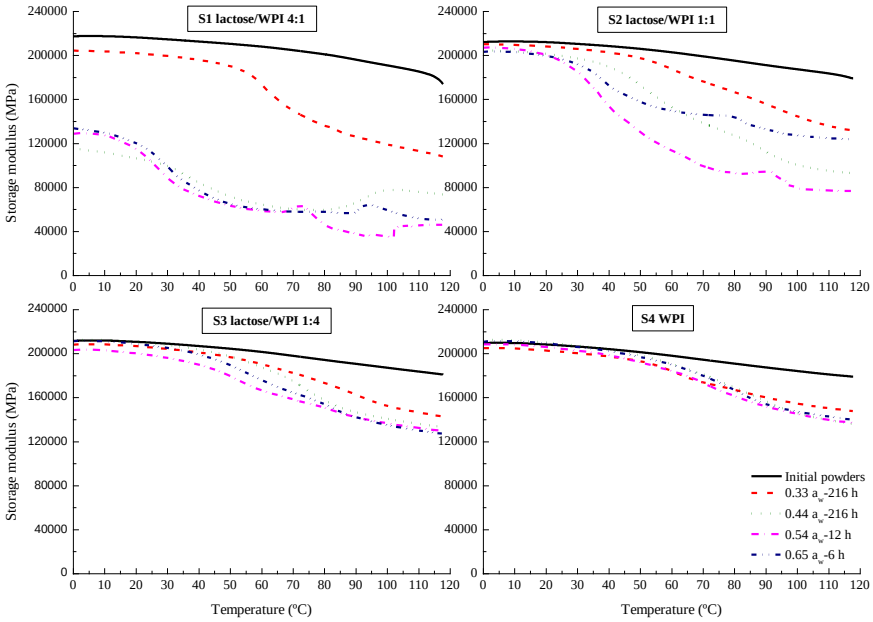
[2] Initial powders were the encapsulated powders after spray drying.

Phase transitions play an important role in encapsulation processes (Whorton, 1995). Levi and Karel (1995) stated that flavor retention was dependent on temperature, water content and the degree of matrix collapse. In the glassy state, flavors have very low diffusion rates in amorphous barriers. Due to the low

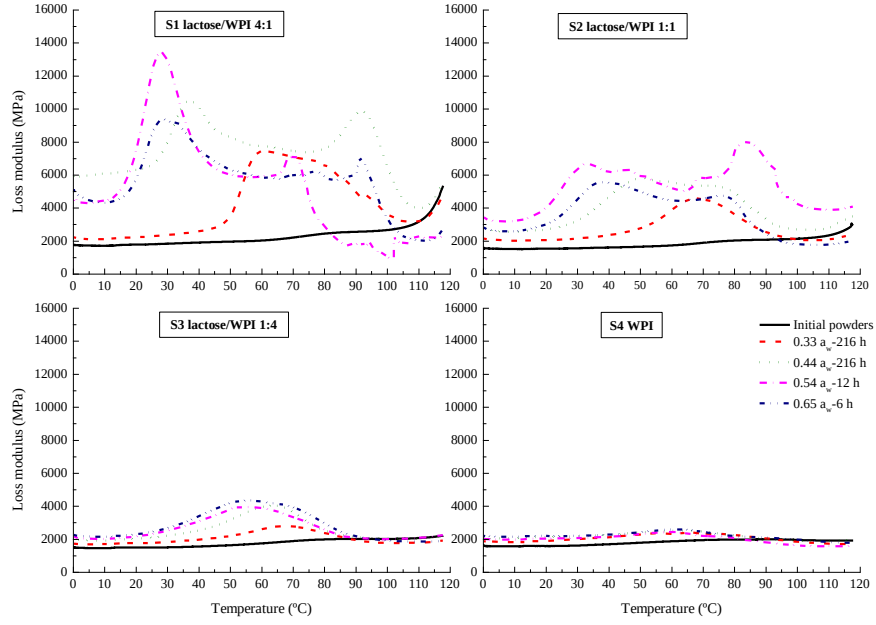
molecular mobility of barriers, flavor release from powders in the glassy state is limited. When a glass is heated to above the glass transition, molecules gain translational mobility and enter the supercooled, liquid-like state. The increase in molecular mobility of amorphous matrix would result in the increase of evaporation of volatile flavors. Since the T_g values of powders were varied according to the storage time, storage RH and wall material compositions, the rate of flavor release was also affected by those conditions. Powders with lower amount of lactose might show lower rate of flavor release at high RH (> 44%).

3.4 Mechanical properties

Many mechanical properties of amorphous materials change dramatically around the glass transition. In this study, the mechanical properties of powders during storage over various RHs were measured using a DMA. The modulus changes of powders equilibration at 0.33-0.65 a_w are shown in Figure 6-2. Since the powders consisting of lactose showed lactose crystallization at 0.54 a_w and 0.65 a_w after storage a period (0.54 a_w: > 12 h; 0.65 a_w: > 6 h), the mechanical properties of powders were only measured before lactose crystallization (Figure 6-2). Additionally, the modulus changes of powders during storage at same RH for different hours are shown in Figure 6-3. Compared to the storage modulus of powders (S1-S4) after spray drying (Initial powders), S1 had significantly higher storage modulus than S2, S3 and S4 at the glassy state. This might be one of the reasons that the encapsulation efficiency of wall material consisting of lactose/WPI (4:1) mixture (S1) was significantly higher than those with lactose/WPI mixtures at ratio 1:1 and 1:4, and WPI (Table 6-1).

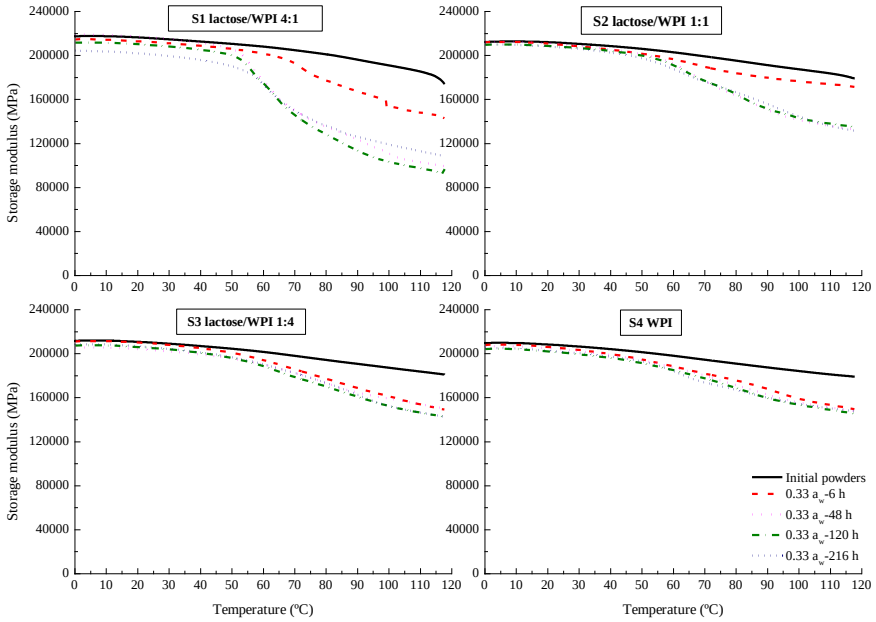


A

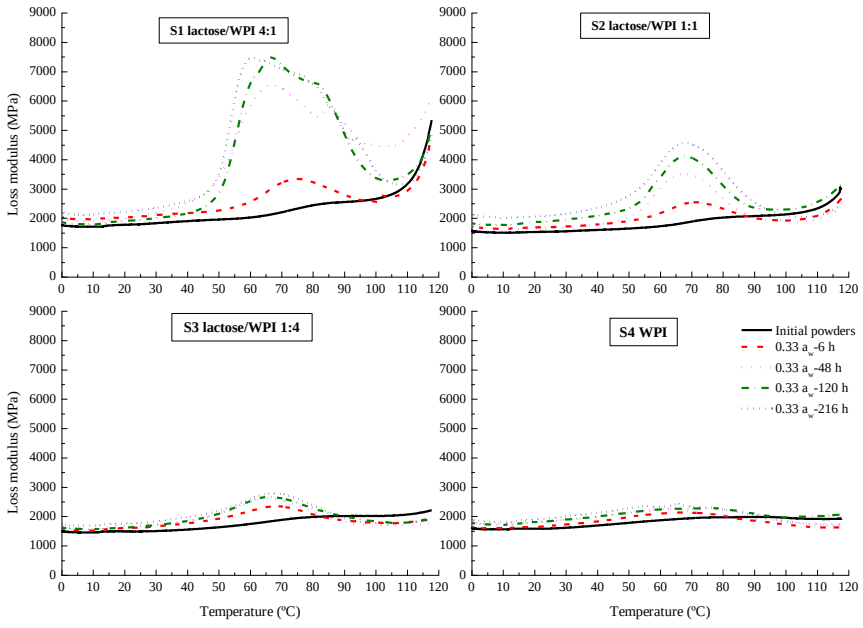


B

Figure 6-2 Storage modulus (A) and loss modulus (B) of powders equilibration at 0.33 a_w and 0.44 a_w for 216 h, 0.54 a_w for 12 h, and 0.65 a_w for 6 h before showing lactose crystallization at 25 ºC. Initial powders were the powders after spray drying.

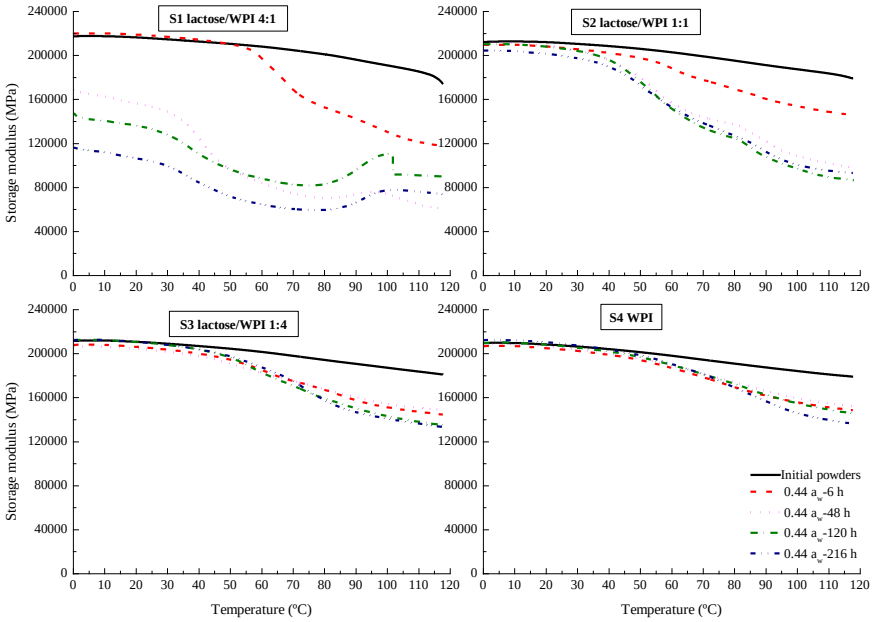


A1

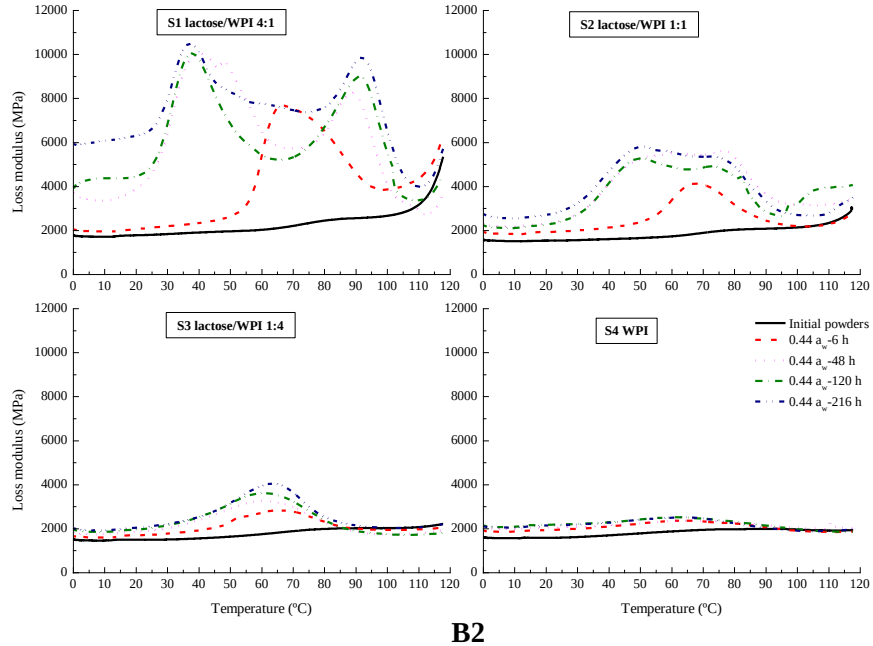


B1

Figure 6-3 Storage modulus (A1 and A2) and loss modulus (B1 and B2) of powders equilibration at 0.33 a_w and 0.44 a_w at 25 ºC for different hours. Initial powders were the encapsulated powders after spray drying.



A2



B2

Figure 6-3 (Continued).

The magnitudes of storage modulus changes for powders were larger at higher water activity (Figure 6-2 A). Moreover, the magnitudes of storage modulus changes

also increased with increasing storage time at same water activity (Figure 6-3 A1 and A2). Since increasing storage RH or storage time caused an increase in the water content of powders, powders with higher water content could result in larger magnitudes of storage modulus changes.

According to previous studies (Roudaut et al., 2004; Silalai & Roos, 2011b), the magnitudes of storage modulus and loss modulus changes were related to molecular mobility of materials. Therefore, increasing water content of powders could increase the molecular mobility of matrix, which might result in a high release rate of flavor in powders. Furthermore, the storage modulus of powders with higher amount of lactose in the wall materials had more significant change when water content increased (Figure 6-2 A). Similar results were also shown when the storage time of powders increased at same water activity (Figure 6-3 A1 and A2). These results indicated that increasing water content or lactose content of powders could increase molecular mobility and free volume of matrix at the glass transition region, which could accelerate the diffusion of flavor molecules during storage.

The changes of loss modulus of powders during equilibration were also measured using a DMA (Figure 6-2 and Figure 6-3). The loss modulus of powders was small and showed minor changes when the temperatures were below glass transition and they increased dramatically and reached peak values with increasing temperature to the glass transition region. This indicated the molecular mobility of powders increased dramatically in the glass transition region. Furthermore, the peak values of loss modulus of powders were affected by the lactose content and water content of matrix. Decreasing water content or lactose content could decrease the molecular

mobility of matrix in the glass transition region. As a result, that might decrease the diffusion of flavor molecules in the glass transition region.

In addition, the α-relaxation temperatures, T_α, were taken from the temperatures of loss modulus peak values at 1 Hz (Table 6-3). The T_α values of powders decreased with increasing water content as a result of water plasticization, which was in agreement with the study of Silalai and Roos (2010a). S1 showed significantly higher T_α values than other encapsulated powders after spray drying. The powder with wall material consisting of lactose/WPI (1:1) mixture (S2) showed the highest T_α values at 0.33 a_w, while powder consisting of only WPI showed the highest T_α values at 0.44 a_w, 0.54 a_w, and 0.65 a_w. The decrease of T_α values of S1 with the highest amount of lactose was larger as compared to those of S2-S4 when water content increased. These results indicated water content showed more significant effect on the structural relaxation of powders with wall materials consisting of higher amount of lactose. Since the diffusion of core materials is governed by the physical properties of the wall materials, such as the matrix structure, increasing water content of powders with wall materials consisting of higher lactose content might result in a higher diffusion of flavor molecules.

3.5 Flavor retention

The effects of water plasticization on the time-course of the flavor release in powders with different composition of wall materials are shown in Figure 6-4. The retention of EB was defined as the ratio of the residual amount of EB in the powder to the initial amount after spray drying. The flavor retention in powders did not show significant change during storage at 0.33 a_w at 25 ºC for 216 h, while the flavor retention of S1 showed a minor decrease with storing at 0.44 a_w. S2 showed the

highest flavor retention at 0.33 a_w and 0.44 a_w, which might be due to its lowest water contents at 0.33 a_w and 0.44 a_w (Figure 6-1). In addition, since the EB content of S1 was significantly higher as compared to those of other powders (S2-S4) after spray drying, S1 still had the highest EB content after storage at 0.33 a_w. However, the flavor retention of S1 dropped sharply with equilibration at 0.54 a_w. Similar result happened to the flavor retention of S1 and S2 when they were stored at 0.65 a_w. These results could be linked to lactose crystallization of encapsulating matrix, which were in agreement with the study of Zhou and Roos (2012). They stated that the amorphous structure protected the entrapped vitamins at low a_w, but crystallization of lactose accelerated vitamin degradation.

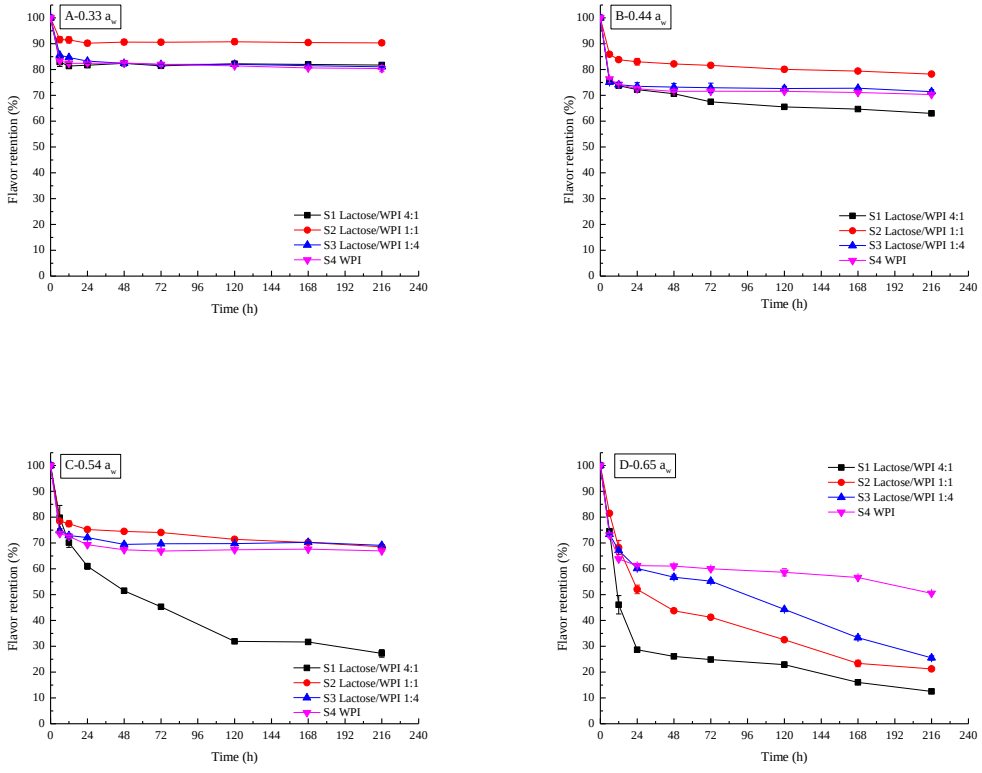


Figure 6-4 Flavor retention in powders equilibration at 0.33 a_w (A), 0.44 a_w (B), 0.54 a_w (C) and 0.65 a_w (D) at 25 ºC for different hours.

Since the T_g values of S1 at 0.54 a_w and 0.65 a_w were below the storage temperature (25 ºC) (Table 6-2), there was a decrease in the viscosity of matrix, and an increase in the diffusivity of flavor molecules. Moreover, collapse of amorphous matrix occurred when lactose showed plasticization. Then the amorphous matrix was unable to support itself against gravity. The flavor was forced from the crystallized matrix to the surface, and the retention of EB decreased sharply. Additionally, the rate of flavor release from S1 decreased as storage time increased at 0.54 a_w and 0.65 a_w. This might be due to the completely collapse of amorphous matrix after lactose crystallization, and then resulted in re-encapsulation of flavor compound in the collapse matrix (Goubet et al., 1998).

In addition, the water plasticization had more significant impact on the flavor retention of powders with wall materials consisting of larger amount of lactose (Figure 6-4). The flavor retention of S4 was larger than 50% even when it was stored at 0.65 a_w for 216 h (Figure 6-4 D). It was due to water plasticization had more significant influence on the molecular mobility and structural relaxation of powders with larger amount of lactose (Figure 6-2 and 6-3), which caused higher diffusion of flavor molecules in the powders with higher amount of lactose. As it also can be seen from Table 6-3, the α-relaxation temperatures of powders with higher amount of lactose decreased more significantly with increasing water content. Therefore, increasing lactose content in wall materials could increase the encapsulation efficiency at low water activities ($\leq$ 0.33 a_w). However, the presence of lactose could result in higher molecular mobility with increasing water content, which leaded to accelerate the rate of flavor release at high water activities ($\geq$ 0.54 a_w).

4. Conclusions

Amorphous encapsulated matrix using lactose/WPI mixtures as wall materials and ethyl butyrate as core materials were prepared by spray drying. The encapsulation efficiency of wall material consisting of lactose/WPI (4:1) mixture was significantly higher compared to wall material consisting of only WPI. However, wall materials with lactose/WPI mixtures at ratios of 1:1 and 1:4 did not show similar result. The different ratios of lactose/WPI in wall materials resulted in the different physical properties of encapsulated powders, including particle size, specific surface area, loose bulk density and particle density, which might affect the storage stability and flavor release of powders. The flavor retention of powders did not show significant change during equilibration at 0.33 a_w, while powder with wall material consisting of lactose/WPI (1:1) mixture had significantly higher flavor retention at 0.33 a_w and 0.44 a_w. Powders with wall materials consisting of higher amount of lactose showed dramatically a decrease in their flavor retention with equilibration at 0.54 a_w and 0.65 a_w, which was as a result of lactose crystallization. Mechanical property study indicated that powder with higher amount of lactose showed higher molecular mobility with increasing water content. Water plasticization showed more significant effect on the glass transition and structural relaxation of powder with higher amount of lactose. Therefore, increasing lactose content could increase the encapsulation efficiency of wall materials during spray drying. However, this also could result in a higher rate of flavor release with storage at high water activity.

CHAPTER SEVEN

Characterization of mechanical and encapsulation properties of lactose/maltodextrin/WPI matrix

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Abstract

In this study, encapsulation systems using lactose/whey protein isolate (WPI) (4:1) or lactose/maltodextrin (MD)/WPI (3:1:1 or 1:3:1) mixtures as wall materials and ethyl butyrate (EB) as core materials were produced by spray drying. Wall material consisting of lactose/WPI (4:1) mixtures had the highest encapsulation efficiency for EB during spray drying, while wall materials consisting of lactose/MD/WPI (1:3:1) mixtures had higher encapsulation efficiency compared to wall materials consisting of lactose/MD/WPI (3:1:1) mixtures. The presence of MD in wall systems delayed the crystallization of amorphous lactose at 0.54-0.76 a_w, which decreased the rate of flavor release from encapsulation systems. Furthermore, the magnitudes of modulus changes for wall systems with higher amount of MD was smaller compared to those with lower amount of MD when water content increased. The addition of MD could increase stiffness and thus, reduce molecular mobility of encapsulation systems. Wall systems consisting with lactose/MD (13-17)/WPI (1:3:1) mixtures and lactose/MD (23-27)/WPI mixtures had higher flavor contents than other wall systems after equilibration at high water activity ($\geq$ 0.54 a_w).

Keywords: Encapsulation; Maltodextrin; Amorphous matrix; Molecular mobility; Flavor release

1. Introduction

Many flavors have been encapsulated, generally in solid matrices which are often produced by spray drying for many years (Bhandari et al., 1992; Sheu & Rosenberg, 1995; Goubet et al., 1998; Arvisenet et al., 2002; Baranauskiene et al., 2007). Those solid matrices are often formed by glass-forming food components. Amorphous carbohydrates in the glassy state are widely used as solid matrices for the encapsulation and stabilization of nutrients, pharmaceutics, and other bioactive compounds (Roos, 2010). Encapsulation matrix in glassy state combines high physical and chemical stability with very high barrier properties with respect to oxygen and organic molecules (Ubbink, 2003). Numerous recent studies have discussed the glass formation of amorphous matrices in encapsulation processes (Vega & Roos, 2006) and emphasized the importance of the glass-forming ability of the encapsulant in protecting sensitive components (Ubbink & Krüger, 2006). In these applications, the glass transition temperature and water content of the amorphous matrix have been used as the central physical parameters for the optimization of processing conditions and storage stability (Townrow et al., 2010).

In amorphous encapsulation systems, the release and stability of core materials is related to the molecular mobility of wall materials, and phase transitions play an important role in most encapsulation processes where the initial objective is to form a stable amorphous glass structure to entrap the flavour compounds and inhibit mobility of molecules. Increasing water content or temperature can result in a transition which occurs in amorphous matrix from the glassy state to the rubbery state. Once an encapsulated matrix has gone through the glass transition and entered the metastable rubbery state, the viscosity decreases while the molecular mobility and free volume of the polymer structure increase. The rates of deteriorative

reactions and diffusion of the flavor from the particle matrix also increase (Whorton, 1995).

Previous studies have indicated that miscible high molecular weight components generally increase viscosity and the average molecular weight, and decrease molecular mobility of amorphous systems (Roos & Karel, 1991; Sillick & Gregson, 2009). Moreover, they may also increase the glass transition temperatures. Furthermore, the addition of a second carbohydrate component to an amorphous system may delay crystallization of amorphous materials (Mazzobre et al., 2001; Potes et al., 2012). Additionally, the primary α-relaxations of solids systems are mainly governed by the miscible solids components and may shift to higher temperature with increasing the contents of high molecular weight components at all a_w (Silalai & Roos, 2011b).

Maltodextrin has been used in encapsulation of food components for several decades (Bhandari et al., 1992; Sheu & Rosenberg, 1995; Gunning et al., 1999; Yoshii et al., 2001; Soottitantawat et al., 2005; Jafari et al., 2007; Bae & Lee, 2008). Previous studies have indicated that sugars in mixtures with maltodextrins of low dextrose equivalent (DE) form systems with high viscosity and are often used to increase the T_g of food solids to improve their dehydration properties and stability (Bhandari et al., 1997; Chronakis, 1998). Sheu and Rosenberg (1995) stated that combinations of whey proteins and high DE maltodextrins or corn syrup solids were effective wall systems for encapsulation of volatiles, and Shiga et al. (2001) indicated that blending of MD in the feed liquid decreased the release rate of *d*-limonene in β-cyclodextrin encapsulation system. Additionally, physical properties, such as wettability and density, were greatly improved by increasing the maltodextrin ratio in the wall systems (Bae & Lee, 2008), which may affect

encapsulation efficiency and flavor release during production and storage. However, there is no further study about how the types and contents of maltodextin affect the encapsulation properties of amorphous matrix, and the relationship between mechanical properties and encapsulation properties. Therefore, a better understanding of the roles of maltodextrin in amorphous encapsulation systems is very important.

Our previous studies have shown that wall material consisting of lactose/whey protein isolate (WPI) (4:1) mixture had significantly ($P < 0.05$) higher encapsulation efficiency compared to wall material consisting of only WPI. The objectives of this study were to investigate the influence of maltodextrin type and contents on mechanical and encapsulation properties of wall systems consisting of lactose/maltodextrin/WPI mixtures. The relationship between flavor release and mechanical properties of encapsulation systems was also studied.

2. Materials and methods

2.1 Materials

α-lactose monohydrate (> 99% purity) was offered by Arla Foods Ingredients (Sønderhøj 10-12, 8260 Viby J, Denmark). WPI, containing 71% β-lactoglobulin and 12% α-lactalbumin, was obtained from Davisco Food International (Le Sueur, MN, USA). Maltodextrin (MD) with dextrose equivalent (DE) values of 4-7, 13-17, and 23-27 were donated by Grain Processing Corporation (Muscatine, lowa 52761-1494, USA). Ethyl butyrate (EB), hydroxylamine hydrochloride, n-hexane and aluminum oxide calcined powder (≥ 99% purity) were purchased from Sigma−Aldrich (St. Louis, MO, USA).

2.2 Emulsion preparation

Wall material solutions were prepared in deionized water at 40 ºC for 2 h and then kept overnight on the magnetic stirrers to ensure complete hydration at room temperature (23-25 ºC). Total solids concentration of wall materials was 25% (w/w), which composed of lactose/WPI (4:1) mixture or lactose/maltodextrin/WPI mixtures. The weight ratios of lactose/maltodextrin/WPI mixtures were 3:1:1 and 1:3:1, respectively, and MD with DE values of 4-7, 13-17, and 23-27 were used, respectively. Then ethyl butyrate was emulsified into the wall solutions at a proportion of 20% (w/w of wall solids). All emulsions (oil in water) were prepared in two stages. Coarse emulsion was prepared using an ULTRA-TURRAX (IKA, Staufen, Germany) operated at 10000 rpm for 1 min. Then the coarse emulsion was further homogenized using a M110-EH Microfluidizer with a 75 μm Y-type ceramic interaction chamber (Microfluidics International Corp., Newton, MA, USA) at 50 MPa for three successive homogenization steps. The homogenization process by microfluidizer was performed at room temperature with running cold water.

2.3 Spray drying

All emulsions were spray-dried by an ANHYDRO single stage spray dryer with a centrifugal atomizer (Copenhagen, Denmark) at the Teagasc Food Research Centre, Moorepark, Fermoy, Co. Cork, Ireland. The inlet air temperature was around 170 ± 2 °C and the outlet temperature around 90 ± 2 °C. Spray-dried solids were kept immediately in desiccators over P_2O_5 at room temperature. Each analysis was carried out within 2 months after spray drying.

2.4 Powder characteristics

2.4.1 Physical properties

Particle density (ρ_p) of encapsulation systems was measured using a Gas Pycnometer (Accupyc II 1340 Gas Pycnometer, Micromeritics Instrument Corporation, USA). Particle size distribution and specific surface area (SSA) of encapsulation systems were determined by laser light scattering using a Malvern Mastersizer 3000 (Malvern Instruments Ltd., Worcestershire, UK). Powder sample was added to the standard venturi disperser with a hopper gap of 2.5 mm and then fed into the dispersion system. Compressed air at 0.75 bar was used to transport and suspend the powder particles through the optical cell. A measurement time of 10 s was used, and background measurements were made using air for 20 s. The laser obscuration level was at 2-10%. In addition, morphological characteristics of encapsulation systems were determined using a Malvern Morphologi G3 S (Malvern Instruments Ltd., Worcestershire, UK). 5 mm^3 volume powder samples were dispersed on the glass plate. 2.5× objective was used for the measurement in this study. In this study, each sample was measured in triplicate to get the average values.

2.4.2 Chemical analysis

Water content was determined using a HR83 Halogen Moisture Analyzer (Mettler Toledo International Inc., Switzerland). Water activity was measured using a water activity meter (Novasina LabMaster AW, Novatron Scientific Ltd, West Susses, UK).

In order to determine encapsulated EB content in powders, EB was extracted from powders according to the method of Kaushik and Roos (2007). 1 g of powder was dissolved in 20 mL of deionized water in glass bottles and 10 mL of hexane was added, followed by mixing with a rota mixer for 1 min. Encapsulated EB was extracted with hexane by heating the samples in glass bottles at 45 ºC in water bath

for 15 min with intermittent mixing. All glass bottles were kept closed with caps and sealed with sealing film during extraction. Then the bottles were cooled to room temperature and hexane was separated from aqueous phase by centrifugation at 4000 r/min for 20 min. The amount of EB present in hexane was quantified by the method of Sheu and Rosenberg (1995). 0.5 mL of centrifuged hexane was mixed with 4.5 mL 50% ethanol solution. Then 4 mL of a fresh reagent mixture consisting of a 1:1 ratio of 3 mol/L sodium hydroxide and 13.9% (w/w) hydroxylamine hydrochloride was added. The mixture was thoroughly mixed by vortex mixer for 30 sec, and incubated for 10 min at 25 ºC. 2 mL of 3 mol/L hydrochloric acid was then added to stop the reaction. The colour was developed after addition of 2 mL 10% (w/w) ferric chloride solution in 0.1 mol/L hydrochloric acid and then measured absorbance with a spectrophotometer at 525 nm. The amount of EB was determined from calibration standard curves. The EB content of each sample was carried out in triplicate.

The ratio of encapsulated EB in powders after spray drying to initial EB added in the emulsion was defined as encapsulation efficiency (%). The ratio of encapsulated EB in powders during equilibration at different relative humidity (RH) to encapsulated EB in powders after spray drying was defined as flavour retention (%).

2.5 Water sorption and flavor release from encapsulation systems

Approximately 1 g of powders was weighed into small glass vials (25 mL). All powders were equilibrated for 216 h in evacuated desiccators over saturated salt solutions of K_2CO_3, $Mg(NO_3)_2$, $NaNO_2$, and NaCl, giving RH of 44%, 54%, 65%, and 76%, respectively. All desiccators were placed at incubators with temperature of 25 °C. 24 vials were prepared for each powder at every RH. Three vials of each powder were taken out from each desiccator at 6, 12, 24, 48, 72, 120, 168 and 216 h,

respectively, and the mass of samples was measured. Then water content of each powder was determined as a function of time. The residual amount of EB in the powders was determined by the method described in 2.4.2. The flavour retention in the powders was calculated as a function of time.

2.6 Glass transition determination

The encapsulation systems were equilibrated at different RHs for 0, 6, 12, 24, 48, 72, 120, 168 and 216 h, respectively. Then the glass transition temperatures, T_g (onset), and initial crystallization temperatures, T_{ic} were determined using a differential scanning calorimeter (DSC Q2000, TA Instruments, Crawley, UK). To determine T_g and T_{ic} values, 10 to 15 mg of powders was transferred to Tzero pans. The DSC pans were hermetically sealed with Tzero hermetic lids and samples were analysed. An empty pan was used as a reference. The temperature range of the scans was varied between -10 ºC and 180 ºC depending on the water content of powders. The heating rate was 5 °C/min and the cooling rate was 10 °C/min during scanning. All measurements were carried out in duplicate. T_g and T_{ic} values were determined using a TA universal analysis software, version 5.1.2 (TA Instruments, Crawley, UK).

2.7 Dynamic mechanical analysis

The encapsulation systems were equilibrated at different RHs for 0, 6, 12, 24, 48, 72, 120, 168 and 216 h, respectively. Then a dynamic mechanical analyser (DMA Q800, TA Instruments, Crawley, UK) was used, in conjunction with a gas cooling accessory (GCA) tank, to determine the dynamic mechanical properties of encapsulation systems. A rectangular stainless steel powder pocket was designed to generate a defined geometry to contain powder with inner dimensions of 60 mm ×

11 mm × 1 mm. A pre-weighed mass of powder mixed with aluminum oxide calcined powder at the ratio 4:1 was evenly spread within this shallow pocket, and the upper lid was then placed onto the top surface of the powder (Mahlin et al., 2009). As aluminum oxide calcined powder showed no effect on mechanical property results of dairy powders, it was added to protect powders from sticking on the pocket during the heating test. The measurements were made at a heating rate of 2 °C /min from 0 to 120 °C. DMA was operated by a sinusoidal deformation applied to the powder pocket at a fixed strain. The amplitude was 15 μm. During dynamic heating, the samples were analysed for storage modulus (E') and loss modulus (E'') using single frequency 1 Hz. Moreover, the α-relaxation temperatures, T_{α}, were determined using TA universal analysis software, version 5.1.2 (TA Instruments, Crawley, UK) and were taken from the peak values of loss modulus at 1 Hz.

2.8 Statistical analysis

Measurement of glass transition and dynamic mechanical analysis were performed in duplicate, with all other analyses performed in triplicate. Results were expressed as mean ± standard deviations (SD). One-way analysis of variance (ANOVA) was used to determine the significant differences between the mean values of each test (Microsoft Office Excel 2010, Microsoft, Inc., Redmond, WA, USA). A significance level of $P < 0.05$ was used throughout the study.

3. Results and discussion

3.1 Powder characteristics

Powder characteristics of encapsulation systems after spray drying are shown in Table 7-1.

Table 7-1 Powder characteristics of encapsulation systems with wall materials consisting of lactose/MD/WPI mixtures after spray drying.

Systems	Water content (%)	Water activity	d_{50} (μm)	SSA (m^2/kg)	Particle density (g/cm^3)	Ester content (mg/g of dry powders)	Encapsulation efficiency (%)
S1 lactose/WPI 4:1	$2.50^{c} \pm 0.24$	$0.12^{f} \pm 0.01$	$23.73^{c} \pm 0.21$	$762.9^{c} \pm 7.1$	$1.1457^{b} \pm 0.0007$	$81.34^{a} \pm 0.93$	$48.80^{a} \pm 0.56$
S2 lactose/MD (4-7)/WPI 3:1:1	$3.13^{b} \pm 0.15$	$0.16^{a} \pm 0.00$	$23.77^{c} \pm 0.54$	$711.0^{d} \pm 14.5$	$1.1646^{a} \pm 0.0009$	$71.67^{c} \pm 1.13$	$43.01^{c} \pm 0.87$
S3 lactose/MD (4-7)/WPI 1:3:1	$3.25^{b} \pm 0.06$	$0.13^{d} \pm 0.00$	$26.50^{a} \pm 0.08$	$584.0^{f} \pm 5.2$	$1.0376^{f} \pm 0.0171$	$77.53^{b} \pm 1.99$	$46.52^{b} \pm 1.12$
S4 lactose/MD (13-17)/WPI 3:1:1	$3.26^{b} \pm 0.11$	$0.14^{c} \pm 0.00$	$23.43^{c} \pm 0.09$	$728.5^{d} \pm 1.6$	$1.0878^{d} \pm 0.0010$	$69.39^{c} \pm 2.57$	$41.63^{c} \pm 1.54$
S5 lactose/MD (13-17)/WPI 1:3:1	$3.61^{a} \pm 0.16$	$0.15^{b} \pm 0.01$	$21.73^{d} \pm 0.09$	$782.8^{b} \pm 3.1$	$1.0843^{de} \pm 0.0095$	$71.84^{c} \pm 0.37$	$43.10^{c} \pm 0.22$
S6 lactose/MD (23-27)/WPI 3:1:1	$3.55^{a} \pm 0.09$	$0.16^{a} \pm 0.00$	$21.57^{d} \pm 0.21$	$818.5^{a} \pm 17.2$	$1.1413^{c} \pm 0.0005$	$61.34^{e} \pm 1.04$	$36.81^{e} \pm 0.62$
S7 lactose/MD (23-27)/WPI 1:3:1	$3.33^{a} \pm 0.11$	$0.16^{a} \pm 0.01$	$25.37^{b} \pm 0.09$	$616.6^{e} \pm 17.6$	$1.0833^{e} \pm 0.0008$	$65.55^{d} \pm 1.19$	$39.33^{d} \pm 0.72$

[1] Values are mean ± standard deviation (n = 3).

[2 a-f] Values within columns with different superscripts are significantly different at $P < 0.05$.

Those seven powders were defined as S1-S7 according to their wall materials (Table 7-1). The EB contents of S1-S7 showed significantly ($P < 0.05$) difference as a result of different composition of wall materials. S1 with wall material consisting of lactose/WPI (4:1) mixture had the highest EB content, which meant wall material consisting of lactose/WPI (4:1) mixture had significantly ($P < 0.05$) higher encapsulation efficiency for EB during spray drying than wall materials consisting of lactose/MD/WPI mixtures. This might be due to the highest lactose content in S1, which could form a large extent of amorphous structure to easily entrap EB molecules during spray drying. For encapsulation systems with wall materials consisting of lactose/MD/WPI mixtures, the lower DE values of MD in the wall materials, the higher was flavor encapsulation efficiency. This was in agreement with the study of Bangs and Reineccius (1982). They reported that volatiles retention in maltodextrin decreased with increasing DE values.

Table 7-2 Morphological characteristics of powders with wall materials consisting of lactose/MD/WPI mixtures.

Systems	Circularity	Elongation	Convexity
S1	$0.9137^{ab} \pm 0.0096$	$0.1603^{ab} \pm 0.0102$	$0.9947^{a} \pm 0.0009$
S2	$0.8970^{b} \pm 0.0029$	$0.1770^{a} \pm 0.0028$	$0.9933^{a} \pm 0.0005$
S3	$0.9210^{a} \pm 0.0028$	$0.1400^{b} \pm 0.0024$	$0.9947^{a} \pm 0.0050$
S4	$0.8873^{c} \pm 0.0025$	$0.1870^{a} \pm 0.0021$	$0.9920^{b} \pm 0.0000$
S5	$0.9093^{ab} \pm 0.0121$	$0.1483^{b} \pm 0.0157$	$0.9940^{a} \pm 0.0008$
S6	$0.8847^{c} \pm 0.0107$	$0.1893^{a} \pm 0.0109$	$0.9920^{b} \pm 0.0008$
S7	$0.8930^{bc} \pm 0.0041$	$0.1763^{a} \pm 0.0049$	$0.9923^{b} \pm 0.0005$

[1] S1-S7: Table 7-1.

[2] Values are mean ± standard deviation (n = 3).

[3] [a-c] Values within columns with different superscripts are significantly different at $P < 0.05$.

In addition, wall materials with the same DE values maltodextrin (S2 and S3, S4 and S5, S6 and S7) had higher flavor encapsulation efficiency when the MD content in the wall systems was higher. This might be due to the addition of miscible high

molecular weight components increasing the viscosity of encapsulation matrix during spray drying.

Moreover, S1 with wall material consisting of lactose/WPI (4:1) mixture showed significantly ($P < 0.05$) lower water content and water activity after spray drying compared to those encapsulation systems with wall materials consisting of lactose/MD/WPI mixtures (Table 7-1), which might affect the flavor retention in encapsulation systems during storage. Particle size and particle density of encapsulation systems (S1-S7) also showed difference as a result of different composition of wall materials (Table 7-1). Moreover, the morphological characteristics of encapsulation systems were also determined and are shown in Table 7-2. In this study, three morphological characteristics (circularity, elongation and convexity) were used to identify the particle shape of encapsulation systems. Powders with MD (DE 23-27) (S6 and S7) had lower circularity and convexity values, while they give higher elongation values, which indicated that the particles of powders with MD (DE 23-27) had less rounded shape and rougher surface than those of powders with MD (DE 4-7) and MD (DE 13-17).

3.2 Water sorption

An overall water sorption behaviour of encapsulation systems at various water activities (0.44-0.76 a_w) was plotted as a function of time (Figure 7-1). Since EB in powders kept releasing during storage period, the water contents of powders shown in Figure 7-1 were not only calculated according to the mass changes of powders during storage, but they were modified according to the mass changes resulting from flavor release during storage.

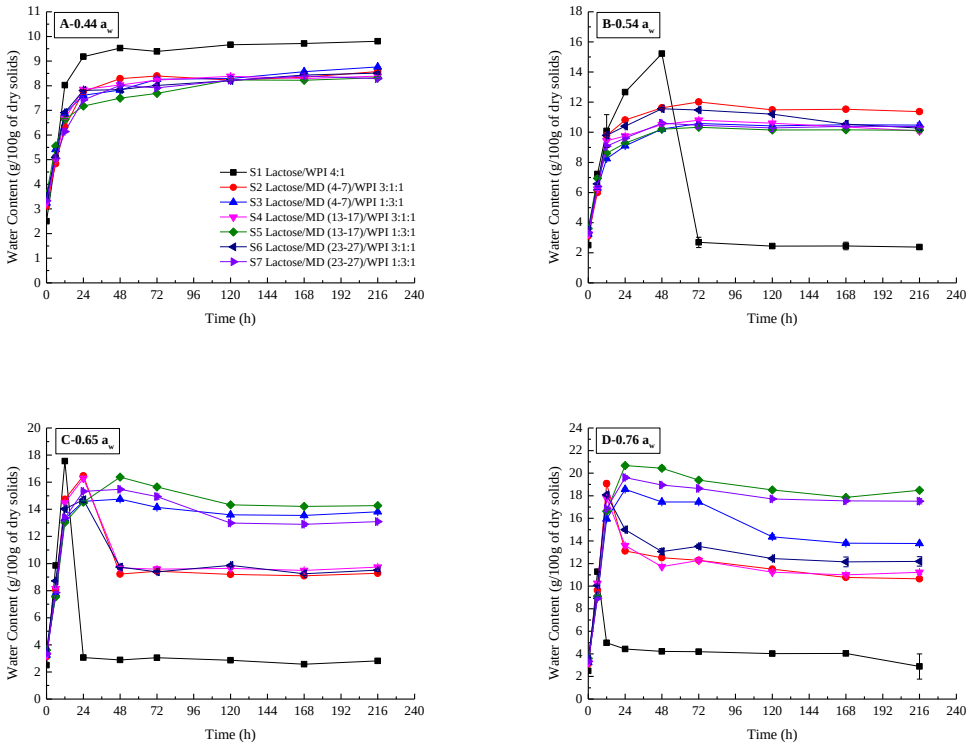


Figure 7-1 Water sorption of powders at 0.44 a_w (A), 0.54 a_w (B), 0.65 a_w (C), and 0.76 a_w (D) at 25 ºC. Loss of sorbed water at 0.54 a_w, 0.65 a_w, and 0.76 a_w indicates lactose crystallization.

The initial water contents of encapsulation systems before equilibration are shown in Table 7-1. S1 with wall material consisting of lactose/WPI (4:1) mixture showed the highest steady water content at 0.44 a_w, while there were only minor difference among the steady water contents of S2-S7 (Figure 7-1 A). At 0.54 a_w, loss of sorbed water was found in S1 after equilibration for 48 h indicating the crystallization of amorphous lactose. However, the water content of encapsulation systems with wall materials consisting of lactose/MD/WPI mixtures did not show significant decrease with equilibration at 0.54 a_w for 216 h (Figure 7-1 B), which was due to the presence of high molecular weight maltodextrin delaying lactose crystallization. Potes et al. (2012) showed similar results. According to their study, interactions between lactose and maltodextrin could reduce or delay the rate of diffusion or mobility of lactose

molecules to form crystals (nucleation) or crystal growth. Loss of sorbed water of encapsulation systems with lactose/MD/WPI (3:1:1) mixtures was obviously observed at 0.65 a_w and 0.76 a_w after storage for 24 h and 12 h, respectively, while only a minor loss of sorbed water was found in encapsulation systems with wall materials consisting of lactose/MD/WPI (1:3:1) mixtures with equilibration at 0.65 a_w and 0.76 a_w for 216 h (Figure 7-1 C and D). Inhibition of lactose crystallization was more pronounced in systems with higher ratios of maltodextrin, which agreed with previous studies (Silalai & Roos, 2011b; Potes et al., 2012). Additionally, encapsulation systems with high DE (13-17 and 23-27) MD showed higher stable water content at 0.65 a_w and 0.76 a_w than those with low DE (4-7) MD, which meant encapsulation systems with a high DE MD showed more significant inhibition of crystallization. That might be due to lower molecular weight carbohydrate present in the high DE MD that could exhibit molecular motions and diffusion rates exceeding those of the higher molecular weight MD carbohydrates (Potes et al., 2012).

The increase of water content in encapsulation systems can lead to an increase in free volume by decreasing the molecular packing of the matrix molecules (van den Dries et al., 2000). According to Rosenberg et al. (1990), water uptake at high relative humidity destroyed the capsule structure and as a result, the release of the encapsulated flavor during storage increased with an increase in relative humidity. Thus, the different water sorption behaviours of encapsulation systems (S1-S7) might result in different rates of flavor diffusion and release in the amorphous matrix. Furthermore, the structure of amorphous matrix was destroyed as lactose crystallization occurred when water content increased at high water activities ($a_w \geqslant$ 0.54), which might result in a quick release of flavor from powders. The addition of MD in wall systems increased viscosity of systems and decrease diffusion of

molecules, which could delay crystallization of amorphous lactose and might reduce the rates of flavor release.

3.3 Glass transition

The glass transition temperatures, T_g (onset), and initial crystallization temperatures, T_{ic}, of encapsulation systems are shown in Table 7-3. T_g values decreased with increasing water activity or storage time, which showed typical water plasticization of amorphous materials (Jouppila et al., 1997; Haque & Roos, 2004a; Potes et al., 2012). The T_g values of encapsulation systems with wall materials consisting of lactose/MD/WPI mixtures (S2-S7) were higher compared to the T_g values of encapsulation system with wall material consisting of lactose/WPI mixtures (S1) with equilibration at 0.44-0.76 a_w before showing lactose crystallization. Silalai and Roos (2011c) reported similar results. They stated that the T_g values of skim milk-maltodextrin (DE9 and DE17) solids were higher than those of skim milk powder at 0-0.76 a_w. Furthermore, the T_g values of encapsulation systems with wall materials consisting of lactose/MD/WPI (1:3:1) mixtures were higher than those of encapsulation systems with wall materials consisting of lactose/MD/WPI (3:1:1) mixtures (Table 7-3), which was more obvious at high water activity ($a_w \geq 0.54$). The lower T_g values of encapsulation systems with lower amount of maltodextrin might account for the presence of high lactose contents, which made low molecular weight sugars dominant and consequently depressed the T_g (Roos & Karel, 1991; Buera et al., 1992;).

Table 7-3 Glass transition temperatures (ºC), T_g, of powders with wall materials consisting of lactose/MD/WPI mixtures storage at 0.44 a_w, 0.54 a_w, 0.65 a_w, and 0.76 a_w, respectively, at 25 ºC for different time.

Water activity	Time (h)	Temperature (ºC)	Systems						
			S1	S2	S3	S4	S5	S6	S7
Initial powders	0	T_g	69 ± 0.5	72 ± 1.0	N/O	68 ± 0.5	84 ± 0.0	66 ± 1.0	70±0.0
		T_{ic}	134 ± 0.0	N/O	N/O	N/O	N/O	N/O	N/O
0.44	6	T_g	37 ± 1.0	55 ± 1.0	N/O	42 ± 1.0	60 ± 1.0	42 ± 0.0	43 ± 1.0
		T_{ic}	110 ± 0.5	N/O	N/O	N/O	N/O	N/O	N/O
	12	T_g	29 ± 0.0	36 ± 0.0	37 ± 1.0	35 ± 1.0	41 ± 1.0	33 ± 1.0	37 ± 1.0
		T_{ic}	88 ± 0.5	113 ± 0.5	102 ± 0.0	110 ± 0.5	N/O	106 ± 1.0	108 ± 0.0
	24	T_g	21 ± 0.0	28 ± 0.5	32 ± 0.5	30 ± 0.5	40 ± 1.0	25 ± 0.0	39 ± 1.0
		T_{ic}	80 ± 1.0	98 ± 1.0	92 ± 1.0	97 ± 1.0	N/O	95 ± 1.0	98 ± 0.0
	48	T_g	20 ± 1.0	28 ± 1.0	29 ± 0.0	27 ± 0.5	40 ± 1.0	25 ± 0.0	39 ± 0.0
		T_{ic}	77 ± 0.0	95 ± 0.5	89 ± 0.5	94 ± 1.0	N/O	93 ± 0.5	95 ± 1.0
	72	T_g	21 ± 0.0	25 ± 0.0	43 ± 1.0	27 ± 0.0	41 ± 1.0	24 ± 0.5	40 ± 0.0
		T_{ic}	77 ± 0.0	92 ± 0.5	87 ± 1.0	92 ± 0.0	N/O	89 ± 1.0	94 ± 0.0
	120	T_g	21 ± 0.5	28 ± 0.0	32 ± 0.5	26 ± 0.5	42 ± 0.0	24 ± 0.5	38 ± 0.0
		T_{ic}	75 ± 0.0	90 ± 1.0	87 ± 0.5	88 ± 0.0	N/O	87 ± 0.5	89 ± 0.0
	168	T_g	21 ± 0.5	28 ± 0.0	32 ± 1.0	26 ± 0.5	42 ± 0.0	24 ± 0.5	38 ± 0.0
		T_{ic}	75 ± 0.0	90 ± 1.0	87 ± 0.5	88 ± 0.0	N/O	87 ± 0.5	89 ± 0.0
	216	T_g	19 ± 1.0	23 ± 1.0	25 ± 1.0	24 ± 0.0	40 ± 1.0	21 ± 0.5	39 ± 0.5
		T_{ic}	73 ± 0.0	87 ± 1.0	83 ± 0.0	86 ± 0.0	N/O	83 ± 0.5	89 ± 0.0
0.54	6	T_g	32 ± 0.5	38 ± 1.0	37 ± 1.0	38 ± 1.0	42 ± 0.0	36 ± 0.0	38 ± 0.5
		T_{ic}	96 ± 0.0	118 ± 1.0	103 ± 0.0	117 ± 0.5	N/O	109 ± 1.0	112 ± 0.0
	12	T_g	10 ± 1.0	16 ± 1.0	28 ± 0.0	16 ± 0.5	36 ± 0.0	14 ± 0.0	32 ± 0.0
		T_{ic}	65 ± 0.5	86 ± 0.0	77 ± 1.0	80 ± 0.0	N/O	79 ± 0.0	82 ± 0.0
0.65	6	T_g	17 ± 1.0	25 ± 1.0	39 ± 1.0	23 ± 0.0	38 ± 1.0	20 ± 0.0	35 ± 1.0
		T_{ic}	73 ± 1.0	97 ± 1.0	90 ± 0.0	92 ± 0.0	N/O	88 ± 0.5	93 ± 0.0
0.76	6	T_g	11 ± 0.0	19 ± 0.0	39 ± 0.5	14 ± 0.0	34 ± 1.0	13 ± 0.0	31 ± 0.5
		T_{ic}	64 ± 1.0	85 ± 0.0	82 ± 1.0	80 ± 0.0	N/O	78 ± 0.0	83 ± 1.0

[1] S1-S7: Table 7-1; Initial powders were the powders after spray drying.

[2] Values are mean ± standard deviation (n = 2); N/O: Not observed.

In addition, encapsulation systems with maltodextrin in the wall systems showed significantly higher initial crystallization temperatures than those of encapsulation system with wall material consisting of lactose/WPI (4:1) mixture at all experimental a_w (Table 7-3), which confirmed that the presence of maltodextrin could delay the crystallization of amorphous sugars.

When the temperature is around or above T_g, various changes such as increase of free volume and specific heat, as well as decrease of viscosity, are noticed in amorphous materials. The stability of encapsulated components was significantly influenced by the state of wall materials (Levi & Karel, 1995; Drusch et al., 2006; Zhou & Roos, 2012). In addition, the influence of T_g on the translational diffusivity or the diffusion of molecules has an important impact on the diffusion-controlled physical and chemical processes. Since the presence of maltodextrin in encapsulation systems could reduce the rate of diffusion or mobility of lactose molecules, the rate of flavor release from encapsulation systems might vary according to the types and contents of maltodextrin in the encapsulation systems (S1-S7).

3.4 Mechanical properties

The mechanical properties of encapsulation systems (S1-S7) were determined using a DMA. The storage and loss modulus changes of encapsulation systems after spray drying and equilibration at 0.44 a_w, 0.54 a_w, and 0.65 a_w at 25 ºC for 216 h, 12 h, and 6 h, respectively are shown in Figure 7-2. Moreover, the modulus changes of encapsulation systems with equilibration at 0.44 a_w for 6 h, 12 h, and 24 h, respectively, are shown in Figure 7-3. Since encapsulation systems showed lactose crystallization after storage at 0.76 a_w for 6 h, the results of storage modulus and loss

modulus for encapsulation systems equilibration at 0.76 a_w were not presented in this study.

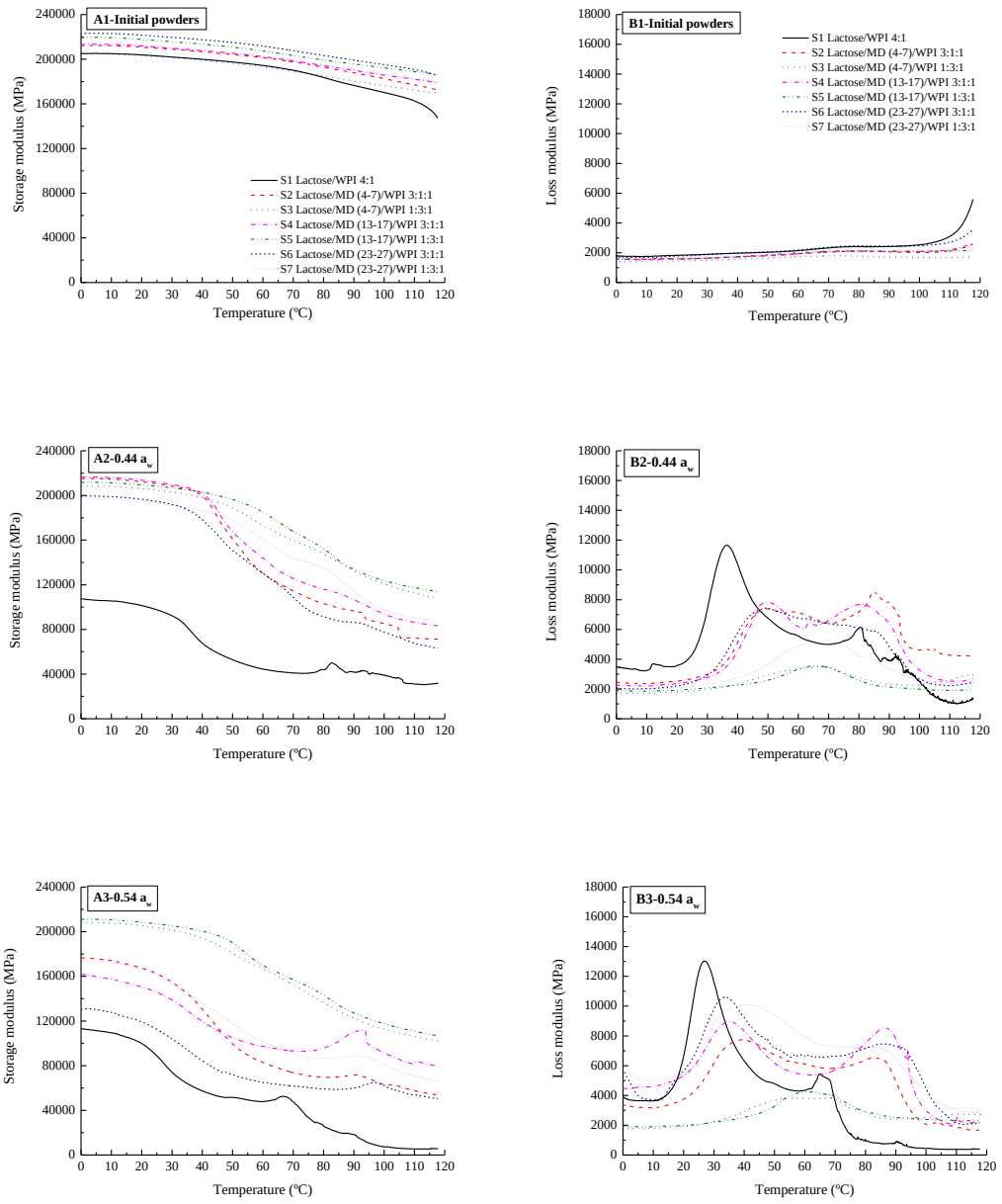


Figure 7-2 Storage modulus (A1, A2, A3, and A4) and loss modulus (B1, B2, B3, and B4) of encapsulation systems after spray drying and equilibration at 0.44 a_w, 0.54 a_w, and 0.65 a_w at 25 ºC for 216 h, 12 h, and 6 h, respectively. Initial powders were the powders after spray drying.

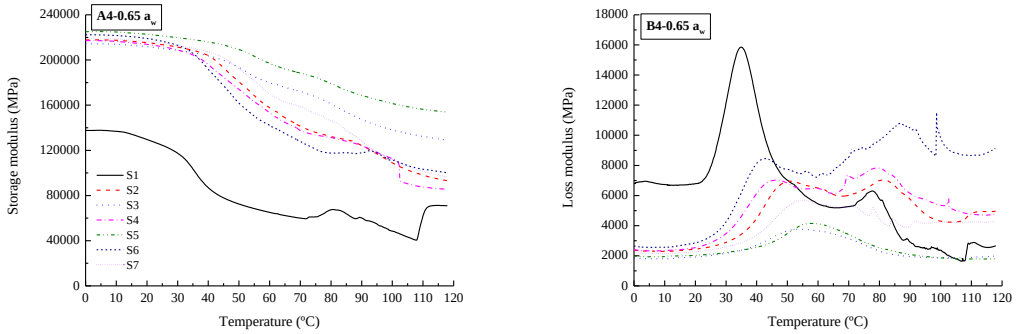


Figure 7-2 (Continued).

The changes of storage modulus and loss modulus for encapsulation systems after spray drying (Initial powders) were small with increasing temperature from 0 to 120 ºC (Figure 7-2 A1 and B1), which was due to the low water content of encapsulation systems (Table 7-1). The storage modulus of encapsulation systems decreased significantly at the glass transition region after equilibration at 0.44 a_w, 0.54 a_w, and 0.65 a_w (Figure 7-2 A2, A3, and A4). Moreover, the magnitudes of storage modulus changes of encapsulation systems increased with increasing storage time at 0.44 a_w (Figure 7-3 A1, A2, and A3). Since previous studies (Roudaut et al., 2004; Silalai & Roos, 2010b) have indicated that the magnitudes of modulus changes were relative to molecular mobility, those results confirmed that increasing water content of solids systems could increase the molecular mobility, which might result in high rates of flavor release from matrix. Furthermore, encapsulation systems with lactose/MD/WPI (3:1:1) mixtures as wall materials showed more significant changes in their storage modulus compared to those with lactose/MD/WPI (1:3:1) mixtures as wall materials, while the storage modulus of S1 without MD in wall systems showed the most significant change with increasing water content. Thus, the addition of maltodextrin in wall systems could increase stiffness and reduce molecular mobility of lactose molecules when water content increased, which was in agreement with previous study (Silalai & Roos, 2011b).

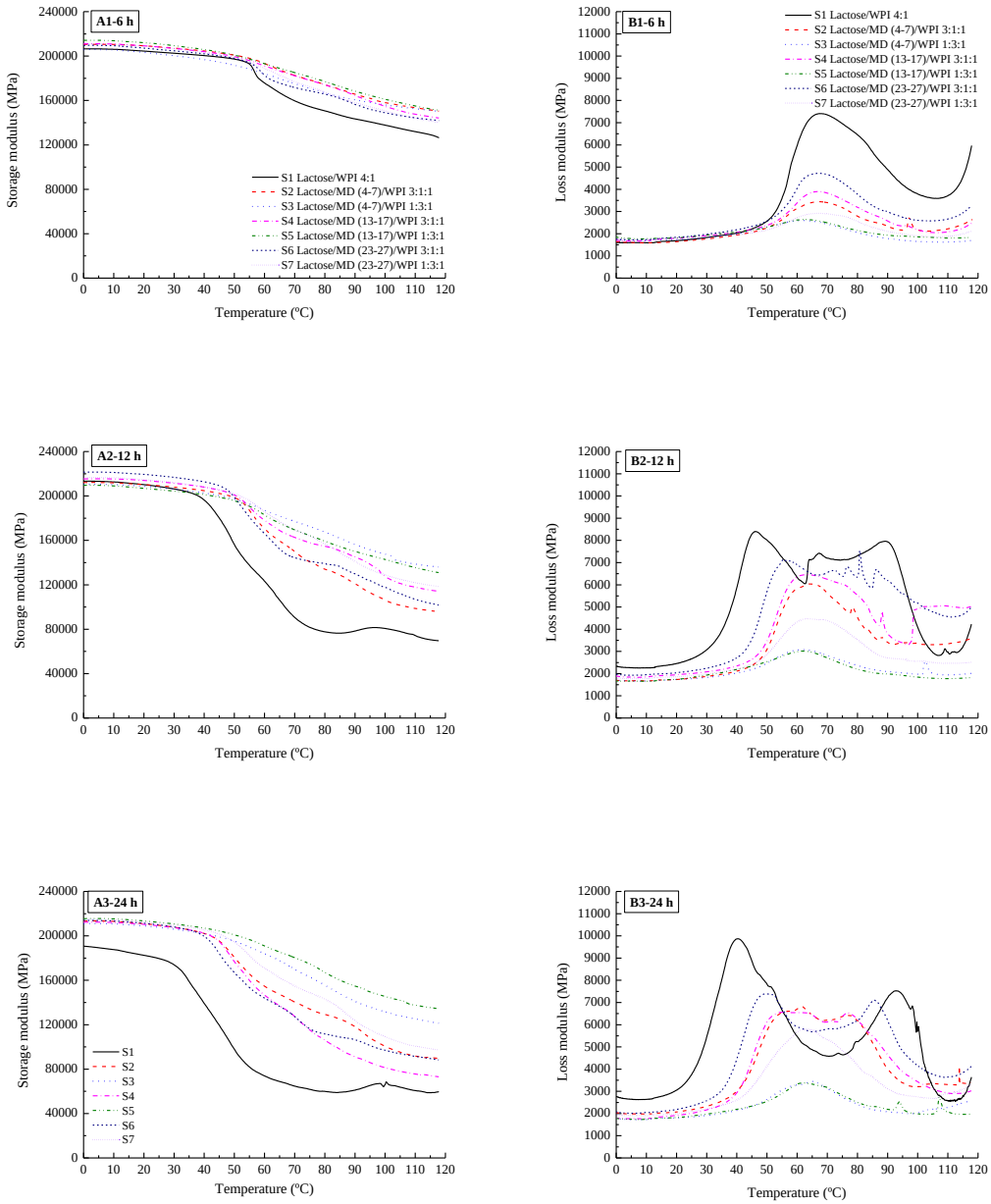


Figure 7-3 Storage modulus (A1, A2, and A3) and loss modulus (B1, B2, and B3) of encapsulation systems equilibration at 0.44 a_w at 25 ºC for 6 h, 12 h, and 24 h, respectively.

In addition, S5 with lactose/MD (13-17)/WPI (1:3:1) mixture showed the smallest magnitudes of storage modulus changes with increasing water content at 0.44-0.65 a_w, which might show excellent flavor encapsulation property with storage at high RH. These results indicated that the addition of maltodextrin in wall systems

decreased molecular mobility of wall systems when water content increased, which might decrease the diffusion of flavor molecules.

The loss modulus of encapsulation systems was small and showed minor changes when the temperatures were below the glass transition and they increased dramatically and reached peak values with increasing temperature to the glass transition region. Furthermore, the magnitudes of loss modulus changes increased with increasing water content (Figure 7-2 B1-B4 and Figure 7-3 B1-B3), which confirmed that the mechanical modulus of the systems were affected by water plasticization and increasing water content could increase the molecular mobility of solids systems. S1 with lactose/WPI (4:1) mixtures showed the largest magnitudes of loss modulus changes, and the magnitudes of loss modulus changes for encapsulation systems with wall materials consisting of lactose/MD/WPI (3:1:1) mixtures (S2, S4, and S6) were larger compared to those with wall materials consisting of lactose/MD/WPI (1:3:1) mixtures (S3, S5, and S7). In addition, S5 and S3 showed smaller magnitudes of loss modulus changes than S7 with high DE maltodextrin. Since the main component responsible for the modulus change around glass transition region of encapsulation systems was the carbohydrate phase (Silalai & Roos, 2011b), the ratios and types of maltodextrin in wall systems affected molecular mobility and free volume of encapsulation matrix significantly, which meant it might influence the diffusion of flavor components. The appearance of transitional mobility of molecules around the glass transition results in the frequency-dependent α-relaxation (Roudaut et al., 2004; Royall et al., 2005; Silalai & Roos, 2011a). The α-relaxation temperatures, T_α, of encapsulation systems equilibration at various water activities were taken from the peak values of loss modulus at 1 Hz (Table 7-4).

Table 7-4 α-relaxation temperatures (ºC), T_{α}, of powders with wall materials consisting of lactose/MD/WPI mixtures storage at 0.44 a_w, 0.54 a_w, 0.65 a_w and 0.76 a_w, respectively, at 25 ºC for different time.

Water activity	Time (h)	Systems						
		S1	**S2**	**S3**	**S4**	**S5**	**S6**	**S7**
Initial powders	**0**	75.4 ± 0.04	76.5 ± 0.04	74.0 ± 0.02	73.6 ± 0.02	72.3 ± 0.01	75.2 ± 0.02	72.2 ± 0.02
0.44	**6**	68.3 ± 0.04	67.2 ± 0.01	61.7 ± 0.03	67.2 ± 0.03	62.8 ± 0.02	67.3 ± 0.05	67.3 ± 0.02
	12	46.1 ± 0.04	64.1 ± 0.01	61.8 ± 0.02	63.1 ± 0.03	61.8 ± 0.03	56.5 ± 0.05	63.2 ± 0.02
	24	40.5 ± 0.04	55.5 ± 0.02	58.3 ± 0.01	53.8 ± 0.01	61.8 ± 0.04	50.3 ± 0.04	61.9 ± 0.08
	216	36.3 ± 0.12	49.3 ± 0.10	56.7 ± 0.10	49.2 ± 0.06	65.1 ± 0.05	48.8 ± 0.12	62.2 ± 0.10
0.54	**6**	52.3 ± 0.04	64.6 ± 0.02	60.0 ± 0.05	67.3 ± 0.04	61.7 ± 0.06	57.9 ± 0.01	65.9 ± 0.01
	12	26.9 ± 0.01	39.3 ± 0.04	52.8 ± 0.01	36.0 ± 0.01	60.6 ± 0.04	33.6 ± 0.02	39.9 ± 0.05
0.65	**6**	34.8 ± 0.05	50.7 ± 0.03	53.8 ± 0.01	46.9 ± 0.08	58.9 ± 0.01	42.8 ± 0.01	55.8 ± 0.00
0.76	**6**	28.6 ± 0.03	39.0 ± 0.01	53.0 ± 0.04	35.4 ± 0.03	58.2 ± 0.05	32.6 ± 0.04	49.6 ± 0.04

[1] S1-S7: Table7-1.

[2] Values are mean ± standard deviation (n = 2).

[3] Initial powders were the powders after spray drying.

The T_α values of encapsulation systems decreased with increasing storage RH or storage time, which was in agreement with previous study (Silalai & Roos, 2011c). Encapsulation systems with wall materials consisting of lactose/MD/WPI mixtures showed higher T_α values than that with wall material consisting of lactose/WPI (4:1) mixtures after equilibration at 0.44 a_w, 0.54 a_w, 0.65 a_w, and 0.76 a_w for 216 h, 12 h, 6 h, and 6 h, respectively, while the T_α values of encapsulation systems with higher amount of maltodextrin (S3, S5, and S7) were higher than those of encapsulation systems with lower amount of maltodextrin (S2, S4, and S6) (Table 7-4). Additionally, S5 gave the highest T_α values after equilibration at 0.44 a_w, 0.54 a_w, 0.65 a_w, and 0.76 a_w for 216 h, 12 h, 6 h, and 6 h, respectively. Thus, the addition of maltodextrin in wall systems decrease the effect of water on structural relaxations of encapsulation systems and viscous flow characteristics of amorphous matrix, which might affect the flavor diffusion and release in powders during storage.

3.5 Flavor retention

The effects of water plasticization on the time-course of the flavor release in encapsulation systems with different wall materials are shown in Figure 7-4. Moreover, the flavor contents in encapsulation systems after equilibration at 0.44-0.76 a_w for 216 h are shown in Table 7-5. The flavor retention in encapsulation systems was affected significantly by storage RH (Figure 7-4). The higher was the storage RH, the lower was the flavor retention. The EB retention in encapsulation systems showed only a minor decrease with storage at 0.44 a_w for 216 h, especially in encapsulation systems with wall systems consisting of lactose/MD (23-27)/WPI (3:1:1) mixture (Figure 7-4 A). Since S1 had the highest encapsulation efficiency after spray drying, it still had the highest EB content after equilibration at 0.44 a_w for

216 h. However, the EB retention in S1 dropped sharply with storage at 0.54 a_w, while the EB retention in S2-S7 showed only slightly decrease with equilibration at 0.54 a_w (Figure 7-4 B). This was due to lactose crystallization in S1 that destroyed the structure of amorphous matrix and EB was expelled from crystallized matrix. For S2-S7, since there was maltodextrin in the wall systems, which could delay lactose crystallization by increasing viscosity and decreasing diffusion of lactose molecules, the EB in those systems were much more stable than that in S1.

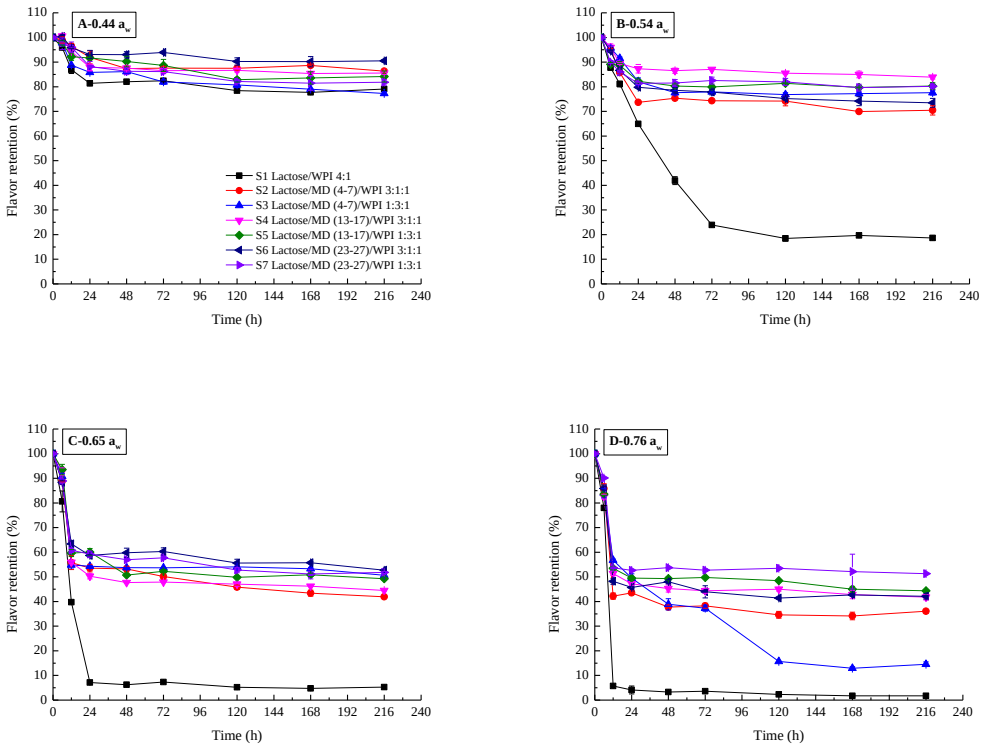


Figure 7-4 Flavor retention in encapsulation systems after equilibration at 0.44 a_w (A), 0.54 a_w (B), 0.65 a_w (C), and 0.76 a_w (D) at 25 ºC for different time.

The EB content of S1 was significantly lower than those of S2-S7 after equilibration at 0.54 a_w for 216 h (Table 7-5). In addition, the rate of EB release from S1 decreased after 72 h at 0.54 a_w, which was corresponding to the result of water sorption at 0.54 a_w (Figure 7-1 B). This might be due to the completely collapse of

amorphous matrix after lactose crystallization, which resulted in re-encapsulation of flavour compound in the collapse matrix (Goubet et al., 1998). Furthermore, EB retention of S1 dropped more sharply with storage at higher relative humidity conditions (Figure 7-4 C and D), which resulted from higher rate of lactose crystallization at higher water activity. At 0.65 a_w, S6 had the highest EB retention, which meant the rate of flavor release from S6 was the lowest. However, since the encapsulation efficiency of S6 was the lowest after spray drying, the EB content of S6 was not higher compared to those of other encapsulation systems with wall materials consisting of lactose/MD/WPI mixtures (Table 7-5).

Table 7-5 Flavor contents of encapsulation systems with wall materials consisting of lactose/MD/WPI mixtures equilibration at 0.44 a_w, 0.54 a_w, 0.65 a_w and 0.76 a_w, respectively, at 25 ºC for 216 h.

Systems	Flavor content (mg/g of dry powders)			
	0.44 a_w	**0.54 a_w**	**0.65 a_w**	**0.76 a_w**
S1	$64.33^{a} \pm 0.48$	$15.15^{d} \pm 0.58$	$4.26^{e} \pm 0.66$	$1.42^{e} \pm 0.51$
S2	$61.87^{b} \pm 0.15$	$50.50^{bc} \pm 1.36$	$30.06^{d} \pm 0.16$	$25.83^{c} \pm 0.52$
S3	$59.92^{bc} \pm 0.49$	$60.15^{a} \pm 0.75$	$39.30^{a} \pm 0.58$	$11.28^{d} \pm 0.73$
S4	$59.36^{c} \pm 0.37$	$58.20^{a} \pm 0.52$	$30.88^{d} \pm 0.13$	$28.99^{bc} \pm 0.78$
S5	$60.44^{bc} \pm 1.62$	$57.68^{a} \pm 0.99$	$35.39^{b} \pm 0.44$	$31.87^{b} \pm 0.18$
S6	$55.52^{d} \pm 0.32$	$45.07^{c} \pm 1.10$	$32.34^{c} \pm 0.13$	$25.83^{c} \pm 0.65$
S7	$53.63^{d} \pm 0.73$	$52.53^{b} \pm 0.66$	$33.95^{b} \pm 0.26$	$33.61^{a} \pm 0.12$

[1] S1-S7: Table 7-1.

[2] Values are mean ± standard deviation (n = 3).

[3 a-e] Values within columns with different superscripts are significantly different at $P < 0.05$.

Additionally, the flavor retentions of encapsulation systems were lower at 0.76 a_w compared to those at 0.65 a_w. The flavor retention of S3 showed rapid decrease again after 72 h storage at 0.76 a_w, while the flavor retention of other encapsulation systems showed only slightly decrease after 12 h. Therefore, wall systems consisting

of lactose/MD (13-17 or 23-27)/WPI (1:3:1) mixtures showed better encapsulation properties for EB at 0.44-0.76 a_w.

Comparing water sorption results and flavor retention results of encapsulation systems (Figure 7-1 and 7-4), the decrease of flavor retention were corresponding to the changes of water contents. The water contents of encapsulation systems increased slowly or decreased sharply after 24 h at 0.44-0.76 a_w, while the flavor retention of encapsulation systems decreased significantly in 24 h. Moreover, the glass transition temperatures of encapsulation systems also decreased significantly with storage at 0.44-0.76 a_w in 24 h (Table 7-3). Furthermore, the magnitudes of modulus changes increased significantly in 24 h of storage at 0.44-0.76 a_w (Figure 7-3). Those results indicated that increasing water content of encapsulation systems depressed the glass transition temperatures and as a result, increased the molecular mobility of wall systems, which accelerated diffusion and release of flavor components. The presence of high molecular weight maltodextrin could delay lactose crystallization and increase the stiffness of wall systems, and restrict the diffusion of flavor molecules during storage.

4. Conclusions

Encapsulation systems with wall materials consisting of lactose/WPI (4:1) mixture and lactose/MD/WPI (3:1:1 or 1:3:1) mixtures were spray dried. Wall systems with lactose/WPI (4:1) mixture had the highest encapsulation efficiency for EB after spray drying. The types and contents of maltodextrin in wall systems had minor impact on particle size and particle density, while the particles of powders with MD (DE 23-27) had less rounded shape and rougher surface than those of powders with MD (DE 4-7) and MD (DE 13-17). The presence of maltodextrin delayed the

crystallization of amorphous lactose with storage at high water activity (≥ 0.54 a_w), while encapsulation systems with high DE (13-17 and 23-27) MD showed higher stable water content at 0.65 a_w and 0.76 a_w than those with low DE (4-7) MD. The T_g values of encapsulation systems with wall materials consisting of lactose/MD/WPI (1:3:1) mixtures were higher than those of encapsulation systems with wall materials consisting of lactose/MD/WPI (3:1:1) mixtures, and encapsulation systems with maltodextrin in wall systems showed higher initial crystallization temperatures than those of encapsulation systems with wall materials consisting of lactose/WPI (4:1) mixtures at all experimental a_w. Moreover, the addition of maltodextrin in wall systems could increase stiffness and reduce molecular mobility of lactose molecules when water content increased, and the presence of high molecular weight maltodextrin could delay lactose crystallization and increase the stiffness of wall systems, and restrict the diffusion of flavor molecules during storage. Wall systems consisting of lactose/MD (13-17 or 23-27)/WPI (1:3:1) mixtures showed better encapsulation properties for EB at 0.44-0.76 a_w.

CHAPTER EIGHT

General discussion

The present study investigated the effects of spray dryer and pre-crystallization on the physical and mechanical properties of model dairy systems (Chapter 2, 3), established the relationships of mechanical properties and flow properties of two dairy based systems--carbohydrate/protein systems and pre-crystallization systems (Chapter 4, 5), and determined the influences of formulation and water plasticization on the encapsulation properties of amorphous matrix (Chapter 6, 7). The current study provided data on structure forming properties with industrial importance and applications, and translated results of structural properties and mechanical properties of model dairy solids systems to an industrially relevant context to achieve improved flow properties and encapsulation properties of dairy powders.

1. Effect of processing conditions on physical and mechanical properties of dairy powders

1.1 Effect of spray dryer

According to previous studies (Finney et al., 2002; Fang et al., 2005), particle size of powders is primarily determined by physical properties of the infeed emulsion (such as viscosity and solids concentration) and the atomization operating parameters, such as the rotational speed and wheel diameter in the case of centrifugal atomization and the orifice size and pressure in the case of nozzle atomization. In the current study, dairy solids were produced by a laboratory-scale spray dryer and a pilot-scale spray dryer, respectively. The particle size of those two systems was significantly different. Particles of S-lactose/MPI solids systems spray-dried by a BÜCHI Mini Spray dryer B-191 had smaller particle size (d_{50}: 6-7 μm), while those of L-lactose/MPI solids systems spray-dried by an ANHYDRO single stage spray dryer had larger particle size (d_{50}: lactose: 24.95 μm; lactose/MPI mixtures: 40-50

μm) (Table 2-1). Water sorption studies indicated that particle size of dairy solids was one of the factors which could affect water sorption properties (Table 2-3). This was in agreement with the study of Haque and Roos (2004b). They found that fine powders sorbed more water than coarse powders at RH ≤ 33%. Powders in small particle size give a large surface area per unit volume, which is related to hygroscopicity (e.g., high degree of moisture absorption). Furthermore, DSC analysis showed that particle size affected water sorption behaviour of dairy solids, which resulted in the difference in their T_g values (Table 2-4). Moreover, mechanical property study indicated that the stiffness of solids systems with smaller size particles was higher compared to solids systems with larger size particles at the amorphous state (Figure 2-2).

As particle size is very important to powder properties (Keogh et al., 2004; Soottitantawat et al., 2005; Jafari et al., 2007; Fu et al., 2012), these findings in present study provided data for industry to achieve improved processing and modification of existing products.

1.2 Effect of pre-crystallization

Crystallization of amorphous components in food products could enhance both physical and chemical stability (Berlin et al., 1968; Roos & Karel, 1991; Miao & Roos, 2004), and changing the crystallinity of lactose in dairy powders often affects product quality (Aguilar & Ziegler, 1994; Roos et al., 1999). In the present study, pre-crystallization was used to produce dairy powders with different crystallinity. Water sorption study showed that the presence of less than 46.8% crystalline lactose in lactose/WPI mixtures had only a minor effect on water sorption behaviour at 0.11-0.44 a_w (Table 3-2). However, according to Bronlund and Paterson (2004) and Ibach

and Kind (2007), the amorphous form of lactose has a much higher water content at a given humidity than the crystalline form. The difference between our study and their studies might be due to the presence of WPI in dairy powders weakening the effect of crystalline lactose on water sorption behaviour of lactose/WPI mixtures. Previous studies have indicated that water contents sorbed by lactose/WPI mixtures were determined by water sorption behaviour of non-crystalline lactose and protein (Fan & Roos, 2015). In addition, powders with higher crystallinity had higher stable water content after showing lactose crystallization (Figure 3-2). Also, the crystallinity of dairy solids affected the initial sorption rate significantly; samples with higher crystallinity showed lower sorption rates (Figure 3-3). There was no significant difference in the T_g values of lactose/WPI mixtures with different levels of crystallinity at the same water activities (Table 3-3), and the T_g values of lactose/WPI mixtures with different amount of crystalline lactose was primarily dependent on the amorphous lactose, which was in agreement with previous studies (Silalai & Roos, 2010a; Potes et al., 2012; Fan & Roos, 2016). They stated that lactose-protein systems showed phase separation and their T_g values were dependent on amorphous lactose. Additionally, the amount of crystalline lactose showed no significant influence on the initial crystallization temperatures, T_{ic} values of the lactose/WPI mixtures (Table 3-3). Unlike amorphous structure, the crystalline state has molecules well arranged, which is in the favourable low energy state. Water plasticization had no significant effect on molecular mobility of crystalline lactose, and only exhibited a minor effect on the modulus changes of dairy powders with higher crystallinity (Figure 3-4). As a result, water plasticisation had a stronger effect on the structural relaxation of dairy powders with lower crystallinity (Figure 3-5). These results suggested that the crystallinity had strong impact on the physical and

mechanical properties of dairy powders. Since pre-crystallization is widely used in dairy industry, those findings may help them to design better formulations.

2. Effect of formulation on flow properties of dairy powders

2.1 Effect of amorphous lactose content

The flow properties of powders depend on their composition and physical characteristics, such as particle size distribution, particle shape, surface structure, particle density, bulk density, water content and chemical composition (Kim et al., 2005; Schulze, 2007; Janjatović et al., 2012; Crowley et al., 2014a). The median particle size (d_{50}) of lactose/MPI solids systems increased with decreasing lactose content (Table 4-1). Particles of dairy solids with higher lactose content had less rounded shape and rougher surface (Table 4-2). In this study, the differences in particle size and particle shape did not show significant influence on the flowability of lactose/MPI mixtures. Crowley et al. (2014a) have also demonstrated that although particle size is considered one of the major factors influencing the flowability of powders, it is often weakly correlated with flowability.

Dairy solids with larger amount of lactose showed more significant change in their flowability when moisture content increased (Figure 4-2). For lactose/WPI mixtures, powders with larger amount of lactose showed better flowability after storage at 0% and 44% RH. This result was similar with the study of Crowley et al. (2014a). They found MPC35, MPC50, and MPC60 showed better flowability than MPC80, MPC85, and MPC90. Furthermore, when moisture content increased, the loose bulk density of lactose showed the most significant change while lactose/MPI mixtures and MPI powders only showed minor changes, especially lactose/MPI (1:1) mixture (Figure 4-4). Moreover, at the same normal stress, wall friction angles of lactose/MPI solids

systems decreased with decreasing lactose content, while their friction angles all increased with increasing water content (Figure 4-5). Many studies have shown that powders with larger amounts of amorphous components are more sensitive to absorbing moisture (Le Meste et al., 2002; Liu et al., 2006; Fitzpatrick et al., 2007a, 2007b; Silalai & Roos, 2010a). High moisture levels affect flowability negatively, due to increased liquid bridging and capillary interactions between particles.

2.2 Effect of pre-crystallization

Bronlund and Paterson (2004) stated that crystalline lactose absorbed approximately 100 times less water than amorphous lactose in the same conditions. Reducing stickiness in materials can be achieved through partial or complete crystallization of sticky components (Chiou et al., 2008). In the present study, dairy powders with larger amounts of crystalline lactose had larger tapped bulk density and particle density (Table 5-1). Morphological characteristics study indicated that the crystallinity of dairy powders had a minor effect on the particle shape (Table 5-2). DSC analysis indicated that dairy solids with 46.8% crystallinity sorbed less water during storage, which might give higher T_g values and protect them from stickiness and caking (Table 5-3). Water plasticization could increase molecular mobility of dairy solids, while increasing protein content or crystalline lactose content of dairy solids could decrease the molecular mobility of dairy solids. In other words, increasing protein content or crystalline lactose content might help dairy solids to delay the formation of stickiness and caking and keep them free-flowing (Figure 5-1). Dairy solids with 11.2% crystallinity showed more easy-flowing than dairy solids with 1.0, 29.2 and 46.8% cystallinity after storage at 0% and 44% RH (Figure 5-2). Fitzpatrick et al. (2007a) indicated that the high amount of crystalline lactose might give rise to greater frictional resistance between the particles or the differences in

surface moisture contents of crystalline and amorphous lactose produce differences in cohesion due to liquid bridging.

In addition, dairy solids with higher crystallinity showed better resistance to develop cohesive when storage at high relative humidity conditions (Table 5-4). The friction angles of dairy solids with higher crystallinity (11.2%, 29.2% and 46.8%) decreased with increasing water content, while the friction angles of dairy powder with 1.0% crystallinity increased with increasing water content (Figure 5-4). Therefore, pre-crystallizing amorphous materials during processing may help to resolve the problem of product stickiness and stability during subsequent storage (Das & Langrish, 2012).

3. Effect of formulation on encapsulation properties of amorphous matrix

3.1 Flavor release in encapsulation systems with wall materials consisting of lactose/WPI mixtures

In the current study, encapsulation systems with lactose/whey protein isolate (WPI) mixtures (4:1, 1:1, and 1:4), or WPI as wall materials and ethyl butyrate as core material were prepared by spray drying. The wall material consisting of lactose/WPI (4:1) mixture showed significantly ($P < 0.05$) higher encapsulation efficiency for ethyl butyrate (Table 6-1). Ubbink and Krüger (2006) announced that encapsulation systems based on amorphous carbohydrates in the glassy state have been very effective in reducing the rate of release of the flavor during storage, and in minimizing the rate of oxidation of oxygen-sensitive flavors by environmental oxygen. Zhou and Roos (2012) addressed that the amorphous structure protected the entrapped vitamins. However, when lactose content was lower than 50% in the wall materials, the present of lactose did not have significant impact on encapsulation

efficiency of wall materials during spray drying (Table 6-1). Rosenberg and Sheu (1996) also showed similar results. According to their study (Rosenberg & Sheu, 1996), the retention of ethyl butyrate in wall system consisting of a 1:1 mixture of WPI and lactose was not higher than that in wall system consisting of WPI when the initial core material load was lower than 30% (w/w), which was in agreement with our study.

The loss of sorbed water was observed in encapsulation systems with wall materials consisting of lactose/WPI mixtures at ratio 4:1, 1:1, and 1:4 after storage at high water activities ($\geq$ 0.54 a_w) (Figure 6-1). The structure of encapsulated matrix was destroyed as a result of lactose crystallization when water content increased at 0.54 a_w and 0.65 a_w. The T_g values decreased with increasing storage time in the range of 0.33-0.65 a_w before showing lactose crystallization, which showed typical water plasticization of amorphous materials (Jouppila et al., 1997; Haque & Roos, 2004a; Potes et al., 2012) (Table 6-2). Since the T_g values of powders were varied according to the storage time, storage RH and wall material compositions, the rate of flavor release was also affected by those conditions. The water plasticization had more significant impact on the flavor retention of powders with wall materials consisting of larger amount of lactose (Figure 6-4). It was due to water plasticization had more significant influence on the molecular mobility and structural relaxation of powders with larger amount of lactose (Figures 6-2 and 6-3), which caused higher diffusion of flavor molecules in the powders with higher amount of lactose. Roussenova et al. (2014) also stated that the main issue in the design of encapsulation matrices with optimal barrier properties is the molecular mobility in the matrix. Therefore, increasing lactose content could increase the encapsulation

efficiency of wall materials during spray drying. However, this also could result in a higher rate of flavor release with storage at high water activity.

3.2 Flavor release in encapsulation systems with wall materials consisting of lactose/maltodextrin/WPI mixtures

Previous studies have indicated that miscible high molecular weight components generally increase viscosity and the average molecular weight, and decrease molecular mobility of amorphous systems (Roos & Karel, 1991; Sillick & Gregson, 2009). Moreover, the addition of a second carbohydrate component to an amorphous system may delay crystallization of amorphous materials (Mazzobre et al., 2001; Potes et al., 2012). In the present study, encapsulation systems using lactose/whey protein isolate (WPI) (4:1) or lactose/maltodextrin (MD)/WPI (3:1:1 or 1:3:1) mixtures as wall materials and ethyl butyrate (EB) as core materials was produced by spray drying. Wall material consisting of lactose/WPI (4:1) mixtures had the highest encapsulation efficiency for EB during spray drying, while wall materials consisting of lactose/MD/WPI (1:3:1) mixtures had higher encapsulation efficiency compared to wall materials consisting of lactose/MD/WPI (3:1:1) mixtures (Table 7-1). Previous studies (Bhandari et al., 1997; Chronakis, 1998) have indicated that sugars in mixtures with maltodextrins of low dextrose equivalent (DE) form systems with high viscosity and are often used to increase the T_g of food solids to improve their dehydration properties and stability. Sheu and Rosenberg (1995) found that combinations of whey proteins and high DE maltodextrins or corn syrup solids were effective wall systems for encapsulation of volatiles, and Shiga et al. (2001) indicated that blending of MD in the feed liquid decreased the release rate of *d*-limonene in β-cyclodextrin encapsulation system.

Additionally, water sorption study showed that the structure of amorphous matrix was destroyed as lactose crystallization occurred when water content increased at high water activities ($a_w \geq 0.54$), which might result in a quick release of flavor from powders (Figure 7-1). However, the water content of encapsulation systems with wall materials consisting of lactose/MD/WPI mixtures did not show significant decrease with equilibration at 0.54 a_w for 216 h (Figure 7-1). Potes et al. (2012) showed similar results. According to their study, interactions between lactose and maltodextrin could reduce or delay the rate of diffusion or mobility of lactose molecules to form crystals (nucleation) or crystal growth. In addition, the decrease of flavor retention was corresponding to the changes of water contents (Figure 7-1 and 7-4). The water contents of encapsulation systems increased slowly or decreased sharply after 24 h at 0.44-0.76 a_w, while the flavor retention of encapsulation systems decreased significantly in 24 h. Moreover, the glass transition temperatures of encapsulation systems also decreased significantly with storage at 0.44-0.76 a_w in 24 h (Table 7-3). Furthermore, the magnitudes of modulus changes increased significantly in 24 h of storage at 0.44-0.76 a_w (Figure 7-3). Those results indicated that increasing water content of encapsulation systems depressed the glass transition temperatures and as a result, increased the molecular mobility of wall systems, which accelerated diffusion and release of flavor components. The presence of high molecular weight maltodextrin could delay lactose crystallization and increase the stiffness of wall systems, and restrict the diffusion of flavor molecules during storage.

4. Overall conclusions

The present study investigated the physical, mechanical and industrially relevant properties of model dairy solids systems. The research included studies of various

physical properties, mechanical properties, flow properties and encapsulation properties of dairy powders giving the following overall conclusions:

- Particle size of dairy powders was significantly affected by the types of spray dryers. Dairy solids with smaller size particles sorbed larger amount of water compared to those with larger size particle after equilibration at 0.11-0.44 a_w, and they had higher steady water content at the end of lactose crystallization.
- Dairy solids with smaller size particles had lower glass transition temperatures at 0.11-0.33 a_w. Water plasticization had stronger effect on the structural relaxation of dairy solids with smaller size particles.
- The presence of less than 46.8% crystalline lactose in lactose/WPI mixtures had only a minor effect on water sorption behaviour at 0.11-0.44 a_w, whereas samples with higher crystallinity had higher stable water content after showing lactose crystallization. Moreover, samples with lower crystallinity showed higher initial sorption rates.
- Increasing the amount of crystalline lactose had no significant influence on the glass transition temperatures and the initial crystallization temperatures at 0.11-0.44 a_w. Dairy powders with higher crystallinity had higher stiffness. Additionally, water plasticisation had a stronger effect on the structural relaxation of dairy powders with lower crystallinity.
- Lactose/MPI mixtures with higher amount of lactose showed better flowability after storage at 0% and 44% RH. At the same normal stress, wall friction angles of dairy solids systems decreased with decreasing lactose content, while their friction angles all increased with increasing water content.
- Lactose/WPI (4:1) mixtures with 11.2% crystallinity was more easy-flowing than lactose/WPI (4:1) mixtures with 1.0%, 29.2% and 46.8% crystallintiy after

storage at 0% and 44% RH storage conditions. Furthermore, dairy solids with higher amount of crystalline lactose showed better resistance to develop cohesive at high RH storage conditions. The friction angle of lactose/WPI (4:1) mixtures with 1.0% crystallinity increased with increasing water content, while friction angles of lactose/WPI (4:1) mixtures with higher crystallinity decreased with increasing water content.

- Increasing lactose content in wall materials could increase the encapsulation efficiency during spray drying (≤ 0.33). However, the presence of lactose could result in higher molecular mobility with increasing water content, which leaded to accelerate the rate of flavor release at high water activities (≥ 0.54).
- The addition of maltodextrin in wall systems could increase stiffness and reduce molecular mobility of lactose molecules when water content increased, and the presence of high molecular weight maltodextrin could also delay lactose crystallization and increase the stiffness of wall systems, and restrict the diffusion of flavor molecules during storage. Wall systems consisting of lactose/MD (13-17 or 23-27)/WPI (1:3:1) mixtures showed better encapsulation properties for EB at 0.44-0.76 a_w.

5. Application of the research findings and future work

The results from present study are helpful to facilitate improvements of formulation of dairy-based food solids using controlled structure formation, and provide data on physico-chemical properties and structural factors affecting capability of food matrices to protect encapsulated components and sensitive and bioactive food ingredients. Moreover, the current study enhanced industrial uses of knowledge-based approaches in food processing and product formulation. The data can be used for improving processing, product development and modification of

existing process and products, as well as to understand food properties beyond consumption release properties and bioavailability.

Real food systems are composed of numerous miscible, partially miscible, immiscible as well as partially crystalline, and partially amorphous components. This makes the understanding of the properties of individual food systems in various processing and storage conditions greatly challenging. It will be helpful to do further study about how low molecular weight sugars, such as sucrose, glucose, fructose, etc., affect the properties of amorphous lactose in the future. Secondly, it is of great importance to investigate the influence of maltodextrin on the flow properties of model dairy solids. Last but not least, it would be interesting to use other flavor components or active components as core materials and test encapsulation efficiency of amorphous matrix.

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APPENDIX

Published Literatures

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Roles of particle size on physical and mechanical properties of dairy model solids

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ABSTRACT

Lactose/milk protein isolate (MPI) solids systems were prepared by laboratory-scale spray dryer (defined as S-lactose/MPI solids systems) and pilot-scale spray dryer (defined as L-lactose/MPI solids systems). Particles of L-lactose/MPI solids systems had more rounded shape, and smoother surface than those of S-lactose/MPI solids systems. Water sorption study showed S-lactose/MPI solids systems sorbed 5–30% larger amount of water than L-lactose/MPI solids systems after equilibrated at different water activities (0.11 a_w–0.44 a_w). Besides, comparing the samples with same composition, dairy solids with small size particles showed higher steady water content at the end of lactose crystallisation. Moreover, S-lactose/MPI solids systems showed lower glass transition temperature (T_g) values than L-lactose/MPI solids systems after equilibration at 0.11 a_w, 0.23 a_w and 0.33 a_w, which might be due to the higher water content of S-lactose/MPI solids systems. The study of mechanical properties indicated the stiffness of S-lactose/MPI solids systems was higher than that of L-lactose/MPI solids systems at 0.23 a_w and 0.33 a_w when temperature was below T_g values. Water plasticization showed stronger effect on relaxation process of dairy solids with smaller size particles.

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1. Introduction

Several single particle characteristics are important to powder properties. These include particle size, shape, surface, density, hardness, adsorption properties, and so on (Bronlund and Paterson, 2004; Fitzpatrick et al., 2004, 2007; Fu et al., 2012). Of these features, particle size is the most essential and important. Particle size of the powder is primarily determined by physical properties of the infeed emulsion (such as viscosity and solids concentration) and the atomization operating parameters, such as the rotational speed and wheel diameter in the case of centrifugal atomization and the orifice size and pressure in the case of nozzle atomization (Finney et al., 2002; Fang et al., 2005). According to Langrish et al. (2006), the dryer type and settings can also be used to control the morphology of the powder particle and the functional properties of the powder. They stated that the powders produced by the laboratory- and pilot-scale dryers were significantly different from the commercially dried powders in both surface composition and morphology.

Although the role of particle size is not clear, it is often desirable to produce large particles to facilitate rehydration (Ji et al., 2015). Small particles tend to disperse very poorly, especially in cold water, and instead form lumps on liquid surface. Large particles can be obtained through appropriate choice of spray dryer operating conditions or the use of agglomeration techniques (Ji et al., 2015). Powders in small particle size give a large surface area per unit volume, which is related to hygroscopicity (e.g., high degree of moisture absorption). The stability of a powder, in terms of physical and chemical properties, is usually impaired by increased water sorption (Bhandari and Hartel, 2005). The study of Haque and Roos (2004) showed that fine powders (size 3–15 μm for pure lactose and 8–20 μm for lactose/proteins mixtures) sorbed more water than coarse powders (size 15–28 μm for pure lactose and 15–35 μm for lactose/proteins mixtures) at relative vapour pressure (RVP) ≤ 33.2%. Besides, powder particle size could also influence the encapsulation efficiency of oils during spray drying (Jafari et al., 2007). Jafari et al. (2007) revealed that larger particles (>63 μm) retained more volatiles than smaller particles (<38 μm), but at the same time there was more unencapsulated oil at the surface of larger particles.

In addition, the bulk density, compressibility, and flowability of

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a food powder are highly dependent on particle size and its distribution. According to Schulze (2007), the flow properties of a fine-grained bulk solid are mainly influenced by adhesive forces due to liquid bridges (if water is present) and van de Waals forces (dominating force for dry, fine-grained bulk solids). Both forces are proportional to particle size. Moreover, for quality control or system property description, it becomes paramount to present the particle size distribution of food powders.

The objective of this study was to study the effect of particle size on physical properties and mechanical properties of lactose/milk protein isolate (MPI) solids systems. In this study two kinds of spray dryers were used to produce dairy solids with different size particles. The aim was to build a better understanding of the roles of particle size on physical properties and mechanical properties of spray-dried dairy solids.

2. Materials and methods

2.1. Materials

α-lactose monohydrate (>99% purity) and MPI were kindly offered by Arla Foods Ingredients (Sønderhøj 10–12, 8260 Viby J, Denmark) and Kerry Ingredients & Flavours (Kerry Group, Tralee, Co. Kerry, Ireland), respectively. MPI contained ≥89% protein and ≤0.35% lactose. Aluminum oxide calcined powder (≥99% purity) was purchased from Sigma–Aldrich (St. Louis, MO, USA).

2.2. Preparation of lactose/MPI solids systems

Aqueous solution (15%) of lactose, and lactose/MPI mixtures (4:1, 1:1, and 1:4) were spray-dried using a laboratory-scale spray dryer BÜCHI Mini Spray dryer B-191 (BÜCHI Laboratoriums-Technik, Flawil, Switzerland) (defined as S-lactose/MPI solids systems) and a pilot-scale spray dryer ANHYDRO spray dryer with centrifugal atomizer (Copenhagen, Denmark) (defined as L-lactose/MPI solids systems), respectively, at Teagasc Food Research Centre, Moorepark, Fermoy, Co. Cork, Ireland. The inlet air temperature was around 170 ± 2 °C and outlet temperature was around 90 ± 2 °C. Spray-dried solids were kept immediately in evacuated desiccators over P_2O_5 at room temperature. Each analysis was carried out within 3 months after spray drying.

2.3. Powder characterisation

Protein content was determined by FP 628 Nitrogen Determinator (LECO Corporation, Lakeview Avenue, St. Joseph, Michigan, USA). Lactose content was determined by Automatic Polarimeter (Autopol 1, Rudolph Research Analytical, Hackettstown, NJ, USA). Chemical analysis of powders was carried out immediately after manufacture. Powder particle size distribution and specific surface area (SSA) were determined by laser light scattering using a Malvern Mastersizer 3000 (Malvern Instruments Ltd, Worcestershire, UK). Powder sample was added to the standard venture disperser with a hopper gap of 2.5 mm and then fed into the dispersion system. Compressed air at 0.75 bar was used to transport and suspend the powder particles through the optical cell. A measurement time of 10 s was used, and background measurements were made using air for 20 s. The laser obscuration level was at 2–10%.

2.4. Morphological characteristics

Morphological characteristics were determined by Malvern Morphologi G3S (Malvern Instruments Ltd, Worcestershire, UK). 5 mm^3 volume powder samples were dispersed on the glass plate. 2.5× objective was used for the measurement in this study. Circularity, elongation and convexity are three commonly used shape factors (Ji et al., 2015). One way to measure shape is to quantify how close the shape is to a perfect circle. Circularity is the ratio of perimeter of a circle with the same area as the particle divided by the perimeter of the actual particle image. Several definitions of circularity could be used but for accuracy the software reports HS Circularity (HS for high sensitivity) in addition to circularity. Circularity has values in the range of 0–1. A perfect circle has a circularity of 1 while a 'spiky' or irregular object has a circularity value closer to 0. Circularity is sensitive to both overall form and surface roughness. Elongation is defined as [1 − aspect ratio] or [1 − width/length]. As the name suggests, it is a measure of elongation and again has values in the range 0–1. A shape symmetrical in all axes, such as a circle or square, has an elongation value of 0; shapes with large aspect ratios have an elongation closer to 1. Convexity is a measurement of the surface roughness of a particle. It is calculated by dividing the convex hull perimeter by the actual particle perimeter. A smooth shape has a convexity of 1 while a very 'spiky' or irregular object has a convexity closer to 0. In this study, each sample was measured in triplicate to get the average value for circularity, elongation and convexity.

2.5. Water sorption and lactose crystallisation

Water sorption for each solid was measured using the static gravimetric method. Approximately 1 g powder was weighed into small glass vials (25 mL). Triplicate samples of spray-dried lactose/MPI solids systems were dried in a vacuum oven (OV-12, Medline Industries, Inc., Mundelein, Illinois, USA) at 50 °C for 48 h to remove residual water. All powders were then equilibrated for 168 h in evacuated desiccators over saturated salt solutions of LiCl, CH_3COOK, $MgCl_2$, K_2CO_3, $Mg(NO_3)_2$, and $NaNO_2$, giving RVP of 11%, 23%, 33%, 44%, 54%, and 65%, respectively. All desiccators were kept in incubators with temperature of 25 °C during equilibration. The samples were weighed at 0, 3, 6, 9, 12 and 24 h, and then at 24-h intervals. All vials were kept closed with caps after the vacuum was released in the desiccators before weighing. Water content of each powder was measured as a function of time and the mean weight of triplicate samples was calculated.

2.6. Differential scanning calorimetry

Glass transition temperatures, T_g (onset), of L- and S-lactose/MPI solids systems were determined using a differential scanning calorimeter (DSC Q2000, TA Instruments, Crawley, UK). To determine the T_g, spray-dried dairy solids (1 g) were transferred to glass vials and dried in the vacuum oven at 50 °C for 48 h. The dehydrated powders were equilibrated in evacuated desiccators over P_2O_5 and saturated salt solutions of LiCl, CH_3COOK, $MgCl_2$, and K_2CO_3 for 168 h. Then 10–15 mg of equilibrated powders was transferred to Tzero pans. The DSC pans were hermetically sealed with Tzero hermetic lids and samples were analysed. An empty pan was used as a reference. At the first scan, the samples were heated over the glass transition temperature region at 5 °C/min and then cooled at 10 °C/min to below glass transition, a 2nd heating scan was then run to far above the glass transition temperature at 5 °C/min. Anhydrous samples were scanned using pans with punctured lids to allow evaporation of residual water during the measurements (Silalai and Roos, 2010b). At the first scan, the samples were heated at 5 °C/min to 100 °C and then cooled at 10 °C/min to below glass transition, a 2nd heating scan was then run to far above the glass transition temperature at 5 °C/min. The first scan was to evaporate the residual water, while the "anhydrous" state of powders during the subsequent heating scans was expected. All

measurements were carried out in duplicate.

2.7. Dynamic mechanical analysis

A Dynamic Mechanical Analyser (DMA Q800, TA Instruments, Crawley, UK) was used, in conjunction with a gas cooling accessory (GCA) tank, to determine dynamic mechanical properties of L- and S-lactose/WPI solids systems. A rectangular stainless steel powder holder was designed to generate a defined geometry to contain powder with inner dimensions of 60 mm × 11 mm × 1 mm. A pre-weighed mass of powder mixed with Aluminum oxide calcined powder at the ratio 4:1 was evenly spread within this shallow container, and the upper lid was then placed onto the top surface of the powder (Mahlin et al., 2009). As Aluminum oxide calcined showed no influence on the mechanical results of dairy solids in the temperature range, Aluminum oxide powder was added to protect dairy powder from sticking on the powder holder during the heating test. The sample holder was mounted in the instrument in a dual cantilever clamp during measurement. For anhydrous samples and samples equilibrated at 0.11 a_w, the measurements were made at a heating rate of 2 °C/min from 0 to 150 °C. For samples equilibrated at 0.23 a_w, 0.33 a_w and 0.44 a_w, the measurements were made at a heating rate of 2 °C/min from 0 to 120 °C. DMA was operated by a sinusoidal deformation applied to the powder sample holder at a fixed strain. The amplitude was 15 μm. During dynamic heating, the samples were analysed for storage modulus (E′) and loss modulus (E″) using single frequency 1 Hz. Frequency of deformation (oscillating frequency) was changed in multiple frequencies of 0.5, 1, 3, 5, 10, and 20 Hz. The α-relaxation times were determined directly from the frequencies (f) using the relationship $\tau_\alpha = 1/(2\pi f)$ (Noel et al., 2000). The temperature dependence of α-relaxation time was modelled using the Vogel–Tamman–Fulcher (VTF) relationship of Eq. (1) (Angell, 2008; Silalai and Roos, 2011a).

$$\tau_\alpha = \mathrm{Aexp}[DT_0/(T - T_0)], \quad (1)$$

where A, D and T_0 are constants.

2.8. Statistical analysis

Measurement of protein content, glass transition, and dynamic mechanical analysis were performed in duplicate, with all other analysis performed in triplicate. Results were expressed as mean ± standard deviations (SD). One-way analysis of variance (ANOVA) was used to determine the significant differences between the mean values of each test (Microsoft Office Excel 2010, Microsoft, Inc., WA, USA). A significance level of $P < 0.05$ was used throughout the study.

3. Results and discussion

3.1. Powder characterisation

Two kinds of lactose/MPI solids systems with different size particles were prepared by spray-drying (Table 1). Particles of S-lactose/MPI solids systems spray-dried by BÜCHI Mini Spray dryer B-191 had small particle size (d_{50}: 6–7 μm), while those of L-lactose/MPI solids spray-dried by ANHYDRO spray dryer had large particle size (d_{50}: lactose: 24.95 μm; lactose/MPI mixtures: 40–50 μm). As SSA values are typically inferred from particle size data (Crowley et al., 2014), SSA is increased as the particle size becomes small. L-lactose/MPI solids systems showed much smaller SSA values than S-lactose/MPI solids systems. The ratios of SSA values for L-lactose/MPI solids systems and S-lactose solids systems were only between 8.2 and 28.3%. The ratio decreased as lactose content decreased. The difference in their SSA values might affect their water sorption behaviour.

3.2. Particle shape

The particle shape of L- and S-lactose/MPI solids systems was also investigated. Three morphological characteristics (circularity, elongation and convexity) were used to identify the particle shape of L- and S-lactose/MPI solids systems (Table 2). The circularity and convexity of L-lactose/MPI solids systems increased as lactose content decreased, while the elongation decreased as lactose content decreased. However, S-lactose/MPI solids systems did not show the similar results. Lactose and lactose/MPI mixtures with small size particles showed similar circularity and convexity, while the elongation decreased as lactose content decreased. Moreover, comparing dairy solids with same composition, dairy solids with small size particles showed 11–16% smaller circularity values and 13–18% larger elongation values than dairy solids with large size particles (Table 2). These results indicated that particles of L-lactose/MPI solids systems had more rounded shape, and smoother surface than those of S-lactose/MPI solids systems with small size particles. Studies showed that particle shape often influenced the final product performance, such as flowability, abrasive efficiency, and bio-availability (Bumiller et al., 2002; Fu et al., 2012). According to their studies, powders consisting of regularly shaped particles flow better than those consisting of irregular shaped particles. Moreover, the more the particles in a powder resemble spheres, the better the powder flows. Coarse powders in general have better flow properties than fine powders.

3.3. Water sorption and lactose crystallisation

Water content of L- and S-lactose/MPI solids systems after equilibration at different water activities are given in Table 3. S-lactose/MPI solids systems sorbed 5–30% larger amount of water than L-lactose/MPI solids systems after equilibrated at same storage conditions. Similar result was also stated by Haque and Roos (2004). They showed that fine powders sorbed more water than coarse powders at $RVP \leq 33\%$. The large SSA values of S-lactose/MPI solids systems might be one of the reasons that S-lactose/MPI solids sorbed larger amount of water during equilibration. Larger surface area of particles meant more area for water molecular. It is also possible that hydrogen bonding between molecules varies, depending on particle size and affects water sorption (Haque and Roos, 2004). The other possible reason might be the difference in their particle shapes. Particles of S-lactose/MPI solids systems had rougher surface (Table 2), which might be easier for water sorption. Besides, L-lactose/MPI mixture at ratio 4:1 sorbed lower amount of water than L-lactose at 0.11 a_w and 0.23 a_w, while S-lactose/MPI mixture at ratio 4:1 showed the opposite result. These results indicated that particle size of dairy solids was one of the factors which could affect water sorption properties.

Sorbed water of L- and S-lactose/MPI solids systems decreased within 24 h at water activities >0.44 as a result of lactose crystallisation (Fig. 1). The steady state water content of L- and S-lactose/MPI solids systems at the end of lactose crystallisation all increased as protein content increased. Loss of sorbed water in pure L- and S-lactose, and L- and S-lactose/MPI (4:1) mixture occurred rapidly at 0.54 a_w, while the amount of sorbed water for L- and S-lactose/MPI mixtures at ratio 1:1 and 1:4 showed minor decrease after equilibrated at 0.54 a_w. These results indicated that milk protein retarded lactose crystallisation of dairy solids, regardless of their particle size. Besides, comparing the samples with same ratios of lactose/MPI, dairy solids with small size particles showed higher steady water content at the end of lactose crystallisation than those with

Table 1
Physical characteristics of L- and S-lactose/MPI solids systems.

Systems	Protein content (%)	Lactose content (%)	d_{50} (μm)	SSA (m^2/kg)
L-Lactose	0	100	$24.95^{d} \pm 0.25$	$678.3^{e} \pm 2.25$
L-Lactose/MPI 4:1	20.48 ± 0.63	78.95 ± 0.12	$40.90^{c} \pm 0.01$	$234.9^{f} \pm 0.95$
L-Lactose/MPI 1:1	46.54 ± 0.36	51.79 ± 0.42	$44.85^{b} \pm 0.15$	$196.7^{g} \pm 0.04$
L-Lactose/MPI 1:4	74.59 ± 0.11	20.52 ± 0.29	$49.20^{a} \pm 0.50$	$182.8^{h} \pm 2.75$
S-Lactose	0	100	$6.73^{g} \pm 0.09$	$2389.0^{a} \pm 2.00$
S-Lactose/MPI 4:1	20.32 ± 0.37	79.21 ± 0.26	$7.41^{e} \pm 0.02$	$2131.0^{c} \pm 29.00$
S-Lactose/MPI 1:1	46.97 ± 0.17	52.03 ± 0.52	$7.11^{f} \pm 0.10$	$2047.0^{d} \pm 20.00$
S-Lactose/MPI 1:4	73.98 ± 0.38	20.96 ± 0.15	$6.70^{g} \pm 0.02$	$2220.0^{b} \pm 17.00$

1 Values are mean ± standard deviation (protein content: n = 2; for the other values, n = 3).
2 $^{a-g}$Values within columns with different superscripts are significantly different ($P < 0.05$).

Table 2
Particle shape of L- and S-lactose/MPI solids systems.

Systems	Circularity	Elongation	Convexity
L-Lactose	$0.8810^{c} \pm 0.0050$	$0.1970^{e} \pm 0.0085$	$0.9923^{b} \pm 0.0005$
L-Lactose/MPI 4:1	$0.9050^{b} \pm 0.0022$	$0.1773^{f} \pm 0.0039$	$0.9933^{b} \pm 0.0005$
L-Lactose/MPI 1:1	$0.9340^{a} \pm 0.0057$	$0.1300^{g} \pm 0.0059$	$0.9960^{a} \pm 0.0008$
L-Lactose/MPI 1:4	$0.9393^{a} \pm 0.0086$	$0.1177^{g} \pm 0.0106$	$0.9960^{a} \pm 0.0008$
S-Lactose	$0.7815^{f} \pm 0.0055$	$0.3140^{a} \pm 0.0010$	$0.9865^{c} \pm 0.0015$
S-Lactose/MPI 4:1	$0.8120^{d} \pm 0.0040$	$0.2840^{b} \pm 0.0050$	$0.9865^{c} \pm 0.0005$
S-Lactose/MPI 1:1	$0.8090^{d} \pm 0.0020$	$0.2715^{d} \pm 0.0005$	$0.9815^{d} \pm 0.0035$
S-Lactose/MPI 1:4	$0.7900^{e} \pm 0.0010$	$0.2740^{c} \pm 0.0000$	$0.9825^{d} \pm 0.0005$

1 Values are mean ± standard deviation (n = 3).
2 $^{a-g}$Values within columns with different superscripts are significantly different ($P < 0.05$).

Table 3
Water content (g/100 g of dry solids) of L- and S-lactose/MPI solids systems equilibration over saturated salt solution at room temperature (25 °C) for 168 h.

Systems	0.11 a_w	0.23 a_w	0.33 a_w	0.44 a_w
L-Lactose	$2.00^{e} \pm 0.08$	$3.88^{e} \pm 0.06$	$6.16^{d} \pm 0.12$	$9.25^{b} \pm 0.10$
L-Lactose/MPI 4:1	$1.99^{e} \pm 0.02$	$3.43^{f} \pm 0.03$	$5.23^{f} \pm 0.03$	$7.42^{f} \pm 0.70$
L-Lactose/MPI 1:1	$2.60^{d} \pm 0.02$	$4.09^{e} \pm 0.03$	$5.76^{e} \pm 0.06$	$7.82^{e} \pm 0.05$
L-Lactose/MPI 1:4	$3.47^{ab} \pm 0.08$	$5.15^{b} \pm 0.07$	$6.70^{c} \pm 0.00$	$8.20^{d} \pm 0.11$
S-Lactose	$2.75^{c} \pm 0.05$	$4.49^{d} \pm 0.02$	$6.79^{bc} \pm 0.02$	$10.21^{a} \pm 0.09$
S-Lactose/MPI 4:1	$3.30^{b} \pm 0.01$	$5.07^{c} \pm 0.05$	$6.92^{b} \pm 0.05$	$9.43^{a} \pm 0.10$
S-Lactose/MPI 1:1	$3.39^{b} \pm 0.09$	$5.06^{c} \pm 0.21$	$6.68^{c} \pm 0.30$	$8.78^{c} \pm 0.26$
S-Lactose/MPI 1:4	$3.75^{a} \pm 0.04$	$5.59^{a} \pm 0.19$	$7.05^{a} \pm 0.26$	$8.71^{c} \pm 0.27$

1 Values are mean ± standard deviation (n = 3).
2 $^{a-f}$Values within columns with different superscripts are significantly different ($P < 0.05$).

large size particles. As a result, L-lactose showed the lowest steady water content (2.49 g/100 g of dry solids) after equilibration, while S-lactose/MPI mixture at ratio 1:4 showed the highest steady water content (10.75 g/100 g of dry solids) after equilibration.

3.4. Glass transition

Glass transition temperatures for anhydrous and water plasticized L- and S-lactose/MPI solids systems were determined using DSC (Table 4). For anhydrous lactose/MPI solids systems, T_g values of S-lactose/MPI solids systems showed 1–5 °C higher than those of L-lactose/MPI solids systems. However, T_g values of S-lactose/MPI solids systems showed 2–9 °C lower than those of L-lactose/MPI solids systems after equilibration at 0.11 a_w, 0.23 a_w and 0.33 a_w (Table 4), which might be due to the higher water content of S-lactose/MPI solids systems (Table 3). But at 0.44 a_w, pure lactose and lactose/MPI mixtures at ratio 4:1 and 1:1 with different size particles showed similar T_g values, while S-lactose/MPI mixture at ratio 1:4 showed a higher T_g value than L-lactose/MPI mixture at ratio 1:4. These results indicated that particle size affected water sorption behaviour of dairy solids, which might result the difference in their T_g values. Besides, all T_g values of L- and S-lactose/MPI solids systems decreased with increasing water content, which showed typical water plasticization of dairy solids with amorphous lactose (Jouppila and Roos, 1994; Haque and Roos, 2004; Schuck et al., 2005; Silalai and Roos, 2010b).

3.5. Mechanical properties

3.5.1. Modulus changes

Changes in physical properties of materials often occur around the glass transition, which also results in an α-relaxation (Roudaut et al., 2004; Silalai and Roos, 2011a, 2011b). Mechanical properties changes at and around glass transition are key factors in governing

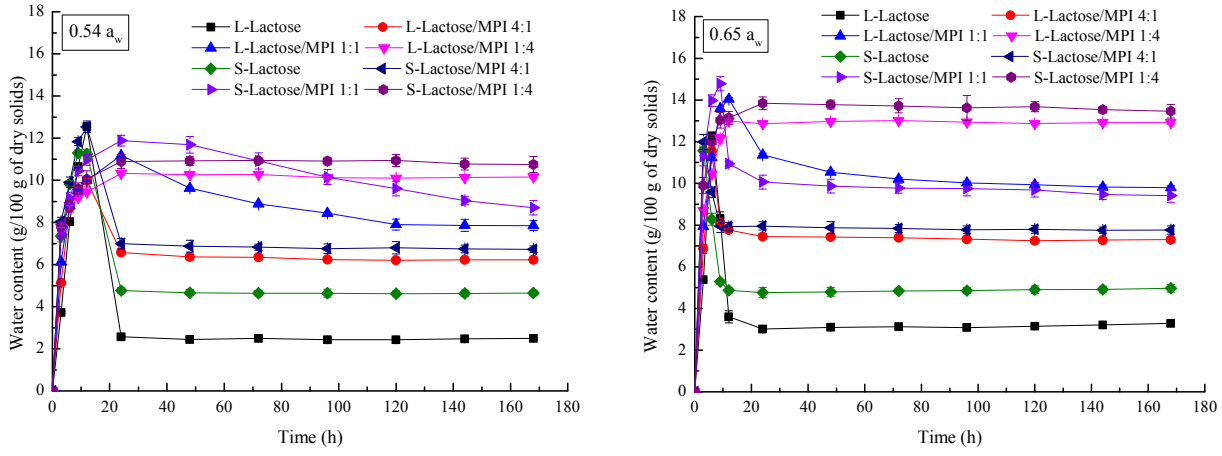


Fig. 1. Lactose crystallisation of L- and S-lactose/MPI solids systems equilibrated at 0.54 a_w and 0.65 a_w at 25 °C for 168 h.

Table 4
Glass transition temperature, T_g, and α-relaxation temperature, T_α, for L- and S-lactose/MPI solids systems equilibration over saturated salt solution at room temperature (25 °C) for 168 h.

Systems		0 a_w	0.11 a_w	0.23 a_w	0.33 a_w	0.44 a_w
L-Lactose	T_g	111 ± 0.0	73 ± 0.5	54 ± 0.0	35 ± 0.0	18 ± 0.5
	T_α	123 ± 0.5	122 ± 0.0	77 ± 0.0	51 ± 0.0	/
L-Lactose/MPI 4:1	T_g	109 ± 0.0	72 ± 0.0	54 ± 0.0	36 ± 1.0	20 ± 0.5
	T_α	124 ± 1.0	124 ± 0.5	77 ± 0.0	52 ± 1.0	40 ± 0.5
L-Lactose/MPI 1:1	T_g	110 ± 0.5	67 ± 0.0	51 ± 0.5	38 ± 0.0	21 ± 0.0
	T_α	129 ± 0.0	130 ± 1.0	73 ± 1.5	67 ± 0.5	45 ± 0.0
L-Lactose/MPI 1:4	T_g	/	67 ± 0.5	50 ± 0.0	43 ± 0.0	33 ± 0.0
	T_α	/	/	69 ± 0.5	65 ± 1.0	61 ± 0.0
S-Lactose	T_g	112 ± 0.5	68 ± 0.0	52 ± 0.5	34 ± 0.0	18 ± 0.0
	T_α	121 ± 1.0	121 ± 1.0	80 ± 0.5	57 ± 0.5	/
S-Lactose/MPI 4:1	T_g	111 ± 1.0	63 ± 0.0	50 ± 0.5	35 ± 1.0	20 ± 0.5
	T_α	126 ± 1.0	122 ± 0.5	78 ± 0.5	60 ± 1.0	38 ± 0.5
S-Lactose/MPI 1:1	T_g	115 ± 0.5	59 ± 1.0	49 ± 0.0	37 ± 0.5	22 ± 0.0
	T_α	130 ± 0.5	130 ± 1.0	78 ± 0.5	71 ± 0.5	49 ± 0.5
S-Lactose/MPI 1:4	T_g	/	63 ± 0.5	50 ± 0.0	45 ± 1.0	37 ± 0.5
	T_α	/	/	73 ± 0.5	66 ± 0.5	66 ± 0.0

1 Values are mean ± standard deviation (n = 2).

the functionality and stability of materials (Peleg, 1993). DMA is the most sensitive technique for monitoring relaxation events, such as glass transitions, as the mechanical properties change dramatically when relaxation behaviour is observed (Menard, 2008). The mechanical properties of L- and S-lactose/MPI solids systems were studied by DMA (Fig. 2). In this study, mechanical α-relaxation of L- and S-lactose/MPI solids systems occurred above the glass transition and was observed from a decrease in storage modulus and a peak in the loss modulus. At temperatures above the glass transition, large changes in viscoelastic properties were expected (Kasapis, 2001; Royall et al., 2005; Silalai and Roos, 2011b). The storage modulus of L- and S-lactose/MPI solids systems decreased significantly in agreement with increasing loss modulus as a result of increasing molecular mobility at glass transition region (Fig. 2).

The storage modulus of S-lactose/MPI solids systems was higher than that of L-lactose/MPI solids systems at 0.23 a_w and 0.33 a_w when temperature was below glass transition temperature (Fig. 2A1 and A2). The storage modulus for S-lactose/MPI solids systems at glassy state increased when water content increased (Fig. 2A1 and A2). However, the storage modulus for L-lactose/MPI solids systems at glassy state decreased as water content increased. For the special case of unconstrained uniaxial tension or compression, Young's modulus can be as a measure of the stiffness of a material. In this study, the results of storage modulus could reflect the changes of stiffness of L- and S-lactose/WPI solids systems. The results of storage modulus indicated that the stiffness of S-lactose/MPI solids systems was higher than that of solids systems with large size particles. Furthermore, the stiffness of S-lactose/MPI solids systems increased with increasing water content, while that of L-lactose/MPI solids systems decreased as water content increased. Dairy solids, spray-dried by different spray dryers, might have different microstructure and hydrogen bonding between molecules, which resulted the difference in their stiffness.

In addition, the magnitude of storage modulus change for L-lactose was around 30% and 20% higher than those for S-lactose

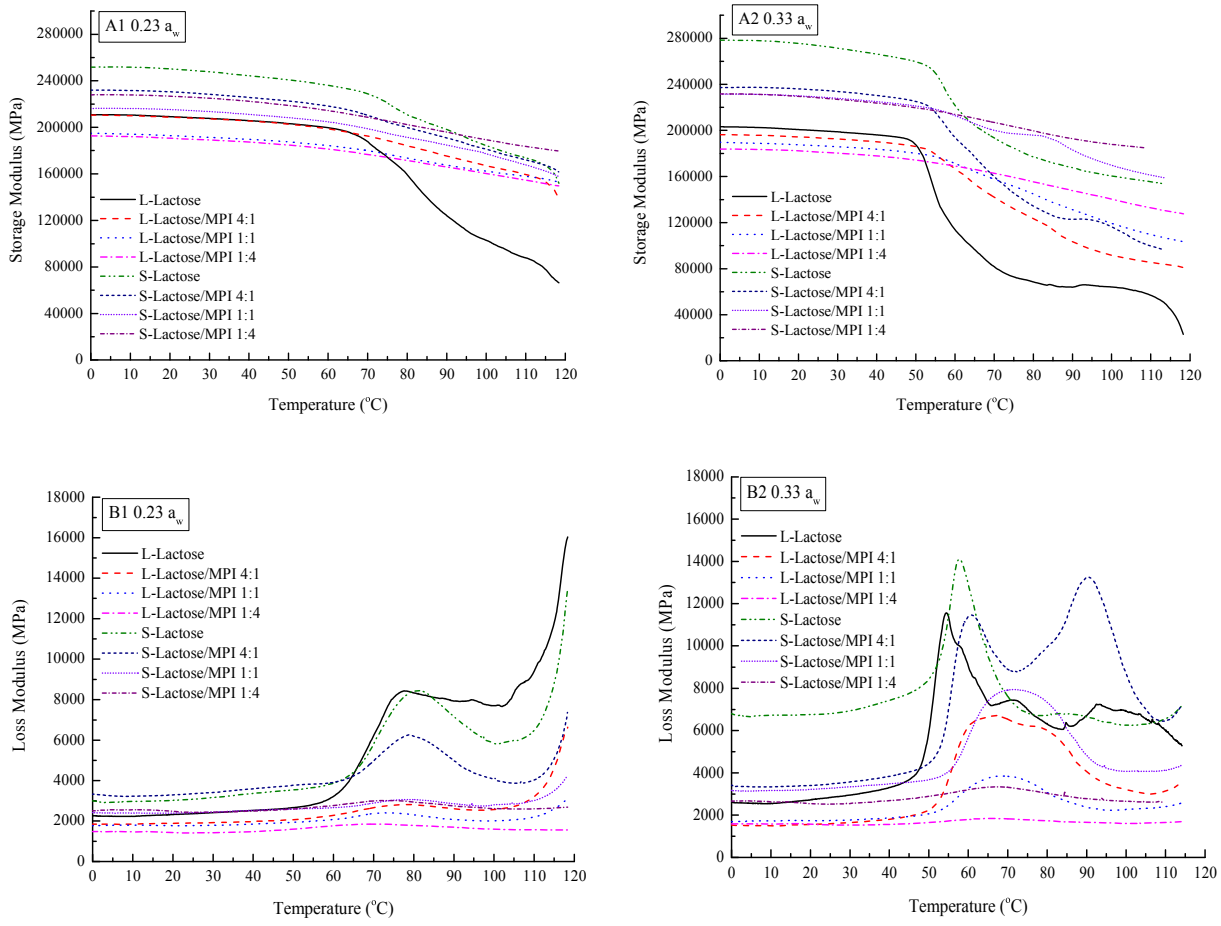


Fig. 2. Storage modulus and loss modulus of L- and S-lactose/WPI solids systems after equilibration at 0.23 a_w and 0.33 a_w at 25 °C for 168 h.

from glassy state to rubbery state at 0.23 a_w and 0.33 a_w, respectively (0.23 a_w: L-lactose: 144,595 MPa, S-lactose: 99,884 MPa; 0.33 a_w: L-lactose: 152,619 MPa, S-lactose: 124,854 MPa). According to Silalai and Roos (2010a), the magnitudes of modulus changes indicated mechanical α-relaxations which were relative to molecular mobility. Therefore, those results showed that L-lactose showed higher molecular mobility than S-lactose at and above glass transition temperatures. But the storage modulus of L-lactose/MPI mixture at ratio 1:4 showed smaller change than that of S-lactose/MPI mixture at ratio 1:4 above glass transition temperature at 0.23 a_w, while the opposite result occurred at 0.33 a_w. Besides, the magnitudes of storage modulus changes of S-lactose/MPI solids systems and L-lactose/MPI systems all increased with increasing water content, which meant water plasticization could increase molecular mobility of solids systems.

The loss modulus changes from glassy state to rubbery state for L- and S-lactose/MPI solids systems were also monitored by DMA (Fig. 2B1 and B2). The loss modulus of L-lactose/MPI solids systems and S-lactose/MPI solids systems showed minor changes in glassy state and rubbery state, while they showed dramatically change in glass transition regions. The magnitudes of loss modulus changes for L-lactose/MPI solids systems and S-lactose/MPI solids systems were different. For pure lactose, the magnitude of loss modulus change of L-lactose was around 10–20% higher than that of S-lactose at 0.23 a_w and 0.33 a_w (0.23 a_w: L-lactose: 6158 MPa, S-lactose: 5430 MPa; 0.33 a_w: L-lactose: 8941 MPa, S-lactose: 7280 MPa). However, for lactose/MPI mixtures, solids with large size particles showed lower magnitudes of loss modulus changes than solids with small size particles at 0.23 a_w and 0.33 a_w. Besides, dairy solids with higher lactose content showed higher magnitudes of loss modulus change. Furthermore, increasing water content of L- and S-lactose/MPI solids systems could also result a higher magnitude of loss modulus (Fig. 2B1 and B2). This was similar as the results of Silalai and Roos (2011b). They stated that the magnitudes of the drop in storage modulus and loss modulus peaks increased dramatically with increasing a_w. As higher magnitudes indicated a higher molecular mobility, particle size as well as amorphous lactose content and water content could affect the molecular mobility of solids systems.

3.5.2. Relaxation time

The appearance of transitional mobility of molecular around the glass transition results in the frequency-dependent α-relaxation (Roudaut et al., 2004; Royall et al., 2005; Silalai and Roos, 2011b). In this study, the α-relaxation temperatures, T_α, were taken from the temperatures of loss modulus peak values determined at different frequencies. T_α values of L- and S-lactose/MPI solids systems at 0.23 a_w and 0.33 a_w are also shown in Table 4. Those T_α values were measured by DMA at 1 Hz. L-lactose/MPI solids systems and S-lactose/MPI solids systems showed similar T_α values at 0 a_w and 0.11 a_w. In addition, S-lactose/MPI solids systems showed higher T_α values at 0.23 a_w, 0.33 a_w and 0.44 a_w than L-lactose/MPI solids systems. Moreover, T_α values of L- and S-lactose/MPI solids systems were also affected by water plasticization. Increasing water content made T_α shift to lower values.

The temperature dependence of α-relaxation times of amorphous materials above the glass transition temperature can be described using the VTF relationship (Angell, 1991, 1997, 2002, 2008). The mechanical α-relaxations for L- and S-lactose/WPI solids systems at 0.23 a_w and 0.33 a_w were measured by DMA using multi-frequency mode. The magnitude of mechanical α-relaxations and T_α values for L- and S-lactose/WPI solids systems decreased with increasing frequency (data not shown). Plots of ln (relaxation time) against $1/(T - T_g)$ gave a linear relationship with regression coefficients of 0.90–0.99. At 0.23 a_w, L-lactose/MPI solids showed higher $(T_\alpha - T_g)$ values than S-lactose/MPI solids for the corresponding relaxation, which meant the α-relaxation occurred at higher temperatures above glass transition temperature as increasing particle size (Fig. 3A). For pure lactose, S-lactose showed more significant change on $(T_\alpha - T_g)$ values than L-lactose, when water content increased (Fig. 3A and B). These results indicated that the viscosity and molecular mobility of dairy solids with smaller size particles had stronger temperature dependence, and water plasticization showed stronger effect on the relaxation process of dairy solids with smaller size particles.

4. Conclusions

The particle size of lactose/MPI solids systems spray-dried by laboratory- and pilot-scale dryers was different. Morphology study showed that particles of L-lactose/MPI solids systems had more rounded shape, and smoother surface than those of S-lactose/MPI solids systems. Water sorption properties of dairy solids were not only governed by the composition of non-fat solids, but also influenced by particle size distribution. Moreover, comparing the samples with the same composition, dairy solids with small size particles showed higher steady water content at the end of lactose crystallisation than those with large size particles. As particle size affected water sorption behaviour of dairy solids, the different in water content of dairy solids resulted difference in their T_g values.

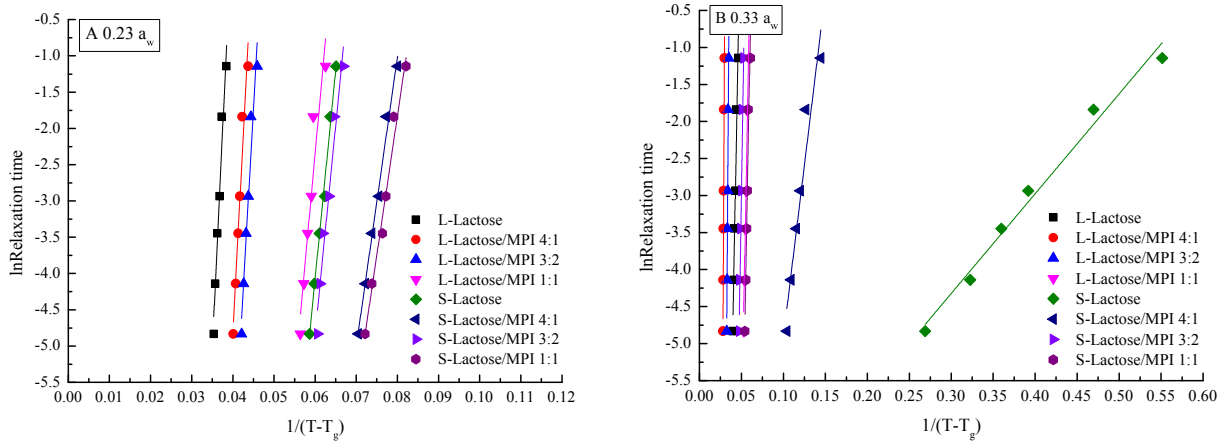


Fig. 3. Plots of ln(relaxation time) against temperature difference $1/(T - T_g)$ for L- and S-lactose/MPI solids systems after equilibration at 0.23 a_w and 0.33 a_w at 25 °C for 168 h.

In addition, the storage modulus of S-lactose/MPI solids systems was higher than that of L-lactose/MPI solids systems at 0.23 a_w and 0.33 a_w when temperature was below glass transition temperature. Thus, the stiffness of S-lactose/MPI solids systems was higher than that of solids systems with large size particles at amorphous state. Furthermore, the stiffness of S-lactose/MPI solids systems increased with increasing water content, while that of L-lactose/MPI solids systems decreased as water content increased. L-lactose/MPI solids systems and S-lactose/MPI solids systems showed similar T_α values at 0 a_w and 0.11 a_w, while S-lactose/MPI solids systems showed higher T_α values at 0.23 a_w, 0.33 a_w and 0.44 a_w than L-lactose/MPI solids systems. The molecular mobility of dairy solids with small size particles showed stronger temperature dependence, and water plasticization showed stronger effect on relaxation process of dairy solids with smaller size particles.

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Physical and mechanical properties of lactose/WPI mixtures: Effect of pre-crystallisation

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ABSTRACT

This study investigated the physical and mechanical properties of spray-dried lactose/whey protein isolate (WPI) (4:1) mixtures with different contents of α-lactose monohydrate (1.0%, 11.2%, 29.2%, and 46.8%, w/w). Particle size of samples with 11.2%, 29.2%, and 46.8% crystallinity was significantly ($P < 0.05$) larger compared with the sample with 1.0% crystallinity. The presence of less than 46.8% crystalline lactose in lactose/WPI mixtures had only a minor effect on water sorption behaviour at a_w 0.11–0.44, whereas samples with higher crystallinity had higher stable water content after showing lactose crystallisation. Moreover, samples with lower crystallinity showed higher initial sorption rates. Increasing the amount of crystalline lactose had no significant influence on the glass transition temperature and the initial crystallisation temperatures at a_w 0.11–0.44. Furthermore, dairy powders with higher crystallinity had higher stiffness and water plasticisation showed a stronger effect on the structural relaxation of dairy powders with lower crystallinity.

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1. Introduction

The main carbohydrate in dairy powders is lactose (Arellano, Aguilera, & Bouchon, 2004), which can exist in various crystalline and non-crystalline forms. The crystalline state is a solid state, having molecules well arranged in regular lattice. According to Haque and Roos (2005), the main types of crystallised lactose are α-lactose monohydrate, anhydrous β-lactose, and anhydrous forms of α- and β-lactose in molar ratios of 5:3 and 4:1. Compared with lactose in the crystalline state, the molecular arrangement of lactose in the amorphous state is disordered. Moreover, amorphous lactose is thermodynamically unstable and hygroscopic, easily absorbing moisture from the surroundings and then plasticising, while the crystalline lactose is thermodynamically stable and much less hygroscopic. These different state forms affect the behaviour of lactose and materials containing lactose, such as dairy powders (McSweeney & Fox, 2009). There has been considerable interest in amorphous components in dairy and pharmaceuticals industries. The presence of even small amounts of amorphous components can have a significant impact on the physico-chemical properties of materials, and subsequently alter product performance (Buckton & Darcy, 1996).

According to Bronlund and Paterson (2004) and Ibach and Kind (2007), the amorphous form of lactose has a much higher water content at a given humidity than the crystalline form and Hogan and Buckton (2001) stated that water sorption can be used to quantify the amorphous content of predominantly crystalline materials. In addition, Bronlund and Paterson (2004) indicated that the amount of water sorbed by crystalline powders at high water activity was dependent on the packing density of the powder particles, and small quantities of amorphous lactose present on crystalline powders caused significant changes to the water sorption behaviour.

In dairy powders, amorphous solids have a liquid-like structure with an extremely high viscosity. The amorphous residue will be changed to a nonequilibrium liquid state when temperature increases. Under the same thermodynamic conditions amorphous solids display higher molecular mobility than crystalline solids (Liu, Bhandari, & Zhou, 2006). The molecular mobility of the amorphous components is of great importance in determining the physical stability of food materials (Hancock, Shamblin, & Zografi, 1995). When the temperature increases from below to above the glass transition temperature (T_g), many of the physical properties of the amorphous materials show a rapid change, including increases in

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the free volume, molecular mobility, and dielectric coefficient. Additionally, large changes in viscoelastic properties of amorphous powders were expected above T_g (Jones, 1999; Kasapis, 2001; Royall et al., 2005). Crystallisation of amorphous components in food products may enhance both physical and chemical stability (Berlin, Anderson, & Pallansch, 1968a, 1968b; Miao & Roos, 2004; Roos & Karel, 1991), and changing the crystallinity of lactose in dairy powders often affects product quality (Aguilar & Ziegler, 1994; Roos, Jouppila, & Söderholm, 1999).

Water sorption behaviour, crystallisation and glass transitions of amorphous lactose, amorphous lactose/protein systems and amorphous lactose/salts mixtures after freeze-drying or spray drying have been widely studied (Bandyopadhyay, Das, & Sharma, 1987; Berlin et al., 1968a, 1968b, 1970; Foster, Bronlund, & Paterson, 2005; Haque & Roos, 2004a, 2004b, 2005, 2006; Haque, Kawai, & Suzuki, 2006; Hermansson, 1977; Hogan & Buckton, 2001; Jouppila, Kansikas, & Roos, 1997; Kaminaski & Al-Bezweni, 1994; Potes, Kerry, & Roos, 2012; Shrestha, Howes, Adhikari, & Bhandari, 2007). Moreover, the amounts of crystalline lactose can affect the sorption behaviour of lactose powders significantly (Bronlund & Paterson, 2004). However, there has been no further study about the effects of crystalline lactose content on mechanical properties of dairy powders, which is essential for dairy research and industry. The objectives of this study were to determine the influence of crystalline lactose content on physical and mechanical properties of lactose/whey protein isolate (WPI) mixtures.

2. Materials and methods

2.1. Materials

Powdered of α-lactose monohydrate (>99% purity) was kindly donated by Arla Foods Ingredients (Viby J, Denmark). WPI, containing 71% β-lactoglobulin and 12% α-lactalbumin, was obtained from Davisco Food International (Le Sueur, MN, USA). Aluminium oxide calcined powder was purchased from Sigma–Aldrich (St. Louis, MO, USA).

2.2. Sample preparation

Lactose/WPI (4:1) mixtures at 40% (w/w) dry matter were prepared in de-ionised water at 65 °C in a water bath for 2 h with a stirring speed of 500 rpm. These solutions were kept at room temperature (20–22 °C) with a stirring speed of 150 rpm for 0, 3, 15 and 20 h pre-crystallisation; these lactose/WPI mixtures were defined as S1, S2, S3 and S4, respectively, according to the pre-crystallisation time. After pre-crystallisation, samples were spray-dried using an ANHYDRO spray dryer with a centrifugal atomiser (Copenhagen, Denmark). The inlet air temperature was around 170 °C, and the outlet temperature was around 90 °C. Spray-dried solids were immediately placed in evacuated desiccators over P_2O_5 at room temperature. Each analysis was carried out within 3 months after spray-drying.

2.3. Powder characterisation

2.3.1. Determination of α-lactose monohydrate content in spray-dried lactose/WPI mixtures

The content of α-lactose monohydrate in spray-dried lactose/WPI mixtures was determined according to the method of Schuck and Dolivet (2002) based on the difference between total water, determined using a Karl Fischer Titration (Mettler Toledo International Inc., Im Langacher Greifensee, Switzerland), and unbound water, determined by weight loss following 6 h drying of 1 g powder at 87 °C. In this study, the content of α-lactose monohydrate was used to represent the crystallinity of lactose/WPI mixtures. It was assumed that there was no bound water in amorphous lactose. Each analysis was carried out in triplicate.

2.3.2. Light microscopy

Lactose crystals were observed with a polarised light microscope fitted with a ProgRes® camera system (JENOPTIK I Optical Systems, Jena, Germany). The lactose/WPI mixtures were spread on slides and one drop of sunflower oil was used to blend with the samples. Coverslips were then placed on the sample, which was observed with a 10× objective. Images were acquired using an Olympus BX51 light microscope (Olympus Optical Co. Ltd., Tokyo, Japan) with polariser filters.

2.3.3. Powder characteristics

Protein content was determined using a FP 628 Nitrogen Determinator (LECO Corporation, Lakeview Avenue, St. Joseph, MI, USA). Lactose content was determined using an Automatic Polarimeter (Autopol 1, Rudolph Research Analytical, Hackettstown, NJ, USA). Water content was determined using a HR83 Hologen Moisture Analyzer (Mettler Toledo International Inc., Im Langacher Greifensee, Switzerland). All chemical analysis of powders was carried out immediately after manufacture. Powder particle size distribution and specific surface area (SSA) were determined by laser light scattering using a Malver Mastersizer 3000 (Malvern Instruments Ltd., Worcestershire, UK).

2.4. Water sorption and lactose crystallisation

Water sorption for each powder was measured using the static gravimetric method and performed in triplicate. Approximately 1 g of spray-dried lactose/WPI mixtures was weighed into small glass vials (25 mL) and dried in a vacuum oven (OV-12, Meline Industies, Inc., Mundelein, IL, USA) at 45 °C for 48 h to remove residual water. After drying, all samples were equilibrated for 240 h in evacuated desiccators over different saturated salt solutions. These saturated salt solutions were LiCl, CH_3COOK, $MgCl_2$, K_2CO_3, $Mg(NO_3)_2$, and $NaNO_2$, which gave relative humidity (RH) of 11%, 23%, 33%, 44%, 54%, and 65%, respectively. All desiccators were placed in incubators set at 25 °C during equilibration. The samples were weighed at 0, 3, 6, 9, 12 and 24 h, and then at 24 h intervals. Water content of each powder was measured as a function of time and the mean weight of triplicate samples was calculated.

The water sorption of lactose/WPI mixtures at 24 h was also monitored using a Multisample Dynamic Moisture Sorption SPS11-10μ (ProUmid GmbH & Co. KG, August-Nagel-Str. 23, Ulm, Germany). The measurement cycles were started at 11%, 23%, 33%, 44%, 54%, and 65% RH, respectively, and ended at 11%, 23%, 33%, 44%, 54%, and 65% RH, respectively. The time for one cycle was 24 h. The measurement temperature was 25 ± 0.1 °C. Sorption rate of spray-dried lactose/WPI mixtures was calculated according to the water sorption results:

$$\text{Sorption rate} = \text{Water content} \Big/ \text{time}\left(\%\text{h}^{-1}\right) \quad (1)$$

2.5. Differential scanning calorimetry

T_g (onset), and initial crystallisation temperatures, (T_{ic}) of lactose/WPI mixtures were determined using a differential scanning calorimeter (DSC Q2000, TA Instruments, Crawley, UK). To determine the T_g, dairy powders (1 g) were transferred to glass vials and dried in a vacuum oven at 45 °C for 48 h. The dehydrated powders were equilibrated in evacuated desiccators over P_2O_5 and

saturated salt solutions of LiCl, CH_3COOK, $MgCl_2$, and K_2CO_3 for 168 h. Then 10–15 mg of equilibrated powders was transferred to Tzero pans (TA Instruments). The DSC pans were hermetically sealed with Tzero hermetic lids and samples were analysed. An empty pan was used as a reference. At the first scan, the samples were heated to at least 20 °C higher than the glass transition temperature region at 5 °C min^{-1} and then cooled at 10 °C min^{-1} to 0 °C; a second heating scan was then run to at least 100 °C higher than the glass transition temperature at 5 °C min^{-1}. Anhydrous samples were scanned using pans with punctured lids to allow evaporation of residual water during the measurements (Silalai & Roos, 2010). At the first scan, the samples were heated at 5 °C min^{-1} to 100 °C to evaporate residual water and then cooled at 10 °C min^{-1} to below glass transition. A second heating scan was then performed on the anhydrous powders to far above the glass transition temperature at 5 °C min^{-1}. All measurements were carried out in duplicate. T_g values were taken as the onset-point of the endothermic baseline shift. T_g and T_{ic} were determined using TA Universal analysis software, version 5.1.2 (TA Instruments).

2.6. Dynamic mechanical analysis

A Dynamic Mechanical Analyser (DMA Q800, TA Instruments) was used, in conjunction with a gas cooling accessory (GCA) tank, to determine the dynamic mechanical properties of lactose/WPI mixtures. A rectangular stainless steel powder holder was designed to generate a defined geometry to contain powder with inner dimensions of 60 mm × 11 mm × 1 mm. A pre-weighed mass of powder mixed with aluminium oxide calcined powder at the ratio 4:1 was evenly spread within this shallow container, and the upper lid was then placed onto the top surface of the powder (Mahlin, Wood, Hawkins, Mahey, & Royall, 2009). As aluminium oxide calcined powder showed no influence on mechanical property results of dairy powders in the temperature range, it was added to protect dairy powder from sticking on the powder holder during the heating test. The sample holder was mounted in the instrument in a dual cantilever clamp during measurement. For anhydrous samples and samples equilibrated at a_w 0.11, the measurements were made at a heating rate of 2 °C min^{-1} from 0 to 150 °C. For samples equilibrated at a_w 0.23, 0.33 and 0.44, the measurements were made at a heating rate of 2 °C min^{-1} from 0 to 120 °C. DMA was operated by a sinusoidal deformation applied to the powder sample holder at a fixed strain. The amplitude was 15 μm. During dynamic heating, the samples were analysed for storage modulus (E′) and loss modulus (E″) using single frequency 1 Hz. Frequency of deformation (oscillating frequency) was changed in multiple frequencies of 0.5, 1, 3, 5, 10, and 20 Hz. The α-relaxation times were determined directly from the frequencies (f) using the relationship of Eq. (2) (Noel, Parker, & Ring, 2000):

$$\tau_a = 1/(2\pi f) \quad (2)$$

The temperature dependence of α-relaxation time was modelled using the Vogel-Tamman-Fulcher (VTF) relationship of Eq. (3) (Angell, 2008; Silalai & Roos, 2011a):

$$\tau_a = A \exp[DT_0/(T_0 - T_0)] \quad (3)$$

where A, D and T_0 are constants.

2.7. Statistical analysis

Measurement of protein content, glass transition, and dynamic mechanical analysis were performed in duplicate, with all other analyses performed in triplicate. Results were expressed as mean ± standard deviations (SD). One-way analysis of variance (ANOVA), followed by Tukey's test, was used to determine the significant differences between the mean values of each test (Microsoft Office Excel 2010, Microsoft, Inc., Redmond, WA, USA). A significance level of $P < 0.05$ was used throughout the study.

3. Results and discussion

3.1. Powder characterisation

The characteristics of lactose/WPI mixtures are shown in Table 1. Crystalline lactose content increased as the pre-crystallisation time was increased (Table 1), yielding samples containing 1.0% (S1), 11.2% (S2), 29.2% (S3) and 46.8% (S4) crystalline lactose. The amount of crystalline lactose is defined as crystallinity of the samples in this study.

The physical appearance of samples is shown in Fig. 1. It was obvious that the amount of crystalline lactose increased from S1 to S4, which further confirmed that the crystallinity of S1, S2, S3 and S4 was different. Lactose crystals were very hard and brittle and its particle shape was different from that of amorphous lactose, which might affect the physical properties and flow properties of dairy powders.

Protein and lactose contents for lactose/WPI mixtures were around 20% and 80%, respectively (Table 1). The particle size of S2, S3, and S4 was significantly larger than S1. However, there were only minor differences in the particle size between samples S2, S3, and S4. As specific surface area (SSA) values are typically inferred from particle size data, S1 with the smallest particle size showed the largest SSA value. These results indicated that pre-crystallisation before spray drying could increase the particle size of dairy powders. But the amount of crystalline lactose showed only a minor effect on the particle size of powders. These differences in particle size and SSA values of dairy powders can affect their physical properties and functionality.

3.2. Water sorption and lactose crystallisation

3.2.1. Water sorption

The experimental water content of lactose/WPI mixtures with different crystallinity equilibration at various RH is shown in Table 2. In lactose/WPI mixtures, the water may be sorbed by proteins, amorphous lactose, crystalline lactose, with some bound as the water of crystallisation 5% of mass of crystals. The amount of water sorbed by S2 with 11.2% crystallinity was significantly higher ($P < 0.05$) than those of S1 (1.0% crystallinity), S3 (29.2% crystallinity), and S4 (46.8% crystallinity) at water activity range of a_w 0.11–0.33, while S3 sorbed the highest amount of water at a_w 0.44. S1, with the lowest crystallinity, did not sorb the highest amount of water at water activity range of a_w 0.11–0.44, but did S1 sorb the highest amount of water at a_w 0.54 and 0.65 before showing loss of sorbed water. According to Bronlund and Paterson (2004), crystalline lactose sorbed very little water over the water activity range (a_w 0–0.85). However, the presence of crystalline lactose in lactose/WPI mixtures did not show significant effect on their water sorption behaviour during equilibration (Table 2). It was assumed that the presence of WPI in dairy powders weakened the effect of crystalline lactose on water sorption behaviour of lactose/WPI mixtures. Previous studies also indicated that water contents sorbed by lactose/WPI mixtures were determined by water sorption behaviour of non-crystalline lactose and protein (Fan & Roos, 2015).

Sorbed water of lactose/WPI mixtures decreased within 24 h at $a_w > 0.44$ as a result of lactose crystallisation (Fig. 2). Loss of sorbed water occurred more rapidly at a_w 0.65 as compared with at a_w 0.54, which was in agreement with the study of Haque and Roos

Table 1
Powder characteristics of lactose/WPI (4:1) mixtures.[a]

System	Crystallinity (%)	Protein content (%)	Lactose content (%)	Water content (%)	d_{50} (μm)	Specific surface area ($m^2\ kg^{-1}$)
S1	1.0 ± 0.58	19.94 ± 0.07	78.91 ± 0.02	2.47 ± 0.04	22.85 ± 0.25^c	714.75 ± 7.45^a
S2	11.2 ± 0.97	19.55 ± 0.04	79.03 ± 0.11	2.93 ± 0.16	25.35 ± 0.05^a	629.95 ± 0.85^c
S3	29.2 ± 0.92	19.45 ± 0.02	78.99 ± 0.06	2.45 ± 0.09	25.20 ± 1.20^{ab}	682.10 ± 9.30^b
S4	46.8 ± 1.11	19.66 ± 0.02	79.45 ± 0.09	2.53 ± 0.15	23.85 ± 0.05^b	695.05 ± 1.05^b

[a] Values are means ± standard deviation (n = 2 for protein content; for the other values, n = 3); values within columns with different superscript letters are significantly different at $P < 0.05$.

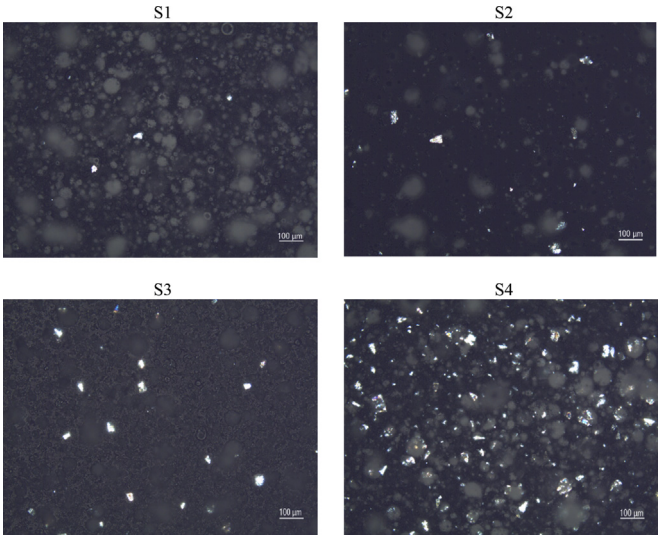


Fig. 1. Images obtained by polarised light microscope for lactose/WPI (4:1) mixtures with 1.0% (S1), 11.2% (S2), 29.2% (S3) and 46.8% (S4) crystallinity.

Table 2
Water content of lactose/WPI (4:1) mixtures with 1.0% (S1), 11.2% (S2), 29.2% (S3) and 46.8% (S4) crystallinity after equilibration at a_w 0.11–0.65 at 25 °C for 240 h.[a]

a_w	S1	S2	S3	S4
0.11	2.48 ± 0.00^b	2.77 ± 0.03^a	2.54 ± 0.09^b	2.45 ± 0.03^b
0.23	4.13 ± 0.11^b	4.33 ± 0.05^a	4.26 ± 0.04^a	4.00 ± 0.04^c
0.33	5.94 ± 0.11^b	6.05 ± 0.05^a	6.04 ± 0.07^a	5.71 ± 0.05^c
0.44	8.69 ± 0.07^b	8.52 ± 0.02^c	8.76 ± 0.11^a	8.43 ± 0.05^d
0.54	5.68 ± 0.04^b	6.78 ± 0.32^a	6.85 ± 0.07^a	6.90 ± 0.06^a
0.65	7.17 ± 0.08^c	7.78 ± 0.13^b	7.85 ± 0.06^b	8.51 ± 0.05^a

[a] Values (g 100 g^{-1} of dry solids) are means ± standard deviation (n = 3); values within columns with different superscript letters are significantly different at $P < 0.05$.

(2004a). Since loss of sorbed water does not occur in crystalline lactose, S2, S3, and S4 showed higher amount of stable water after lactose crystallisation than those of S1 without pre-crystallisation at a_w 0.54 and 0.65 (Fig. 2). These results indicated that the crystallinity showed minor influence on the water sorption behaviour of dairy powders containing protein at a_w 0.11–0.44. However, dairy powders with higher crystallinity showed higher stable water content after lactose crystallisation.

3.2.2. Sorption rate

Water sorption behaviour of lactose/WPI mixtures with different crystallinity was also measured using a Multisample Dynamic Moisture Sorption SPS11-10μ. Water sorption of lactose/WPI mixtures were near equilibrium within 24 h (raw data not shown). Using the water sorption results, sorption rates in the first hour of equilibration were calculated (Fig. 3). The sorption rates of lactose/WPI mixtures increased with increasing storage relative humidity (Fig. 3A–F). The sorption rates of lactose/WPI mixtures decreased and then arrived at constant values (Fig. 3), and the final constant sorption rates of S1, S2, S3 and S4 were not significantly different at a_w 0.11 (Fig. 3A). The sorption rates of S2, with 11.2% crystallinity, were higher than those of S1, S3, and S4 at a_w 0.23–0.65. In addition, the initial sorption rates of lactose/WPI mixtures were divided into two groups, higher initial sorption rate group for S1 and S2 with lower crystallinity, and lower initial sorption rate group for S3 and S4 with higher crystallinity (Fig. 3). It was obvious that the difference between two groups increased with increasing storage relative humidity. Therefore, the crystallinity affected the initial sorption rate of the lactose/WPI mixtures significantly; samples with higher crystallinity showed lower sorption rates.

3.3. Glass transition

The T_g and T_{ic} values for anhydrous and equilibrated lactose/WPI mixtures are shown in Table 3. It was obvious that the T_g values of lactose/WPI mixtures decreased with increasing water content, which showed typical water plasticisation of dairy powders

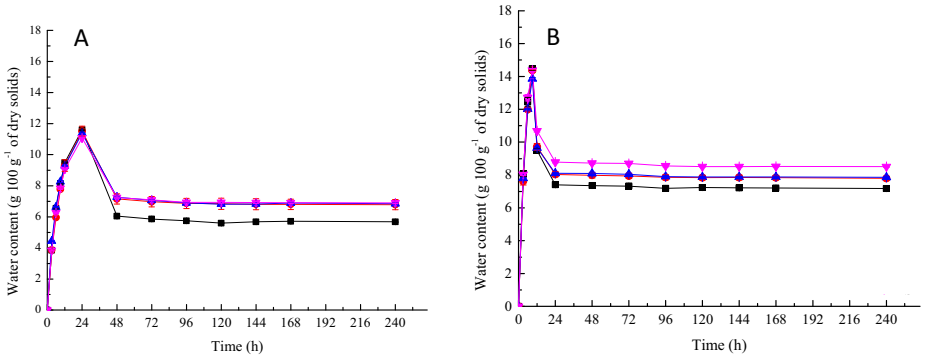


Fig. 2. Lactose crystallisation at (A) a_w 0.54 and (B) a_w 0.65 at 25 °C of lactose/WPI (4:1) mixtures with 1.0% (S1), 11.2% (S2), 29.2% (S3) and 46.8% (S4) crystallinity.

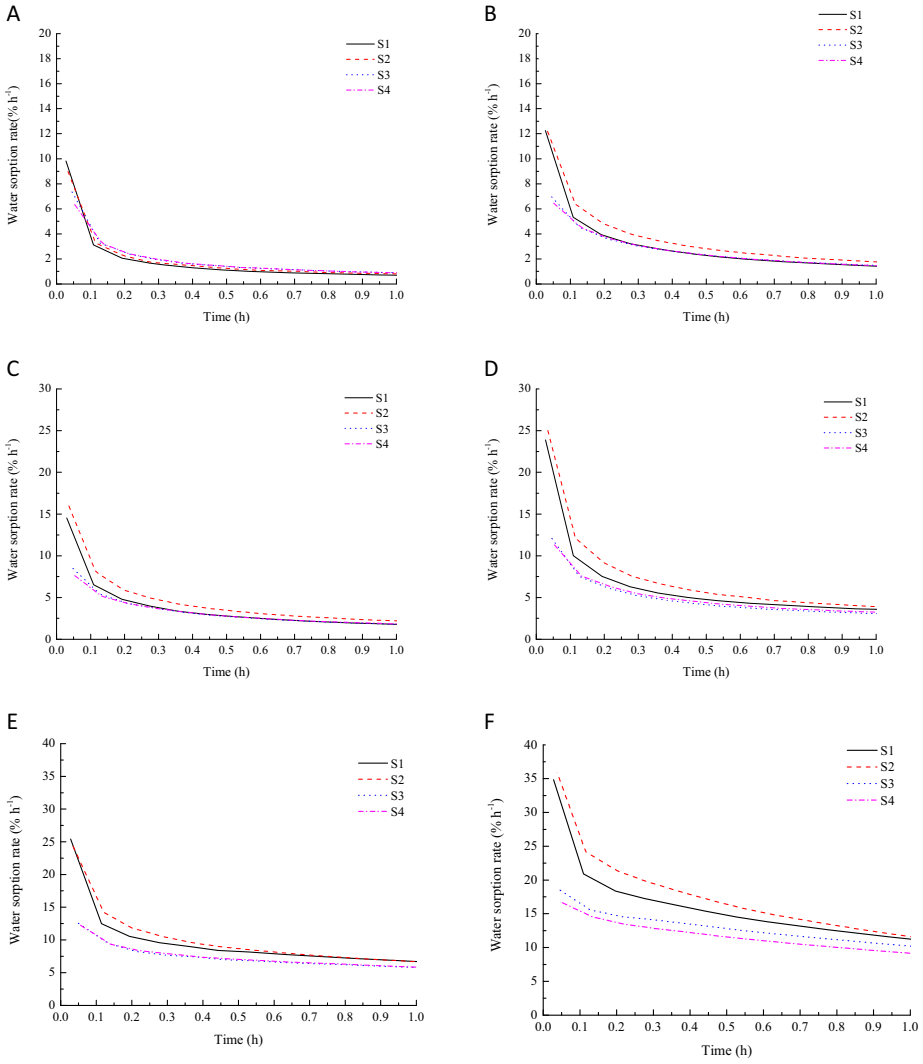


Fig. 3. Sorption rate of lactose/WPI (4:1) mixtures with 1.0% (solid line, S1), 11.2% (dashed line, S2), 29.2% (dotted line, S3) and 46.8% (dot-dash line, S4) crystallinity during equilibration for 24 h at 25 °C at a_w of: A, 0.11; B, 0.23; C, 0.33; D, 0.44: E, 0.54; F, 0.65.

containing lactose (Haque et al., 2006; Jouppila et al., 1997; Potes et al., 2012). There was no significant difference in the T_g values of lactose/WPI mixtures with different levels of crystalline lactose at the same water activities. Therefore, the T_g values of lactose/WPI mixtures with different amount of crystalline lactose was primarily dependent on the amorphous lactose, which was in agreement with previous studies. According to previous studies (Fan & Roos, 2015; Potes et al., 2012; Silalai & Roos, 2010), lactose-protein systems showed phase separation and their T_g values were dependent on amorphous lactose. The T_g values of lactose/WPI mixtures in this study were higher than those reported by Haque and Roos (2004b) and Fan and Roos (2015) for lactose/WPI mixtures at corresponding water activities. As water content significantly affected T_g values of dairy powders, the differences in the T_g values between our study and other studies were probably a result of different water contents with equilibration at a_w 0.11–0.44. Haque and Roos (2004a) have indicated that drying methods, storage time, and storage temperature could result in the differences in final water content of lactose/protein mixtures. In addition, the T_{ic} values of lactose/WPI mixtures also decreased with increasing water content (Table 3). Since lactose crystallisation could be delayed by the presence of protein, the T_{ic} values of lactose/WPI mixtures was higher than that of pure lactose (Haque & Roos, 2004b; Zhou & Roos, 2012). Lactose/WPI mixtures with different amount of crystalline lactose showed similar T_{ic} values in the range of a_w 0.11–0.44. Therefore, the amount of crystalline lactose showed no significant influence on the T_{ic} values of the lactose/WPI mixtures.

Table 3
Glass transition temperature (T_g), initial crystallisation temperature (T_{ic}), and α-relaxation temperature (T_α) of lactose/WPI (4:1) mixtures with 1.0% (S1), 11.2% (S2), 29.2% (S3) and 46.8% (S4) crystallinity equilibrated at a_w 0–0.44 at 25 °C for 168 h.[a]

Systems		Water activity (a_w)				
		0	0.11	0.23	0.33	0.44
S1	T_g	105 ± 0.5	71 ± 0.0	58 ± 0.5	40 ± 0.0	21 ± 0.5
	T_{ic}	/	127 ± 1.0	115 ± 0.5	94 ± 0.5	72 ± 0.0
	T_α	126.5 ± 0.4	126.6 ± 0.4	80.0 ± 0.3	70.6 ± 0.9	44.4 ± 1.1
S2	T_g	105 ± 0.0	70 ± 0.0	58 ± 0.5	40 ± 0.5	22 ± 0.0
	T_{ic}	/	125 ± 0.5	112 ± 0.0	92 ± 0.5	73 ± 0.5
	T_α	125.8 ± 0.1	125.1 ± 0.3	77.8 ± 0.7	66.4 ± 0.9	37.4 ± 0.9
S3	T_g	104 ± 0.5	70 ± 0.0	58 ± 1.0	39 ± 0.0	21 ± 0.0
	T_{ic}	/	126 ± 1.0	114 ± 0.5	93 ± 0.0	73 ± 0.5
	T_α	127.0 ± 0.3	127.0 ± 0.3	78.9 ± 0.3	61.0 ± 0.6	38.0 ± 0.9
S4	T_g	105 ± 0.0	70 ± 0.5	58 ± 0.0	38 ± 0.5	21 ± 0.5
	T_{ic}	/	127 ± 0.5	113 ± 0.5	93 ± 0.5	72 ± 0.0
	T_α	127.0 ± 0.4	126.3 ± 0.2	77.9 ± 0.5	62.0 ± 0.8	41.0 ± 0.9

[a] Values are mean ± standard deviation (n = 2).

3.4. Mechanical properties

3.4.1. Modulus and stiffness

The physical properties of amorphous materials often change around the glass transition temperatures, which may result in an α-relaxation (Roudaut, Simatos, Champion, Contreras-Lopez, & Le Meste, 2004; Silalai & Roos, 2011a, 2011b). The mechanical properties of lactose/WPI mixtures with different amount of crystalline lactose were measured by DMA. A loss of water occurred during dynamic measurements for dairy powders with lower water activities (a_w < 0.23), which was also reported by Silalai and Roos (2011b). Moreover, lactose/WPI mixtures showed lactose crystallisation during storage at a_w 0.54 and 0.65. Therefore, the results of mechanical properties of lactose/WPI mixtures at a_w 0.11, 0.54 and 0.65 are not shown. Mechanical α-relaxation of lactose/WPI mixtures occurred above T_g and was observed from a sharp decrease in their storage modulus and a peak in their loss modulus (Fig. 4). The storage modulus shows the amount of energy that the material stores (Edward, Kirui, Omolo, Ngumbu, & Odhiambo, 2014). Furthermore, the magnitudes of storage modulus and loss modulus changes are relative to molecular mobility (Roudaut et al., 2004; Silalai & Roos, 2010, 2011b). As it can be seen from Fig. 4 A, C, and E, samples S4, with the highest crystallinity, showed higher storage modulus than samples S1, S2, and S3 at the glassy state at a_w 0.23–0.44. Additionally, the difference in storage modulus of lactose/WPI mixtures increased with increasing storage RH (Fig. 4 A, C, and E). At the glassy state, the storage modulus of lactose/WPI mixtures with lower crystallinity (S1 and S2) decreased significantly from a_w 0.33 to a_w 0.44 (from 208,295 MPa to 135,679 MPa for S1; from 214,528 MPa to 110,495 MPa for S2) (Fig. 4 C and E). The storage modulus of S4 with 46.8% crystallinity showed the smallest change at the glassy state with increasing water content (222,785 MPa at a_w 0.33; 214,190 MPa at a_w 0.44). These results indicated that the addition of crystalline lactose could maintain the stiffness of dairy powders when water content is increased. This might be due to the different molecular mobility and free volume of amorphous and crystalline state lactose. According to Kilburn et al. (2004), the effect of water plasticisation in carbohydrates solids is related to hydrogen bond formation and disruption, and also involves to the changes in free volume. Unlike amorphous structure, the crystalline state has molecules well arranged, which is in the favourable low energy state. Water plasticisation showed no significant effect on molecular mobility of crystalline lactose, and only exhibited a minor effect on the storage modulus of dairy powders with higher crystallinity. At the glass transition region, the storage modulus of lactose/WPI mixtures decreased significantly at a_w 0.23,

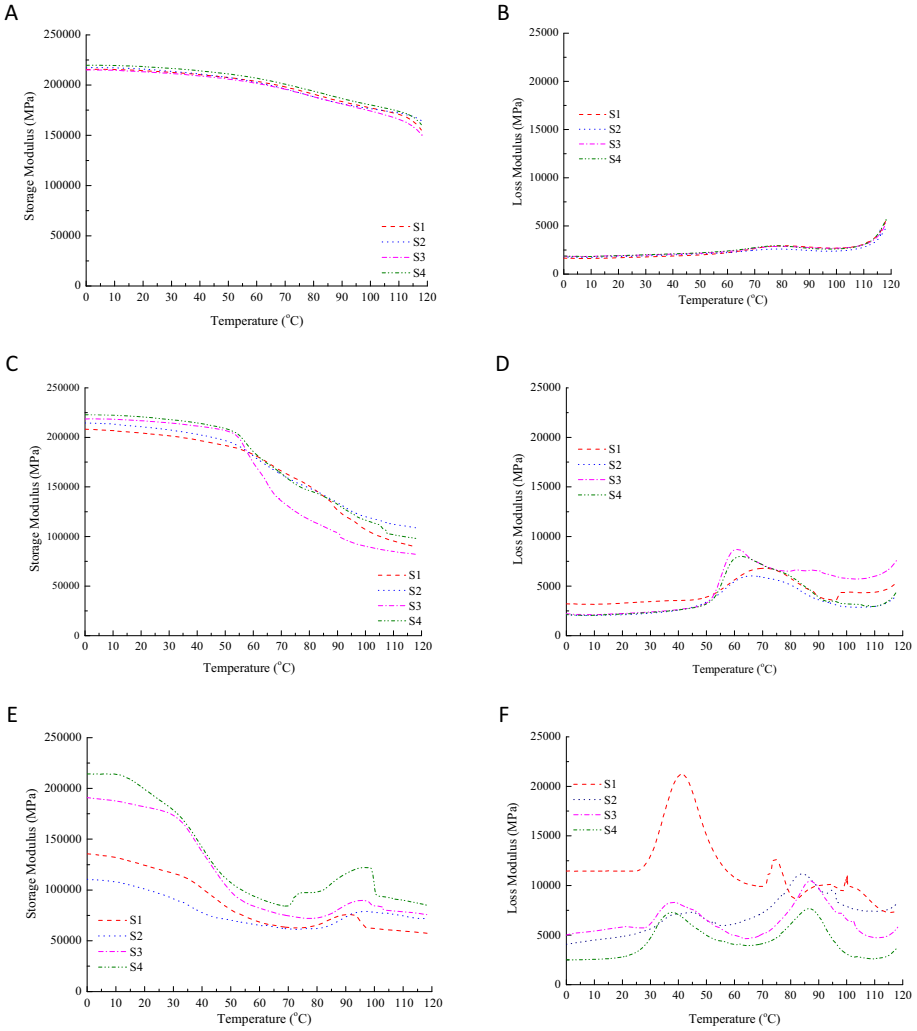


Fig. 4. Storage modulus (A, C, E) and loss modulus (B, D, F) of lactose/WPI (4:1) mixtures with 1.0% (dashed line, S1), 11.2% (dotted line, S2), 29.2% (dash-dot line, S3) and 46.8% (dash-dot-dot line, S4) crystallinity during equilibration at 25 °C for 168 h at a_w of: A and B, 0.23; C and D, 0.33; E and F, 0.44.

0.33 and 0.44 as a result of increasing molecular mobility (Fig. 4 A, C, and E). A greater change in the storage modulus was experienced with lactose/WPI mixtures at a_w 0.33 and 0.44 compared with at a_w 0.23, which indicated that lactose/WPI mixtures with higher water content showed higher molecular mobility at the glass transition region. Therefore, the magnitude of the storage modulus changes of lactose/WPI mixtures were affected by the amount of crystalline lactose and water. Dairy powders with higher crystallinity showed lower molecular mobility with increasing temperature.

Stiffness of materials refers to the ability to carry stress without changing dimension (Ebewele, 2000). For the measurement of unconstrained uniaxial tension or compression, Young's modulus can be used as a measure of the stiffness of a material. In this study, the change of storage modulus could reflect the change of stiffness of lactose/WPI mixtures. The changes of stiffness for lactose/WPI mixtures were directly related to the storage modulus when temperature increased from 0 to 120 °C at 1 Hz (the stiffness results were not shown). S4 with the highest crystallinity gave the largest storage modulus at a_w 0.23, 0.33 and 0.44 (Fig. 4 A, C, and E), which meant S4 had the highest stiffness at a_w 0.23 to 0.44. However, S1 and S2 with lower crystallinity showed lower stiffness at a_w 0.33 and 0.44. These results indicated that dairy powders with higher amount of crystalline lactose had higher stiffness, which might be due to the physical properties of crystalline lactose. As crystallinity is the result of a highly ordered arrangement of the lactose molecules, lactose crystals are very hard and stiff.

The changes of loss modulus for lactose/WPI mixtures with different crystallinity were also determined using the DMA. The loss modulus, E″, of lactose/WPI mixtures showed minor changes at the glassy state and the rubbery state, while they increased dramatically and arrived at the peak values in the glass transition region (Fig. 4 B, D, and F). This result could be explained from the point of mechanical internal friction (Guo, Feng, Wang, Hu, & Zhang, 2013). According to Guo et al. (2013), the chain segment motion of lactose and proteins molecules is in a frozen state when in the glassy state, and is in a free moving state when in the rubbery state. The chain segment motion changes from a frozen state to a free moving state during the glass transition region. This change of motion leads to large internal loss. The internal friction loss approaches maximum as the temperature reaches glass transition temperature, which is reflected from the peak of loss modulus. Since the physical state of amorphous powders is strongly affected by the concentration of water, the peak values of loss modulus for lactose/WPI mixtures increased as water content was increased (Fig. 4 B, D, and F). Moreover, the loss modulus of lactose/WPI mixtures in the glassy state also increased with increasing water content, especially for S1 with the lowest crystallinity (3211 MPa at a_w 0.33; 11,442 MPa at a_w 0.44). Since the magnitude of loss modulus changes is also related to the molecular mobility, dairy powders with lower crystallinity showed higher molecular mobility as water content was increased.

3.4.2. Mechanical structural relaxation

In this study, the α-relaxation temperatures, T_α, were taken from the temperatures of loss modulus peak values at 1 Hz. T_α values of dairy powders shifted to lower temperatures with increasing water content (Table 3), which was in agreement with previous studies (Li, Roos, & Miao, 2016; Potes et al., 2012; Silalai & Roos, 2011b). Lactose/WPI mixtures with different crystallinity showed similar T_α values at a_w 0 and 0.11, while S1 with the lowest amount of crystalline lactose showed the highest T_α values at a_w 0.23–0.44. Furthermore, the mechanical α-relaxations for lactose/WPI mixtures at a_w 0.23, 0.33, and 0.44 were determined by DMA using multi-frequency mode. The magnitude of mechanical α-relaxations for lactose/WPI mixtures decreased when frequency was increased (data not shown).

Many studies have indicated that the Vogel-Tammann-Fulcher (VTF) relationship can be used to describe the temperature dependence of relaxation times for amorphous materials at temperatures above glass transition (Angell, 1995, 2008; Angell, Ngai, McKenna, McMillan, & Martin, 2000; Potes et al., 2012; Silalai & Roos, 2011b). The VTF plots indicated that the T_α values of lactose/WPI mixtures at various frequencies were at higher temperatures with increasing frequency (Fig. 5). Moreover, lower T-T_g values were shown by S1 for the corresponding relaxation at a_w 0.23–0.44, which meant α-relaxation of S1 occurred at lower temperatures above T_g values than those of S2, S3, and S4. Comparing the VTF plots at a_w 0.23 and 0.33 (Fig. 5A and B), the α-relaxations of lactose/WPI mixtures occurred at higher T-T_g values as water content was increased. Then the T-T_g values of S1 and S2 decreased when a_w was increased from 0.33 to 0.44 (Fig. 5B and C), while those of S3 and S4 showed only minor changes. According to

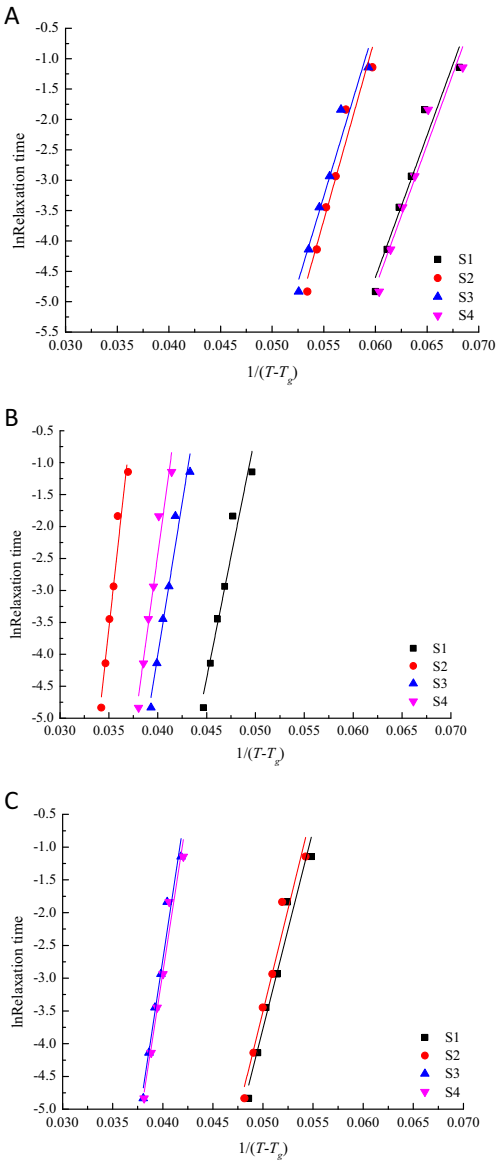


Fig. 5. Plots of ln relaxation time against temperature difference $1/(T - T_g)$ for lactose/WPI (4:1) mixtures with 1.0% (■, S1), 11.2% (●, S2), 29.2% (▲, S3) and 46.8% (▼, S4) crystallinity during equilibration at 25 °C for 168 h at a_w of: A, 0.23; B, 0.33; C, 0.44.

Liu et al. (2006), the viscosity and molecular mobility of S1 and S2 with lower crystallinity might have strong temperature dependence. Thus, they exhibit larger changes on relaxation time in the vicinity of the glass transition than dairy powders with higher crystallinity. Therefore, water plasticisation had a stronger effect on the structural relaxation of dairy powders with lower crystallinity.

4. Conclusions

As crystalline lactose and amorphous lactose have different molecular arrangement, they show different behaviour in physical properties and functionality. Lactose/WPI mixtures with different amount of crystalline lactose were prepared by pre-crystallisation. Particle size of dairy powders with 11.2%, 29.2%, and 46.8% crystallinity was significantly ($P < 0.05$) larger than that of dairy powder with 1.0% crystallinity. Since physical properties, flowability and functionality of dairy powders are highly dependent on the particle size of powders, pre-crystallisation could have a significant impact on the final properties of dairy powers. The presence of less than 46.8% crystalline lactose in dairy powders showed only a minor effect on water sorption behaviour of dairy powder at a_w 0.11–0.44. Dairy powders with higher crystallinity showed higher stable water content after lactose crystallisation. Furthermore, dairy powders with lower amount of crystalline lactose showed higher sorption rates at the beginning of water sorption. Increasing the amount of crystalline lactose in dairy powders did not have significant influence on the T_g and T_{ic} values. The mechanical property study showed that lactose/WPI mixtures with higher amount of crystalline lactose had higher stiffness, and the addition of crystalline lactose could maintain the stiffness of dairy powders when water content is increased. Water plasticisation had a stronger effect on the structural relaxation of dairy powders with lower amount of crystalline lactose. Since pre-crystallisation of lactose is widely used in the production of dairy powders, the findings of this study could be very useful in the dairy industry.

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The effect of water plasticization and lactose content on flow properties of dairy model solids

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ABSTRACT

The flow properties of spray-dried solids depend on their composition and physical characteristics. This study investigated the influence of water plasticization and lactose content on flow properties of lactose/milk protein isolate (MPI) solids systems. Median particle size (d_{50}) of lactose/MPI solids systems increased as lactose content decreased, and lactose showed the largest specific surface area (SSA). Particle shape of dairy solids with higher lactose content had less rounded shape, rougher surface and lower ratio of width/length. T_g values of lactose/MPI mixtures (protein content $\leq$ 60%) showed only minor difference as comparing to T_g values of pure lactose in this study. Mechanical study showed that the higher was the lactose content in dairy solids, the more significant was the change in their modulus at glass transition region. Lactose/MPI mixtures with higher lactose contents showed better flowability in this study, but they gave bigger friction angles after storage at same relative humidity.

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1. Introduction

Spray-dried dairy solids are very important ingredients in many food and dairy products. There is a need for information about handling and processing characteristics of spray-dried dairy solids. Flow properties of spray-dried dairy solids are very important in handling and processing operations (Knowlton et al., 1994; Fitzpatrick et al., 2007a). Flow problems in hoppers, silos and transport containers are severe problems for engineers and process operatives (Marinelli and Carson, 1992; Fitzpatrick et al., 2007a). Food powders are commonly stored in bulk silos before packaging, dry-mixing with other powders or dehydration (Crowley et al., 2014b).

The flow properties of powders depend on their composition and physical characteristics, such as particle size distribution, particle shape, surface structure, particle density, bulk density, water content and chemical composition (Crowley et al., 2014b; Janjatović et al., 2012; Kim et al., 2005; Schulze, 2007). Many food powders and food ingredient mixes are rendered complicated by the fact that they contain many different components, and this makes it difficult to predict their flow behaviour (Fitzpatrick et al., 2007a). Crowley et al. (2014a,b) demonstrated that composition and processing of milk protein concentrates across a range of protein concentrations resulted in powders with different physical characteristics, which, in turn, affected their flow properties. Study also showed the presence of free-fat on the powder surface was critical to the deterioration of dairy powder flowability (Kim et al., 2005). Fitzpatrick et al. (2007b) stated that the dominant compositional factors affecting the cohesiveness of dairy powders were moisture, amorphous lactose and state transitions.

In addition, stickiness of powder particles is responsible for impaired flow properties (Lazar et al., 1956). Stickiness and caking of powders resulted from formation of liquid bridges between individual particles (Peleg, 1977). Many studies showed that powders with larger amounts of amorphous components were more sensitive to absorbing moisture (Meste et al., 2002; Fitzpatrick et al., 2007a,b; Liu et al., 2006; Silalai and Roos, 2010). High moisture levels affect flowability negatively, due to increased liquid bridging and capillary interactions between particles. This would result in lumping and caking problems for powders. Moreover, as amorphous solid has a kinetically frozen liquid-like structure and is not in a thermodynamic equilibrium state, amorphous materials exhibit increased molecular mobility and rapidly decreasing viscosity above the glass transition (Roos and Karel, 1991; Champion et al., 2000; Roudaut et al., 2004). Several studies have confirmed that stickiness was controlled by the glass transition (Hennigs et al.,

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2001; Ozmen and Langrish, 2002; Silalai and Roos, 2011a). Besides, changes in mechanical α-relaxations of milk solids/maltodextrin systems were also associated with powder stickiness, which was also as a result of increasing molecular mobility above the glass transition of powder components (Silalai and Roos, 2011b). Thus, amorphous lactose content of dairy solids might affect their flow properties, as lactose causes caking and stickiness during storage and transportation.

However, there are only a few studies about the relationship between amorphous lactose content and flow function of dairy solids. The objectives of this study were to investigate the glass transition, mechanical properties and flow properties of lactose/MPI solids systems, to study the effect of water plasticization and amorphous lactose content on the flow function of dairy model solids.

2. Materials and methods

2.1. Materials

α-lactose monohydrate (>99% purity) and milk protein isolate (MPI) were kindly offered by Arla Foods Ingredients (Denmark) and Kerry Ingredients & Flavours (Listowel, Ireland), respectively. MPI contained ≥89% protein and ≤0.35% lactose. Aluminium oxide calcined powder (≥99% purity) was purchased from Sigma–Aldrich (St. Louis, MO, USA).

2.2. Lactose/MPI mixtures preparation

Dairy solids with different ratios of lactose/MPI, were spray-dried at Teagasc Food Research Centre, Moorepark, Fermoy, Co. Cork, Ireland. These were lactose, lactose/MPI (4:1, 3:2, 1:1, 2:3, and 1:4), and MPI. Solution of lactose/MPI mixtures was prepared at room temperature while the solid concentration was 15% for lactose and lactose/MPI mixtures, and 10% for MPI (w/w). All sample solutions were spray-dried by an ANHYDRO spray dryer with centrifugal atomizer (Copenhagen, Denmark) at Teagasc Food Research Centre, Moorepark, Fermoy, Co. Cork, Ireland. The inlet air temperature was around 170 °C and outlet temperature around 90 °C. Spray-dried solids were kept immediately in vacuum desiccators over P_2O_5 at room temperature. Each analysis was carried out within 3 months after spray drying.

2.3. Powder characterisation

Protein content was determined by FP 628 Nitrogen Determinator (LECO Corporation, USA). Lactose content was determined by Automatic Polarimeter (Autopol 1, Rudolph Research Analytical, USA). Water content was determined by HR83 Hologen Moisture Analyser (Mettler Toledo International Inc., Switzerland). Ash content was determined after overnight incineration at 550 °C furnace. All chemical analysis of powders was carried out immediately after manufacture. Powder particle size distribution and specific surface area (SSA) were determined by laser light scattering using a Malver Mastersizer 3000 (Malvern Instruments, Worcestershire, UK). Particle density was determined using a Gas Pycnometer (Accupyc II 1340 Gas Pycnometer, Micromeritics Instrument Corporation, USA).

2.4. Morphological characteristics

Morphological characteristics were determined by Malvern Morphologi G3 S (Malvern Instruments, Worcestershire, UK). 5 mm^3 volume powder samples were dispersed on the glass plate. 2.5X objective was used for the measurement in this study. Circularity, convexity and elongation are three commonly used shape factors. One way to measure shape is to quantify how close the shape is to a perfect circle. Circularity is the ratio of perimeter of a circle with the same area as the particle divided by the perimeter of the actual particle image. Several definitions of circularity could be used but for accuracy the software reports HS Circularity (HS for high sensitivity) in addition to circularity. Circularity has values in the range 0–1. A perfect circle has a circularity of 1 while a 'spiky' or irregular object has a circularity value closer to 0. Circularity is sensitive to both overall form and surface roughness. Convexity is a measurement of the surface roughness of a particle. It is calculated by dividing the convex hull perimeter by the actual particle perimeter. A smooth shape has a convexity of 1 while a very 'spiky' or irregular object has a convexity closer to 0. Elongation is defined as [1-aspect ratio] or [1-width/length]. As the same suggests, it is a measure of elongation and again has values in the range 0–1. A shape symmetrical in all axes, such as a circle or square, has an elongation value of 0; shapes with large aspect ratios have an elongation closer to 1. In this study, each sample was measured in triplicate to get the average value for circularity, convexity and elongation.

2.5. Powder preparation for flow function test

In order to study the flow function of dairy solids with different water content, two moisture levels of spray-dried dairy solids were prepared in the vacuum oven (OV-12, Meline Industies, Inc., USA). For dairy solids with low moisture (LM) content, the powders were placed in the vacuum oven at 45 °C for 36 h. For dairy solids with high moisture (HM) content, spray-dried dairy solids were firstly dried at 45 °C in the vacuum oven for 36 h, and then equilibrated over saturated K_2CO_3 solution (giving 44% relative humidity) at 25 °C for 5 days in the vacuum oven. During equilibration, all powders were put in petri dishes with thickness around 10 mm. The final water content was measured in triplicate using HR83 Hologen Moisture Analyser (Mettler Toledo International Inc., Switzerland) before measuring the flow properties.

2.6. Differential scanning calorimetry

Glass transition temperatures, T_g (onset), of spray-dried dairy solids were determined using a differential scanning calorimeter (DSC Q2000, TA Instruments, Crawley, UK). To determine the T_g, spray-dried solids (1 g) were transferred to glass vials and dried in the vacuum oven at 45 °C for 48 h. The dehydrated powders were equilibrated in evacuated desiccators over P_2O_5 and saturated salt solutions of LiCl, CH_3COOK, $MgCl_2$, and K_2CO_3 for 144 h. Then 10–15 mg of equilibrated powders was transferred to DSC aluminium pans (Tzero pan and lid, Switzerland). The DSC pans were hermitically sealed and samples were analysed. An empty pan was used as a reference. At the first scan, the samples were heated over the glass transition temperature region at 5 °C/min and then cooled at 10 °C/min to below glass transition, a 2nd heating scan was then run to far above the glass transition temperature at 5 °C/min. Anhydrous samples were scanned using pans with punctured lids to allow evaporation of residual water during the measurements (Silalai and Roos, 2010). At the first scan, the samples were heated at 5 °C/min to 100 °C and then cooled at 10 °C/min to below glass transition, a 2nd heating scan was then run to far above the glass transition temperature at 5 °C/min. The first scan was to evaporate the residual water, while the "anhydrous" state of powders during the rest heating scans was expected. T_g values of spray-dried solids with different moisture contents were determined by DSC before flow function test. All measurements were carried out in duplicate.

2.7. Dynamic mechanical analysis

A Dynamic Mechanical Analyser (DMA Q800, TA Instruments, Crawley, UK) was used, in conjunction with a gas cooling accessory (GCA) tank, to determine dynamic mechanical properties of spray-dried dairy solids. A rectangular stainless steel powder holder was designed to generate a defined geometry to contain powder with inner dimensions of 60 mm × 11 mm × 1 mm. A pre-weighed mass of powder mixed with Aluminium oxide calcined powder, with the ratio of 4:1 (dairy powder/Aluminium oxide calcined powder), was evenly spread within this shallow container, and the upper lid was then placed onto the top surface of the powder (Mahlin et al., 2009). As Aluminum oxide calcined showed no influence on the mechanical property results of dairy solids in the temperature range, it was added to protect dairy powder from sticking on the powder holder during the heating test. The sample holder was mounted in the instrument in a dual cantilever clamp so that during measurement, the DMA oscillated the sample perpendicularly to the base plane of the sample holder by a vertical motion of the middle clamp. For anhydrous samples and samples equilibrated at 0.11 a_w, the measurements were made at a heating rate of 2 °C/min from 0 to 150 °C. For samples equilibrated at 0.23 a_w, 0.33 a_w and 0.44 a_w, the measurements were made at a heating rate of 2 °C/min from 0 to 120 °C. DMA was operated by a sinusoidal deformation applied to the powder sample holder at a fixed strain. The amplitude was 15 μm. During dynamic heating, the samples were analysed for storage modulus (E′) and loss modulus (E″) using single frequency 1 Hz. All measurements were carried out in duplicate.

2.8. Powder flow testing

The flow properties of lactose/MPI solids systems were determined by a Powder Flow Tester (PFT) (Brookfield Engineering Laboratories, Inc., Middleboro, MA, USA). The axial and torsional speeds for the PFT were 1.0 mm s^{-1} and 1 rev h^{-1}, respectively. Samples were filled into the aluminium trough of the annular shear cell at room temperature (22–25 °C). Curved- or flat-profiled shaping blades were used to level the powder surface in the trough for flow- or wall fiction-testing, respectively. The mass of the powder was recorded before testing, with axial distance between the lid and the powder used to calculate changes in the volume of powder during testing. Vane- or flat-profiled lids were attached to compression plate of the PFT for flow- or wall friction-testing. Flowability, cohesion and bulk density were measured using standard flow function test. Friction angle was determined using standard wall friction test. For standard flow function test, the involved uniaxial normal stresses were between 0.2 and 4.8 kPa. For standard wall friction test, ten normal stresses, between 0.4 and 4.8 kPa, were applied to measure the wall friction angles.

2.9. Statistical analysis

Measurement of protein content, glass transition, dynamic mechanical analysis, standard flow function test and wall friction test were performed in duplicate, with all other analyses performed in triplicate. Results were expressed as mean ± standard deviations (SD). One-way analysis of variance (ANOVA), followed by Tukey's test, was used to determine the significant differences between the mean values of each test (Microsoft Office Excel 2010, Microsoft, Inc., U.S.A.). A significance level of $p < 0.05$ was used throughout the study.

3. Results and discussion

3.1. Powder characterisation

Protein contents ranged from 0 to 89.91%, and lactose contents were from 100 to 1.29% for lactose/MPI solids systems. Particle size distribution study showed that the median particle size (d_{50}) increased as lactose content decreased (Table 1). As specific surface area (SSA) values are typically inferred from particle size data, lactose powder gave the largest SSA value (Table 1). Particle size distribution has a major influence on powder flowability (Fitzpatrick et al., 2004). However, lactose/MPI mixtures (2:3) had the lowest SSA while its median particle size (d_{50}) was not the largest one, which indicated that the difference in SSA values might not have been only due to difference in particle size alone, suggesting that alterations to surface morphology might have been a contributing factor (Crowley et al., 2014b). Fitzpatrick et al. (2004) stated that a significant disimprovement in flowability would be expected if the powder is reduced in size by an order of magnitude. According to Fitzpatrick et al. (2004) this reduction in flowability at smaller particle size was due to the increased surface area per unit mass of powder. More surface area is available for cohesive forces, in particular, and frictional forces to resist flow. Thus, the difference in particle size distribution and SSA values of spray-dried lactose/MPI solids systems might affect their flowability. For lactose/MPI mixtures, particle density increased as lactose content decreased. This might due to decrease in the volume of occluded air with increasing protein content in lactose/MPI mixtures and MPI (Crowley et al., 2014b).

3.2. Particle shape

The morphological properties of spray-dried dairy solids were investigated. Three morphological characteristics (circularity, convexity, and elongation) were used to identify the particle shape of lactose/MPI solids systems. Table 2 shows that the circularity and convexity of lactose/MPI solids systems increased as lactose content decreased, while the elongation decreased as lactose content decreased. These results indicated that particle shape of lactose/MPI solids systems with higher content of lactose had less rounded shape, rougher surface and lower ratio of width/length. Particle shape often has a significant influence on final product performance parameters such as flowability, abrasive efficiency, bioavailability, etc. Powders consisting of regularly shaped particles flow better than those consisting of irregular shaped particles. Moreover, the more the particles in a powder resemble spheres the better the powder flows. Coarse powders in general have better flow properties than fine powders. Consequently, the difference in particle shape of lactose/MPI solids systems might influence the final flow properties of spray-dried dairy solids.

3.3. Glass transition

Glass transitions for anhydrous and water plasticized lactose and lactose/MPI mixtures were determined using DSC. Lactose/MPI mixtures showed slightly lower T_g values than pure lactose at 0.11 a_w and 0.23 a_w (Table 3). However, at 0.33 a_w and 0.44 a_w, lactose/MPI mixtures showed slightly higher T_g values than pure lactose. The lower T_g values of lactose/MPI mixtures might relate to the change in water sorption properties. Pure lactose sorbed less water during storage at $a_w \leq 0.23$ and more water at 0.33 a_w and 0.44 a_w. Haque and Roos (2004) also showed similar results. They stated that T_g of lactose/protein mixtures were lower than T_g of pure lactose in humidified samples at a_w 0.23 and below, but slightly higher at 0.33 a_w and above (Haque and Roos, 2004). In addition, T_g

Table 1
Physical properties of lactose/MPI solids systems.

Systems	Protein content (%)	Lactose content (%)	Water content (%)	Ash content (%)	d_{50} (μm)	SSA (m^2/kg)	ρ_p (g/cm^3)
Lactose	0 ± 0.00	100 ± 0.00	3.47 ± 0.07	0.12 ± 0.01	24.95 ± 0.25	678.25 ± 2.25	1.22 ± 0.00
Lactose/MPI 4:1	20.48 ± 0.50	78.95 ± 0.92	2.63 ± 0.13	1.56 ± 0.01	40.90 ± 0.01	234.85 ± 0.95	1.05 ± 0.02
Lactose/MPI 3:2	36.92 ± 0.42	62.04 ± 0.23	3.25 ± 0.12	2.55 ± 0.02	40.70 ± 0.10	224.55 ± 0.45	1.05 ± 0.02
Lactose/MPI 1:1	46.54 ± 0.51	51.79 ± 0.60	3.13 ± 0.10	3.28 ± 0.07	44.85 ± 0.15	196.65 ± 0.04	1.14 ± 0.04
Lactose/MPI 2:3	56.95 ± 0.36	40.61 ± 0.52	2.35 ± 0.16	3.87 ± 0.02	49.50 ± 0.00	160.25 ± 0.65	1.21 ± 0.04
Lactose/MPI 1:4	74.59 ± 0.48	20.52 ± 0.34	3.76 ± 0.09	5.05 ± 0.05	49.20 ± 0.50	182.75 ± 2.75	1.25 ± 0.05
MPI	89.91 ± 0.61	1.29 ± 0.00	4.53 ± 0.16	6.01 ± 0.04	50.90 ± 0.30	182.60 ± 0.50	1.28 ± 0.02

Values are mean ± standard deviation (protein content: n = 2; for the other values, n = 3).

Table 2
Morphological characteristics of lactose/MPI solids systems.

Systems	Circularity	Elongation	Convexity
Lactose	0.8810 ± 0.0050	0.1970 ± 0.0085	0.9923 ± 0.0005
Lactose/MPI 4:1	0.9050 ± 0.0022	0.1773 ± 0.0039	0.9933 ± 0.0005
Lactose/MPI 3:2	0.9283 ± 0.0045	0.1403 ± 0.0068	0.9950 ± 0.0000
Lactose/MPI 1:1	0.9340 ± 0.0057	0.1300 ± 0.0059	0.9960 ± 0.0008
Lactose/MPI 2:3	0.9347 ± 0.0062	0.1300 ± 0.0051	0.9960 ± 0.0008
Lactose/MPI 1:4	0.9393 ± 0.0086	0.1177 ± 0.0106	0.9960 ± 0.0008
MPI	0.9420 ± 0.0042	0.1213 ± 0.0090	0.9970 ± 0.0000

Values are mean ± standard deviation (n = 3).

values of lactose and lactose/MPI mixtures decreased with increasing water content as shown in Table 3, which showed typical water plasticization of dairy powders containing lactose (Jouppila and Roos, 1994; Haque and Roos, 2004; Schuck et al., 2005; Silalai and Roos, 2010).

Lactose/MPI solids systems showed difference in glass transition temperature after storage at different relative humidity (Table 4). Water plasticization depressed glass transition temperature of lactose and lactose/MPI mixtures. Fitzpatrick et al. (2007b) announced that lactose glass transition had a major influence on the development of cake strength and it was influencing the initial development of cake strength. This difference in cake strength might influence the flowability of dairy solids.

3.4. Dynamic mechanical properties

The mechanical properties of dairy solids storage at 0% and 44% RH were investigated by DMA. Mechanical changes at and around their glass transition are key factors in their functionality and stability (Peleg, 1993). DMA is the most sensitive technique for monitoring relaxation events, such as glass transitions, as the mechanical properties change dramatically when relaxation behaviour is observed (Menard, 2008). In the present study, mechanical α-relaxation of lactose/MPI solids systems occurred above the glass transition and was observed from a decrease in storage modulus and a peak in the loss modulus (Fig. 1). At temperatures above the glass transition, large changes in viscoelastic properties were expected (Royall et al., 2005; Silalai and Roos, 2011b; Roos, 2013). From Fig. 1A1 and 1B1, it could be seen that the storage modulus of spray-dried dairy solids decreased slowly in the amorphous state at the beginning of heating. In the glass transition region, the storage modulus dropped sharply from the original value at glassy state to the value at rubbery state. The magnitudes of modulus changes indicated mechanical α-relaxations which were relative to molecular mobility (Roudaut et al., 2004; Silalai and Roos, 2011b). Magnitudes of storage modulus for lactose/MPI solids systems with higher lactose content showed more significant change at glass transition region (Fig. 1A1 and 1B1). The storage modulus showed a smaller decrease and remained at a higher level for the rubbery

Table 3
Glass transition temperatures, T_g, α-relaxation temperature, T_α, and water content, m, for spray-dried lactose and lactose/MPI mixtures equilibrated over saturated salt solution at room temperature (25 °C) for 144 h.

Systems		0 a_w	0.11 a_w	0.23 a_w	0.33 a_w	0.44 a_w
Lactose	m	0 ± 0.00	2.00 ± 0.08	3.88 ± 0.06	6.16 ± 0.12	9.25 ± 0.10
	T_g	108 ± 0.0	73 ± 0.5	54 ± 0.0	35 ± 0.0	18 ± 0.5
	T_α	123 ± 0.5	122 ± 0.0	77 ± 0.0	51 ± 0.0	–
Lactose/MPI 4:1	m	0 ± 0.00	1.99 ± 0.02	3.43 ± 0.03	5.23 ± 0.03	7.42 ± 0.7
	T_g	109 ± 0.0	72 ± 0.0	54 ± 0.0	36 ± 1.0	20 ± 0.5
	T_α	124 ± 1.0	124 ± 0.5	77 ± 0.0	52 ± 1.0	40 ± 0.5
Lactose/MPI 3:2	m	0 ± 0.00	2.50 ± 0.02	4.04 ± 0.09	5.81 ± 0.06	8.14 ± 0.07
	T_g	109 ± 0.5	70 ± 0.0	51 ± 0.0	36 ± 0.5	20 ± 1.0
	T_α	128 ± 1.0	126 ± 0.5	76 ± 0.0	68 ± 1.5	38 ± 0.5
Lactose/MPI 1:1	m	0 ± 0.00	2.60 ± 0.02	4.09 ± 0.03	5.76 ± 0.06	7.82 ± 0.05
	T_g	110 ± 0.5	67 ± 0.0	51 ± 0.5	38 ± 0.0	21 ± 0.0
	T_α	129 ± 0.0	130 ± 1.0	73 ± 1.5	67 ± 0.5	45 ± 0.0
Lactose/MPI 2:3	m	0 ± 0.00	2.68 ± 0.06	4.31 ± 0.02	5.99 ± 0.01	7.65 ± 0.02
	T_g	109 ± 0.5	67 ± 0.0	51 ± 0.0	37 ± 0.0	22 ± 0.0
	T_α	–	–	70 ± 0.5	64 ± 0.0	64 ± 0.5
Lactose/MPI 1:4	m	0 ± 0.00	3.47 ± 0.08	5.15 ± 0.07	6.70 ± 0.00	8.20 ± 0.11
	T_g	–	67 ± 0.5	50 ± 0.0	43 ± 0.0	33 ± 0.0
	T_α	–	–	69 ± 0.5	65 ± 1.0	61 ± 0.0
MPI	m	0 ± 0.00	3.91 ± 0.04	5.83 ± 0.12	7.59 ± 0.23	9.20 ± 0.12
	T_g	–	–	–	–	–
	T_α	–	–	66 ± 0.5	59 ± 0.0	65 ± 0.0

m = water content (g/100 g dry solids).
T_g = onset temperature (°C).
T_α = α-relaxation temperature (°C).
Values are mean ± standard deviation (m values: n = 3; T_g and T_α values: n = 2).

Table 4
Water content, m, T_g, T_α and flow index values of lactose/MPI solids systems storage at different humidity conditions (0 RH and 44% RH).

System	m (%)		T_g (°C)		T_α (°C)		Flow index	
	LM	HM	LM	HM	LM	HM	LM	HM
Lactose	1.50 ± 0.05	5.29 ± 0.31	73 ± 0.0	32 ± 0.0	121 ± 0.5	46 ± 0.0	0.17 ± 0.005	0.22 ± 0.000
Lactose/MPI 4:1	1.89 ± 0.34	5.86 ± 0.09	74 ± 0.0	31 ± 0.5	125 ± 1.0	52 ± 0.0	0.11 ± 0.000	0.15 ± 0.005
Lactose/MPI 3:2	1.96 ± 0.15	6.43 ± 0.06	73 ± 0.5	29 ± 0.0	125 ± 0.5	55 ± 0.0	0.11 ± 0.005	0.16 ± 0.005
Lactose/MPI 1:1	2.24 ± 0.16	5.93 ± 0.12	75 ± 0.5	31 ± 0.5	130 ± 0.0	64 ± 0.5	0.17 ± 0.005	0.20 ± 0.000
Lactose/MPI 2:3	2.19 ± 0.14	5.91 ± 0.07	76 ± 0.5	31 ± 0.0	–	64 ± 0.5	0.19 ± 0.000	0.22 ± 0.000
Lactose/MPI 1:4	2.22 ± 0.13	6.37 ± 0.09	73 ± 0.0	44 ± 0.5	–	64 ± 0.0	0.23 ± 0.000	0.24 ± 0.005
MPI	3.06 ± 0.01	7.53 ± 0.19	–	–	–	51 ± 0.0	0.25 ± 0.005	0.24 ± 0.005

Values are mean ± standard deviation (free water content: n = 3; T_g, T_α and flow index values: n = 2).

plateau for dairy solids with lower lactose contents. These results indicated that the magnitude of the modulus change of lactose/MPI solids systems was relative to the ratio of lactose/MPI. In addition, all dairy solids sorbed much water from air during storage at 44% RH (Table 4). Water, acting as a plasticizer in lactose/MPI solids systems, could increase the free volume between the molecules and decrease T_g values (Fig. 1A1 and 1B1). Kilburn et al. (2004) concluded that the plasticization effect of water in carbohydrates is via a complex mechanism involving both hydrogen bond formation and disruption and changes in the matric free volume.

Stiffness refers to the ability to carry stress without changing dimension (Ebewele, 2000). For the special case of unconstrained uniaxial tension or compression, Young's modulus can be thought of as a measure of the stiffness of a material. In this study, the change of storage modulus could reflect the change of stiffness for dairy solids. The stiffness of spray-dried dairy solids showed the same trend in change as storage modulus did when temperature increased from 0 to 120 °C. Pure lactose showed the largest stiffness at glassy state after equilibrated at 0 and 44% RH, while diary solids with lower lactose content showed higher stiffness at and above glass transition temperature. Silalai and Roos (2011b) showed the similar results. They stated that the addition of high molecular weight compounds, such as maltodextrins, could increase stiffness, and thus, reduce the molecular mobility of lactose molecules due to a high degree of association as observed from the small magnitudes of modulus changes.

The results of loss modulus were shown in Fig. 1A2 and 1B2. The values of loss modulus for lactose/MPI solids systems with different water content were small and had minor changes when they were in the amorphous state (Fig. 1A2 and 1B2). However, when they

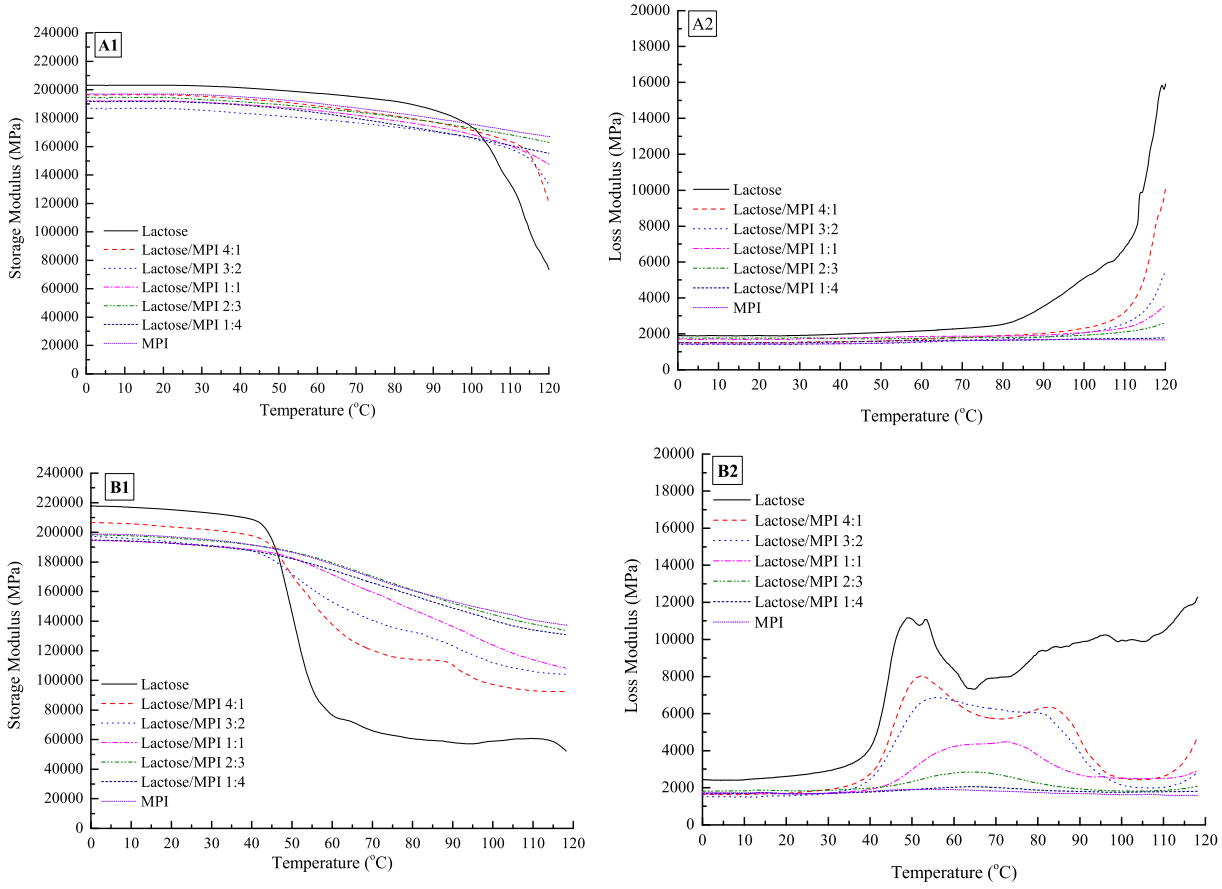


Fig. 1. Storage modulus and loss modulus for lactose/MPI solids systems with low moisture (LM) content (A1 and A2) and high moisture (HM) content (B1 and B2).

were in the glass transition region, the loss modulus of spray-dried dairy solids increased dramatically and reached the peak values. This result could be explained from the theory of mechanical internal friction (Guo et al., 2013). According to Guo et al. (2013), in the glassy state, the chain segment motion of lactose and proteins molecules is frozen. No relative slipping can occur between different chain segments, so the internal loss is very small, which was reflected in the minor change of loss modulus. In the rubbery state, the chain segment could move freely, so the internal loss is also small when the chain segment relatively slipped. In the glass transition region, the chain segment changes from the frozen state to the free moving state. The motion needs to overcome the larger friction leading to larger internal loss. The loss will approach maximum when the temperature reaches glass transition region. Thus, the values of loss modulus are related to molecular mobility. In our study, the peak values of loss modulus for lactose/MPI solids systems decreased as lactose content decreased (Fig. 1A2 and 1B2). As the magnitudes of modulus changes indicated mechanical α-relaxations which were relative to molecular mobility (Roudaut et al., 2004; Silalai and Roos, 2011b), lactose/MPI solids systems with larger amount of lactose showed higher molecular mobility when temperature was near T_g.

Moreover, in this study, the α-relaxation temperatures, T_α, were taken from the temperatures of loss modulus peak (Table 3). T_α of the systems was found to decrease when a_w was increased. Dairy solids with higher lactose content had lower T_α values at 0.23 a_w and below, while they gave slightly higher T_α values at 0.33 a_w and above (Table 4). The lower T_α values of lactose/MPI mixtures might also relate to the change in water sorption properties. Pure lactose sorbed less water during storage at $a_w \leq 0.23$ and more water at 0.33 a_w and 0.44 a_w. Besides, according to Hancock and Zografi (1997), the molecular mobility in lower molecular weight solids changes more rapidly near Tg. Therefore, its molecular arrangement or its configuration structure is broken down more rapidly as well at higher a_w (Hancock and Zografi, 1997).

3.5. Flow properties

Standard flow function test and wall friction test of lactose/MPI solids systems was conducted using Powder Flow Tester. The flowability of powders is usually stress-dependent (Schulze, 2007). Flow function results showed that lactose/MPI solids systems were easy-flowing or cohesive depending on the major principle consolidating stress applied (<12.5 kPa) (Fig. 2). After storage at 0% RH, lactose/MPI mixtures at ratios 1:1 and 2:3, which were easy flowing at major principle consolidating stress >2.7 kPa, were cohesive at major principle consolidating stress ≤2.7 kPa (Fig. 2A). For lactose/MPI mixtures (1:4) and MPI powders, major principle consolidating stress should be above 6 kPa to make them easy-flowing (Fig. 2A). Increasing moisture content of dairy solids decreased their flowability, especially for lactose (Fig. 2B). Lactose fell into cohesive region after placed at 44% RH at 25 °C for 5 days even when major principle consolidating stress was over 9 kPa. MPI powders without amorphous lactose showed no significant change in its flowability as increasing moisture content (Fig. 2), which could also be seen from its flow index (Table 4). Dairy solids with higher amount of lactose showed more significant change in their flowability when moisture content increased. The flow index of lactose showed the greatest increase as moisture content increased (Table 4). Besides, for lactose/MPI mixtures storage at 0% and 44% RH, powders with higher amount of lactose showed better flowability (Fig. 2), while the particle size of those solids with higher lactose content was smaller. Moreover, particle shape of those solids with higher content of lactose had less rounded shape. These results indicated that particle size and particle shape did not show significant influence on the flowability of lactose/MPI mixtures.

Cohesion of lactose/MPI solids systems showed the same tendency as their flowability after storage at 0% and 44% RH (Figs. 2 and 3). Lactose showed the most significant change in cohesion as free moisture content increased. Cohesion of MPI powder after storage at 44% RH showed the same as it was storage at 0% RH. According to Peleg, interparticle forces play a significant role in free flowing and cohesive powders (Peleg, 1977). Higher cohesion means worse flow behaviour at the same major principle consolidating stress.

The bulk density of lactose/MPI solids systems increased as major principle consolidating stress increased (Fig. 4). All dairy solids became compressed on the application of increasing major principle consolidating stress. Spray-dried lactose/MPI mixtures showed difference in loose bulk density. Dairy solids with higher lactose content had higher loose bulk density after storage at 0% RH (Fig. 4A). Increasing moisture content, the loose bulk density of lactose showed the most significant change while lactose/MPI mixtures and MPI powders showed minor changes, especially lactose/MPI mixture with the ratio of 1:1 (Fig. 4).

The wall friction angles of lactose/MPI solids systems were measured at different normal stress using standard wall friction test (Fig. 5). At the same normal stress, wall friction angles of lactose/MPI solids systems decreased as lactose content decreased.

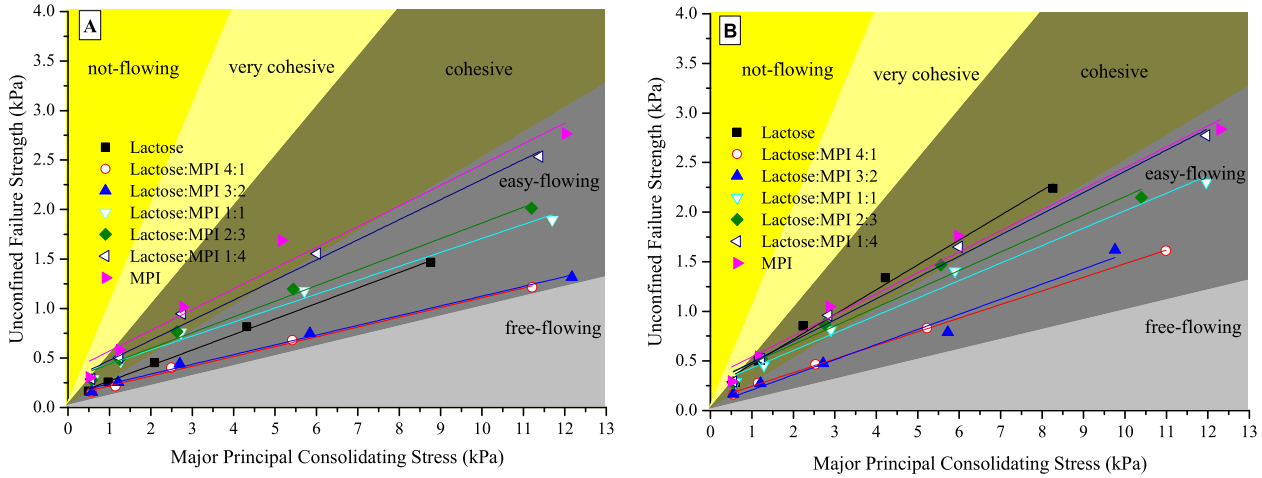


Fig. 2. Flow function curves showing unconfined strength as a function of major principal consolidating stress for lactose/MPI solids systems with low moisture (LM) content (A) and high moisture (HM) content (B).

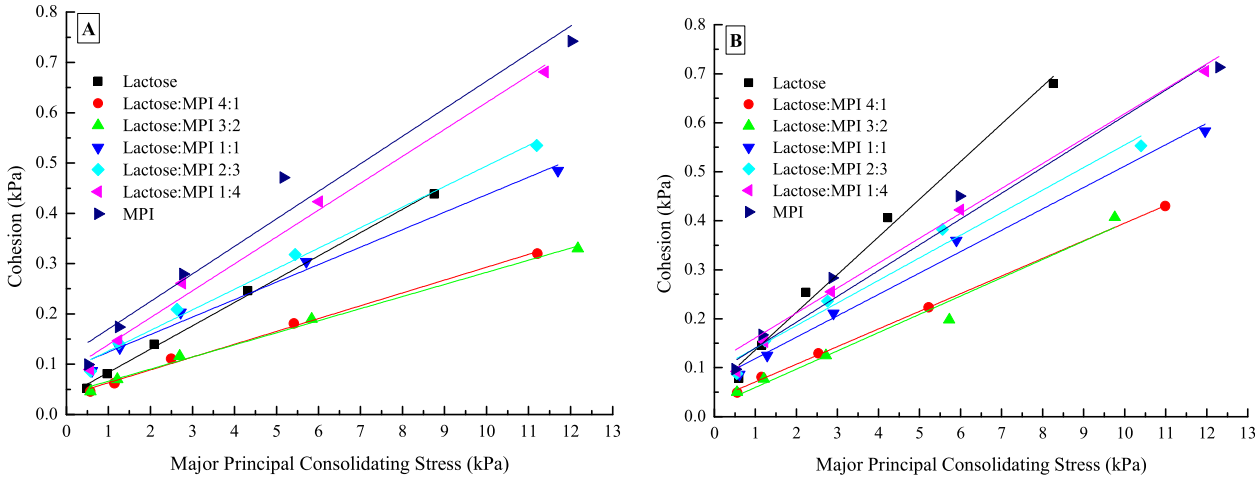


Fig. 3. Cohesions as a function of major principal consolidating stress for lactose/MPI solids systems with low moisture (LM) content (A) and high moisture (HM) content (B).

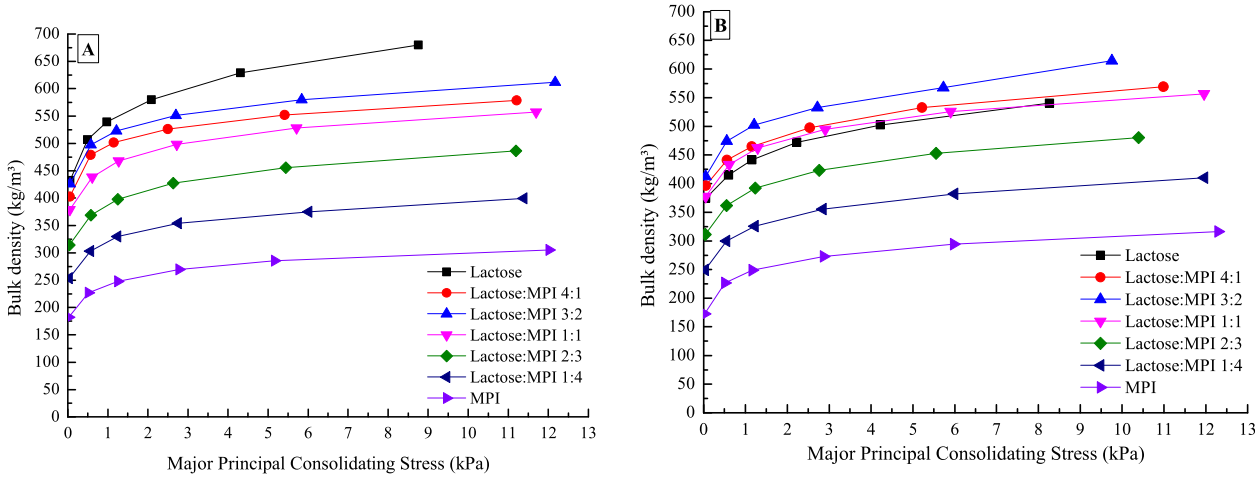


Fig. 4. Bulk density as a function of major principal consolidating stress for lactose/MPI solids systems with low moisture (LM) content (A) and high moisture (HM) content (B).

All lactose/MPI solids systems sorbed moisture when exposed to air with relative humidity 44% (Table 4). As a result, friction angles of lactose/MPI solids systems increased with increasing moisture content (Fig. 5A and B). The wall friction angle, φ_{χ}, quantifies the effort required to move a bulk solid across the surface of a specific wall material. The larger the wall friction angle, the greater is wall friction, which can result in deposition or segregation of powder (Iqbal and Fitzpatrick, 2006). Besides, Iqbal and Fitzpatrick (2006)

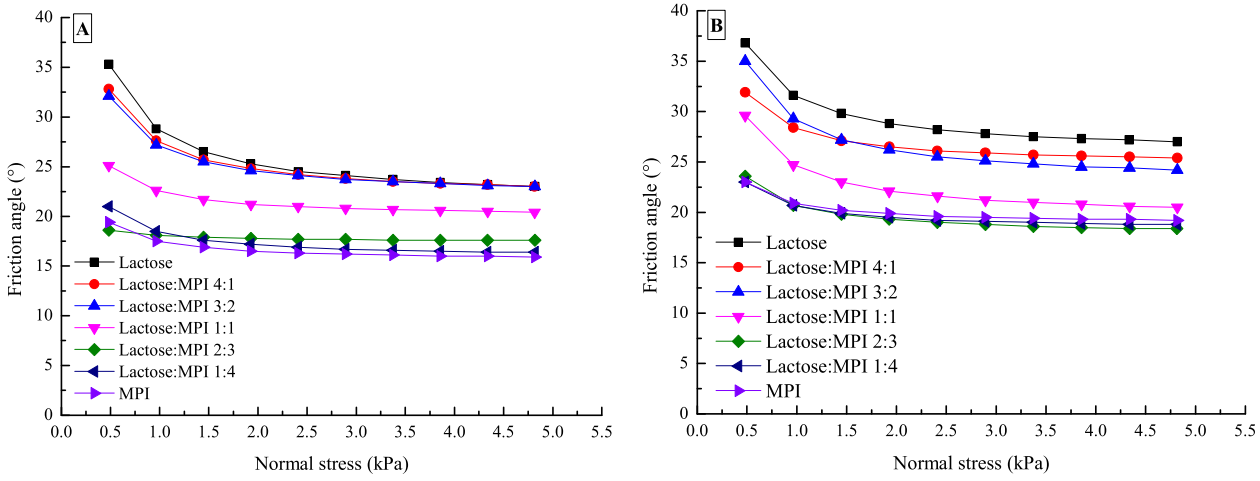


Fig. 5. Fiction angle as a function of normal stress for lactose/MPI solids systems with low moisture (LM) content (A) and high moisture (HM) content (B).

stated that the composition, moisture content and particle size distribution of bulk solids will influence their wall friction characteristics. Powders with smaller particle sizes tend to increase wall friction, as there is greater contact surface area between smaller particles and the wall surface. This might be one reason that friction angles of lactose/MPI solids systems decreased as lactose content decreased (Fig. 5).

4. Conclusions

Dairy powders with amorphous components, such as amorphous lactose, could become sticky and caking, as a result of poor flowability, when temperature is at or above glass transition temperature or sorb certain amount of water from environment. The increased in moisture content could increase adhesive forces between individual particles. Adhesive forces are the source of poor flowability or caking of powders (Schulze, 2007). In addition, water plasticization also reduces the lactose glass transition temperature T_g, while the temperature difference between the powder and the glass transition represents a driver for greater molecular mobility, powder stickiness and caking (Fitzpatrick et al., 2007b). This study investigated the influence of water plasticization and lactose content on the flow properties of dairy model solids. Median particle size (d_{50}) of lactose/MPI solids systems increased as lactose content decreased. Pure lactose showed the largest SSA values, while there is only slightly difference in SSA values of lactose/MPI mixtures and MPI powders. Moreover, particle morphology study showed that lactose/MPI solids systems with higher content of lactose had less regular particle shape. According to studies, those powder characteristics might affect the flow properties of lactose/MPI solids systems. However, flow function study showed that for lactose/MPI mixtures storage at 0% and 44% RH, powders with higher amount of lactose showed better flowability, while pure lactose also showed easy-flowing after storage at 0% RH. Smaller particle size and less rounded particle shape of lactose and lactose/MPI mixtures with higher lactose content did not show significant influence on their flowability.

As amorphous lactose is hygroscopic and readily sorbs water from air, pure lactose sorbed less water during storage at $a_w \leq 0.23$ and more water at 0.33 a_w and 0.44 a_w. Water plasticization depressed glass transition temperature of lactose and lactose/MPI mixtures after storage at 44% RH. Lactose/MPI mixture at ratio 1:4 showed the largest T_g value than those of lactose and other lactose/MPI mixtures, which might be one reason that its flow index showed the smallest increase after storage at 44% RH. DMA study indicated that magnitudes of storage modulus and loss modulus for lactose/MPI solids systems with higher lactose content showed more significant change at glass transition region, which meant dairy solids with higher lactose content had higher molecular mobility. This might cause pure lactose the highest cohesion after storage at 44% RH. Besides, at the same normal stress, wall friction angles of lactose/MPI solids systems decreased as lactose content decreased, while their friction angles all increased as increasing water content.

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Influence of pre-crystallisation and water plasticization on flow properties of lactose/WPI solids systems

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ABSTRACT

This study investigated the influence of pre-crystallisation and water plasticization on flow properties of lactose/whey protein isolate (WPI) solids systems. Powder characteristics of lactose/WPI mixtures with different amounts of α-lactose monohydrate (1.01%, 11.18%, 29.20%, and 46.84%, w/w) were studied. Dairy powders with higher amounts of crystalline lactose showed larger tapped bulk density and particle density. Morphological characteristic study indicated that dairy solids with higher crystallinity had less rounded shape and rougher surface. Increasing protein content or crystalline lactose content could decrease the molecular mobility of dairy solids. Flow function tests indicated that dairy solid with 11.18% crystallinity was more easy-flowing than lactose/WPI mixtures with 1.01%, 29.20% and 46.84% crystallinity at 0% and 44% relative humidity (RH) storage conditions. Furthermore, dairy solids with higher amount of crystalline lactose showed better resistance to develop cohesive at high RH storage conditions. The friction angle of dairy solid with 1.01% crystallinity increased with increasing water content, while friction angles of lactose/WPI mixtures with higher crystallinity decreased with increasing water content.

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1. Introduction

Flow properties of spray-dried dairy solids are very important in handling and processing operations [1,2]. Previous studies indicated that flow properties depend on the composition and physical properties of powders, such as particle size and shape, surface structure, amorphous lactose content, and water content [3–8]. Stickiness and caking of powders usually result from formation of liquid bridges between individual particles [9], and they are responsible for impaired flow properties [10]. Many studies showed that powders with greater amounts of amorphous components, such as amorphous lactose, were more sensitive to absorbing moisture, giving rise to lumping and caking problems [2,4,11–13].

Lactose in dairy systems can exist in various crystalline and non-crystalline forms. The crystalline state is a solid state having molecules well arranged in regular lattice. For lactose in amorphous state, the molecular arrangement is disordered. Amorphous lactose is thermodynamically unstable and hygroscopic, absorbing moisture from the surroundings and subsequently plasticizing, while crystalline lactose is thermodynamically stable and significantly less hygroscopic. Reducing stickiness in materials can be achieved through partial or complete crystallisation of sticky components [14]. Bronlund and Paterson [15] stated that crystalline lactose absorbed approximately 100 times less water than amorphous lactose in the same conditions. Therefore, pre-crystallising those amorphous materials during processing may help to resolve the problem of product stickiness and stability during subsequent storage [16].

Since lactose is around 70% of the dry matter in whey powder, the hygroscopicity of lactose makes whey powder become sticky and adhere to the chamber walls during spray drying [17]. Pre-crystallisation of lactose in whey concentrates before drying is a successful remedial measure in manufacturing process, and is widely used in the production of whey powder in dairy industry [18]. Powder hygroscopicity and caking are brought under control by lowering the level of amorphous lactose.

Moreover, previous studies indicated that particle shape affected the bulk behaviour and flow properties of dairy solids [5,19]. According to the study of Thomas et al. [20], morphological changes, such as surface deformation, occurred due to the build-up of lactose crystals in dairy powders. This difference in the particle shape of crystalline lactose and amorphous lactose may influence the flow properties of dairy powders and subsequently affect the handling and processing operations. Thus, comparing with amorphous lactose, crystalline lactose shows different physical properties and water sorption behaviour during processes of production and storage [15,19], which may finally influence the flow properties of dairy solids.

However, how pre-crystallisation and crystalline component content, such as α-lactose monohydrate, that affects the flow properties of dairy solids has not been reported so far. The objectives of this

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study were to investigate the effect of crystalline lactose content on the flow properties of lactose/whey protein isolate (WPI) solids systems. Pre-crystallisation of lactose before spray drying was used to prepare dairy solids with different amounts of crystalline lactose in this study.

2. Materials and methods

2.1. Materials

α-Lactose monohydrate (>99% purity) was kindly donated by Arla Foods Ingredients (Sønderhøj 10-12, 8260 Viby J, Denmark). WPI, containing 71% β-lactoglobulin and 12% α-lactalbumin, was obtained from Davisco Food International (Le Sueur, MN, USA). Aluminum oxide calcined powder and α-lactose (≥99% purity) were purchased from Sigma-Aldrich (St. Louis, MO, USA).

2.2. Powder preparation

Solution of lactose and lactose/WPI mixtures at the ratio 4:1 was prepared in de-ionised water at 65 °C in a water bath for 2 h with a stirring speed of 500 rpm. The total solid concentration of lactose and lactose/WPI mixtures solution was 40% (w/w). Then the solution of lactose/WPI mixtures was cooled to room temperature (20–22 °C) and kept at room temperature (20–22 °C) for different hours to pre-crystallise. The stirring speed was 150 rpm during pre-crystallisation. The pre-crystallisation time for lactose/WPI mixtures was 0, 3, 15 and 20 h, respectively. They were defined as S2 (0 h), S3 (3 h), S4 (15 h) and S5 (20 h) according to the pre-crystallisation time. Pure lactose without pre-crystallisation and WPI were defined as S1 and S6, respectively. They were all spray-dried by an ANHYDRO spray dryer with a centrifugal atomizer (Copenhagen, Denmark) at the Teagasc Food Research Centre, Moorepark, Fermoy, Co. Cork, Ireland. The inlet air temperature was around 170 ± 2 °C and the outlet temperature around 90 ± 2 °C. Spray-dried solids were kept immediately in evacuated desiccators over P_2O_5 at room temperature. Each analysis was carried out within three months after spray drying.

2.3. Powder characterisation

2.3.1. Determination of α-lactose monohydrate content in spray-dried lactose/WPI mixtures

The content of α-lactose monohydrate (% C°) in spray-dried lactose/WPI mixtures was determined according to the method of Schuck and Dolivet [21]. In this study, the content of α-lactose monohydrate was used to represent the crystallinity of dairy solids. The water of crystallisation (%) of a powder is the difference between total water and non-bound water. The formula is as below:

$$\%C^{\circ} = (BWL*19/L)*100 \quad (1)$$

where

BWL bound water content in the lactose (g/kg);
L lactose content (g/kg).

The bound water content in lactose was calculated according to the following formula:

$$BWL = TW - FW - (0.005*WPC) \quad (2)$$

where

BWL bound water content in lactose (g/kg);
TW total water content (g/kg);
FW non-bound water content (g/kg);
WPC whey protein content (g/kg); 0.005: 0.50 g of bound water per 100 g of whey protein.

Non-bound water content of lactose/WPI mixtures was measured using GEA Niro analytical method A 1 c [22]. The total water content of lactose/WPI mixtures was determined using a Karl Fischer Titration (Mettler Toledo International Inc., Im Langacher Greifensee, Switzerland). Each analysis was carried out in triplicate.

2.3.2. Powder characteristics

Water content was determined using an HR83 Halogen Moisture Analyzer (Mettler Toledo International Inc., Im Langacher Greifensee, Switzerland). Powder particle size distribution and specific surface area (SSA) were determined by laser light scattering using a Malvern Mastersizer 3000 (Malvern Instruments Ltd., Worcestershire, UK). Powder sample was added to the standard venturi disperser with a hopper gap of 2.5 mm and then fed into the dispersion system. Compressed air at 0.75 bar was used to transport and suspend the powder particles through the optical cell. A measurement time of 10 s was used, and background measurements were made using air for 20 s. The laser obscuration level was at 2–10%.

2.4. Bulk density, particle density and porosity

Loose and tapped (100 taps) bulk densities (ρ_{tapped}) of lactose/WPI solids systems was measured as per GEA Niro [23], using a Jolting volumeter (Funke Gerber, Berlin, Germany). Particle density (ρ_p) was measured as per GEA Niro [24], using a Gas Pycnometer (Accupyc II 1340 Gas Pycnometer, Micromeritics Instrument Corporation, USA). Since the definition of porosity of a porous media corresponds to extra particle void space, the corresponding porosity of dairy solids was calculated as Eq. (3):

$$\varepsilon = 1 - \rho_{tapped}/\rho_p. \quad (3)$$

2.5. Morphological characteristics

Morphological characteristics were determined using a Malvern Morphologi G3 S (Malvern Instruments Ltd., Worcestershire, UK). 5 mm^3 volume powder samples were dispersed on the glass plate. 2.5× objective was used for the measurement in this study. Circularity, convexity and elongation are three commonly used shape factors. One way to measure shape is to quantify how close the shape is to a perfect circle. Circularity is the ratio of perimeter of a circle with the same area as the particle divided by the perimeter of the actual particle image. Several definitions of circularity could be used but for accuracy the software reports HS Circularity (HS for high sensitivity) in addition to circularity. Circularity has values in the range 0–1. A perfect circle has a circularity of 1 while a 'spiky' or irregular object has a circularity value closer to 0. Circularity is sensitive to both overall form and surface roughness. Elongation is defined as [1-aspect ratio] or [1-width/length]. As the name suggests, it is a measure of elongation and again has values in the range 0–1. A shape symmetrical in all axes, such as a circle or square, has an elongation value of 0; shapes with large aspect ratios have an elongation closer to 1. Convexity is a measurement of the surface roughness of a particle. It is calculated by dividing the convex hull perimeter by the actual particle perimeter. A smooth shape has a convexity of 1 while a very 'spiky' or irregular object has a convexity closer to 0. In this study, each sample was measured in triplicate to get the average value.

2.6. Powder preparation for flow function test

Two moisture levels of lactose/WPI solids systems were prepared in a vacuum oven (OV-12, Medline Industries, Inc., Mundelein, Illinois,

USA). For dairy solids with low moisture (LM) content, the powders were placed in a vacuum oven at 45 °C for 36 h. For dairy solids with high moisture (HM) content, spray-dried dairy solids were firstly dried at 45 °C in a vacuum oven for 36 h, and then equilibrated over saturated K_2CO_3 solution (giving 44% relative humidity) at 25 °C for 48 h in a vacuum oven. During equilibration, all powders were put in petri dishes with thickness around 8 mm. The final water content was measured in triplicate using an HR83 Halogen Moisture Analyzer (Mettler Toledo International Inc., Im Langacher Greifensee, Switzerland) before measuring the flow properties.

2.7. Glass transition

Glass transition temperatures, T_g (onset), of lactose and lactose/WPI mixtures were determined using a differential scanning calorimeter (DSC Q2000, TA Instruments, Crawley, UK). 10–15 mg of dairy solids was transferred to DSC aluminium pans (Tzero pan and lid, Switzerland). Then DSC pans were hermetically sealed and samples were analysed. An empty pan was used as a reference. At the first scan, the samples were heated over the glass transition temperature region at 5 °C/min and then cooled at 10 °C/min to below glass transition, a 2nd heating scan was then run to above the glass transition temperature at 5 °C/min. All measurements were carried out in duplicate. Glass transition temperatures were determined using TA universal analysis software, version 5.1.2 (TA Instruments, Crawley, UK).

2.8. Dynamic mechanical analysis

A dynamic mechanical analyser (DMA Q800, TA Instruments, Crawley, UK) was used, in conjunction with a gas cooling accessory (GCA) tank, to determine dynamic mechanical properties of spray-dried dairy solids. A rectangular stainless steel powder holder was designed to generate a defined geometry to contain powder with inner dimensions of 60 mm × 11 mm × 1 mm. A pre-weighed mass of dairy solids mixed with aluminum oxide calcined powder at the ratio of 4:1 was evenly spread within this shallow container, and the upper lid was then placed onto the top surface of the powder [25]. As aluminum oxide calcined powder showed no effect on mechanical property results of dairy solids, it was added to protect dairy powder from sticking on the powder holder during the heating test. The sample holder was mounted in the instrument in a dual cantilever clamp so that during measurement, the DMA oscillated the sample perpendicularly to the base plane of the sample holder by a vertical motion of the middle clamp. The measurements were made at a heating rate of 2 °C/min from 0 to 140 °C for dairy solids with low moisture content and from 0 to 120 °C for dairy solids with high moisture content. DMA was operated by a sinusoidal deformation applied to the powder sample holder at a fixed strain. The amplitude was 15 μm. During dynamic heating, the samples were analysed for storage modulus (E′) and loss modulus (E″) using single frequency 1 Hz.

2.9. Powder flow testing

The flow function of lactose/WPI solids systems was determined using a Powder Flow Tester (PFT) (Brookfield Engineering Laboratories, Inc., Middleboro, MA, USA). The axial and torsional speeds for the PFT were 1.0 mm/s and 1 rev/h, respectively. Samples were filled into the aluminium trough of the annular shear cell at room temperature (22–25 °C). Curved- or flat-profiled shaping blades were used to level the powder surface in the trough for flow- or wall fiction-testing, respectively. The mass of the powder was recorded before testing, with axial distance between the lid and the powder used to calculate changes in the volume of powder during testing. Vane- or flat-profiled lids were attached to compression plate of the PFT for flow- or wall friction-testing. Flowability, cohesion and bulk density were measured using standard flow function test. Friction angle was determined using standard wall friction test. For standard flow function test, the involved uniaxial normal stresses were between 0.2 and 4.8 kPa. For standard wall friction test, ten normal stresses, between 0.4 and 4.8 kPa, were applied to measure the wall friction angles.

2.10. Statistical analysis

Measurement of glass transition, and dynamic mechanical analysis were performed in duplicate, with all other analysis performed in triplicate. Results were expressed as mean ± standard deviations (SD). One-way analysis of variance (ANOVA) was used to determine the significant differences between the mean values of each test (Microsoft Office Excel 2010, Microsoft, Inc., WA, USA). A significance level of $P < 0.05$ was used throughout the study.

3. Results and discussion

3.1. Powder characterisation

The powder characteristics of lactose/WPI solids systems are shown in Table 1. The amount of crystalline lactose for lactose/WPI mixtures (S2–S5) increased with increasing the pre-crystallised time (Table 1). After pre-crystallisation, four kinds of lactose/WPI mixtures with different amounts of α-lactose monohydrate were ready for analysis. As the amount of crystalline lactose was defined as the crystallinity of dairy solids in this study, the crystallinity of lactose/WPI mixtures (S2–S5) were 1.01%, 11.18%, 29.20% and 46.84%, respectively. Lactose (S1) was spray-dried without pre-crystallisation and was assumed to be in the amorphous form. Particle size study showed that the particle size of S3, S4, and S5 was higher than S2 (Table 1), which indicated that pre-crystallisation increased the particle size of dairy solids. As specific surface area (SSA) values are typically inferred from particle size data, S2 with 1.01% crystallinity showed the largest SSA value, while WPI powder gave the smallest SSA value. It is well known that particle size influences flowability [6,26]. For example, fine particles tend to be more cohesive and therefore less free-flowing, whereas larger particles tend to be free flowing. Moreover, according to Fitzpatrick et al. [26], the

Table 1
Physical characteristics of lactose/WPI solids systems.

Systems	Crystallinity (%)	d_{50} (μm)	SSA (m^2/kg)	Loose bulk density (g/cm^3)	Tapped bulk density (g/cm^3)	Particle density (g/cm^3)	Porosity
S1	0.00	$29.25^{a} \pm 0.25$	$620.50^{c} \pm 6.50$	$0.5458^{a} \pm 0.0138$	$0.7110^{a} \pm 0.0096$	$1.2900^{a} \pm 0.0055$	$0.4488^{e} \pm 0.0074$
S2	1.01 ± 0.58	$22.85^{d} \pm 0.25$	$714.75^{a} \pm 7.45$	$0.3282^{d} \pm 0.0027$	$0.3807^{d} \pm 0.0027$	$1.2168^{e} \pm 0.0019$	$0.6871^{b} \pm 0.0023$
S3	11.18 ± 0.97	$25.35^{b} \pm 0.05$	$629.95^{c} \pm 0.85$	$0.3297^{d} \pm 0.0037$	$0.3731^{e} \pm 0.0023$	$1.2182^{e} \pm 0.0016$	$0.6778^{c} \pm 0.0020$
S4	29.20 ± 0.92	$25.20^{b} \pm 1.20$	$682.10^{b} \pm 9.30$	$0.3418^{c} \pm 0.0030$	$0.4022^{c} \pm 0.0044$	$1.2443^{d} \pm 0.0014$	$0.6768^{c} \pm 0.0012$
S5	46.84 ± 1.11	$23.85^{c} \pm 0.05$	$695.05^{b} \pm 1.05$	$0.3614^{b} \pm 0.0070$	$0.4226^{b} \pm 0.0036$	$1.2485^{c} \pm 0.0021$	$0.6615^{d} \pm 0.0031$
S6	0.00	$26.10^{b} \pm 0.50$	$536.00^{d} \pm 6.60$	$0.1916^{e} \pm 0.0007$	$0.2381^{f} \pm 0.0015$	$1.2814^{b} \pm 0.0019$	$0.8142^{a} \pm 0.0018$

1. S1–S6: S1: amorphous lactose; S2–S5: lactose/WPI mixtures at ratio 4:1 with 1.01%, 11.18%, 29.20% and 46.84% crystallinity, respectively; S6: WPI.
2. Values are mean ± standard deviation (n = 3).
3. $^{a–f}$ Values within columns with different superscripts are significantly different at $P < 0.05$.

Table 2
Morphological characteristics of lactose/WPI solids systems.

Systems	Circularity	Elongation	Convexity
S1	$0.9120^{a} \pm 0.0010$	$0.1590^{c} \pm 0.0010$	$0.9940^{a} \pm 0.0000$
S2	$0.8593^{b} \pm 0.0074$	$0.2477^{b} \pm 0.0082$	$0.9920^{b} \pm 0.0008$
S3	$0.8430^{bc} \pm 0.0123$	$0.2533^{b} \pm 0.0109$	$0.9900^{bc} \pm 0.0008$
S4	$0.8473^{bc} \pm 0.0012$	$0.2507^{ab} \pm 0.0009$	$0.9903^{bc} \pm 0.0005$
S5	$0.8350^{c} \pm 0.0071$	$0.2630^{a} \pm 0.0050$	$0.9890^{c} \pm 0.0008$
S6	$0.8355^{c} \pm 0.0055$	$0.2570^{a} \pm 0.0030$	$0.9890^{c} \pm 0.0010$

1. S1–S6: Table 1.
2. Values are mean ± standard deviation (n = 3).
3. $^{a–c}$ Values within columns with different superscripts are significantly different at $P < 0.05$.

increased surface area per unit mass of powder means more surface area is available for cohesive forces and frictional forces to resist flow. Therefore, the difference in particle size and SSA values of lactose/WPI mixtures with different crystalline lactose content might affect their flowability.

Powder density is an important characteristic for calculating the capacity of packaging materials, containers, hoppers, bins, and silos, and also for filling of the die of tableting machines and for capsule filling. Pure lactose (S1) had the largest bulk density and particle density, and the smallest porosity, while WPI powder (S6) gave the opposite results (Table 1). For lactose/WPI mixtures (S2–S5), dairy solids with higher amount of crystalline lactose showed larger loose bulk density, tapped bulk density and particle density (Table 1). Furthermore, dairy solids with higher crystallinity showed lower porosity (Table 1).

3.2. Morphological characteristics

The particle shapes of lactose/WPI solids systems were investigated using a Morphologi G3 S. The Morpholigi G3 S reports a number of particle shape factors. In this study, three morphological characteristics (circularity, elongation and convexity) were used to identify the particle shape of lactose/WPI solids systems. The results in Table 2 showed that particles of pure lactose (S1) were more circular than those of lactose/WPI mixtures and WPI. The circularity of particle shape of lactose/WPI mixtures decreased as the crystallinity increased. Moreover, particle shape of S5 with the highest amount of crystalline lactose had the lowest ratio of width/length and the roughest surface. Those results indicated dairy solids with higher amount of crystalline lactose had less rounded shape, and rougher surface. Fu et al. [19] stated that particle shape significantly affected the flow characteristics of powder over a wide range of stress conditions. Powders consisting of regularly shaped particles flow better than those consisting of irregular shaped particles. Thus, different particle shapes of lactose/WPI solids systems may link to their flow behaviours in this study.

3.3. Glass transition

After storage at different humidity conditions, lactose/WPI solids systems with different moisture contents were prepared (Table 3). There was no trend for the water content of lactose/WPI mixtures with different crystallinity after storage at 44% RH, which might be due to the presence of WPI in dairy powders weakening the effect of crystalline lactose on water sorption behaviour of lactose/WPI mixtures. Water activities of lactose/WPI solids systems with low moisture (LM) content and high moisture (HM) content were around 0.11 a_w and 0.33 a_w, respectively (Table 3). Lactose and lactose/WPI mixtures showed significant difference in their glass transition temperatures after storage at different relative humidity conditions (Table 3). Water plasticization depressed glass transition temperatures of lactose and lactose/WPI mixtures. For lactose/WPI mixtures (S2–S5), S5 showed the lowest water content after storage at 44% RH, which resulted in the highest T_g value of S5. This might be due to the different water sorption behaviours of amorphous lactose and crystalline lactose. Similar results were also stated by Fitzpatrick et al. [4]. According to their study, the powders with larger amount of amorphous lactose were more sensitive to absorbing moisture when in intimate contact with air. According to Fitzpatrick et al. [2], powders with amorphous components, such as amorphous lactose, may become sticky if the powder temperature is elevated above the components glass transition temperature and into the sticky temperature region. This can lead to the powder becoming much more cohesive and eventually caking, and can also cause a powder to adhere more to a surface. These indicated dairy solids with 46.84% crystallinity sorbed less water during storage, which might give higher T_g values and protect them from stickiness and caking.

3.4. Mechanical properties

The mechanical properties of lactose/WPI solids systems storage at 0% and 44% RH were measured using a DMA. Mechanical α-relaxation of lactose/WPI solids systems occurred above the glass transition and was observed from a decrease in storage modulus and a peak in the loss modulus (Fig. 1). At temperatures above the glass transition, large changes in viscoelastic properties were expected [27,28]. The storage modulus of lactose/WPI solids systems decreased slowly in the amorphous state, while it dropped sharply from the original value at the glassy state to the value at the rubbery state in the glass transition region (Fig. 1A1 and B1). There were minor differences in the magnitude of storage modulus change for lactose/WPI mixtures with low moisture content, while pure lactose (S1) with low moisture content showed the most significant change in its storage modulus at the glass transition region (Fig. 1A1). All dairy solids sorbed much water from air during storage at 44% RH (Table 3), which resulted in lactose/WPI solids systems showed more significant change in their storage modulus at the glass transition region. The storage modulus of pure lactose still showed the most significant change after storage at 44% RH (Fig. 1B1). However, for lactose/WPI mixtures, S5 with the highest crystallinity showed the smallest change of storage modulus during the glass transition region (Fig. 1B1). Comparing S2 and S5, S2 with lower crystallinity showed higher magnitude of storage modulus change than S5. The magnitudes of modulus changes indicated mechanical α-relaxations which were relative to molecular mobility [28,29]. Higher molecular mobility could contribute to the formation of inter-particle bridges and stickiness

Table 3
Water content, m, water activity, a_w, glass transition temperature, T_g, and α-relaxation temperature, T_α of lactose/WPI solids systems storage at different humidity conditions (0% RH and 44% RH).

Systems	m		a_w		T_g (°C)		T_α (°C)	
	LM	HM	LM	HM	LM	HM	LM	HM
S1	1.35 ± 0.01	4.67 ± 0.02	0.16 ± 0.001	0.34 ± 0.002	72.0 ± 0.1	50.0 ± 0.2	122.1 ± 0.04	69.6 ± 0.02
S2	2.21 ± 0.25	4.80 ± 0.21	0.09 ± 0.001	0.32 ± 0.001	68.9 ± 0.2	47.8 ± 0.0	126.6 ± 0.03	69.7 ± 0.03
S3	2.34 ± 0.15	6.14 ± 0.08	0.09 ± 0.002	0.35 ± 0.003	66.1 ± 0.1	35.9 ± 0.2	125.1 ± 0.05	63.2 ± 0.04
S4	2.40 ± 0.04	6.22 ± 0.11	0.11 ± 0.001	0.34 ± 0.000	67.3 ± 0.3	37.0 ± 0.1	127.0 ± 0.02	58.6 ± 0.04
S5	2.11 ± 0.04	4.78 ± 0.12	0.09 ± 0.003	0.33 ± 0.003	71.4 ± 0.2	48.8 ± 0.4	126.3 ± 0.02	73.2 ± 0.05
S6	3.49 ± 0.01	7.87 ± 0.06	0.09 ± 0.001	0.33 ± 0.000	/	/	/	/

1. S1–S6: Table 1.
2. Values are mean ± standard deviation (water content: n = 3; T_g and T_α: n = 2).

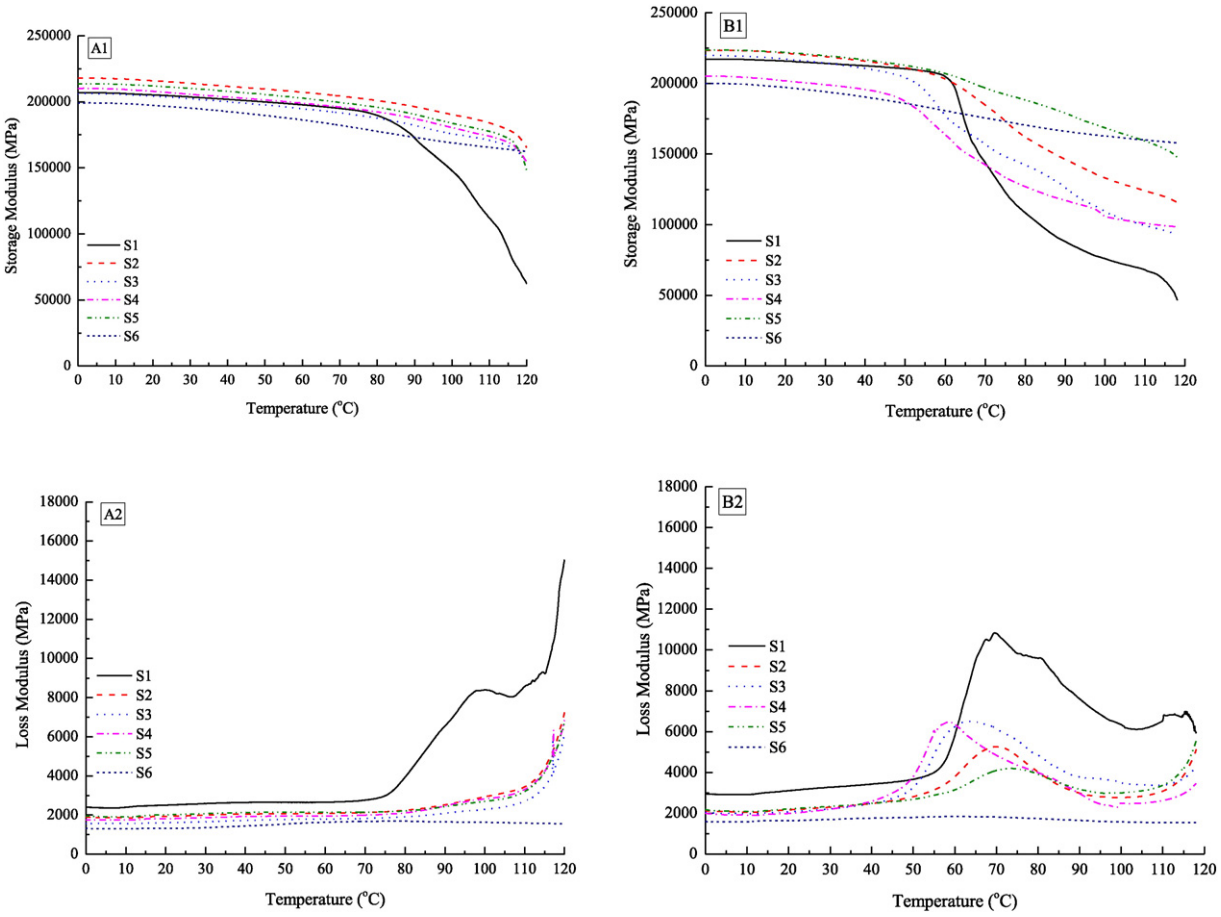


Fig. 1. Storage modulus and loss modulus of lactose/WPI solids systems with low moisture (LM) content (A1 and A2) and high moisture (HM) content (B1 and B2). S1–S6: S1: amorphous lactose; S2–S5: lactose/WPI (4:1) mixtures with 1.01%, 11.18%, 29.20% and 46.84% crystallinity, respectively; S6: WPI.

[9,28]. Consequently, water plasticization could increase molecular mobility of dairy solids, while increasing protein content or crystalline lactose content of dairy solids could decrease the molecular mobility of dairy solids. In other words, increasing protein content or crystalline lactose content might help dairy solids to delay the formation of stickiness and caking and keep them free-flowing.

Stiffness of materials refers to the ability to carry stress without changing dimension [30]. For the measurement of unconstrained uniaxial tension or compression, Young's modulus can be as a measure of the stiffness of a material. In this study, the change of storage modulus could reflect the change of stiffness for dairy solids. The stiffness of spray-dried dairy solids showed the same trend as the change of storage modulus when temperature increased from 0 to 120 °C. The results of storage modulus indicated that dairy solids with higher crystallinity had higher stiffness at high moisture content, which might help dairy solids to maintain their flowability after storage at high relative humidity environment.

The changes of loss modulus for lactose/WPI solids systems are shown in Fig. 1A2 and B2. Loss modulus of lactose/WPI solids systems showed minor changes in the amorphous state and the rubbery state,

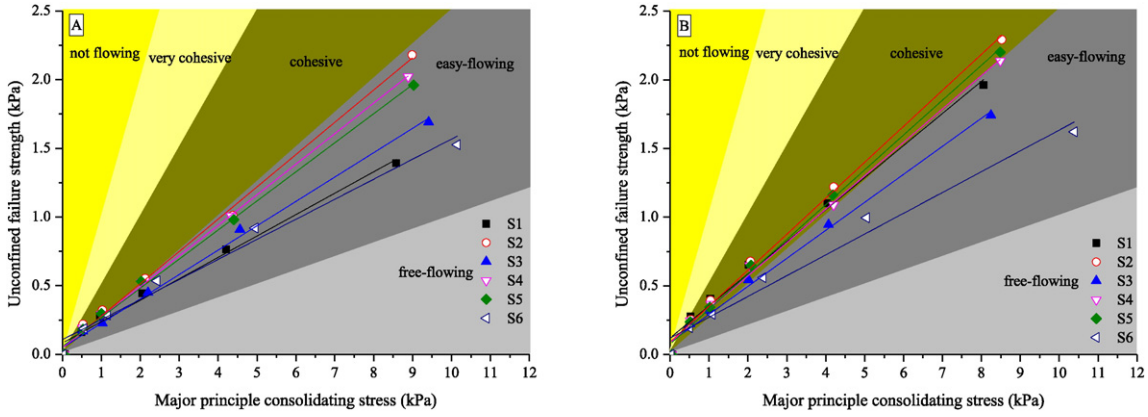


Fig. 2. Flow function curves showing unconfined strength as a function of major principal consolidating stress for lactose/WPI solids systems with low moisture (LM) content (A) and high moisture (HM) content (B). S1–S6: S1: amorphous lactose; S2–S5: lactose/WPI (4:1) mixtures with 1.01%, 11.18%, 29.20% and 46.84% crystallinity, respectively; S6: WPI.

Table 4
Values relating to flow properties of lactose/WPI solids systems derived from standard flow function test using a Powder Flow Tester ($D_{arching}$: minimum outlet diameter to prevent arching; δ_J: effective angle of internal friction).

Systems	Critical stress		$D_{arching}$ (m)		Flow index		δ_J	
	LM	HM	LM	HM	LM	HM	LM	HM
S1	$0.154^{b} \pm 0.001$	$0.264^{a} \pm 0.001$	$0.060^{bc} \pm 0.001$	$0.113^{b} \pm 0.001$	$6.25^{c} \pm 0.01$	$4.17^{bc} \pm 0.01$	$36.3^{d} \pm 0.1$	$44.4^{b} \pm 0.1$
S2	$0.099^{e} \pm 0.000$	$0.210^{b} \pm 0.003$	$0.056^{c} \pm 0.000$	$0.120^{c} \pm 0.002$	$4.17^{a} \pm 0.01$	$3.70^{a} \pm 0.00$	$40.7^{b} \pm 0.1$	$45.2^{a} \pm 0.0$
S3	$0.096^{e} \pm 0.001$	$0.181^{d} \pm 0.001$	$0.056^{c} \pm 0.001$	$0.108^{d} \pm 0.002$	$5.56^{b} \pm 0.20$	$4.76^{c} \pm 0.00$	$39.4^{c} \pm 0.1$	$43.4^{c} \pm 0.0$
S4	$0.106^{d} \pm 0.001$	$0.192^{c} \pm 0.001$	$0.056^{c} \pm 0.001$	$0.101^{d} \pm 0.001$	$4.35^{a} \pm 0.00$	$4.00^{b} \pm 0.01$	$40.1^{c} \pm 0.1$	$45.2^{a} \pm 0.0$
S5	$0.122^{c} \pm 0.000$	$0.175^{d} \pm 0.001$	$0.064^{b} \pm 0.001$	$0.097^{e} \pm 0.001$	$4.55^{a} \pm 0.00$	$3.85^{ab} \pm 0.01$	$40.7^{b} \pm 0.1$	$44.0^{b} \pm 0.1$
S6	$0.193^{a} \pm 0.001$	$0.216^{b} \pm 0.001$	$0.179^{a} \pm 0.001$	$0.199^{a} \pm 0.000$	$6.67^{c} \pm 0.00$	$6.25^{d} \pm 0.00$	$41.1^{a} \pm 0.1$	$40.7^{e} \pm 0.1$

1. S1–S6: Table 1.
2. Values are mean ± standard deviation (n = 3).
3. $^{a–e}$ Values within columns with different superscripts are significantly different at $P < 0.05$.

while they increased dramatically and reached the peak values in the glass transition region (Fig. 1B1 and B2). The magnitudes of loss modulus increased with increasing water content of lactose/WPI solids systems. Although S2 and S5 showed similar water content after storage at 44% RH, S5 with the highest amount of crystalline lactose showed smaller magnitude of loss modulus change. In addition, in this study, the α-relaxation temperatures, T_α, were taken from the temperatures of loss modulus peak (Table 3). T_α values of lactose and lactose/WPI mixtures decreased as moisture content increased. S5 showed the highest T_α values, which might be due to its highest crystallinity and lower moisture content. Those results of storage modulus and loss modulus indicated that the crystallinity of dairy solids affected the mechanical properties of dairy solids.

3.5. Flow properties

Standard flow function test and standard wall friction test of lactose/WPI solids systems were conducted using a Powder Flow Tester. The flowability results are shown in Fig. 2. According to Schulze [6], the flowability of powders is usually stress-dependent. For lactose/WPI solids systems with low moisture content, they were easy-flowing or cohesive when the major principle consolidating stress was below 3 kPa, while they were all easy-flowing at major principle consolidating stress >3 kPa (Fig. 2A). However, for dairy solids with high moisture content, lactose/WPI mixtures with 1.01%, 29.20% and 46.84% amount of crystalline lactose fell into cohesive area even when major principle consolidating stress was over 8 kPa. Therefore, increasing water content decreased flowability of dairy solids, which might be due to the increase in liquid bridges and capillary forces acting between the powder particles. For lactose/WPI mixtures (S2–S5), S3 with 11.18% crystallinity showed more easy-flowing than S2, S4 and S5 after storage at 0% and 44% RH. This could also be derived from the flow index results (Table 4). S3 gave higher flow index values than other lactose/WPI mixtures. S4 and S5 with higher amount of crystalline lactose did not show better flowability than S3. According to Fitzpatrick et al. [4], this might be due to the high amount of crystalline lactose for S4 and S5, which gave rise to greater frictional resistance between the particles or the differences in surface moisture contents of crystalline and amorphous lactose producing differences in cohesion due to liquid bridging. In addition, S4 and S5 had smaller particle size and larger SSA values than S3 (Table 1), which meant they had more surface area for cohesive forces and frictional forces to resist flow. Furthermore, morphological study showed that dairy solids with lower crystallinity had more rounded shape, and smoother surface (Table 2), which might result that S3 was more easy-flowing than S4 and S5.

In addition, for lactose/WPI mixtures with low moisture content, S5 had a significant higher ($P < 0.05$) critical stress value than other lactose/WPI mixtures (S2, S3, and S4) (Table 4), indicating that it had a tendency to develop cohesive arches which required greater stress to collapse [6,8]. However, after storage at 44% RH, S5 gave a significant lower critical stress value than other lactose/WPI mixtures (S2, S3, and S4). Moreover, $D_{arching}$ value of S5 with low moisture content was significant higher than other lactose/WPI mixtures (S2, S3, and S4), while S5 gave the opposite result after storage at 44% RH. As a result, S5 with the highest crystallinity showed the smallest change in its critical stress and $D_{arching}$ value with increasing water content. It was clear from these results that dairy solids with higher crystallinity showed better resistance to develop cohesive when storage at high relative humidity conditions.

The bulk densities of lactose/WPI solids systems increased as major principle consolidating stress increased (Fig. 3). All dairy solids became compressed on the application of increasing major principle consolidating stress. There was only minor difference in the bulk density of lactose/WPI mixtures with different crystallinity. Increasing water

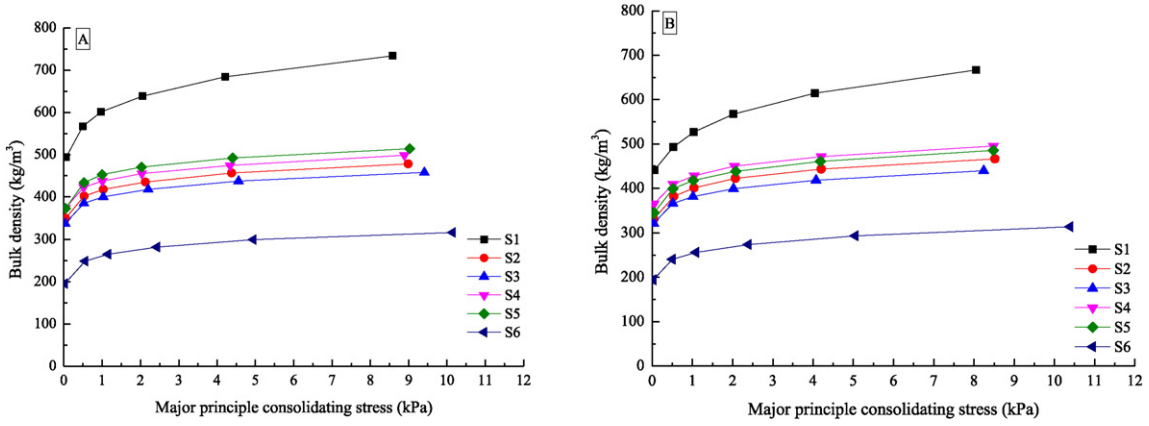


Fig. 3. Bulk density as a function of major principal consolidating stress for lactose/WPI solids systems with low moisture (LM) content (A) and high moisture (HM) content (B). S1–S6: S1: amorphous lactose; S2–S5: lactose/WPI (4:1) mixtures with 1.01%, 11.18%, 29.20% and 46.84% crystallinity, respectively; S6: WPI.

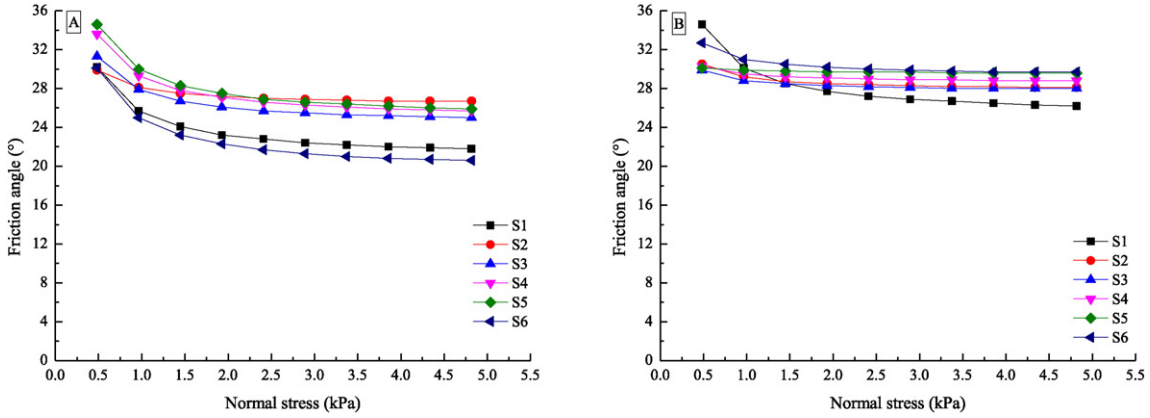


Fig. 4. Fiction angle as a function of normal stress for lactose/WPI solids systems with low moisture (LM) content (A) and high moisture (HM) content (B). S1–S6: S1: amorphous lactose; S2–S5: lactose/WPI (4:1) mixtures with 1.01%, 11.18%, 29.20% and 46.84% crystallinity, respectively; S6: WPI.

content decreased the bulk density of lactose (S1) significantly, while the bulk densities of lactose/WPI mixtures and WPI solids only showed minor decrease.

Wall friction is the dominant parameter in determining the minimum hopper angle (between the hopper wall and the horizontal) required to ensure mass flow. In this study, the wall friction angles of lactose/WPI solids systems were also determined at different normal stresses using standard wall friction test (Fig. 4). For lactose/WPI mixtures with low moisture content, friction angles increased as crystallinity was increased at 0.483 kPa (Fig. 4A). However, for lactose/WPI mixtures with high moisture content, the friction angles decreased with increasing crystallinity at 0.483 kPa (Fig. 4B). Comparing the friction angles of dairy solids with different water contents (Fig. 4A and B), the friction angles of S2 increased with increasing water content, and the friction angles of S3, S4, and S5 decreased with increasing water content. This might be due to amorphous powders (S2) that were more cohesive with increasing water content. However, for S3, S4, and S5, the increased moisture might act as a lubricant and decreased friction angles for partially crystallised powders [4].

Additionally, the effective angles of internal friction (δ_J) for lactose/WPI solids systems are also shown in Table 4. δ_J values of lactose/WPI solids systems increased with increasing water content. For lactose/WPI solids systems (S1–S6) with low water content, pure lactose (S1) showed the smallest δ_J and WPI (S6) showed the largest δ_J, while the opposite result was shown as water content increasing (Table 4). This result indicated increasing protein content decreased the effect of water plasticization on the internal friction of dairy solids.

4. Conclusions

As amorphous lactose and crystalline lactose show different physical and mechanical properties, this study investigated the influence of crystalline lactose content and water plasticization on the flow properties of lactose/WPI solids systems. Particle size study indicated that pre-crystallisation increased the particle size of dairy powders. SSA values results showed that S2 with 1.01% crystallinity gave the largest SSA value, while WPI powder showed the smallest SSA value. For lactose/WPI mixtures (S2–S5), dairy solids with higher crystallinity had larger loose bulk density, tapped bulk density and particle density, whereas they gave lower porosity. Moreover, the crystallinity of dairy powders had a minor effect on the particle shape. Those differences in particle size, SSA, bulk density, particle density and particle shape resulting from the crystallinity might affect their flow properties.

The results of mechanical property study indicated that water plasticization could increase molecular mobility of dairy solids, while increasing protein content or crystalline lactose content of dairy solids might decrease the molecular mobility of dairy solids and maintain their stiffness. Therefore, the presence of protein or crystalline lactose might protect dairy solids from stickiness and caking at high relative humidity conditions. Flow function test showed that for lactose/WPI mixtures with different crystallinity, S3 with 11.18% crystallinity was more easy-flowing than S2 (1.01% crystallinity), S4 (29.20% crystallinity) and S5 (46.84% crystallinity) at 0% and 44% RH storage conditions. Increasing water content reduced the flowability of dairy solids with different levels of crystalline lactose. Moreover, dairy solids with higher crystallinity showed better resistance to develop cohesive when they were at high relative humidity conditions. The friction angles of dairy solids with higher crystallinity (S3, S4, and S5) decreased with increasing water content, while the friction angles of S2 increased with increasing water content. Since pre-crystallisation of lactose is widely used in the production of dairy powders, the findings in this study will be very useful in handling and processing of dairy powders.

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Flavor release from spray-dried amorphous matrix: Effect of lactose content and water plasticization

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ABSTRACT

Glass-forming carbohydrates are widely used as matrix for encapsulation of nutrients and bioactive compounds. In this study, encapsulation systems with lactose/whey protein isolate (WPI) mixtures (4:1, 1:1, and 1:4), or WPI as wall materials and ethyl butyrate as core material were prepared by spray drying. The effects of lactose content and water plasticization on encapsulation efficiency and flavor release were investigated. Wall material consisting of lactose/WPI (4:1) mixture had significantly ($P < 0.05$) higher encapsulation efficiency. The flavor retention in powders did not have significant decrease with equilibration at 0.33 a_w, while it was dramatically decreased at 0.54 a_w and 0.65 a_w as a result of lactose crystallisation. Mechanical property study showed that the molecular mobility and free volume of encapsulation systems with higher lactose content increased more significantly with increasing water content, which accelerated the diffusion of flavor molecules. Those results may use in the assessment of protection and release characteristics of flavor components in formulated systems.
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1. Introduction

In food industry, there is a growing interest for encapsulation technologies, which are designed to protect the encapsulated materials and to allow controlled release. Many volatile compounds are encapsulated in solid carriers to increase their protection, reduce evaporation, and promote easier handling (Bae & Lee, 2008; Baranauskiene, Bylaite, Zukauskaite, & Venskutonis, 2007; Beristain, Vazquez, Garcia, & Vernon-Carter, 1996; Chin et al., 2010; Goubet, Le Quere, & Voilley, 1998; Jafari, He, & Bhandari, 2007; Kaushik & Roos, 2007). Since flavoring components are prone to loss by evaporation, oxidation or ingredient interactions, the encapsulation of flavor ingredients is among the most important applications in the food industry (Baranauskiene et al., 2007). Encapsulation matrix for flavor compounds can be selected from a wide variety of polymers, depending on the core materials and desired characteristics of the microcapsule. Typical wall materials include proteins (sodium caseinate, whey proteins, soy proteins and gelatin) and hydrocolloids (modified starch and gum Arabic). Among proteins, whey proteins have been shown to be an excellent encapsulating agent for microencapsulation of oils/fats and volatiles (Bae & Lee, 2008; Charve & Reineccius, 2009; Moreau & Rosenberg, 1996; Rodea-González et al., 2012; Rosenberg & Sheu, 1996; Sheu & Rosenberg, 1995). Moreover, although a variety of methods have been proposed to encapsulate flavors, spray-drying and extrusion are still the most common techniques. It has been shown that wall systems of spray-dried microcapsules consisting of whey proteins provide effective protection against core oxidation (Bylaitë, Venskutonis, & Maþdþierienë, 2001; Kim & Morr, 1996).

Previous studies have indicated that the addition of small quantities of specific low molecular weight compounds to matrices can improve the storage stability of bioactive (Roussenova, Murith, Alam, & Ubbink, 2010). These low molecular weight compounds act as packing enhancer, leading to a reduction of the molecular hole size in the glassy state, which could explain the improved glassy-state barrier properties and encapsulation performance. According to Rosenberg and Sheu (1996), the addition of lactose into WPI-based wall systems improves the volatile retention during spray drying and limits the core extractability. This is due to lactose in its amorphous state acting as a hydrophilic sealant that significantly limits diffusion of the hydrophobic core through the wall and thus leads to high microencapsulation efficiency values. Furthermore, amorphous carbohydrates in the glassy state are widely used as matrix for the encapsulation and stabilization of nutrients, pharmaceutics, and other bioactive compounds (Drusch, Serfert, Van Den Heuvel, & Schwarz, 2006; Fäldt & Bergenståhl, 1996a, 1996b; Kaushik & Roos, 2008; Levi & Karel, 1995; Lim, Griffin, & Roos, 2014; Lim & Roos, 2015; Naknean & Meenune, 2010; Zhou & Roos, 2012). In these applications, the glass transition temperature of amorphous matrix has been used as the central physical parameter for the optimization of processing conditions and storage stability (Soottitantawat et al., 2004; Townrow, Roussenova, Giardiello, Alam, & Ubbink, 2010). When the temperature increases from below to above the glass transition

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temperature, many of the physical properties of the amorphous matrix show a rapid change, including increases in the free volume, molecular mobility, and dielectric coefficient. Large changes in viscoelastic properties of amorphous powders also occur above the glass transition temperatures (Jones, 1999; Kasapis, 2001; Royall et al., 2005). Once an encapsulation matrix has gone through the glass transition and entered the metastable rubbery state, the rates of deteriorative reactions and diffusion of the flavor from the particle matrix may increase dramatically (Risch & Reineccius, 1995; Whorton, 1995).

In addition, since the presence of high molecular weight protein or carbohydrate in the amorphous lactose-based systems could increase diffusion distance (Potes, Kerry, & Roos, 2012; Silalai & Roos, 2010, 2011), the ratios of low molecular weight compounds in encapsulation systems could affect the properties of whey protein-based systems. Furthermore, water is a highly efficient plasticizer of carbohydrates and the glass transition temperature of an amorphous carbohydrate matrix decreases strongly with increasing water content (Jouppila, Kansikas, & Roos, 1997; Jouppila & Roos, 1994; Partanen et al., 2008; Velasco, Holgado, Dobarganes, & Márquez-Ruiz, 2009; Zhou & Roos, 2012). According to Kilburn et al. (2004), the diffusional mobility of small molecules such as water, gases, or volatile organic compounds increases rapidly with increasing water content in both the glassy and rubbery states. The water content and water activity of the encapsulation matrix are key parameters for understanding the physical behavior and barrier properties of amorphous carbohydrates (Ubbink, 2003). Levi and Karel (1995) stated that water resulted in a lowering of T_g and acceleration of relaxation processes, which increased the release of 1-n-propanol in amorphous carbohydrate glasses. However, there is no further study about the roles of lactose content and water plasticization on the encapsulation properties of wall systems, and especially the relationship between the mechanical properties of amorphous matrix and their barrier properties.

Therefore, the aim of present study was to investigate the effect of amorphous lactose content and water plasticization on encapsulation properties and flavor release in dairy-based powders. How the physical and mechanical properties of wall systems affect flavor release was also investigated.

2. Materials and methods

2.1. Materials

α-Lactose monohydrate (>99% purity, Batch No. F051621) was kindly donated by Arla Foods Ingredients (Sønderhøj 10–12, 8260 Viby J, Denmark). Whey protein isolate (WPI), containing 71% β-lactoglobulin and 12% α-lactalbumin, was obtained from Davisco Food International (Le Sueur, MN, USA). Ethyl butyrate (EB), hydroxylamine hydrochloride, n-hexane and aluminum oxide calcined powder (≥99% purity) were purchased from Sigma-Aldrich (St. Louis, MO, USA).

2.2. Emulsion preparation

Wall material solutions were prepared in deionized water at 40 °C for 2 h and then kept overnight on the magnetic stirrers to ensure complete hydration at room temperature (23–25 °C). Total solids concentration of wall materials was 25% (w/w), which composed of lactose/WPI mixtures or WPI. The mass ratios of 4:1, 1:1, and 1:4 for lactose/WPI mixtures were used in this study. They were defined as S1 (lactose/WPI (4:1) mixture), S2 (lactose/WPI (1:1) mixture), S3 (lactose/WPI (1:4) mixture), and S4 (WPI) according to the wall materials. Then ethyl butyrate was emulsified into the wall solutions at a proportion of 20% (w/w of wall solids). All emulsions (oil in water) were prepared in two stages. Coarse emulsion was prepared using an ULTRA-TURRAX (IKA, Staufen, Germany) operated at 10,000 rpm for 1 min. Then the coarse emulsion was further homogenized using a M110-EH Microfluidizer with a 75 μm Y-type ceramic interaction chamber (Microfluidics International Corp., Newton, MA, USA) at 50 MPa for three successive homogenization steps. The homogenization process by microfluidizer was performed at room temperature with running cold water.

2.3. Spray drying

All emulsions were spray-dried by an ANHYDRO single stage spray dryer with a centrifugal atomizer (Copenhagen, Denmark) at the Teagasc Food Research Centre, Moorepark, Fermoy, Co. Cork, Ireland. The inlet air temperature was around 170 ± 2 °C and the outlet temperature around 90 ± 2 °C. Spray-dried solids were kept immediately in desiccators over P_2O_5 at room temperature. Each analysis was carried out within 2 months after spray drying.

2.4. Physical properties

Loose bulk density of powders was measured using a Jolting volumeter (Funke Gerber, Berlin, Gerrmany). Particle density (ρ_p) was measured using a Gas Pycnometer (Accupyc II 1340 Gas Pycnometer, Micromeritics Instrument Corporation, USA). Particle size distribution and specific surface area (SSA) of powder particles were determined by laser light scattering using a Malvern Mastersizer 3000 (Malvern Instruments Ltd., Worcestershire, UK).

2.5. Chemical analysis

Protein content in powders was determined using a FP 628 Nitrogen Determinator (LECO Corporation, Lakeview Avenue, St. Joseph, Michigan, USA). Lactose content was determined using an Automatic Polarimeter (Autopol 1, Rudolph Research Analytical, Hackettstown, NJ, USA). Water content was determined using a HR83 Halogen Moisture Analyzer (Mettler Toledo International Inc., Im Langacher Greifensee, Switzerland). Water activity was measured using a water activity meter (Novasina LabMaster AW, Novatron Scientific Ltd., West Susses, UK).

In order to determine encapsulated EB content in powders, EB was extracted from powders according to the method of Kaushik and Roos (2007). 1 g of powder was dissolved in 20 mL of deionized water in glass bottles and 10 mL of hexane was added, followed by mixing with a rota mixer for 1 min. Encapsulated EB was extracted with hexane by heating the samples in glass bottles at 45 °C in a water bath for 15 min with intermittent mixing. All glass bottles were kept closed with caps and sealed with sealing film during extraction. Then the bottles were cooled to room temperature and hexane was separated from aqueous phase by centrifugation at 4000 rpm for 20 min. The amount of EB present in hexane was quantified by the method of Sheu and Rosenberg (1995). 0.5 mL of centrifuged hexane was mixed with 4.5 mL 50% ethanol solution. The colour of the solution containing EB was developed and then measured absorbance with a spectrophotometer at 525 nm. The amount of EB was determined from calibration standard curves. More details about the method of EB determination were presented in the work of Sheu and Rosenberg (1995). The EB content of each sample was carried out in triplicate.

The ratio of encapsulated EB content in powders after spray drying to initial EB content added into the emulsion was defined as encapsulation efficiency (%). The ratio of encapsulated EB content in powders during equilibration at different relative humidity (RH) to encapsulated EB content after spray drying was defined as flavor retention (%).

2.6. Water sorption and flavor release from powders at different RHs

Approximately 1 g of powders was weighed into small glass vials (25 mL). All vials were equilibrated for 216 h in evacuated desiccators over saturated salt solutions of $MgCl_2$, K_2CO_3, $Mg(NO_3)_2$, and $NaNO_2$, giving RH of 33%, 44%, 54%, and 65%, respectively. All desiccators were

placed at incubators with temperature of 25 °C during equilibration. 24 vials were prepared for each powder at every RH. Three vials of each powder were taken out from every desiccator at 6, 12, 24, 48, 72, 120, 168 and 216 h, respectively, and the mass of samples was measured. Then water content of each powder was determined as a function of time. The residual amount of EB in the powder was determined by the method described above. The flavor retention was calculated as a function of time.

2.7. Glass transition determination

The powders were equilibrated at different RHs for 0, 6, 12, 24, 48, 72, 120, 168 and 216 h, respectively. Then the glass transition temperatures, T_g (onset), were determined using a differential scanning calorimeter (DSC Q2000, TA Instruments, Crawley, UK). To determine T_g values, 10–15 mg of equilibrated powders was transferred to Tzero pans. The DSC pans were hermetically sealed with Tzero hermetic lids and samples were analysed. An empty pan was used as a reference. The temperature range of the scans was between −10 °C and 180 °C depending on the water contents of powders. The heating rate was 5 °C/min and the cooling rate was 10 °C/min during scanning. All measurements were carried out in duplicate. T_g values were determined using TA universal analysis software, version 5.1.2 (TA Instruments, Crawley, UK) and were taken as the onset-point of the endothermic baseline shift.

2.8. Dynamic mechanical analysis

The powders were equilibrated at different RHs for 0, 6, 12, 24, 48, 72, 120, 168 and 216 h, respectively. Then a dynamic mechanical analyzer (DMA Q800, TA Instruments, Crawley, UK) was used, in conjunction with a gas cooling accessory (GCA) tank, to determine the dynamic mechanical properties of powders. A rectangular stainless steel powder holder was designed to generate a defined geometry to contain powder with inner dimensions of 60 mm × 11 mm × 1 mm. A pre-weighed mass of powder mixed with aluminum oxide calcined powder at the ratio 4:1 was evenly spread within this shallow container, and the upper lid was then placed onto the top surface of the powder (Mahlin, Wood, Hawkins, Mahey, & Royall, 2009). As aluminum oxide calcined powder showed no effect on mechanical property results of dairy solids, it was added to protect dairy powder from sticking on the powder holder during the heating test. The measurements were made at a heating rate of 2 °C/min from 0 to 120 °C. DMA was operated by a sinusoidal deformation applied to the powder sample holder at a fixed strain. During dynamic heating, the samples were analysed for storage modulus (E') and loss modulus (E") using single frequency 1 Hz. The α-relaxation temperatures, T_α, were determined using TA universal analysis software, version 5.1.2 (TA Instruments, Crawley, UK).

2.9. Statistical analysis

Measurement of protein content, glass transition, and dynamic mechanical analysis were performed in duplicate, with all other analyses performed in triplicate. Results were expressed as mean ± standard deviations (SD). One-way analysis of variance (ANOVA) was used to determine the significant differences between the mean values of each test (Microsoft Office Excel 2010, Microsoft, Inc., Redmond, WA, USA). A significance level of $P < 0.05$ was used throughout the study.

3. Results and discussion

3.1. Powder characteristics

The powder characteristics of encapsulation systems after spray drying are shown in Table 1. The EB content in the powder with wall material consisting of lactose/WPI (4:1) mixture was significantly ($P < 0.05$) higher than in the powders with wall materials consisting of lactose/WPI mixtures at ratio of 1:1 and 1:4, and WPI. As a result, the wall material consisting of lactose/WPI (4:1) mixture had significantly ($P < 0.05$) higher encapsulation efficiency than S2, S3 and S4. This might be due to the highest lactose content in S1, which could form a large extent of amorphous structure to entrap EB during spray drying. According to Roussenova et al. (2010), the density of the amorphous matrix increased when the molecular weight of a glassy carbohydrate matrix decreased. Therefore, the glass structure and increase in density of amorphous matrix might improve the barrier properties of wall materials with higher amount of lactose, and resulted in the higher encapsulation efficiency of wall materials with lactose/WPI (4:1) mixture. However, when lactose content was lower than 50% in the wall materials, the present of lactose did not have significant impact on encapsulation efficiency of wall materials during spray drying (Table 1). Rosenberg and Sheu (1996) also showed similar results. According to their study, the retention of EB in wall system consisting of a 1:1 mixture of WPI and lactose was not higher than in wall system consisting of WPI when the initial core material load was lower than 30% (w/w), which was in agreement with our study. Therefore, the addition of lactose in WPI-based wall systems did not have significant improvement in the barrier properties when the lactose content was lower than 50%. Additionally, the water content of powders with lower ratios of lactose of wall systems was significantly ($P < 0.05$) higher, while all powders had similar water activities. Moreover, the particle size of powders with higher amount of lactose was smaller, and the SSA values of them were larger. Furthermore, the powders with higher amount of lactose showed smaller particle density, but they showed higher loose bulk density.

3.2. Water sorption

Water sorption of powders over various water activities was plotted as a function of time, as shown in Fig. 1. Since EB in powders kept releasing during storage period, the water contents of powders shown in Fig. 1 were not only calculated according to the mass changes of powders during storage, but they were modified according to the mass change resulting from flavor release during storage. The initial water contents before equilibration are shown in Table 1. The wall system consisting of only WPI (S4) sorbed the highest amount of water in the range of 0.33–0.65 a_w. S2 with wall material consisting of lactose/WPI (1:1) mixture sorbed the lowest amount of water at 0.33 a_w and 0.44 a_w. At 0.54 a_w, loss of sorbed water was found in S1 with wall material consisting of

Table 1
Powder characteristics of encapsulation systems.

Systems	Water content (%)	Water activity	d_{50} (μm)	SSA (m^2/kg)	Particle density (g/cm^3)	Loose bulk density (g/cm^3)	Ester content (mg/g of dry solids)	Encapsulation efficiency (%)
S1 lactose/WPI 4:1	$2.52^{d} \pm 0.03$	$0.17^{ab} \pm 0.00$	$26.20^{c} \pm 0.00$	$646.73^{a} \pm 3.27$	$1.0986^{c} \pm 0.0031$	$0.4117^{a} \pm 0.0002$	$71.04^{a} \pm 0.85$	$42.62^{a} \pm 0.51$
S2 lactose/WPI 1:1	$2.69^{c} \pm 0.02$	$0.16^{b} \pm 0.00$	$24.30^{d} \pm 0.43$	$672.93^{a} \pm 5.32$	$1.0949^{c} \pm 0.0093$	$0.3189^{b} \pm 0.0051$	$61.48^{b} \pm 3.65$	$36.89^{b} \pm 2.19$
S3 lactose/WPI 1:4	$4.07^{b} \pm 0.06$	$0.18^{a} \pm 0.00$	$27.20^{b} \pm 0.08$	$608.27^{b} \pm 5.94$	$1.1342^{a} \pm 0.0043$	$0.2763^{c} \pm 0.0010$	$60.44^{b} \pm 1.54$	$36.26^{b} \pm 0.92$
S4 WPI	$4.26^{a} \pm 0.05$	$0.16^{ab} \pm 0.01$	$30.37^{a} \pm 0.09$	$506.53^{c} \pm 3.85$	$1.1232^{b} \pm 0.0001$	$0.2466^{d} \pm 0.0011$	$62.52^{b} \pm 3.55$	$37.51^{b} \pm 2.13$

Values are mean ± standard deviation ($n = 3$).
[a–d]Values within columns with different superscripts are significantly different at $P < 0.05$.

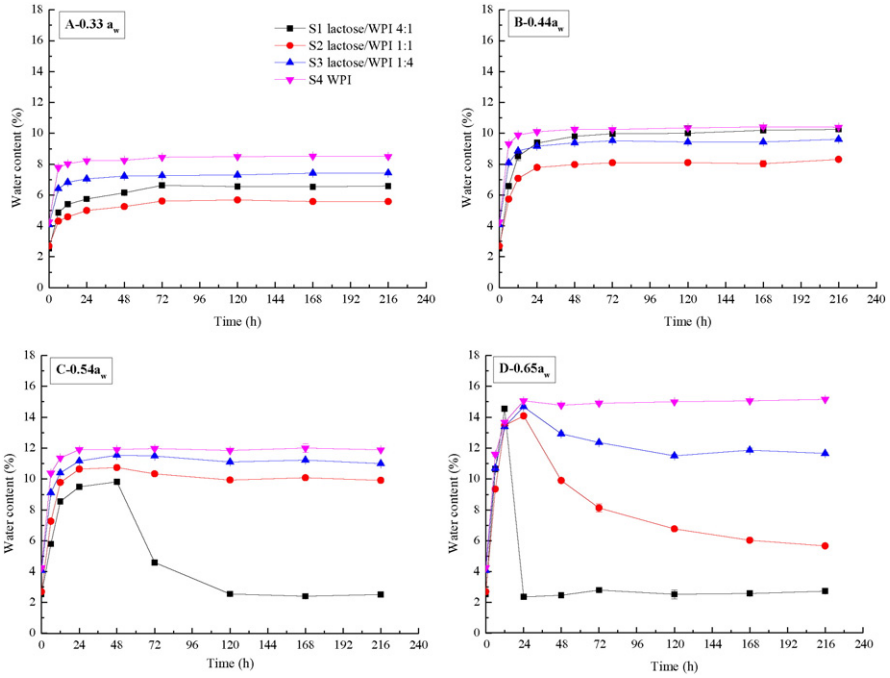


Fig. 1. Water sorption of encapsulation systems equilibration at 0.33 a_w (A), 0.44 a_w (B), 0.54 a_w (C), and 0.65 a_w (D) at 25 °C. Loss of sorbed water at 0.54 a_w and 0.65 a_w indicates lactose crystallisation.

lactose/WPI (4:1) mixture after 48 h of storage, while only small amount of sorbed water lost in S2 with wall material consisting of lactose/WPI (1:1) mixture after 72 h of storage. The rates of water sorption and lactose crystallisation for powders at 0.65 a_w were higher than those at 0.54 a_w. The loss of sorbed water was observed in powders with wall materials consisting of lactose/WPI mixtures at ratio 4:1, 1:1, and 1:4 after 12 h, 24 h, and 24 h of storage at 0.65 a_w, respectively. However, only a minor loss of sorbed water was observed in S3 with wall material consisting of lactose/WPI (1:4) mixture. In the present study, the presence of high molecular weight protein delayed lactose crystallisation at 0.54 a_w and 0.65 a_w, which agreed with the previous studies (Fan & Roos, 2015; Haque & Roos, 2004a, 2004b). The presence of protein might result in the physical blocking or steric hindrance, which could reduce molecular diffusion and delay lactose crystallisation (Fan & Roos, 2015).

Since the increase of water content can lead to an increase in free volume by decreasing the molecular packing of the matrix molecules (van den Dries, van Dusschoten, Hemminga, & van der Linden, 2000), the difference in water content of encapsulated systems (S1–S4) during storage at various water activities might result in different rates of flavor release in the amorphous matrix. Furthermore, the structure of encapsulated matrix was destroyed as lactose crystallisation occurred when water content increased at 0.54 a_w and 0.65 a_w, which might result in a quick release of flavor from powders. In addition, the collapse of amorphous matrix might also reduce flavor molecular diffusion through the matrix and result in re-encapsulation of flavor compound when lactose crystallized (Goubet et al., 1998).

3.3. Glass transition

The glass transition temperatures of powders (S1–S3) equilibration at various RHs during water sorption were measured using a DSC and are shown in Table 2. The T_g values decreased with increasing storage time in the range of 0.33–0.65 a_w before showing lactose crystallisation (Table 2), which showed typical water plasticization of amorphous materials (Haque & Roos, 2004a, 2004b; Jouppila et al., 1997; Potes et al., 2012; Zhou & Roos, 2011). Moreover, the T_g values of lactose decreased when the storage RH was increased. Powder with wall material of lactose/WPI (1:4) mixture showed higher T_g values than those with wall materials of lactose/WPI mixtures at ratio 4:1 and 1:1 at 0.44–0.65 a_w. This was in agreement with the results of Fan and Roos (2016). They indicated the T_g value of lactose/WPI mixture at ratio 3:7 was higher than those of lactose/WPI mixtures at ratios 7:3 and 1:1 at 0.33 a_w. The increasing effect of T_g values in powder with lactose/WPI (1:4) mixture

Table 2
Glass transition temperatures (°C), T_g, of powders with wall materials consisting of lactose/WPI mixtures storage at 0.33 a_w, 0.44 a_w, 0.54 a_w, and 0.65 a_w at 25 °C for different time.

Water activity	Time (h)	Systems		
		S1 lactose/WPI 4:1	S2 lactose/WPI 1:1	S3 lactose/WPI 1:4
Initial powders	**0**	64 ± 0.5	57 ± 0.0	65 ± 0.0
0.33	**6**	55 ± 1.0	56 ± 1.0	63 ± 1.0
	12	46 ± 0.5	46 ± 0.5	45 ± 1.0
	24	46 ± 0.5	47 ± 0.0	47 ± 0.5
	48	45 ± 0.0	46 ± 0.5	49 ± 0.0
	72	41 ± 0.0	44 ± 0.5	45 ± 0.5
	120	40 ± 0.0	42 ± 0.0	42 ± 0.0
	168	39 ± 0.5	42 ± 0.0	43 ± 0.5
	216	40 ± 0.0	41 ± 0.5	43 ± 0.0
0.44	**6**	40 ± 0.0	41 ± 0.0	40 ± 0.0
	12	30 ± 0.0	31 ± 0.0	37 ± 0.0
	24	24 ± 0.5	28 ± 0.5	36 ± 1.0
	48	22 ± 0.0	25 ± 0.5	36 ± 0.0
	72	22 ± 0.0	25 ± 0.0	35 ± 0.0
	120	22 ± 0.5	25 ± 0.5	35 ± 0.5
	168	21 ± 0.5	25 ± 0.0	34 ± 0.0
	216	21 ± 0.0	25 ± 0.5	34 ± 0.5
0.54	**6**	33 ± 0.5	33 ± 0.5	38 ± 0.5
	12	13 ± 0.5	16 ± 0.0	33 ± 0.0
0.65	**6**	15 ± 0.5	16 ± 0.0	34 ± 1.0

Values are mean ± standard deviation ($n = 2$).
Initial powders were the powders after spray drying.

might be due to the presence of high amount of protein with high molecular weight.

Phase transitions play an important role in encapsulation processes (Whorton, 1995). Levi and Karel (1995) stated that flavor retention was dependent on temperature, water content and the degree of matrix collapse. In the glassy state, flavors have very low diffusion rates in amorphous barriers. Due to the low molecular mobility of barriers, flavor release from powders in the glassy state is limited. When a glass is heated to above the glass transition, molecules gain translational mobility and enter the supercooled, liquid-like state. The increase in molecular mobility of amorphous matrix would result in the increase of evaporation of volatile flavors. Since the T_g values of powders were varied according to the storage time, storage RH and wall material compositions, the rate of flavor release was also affected by those conditions. Powders with lower amount of lactose might show lower rate of flavor release at high RH (>44%).

3.4. Mechanical properties

Many mechanical properties of amorphous materials change dramatically at glass transition region. In this study, the mechanical properties of powders during storage over various RHs were measured using a DMA. The modulus changes of powders equilibration at 0.33–0.65 a_w are shown in Fig. 2. Since the powders consisting of lactose showed lactose crystallisation at 0.54 a_w and 0.65 a_w after storage a period (0.54 a_w: >12 h; 0.65 a_w: >6 h), the mechanical properties of powders were only

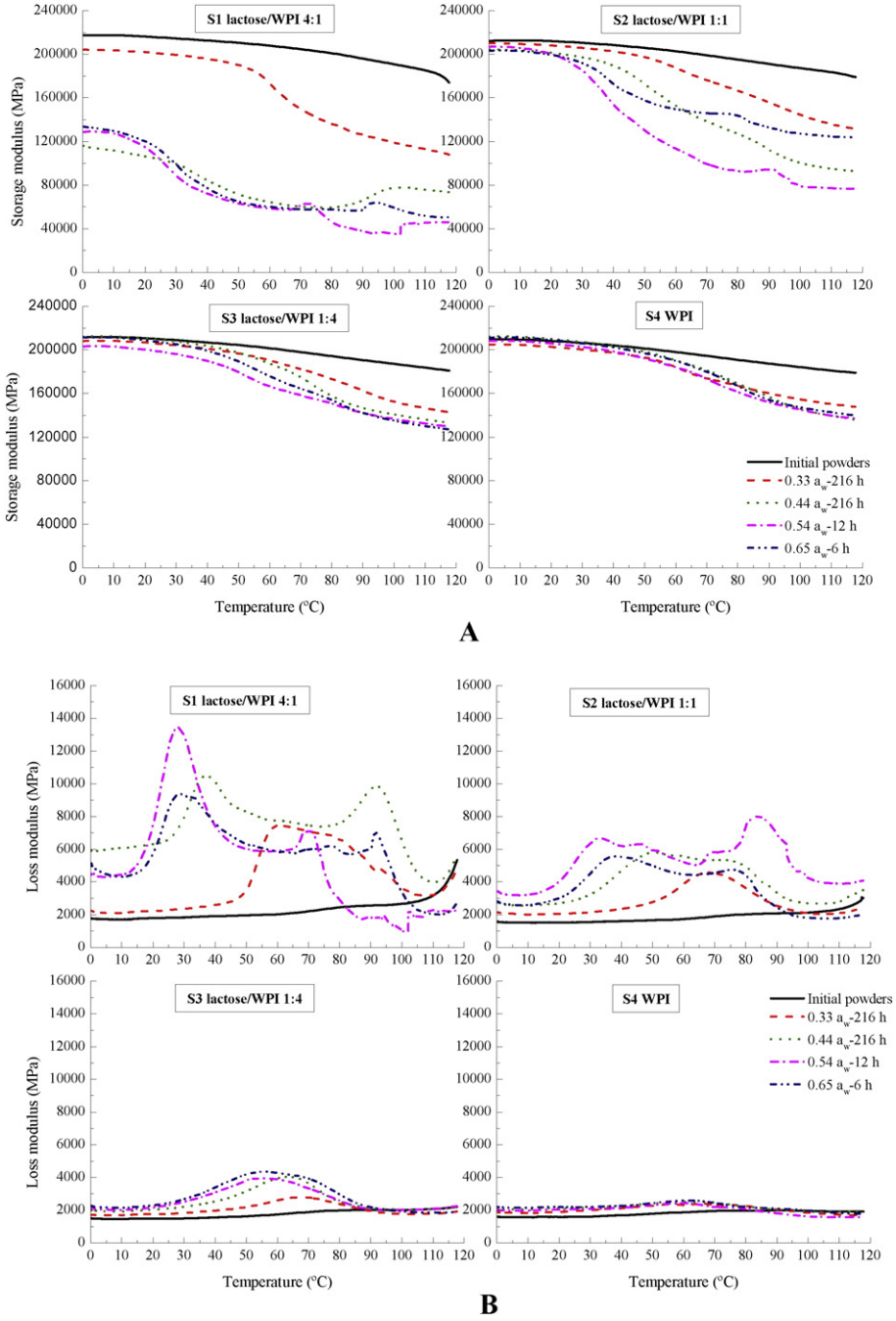


Fig. 2. Storage modulus (A) and loss modulus (B) of encapsulation systems equilibration at 0.33 a_w and 0.44 a_w for 216 h, 0.54 a_w for 12 h, and 0.65 a_w for 6 h before showing lactose crystallisation at 25 °C. Initial powders were the powders after spray drying.

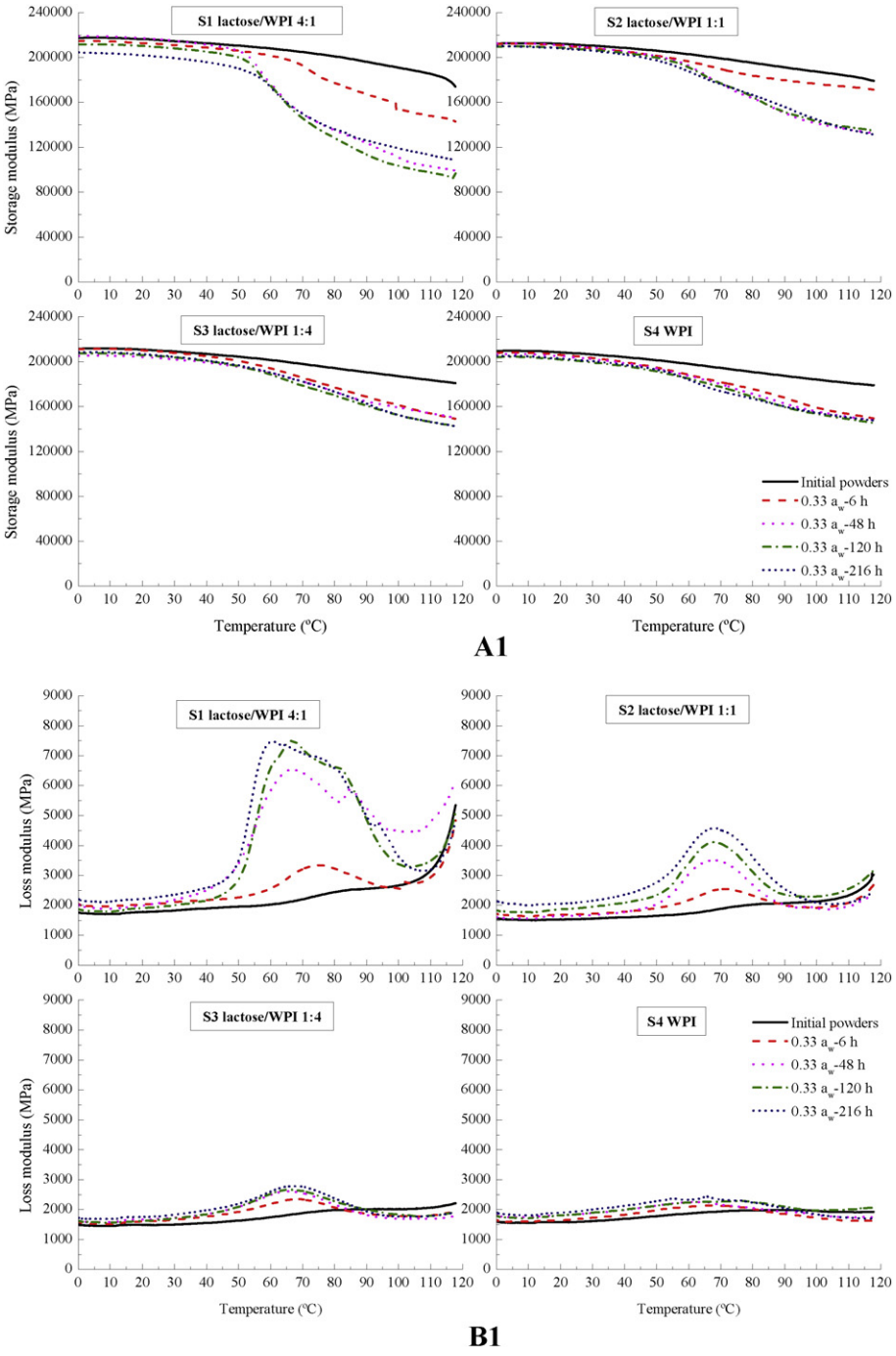


Fig. 3. Storage modulus (A1 and A2) and loss modulus (*B*1 and B2) of encapsulation systems equilibration at 0.33 a_w and 0.44 a_w at 25 °C for different time. Initial powders were the powders after spray drying.

measured before lactose crystallisation (Fig. 2). Additionally, the modulus changes of powders during storage at the same RH for different time are shown in Fig. 3. Compared with the storage modulus of powders (S1–S4) after spray drying (Initial powders), S1 had significantly higher storage modulus than S2, S3 and S4 at the glassy state. This might be one of the reasons that the encapsulation efficiency of wall material consisting of lactose/WPI (4:1) mixture (S1) was significantly higher than those with lactose/WPI mixtures at ratio 1:1 and 1:4, and WPI (Table 1). The magnitudes of storage modulus changes for powders were larger at higher water activity (Fig. 2 A). Moreover, the magnitudes of storage modulus changes also increased with increasing storage time at same water activity (Fig. 3 A1 and A2). Since increasing storage RH or storage time caused an increase in the water contents of powders, powders with higher water content could result in larger magnitudes of storage modulus changes. According to previous studies (Roudaut, Simatos, Champion, Contreras-Lopez, & Le Meste, 2004; Silalai & Roos, 2011), the magnitudes of storage modulus and loss modulus changes were related to molecular mobility of materials. Therefore, increasing water content of powders could increase the molecular mobility of matrix, which might result in a high release rate of flavor in powders. Furthermore, the storage modulus of powders with higher amount of lactose in the wall materials had more significant change when water content increased (Fig. 2 A). Similar results were also shown when the storage time of powders increased at same water

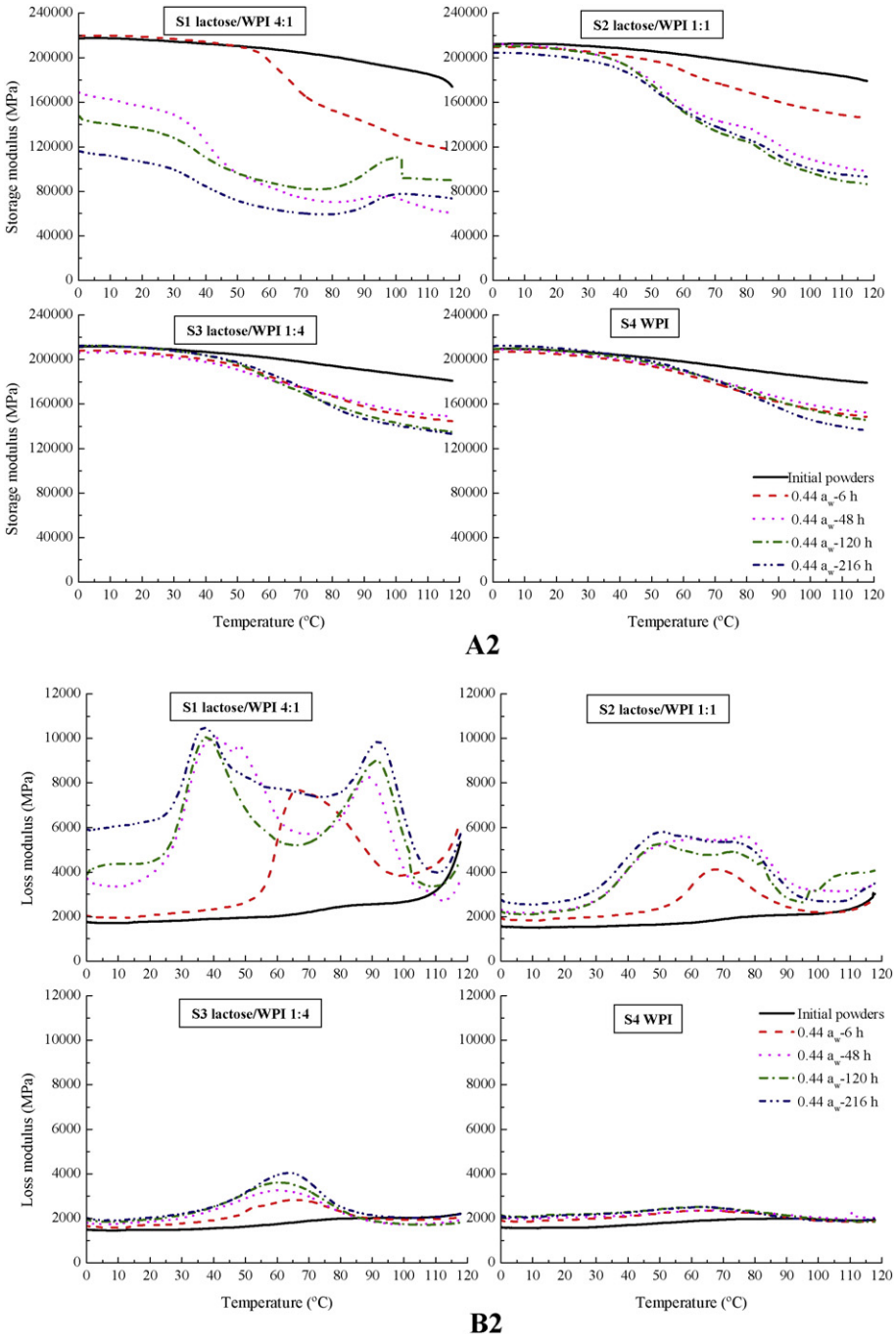


Fig. 3 (*continued*).

activity (Fig. 3 A1 and A2). These results indicated that increasing water content or lactose content of powders could increase molecular mobility and free volume of matrix at the glass transition region, which could accelerate the diffusion of flavor molecules during storage.

The changes of loss modulus of powders during equilibration were also measured using a DMA (Figs. 2 and 3). The loss modulus of powders was small and showed minor changes when the temperatures were below glass transition and they increased dramatically and reached peak values with increasing temperature to the glass transition region. This indicated the molecular mobility of powders increased dramatically in the glass transition region. Furthermore, the peak values of loss modulus of powders were affected by the lactose content and water content of matrix. Decreasing water content or lactose content could decrease the molecular mobility of matrix in the glass transition region.

In addition, the α-relaxation temperatures, T_α, were taken from the temperatures of loss modulus peak values at 1 Hz (Table 3). The T_α values of powders decreased with increasing water content as a result of water plasticization, which was in agreement with the study of Silalai and Roos (2010). S1 showed significantly higher T_α values than other powders after spray drying. The powder with wall material consisting of lactose/WPI (1:1) mixture (S2) showed the highest T_α values at 0.33 a_w, while powder consisting of only WPI showed the highest T_α values at 0.44 a_w, 0.54 a_w, and 0.65 a_w. The decrease of T_α values of S1 with the highest amount of lactose was larger as compared to those of S2–S4 when water content increased. These results indicated

Table 3
α-Relaxation temperatures (°C), T_α, of powders storage at 0.33 a_w, 0.44 a_w, 0.54 a_w, and 0.65 a_w at 25 °C for different time.

Water activity	Time (h)	Systems			
		S1 lactose/WPI 4:1	S2 lactose/WPI 1:1	S3 lactose/WPI 1:4	S4 WPI
Initial powders	**0**	81.9 ± 0.04	78.5 ± 0.01	76.7 ± 0.02	77.3 ± 0.08
0.33	**6**	73.9 ± 0.06	71.3 ± 0.02	68.2 ± 0.02	68.2 ± 0.05
	48	65.7 ± 0.10	68.2 ± 0.05	65.9 ± 0.03	61.2 ± 0.03
	120	65.7 ± 0.07	68.8 ± 0.10	65.9 ± 0.06	61.2 ± 0.07
	216	65.9 ± 0.08	68.1 ± 0.05	65.8 ± 0.09	61.3 ± 0.04
0.44	**6**	66.4 ± 0.05	67.3 ± 0.01	64.7 ± 0.01	67.9 ± 0.04
	48	40.0 ± 0.02	53.2 ± 0.04	63.8 ± 0.06	65.4 ± 0.05
	120	37.5 ± 0.04	50.7 ± 0.05	62.0 ± 0.04	64.1 ± 0.04
	216	36.6 ± 0.02	49.8 ± 0.03	61.1 ± 0.01	62.9 ± 0.04
0.54	**6**	52.4 ± 0.02	60.2 ± 0.03	63.0 ± 0.04	66.0 ± 0.01
	12	27.5 ± 0.04	31.9 ± 0.04	56.6 ± 0.03	60.3 ± 0.02
0.65	**6**	28.1 ± 0.06	37.1 ± 0.03	55.8 ± 0.05	64.0 ± 0.05

[1]Values are mean ± standard deviation ($n = 2$).
[2]Initial powders were the powders after spray drying.

water content showed more significant effect on the structural relaxation of powders with wall materials consisting of higher amount of lactose. Since the diffusion of core materials is governed by the physical properties of the wall materials, such as the matrix structure, increasing water content of powders with wall materials consisting of higher lactose content might result in a higher diffusion of flavor molecules.

3.5. Flavor retention

The effects of water plasticization on the time-course of the flavor release in powders with different composition of wall materials are shown in Fig. 4. The retention of EB was defined as the ratio of the residual amount of EB in the powder to the initial amount after spray drying. The flavor retention in powders did not show significant change during storage at 0.33 a_w at 25 °C for 216 h, while the flavor retention of S1 showed a minor decrease with storing at 0.44 a_w. S2 showed the highest flavor retention at 0.33 a_w and 0.44 a_w, which might be due to its lowest water contents at 0.33 a_w and 0.44 a_w (Fig. 1). In addition, since the EB content of S1 was significantly higher compared to those of other powders (S2–S4) after spray drying, S1 still had the highest EB content after storage at 0.33 a_w. However, the flavor retention of S1 dropped sharply with equilibration at 0.54 a_w. Similar result happened to the flavor retention of S1 and S2 when they were stored at 0.65 a_w. These results could be linked to lactose crystallisation of encapsulating matrix, which were in agreement with the study of Zhou and Roos (2012). They stated that the amorphous structure protected the entrapped vitamins at low a_w, but crystallisation of lactose destroyed the structure. Since the T_g values of S1 at 0.54 a_w and 0.65 a_w were below the storage temperature (25 °C) (Table 2), there was a decrease in the viscosity of matrix, and an increase in the diffusivity of flavor molecules. Moreover, collapse of amorphous matrix occurred when lactose showed plasticization. Then the amorphous matrix was unable to support itself against gravity. The flavor was expelled from the crystallized matrix to the surface, and the retention of EB decreased sharply. Additionally, the rate of flavor release from S1 decreased as storage time increased at 0.54 a_w and 0.65 a_w. This might be due to the completely collapse of amorphous matrix after lactose crystallisation, and then resulted in re-encapsulation of flavor compound in the collapse matrix (Goubet et al., 1998).

In addition, the water plasticization had more significant impact on the flavor retention of powders with wall materials consisting of larger amount of lactose (Fig. 4). The flavor retention of S4 was higher than 50% even when it was stored at 0.65 a_w for 216 h (Fig. 4 D). It was due to water plasticization had more significant influence on the molecular mobility and structural relaxation of powders with larger amount of lactose (Figs. 2 and 3), which caused higher diffusion of flavor molecules in the encapsulation systems with higher amount of lactose. As it also can be seen from Table 3, the α-relaxation temperatures of powders with higher amount of lactose decreased more significantly with increasing water content. Therefore, increasing lactose content in wall materials could increase the encapsulation efficiency at low water activities (≤0.33). However, the presence of lactose could result in higher molecular mobility with increasing water content, which leaded to accelerate the rate of flavor release at high water activities (≥0.54).

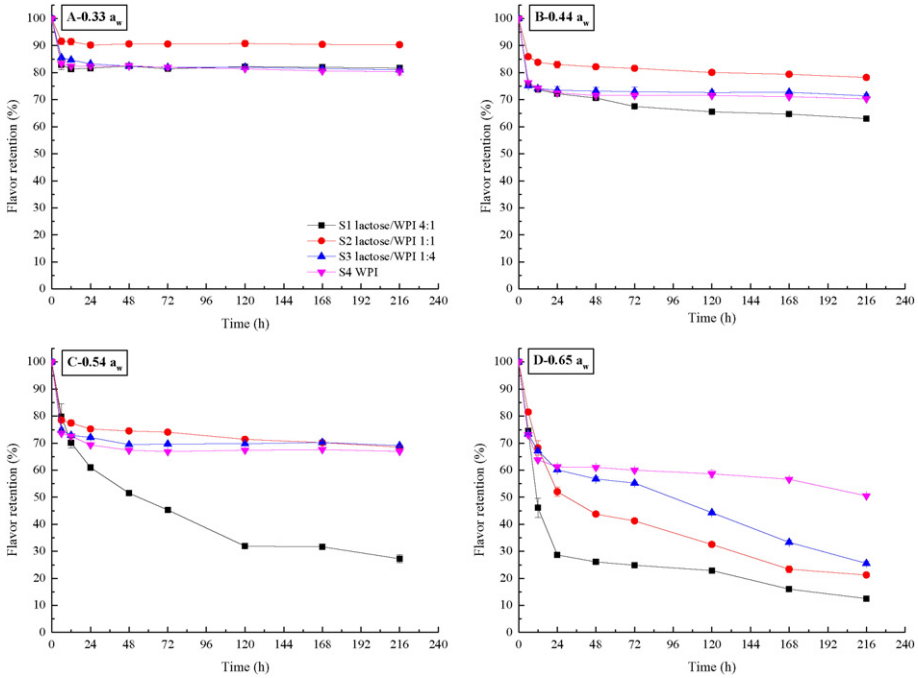


Fig. 4. Flavor retention in powders equilibration at 0.33 a_w (A), 0.44 a_w (B), 0.54 a_w (C) and 0.65 a_w (D) at 25 °C for different time.

4. Conclusions

Amorphous encapsulated matrix using lactose/WPI mixtures as wall materials and ethyl butyrate as core materials were prepared by spray drying. The encapsulation efficiency of wall material consisting of lactose/WPI (4:1) mixture was significantly higher compared to wall material consisting of only WPI. However, wall materials with lactose/WPI mixtures at ratios of 1:1 and 1:4 did not show similar result. The different ratios of lactose/WPI in wall materials resulted in the different physical properties of encapsulation systems, including particle size, specific surface area, loose bulk density and particle density, which might affect the storage stability and flavor release of powders. The flavor retention of powders did not show significant change during equilibration at 0.33 a_w, while powder with wall material consisting of lactose/WPI (1:1) mixture had significantly higher flavor retention at 0.33 a_w and 0.44 a_w. Powders with wall materials consisting of higher amount of lactose showed dramatically decrease in their flavor retention with equilibration at 0.54 a_w and 0.65 a_w, which was as a result of lactose crystallisation. Mechanical property study indicated that powder with higher amount of lactose showed higher molecular mobility with increasing water content, and water plasticization had more significant impact on the glass transition and structural relaxation of powder with higher amount of lactose. Therefore, increasing lactose content could increase the encapsulation efficiency of wall materials during spray drying. However, this also could result in a higher rate of flavor release with storage at high water activity.

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Characterization of mechanical and encapsulation properties of lactose/maltodextrin/WPI matrix

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ABSTRACT

In this study, encapsulation systems using lactose/whey protein isolate (WPI) (4:1) or lactose/maltodextrin (MD)/WPI (3:1:1 or 1:3:1) mixtures as wall materials and ethyl butyrate (EB) as core materials were produced by spray drying. Wall material consisting of lactose/WPI (4:1) mixtures had the highest encapsulation efficiency for EB during spray drying, while wall materials consisting of lactose/MD/WPI (1:3:1) mixtures had higher encapsulation efficiency compared to wall materials consisting of lactose/MD/WPI (3:1:1) mixtures. The presence of MD in wall systems delayed the crystallisation of amorphous lactose at 0.54–0.76 a_w, which decreased the rate of flavor release from encapsulation systems. Furthermore, the magnitudes of modulus changes for wall systems with higher amount of MD was smaller compared to those with lower amount of MD when water content increased. The addition of MD could increase the stiffness of encapsulation systems and thus, reduce molecular mobility of wall materials. Wall systems consisting with lactose/MD (13–17)/WPI (1:3:1) mixtures and lactose/MD (23–27)/WPI mixtures had higher flavor retention than other wall systems after equilibration at high water activity ($\geq$0.54 a_w).

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1. Introduction

Many flavors have been encapsulated, generally in solid matrices which are often produced by spray drying (Arvisenet, Voilley, & Cayot, 2002; Baranauskiene, Bylaite, Zukauskaite, & Venskutonis, 2007; Bhandari, Dumoulin, Richard, Noleau, & Lebert, 1992; Goubet, Le Quere, & Voilley, 1998; Sheu & Rosenberg, 1995). Those solid matrices are often formed by glass-forming food components, and amorphous carbohydrates in the glassy state are widely used as solid matrices for the encapsulation and stabilization of nutrients, pharmaceutics, and other bioactive compounds (Roos, 2010). Encapsulation matrix in the glassy state combines high physical and chemical stability with very high barrier properties with respect to oxygen and organic molecules (Ubbink, 2003). Numerous recent studies have discussed the glass formation of amorphous matrices in encapsulation processes (Vega & Roos, 2006) and emphasized the importance of the glass-forming ability of the encapsulant in protecting sensitive components (Ubbink & Krüger, 2006). In these applications, the glass transition temperature and water content of the amorphous matrix have been used as the central physical parameters for the optimization of processing conditions and storage stability (Townrow, Roussenova, Giardiello, Alam, & Ubbink, 2010).

In amorphous encapsulation systems, the release and stability of core materials are related to the molecular mobility of wall materials, and phase transitions play an important role in most encapsulation processes where the initial objective is to form a stable amorphous glass structure to entrap the flavor compounds and inhibit mobility of molecules. Increasing water content or temperature can result in a transition which occurs in amorphous matrix from the glassy state to the rubbery state. Once an encapsulated matrix has gone through the glass transition and entered the metastable rubbery state, the viscosity decreases while the molecular mobility and free volume of the polymer structure increase. The rates of deteriorative reactions and diffusion of the flavor from the particle matrix also increase (Whorton, 1995).

Previous studies have indicated that miscible high molecular weight components generally increase viscosity and the average molecular weight, and decrease molecular mobility of amorphous systems (Roos & Karel, 1991; Sillick & Gregson, 2009). Moreover, they may also increase the glass transition temperatures.

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Furthermore, the addition of a second carbohydrate component to an amorphous system may delay the crystallisation of amorphous materials (Mazzobre, Soto, Aguilera, & Buera, 2001; Potes, Kerry, & Roos, 2012). Additionally, the primary α-relaxations of solids systems are mainly governed by the miscible solids components and may shift to higher temperature with increasing the contents of high molecular weight components at all a_w (Silalai & Roos, 2011b).

As a food ingredient, maltodextrin (MD) has been used in the encapsulation of food components for several decades (Bae & Lee, 2008; Bhandari et al., 1992; Gunning et al., 1999; Jafari, He, & Bhandari, 2007; Sheu & Rosenberg, 1995; Soottitantawat et al., 2005; Yoshii et al., 2001). Previous studies have indicated that sugars in mixtures with maltodextrins of low dextrose equivalent (DE) form systems with high viscosity and are often used to increase the T_g of food solids to improve their dehydration properties and stability (Bhandari, Datta, Crooks, Howes, & Rigby, 1997; Chronakis, 1998). Sheu and Rosenberg (1995) stated that combinations of whey proteins and high DE maltodextrins or corn syrup solids were effective wall systems for encapsulation of volatiles, and Shiga et al. (2001) indicated that blending of MD in the feed liquid decreased the release rate of *d*-limonene in β-cyclodextrin encapsulation system. Additionally, physical properties, such as wettability and density, were greatly improved by increasing the maltodextrin ratio in the wall systems (Bae & Lee, 2008), which may affect encapsulation efficiency and flavor release during production and storage. However, there is no further study about how the types and contents of maltodextrin affect the encapsulation properties of amorphous matrix. Moreover, it is also essential to investigate the relationship between mechanical properties and flavor release in amorphous matrix. Therefore, a better understanding of the roles of maltodextrin in amorphous encapsulation systems is very important to improve product development and modification of existing process and products.

Our previous studies have shown that wall material consisting of lactose/whey protein isolate (WPI) (4:1) mixtures had significantly ($P < 0.05$) higher encapsulation efficiency compared to wall material consisting of only WPI (Li, Roos, & Miao, 2016b). The objectives of this study were to investigate the influence of maltodextrin type and contents on mechanical and encapsulation properties of wall systems consisting of lactose/maltodextrin/WPI mixtures. The relationship between flavor release and mechanical properties of encapsulation systems was also studied.

2. Materials and methods

2.1. Materials

α-lactose monohydrate (>99% purity) was kindly offered by Arla Foods Ingredients (Sønderhøj 10–12, 8260 Viby J, Denmark), while WPI, containing 71% β-lactoglobulin and 12% α-lactalbumin, was obtained from Davisco Food International (Le Sueur, MN, USA). Maltodextrin with DE values of 4–7, 13–17, and 23–27 were donated by Grain Processing Corporation (Muscatine, lowa 52761–1494, USA). Ethyl butyrate (EB), hydroxylamine hydrochloride, n-hexane and aluminum oxide calcined powder (≥99% purity) were purchased from Sigma–Aldrich (St. Louis, MO, USA).

2.2. Emulsion preparation

Wall material solutions were prepared in deionized water at 40 °C for 2 h and then kept overnight on the magnetic stirrers to ensure complete hydration at room temperature (23–25 °C). Total solids concentration of wall materials was 25% (w/w), which composed of lactose/WPI (4:1) mixture or lactose/maltodextrin/WPI mixtures. The weight ratios of lactose/maltodextrin/WPI were 3:1:1 and 1:3:1, respectively. MD with DE values of 4–7, 13–17, and 23–27 were used, respectively. Then ethyl butyrate was emulsified into the wall solutions at a proportion of 20% (w/w of wall solids). All emulsions (oil in water) were prepared in two stages. Coarse emulsion was prepared using an ULTRA-TURRAX (IKA, Staufen, Germany) operated at 10000 rpm for 1 min. Then the coarse emulsion was further homogenized using a M110-EH Microfluidizer with a 75 μm Y-type ceramic interaction chamber (Microfluidics International Corp., Newton, MA, USA) at 50 MPa for three successive homogenization steps. The homogenization process by microfluidizer was performed at room temperature with running cold water.

2.3. Spray drying

All emulsions were spray-dried by an ANHYDRO single stage spray dryer with a centrifugal atomizer (Copenhagen, Denmark) at the Teagasc Food Research Centre, Moorepark, Fermoy, Co. Cork, Ireland. The inlet air temperature was around 170 ± 2 °C and the outlet temperature around 90 ± 2 °C. Spray-dried solids were kept immediately in desiccators over P_2O_5 at room temperature. Each analysis was carried out within 2 months after spray drying.

2.4. Powder characteristics

2.4.1. Physical properties

Particle density (ρ_p) of encapsulation systems was measured using a Gas Pycnometer (Accupyc II 1340 Gas Pycnometer, Micromeritics Instrument Corporation, USA). Particle size distribution and specific surface area (SSA) of encapsulation systems were determined by laser light scattering using a Malvern Mastersizer 3000 (Malvern Instruments Ltd., Worcestershire, UK). In addition, morphological characteristics of encapsulation systems were determined using a Malvern Morphologi G3 S (Malvern Instruments Ltd., Worcestershire, UK). 5 mm^3 volume powder samples were dispersed on the glass plate. 2.5 × objective was used for the measurement in this study. In this study, each sample was measured in triplicate to get the average values.

2.4.2. Compositional analysis

Water content was determined using a HR83 Halogen Moisture Analyzer (Mettler Toledo International Inc., Switzerland). Water activity was measured using a water activity meter (Novasina LabMaster AW, Novatron Scientific Ltd., West Susses, UK).

In order to determine encapsulated EB content in powders, EB was extracted from powders according to the method of Kaushik and Roos (2007). 1 g of powder was dissolved in 20 mL of deionized water in glass bottles and 10 mL of hexane was added, followed by mixing with a rota mixer for 1 min. Encapsulated EB was extracted with hexane by heating the samples in glass bottles at 45 °C in water bath for 15 min with intermittent mixing. All glass bottles were kept closed with caps and sealed with sealing film during extraction. Then the bottles were cooled to room temperature and hexane was separated from aqueous phase by centrifugation at 4000 rpm for 20 min. The amount of EB present in hexane was quantified by the method of Sheu and Rosenberg (1995). 0.5 mL of centrifuged hexane was mixed with 4.5 mL 50% ethanol solution. The colour of the solution containing EB was developed and then measured absorbance with a spectrophotometer at 525 nm. The amount of EB was determined from calibration standard curves. More details about the method of EB determination were presented in the work of Sheu and Rosenberg (1995). The EB content of each sample was carried out in triplicate.

The ratio of encapsulated EB content in powders after spray drying to initial EB content added in the emulsion was defined as

encapsulation efficiency (%). The ratio of encapsulated EB content in powders during equilibration at different relative humidity (RH) to encapsulated EB content in powders after spray drying was defined as flavor retention (%).

2.5. Water sorption and flavor release from encapsulation systems

Approximately 1 g of powders was weighed into small glass vials (25 mL), and then all powders were equilibrated for 216 h in evacuated desiccators over saturated salt solutions of K_2CO_3, $Mg(NO_3)_2$, $NaNO_2$, and NaCl, giving RH of 44%, 54%, 65%, and 76%, respectively. All desiccators were placed at 25 °C in incubators. 24 vials were prepared for each powder at every RH. Three vials of each powder were taken out from each desiccator at 6, 12, 24, 48, 72, 120, 168 and 216 h, respectively, and the mass of samples was measured. Then water content of each powder was determined as a function of time. The residual amount of EB in the powders was determined by the method described in 2.4.2. The flavor retention in the powders was calculated as a function of time.

2.6. Glass transition determination

The encapsulation systems were equilibrated at different RHs for 0, 6, 12, 24, 48, 72, 120, 168 and 216 h, respectively. Then the glass transition temperatures, T_g (onset), and initial crystallisation temperatures, T_{ic} (onset), were determined using a differential scanning calorimeter (DSC Q2000, TA Instruments, Crawley, UK). To determine T_g and T_{ic} values, 10–15 mg of powders was transferred to Tzero pans. The DSC pans were hermetically sealed with Tzero hermetic lids and samples were analysed. An empty pan was used as a reference. The temperature range of the scans was varied between −10 °C and 180 °C depending on the water content of powders. The heating rate was 5 °C/min and the cooling rate was 10 °C/min during scanning. All measurements were carried out in duplicate. T_g and T_{ic} values were determined using a TA universal analysis software, version 5.1.2 (TA Instruments, Crawley, UK).

2.7. Dynamic mechanical analysis

The encapsulation systems were equilibrated at different RHs for 0, 6, 12, 24, 48, 72, 120, 168 and 216 h, respectively. Then a dynamic mechanical analyzer (DMA Q800, TA Instruments, Crawley, UK) was used, in conjunction with a gas cooling accessory (GCA) tank, to determine the dynamic mechanical properties of encapsulation systems. A pre-weighed mass of powder mixed with aluminum oxide calcined powder at the ratio 4:1 was evenly spread within this shallow pocket, and the upper lid was then placed onto the top surface of the powder (Mahlin, Wood, Hawkins, Mahey, & Royall, 2009). As aluminum oxide calcined powder showed no effect on mechanical property results of dairy powders, it was added to protect powders from sticking on the pocket during the heating test. The measurements were made at a heating rate of 2 °C/min from 0 to 120 °C. DMA was operated by a sinusoidal deformation applied to the powder pocket at a fixed strain. The amplitude was 15 μm. During dynamic heating, the samples were analysed for storage modulus (E′) and loss modulus (E″) using single frequency 1 Hz. Moreover, the α-relaxation temperatures, T_α, were determined using TA universal analysis software, version 5.1.2 (TA Instruments, Crawley, UK) and were taken from the peak values of loss modulus at 1 Hz.

2.8. Statistical analysis

Measurement of glass transition and dynamic mechanical analysis were performed in duplicate, with all other analyses performed in triplicate. Results were expressed as mean ± standard deviations (SD). One-way analysis of variance (ANOVA) was used to determine the significant differences between the mean values of each test (Microsoft Office Excel 2010, Microsoft, Inc., Redmond, WA, USA). A significance level of $P < 0.05$ was used throughout the study.

3. Results and discussion

3.1. Powder characteristics

Powder characteristics of encapsulation systems after spray drying are shown in Table 1. Those seven powders were defined as S1–S7 according to their wall materials (Table 1). The EB contents of S1–S7 showed significantly ($P < 0.05$) difference as a result of different composition of wall materials. S1 with wall material consisting of lactose/WPI (4:1) mixtures had the highest EB content, which meant wall material consisting of lactose/WPI (4:1) mixtures had significantly ($P < 0.05$) higher encapsulation efficiency for EB during spray drying than wall materials consisting of lactose/MD/WPI mixtures. This might be due to the highest lactose content in S1, which could form a large extent of amorphous structure to easily entrap EB molecules during spray drying. For encapsulation systems with wall materials consisting of lactose/MD/WPI mixtures, the lower DE values of MD in the wall materials, the higher was flavor encapsulation efficiency. This was in agreement with the study of Bangs and Reineccius (1982). They reported that volatiles retention in maltodextrin decreased with increasing DE values. In addition, wall materials with the same DE values maltodextrin (S2 and S3, S4 and S5, S6 and S7) had higher flavor encapsulation efficiency when the MD content in the wall systems was higher. This might be due to the addition of miscible high molecular weight components increasing the viscosity of encapsulation matrix during spray drying.

In addition, S1 with wall material consisting of lactose/WPI (4:1) mixtures showed significantly ($P < 0.05$) lower water content and water activity after spray drying compared to those encapsulation systems with wall materials consisting of lactose/MD/WPI mixtures (Table 1), which might affect the flavor retention in encapsulation systems during storage. Particle size and particle density of encapsulation systems (S1–S7) also showed difference as a result of different composition of wall materials (Table 1). Moreover, the morphological characteristics of encapsulation systems were also determined and are shown in Table 2. In this study, three morphological characteristics (circularity, elongation and convexity) were used to identify the particle shape of encapsulation systems (Li, Roos, & Miao, 2016a). Powders with MD (DE 23–27) (S6 and S7) had lower circularity and convexity values, while they give higher elongation values, which indicated that the particles of powders with MD (DE 23–27) had less rounded shape and rougher surface than those of powders with MD (DE 4–7) and MD (DE 13–17).

3.2. Water sorption

An overall water sorption behaviour of encapsulation systems at various water activities (0.44–0.76 a_w) was plotted as a function of time (Fig. 1). Since EB in powders kept releasing during storage period, the water contents of encapsulation systems shown in Fig. 1 were not only calculated according to the mass changes of encapsulation systems during storage, but they were modified according to the mass changes resulting from flavor release during storage. The initial water contents of encapsulation systems before equilibration are shown in Table 1. S1 with wall material consisting of lactose/WPI (4:1) mixtures showed the highest steady water

Table 1
Powder characteristics of encapsulation systems with wall materials consisting of lactose/MD/WPI mixtures after spray drying.

Systems	Water content (g/100 g of solids)	Water activity	d_{50} (μm)	SSA (m^2/kg)	Particle density (g/cm^3)	Ester content (mg/g of dry powders)	Encapsulation efficiency (%)
S1 lactose/WPI 4:1	2.50^{c}±0.24	0.12^{f}±0.01	23.73^{c}±0.21	762.9^{c}±7.1	1.1457^{b} ± 0.0007	81.34^{a}±0.93	48.80^{a}±0.56
S2 lactose/MD (4–7)/WPI 3:1:1	3.13^{b} ± 0.15	0.16^{a}±0.00	23.77^{c}±0.54	711.0^{d} ± 14.5	1.1646^{a}±0.0009	71.67^{c}±1.13	43.01^{c}±0.87
S3 lactose/MD (4–7)/WPI 1:3:1	3.25^{b} ± 0.06	0.13^{d} ± 0.00	26.50^{a}±0.08	584.0^{f}±5.2	1.0376^{f}±0.0171	77.53^{b} ± 1.99	46.52^{b} ± 1.12
S4 lactose/MD (13–17)/WPI 3:1:1	3.26^{b} ± 0.11	0.14^{c}±0.00	23.43^{c}±0.09	728.5^{d} ± 1.6	1.0878^{d} ± 0.0010	69.39^{c}±2.57	41.63^{c}±1.54
S5 lactose/MD (13–17)/WPI 1:3:1	3.61^{a}±0.16	0.15^{b} ± 0.01	21.73^{d} ± 0.09	782.8^{b} ± 3.1	1.0843^{de} ± 0.0095	71.84^{c}±0.37	43.10^{c}±0.22
S6 lactose/MD (23–27)/WPI 3:1:1	3.55^{a}±0.09	0.16^{a}±0.00	21.57^{d} ± 0.21	818.5^{a}±17.2	1.1413^{c}±0.0005	61.34^{e}±1.04	36.81^{e}±0.62
S7 lactose/MD (23–27)/WPI 1:3:1	3.33^{a}±0.11	0.16^{a}±0.01	25.37^{b} ± 0.09	616.6^{e}±17.6	1.0833^{e}±0.0008	65.55^{d} ± 1.19	39.33^{d} ± 0.72

[1] Values are mean ± standard deviation (n = 3).
[2] $^{a-f}$ Values within columns with different superscripts are significantly different at $P < 0.05$.

Table 2
Morphological characteristics of encapsulation systems with wall materials consisting of lactose/MD/WPI mixtures.

Systems	Circularity	Elongation	Convexity
S1	0.9137^{ab} ± 0.0096	0.1603^{ab} ± 0.0102	0.9947^{a}±0.0009
S2	0.8970^{b} ± 0.0029	0.1770^{a}±0.0028	0.9933^{a}±0.0005
S3	0.9210^{a}±0.0028	0.1400^{b} ± 0.0024	0.9947^{a}±0.0050
S4	0.8873^{c}±0.0025	0.1870^{a}±0.0021	0.9920^{b} ± 0.0000
S5	0.9093^{ab} ± 0.0121	0.1483^{b} ± 0.0157	0.9940^{a}±0.0008
S6	0.8847^{c}±0.0107	0.1893^{a}±0.0109	0.9920^{b} ± 0.0008
S7	0.8930^{bc}±0.0041	0.1763^{a}±0.0049	0.9923^{b} ± 0.0005

[1] S1–S7: Table 1.
[2] Values are mean ± standard deviation (n = 3).
[3] $^{a-c}$ Values within columns with different superscripts are significantly different at $P < 0.05$.

content at 0.44 a_w, while there were only minor difference among the steady water contents of S2–S7 (Fig. 1A). At 0.54 a_w, loss of sorbed water was found in S1 after equilibration for 48 h indicating the crystallisation of amorphous lactose. However, the water content of encapsulation systems with wall materials consisting of lactose/MD/WPI mixtures did not show significant decrease with equilibration at 0.54 a_w for 216 h (Fig. 1B), which was due to the presence of high molecular weight maltodextrin delaying lactose crystallisation. Potes et al. (2012) also showed similar results. According to their study, interactions between lactose and maltodextrin could reduce or delay the rate of diffusion or mobility of lactose molecules to form crystals (nucleation) or crystal growth.

Loss of sorbed water of encapsulation systems with lactose/MD/WPI (3:1:1) mixtures was obviously observed at 0.65 a_w and 0.76 a_w after storage for 24 h and 12 h, respectively, while only a minor loss of sorbed water was found in encapsulation systems with wall materials consisting of lactose/MD/WPI (1:3:1) mixtures with equilibration at 0.65 a_w and 0.76 a_w for 216 h (Fig. 1C and D). Inhibition of lactose crystallisation was more pronounced in systems with higher ratios of maltodextrin, which agreed with previous studies (Potes et al., 2012; Silalai & Roos, 2011b). Additionally, encapsulation systems with high DE (13–17 and 23–27) MD showed higher stable water content at 0.65 a_w and 0.76 a_w than those with low DE (4–7) MD, which meant encapsulation systems with a high DE MD showed more significant inhibition of lactose crystallisation. That might be due to lower molecular weight carbohydrate present in the high DE MD that could exhibit molecular motions and diffusion rates exceeding those of the higher molecular weight MD carbohydrates (Potes et al., 2012).

The increase of water content in encapsulation systems can lead to an increase in free volume by decreasing the molecular packing of the matrix molecules (van den Dries, van Dusschoten, Hemminga, & van der Linden, 2000). According to Rosenberg, Kopelman, and Talmon (1990), water uptake at high relative humidity destroyed the capsule structure and as a result, the release of the encapsulated flavor during storage increased with an increase in relative humidity. Thus, the different water sorption behaviours of encapsulation systems (S1–S7) might result in different rates of flavor diffusion and release in the amorphous matrix. Furthermore, the structure of amorphous matrix collapsed as lactose crystallisation occurred when water content increased at high water activities ($a_w \geq 0.54$), which might result in a quick release of flavor from encapsulation systems. The addition of MD in wall systems increased viscosity of systems and decrease diffusion of molecules, which could delay the crystallisation of amorphous lactose and might reduce the rates of flavor release.

3.3. Glass transition

The glass transition temperatures, T_g (onset), and initial crystallisation temperatures, T_{ic}, of encapsulation systems are shown in Table 3. T_g values decreased with increasing water activity or storage time, which showed typical water plasticization of amorphous materials (Haque & Roos, 2004; Jouppila, Kansikas, & Roos, 1997; Potes et al., 2012).

The T_g values of encapsulation systems with wall materials consisting of lactose/MD/WPI mixtures (S2–S7) were higher compared to the T_g values of encapsulation system with wall material consisting of lactose/WPI mixtures (S1) with equilibration at 0.44–0.76 a_w before showing lactose crystallisation. Silalai and Roos (2011c) reported similar results. They stated that the T_g values of skim milk-maltodextrin (DE9 and DE17) solids were higher than those of skim milk powder at 0–0.76 a_w. Furthermore, the T_g values of encapsulation systems with wall materials consisting of lactose/MD/WPI (1:3:1) mixtures were higher than those of encapsulation systems with wall materials consisting of lactose/MD/WPI (3:1:1) mixtures (Table 3), which was more obvious at high water activity ($a_w \geq 0.54$). The lower T_g values of encapsulation systems with lower amount of maltodextrin might account for the presence of high lactose contents, which made low molecular weight sugars dominant and consequently depressed the T_g (Buera, Levi, & Karel, 1992; Roos & Karel, 1991). In addition, encapsulation systems with maltodextrin in the wall systems showed significantly higher initial crystallisation temperatures than those of encapsulation system with wall material consisting of lactose/WPI (4:1) mixtures at all experimental a_w (Table 3), which confirmed that the presence of maltodextrin could delay the crystallisation of amorphous sugars.

When the temperature is around or above T_g, various changes such as increase of free volume and specific heat, as well as decrease of viscosity, are noticed in amorphous materials. The stability of encapsulated components was significantly influenced by the state of wall materials (Drusch, Serfert, Van Den Heuvel, & Schwarz, 2006; Levi & Karel, 1995; Zhou & Roos, 2012). In addition, the influence of T_g on the translational diffusivity or the diffusion of molecules has an important impact on the diffusion-

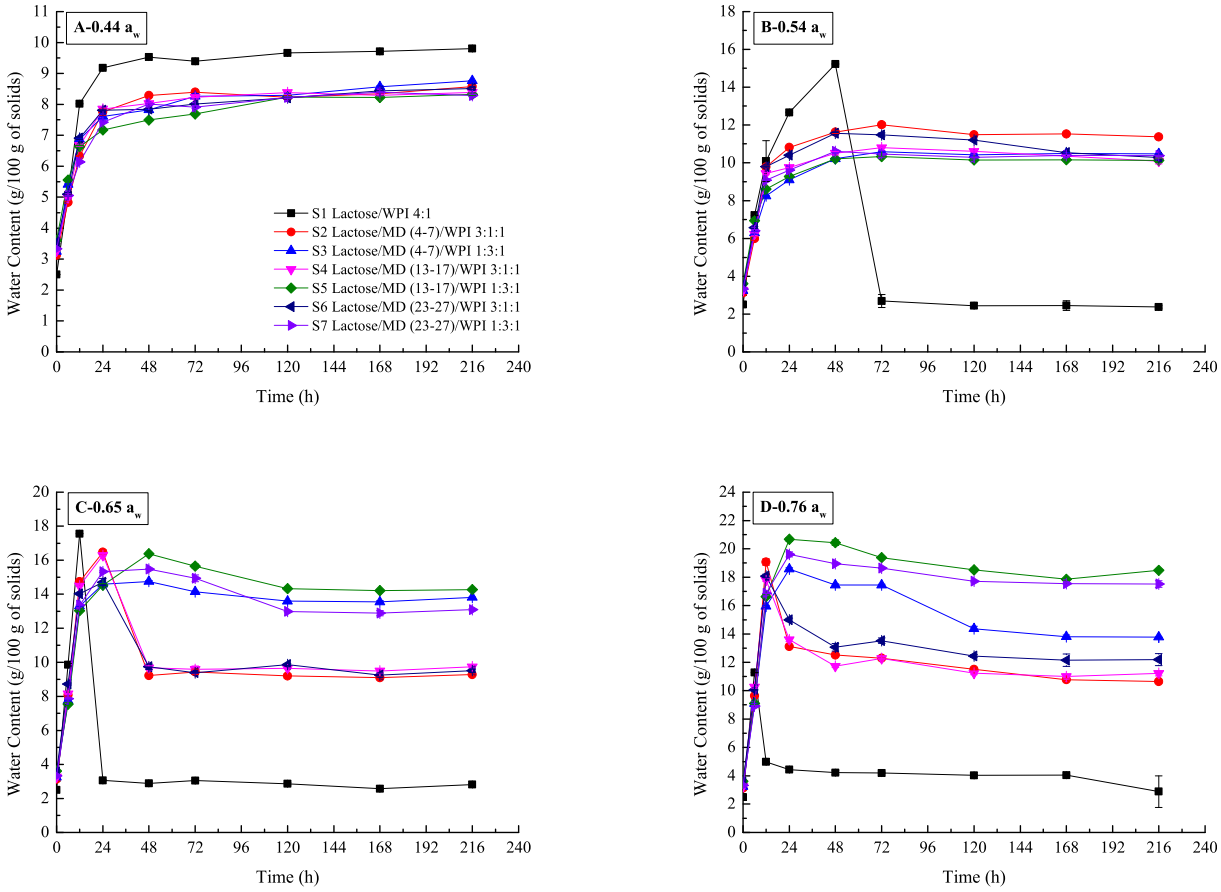


Fig. 1. Water sorption of encapsulation systems equilibration at 0.44 aw (A), 0.54 aw (B), 0.65 aw (C), and 0.76 aw (D) at 25 °C. Loss of sorbed water at 0.54 aw, 0.65 aw, and 0.76 aw indicates lactose crystallisation.

controlled physical and chemical processes. Since the presence of maltodextrin in encapsulation systems could reduce the rate of diffusion or mobility of lactose molecules, the rate of flavor release from encapsulation systems might vary according to the types and contents of maltodextrin in the encapsulation systems (S1–S7).

3.4. Mechanical properties

The mechanical properties of encapsulation systems (S1–S7) were determined using a DMA. The storage and loss modulus changes of encapsulation systems after spray drying and equilibration at 0.44 a_w, 0.54 a_w, and 0.65 a_w at 25 °C for 216 h, 12 h, and 6 h, respectively are shown in Fig. 2. Moreover, the modulus changes of encapsulation systems with equilibration at 0.44 a_w for 6 h, 12 h, and 24 h, respectively, are shown in Fig. 3. Since encapsulation systems showed lactose crystallisation after storage at 0.76 a_w for 6 h, the results of storage modulus and loss modulus for encapsulation systems equilibration at 0.76 a_w were not presented in this study. The changes of storage modulus and loss modulus for encapsulation systems after spray drying (Initial powders) were small with increasing temperature from 0 to 120 °C (Fig. 2A1 and B1), which was due to the low water content of encapsulation systems (Table 1). The storage modulus of encapsulation systems decreased significantly at the glass transition region after equilibration at 0.44 a_w, 0.54 a_w, and 0.65 a_w (Fig. 2A2, A3, and A4). Moreover, the magnitudes of storage modulus changes of encapsulation systems increased with increasing storage time at 0.44 a_w (Fig. 3A1, A2, and A3). Since previous studies (Roudaut, Simatos, Champion, Contreras-Lopez, & Le Meste, 2004; Silalai & Roos, 2010) have indicated that the magnitudes of modulus changes were relative to molecular mobility, those results confirmed that increasing water content of solids systems could increase the molecular mobility, which might result in high rates of flavor release from matrix.

Furthermore, encapsulation systems with lactose/MD/WPI (3:1:1) mixtures as wall materials showed more significant changes in their storage modulus compared to those with lactose/MD/WPI (1:3:1) mixtures as wall materials, while the storage modulus of S1 without MD in wall systems showed the most significant change with increasing water content. Thus, the addition of maltodextrin in wall systems could increase stiffness and reduce molecular mobility of lactose molecules when water content increased, which was in agreement with previous study (Silalai & Roos, 2011b). In addition, S5 with lactose/MD (13–17)/WPI (1:3:1) mixtures showed the smallest magnitudes of storage modulus changes with increasing water content at 0.44–0.65 a_w, which might show excellent flavor encapsulation property with storage at high RH. These results indicated that the addition of maltodextrin in wall systems decreased molecular mobility of wall systems when water content increased, which might decrease the diffusion of flavor molecules.

The loss modulus of encapsulation systems was small and showed minor changes when the temperatures were below the glass transition and they increased dramatically and reached peak values with increasing temperature to the glass transition region. Furthermore, the magnitudes of loss modulus changes increased

Table 3
Glass transition temperatures, T_g, and initial crystallisation temperatures, T_{ic}, of encapsulation systems with wall materials consisting of lactose/MD/WPI mixtures storage at 0.44 a_w, 0.54 a_w, 0.65 a_w, and 0.76 a_w, respectively, at 25 °C for different time.

Water activity	Time (h)	Temperature (°C)	Systems						
			S1	S2	S3	S4	S5	S6	S7
Initial powders	0	T_g	69 ± 0.5	72 ± 1.0	N/O	68 ± 0.5	84 ± 0.0	66 ± 1.0	70 ± 0.0
		T_{ic}	134 ± 0.0	N/O	N/O	N/O	N/O	N/O	N/O
0.44	6	T_g	37 ± 1.0	55 ± 1.0	N/O	42 ± 1.0	60 ± 1.0	42 ± 0.0	43 ± 1.0
		T_{ic}	110 ± 0.5	N/O	N/O	N/O	N/O	N/O	N/O
	12	T_g	29 ± 0.0	36 ± 0.0	37 ± 1.0	35 ± 1.0	41 ± 1.0	33 ± 1.0	37 ± 1.0
		T_{ic}	88 ± 0.5	113 ± 0.5	102 ± 0.0	110 ± 0.5	N/O	106 ± 1.0	108 ± 0.0
	24	T_g	21 ± 0.0	28 ± 0.5	32 ± 0.5	30 ± 0.5	40 ± 1.0	25 ± 0.0	39 ± 1.0
		T_{ic}	80 ± 1.0	98 ± 1.0	92 ± 1.0	97 ± 1.0	N/O	95 ± 1.0	98 ± 0.0
	48	T_g	20 ± 1.0	28 ± 1.0	29 ± 0.0	27 ± 0.5	40 ± 1.0	25 ± 0.0	39 ± 0.0
		T_{ic}	77 ± 0.0	95 ± 0.5	89 ± 0.5	94 ± 1.0	N/O	93 ± 0.5	95 ± 1.0
	72	T_g	21 ± 0.0	25 ± 0.0	43 ± 1.0	27 ± 0.0	41 ± 1.0	24 ± 0.5	40 ± 0.0
		T_{ic}	77 ± 0.0	92 ± 0.5	87 ± 1.0	92 ± 0.0	N/O	89 ± 1.0	94 ± 0.0
	120	T_g	21 ± 0.5	28 ± 0.0	32 ± 0.5	26 ± 0.5	42 ± 0.0	24 ± 0.5	38 ± 0.0
		T_{ic}	75 ± 0.0	90 ± 1.0	87 ± 0.5	88 ± 0.0	N/O	87 ± 0.5	89 ± 0.0
	168	T_g	21 ± 0.5	28 ± 0.0	32 ± 1.0	26 ± 0.5	42 ± 0.0	24 ± 0.5	38 ± 0.0
		T_{ic}	75 ± 0.0	90 ± 1.0	87 ± 0.5	88 ± 0.0	N/O	87 ± 0.5	89 ± 0.0
	216	T_g	19 ± 1.0	23 ± 1.0	25 ± 1.0	24 ± 0.0	40 ± 1.0	21 ± 0.5	39 ± 0.5
		T_{ic}	73 ± 0.0	87 ± 1.0	83 ± 0.0	86 ± 0.0	N/O	83 ± 0.5	89 ± 0.0
0.54	6	T_g	32 ± 0.5	38 ± 1.0	37 ± 1.0	38 ± 1.0	42 ± 0.0	36 ± 0.0	38 ± 0.5
		T_{ic}	96 ± 0.0	118 ± 1.0	103 ± 0.0	117 ± 0.5	N/O	109 ± 1.0	112 ± 0.0
	12	T_g	10 ± 1.0	16 ± 1.0	28 ± 0.0	16 ± 0.5	36 ± 0.0	14 ± 0.0	32 ± 0.0
		T_{ic}	65 ± 0.5	86 ± 0.0	77 ± 1.0	80 ± 0.0	N/O	79 ± 0.0	82 ± 0.0
0.65	6	T_g	17 ± 1.0	25 ± 1.0	39 ± 1.0	23 ± 0.0	38 ± 1.0	20 ± 0.0	35 ± 1.0
		T_{ic}	73 ± 1.0	97 ± 1.0	90 ± 0.0	92 ± 0.0	N/O	88 ± 0.5	93 ± 0.0
0.76	6	T_g	11 ± 0.0	19 ± 0.0	39 ± 0.5	14 ± 0.0	34 ± 1.0	13 ± 0.0	31 ± 0.5
		T_{ic}	64 ± 1.0	85 ± 0.0	82 ± 1.0	80 ± 0.0	N/O	78 ± 0.0	83 ± 1.0

[1] S1–S7: Table 1; Initial powders were the powders after spray drying.
[2] Values are mean ± standard deviation (n = 2); N/O: Not observed.

with increasing water content (Fig. 2B1–B4 and Fig. 3B1–B3), which confirmed that the mechanical modulus of the systems were affected by water plasticization and increasing water content could increase the molecular mobility of solids systems. S1 with lactose/WPI (4:1) mixtures showed the largest magnitudes of loss modulus changes, and the magnitudes of loss modulus changes for encapsulation systems with wall materials consisting of lactose/MD/WPI (3:1:1) mixtures (S2, S4, and S6) were larger compared to those with wall materials consisting of lactose/MD/WPI (1:3:1) mixtures (S3, S5, and S7). In addition, S3 and S5 showed smaller magnitudes of loss modulus changes than S7 with high DE maltodextrin. Since the main component responsible for the modulus change around glass transition region of encapsulation systems was the carbohydrate phase (Silalai & Roos, 2011b), the ratios and types of maltodextrin in wall systems affected molecular mobility and free volume of encapsulation matrix significantly, which meant it might influence the diffusion of flavor components.

The appearance of transitional mobility of molecules around the glass transition results in the frequency-dependent α-relaxation (Roudaut et al., 2004; Royall et al., 2005; Silalai & Roos, 2011a). The α-relaxation temperatures, T_α, of encapsulation systems with equilibration at various water activities were taken from the peak values of loss modulus at 1 Hz (Table 4). The T_α values of encapsulation systems decreased with increasing storage RH or storage time, which was in agreement with previous study (Silalai & Roos, 2011c). Encapsulation systems with wall materials consisting of lactose/MD/WPI mixtures showed higher T_α values than that with wall material consisting of lactose/WPI (4:1) mixtures after equilibration at 0.44 a_w, 0.54 a_w, 0.65 a_w, and 0.76 a_w for 216 h, 12 h, 6 h, and 6 h, respectively, while the T_α values of encapsulation systems with higher amount of maltodextrin (S3, S5, and S7) were higher than those of encapsulation systems with lower amount of maltodextrin (S2, S4, and S6) (Table 4). Additionally, S5 gave the highest T_α values after equilibration at 0.44 a_w, 0.54 a_w, 0.65 a_w, and 0.76 a_w for 216 h, 12 h, 6 h, and 6 h, respectively. Thus, the addition of maltodextrin in wall systems decrease the effect of water plasticization on structural relaxations of encapsulation systems and viscous flow characteristics of amorphous matrix, which might affect the flavor diffusion and release in encapsulation systems during storage.

3.5. Flavor retention

The effects of water plasticization on the time-course of the flavor release in encapsulation systems with different wall materials are shown in Fig. 4. Moreover, the flavor contents in encapsulation systems after equilibration at 0.44–0.76 a_w for 216 h are shown in Table 5. The flavor retention in encapsulation systems was affected significantly by storage RH (Fig. 4). The higher was the storage RH, the lower was the flavor retention. The EB retention in encapsulation systems showed only a minor decrease with storage at 0.44 a_w for 216 h, especially in encapsulation systems with wall systems consisting of lactose/MD (23–27)/WPI (3:1:1) mixtures (Fig. 4A). Since S1 had the highest encapsulation efficiency after spray drying, it still had the highest EB content after equilibration at 0.44 a_w for 216 h (Table 5). However, the EB retention in S1 dropped sharply with storage at 0.54 a_w, while the EB retention in S2–S7 showed only slightly decrease with equilibration at 0.54 a_w (Fig. 4B). This was due to the lactose crystallisation in S1 that destroyed the structure of amorphous matrix and EB was expelled from crystallized matrix. For S2–S7, since there was maltodextrin in the wall systems, which could delay lactose crystallisation by increasing viscosity and decreasing diffusion of lactose molecules, the EB in those systems were much more stable than that in S1. The EB content of S1 was significantly lower than those of S2–S7 after equilibration at 0.54 a_w for 216 h (Table 5). In addition, the rate of EB release from S1 decreased after 72 h at 0.54 a_w, which was corresponding to the result of water sorption at 0.54 a_w (Fig. 1B). This

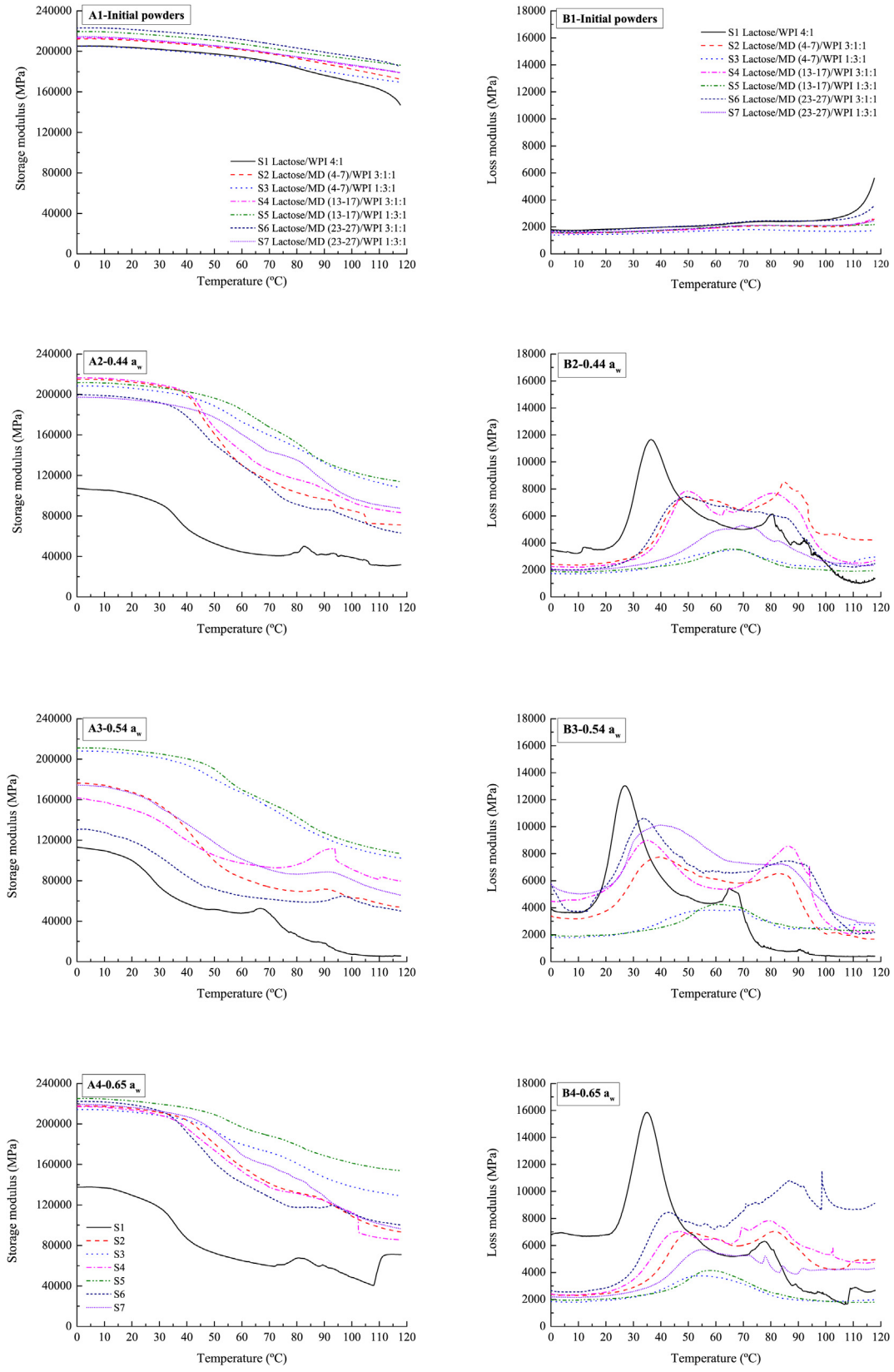


Fig. 2. Storage modulus (A1, A2, A3, and A4) and loss modulus (B1, B2, B3, and B4) of encapsulation systems after spray drying and equilibration at 0.44 aw, 0.54 aw, and 0.65 aw at 25 °C for 216 h, 12 h, and 6 h, respectively. Initial powders were the powders after spray drying.

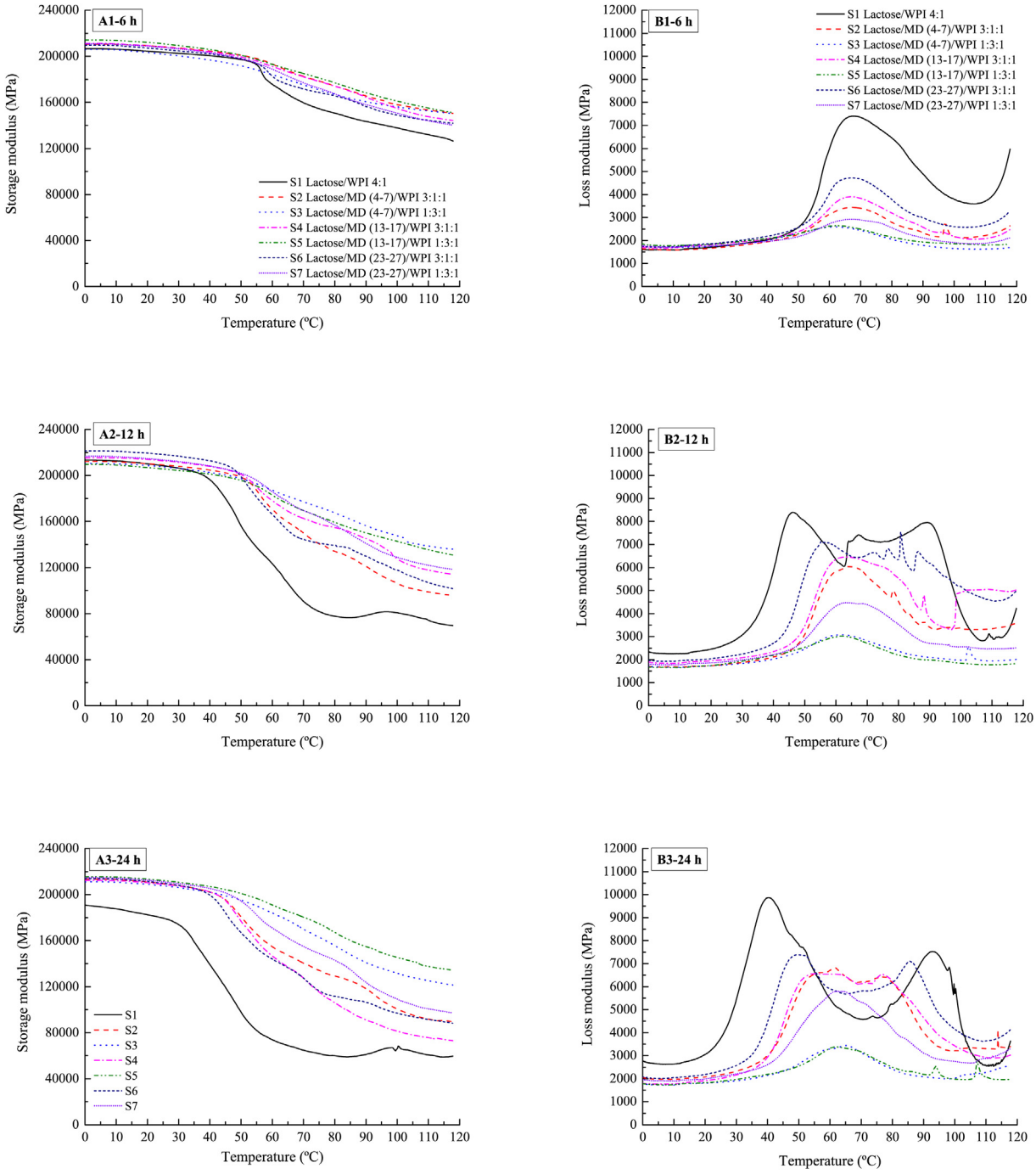


Fig. 3. Storage modulus (A1, A2, and A3) and loss modulus (B1, B2, and B3) of encapsulation systems equilibration at 0.44 aw at 25 °C for 6 h, 12 h, and 24 h, respectively.

might be due to the completely collapse of amorphous matrix after lactose crystallisation, which resulted in re-encapsulation of flavour compound in the collapse matrix (Goubet et al., 1998). Furthermore, EB retention of S1 dropped more sharply with storage at higher relative humidity conditions (Fig. 4C and D), which resulted from higher rate of lactose crystallisation at higher water activity. At 0.65 a_w, S6 had the highest EB retention, which meant the rate of flavor release from S6 was the lowest. However, since the encapsulation efficiency of S6 was the lowest after spray drying, the EB content of S6 was not higher compared to those of other encapsulation systems with wall materials consisting of lactose/MD/WPI mixtures (Table 5). Additionally, the flavor retentions of encapsulation systems were lower at 0.76 a_w compared to those at 0.65 a_w. The flavor retention of S3 showed rapid decrease again after 72 h storage at 0.76 a_w, while the flavor retention of other encapsulation systems showed only slightly decrease after 12 h. Therefore, wall systems consisting of lactose/MD (13–17 or 23–27)/WPI (1:3:1) mixtures showed better encapsulation properties for EB at 0.44–0.76 a_w.

Comparing water sorption results and flavor retention results of encapsulation systems (Figs. 1 and 4), the decrease of flavor retention were corresponding to the changes of water contents. The water contents of encapsulation systems increased slowly or decreased sharply after 24 h at 0.44–0.76 a_w, while the flavor

Table 4
α-relaxation temperatures (°C), T_α, of encapsulation systems with wall materials consisting of lactose/MD/WPI mixtures storage at 0.44 a_w, 0.54 a_w, 0.65 a_w and 0.76 a_w, respectively, at 25 °C for different time.

Water activity	Time (h)	Systems						
		S1	S2	S3	S4	S5	S6	S7
Initial powders	0	75.4 ± 0.04	76.5 ± 0.04	74.0 ± 0.02	73.6 ± 0.02	72.3 ± 0.01	75.2 ± 0.02	72.2 ± 0.02
0.44	6	68.3 ± 0.04	67.2 ± 0.01	61.7 ± 0.03	67.2 ± 0.03	62.8 ± 0.02	67.3 ± 0.05	67.3 ± 0.02
	12	46.1 ± 0.04	64.1 ± 0.01	61.8 ± 0.02	63.1 ± 0.03	61.8 ± 0.03	56.5 ± 0.05	63.2 ± 0.02
	24	40.5 ± 0.04	55.5 ± 0.02	58.3 ± 0.01	53.8 ± 0.01	61.8 ± 0.04	50.3 ± 0.04	61.9 ± 0.08
	216	36.3 ± 0.12	49.3 ± 0.10	56.7 ± 0.10	49.2 ± 0.06	65.1 ± 0.05	48.8 ± 0.12	62.2 ± 0.10
0.54	6	52.3 ± 0.04	64.6 ± 0.02	60.0 ± 0.05	67.3 ± 0.04	61.7 ± 0.06	57.9 ± 0.01	65.9 ± 0.01
	12	26.9 ± 0.01	39.3 ± 0.04	52.8 ± 0.01	36.0 ± 0.01	60.6 ± 0.04	33.6 ± 0.02	39.9 ± 0.05
0.65	6	34.8 ± 0.05	50.7 ± 0.03	53.8 ± 0.01	46.9 ± 0.08	58.9 ± 0.01	42.8 ± 0.01	55.8 ± 0.00
0.76	6	28.6 ± 0.03	39.0 ± 0.01	53.0 ± 0.04	35.4 ± 0.03	58.2 ± 0.05	32.6 ± 0.04	49.6 ± 0.04

[1] S1–S7: Table 1.
[2] Values are mean ± standard deviation (n = 2).
[3] Initial powders were the powders after spray drying.

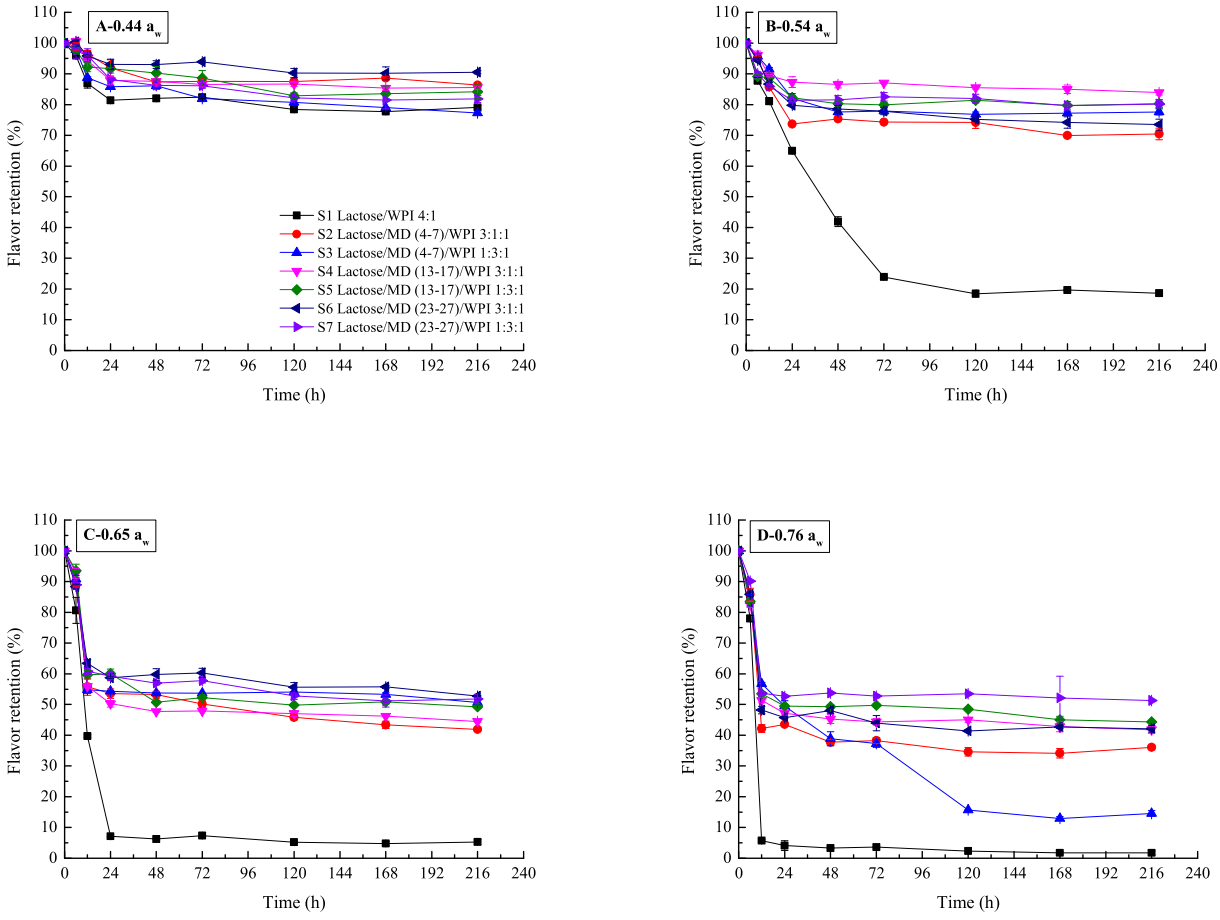


Fig. 4. Flavor retention in encapsulation systems after equilibration at 0.44 aw (A), 0.54 aw (B), 0.65 aw (C), and 0.76 aw (D) at 25 °C for different time.

retention of encapsulation systems decreased significantly in 24 h. Moreover, the glass transition temperatures of encapsulation systems also decreased significantly with storage at 0.44–0.76 a_w in 24 h (Table 3). Furthermore, the magnitudes of modulus changes increased significantly in 24 h of storage at 0.44–0.76 a_w (Fig. 3). Those results indicated that increasing water content of encapsulation systems depressed the glass transition temperatures and as a result, increased the molecular mobility of wall systems, which accelerated diffusion and release of flavor components. The presence of high molecular weight maltodextrin could delay lactose crystallisation and increase the stiffness of wall systems, and restrict the diffusion of flavor molecules during storage.

4. Conclusions

Encapsulation systems with wall materials consisting of lactose/WPI (4:1) mixtures and lactose/MD/WPI (3:1:1 or 1:3:1) mixtures were spray dried. Wall systems with lactose/WPI (4:1) mixtures had the highest encapsulation efficiency for EB after spray drying. The types and contents of maltodextrin in wall systems had minor impact on particle size and particle density, while the particles of powders with MD (DE 23–27) had less rounded shape and rougher

Table 5
Flavor contents of encapsulation systems with wall materials consisting of lactose/MD/WPI mixtures after equilibration at 0.44 a_w, 0.54 a_w, 0.65 a_w and 0.76 a_w, respectively, at 25 °C for 216 h.

Systems	Flavor content (mg/g of dry powders)			
	0.44 a_w	0.54 a_w	0.65 a_w	0.76 a_w
S1	64.33^{a}±0.48	15.15^{d} ± 0.58	4.26^{e}±0.66	1.42^{e}±0.51
S2	61.87^{b} ± 0.15	50.50^{bc}±1.36	30.06^{d} ± 0.16	25.83^{c}±0.52
S3	59.92^{bc}±0.49	60.15^{a}±0.75	39.30^{a}±0.58	11.28^{d} ± 0.73
S4	59.36^{c}±0.37	58.20^{a}±0.52	30.88^{d} ± 0.13	28.99^{bc}±0.78
S5	60.44^{bc}±1.62	57.68^{a}±0.99	35.39^{b} ± 0.44	31.87^{b} ± 0.18
S6	55.52^{d} ± 0.32	45.07^{c}±1.10	32.34^{c}±0.13	25.83^{c}±0.65
S7	53.63^{d} ± 0.73	52.53^{b} ± 0.66	33.95^{b} ± 0.26	33.61^{a}±0.12

[1] S1–S7: Table 1.
[2] Values are mean ± standard deviation (n = 3).
[3] $^{a-e}$ Values within columns with different superscripts are significantly different at $P < 0.05$.

surface than those of powders with MD (DE 4–7) and MD (DE 13–17). The presence of maltodextrin delayed the crystallisation of amorphous lactose with storage at high water activity (≥0.54 a_w), while encapsulation systems with high DE (13–17 and 23–27) MD showed higher stable water content at 0.65 a_w and 0.76 a_w than those with low DE (4–7) MD. The T_g values of encapsulation systems with wall materials consisting of lactose/MD/WPI (1:3:1) mixtures were higher than those of encapsulation systems with wall materials consisting of lactose/MD/WPI (3:1:1) mixtures, and encapsulation systems with maltodextrin in wall systems had higher initial crystallisation temperatures than those of encapsulation systems with wall materials consisting of lactose/WPI (4:1) mixtures at all experimental a_w. Moreover, the addition of maltodextrin in wall systems could increase stiffness and reduce molecular mobility of lactose molecules when water content increased, and the presence of high molecular weight maltodextrin could delay lactose crystallisation and increase the stiffness of wall systems, and restrict the diffusion of flavor molecules during storage. Wall systems consisting of lactose/MD (13–17 or 23–27)/WPI (1:3:1) mixtures showed better encapsulation properties for EB at 0.44–0.76 a_w. Those results from present study are helpful to provide data on mechanical properties and structural factors affecting encapsulation properties of food matrices, and improve the formulation of dairy-based food solids. For the future study, it would be interesting to use other flavor components or active components as core materials and test encapsulation efficiency of amorphous matrix.

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