

Title	Development of active, nanoparticle, antimicrobial technologies for muscle-based packaging applications
Authors	Morris, Michael A.;Padmanabhan, Sibu C.;Cruz-Romero, Malco C.;Cummins, Enda;Kerry, Joseph P.
Publication date	2017-04-28
Original Citation	Morris, M. A., Padmanabhan, S. C., Cruz-Romero, M. C., Cummins, E. and Kerry, J. P. (2017) 'Development of active, nanoparticle, antimicrobial technologies for muscle-based packaging applications', Meat Science, 132, pp. 163-178. doi:10.1016/j.meatsci.2017.04.234
Type of publication	Article (peer-reviewed)
Link to publisher's version	10.1016/j.meatsci.2017.04.234
Rights	© 2017, American Meat Science Association. Published by Elsevier B.V. All rights reserved. This manuscript version is made available under the CC-BY-NC-ND 4.0 license. - <a href="http://creativecommons.org/licenses/by-nc-nd/4.0/">http://creativecommons.org/licenses/by-nc-nd/4.0/</a>
Download date	2024-04-20 14:21:13
Item downloaded from	<a href="https://hdl.handle.net/10468/4594">https://hdl.handle.net/10468/4594</a>

## Accepted Manuscript

Development of active, nanoparticle, antimicrobial technologies for muscle-based packaging applications

Michael A. Morris, Siby C. Padmanabhan, Malco C. Cruz-Romero, Enda Cummins, Joseph P. Kerry



PII: S0309-1740(17)30281-4

DOI: doi: [10.1016/j.meatsci.2017.04.234](https://doi.org/10.1016/j.meatsci.2017.04.234)

Reference: MESC 7255

To appear in: *Meat Science*

Received date: 3 March 2017

Revised date: 19 April 2017

Accepted date: 27 April 2017

Please cite this article as: Michael A. Morris, Siby C. Padmanabhan, Malco C. Cruz-Romero, Enda Cummins, Joseph P. Kerry, Development of active, nanoparticle, antimicrobial technologies for muscle-based packaging applications. The address for the corresponding author was captured as affiliation for all authors. Please check if appropriate. *Mesc*(2017), doi: [10.1016/j.meatsci.2017.04.234](https://doi.org/10.1016/j.meatsci.2017.04.234)

This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting proof before it is published in its final form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.

## Development of active, nanoparticle, antimicrobial technologies for muscle-based packaging applications

*Michael A. Morris<sup>1\*</sup>, Siby C. Padmanabhan<sup>1,2</sup>, Malco C. Cruz-Romero<sup>3</sup>, Enda Cummins<sup>4</sup>, Joseph P. Kerry<sup>3\*</sup>*

<sup>1</sup>Advanced Materials and Bioengineering Research (AMBER) and School of Chemistry, Trinity College Dublin, College Green, Dublin 2, Ireland

<sup>2</sup>Department of Chemistry, University College Cork, Cork, Ireland

<sup>3</sup>Food Packaging Group, School of Food & Nutritional Sciences, University College Cork, Cork, Ireland.

<sup>4</sup>School of Biosystems & Food Engineering, Agriculture and Food Science, Belfield, Dublin.

\*corresponding authors

J.P. Kerry

E-mail: Joe.Kerry@ucc.ie

Tel: +353 (0)21 4903798

M.A. Morris

E-mail: morrism2@tcd.ie

Tel: +353 (0)1 8963096

### Abstract

Fresh and processed muscle-based foods are highly perishable food products and packaging plays a crucial role in providing containment so that the full effect of preservation can be achieved through the provision of shelf life extension. Conventional packaging materials and systems have served the industry well, however, greater demands are being placed upon industrial packaging formats owing to the movement of muscle-based products to

increasingly distant markets, as well as increased customer demands for longer product shelf-life and storage capability. Consequently, conventional packaging materials and systems will have to evolve to meet these challenges. This review presents some of the new strategies that have been developed by employing novel nanotechnological concepts which have demonstrated some promise in significantly extending the shelf-life of muscle-based foods by providing commercially-applicable, antimicrobially-active, smart packaging solutions. The primary focus of this paper is applied to subject aspects, such as; material chemistries employed, forming methods utilised, interactions of the packaging functionalities including nanomaterials employed with polymer substrates and how such materials ultimately affect microbes. In order that such materials become industrially feasible, it is important that safe, stable and commercially-viable packaging materials are shown to be producible and effective in order to gain public acceptance, legislative approval and industrial adoption.

## 1. Introduction

Food wastage is a significant cost to the food industry. According to the Food & Agriculture Organisation of the United Nations, approximately one-third or over 1.3 billion metric tons of all edible food produced, including muscle-based foods, for human consumption is lost or wasted annually throughout the supply chain due to poor practices in harvesting, storage and transport; as well as through market and consumer wastage (UN, 2017; "World Health Organization: WHO Model of Essential Medicines. [<http://www.who.int/medicines/publications/essentialmedicines/en/index.html>],"). Tackling food wastage directly could potentially result in our ability to feed our growing future predicted global population, as an alternative strategy; rather than simply focussing on our capabilities to develop ever increasing quantities of food. A reduction in food wastage would enable sustainable food production and enhance market development.

Microbial contamination is the primary cause of food wastage (Sperber, 2009). Microbial contamination of food reduces quality, limits product shelf-life and increases food-borne illness risks to consumers. Contamination occurs primarily on the surface of foods, especially for muscle-based food products. For the food industry, prevention of food spoilage is an important variable when determining profit. Moreover, prevention of food spoilage can prolong the shelf-life of products and, thus, extend market boundaries, resulting in increased market size, product placement, sales and consequently, increased profits. The growth of microorganisms on muscle-based food products largely occurs post-processing and primarily during storage, therefore, adequate packaging of such food products is paramount among all possible processing technologies in terms of delivering longer product storage stability and shelf-life (Appendini & Hotchkiss, 2002; Kerry, O'Grady, & Hogan, 2006). Additionally, post-process contamination of muscle-based food products render such as dangerous if contaminated with microbes of public health significance. Therefore, the control of such microbes in long shelf-life product packs is critically important.

Present packaging technologies work synergistically with a variety of physical, chemical and biological processes and agents to preserve food and prevent the growth and transmission of associated microorganisms (M. C. Cruz-Romero & Kerry, 2011; Rodríguez-Calleja, Cruz-Romero, O'Sullivan, García-López, & Kerry, 2012). These solutions comprise; gaseous control within packs, modification of internal pack pressures, moisture control, active packaging modifications, ingredient modification, various chilling regimes, freezing, pasteurization, cooking, fermentation, irradiation etc. (Chouliara, Badeka, Savvaidis, & Kontominas, 2008); however, usage of non-packaging processes are product-specific.

Developments in material science, particularly in the area of nanotechnology, has enabled scientific progress in many scientific spheres and allowed industrial uptake and application. Recent progress in nanoscience and surface engineering offers great promise in addressing

some of the significant problems faced by the food industry in general. One particular area which is ideal and perfectly positioned for uptake is the food packaging sector. The development of novel, natural and synthetic nanomaterials, which are antimicrobially-active, is significant and offers the potential of developing novel advanced materials and solutions for addressing the primary concerns of microbial contamination and growth in food, particularly muscle-based food products (Cushen, Kerry, Morris, Cruz-Romero, & Cummins, 2012). The global nanoenabled packaging for food and beverage markets attained revenues worth US\$6.5 billion in 2013. The market is estimated to be worth US\$15.0 billion by the end of 2020, expanding at a CAGR of 12.7% over 2014-2020 (Valdes, Mellinas, Ramos, Garrigos, & Jimenez, 2014). Tuning the size, morphology, surface and interfacial properties, development of novel nanocomplexes and composites have all enabled the development of new and improved antimicrobial systems through their integration into host systems such as plastics and laminates manufactured by the packaging industry (Azeredo, 2009; Azlin-Hasim, Cruz-Romero, Ghoshal, et al., 2015; Azlin-Hasim, Cruz-Romero, Morris, et al., 2016; Duncan, 2011; Kumar, Howdle, & Münstedt, 2005).

Polymeric compounds, owing to their many beneficial characteristics, including; high durability, high ductility and good tensile strength are used for manufacturing a major share of packaging materials. Different types and forms of plastics such as polyethylenes, polypropylenes, polyvinyl acetates, polyvinyl alcohols, polyvinyl chlorides, polyethylene terephthalates, polyamides etc. are the primary polymers used in plastic and laminate manufacture in the packaging industry (Marsh & Bugusu, 2007) for food usage. Despite their many advantages, they all possess some drawbacks. For example, micropore formation in plastics during manufacture is one drawback that compromises both containment and barrier properties.

Of all of the plastics available on the market for food usage, low density polyethylene (LDPE) requires special mention. LDPE is a widely used plastic in food packaging applications owing to its many advantages, such as; low cost, ease of processing and forming, optical properties (transparency, colour), water impermeability, but especially, because of its low processing temperature and heat-sealing ability. It is because of these latter properties that LDPE is predominantly used as the food contact plastic layer in most plastic-based laminated structures used for fresh and processed meat products. However, owing to its very hydrophobic nature and low reactivity, LDPE presents itself as a difficult substrate to functionalize and consequently, to target as a material layer for functionalisation to create antimicrobial surfaces. However, if it were possible to surface coat LDPE in a facile manner, so as to functionalize its surfaces to deliver antimicrobial activity, this surface coating could in turn improve its gas barrier and other physical properties. For example, incorporation of silver into a polymeric matrix has been shown, in addition to producing antimicrobial properties, to enhance the tensile modulus, strength, and elongation at break of formed films.

Recent progress in the areas of nanotechnology and surface engineering concepts now enable food technologists to design novel nanocomplexes and composites and integrate them in these polymer systems, either through incorporation into host matrices or onto their surfaces by utilising processes, such as; polymer blending, micro-perforation, co-extrusion, lamination, solvent casting or coating (Liu et al., 2012; Martínez-Abad, Lagaron, & Ocio, 2012). By selecting the required active/passive functionalities and processes, new packaging systems with superior properties can be developed. The dependence of product-innovation on packaging technologies makes such technologies highly desirable. Furthermore, the ever-increasing demands for more diverse high-quality consumer food-products, including that of muscle-based food products, underline the need for feasible and cost-effective innovative packaging technologies (Troy & Kerry, 2010).

Smart packaging technologies, including novel active and intelligent packaging systems, have been available on global markets for some time and have enormous potential and scope for product application. However, many initial technologies are considered bulky, labour intensive and potentially interfere in recycling programmes. However, many of the initial technologies have evolved to address these issues and the approaches adopted now aim to use minimal amounts of smart packaging components which are more effective in function and that are strategically integrated into conventional packaging materials without the need for specialised application equipment. Research developments in the areas of active and intelligent packaging technologies are, therefore, progressing rapidly and commercial applications now a reality. More recent developments suggest that smart nanotechnology-based packaging technologies are near to market. Therefore, the purpose of this review is to examine the smart packaging technologies and systems that have been, or are currently being, used for meat and meat product application and highlight those new and developing systems that may have potential for commercial use with muscle-based food packaging systems in the future.

## **2. Nanomaterials and concepts in food packaging**

Food nanotechnology is an emerging field that is still in its' adolescence stage, but has enormous potential to revolutionize the global food industry, with wide applications in food engineering, food nanosensing, development of nanostructured ingredients, food quality control, safety evaluation, food processing, preservation and food packaging. Nanotechnology has enabled almost all areas of food science from agriculture to food processing to security to nutrition and nutraceuticals to packaging. The potential for developing feasible food packaging solutions based around nanomaterials-based antimicrobials are enormous.



Nanomaterials refer to materials in which at least one of its dimensions is below 100 nm. A material's size reduction below 100 nm is normally associated with dramatic changes in their optical, electric, electronic and functional properties owing, in general, to their large surface-to-volume ratio and quantum size effects (for materials of <10 nm) (Drexler, 1986). A similar trend for antimicrobial activity was envisaged and current studies, including that from our group, underline this concept (M. C. Cruz-Romero, Murphy, Morris, Cummins, & Kerry, 2013). However, the potential antimicrobial application of a given nanoparticle (NP) depends on many factors, including; material type, (Ren et al., 2009; Ruparelia, Chatterjee, Duttagupta, & Mukherji, 2008) particle size, shape, (R. H. Wang, Xin, & Tao, 2005) functionality, hydrophilic-hydrophobic properties and usage concentration (Kim, Kim, Cho, & Cho, 2003).

Food materials, in particular, meat products naturally support the onset and proliferation of microbes on their surface due to the presence of a myriad of complex chemical species in them that can be ideal hosts of microbes. This feature, however, causes a diminishing effect on an antimicrobial's activity and the multitude of chemical species present in meat can nullify the efficiency of the antimicrobial in question by complexing with it. Therefore, instead of a direct mixing or coating of antimicrobials into or onto a film matrix, respectively, incorporating them instead into another medium which retains their functional properties and allows their application onto the chosen product is considered to be the best approach. In other words, technologies that enable the controlled supply of antimicrobials, when and where required, represent the best approach to creating functional materials. This has led to the creation of active antimicrobial packaging concepts which have resulted in active antimicrobials being incorporated as sachets into food packs, active agents dispersed within the packaging materials, coatings and immobilizing active agents located on the surfaces of packaging materials, or applying biocompatible antimicrobial materials onto or into edible

films. Although considerable research has been carried out using these concepts, marketable solutions which have been both effective and affordable have been limited. However, further innovation is happening where natural and synthetic antimicrobials are being prepared in nanoform and integrated into the packaging for improved activity, application and cost. For example, inorganic- and metal-based NPs utilised as polymeric nanocomposites, natural antimicrobial-based nanoemulsions, nanocapsules and nanocomposites, as well as coatings, are being researched and developed currently. These will all be discussed as part of this review. There are a number of established surface deposition methods that have shown potential in the development of antimicrobial active packaging materials. This review will discuss them briefly. The main surface deposition technologies for the development of antimicrobial active packaging and novel strategies for the improvement of the deposition of antimicrobials will also be discussed.

### **3. Surface activation and antimicrobial deposition procedures for the development of active packaging materials**

The commercial polymeric films used widely in food packaging applications, such as LDPE and PP, are generally inert, hydrophobic in nature and have low surface energies. Therefore, surface modification is often required to facilitate the development of polymer film surfaces with desirable functionalities or polar groupings for the attachment or deposition of antimicrobial materials. The surface modification of polymer materials involves three sequential steps: 1) cleaning or etching by removal of materials/contaminants from the surface 2) surface reactions producing functional groups and cross-linking and 3) deposition of target materials on the surface (Pelagade et al., 2010). Considering the surface chemistries of polymer substrates used for packaging muscle-based food products, especially LDPE surfaces which are chemically stable and inert, surface activation/functionalisation will be the defining step in the antimicrobial deposition process. A range of chemically-based (oxidation

by strong acids, ammonium persulfates, chemisorption or flame treatment), and radiation-based (glow plasma discharge, corona discharge, UV/ozone treatment, photoactivation (UV), laser, ion beam, electron beam and gamma radiation) surface activation processes can be used for activating the surfaces (Lee & Coote, 2016).

### **3.1. Surface functionalisation of polymer surfaces**

#### **3.1.1 Oxidation by strong acids**

For functionalising the surface of polymers by chemical solutions, polymer substrates are immersed/dipped in an appropriate volume ratio of respective chemical solution at a desired temperature (normally 50-70°C) for a desired duration (normally more than 30 min.). The most commonly used strong acids solutions for surface modification of the polymers are:

Chromic acid ( $K_2Cr_2O_7/H_2O/H_2SO_4$ ; 1:2:18, 1:5:184 and 4:5:184, mass ratio): The chromic acid solution used for treating plastics is a mixture of potassium dichromate, water and sulfuric acid in a suitable proportion (Bag, Kumar, & Maiti, 1999).

Ammonium persulfate +  $(FeNO_3)_3$ : A mixture of ammonium persulfate,  $Fe(NO_3)_3$  and water is used in suitable proportion (Bandopadhyay, Tarafdar, Panda, & Pramanik, 2004).

Piranha solution: A mixture of  $H_2O_2$  (30 %),  $H_2SO_4$  and water in a suitable proportion (Barish & Goddard, 2011).

After treatment with acid solutions, the films are dipped or rinsed and washed with water and dried (50-70°C). In all these treatments, polar groups like -OH, -CO and -COOH will be generated on the surface of the LDPE films (Bandopadhyay et al., 2004). The strong oxidising species in all these processes attack the double bonds ( $-C=C-$ ) on the surface of the polymers producing these functionalities. In the ammonium persulfate process; however, the persulfate first attack the double bond to form epoxy or diol groups, which on further oxidation by

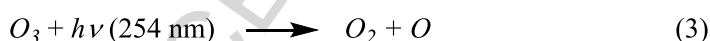
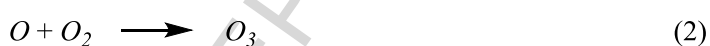
$\text{FeO}^{2+}$ , will be converted to the polar functional groups (-OH, -CO and -COOH) (Louwerse & Jan Baerends, 2007). In these chemical treatments, however, a longer period of treatment can affect/deteriorate their bulk properties as compared to shorter treatment periods (< 1 hr) which produce only surface effects (Barish & Goddard, 2011). Finally, though these treatments show good surface activation potential, they are not favoured in industrial processes owing to their negative environmental effects.

### 3.1.2 Radiation based surface activation

Glow plasma discharge, corona discharge, UV/ozone treatment and UV photoactivation are the conventionally used surface activation processes for polymers. Though the efficiency and amount of functional groups formed will differ between these processes (which require different process parameters such as time duration, power used and intensity), they all produce hydroxyl (-OH) or carboxyl (-COOH) functionalities on the plastic surface. Plasmas are ionised gases, which consist of positive and negative ions, atoms, electrons, radicals, as well as neutral species (Bogaerts, Neyts, Gijbels, & van der Mullen, 2002). Plasma treatment is a low environmental impact process with potential to make pinhole-free coatings on polymer substrates without changing the bulk properties of the material. Polymer surface activation by the plasma activated gaseous species involves the modification of the surface chemistry and structure (Yameen, 2008), where reactions between the plasma-derived gas-phase species and the surface produce functional groups and cross-linking at the surface. For example, oxygen plasma can react with the polymers to produce a variety of oxygen functional groups, including C-O, C=O, O-C=O, C-O-O and  $\text{CO}_3$  (Sanchis, Blanes, Blanes, Garcia, & Balart, 2006; J. Wang et al., 2008). In oxygen plasma, the reaction occurs between the active species from the plasma and the surface atoms, where two processes occur simultaneously: etching of the polymer through the reactions of oxygen atoms with the surface carbon atoms, giving rise to volatile reaction products, and the formation of oxygen-

rich functional groups or polar groups at the polymer surface. Glow discharge plasmas are generally used for the surface modification of polymers because the processes involved are solvent-free and dry, the consumption of chemicals is extremely low and need for sterilization of the products is eliminated (Clarke et al., 2017; Guruvenket, Rao, Komath, & Raichur, 2004; Lehocký et al., 2003; Sanchis et al., 2006). Corona discharge is a form of plasma that operates at a standard atmospheric pressure. Corona discharge also produces similar excited species as plasma process and affects the surface in a similar manner, although the effectiveness can be different.

For UV/ozone treatment, the major reactive substances generated are ozone and atomic oxygen. In the presence of the high-energy UV radiation at 185 nm, oxygen molecules will become excited and reactive atomic oxygen species are formed (Eq. 1). This reactive atomic oxygen species further react with oxygen molecules to form ozone (Eq. 2). Subsequently, the formed ozone absorbs UV radiation at 254 nm and decomposes by photo-dissociation to molecular and atomic oxygen (Eq. 3) having high oxidising potential (Jofre-Reche and Martín-Martínez 2013).



The formed ozone and atomic oxygen react with polymer surfaces and create C-O and C=O polar groups in the gas phase and –OH and –COOH surfaces in the liquid phase. An unpublished study by our group showed that the UV/ozone treatment increased ( $p < 0.05$ ) the generation of polar groups on polymer film surfaces and that the increase detected was dependent directly to exposure time. An optimisation process indicated that oxygen flow rate and exposure time increased ( $p < 0.05$ ) the formation of carboxylic groups, with optimum

effects observed when the UV/ozone treatment was carried out at  $0.5 \text{ L min}^{-1}$  oxygen flow rate for 30 min.[PhD Dissertation, Azlin-Hasim, University College Cork, 2016]

### 3.2 Antimicrobial deposition/coating methods

In the following step (step 2), the formed surface functionalities are used as an anchoring platform for further deposition of the active functionalities. For the development of antimicrobial-active packaging for food applications, inorganic- or metal-based antimicrobial NPs such as Ag, Cu, ZnO, TiO<sub>2</sub>, MgO or nanoemulsions or nanoencapsulations containing active natural antimicrobial materials can be attached through covalent, electrostatic or through hydrogen bonding interactions, covalent interactions being the most preferred. For example, and in general, silver NPs can be attached to a plastic substrate by following these sequential steps: surface activation of plastic to provide –COOH functionality, modification of the activated surface with a chelating agent (for example, a diamine such as 1,2-ethylenediamine (EDA)), and deposition of Ag or Ag NP onto the amine functional group. The Ag NP can be further protected with suitable functional groups to stabilize it against dissolution so that only a slow dissolution occurs. This slow dissolution in applications like active food packaging can be advantageous for providing a longer shelf-life of packaged food by controlled release of Ag ions, thereby achieving a lower Ag migration into the food. The chemistry behind the process (Fig. 1) is a spontaneous reaction between an acidic functional group (–COOH) and an amine group (–NH<sub>2</sub>) to yield a urethane linkage (–CO–NH–) followed by the binding of silver by amine, which occurs due to the high affinity of amines for silver (Fan, Thompson, Andrade, & Brolo, 2010).

Many variations of chemical reagents can be used to create silver loaded plastics, depending on the application, such as different diamines, different silver stabilizing molecules, etc. For example, hydrophilically-functionalised, hydrophobically-functionalised or a hydrophilic-hydrophobic-functionalised, but balanced chelating compound (e.g., nanoemulsions), can be

prepared by selecting suitable functional molecules from a variety of available ligands, chelating agents and surfactants. It is to be noted that the modification procedure of other more energetic polymeric substrates used in packaging applications with inherent functionalities (e.g., PVC, PVA, EVA etc.) are less cumbersome and therefore, processed by similar approaches. Furthermore, other methods like chemical or physical vapour deposition can be applied to deposit inorganic or metal NPs or other active inorganic nanomaterials onto activated surfaces, but these are more expensive processes, requiring sophisticated processing equipment. The chemical deposition of oxides (ZnO, TiO<sub>2</sub>, MgO and CuO) from solution can be a rather inexpensive method which can utilise similar processes as that employed for silver. Their readily available oxide surfaces make them good candidates for surface functionalization and deposition (Iijima & Kamiya, 2010).

### **3.2.1 Layer-by-layer (LBL) process**

The activated surface can also be used as a platform to deposit active antimicrobial materials (inorganic, metal or natural) by a LBL deposition process. The method is based on a sequential electrostatic-based adsorption of polycationic and polyanionic compounds from solution (Fig. 2). Other weak interactions such as van der Waals forces, hydrogen bonding and weak coordination bonding can also be used to stack layers by LBL method. For example, chitosan (polycationic) and alginate (polyanionic) are two biodegradable polymers applicable in food packaging. Sequential dip/spray coatings of these compounds or their nano-equivalents (e.g., chitosan NPs) from their dispersed solutions will produce an antimicrobial surface on the polymer substrate. These two alternate deposition steps can be repeated to make a thick coating. Similarly, inorganic (Iijima & Kamiya, 2010) and metal NPs can also be surface modified and dispersed in suitable solvents and deposited onto polymeric substrates using this approach (Antunes et al., 2011; Yang, He, Duan, Cui, & Li, 2007; Ye, Wang, Liu, & Tong, 2005). This technique, although used to assemble a wide

range of materials including DNA, enzymes, EOs, proteins, polymers etc., have seldom been used in food packaging technologies. Developmental research on these techniques are hence of high importance for developing new technologies and food packaging solutions (Fabra et al., 2016; Yang et al., 2007).

Ag and Cu, owing to their similarity in surface chemistries, can be processed by similar approaches. i.e., similar processes can be used to deposit them using the aforementioned methods (Azlin-Hasim, Cruz-Romero, Morris, et al., 2016). Similarly, metal oxide NPs ( $\text{TiO}_2$ , ZnO and MgO) can also be processed, though with required changes, depending on their other chemical aspects such as point of zero charge which determines their surface properties. These metal oxide NPs can be produced in a range of primary particle sizes. The most common procedure for the synthesis of  $\text{TiO}_2$  NPs utilizes the hydrolysis of its salt/alkoxide in an acidic solution (Sibu, Kumar, Mukundan, & Warriar, 2002; Sivakumar, Sibu, Mukundan, Pillai, & Warriar, 2004). ZnO and MgO NPs are commonly prepared by sol-gel, hydrothermal or vapour deposition processes (Jin, Sun, Su, Zhang, & Sue, 2009; Tang & Lv, 2014; Znaidi, Chhor, & Pommier, 1996). Methods such as chemical vapour condensation or nucleation from sol-gel can control the structure, size and shape of these NPs (Jin et al., 2009; Xingping et al., 2008; Znaidi et al., 1996).

### 3.2.2 Sol-gel coating process

The sol-gel process is a simple hydrolysis-condensation process by which a variety of high purity metal oxide NPs, as well as organic-inorganic hybrid systems, can be prepared. The NPs formed by sol-gel reactions are predominantly transparent owing to their nanosize dimension. A typical sol-gel reaction starts with the hydrolysis of a metal salt or metalorganic precursor (e.g. metal alkoxide) followed by extensive condensation reactions leading to extended metal oxide frameworks. One particular advantage of sol-gel process is the ease to prepare organic-inorganic frameworks, (Marini et al., 2007) mixed oxide systems,



(Sivakumar et al., 2004) or carefully doped systems (Padmanabhan et al., 2007; Sibin et al., 2002) by mixing their respective precursors and salts and allowing them to hydrolyse and polycondensate to form the gel network, followed by drying (xerogel) and annealing to form the final product. Sols can be used directly for coating on substrates, and on surface gelation, drying and heating, will be converted to the respective oxide forms. Antimicrobial silver NP-metal oxide systems and titania systems prepared through sol-gel process have shown great potential for this technique to be applied in developing antimicrobial surfaces for food packaging applications (Marini et al., 2007).

### **3.2.3 Electrospinning**

Electrospinning is a simple method, where a polymer solution jet is accelerated towards a target by an applied high voltage (tens of kV) and deposited as ultrathin polymer fibres. The conventional electrospinning system consists of three parts: 1) a source of high voltage, 2) a spinneret and 3) a grounded collector. In the electrospinning process, the high voltage connected to the end of the capillary containing liquid solution produces a high intensity electric field. With this increased field intensity, the hemispherical surface of the liquid at the end of the capillary extends and creates a conical shape known as a Taylor cone. When increasing the electric field further, the repulsive electrostatic force overcomes the surface tension of the liquid that holds it together (critical limit) and the charged strand jets out of the end of the Taylor cone. This strand of polymer solution undergoes a process of lengthening and instability during which solvent evaporates. The fibers are subsequently deposited on the collector as a non-woven fibrous layer. These fibres can be prepared into sub-micrometer sizes and antimicrobial agents can be added onto the fibres or they can be incorporated into the polymer solution beforehand and electrospun (Torres-Giner, 2011; Zhang & Yu, 2014). Antimicrobial Ag containing electrospun polymer fibres including poly(acrylonitrile) (PAN), cellulose acetate, PVP, polyvinyl acetate (PVA), PVA/polyacrylic acid (PVA/PAA) and

PMMA have been reported to show food packaging applicability (Kong & Jang, 2008; Son, Youk, & Park, 2006).

### **3.2.4 Electrospraying**

In electrospraying, a polymer solution is made to flow through an emitter applied with a high voltage at its tip. The principle is similar to that of electrospinning. When the energy of the electric field overcomes the surface tension of the solution, influenced by electrostatic forces, a Taylor's cone forms from which the solution breaks into small charged particles. The solvent evaporates from the surface of these droplets on its way out of the cone. The particle size can be tuned by controlling solution properties such as concentration and conductivity, and processing parameters such as flow rate and applied voltage. Electrospraying enables the generation of micro- and nano-sized particles simply by applying a high voltage electric field.

### **3.2.5 Chemical vapour deposition (CVD)**

In the CVD process, the material to be coated, or its chemical precursor, is vapourised and deposited onto the substrate placed inside a vacuum chamber. The vapourisation can be realised by either heating the material or its precursor, or by reducing the pressure in the chamber until it vapourises. The precursor can also be vapourised externally and introduced into the chamber. The vapourised material subsequently starts to deposit onto the substrate and a uniform coating is formed. The thickness of the coating can be controlled by adjusting the temperature and duration of the process. When high temperatures are required to deposit metals, like Ag, the polymer deposition involves low temperatures. However, the polymer process requires the introduction of two or more monomeric precursors, depending on the required end product and initiators into the chamber where they react to form polymers as they deposit on the surface. CVD can produce uniform, pure coatings of metals and polymers.

### 3.2.6 Self-assembly of block co-polymer (BCP) systems

The scope of BCP self-assembly based surface deposition of nanostructured antimicrobial materials (Ag, Cu, TiO<sub>2</sub>, ZnO, MgO and natural antimicrobials) on polymers that are widely used in food packaging materials have recently been demonstrated by our research group (Azlin-Hasim, Cruz-Romero, Ghoshal, et al., 2015). The advantages of this technique are the ability to strictly control nanoparticle size and spacing, as well as allow direct deposition onto a range of substrates. Self-assembly is a process of self-organisation of materials or components into patterns or structures without the assistance of any external forces or manipulation. In the BCP-based self-assembly process, generally, BCPs with chemically distinct polymer blocks which are linked together by a covalent bond are used. In a typical self-assembly process, a BCP such as polystyrene-*b*-polyethylene (PS-PEO) is allowed to self-assemble on a substrate at a slightly elevated temperature (<60°C) in the presence of a suitable solvent or solvent mixture that selectively swells one (or both) of the component block(s) of the BCP. The swelling allows free movement of the component groups in the structure that may have been entangled when coated, which on evaporation of the solvent(s), freezes into an energetically stable (low energy) structure. The energetically stable structures in BCPs are normally formed when the component blocks are separated to their maximum extent, possibly in order to share their interfaces to the minimum possible extent. Due to the presence of the covalent linkage in the middle, however, the movement apart of these structures are restricted, thereby causing them to freeze within a phase separated nanoscale structure. One particular advantage of the BCP self-assembly process is its ability to produce a variety of structures such as spheres, lamellae, cylinders, gyroid structures etc., thereby enabling this process to be a promising method in terms of manipulating the structure and shape of nanoscale materials.

#### 3.2.6.1 Chemistry of BCP self-assembly in brief

BCPs are composed of two or more chemically distinct polymeric segments that are usually immiscible with each other. Several types of BCPs have been reported to be capable of forming phase separated nanopatterns, including; PS-*b*-PEO, PS-*b*-PMMA, PS-poly(2-vinylpyridine) (PS-*b*-P2VP), PS-poly(4-vinylpyridine) (PS-*b*-P4VP), PS-poly(dimethylsiloxane) (PS-*b*-PDMS) and PS-poly(lactic acid) (PS-*b*-PLA) (Cummins, Ghoshal, Holmes, & Morris, 2016). The self-assembly of BCPs can be controlled by selecting BCP blocks with different molecular weight, degree of polymerisation ( $N$ ) and volume fraction ( $f$ ), which in turn will define the strength of the interaction between the blocks (represented by the A-B Flory-Huggins interaction parameter  $\chi$ ). In other words, the architecture and composition (e.g., molecular weight, molar ratio) of BCPs affect the morphologies of the self-assembled structure and form phases such as spherical, cylindrical, bicontinuous porous, or lamellar (Bates and Fredrickson 1999). The self-assembly of BCP and current research on BCP materials impregnated with various inorganic materials have been discussed in detail previously (Mai & Eisenberg; Cummins et al., 2016).

Owing to the simplicity and effectiveness of the BCP patterning technique, it was used for generating Ag nanodots on various substrates by our research group and demonstrated that this approach has the potential to be used as a simple method for developing antimicrobially-active packaging materials. Briefly, a prepared self-assembled PS-*b*-PEO pattern was used as a template to create Ag nanodots by depositing an ethanolic solution of AgNO<sub>3</sub>, which on subsequent drying and curing, was attached to the BCP pattern. The schematic of the methodology that can be used for antimicrobial deposition on the surface of the polymer is illustrated in Fig. 4. The BCP coated onto a substrate surface was microphase separated by an annealing process into a cylindrical pattern (a), the active antimicrobial Ag was subsequently incorporated onto the nanocylinders by dip- or spray-coating and a low temperature heating process (<60°C) produced an intact Ag-coated surface (b). Such self-assembled PS-*b*-PEO or

any other suitable BCP pattern can be used as templates to coat antimicrobial materials, from preformed NP solutions (Ag, Cu, TiO<sub>2</sub>, ZnO, MgO and a host of naturally-occurring antimicrobials) or their precursor salt solution.

### 3.2.7 Gravure printing

Gravure printing is a fast (beyond 15 m/sec) high-volume printing method conventionally used for printing magazines, catalogues or packaging materials. The working principle is illustrated in Fig. 5. The gravure system consists of a gravure cylinder and an impression cylinder. The gravure cylinder is made of steel and the printing image on its surface consists of engraved cells worked into a thin layer of copper, which is further coated with a chromium layer to enhance the wearing resistance of the copper. Depending on the application and the desired printing results, the depths, sizes, shape or screen ruling of the cells worked into the copper layer can be altered to adjust the print volume in ml/m<sup>2</sup>. The printing cylinder is immersed in an ink bath, which on rotation, carries the metered ink in the cells. The doctor blade attached just above the tank scrapes off excess ink, thereby leaving the unpatterned chrome surface blank. In a slightly different set up, the ink can be kept in an enclosed system with a chambered blade and transferred to the substrate through surface interactions of the nip zone between gravure cylinder and the impression cylinder. The ink rheology, complex interactions between the cell characteristics and the printing parameters used normally defines the ink transfer rate. The low viscosity ink solutions normally require levelling after deposition to form a homogeneous layer due to the structured printing image based on small cells. To offset this issue, the inked gravure cylinder first transfers the ink to a soft blanket roller and this in turn is then transferred onto the substrate.

### 3.2.8 Flexographic printing

Flexographic printing is an industrially used, very fast method for a wide range of substrates with web widths beyond 1.5m that can run at hundreds of meters per minute. The working principle is illustrated in Fig. 6. In contrast to the gravure method, it uses a soft, flexible printing plate made of rubber or a photopolymer with different hardness and material quality depending on the intended application and the ink employed. The set up consists of three parts and an impression cylinder. The first part is a fountain roller immersed in an ink bath. The second part of the printing unit is the anilox roller, normally made from ceramics. The surface of the anilox roller is engraved with small cavities or cells of a certain ink volume ( $\text{ml/m}^2$ ) to carry ink and transfer to the substrate. In a three roller system, the fountain roller supplies ink to the anilox roller and in a two roller system, the anilox roller is directly connected to a closed chambered blade system. Excess ink in the anilox roller is scraped off with a doctor blade. It is then brought into contact with the printing form cylinder that picks out the ink and transfers it to the substrate. The printing plate is either taped onto the printing cylinder or manufactured as a gapless sleeve. The plates are made by either direct laser engraving, or through light exposure, developing and washing techniques. This technique uses low to medium viscosities of inks below 500 mPa·s, which is similar to gravure printing.

### 3.2.9 Inkjet printing

There are two types of inkjet printing; continuous inkjet (CIJ) and drop-on-demand (DOD) inkjet. In DOD inkjet printing, which is used in most current applications, piezoelectrically actuated transducers are used to eject droplets from the nozzle on demand. The working principle is illustrated in Fig. 7. The ink held in the chamber is ejected by a pressure pulse generated by mechanical actuation produced by a voltage waveform (firing pulse) applied to the piezo. Ink is held inside the chamber due to surface tension and static pressure that stabilizes the meniscus at the nozzle and this is ejected as droplets once the pressure exceeds

the threshold at the nozzle. For roll-to-roll (R2R) systems, inkjet heads with large print swathe widths are preferred. They often have >1000 nozzles and can print >70mm wide at speeds beyond 50m/min<sup>1</sup>. The choice of solvent mixtures (low and high boiling point) and print parameter settings have a crucial impact on the layer print results. It is a very complex technology with a huge parameter space that needs to be taken into account for the fabrication of functional structures. The big advantage, however, is the virtually waste-free nature of this printing process which employs additive processes and digital printing forms which are literally free and can be changed on-the-fly.

### **3.2.10 Slot die coating**

Slot-die coating is a non-contact large-area processing method for the deposition of homogeneous wet films with high cross-directional uniformity. It works with solutions of a broad range of viscosities between less than 1 mPa·s and several thousand Pa·s and speeds between less than 1 m min<sup>-1</sup> and more than 600 m min<sup>-1</sup>. The method allows coating of all of the supplied liquid onto the substrate, where the wet film thickness is controlled by the flow rate, coating width and speed. The working principle is shown in Fig. 8.

## **4. Solvent casting or extrusion techniques**

Techniques such as solvent casting and extrusion are commonly used for making polymer-NP nanocomposites for packaging applications; however, the homogeneous dispersion of NPs in the polymer matrix has been an issue that generally affects the material's mechanical and barrier properties, thereby indirectly affecting antimicrobial activity. This happens mainly because of the different polarities of the polymer matrix and the additives (particles or compounds). Simple mixing or blending of particles with polymer will result in the aggregation of particles. One potential approach to achieve a uniform dispersion is by functionalising the NPs with polymer matrix-compatible organic molecules or surfactants.

Use of diacids was reported as a suitable procedure to disperse Ag NPs (Jiang, Moon, Li, & Wong, 2006). Selecting NP-binding metalorganic compounds with similar chemistries and polarities of that of the polymer matrix material such as vinyltriethoxysilane (VTES) or vinyltrimethoxysilane (VTMS) or any analogue of such compounds could be another potential approach (Melo, Aguiar, & Marques, 2015). Due to their chemical similarity and polarity, they can mix effectively in the polymer matrix without significant disturbance to their extensive linkage, thereby minimally affecting their mechanical and barrier properties which mainly depend on the extensive polymer-polymer linkages and crystallinity.

#### **5. Application of antimicrobial nanocomposites with particular emphasis on muscle-based food products**

Packaging technologies used by the meat industry fundamentally provides product protection, convenience and safety, while also addressing consumer expectation for quality and product freshness through the delivery of meat products of high quality, colour, flavour and texture (M. Cruz-Romero & Kerry, 2017; Walsh & Kerry, 2012). Packaging is also a critical component of value-added meat products offered for both export and domestic markets. In order to preserve the quality of muscle-based food products, mechanical, optical, barrier, antioxidant and antimicrobial properties are the most relevant properties required for the packaging materials (Atarés & Chiralt, 2016).

The shelf-life of a muscle-based food product is defined as the length of time that a meat product in a container will remain in an acceptable condition for its use or application, under specific conditions of storage (Morris et al., 2010). The shelf-life of muscle-based food products depends largely on the initial quality of the raw material (Carbone et al., 2016). The shelf-life of a food product is influenced by three factors: 1) product characteristics, including formulation and processing parameters (intrinsic factors), 2) the properties of the package and



3) the environment to which the product is exposed during distribution and storage (extrinsic factors) (Emblem, 2012a). Intrinsic factors include; pH, water activity ( $a_w$ ), enzymes, microorganisms and concentration of reactive compounds and many of these factors can be controlled by appropriately selecting the raw materials and ingredients, as well as the choice of processing parameters. Extrinsic factors include; temperature, relative humidity, light, total pressure and partial pressure of different gases, as well as mechanical stresses including consumer handling. Many of these extrinsic factors can affect the deterioration reactions rates that occur during storage of the food product. When considering the preservation function of packaging, it is important to recognise that whilst packaging can and does contribute to shelf-life, it cannot overcome inherent product problems, if the product at the point of packaging is unsafe or of poor quality, it is likely that the packaged product will remain unsafe or of poor quality, as packaging systems can only maintain the initial quality of the product in question. Additionally, if temperature is a key preservation factor, e.g. chilling or freezing, the packaging has only a “supporting” role to play as if temperature of the packaged muscle-based food product is allowed to rise to the point where deterioration occurs, the packaging will not compensate for this failure to manage storage conditions (Emblem, 2012b).

In order to determine the optimum packaging required to extend shelf-life of muscle-based food products, within the limitations mentioned above, it is necessary to define the cause of deterioration, i.e. what is the spoilage mechanism? It is then necessary to understand what process (if any) will be used to prevent/delay spoilage and the extent to which this will affect the packaging used and, therefore, determine its key properties (Emblem, 2012b).

The increased demand for fresh muscle-based food products with an extended shelf-life and enhanced safety, as well as changes in consumer preferences, has led to the development of innovative and novel approaches in food packaging technologies (Angiolillo, Conte, & Del Nobile, 2016). There is a growing demand in the meat industry for the use of antimicrobial

packaging, which can play a crucial role in extending the shelf-life of muscle-based food products. Over the last few years, different strategies in manufacturing packaging materials with high antibacterial efficacy have been explored for food preservation and storage purposes. As in most fresh or processed meat products, microbial contamination is found principally on the product surface. Therefore, the application of antimicrobially-active packaging can be more efficient than the addition of antimicrobial additives directly into the foodstuff (Falguera, Quintero, Jiménez, Muñoz, & Ibarz, 2011) as the packaging can actively interact with the product and the environment (Angiolillo et al., 2016). Recent developments in nanosciences and nanotechnologies offer new prospects for the development of novel antimicrobial packaging materials. Nanocomposite materials, which contain certain NPs that possess good antimicrobial activity, have been proposed as promising candidates for the development of antimicrobial packaging materials. Given the number of publications that cite antimicrobial food packaging as one of the main applications for nanotechnology and nanomaterials in the agriculture, feed and food sectors (Amenta et al., 2015; Cushen et al., 2012), it is then rather surprising to find that the number of publications which report the application of antimicrobial nanocomposite materials for the purposes of extending the shelf-life or improving the safety of actual packaged food components, especially for muscle-based food products, is surprisingly small.

Active antimicrobial packaging composites interact with packaged food and headspace to reduce, delay, or even inhibit the growth of spoilage and pathogenic microorganisms (Otoni, Espitia, Avena-Bustillos, & McHugh, 2016). The incorporation of certain antimicrobial NPs in polymers has led to the development of antimicrobially-active packaging materials that have the capability to prevent growth or inactivate microorganisms and hence, preserve the quality of muscle-based food products during transportation and storage. The antimicrobial effect that a nanocomposite packaging has on a food depends on its active ingredient,

namely; the composition of the nanomaterial that is being applied. The use of inorganic nanomaterials, such as silver NPs, titanium oxide and zinc oxide NPs and organic nanomaterials, such as chitosan and essential oils (EOs), have been reported in the literature. The polymer matrix may also have a role to play in controlling the action of the nanocomposite; for example, it may influence particle release rate, as density determines the rate of release of bioactive compounds which may be required to be either bound (immobilised) in the matrix or be released over time. Therefore, the choice of polymer matrix is a major factor in the release efficacy of the active components in the nanocomposite film (Cushen et al., 2012). The polymers commonly used in the manufacture of nanocomposites, include; polyamides (PA), nylons, polyolefins, polystyrene (PS), ethylene-vinylacetate (EVA) copolymer, epoxy resins, polyurethane, polyimides and polyethyleneterephthalate (PET) (Simon, Chaudhry, & Bakos, 2008). Since microbial contamination of most food products occurs predominantly at the surface, mainly due to post-process handling, attempts have been made to improve safety and to delay spoilage through the use of antimicrobially-active packaging films to effectively control the microbial growth on the surface of the food (Azlin-Hasim, Cruz-Romero, Morris, Cummins, & Kerry, 2015; Azlin-Hasim, Cruz-Romero, Morris, et al., 2016).

Many studies have assessed the antibacterial properties of nanocomposites involving various NPs and polymers. Fedotova et al. (2010) immobilised silver NPs in cellulose and collagen sausage casings and found that these materials exhibited high bactericidal activity against *Escherichia coli* (*E. coli*) and *Staphylococcus aureus* (*S. aureus*). The authors also reported that these materials, while exhibiting high bioactivity to different forms of microorganisms, were deemed to be non-toxic to humans and the environment.

Kumar and Münstedt (Kumar & Münstedt, 2005b) and Damm *et al.* (Damm, Münstedt, & Rösch, 2007) studied the antimicrobial effect of Ag in polyamide (PA)-based composites.

The Ag-PA nanocomposite was an effective antimicrobial against *E. coli* and *S. aureus* and that the effectiveness of the antimicrobial nanocomposite was still discernible after 28 days of testing. Damm *et al.* (Damm et al., 2007) reduced silver acetate thermally during the melting of polyamide 6/silver-nanocomposites producing polyamide 6/silver-nanocomposites with 20 nm Ag NPs. The antibacterial activity of the polyamide 6/silver-nanocomposite against *E. coli* was excellent and complete removal of this organism was achieved. Nanocomposite samples immersed in water for 100 days were found to be equally as effective as only 3% of the available  $\text{Ag}^+$  had been released after 100 days of immersion, suggesting that the antimicrobial lifetime of the nanocomposite produced could be potentially much longer than 100 days (Damm et al., 2007). For comparative purposes, poly(methyl methacrylate) (PMMA) was used to produce a PMMA-Ag nanocomposite. Although, antibacterial properties of this material was not investigated,  $\text{Ag}^+$  release was tracked and it was found that  $\text{Ag}^+$  release from the PMMA-based composite was much lower than that of its PA-based counterpart over the course of a 25-day immersion in water. Presumably this could have resulted in lower antimicrobial activity due to the role of  $\text{Ag}^+$  in the antibacterial mechanism of Ag NPs. Therefore, the polymer used, as well as the NP characteristics, can greatly influence the antibacterial properties of a nanocomposite. In the case of PA and PMMA, the authors attributed a much greater Ag ion release from PA due to its greater hydrophilicity. As ion release is dependent on hydration, the greater hydrophilicity of the polymer results in greater hydration of the NPs and, in turn, greater Ag ion release (Damm et al., 2007). Kumar and Münstedt (Kumar & Münstedt, 2005a) discussed some of the effects of the base polymer of the composites in more detail. It was found that PA crystallinity in PA-Ag composites influenced  $\text{Ag}^+$  release from the composites. The effect of initial silver concentration (% w/w) on silver ion release has also been investigated (Kumar & Münstedt, 2005a) and a greater initial silver concentration resulted in greater  $\text{Ag}^+$  release. For all samples tested, the

increased  $\text{Ag}^+$  release was non-linear as a function of time. For the first 6 days of the 14-day analysis, differences in  $\text{Ag}^+$  release from nanocomposite samples containing 2%, 4% and 8% (w/w) silver, respectively, were not significantly different. However, after day 6, a marked increase in  $\text{Ag}^+$  release was noticed in samples containing 4% and 8% silver. However, nanocomposites containing 2% silver, released  $\text{Ag}^+$  at approximately the same rate for the duration of the test and this was attributed to the characteristics of the PA-Ag nanocomposite.  $\text{Ag}^+$  release is governed by the oxidation of the silver particles to produce ions; therefore, the rate of water diffusion is an important factor, as oxidation takes place in the presence of water. The researchers determined that the rate of water diffusion increased after day 6, which led to greater oxidation and therefore more  $\text{Ag}^+$  release. Effectively,  $\text{Ag}^+$  release was limited by the rate of water diffusion over the first 6 days of the test, which explains small initial differences between samples from different silver concentrations.

(Pongnop, Sombatsompop, Kositchaiyong, & Sombatsompop, 2011) studied the effects of antibacterial activity against *E. coli* of nanosilver colloid content and silver polymer contact time for medium-density polyethylene (MDPE), PS, PET and polyvinyl chloride (PVC) containing nanosilver colloids incorporated using spray-coating and melt-blending techniques. It was observed that the viable cell count decreased with increasing concentration of nanosilver colloid and that the contact time of 150 min was sufficient for 99.9 % reduction of *E. coli* at the optimum silver content of 50 ppm for PS, PET and PVC and of 75 ppm for MDPE. However, PVC exhibited the highest percentage of *E. coli* reduction, due to higher silver release. For a given silver content, the spray-coating technique produced a better dispersion level of silver throughout the thermoplastic films and this led to more effective antibacterial performance as compared with the dry-blending technique. The antibacterial performance of the silver incorporated thermoplastic films was dependent on the chemical structure and polarity of thermoplastics only at low silver content of 25ppm. However, at

higher concentrations, the antimicrobial performance was influenced by silver content. Dispersion and agglomeration of silver particles significantly affected the antibacterial performance of the thermoplastics used. Among the thermoplastics assessed, PVC gave the highest percentage reduction of *E. coli* as the silver release from PVC was greater than that observed for MDPE, PS or PET.

(Busolo, Fernandez, Ocio, & Lagaron, 2010) obtained solvent casted antimicrobial active polylactic acid biocomposite films containing a novel silver-based antimicrobial layered silicate additive. The developed films were highly transparent with enhanced water barrier and strong biocidal properties and showed potential in extending the shelf-life of food products, including meat. Mahdi et al. (Mahdi, Vadood, & Nourdahr, 2012) evaluated the antimicrobial effect of using a nanosilver treated tray to extend the shelf-life of minced beef during storage at 3°C. The study indicated that the nanosilver tray increased the shelf-life of mince beef to 7 days compared to a shelf-life of only 2 days for common control trays and that the antimicrobial effect of the nanosilver tray was affected by the thickness of the minced meat packaged, with greater effectiveness on minced meat of 1cm in thickness compared to minced meat with a thickness of 1.5cm.

Researchers (Angiolillo et al., 2016; Nobile et al., 2004) produced polyethylene-based antimicrobial films containing silver NPs of 90nm *via* a sputtering/deposition process. These authors indicated that growth medium can affect the growth characteristics of bacteria, as the release of silver ions ( $\text{Ag}^+$ ) was affected by the growth medium, with higher  $\text{Ag}^+$  release observed in microbiological media than in real food products. However, when distilled water was used as a comparison, release of a greater concentration of silver ions was observed. Therefore, the ionic strength of the medium governed silver ion release and therefore, influenced the antimicrobial activity of the film. This may indicate that the antimicrobial activity of the antimicrobial nanocomposites can also depend on the food product used;

indicating that careful consideration should be given when choosing the food product against a particular antimicrobial nanomaterial. Brody, Strupinsky & Kline (2002) stated that certain kinds of amino acids and proteins present in the food product can affect antimicrobial activity. Therefore, it is necessary to consider the quality and quantity of amino acids and proteins in foods in terms of antimicrobial activity when films containing Ag are applied for food-quality preservation. Ishitani (1997) reported that there are largely three types of amino acids and related compounds that can affect the elution pattern of Ag and thus, influence its antimicrobial activity. The glycine-type amino acid stimulates the elution of Ag, but does not interfere in the action of Ag ions as the reaction with Ag is weak. In the lysine-type, the elution of Ag ions is weaker than with glycine; however, the association with Ag ions is relatively strong, thereby inhibiting antimicrobial activity. With cysteine-type amino acids, both the elution and association with Ag are strong; therefore cysteine significantly inhibits the antimicrobial activity of Ag (Ishitani, 1997).

Ho et al. (Ho, Tobis, Sprich, Thomann, & Tiller, 2004) developed an innovative silver-containing PEI-MA/HEA (Poly(ethylene imine)-methacrylate/2-hydroxyethyl acrylate) nanocomposite that was antibacterial on two levels. Like the other films described, the material releases  $\text{Ag}^+$ , giving it biocidal properties; however, the material also contained polyethylene glycol (PEG), which repelled microbes. The film inactivated 99.9% of *S. aureus* cells; however, when the film was intensively washed with saline solution for 6 hours, they observed only a reduction in its' antibacterial properties. Thus, even after the (complete) removal of Ag ions from the film, PEG continued repelling microbes, thereby making it a promising antimicrobial material. Li, Lee, Sheng, Cohen and Rubner (2006) also produced films which were capable of antibacterial action by both "release killing" and "contact killing" abilities. The antimicrobial films were produced *via* a "layer-by-layer" (LbL) technique, in which the material had a reservoir for releasing biocidal materials, quaternary

ammonium salts, as well as an Ag NP layer which compliments the material's contact killing properties. The antimicrobial film produced was effective, reducing 99.9 % of *S. epidermidis* and *E. coli* counts. Similarly in our research group, Azlin-Hasim et al. (Azlin-Hasim, Cruz-Romero, Cummins, Kerry, & Morris, 2016) used a LbL technique to coat commercial LDPE films with antimicrobial silver NPs. The coated LDPE films containing antimicrobial Ag had good antimicrobial activity against Gram-positive (*S. aureus*) and Gram-negative bacteria (*Pseudomonas fluorescens*) demonstrating that the LbL technique has the potential to be used as a coating method containing antimicrobial Ag NPs and that the manufactured films could potentially be applied as antimicrobial packaging.

De Silva, Prabakhsh, Lee & Kit (2015) manufactured ZnO deposited/encapsulated halloysite–poly (lactic acid) (PLA) nanocomposites for high performance packaging films with improved mechanical and antimicrobial properties. ZnO NPs were deposited on the outer and inner surfaces of halloysite nanotubes (Hal) using a novel solvothermal method and these ZnO deposited Hal (ZnO-Hal) NPs were incorporated into the PLA matrix as a reinforcing filler. PLA nanocomposite films were fabricated using the solution casting method with different filler loadings (0–10 mass %). PLA nanocomposite films with ZnO had inferior mechanical properties, while PLA films with ZnO-Hal showed significantly improved mechanical properties, where tensile strength and modulus increased by 30% and 65% with the addition of 5 mass %, respectively. Antimicrobial tests revealed that ZnO-Hal reduced bacterial counts for *E. coli* and *S. aureus* by more than 99%.

The antimicrobial activity spectrum of any antimicrobial can be enhanced by combining different antimicrobials. Metat (2015) studied the effects of commercial antimicrobial nanocomposite based nano-Ag and nano-titanium dioxide (TiO<sub>2</sub>) on PE food containers and demonstrated that nano-Ag antimicrobial food packaging applications are a novel approach toward the preservation of foods and the extension of their shelf-life. The presence of both



NPs with a concentration of 1% nano-Ag and 0.1% nano-TiO<sub>2</sub> in the commercial antimicrobial nano-Ag food packaging containers was confirmed. The structural morphology showed the intercalation of Ag and TiO<sub>2</sub> NPs in the 20-70nm range, both of spherical shape NPs, within the bulk polymer and this explained the significant antimicrobial effect observed.

Panea, Ripoll, González, Fernández-Cuello, & Albertí (2014) developed antimicrobial LDPE nanocomposite packaging materials containing a combination of ZnO and silver. The LDPE/ZnO+Ag nanocomposite inactivated the pathogenic bacteria present in meat products such as *E. coli*, *Pseudomonas aeruginosa* and *Listeria monocytogenes* (*L. monocytogenes*) and increased the shelf-life of chicken breast fillets delaying the growth of bacteria and lipid oxidation.

Morsy, Khalaf, Sharoba, El-Tanahi & Cutter (2014) incorporated 2% oregano EO, 2% rosemary EO, 100nm Ag and 110nm zinc oxide NPs into pullulan films. The developed pullulan films containing the EOs and NPs when applied to fresh turkey, raw beef or further processed ready-to-eat turkey deli meat inhibited foodborne pathogens *S. aureus*, *L. monocytogenes*, *E. coli* O157:H7 and *Salmonella Typhimurium* over a 3-week vacuum-packaged storage trial at 4°C. The authors concluded that antimicrobial films containing EOs and NPs have the potential to improve the safety and quality of muscle foods, thereby meeting the expectations of both food manufacturers and consumers. Rhim, Hong, Park and Ng (2006) developed chitosan-silver nanocomposite using a solvent-casting method. The chitosan-Ag nanocomposite showed good antimicrobial activity against food pathogenic bacteria, including; *S. aureus*, *L. monocytogenes*, *Salmonella typhimurium* and *E. coli* O157:H7, which are found in fresh or processed meat products. Wen et al. (2016) incorporated cinnamon EO- $\beta$ -cyclodextrin inclusion complex (CEO/ $\beta$ -CD-IC) into PLA nanofibers via electrospinning technique. The resulting PLA/CEO/ $\beta$ -CD nanofilm had excellent antimicrobial activity against both Gram-positive (*S. aureus*) and Gram-negative (*E.*

*coli*) bacteria and prolonged the shelf-life of fresh pork to 8 days compared to a shelf-life of only 3 days for control samples.

Hurdle technology refers to the intelligent combination of different preservation factors or techniques ('hurdles') in order to achieve multi-target, mild but reliable preservation effects (Chen et al., 2012; Leistner, 2000; Rodríguez-Calleja et al., 2012). Hurdle technology not only ensures the safety of muscle-based food products but maintains the high quality of the treated muscle-based food products as the intensity of the treatments is reduced. Based on the hurdle concept numerous investigations have been carried out to assess the efficiency of a combination of antimicrobial nanocomposite packaging systems and other mild preservation technologies. Azlin-Hasim *et al.* (Azlin-Hasim, Cruz-Romero, Morris, et al., 2015) manufactured LDPE nanocomposite films containing different concentrations of Ag NPs (0.5 and 1 % of polymer weight, (w/w)) *via* extrusion and assessed the shelf-life of chicken breast fillets wrapped with Ag/LDPE nanocomposite films in combination with modified atmosphere packaging (using conventional laminates and employing a gas mix of 40% CO<sub>2</sub>:60% N<sub>2</sub>). Independent of the concentration of Ag NPs used, the Ag/LDPE nanocomposite films significantly extended the shelf-life of the chicken breast fillets and also significantly enhanced the oxidative stability compared to the control film. The authors indicated that LDPE nanocomposite films containing Ag NPs can potentially be used as antimicrobial packaging for food applications, and that in combination with MAP, it can significantly extend the shelf-life of muscle-based food products.

Stability of the antimicrobial nanocomposite films during storage is an important parameter that is to be taken into consideration as antimicrobials can lose activity when stored for long periods. Khalaf, Sharoba, El-Tanahi, & Morsy (2013) studied the stability of pullullan films containing silver or ZnO NPs and oregano or rosemary EOs. Antimicrobial activity of the films during storage at different temperatures (4, 25, 37 and 55°C against *S. aureus* and *L.*

*monocytogenes* during 7 weeks storage) was carried out. The authors concluded that in order to maintain the antimicrobial activity of films containing EOs and NPs, films should be stored at temperatures below 25°C, as temperatures higher than 25°C significantly decreased the antimicrobial activity of films incorporating EOs or NPs.

Azlin-Hasim et al. (2016) manufactured antimicrobial Ag/PVC nanocomposite films by solvent casting and assessed their mechanical, thermal, antimicrobial (against *E. coli*, *S. aureus*, *B. cereus*, *P. fluorescens* and microflora derived from raw chicken) and shelf-life properties (chicken breast fillets). Ag/PVC nanocomposite films containing 0.5% (w/w) Ag (of 5g PVC) were prepared by dissolving PVC in THF and adding Ag NPs of 20 nm, prepared by a polyvinylpyrrolidone (PVP; 0.1M) reduction of AgNO<sub>3</sub> (0.1M), along with a plasticizer 2-bis-ethylhexyl adipate (DEHA) (30% (w/w) of PVC). The solution was homogenised and cast into a 500 µm thick film using a hand-held applicator. The agar diffusion method was used for antibacterial studies. For shelf-life studies, chicken breast fillets were wrapped with the Ag/PVC nanocomposite films in combination with a modified atmosphere packaging (using conventional laminates and employing a gas mix of 60% N<sub>2</sub>/40% CO<sub>2</sub>). The authors showed that there was an increased shelf-life of 8 days against PVC control films (6 days) and a reduction in the lipid oxidation profile. In line with the poultry industry's requirements which uses data such as total viable count (TVC), *Pseudomonas* spp., lactic acid bacteria (LAB) and total coliform counts (TCC) as indicators of processing hygiene and microbiological quality (Bolton, Meredith, Walsh, & McDowell, 2014), these authors employed these guidelines. A microbiological acceptability limit of 6 log CFU g<sup>-1</sup> for TVC was set (Azlin-Hasim et al., 2016) and the obtained changes in TVC, *Pseudomonas* spp. and LAB of MAP-packed chicken breast fillets during chilled storage was reported (Fig. 9). Furthermore, investigation of the migration features of Ag/PVC films showed that only low amounts of Ag migrated

(8.85mg/kg or 0.84mg/dm<sup>2</sup>) to the chicken meat from the film, which was well below the legal limits set by the European Union for Ag intended to come into contact with foodstuffs (not more than 60mg/kg or 10mg/dm<sup>2</sup> (EC 2002)) (Cushen et al., 2012).

As seen throughout this review, many publications in the area of antimicrobial packaging have focused on the direct insertion of antimicrobials including Ag NPs into a bulk polymer matrix *via* casting, lamination, extrusion or co-extrusion (Ghosh & Maiti, 1996; Rhim, Wang, & Hong, 2013; Sánchez-Valdes, Ortega-Ortiz, Ramos-de Valle, Medellín-Rodríguez, & Guedea-Miranda, 2009; Yeo & Jeong, 2003). These methods of insertion can be of limited effectiveness since the dispersion of the NPs can be non-homogeneous and furthermore, the antimicrobial effects become highly mass transport limited (Kumar et al., 2005). Novel methods, such as atomic layer deposition, oxygen plasma, electrochemical deposition, UV irradiation, ion implantation and sputtering (Goddard & Hotchkiss, 2007), can be used to attach Ag NPs to substrates. However, these techniques are expensive and need specialised equipment (Marini et al., 2007). From all studies to date, it has been observed that the stabilization of silver in its smallest NP or ionic state enhances its bioavailability. The higher activity of smaller silver NPs, over larger entities, may be due to more silver being available for surface contact with microorganisms owing to their larger surface-to-volume ratio. The challenge in effectively applying silver in food packaging technologies resides in minimising the silver concentration used and keeping it more bioavailable by stabilizing it with suitable agents. Citrate-based silver complex is a well-established silver formulation for antibacterial applications (Djokić, 2008). Furthermore, processes that enable the inclusion of active agents have been associated with a decrease in their mechanical and barrier properties.

Intense research is ongoing to achieve high levels of antimicrobial activities with low loads of silver by complexing and stabilizing it with harmless, biocompatible agents/ligands. The concept of direct contact materials having ultralow levels of antimicrobial material (natural or

silver) is a potentially marketable technology in the food packaging sphere. Consistent with a surface deposition approach, our group has recently reported a novel surface coating method for polymer films, avoiding bulk inclusion techniques (Azlin-Hasim, Cruz-Romero, Ghoshal, et al., 2015). This involved two steps, where a polymer film (e.g., LDPE) was first functionalised with a self-assembling, long range ordered block-copolymer (BCP) by deposition from a solvent. In this instance, we used a PS-*b*-PEO polymer (of number average molecular weight (kg/mol),  $M_n$ , of 42-b-11.5; PS is polystyrene and PEO is polyethylene oxide). The deposited film was phase separated by solvent annealing in mixed solvents (toluene/water) to form a self-assembled pattern. Subsequently, a simple ethanolic-Ag ion solution was used to selectively deposit metal into the hydrophilic PEO block and simple processing yielded a metal nanodot array on the substrate surface that mimicked the original BCP pattern formed by the self-assembly process. The molecular weight of the BCP used controlled the size of nanodots formed, however it was noted that the size and structure of the nanodot arrays could also be controlled using different concentrations of the Ag precursor. The results suggested that the concentration of the Ag precursor used and surface coverage (%) were the most important determinants of antimicrobial activity, since they strongly correlated to the presence of a higher amount of Ag. The results also showed enhanced antimicrobial activity against *P. fluorescens* and *S. aureus*. The simple deposition process reported possesses great potential for incorporating antimicrobial NPs (natural and synthetic) onto the surfaces of most polymeric films used in the packaging industry. The atomic force micrograph (AFM) images of silver nanodots prepared by changing the molecular weight and ratio of BCP are presented in Fig. 10 to illustrate the process. Scanning electron micrograph (SEM) images of the Ag film formed with different silver precursor concentrations, as well as a schematic diagram showing the Ag deposition process is presented in Fig. 11.

## 6. Risks and chemical migration

With the introduction of nanotechnology into food packaging, the perception of risk, health and safety is also increased among consumers. Identifying and quantifying the hazards presented by nanoparticles, if any, and addressing them in order to reduce eventually determined risks are, and will be, a key research topic in the future of food packaging research. A good number of studies have been targeted at the identification of nanomaterial hazards in food packaging, however, it is acknowledged that there is still considerable uncertainty about the potential harmful effects associated with nanoscale particles (Cushen, Kerry, Morris, Cruz-Romero, & Cummins, 2013, 2014a, 2014b; Hannon et al., 2015; Kuorwel, Cran, Orbell, Buddhadasa, & Bigger, 2015; Llorens, Lloret, Picouet, Trbojevič, & Fernandez, 2012; Panea, Ripoll, González, Fernández-Cuello, & Albertí, 2014). Nanoparticles, especially when their sizes fall within the range of that associated with biomolecules and biomacromolecules, can get adsorbed and could eventually induce chemical and structural transformations. The small size of nanoparticles provide them with unique chemical, physical and functional properties that can be entirely different from their macroscale chemical counterparts. The larger surface area, nanosize, shape, surface chemistry, chemical composition and dose can also influence their adsorption or uptake by biomolecules (Donaldson, Stone, Tran, Kreyling, & Borm, 2004; Goodman, McCusker, Yilmaz, & Rotello, 2004; Sun, Fu, Lin, & Huang, 2002). Nanoparticles of a few nanometers in size can also cross the cell membrane and enter the cell cytoplasm. However, with the development of nanotechnology, it needs to be acknowledged that many (Salata, 2004), nanomaterials are currently being used in biological and medicinal applications, including; drug delivery, gene therapy, tissue engineering, as fluorescent biological labels, imaging contrast agents, DNA probes and nanoscale biochips (Kohli & Alpar, 2004; Salata, 2004).

The current level of applications of nanomaterials in food packaging is at an elementary stage; however, it is widely expected that more and more products will be available in the market over the coming years in this space. A probable increase in available nanotechnology related products will inevitably increase both human and environmental exposure to nanomaterials. Therefore, thorough risk assessment in the area of nanotechnology in the food packaging sector should clarify potential risks (O'Brien & Cummins, 2011). Although there have been studies aimed at understanding the interaction, adsorption, uptake and retention of nanomaterials that have potential in food packaging, especially non-natural antimicrobial materials based on Ag, TiO<sub>2</sub>, ZnO, Cu etc., the risk assessment of these materials are not complete (Cushen et al., 2013, 2014a; Golja et al., 2017; Panea et al., 2014). Studies showed that amongst the nanomaterials studies, those having less solubility and degradability in the biological medium, can be more dangerous compared to the soluble ones. In this regard, antimicrobials based on silver, which are the most promising inorganic antimicrobials for food application, may prove not to be problematic at all, however, detailed toxicokinetic properties including their retention in organs and secretion from the body need to be assessed. Reducing the possibility of migration in food contact packaging materials below the allowed limit is however the first and foremost step in the commercialization of antimicrobial packaging materials and technology. As part of a programme to systematically evaluate migration from different packaging materials and assess the risk of exposure, our research team has carried out a number of studies (Cushen et al., 2014b; Hannon et al., 2015). These studies used either food simulants (3% aqueous acetic acid solution or deionised water) or a selected food product (chicken breast fillets) and studied the effects of time, temperature, food and food simulant on migration. In the experiments with chicken, the migration of silver to chicken breast fillet was estimated from plasticised PVC-silver and PE-silver nanocomposites following varying storage time and temperature conditions using inductively

coupled plasma mass spectroscopy (ICPMS) and migration was found to occur within a range of 0.03–8.4 mg/kg (Cushen et al., 2013) and 0.003-0.005 mg/dm<sup>2</sup>, respectively (Cushen et al., 2014a). A sensitivity analysis revealed that silver migration from the nanocomposite to the food surface was influenced most by the percentage fill ( $p < 0.01$ ), followed by storage time ( $p < 0.01$ ) and storage temperature ( $p < 0.05$ ).

Another approach to reduce the risk associated with the use of synthetic or metal-based nanomaterials in the short-term is to continue to investigate the antimicrobial and antioxidant properties of nanoparticled materials derived from foodstuffs themselves. Continued investigation of such materials as chitin/chitosan, essential oils, organic acids etc. in nanoparticle form may ultimately prove to be the most acceptable route to developing antimicrobially-active packaging materials through the employment of chemical approaches used for attaching synthetic and metal-based NPs to packaging material surfaces.

However, all approaches to the development of the technologies described for the creation of active packaging materials for potential commercial uptake are in their initial stages of development at present and tolerance, patience and time to allow study and perfect these technologies should be provided by bodies and organisations which have the capacity to create negativity around such technologies without necessarily possessing all of the scientific facts, primarily as these facts still remain to be determined by those researchers working within the area.

## **7. Conclusion/ outlook**

The possibility of applying antimicrobials and natural antioxidants as NPs present enormous opportunities for the food scientists and stakeholders to identify, design and develop new strategies in terms of their synthesis and manipulation of matter at the nanoscale for advanced applications and market gains. Although extensive research has been carried out in the



development of antimicrobial packaging solutions, this type of active packaging has had limited commercial success mainly due to regulatory issues and also technical limitations that need to be solved (Realini and Marcos, 2014). Antimicrobial active packaging may play a role in the preservation and protection of perishable foods such as high-value meat products. For a manufacturer to invest in a new packaging system, the benefits of the packaging must be sufficient to warrant investment (Cushen & Cummins, 2017). Prolonging the shelf life of muscle-based food products has the added incentive of extending the geographical export market boundaries. High-value muscle-based food products are most likely to warrant investment in packaging to prolong the product shelf life. For consumers to accept the product in a new packaging (that uses unfamiliar technologies such as nanotechnology), the benefits of this product over a traditionally packaged counterpart must be communicated to them (Cushen & Cummins, 2017; O'Callaghan & Kerry, 2016; Troy, Ojha, Kerry, & Tiwari, 2016).

Most food chain crises are preventable with timely actions and the right investments. A multidisciplinary, collaborative and integrated approach would help develop novel technologies to address problems and bridge gaps to feed more and more people good quality food in a timely and effective manner. Therefore, the need to develop and commercialize smart and intelligent packaging technologies is higher than ever to support both food safety and security.

Cost is the defining component in the commercialization path of any technologies. If the benefits, in terms of economics, utility, applicability and consumer satisfaction derived from the technologies is consistent with sustainable manufacturing costs, then the technology can be considered as cost-effective. In this respect, if a novel smart antimicrobial packaging can be marketed that reduces the spoilage significantly by extending shelf life and, therefore, helps sustainable food production, a slight increase in price would be accepted as sustainable.

It is important for food packaging to contain food in a cost-effective way that satisfies industry requirements and consumer desires, maintains food safety and minimizes environmental impact.

## Acknowledgements

This work was funded under the National Development, through the Food Institutional Research Measure (FIRM) administered by the Department of Agriculture, Food and the Marine (Project no. 11/F/038), Enterprise Ireland Commercialisation Fund (CF/2014/4370) and Science Foundation Ireland through the AMBER Research Centre Grant (12/RC/2278).

## References

- Amenta, V., Aschberger, K., Arena, M., Bouwmeester, H., Botelho Moniz, F., Brandhoff, P., . . . Peters, R. J. (2015). Regulatory aspects of nanotechnology in the agri/feed/food sector in EU and non-EU countries. *Regulatory Toxicology and Pharmacology*, 73(1), 463-476. doi: <http://dx.doi.org/10.1016/j.yrtph.2015.06.016>
- Angiolillo, L., Conte, A., & Del Nobile, M. A. (2016). Packaging and Shelf Life of Produce *Reference Module in Food Science*: Elsevier.
- Antunes, J. C., Pereira, C. L., Molinos, M., Ferreira-da-Silva, F., Dessì, M., Gloria, A., . . . Barbosa, M. A. (2011). Layer-by-Layer Self-Assembly of Chitosan and Poly( $\gamma$ -glutamic acid) into Polyelectrolyte Complexes. *Biomacromolecules*, 12(12), 4183-4195. doi: 10.1021/bm2008235
- Appendini, P., & Hotchkiss, J. H. (2002). Review of antimicrobial food packaging. *Innovative Food Science & Emerging Technologies*, 3(2), 113-126. doi: [http://dx.doi.org/10.1016/S1466-8564\(02\)00012-7](http://dx.doi.org/10.1016/S1466-8564(02)00012-7)
- Atarés, L., & Chiralt, A. (2016). Essential oils as additives in biodegradable films and coatings for active food packaging. *Trends in Food Science & Technology*, 48, 51-62. doi: <http://dx.doi.org/10.1016/j.tifs.2015.12.001>
- Azeredo, H. M. C. d. (2009). Nanocomposites for food packaging applications. *Food Research International*, 42(9), 1240-1253. doi: <http://dx.doi.org/10.1016/j.foodres.2009.03.019>
- Azlin-Hasim, S., Cruz-Romero, M. C., Cummins, E., Kerry, J. P., & Morris, M. A. (2016). The potential use of a layer-by-layer strategy to develop LDPE antimicrobial films coated with silver nanoparticles for packaging applications. *J Colloid Interface Sci*, 461, 239-248. doi: 10.1016/j.jcis.2015.09.021
- Azlin-Hasim, S., Cruz-Romero, M. C., Ghoshal, T., Morris, M. A., Cummins, E., & Kerry, J. P. (2015). Application of silver nanodots for potential use in antimicrobial packaging applications. *Innovative Food Science & Emerging Technologies*, 27, 136-143. doi: <http://dx.doi.org/10.1016/j.ifset.2014.10.012>
- Azlin-Hasim, S., Cruz-Romero, M. C., Morris, M. A., Cummins, E., & Kerry, J. P. (2015). Effects of a combination of antimicrobial silver low density polyethylene nanocomposite films and modified atmosphere packaging on the shelf life of chicken breast fillets. *Food Packaging and Shelf Life*, 4, 26-35. doi: <http://dx.doi.org/10.1016/j.fpsl.2015.03.003>
- Azlin-Hasim, S., Cruz-Romero, M. C., Morris, M. A., Padmanabhan, S. C., Cummins, E., & Kerry, J. P. (2016). The Potential Application of Antimicrobial Silver Polyvinyl Chloride Nanocomposite

- Films to Extend the Shelf-Life of Chicken Breast Fillets. *Food and Bioprocess Technology*, 9(10), 1661-1673. doi: 10.1007/s11947-016-1745-7
- Bag, D. S., Kumar, V. P., & Maiti, S. (1999). Chemical modification of LDPE film. *Journal of Applied Polymer Science*, 71(7), 1041-1048. doi: 10.1002/(SICI)1097-4628(19990214)71:7<1041::AID-APP1>3.0.CO;2-R
- Bandopadhyay, D., Tarafdar, A., Panda, A. B., & Pramanik, P. (2004). Surface modification of low-density polyethylene films by a novel solution base chemical process. *Journal of Applied Polymer Science*, 92(5), 3046-3051. doi: 10.1002/app.20291
- Barish, J. A., & Goddard, J. M. (2011). Topographical and chemical characterization of polymer surfaces modified by physical and chemical processes. *Journal of Applied Polymer Science*, 120(5), 2863-2871. doi: 10.1002/app.33310
- Bogaerts, A., Neyts, E., Gijbels, R., & van der Mullen, J. (2002). Gas discharge plasmas and their applications. *Spectrochimica Acta Part B: Atomic Spectroscopy*, 57(4), 609-658. doi: [http://dx.doi.org/10.1016/S0584-8547\(01\)00406-2](http://dx.doi.org/10.1016/S0584-8547(01)00406-2)
- Bolton, D. J., Meredith, H., Walsh, D., & McDowell, D. A. (2014). The effect of chemical treatments in laboratory and broiler plant studies on the microbial status and shelf-life of poultry. *Food Control*, 36(1), 230-237. doi: <http://dx.doi.org/10.1016/j.foodcont.2013.08.027>
- Busolo, M. A., Fernandez, P., Ocio, M. J., & Lagaron, J. M. (2010). Novel silver-based nanoclay as an antimicrobial in polylactic acid food packaging coatings. *Food Addit Contam Part A Chem Anal Control Expo Risk Assess*, 27(11), 1617-1626. doi: 10.1080/19440049.2010.506601
- Chen, J. H., Ren, Y., Seow, J., Liu, T., Bang, W. S., & Yuk, H. G. (2012). Intervention Technologies for Ensuring Microbiological Safety of Meat: Current and Future Trends. *Comprehensive Reviews in Food Science and Food Safety*, 11(2), 119-132. doi: 10.1111/j.1541-4337.2011.00177.x
- Chouliara, E., Badeka, A., Savvaidis, I., & Kontominas, M. G. (2008). Combined effect of irradiation and modified atmosphere packaging on shelf-life extension of chicken breast meat: microbiological, chemical and sensory changes. *European Food Research and Technology*, 226(4), 877-888. doi: 10.1007/s00217-007-0610-3
- Clarke, D., Tyuftin, A. A., Cruz-Romero, M. C., Bolton, D. J., Fanning, S., Pankaj, S. K., . . . Kerry, J. P. (2017). Surface attachment of active antimicrobial coatings onto conventional plastic-based laminates and performance assessment of these materials on the storage life of vacuum packaged beef sub-primals. *Food Microbiology*, 62, 196-201. doi: <http://dx.doi.org/10.1016/j.fm.2016.10.022>
- Cruz-Romero, M., & Kerry, J. P. (2017). Packaging systems and materials used for meat products with particular emphasis on the use of oxygen scavenging systems *Emerging Technologies in Meat Processing* (pp. 231-263): John Wiley & Sons, Ltd.
- Cruz-Romero, M. C., & Kerry, J. P. (2011). 26 - Packaging of cooked meats and muscle-based, convenience-style processed foods *Processed Meats* (pp. 666-705): Woodhead Publishing.
- Cruz-Romero, M. C., Murphy, T., Morris, M., Cummins, E., & Kerry, J. P. (2013). Antimicrobial activity of chitosan, organic acids and nano-sized solubilisates for potential use in smart antimicrobially-active packaging for potential food applications. *Food Control*, 34(2), 393-397. doi: <http://dx.doi.org/10.1016/j.foodcont.2013.04.042>
- Cummins, C., Ghoshal, T., Holmes, J. D., & Morris, M. A. (2016). Strategies for Inorganic Incorporation using Neat Block Copolymer Thin Films for Etch Mask Function and Nanotechnological Application. *Advanced Materials*, 28(27), 5586-5618. doi: 10.1002/adma.201503432
- Cushen, M., & Cummins, E. J. (2017). Smart packaging solutions encompassing nanotechnology *Emerging Technologies in Meat Processing* (pp. 265-284): John Wiley & Sons, Ltd.
- Cushen, M., Kerry, J., Morris, M., Cruz-Romero, M., & Cummins, E. (2012). Nanotechnologies in the food industry – Recent developments, risks and regulation. *Trends in Food Science & Technology*, 24(1), 30-46. doi: <http://dx.doi.org/10.1016/j.tifs.2011.10.006>

- Cushen, M., Kerry, J., Morris, M., Cruz-Romero, M., & Cummins, E. (2013). Migration and exposure assessment of silver from a PVC nanocomposite. *Food Chemistry*, 139(1–4), 389–397. doi: <http://doi.org/10.1016/j.foodchem.2013.01.045>
- Cushen, M., Kerry, J., Morris, M., Cruz-Romero, M., & Cummins, E. (2014a). Evaluation and simulation of silver and copper nanoparticle migration from polyethylene nanocomposites to food and an associated exposure assessment. [Article]. *Journal of Agricultural and Food Chemistry*, 62(6), 1403–1411. doi: 10.1021/jf404038y
- Cushen, M., Kerry, J., Morris, M., Cruz-Romero, M., & Cummins, E. (2014b). Silver migration from nanosilver and a commercially available zeolite filler polyethylene composites to food simulants. [Article]. *Food Additives and Contaminants - Part A Chemistry, Analysis, Control, Exposure and Risk Assessment*, 31(6), 1132–1140. doi: 10.1080/19440049.2014.905874
- Damm, C., Münstedt, H., & Rösch, A. J. (2007). Long-term antimicrobial polyamide 6/silver-nanocomposites. *Journal of Materials Science*, 42(15), 6067–6073.
- Djokić, S. (2008). Synthesis and Antimicrobial Activity of Silver Citrate Complexes. *Bioinorganic Chemistry and Applications*, 2008, 436458. doi: 10.1155/2008/436458
- Donaldson, K., Stone, V., Tran, C. L., Kreyling, W., & Borm, P. J. A. (2004). Nanotoxicology. *Occupational and Environmental Medicine*, 61(9), 727–728. doi: 10.1136/oem.2004.013243
- Drexler, K. E. (1986). *Engines of Creation*: Anchor Press/Doubleday.
- Duncan, T. V. (2011). Applications of nanotechnology in food packaging and food safety: Barrier materials, antimicrobials and sensors. *Journal of Colloid and Interface Science*, 363(1), 1–24. doi: <http://dx.doi.org/10.1016/j.jcis.2011.07.017>
- Emblem, A. (2012a). Plastic properties for packaging materials. In A. Emblem & H. Emblem (Eds.), *Packaging technology: Fundamentals, materials and processes* (pp. 287–309). Cambridge: Woodhead Publishing Ltd.
- Emblem, A. (2012b). Packaging functions. In A. Emblem & H. Emblem (Eds.), *Packaging technology: Fundamentals, materials and processes* (pp. 24–49). Cambridge: Woodhead Publishing Ltd.
- Fabra, M. J., Flores-López, M. L., Cerqueira, M. A., de Rodriguez, D. J., Lagaron, J. M., & Vicente, A. A. (2016). Layer-by-Layer Technique to Developing Functional Nanolaminate Films with Antifungal Activity. *Food and Bioprocess Technology*, 9(3), 471–480. doi: 10.1007/s11947-015-1646-1
- Falguera, V., Quintero, J. P., Jiménez, A., Muñoz, J. A., & Ibarz, A. (2011). Edible films and coatings: Structures, active functions and trends in their use. *Trends in Food Science & Technology*, 22(6), 292–303. doi: <http://dx.doi.org/10.1016/j.tifs.2011.02.004>
- Fan, M., Thompson, M., Andrade, M. L., & Brolo, A. G. (2010). Silver Nanoparticles on a Plastic Platform for Localized Surface Plasmon Resonance Biosensing. *Analytical Chemistry*, 82(15), 6350–6352. doi: 10.1021/ac101495m
- Ghosh, K., & Maiti, S. N. (1996). Mechanical properties of silver-powder-filled polypropylene composites. *Journal of Applied Polymer Science*, 60(3), 323–331. doi: 10.1002/(SICI)1097-4628(19960418)60:3<323::AID-APP5>3.0.CO;2-N
- Goddard, J. M., & Hotchkiss, J. H. (2007). Polymer surface modification for the attachment of bioactive compounds. *Progress in Polymer Science*, 32(7), 698–725. doi: <http://dx.doi.org/10.1016/j.progpolymsci.2007.04.002>
- Golja, V., Dražić, G., Lorenzetti, M., Vidmar, J., Ščančar, J., Zalaznik, M., . . . Novak, S. (2017). Characterisation of food contact non-stick coatings containing TiO<sub>2</sub> nanoparticles and study of their possible release into food. [Article]. *Food Additives and Contaminants - Part A Chemistry, Analysis, Control, Exposure and Risk Assessment*, 34(3), 421–433. doi: 10.1080/19440049.2016.1269954
- Goodman, C. M., McCusker, C. D., Yilmaz, T., & Rotello, V. M. (2004). Toxicity of Gold Nanoparticles Functionalized with Cationic and Anionic Side Chains. *Bioconjugate Chemistry*, 15(4), 897–900. doi: 10.1021/bc049951i

- Guruvenket, S., Rao, G. M., Komath, M., & Raichur, A. M. (2004). Plasma surface modification of polystyrene and polyethylene. *Applied Surface Science*, 236(1–4), 278-284. doi: <http://dx.doi.org/10.1016/j.apsusc.2004.04.033>
- Hannon, J. C., Kerry, J. P., Cruz-Romero, M., Azlin-Hasim, S., Morris, M., & Cummins, E. (2015). Assessment of the migration potential of nanosilver from nanoparticle-coated low-density polyethylene food packaging into food simulants. [Article]. *Food Additives and Contaminants - Part A Chemistry, Analysis, Control, Exposure and Risk Assessment*, 33(1), 167-178. doi: 10.1080/19440049.2015.1114184
- Ho, C. H., Tobis, J., Sprich, C., Thomann, R., & Tiller, J. C. (2004). Nanoseparated Polymeric Networks with Multiple Antimicrobial Properties. *Advanced Materials*, 16(12), 957-961. doi: 10.1002/adma.200306253
- Iijima, M., & Kamiya, H. (2010). Layer-by-Layer Surface Modification of Functional Nanoparticles for Dispersion in Organic Solvents. *Langmuir*, 26(23), 17943-17948. doi: 10.1021/la1030747
- Ishitani, T. (1997). Active packaging for food quality preservation in Japan. In P. Ackerman, M. Jagerstad & T. Ohlsson (Eds.), *Foods and Packaging Materials- Chemical interactions* (pp. 177-188). Cambridge: The Royal Society of Chemistry.
- Jiang, H., Moon, K.-s., Li, Y., & Wong, C. P. (2006). Surface Functionalized Silver Nanoparticles for Ultrahigh Conductive Polymer Composites. *Chemistry of Materials*, 18(13), 2969-2973. doi: 10.1021/cm0527773
- Jin, T., Sun, D., Su, J. Y., Zhang, H., & Sue, H. J. (2009). Antimicrobial efficacy of zinc oxide quantum dots against *Listeria monocytogenes*, *Salmonella Enteritidis*, and *Escherichia coli* O157:H7. *J Food Sci*, 74(1), M46-52. doi: 10.1111/j.1750-3841.2008.01013.x
- Kerry, J. P., O'Grady, M. N., & Hogan, S. A. (2006). Past, current and potential utilisation of active and intelligent packaging systems for meat and muscle-based products: A review. *Meat Science*, 74(1), 113-130. doi: 10.1016/j.meatsci.2006.04.024
- Kim, B., Kim, D., Cho, D., & Cho, S. (2003). Bactericidal effect of TiO<sub>2</sub> photocatalyst on selected food-borne pathogenic bacteria. *Chemosphere*, 52(1), 277-281. doi: [http://dx.doi.org/10.1016/S0045-6535\(03\)00051-1](http://dx.doi.org/10.1016/S0045-6535(03)00051-1)
- Kohli, A. K., & Alpar, H. O. (2004). Potential use of nanoparticles for transcutaneous vaccine delivery: effect of particle size and charge. *International Journal of Pharmaceutics*, 275(1–2), 13-17. doi: <http://dx.doi.org/10.1016/j.ijpharm.2003.10.038>
- Kong, H., & Jang, J. (2008). Antibacterial Properties of Novel Poly(methyl methacrylate) Nanofiber Containing Silver Nanoparticles. *Langmuir*, 24(5), 2051-2056. doi: 10.1021/la703085e
- Kumar, R., Howdle, S., & Münstedt, H. (2005). Polyamide/silver antimicrobials: Effect of filler types on the silver ion release. *Journal of Biomedical Materials Research Part B: Applied Biomaterials*, 75B(2), 311-319. doi: 10.1002/jbm.b.30306
- Kumar, R., & Münstedt, H. (2005a). Polyamide/silver antimicrobials: effect of crystallinity on the silver ion release. *Polymer International*, 54(8), 1180-1186. doi: 10.1002/pi.1828
- Kumar, R., & Münstedt, H. (2005b). Silver ion release from antimicrobial polyamide/silver composites. *Biomaterials*, 26(14), 2081-2088. doi: <http://dx.doi.org/10.1016/j.biomaterials.2004.05.030>
- Kuorwel, K. K., Cran, M. J., Orbell, J. D., Buddhadasa, S., & Bigger, S. W. (2015). Review of Mechanical Properties, Migration, and Potential Applications in Active Food Packaging Systems Containing Nanoclays and Nanosilver. *Comprehensive Reviews in Food Science and Food Safety*, 14(4), 411-430. doi: 10.1111/1541-4337.12139
- Lee, R., & Coote, M. L. (2016). Mechanistic insights into ozone-initiated oxidative degradation of saturated hydrocarbons and polymers. [10.1039/C6CP05064F]. *Physical Chemistry Chemical Physics*, 18(35), 24663-24671. doi: 10.1039/C6CP05064F
- Lehocký, M., Drnovská, H., Lapčíková, B., Barros-Timmons, A. M., Trindade, T., Zembala, M., & Lapčík Jr, L. r. (2003). Plasma surface modification of polyethylene. *Colloids and Surfaces A*:

- Physicochemical and Engineering Aspects*, 222(1–3), 125–131. doi: [http://dx.doi.org/10.1016/S0927-7757\(03\)00242-5](http://dx.doi.org/10.1016/S0927-7757(03)00242-5)
- Leistner, L. (2000). Basic aspects of food preservation by hurdle technology. *International Journal of Food Microbiology*, 55(1–3), 181–186. doi: [http://dx.doi.org/10.1016/S0168-1605\(00\)00161-6](http://dx.doi.org/10.1016/S0168-1605(00)00161-6)
- Liu, F., Liu, H., Li, X., Zhao, H., Zhu, D., Zheng, Y., & Li, C. (2012). Nano-TiO<sub>2</sub>@Ag/PVC film with enhanced antibacterial activities and photocatalytic properties. *Applied Surface Science*, 258(10), 4667–4671. doi: <http://dx.doi.org/10.1016/j.apsusc.2012.01.058>
- Llorens, A., Lloret, E., Picouet, P. A., Trbojević, R., & Fernandez, A. (2012). Metallic-based micro and nanocomposites in food contact materials and active food packaging. [Review]. *Trends in Food Science and Technology*, 24(1), 19–29. doi: 10.1016/j.tifs.2011.10.001
- Louwerse, M. J., & Jan Baerends, E. (2007). Oxidative properties of FeO<sub>2</sub><sup>+</sup>: electronic structure and solvation effects. [10.1039/B613182D]. *Physical Chemistry Chemical Physics*, 9(1), 156–166. doi: 10.1039/B613182D
- Mahdi, S. S., Vadood, R., & Nourdahr, R. (2012). Study on the antimicrobial effect of nanosilver tray packaging of minced beef at refrigerator temperature. *Global Vet*, 9(3), 284–289.
- Marini, M., De Niederhausern, S., Iseppi, R., Bondi, M., Sabia, C., Toselli, M., & Pilati, F. (2007). Antibacterial Activity of Plastics Coated with Silver-Doped Organic–Inorganic Hybrid Coatings Prepared by Sol–Gel Processes. *Biomacromolecules*, 8(4), 1246–1254. doi: 10.1021/bm060721b
- Marsh, K., & Bugusu, B. (2007). Food Packaging—Roles, Materials, and Environmental Issues. *Journal of Food Science*, 72(3), R39–R55. doi: 10.1111/j.1750-3841.2007.00301.x
- Martínez-Abad, A., Lagaron, J. M., & Ocio, M. J. (2012). Development and Characterization of Silver-Based Antimicrobial Ethylene–Vinyl Alcohol Copolymer (EVOH) Films for Food-Packaging Applications. *Journal of Agricultural and Food Chemistry*, 60(21), 5350–5359. doi: 10.1021/jf300334z
- Melo, R. P. d., Aguiar, V. d. O., & Marques, M. d. F. V. (2015). Silane Crosslinked Polyethylene from Different Commercial PE s: Influence of Comonomer, Catalyst Type and Evaluation of HLPB as Crosslinking Coagent. *Materials Research*, 18, 313–319.
- Morris, B. A., Darby, D., Wininger, J., Marsh, K. S., Fiedler, R. M., Spottiswode, B., . . . Yam, K. L. (2010). *S The Wiley Encyclopedia of Packaging Technology* (pp. 1089–1183): John Wiley & Sons, Inc.
- Nobile, M. A. d., Cannarsi, M., Altieri, C., Sinigaglia, M., Favia, P., Iacoviello, G., & D'Agostino, R. (2004). Effect of Ag-containing Nano-composite Active Packaging System on Survival of *Alicyclobacillus acidoterrestris*. *Journal of Food Science*, 69(8), E379–E383. doi: 10.1111/j.1365-2621.2004.tb09899.x
- O'Callaghan, K. A. M., & Kerry, J. P. (2016). Consumer attitudes towards the application of smart packaging technologies to cheese products. *Food Packaging and Shelf Life*, 9, 1–9. doi: 10.1016/j.fpsl.2016.05.001
- O'Brien, N. J., & Cummins, E. J. (2011). A Risk Assessment Framework for Assessing Metallic Nanomaterials of Environmental Concern: Aquatic Exposure and Behavior. *Risk Analysis*, 31(5), 706–726. doi: 10.1111/j.1539-6924.2010.01540.x
- Otoni, C. G., Espitia, P. J. P., Avena-Bustillos, R. J., & McHugh, T. H. (2016). Trends in antimicrobial food packaging systems: Emitting sachets and absorbent pads. *Food Research International*, 83, 60–73. doi: <http://dx.doi.org/10.1016/j.foodres.2016.02.018>
- Padmanabhan, S. C., Pillai, S. C., Colreavy, J., Balakrishnan, S., McCormack, D. E., Perova, T. S., . . . Kelly, J. M. (2007). A Simple Sol–Gel Processing for the Development of High-Temperature Stable Photoactive Anatase Titania. *Chemistry of Materials*, 19(18), 4474–4481. doi: 10.1021/cm070980n
- Panea, B., Ripoll, G., González, J., Fernández-Cuello, Á., & Albertí, P. (2014). Effect of nanocomposite packaging containing different proportions of ZnO and Ag on chicken breast meat quality.

- Journal of Food Engineering*, 123, 104-112. doi: <http://doi.org/10.1016/j.jfoodeng.2013.09.029>
- Pelagade, S., Singh, N. L., Sejal, S., Anjum, Q., Rane, R. S., Mukherjee, S., . . . Shripathi, T. (2010). Surface free energy analysis for bipolar pulsed argon plasma treated polymer films. *Journal of Physics: Conference Series*, 208(1), 012107.
- Pongnop, W., Sombatsompop, K., Kositchaiyong, A., & Sombatsompop, N. (2011). Effects of incorporating technique and silver colloid content on antibacterial performance for thermoplastic films. *Journal of Applied Polymer Science*, 122(5), 3456-3465. doi: 10.1002/app.34448
- Ren, G., Hu, D., Cheng, E. W. C., Vargas-Reus, M. A., Reip, P., & Allaker, R. P. (2009). Characterisation of copper oxide nanoparticles for antimicrobial applications. *International Journal of Antimicrobial Agents*, 33(6), 587-590. doi: <http://dx.doi.org/10.1016/j.ijantimicag.2008.12.004>
- Rhim, J. W., Wang, L. F., & Hong, S. I. (2013). Preparation and characterization of agar/silver nanoparticles composite films with antimicrobial activity. *Food Hydrocolloids*, 33(2), 327-335. doi: <http://dx.doi.org/10.1016/j.foodhyd.2013.04.002>
- Rodríguez-Calleja, J. M., Cruz-Romero, M. C., O'Sullivan, M. G., García-López, M. L., & Kerry, J. P. (2012). High-pressure-based hurdle strategy to extend the shelf-life of fresh chicken breast fillets. *Food Control*, 25(2), 516-524. doi: <http://dx.doi.org/10.1016/j.foodcont.2011.11.014>
- Ruparelia, J. P., Chatterjee, A. K., Duttagupta, S. P., & Mukherji, S. (2008). Strain specificity in antimicrobial activity of silver and copper nanoparticles. *Acta Biomaterialia*, 4(3), 707-716. doi: <http://dx.doi.org/10.1016/j.actbio.2007.11.006>
- Salata, O. (2004). Applications of nanoparticles in biology and medicine. [journal article]. *Journal of Nanobiotechnology*, 2(1), 3. doi: 10.1186/1477-3155-2-3
- Sánchez-Valdes, S., Ortega-Ortiz, H., Ramos-de Valle, L. F., Medellín-Rodríguez, F. J., & Guedea-Miranda, R. (2009). Mechanical and antimicrobial properties of multilayer films with a polyethylene/silver nanocomposite layer. [Article]. *Journal of Applied Polymer Science*, 111(2), 953-962. doi: 10.1002/app.29051
- Sanchis, M. R., Blanes, V., Blanes, M., Garcia, D., & Balart, R. (2006). Surface modification of low density polyethylene (LDPE) film by low pressure O<sub>2</sub> plasma treatment. *European Polymer Journal*, 42(7), 1558-1568. doi: <http://dx.doi.org/10.1016/j.eurpolymj.2006.02.001>
- Sibu, C. P., Kumar, S. R., Mukundan, P., & Warriar, K. G. K. (2002). Structural Modifications and Associated Properties of Lanthanum Oxide Doped Sol-Gel Nanosized Titanium Oxide. *Chemistry of Materials*, 14(7), 2876-2881. doi: 10.1021/cm010966p
- Simon, P., Chaudhry, Q., & Bakos, D. (2008). Migration of engineered nanoparticles from polymer packaging to food - a physicochemical view. *Journal of Food & Nutrition Research*, 47(3), 105-113.
- Sivakumar, S., Sibu, C. P., Mukundan, P., Pillai, P. K., & Warriar, K. G. K. (2004). Nanoporous titania-alumina mixed oxides—an alkoxide free sol-gel synthesis. *Materials Letters*, 58(21), 2664-2669. doi: <http://dx.doi.org/10.1016/j.matlet.2004.03.050>
- Son, W. K., Youk, J. H., & Park, W. H. (2006). Antimicrobial cellulose acetate nanofibers containing silver nanoparticles. *Carbohydrate Polymers*, 65(4), 430-434. doi: <http://dx.doi.org/10.1016/j.carbpol.2006.01.037>
- Sperber, W. H. (2009). Introduction to the Microbiological Spoilage of Foods and Beverages. In W. H. Sperber & M. P. Doyle (Eds.), *Compendium of the Microbiological Spoilage of Foods and Beverages* (pp. 1-40). New York, NY: Springer New York.
- Sun, Y.-P., Fu, K., Lin, Y., & Huang, W. (2002). Functionalized Carbon Nanotubes: Properties and Applications. *Accounts of Chemical Research*, 35(12), 1096-1104. doi: 10.1021/ar010160v
- Tang, Z.-X., & Lv, B.-F. (2014). MgO nanoparticles as antibacterial agent: preparation and activity. *Brazilian Journal of Chemical Engineering*, 31, 591-601.

- Torres-Giner, S. (2011). 5 - Electrospun nanofibers for food packaging applications A2 - Lagarón, José-María *Multifunctional and Nanoreinforced Polymers for Food Packaging* (pp. 108-125): Woodhead Publishing.
- Troy, D. J., & Kerry, J. P. (2010). Consumer perception and the role of science in the meat industry. *Meat Science*, 86(1), 214-226. doi: 10.1016/j.meatsci.2010.05.009
- Troy, D. J., Ojha, K. S., Kerry, J. P., & Tiwari, B. K. (2016). Sustainable and consumer-friendly emerging technologies for application within the meat industry: An overview. *Meat Science*, 120, 2-9. doi: 10.1016/j.meatsci.2016.04.002
- UN, F. A. O. o. t. (2017). <http://www.fao.org/save-food/resources/keyfindings/en/>, from <http://www.fao.org/save-food/resources/keyfindings/en/>
- Valdes, A., Mellinas, A. C., Ramos, M., Garrigos, M. C., & Jimenez, A. (2014). Natural additives and agricultural wastes in biopolymer formulations for food packaging. *Frontiers in Chemistry*, 2. doi: 10.3389/fchem.2014.00006
- Walsh, H., & Kerry, J. P. (2012). Packaging of ready-to-serve and retail-ready meat, poultry and seafood products. In J. P. Kerry (Ed.), *Advances in Meat, Poultry and Seafood Packaging* (pp. 406-436).
- Wang, J., Chen, P., Li, H., Li, W., Wang, B., Zhang, C., & Ni, R. (2008). Surface characteristic of poly(p-phenylene terephthalamide) fibers with oxygen plasma treatment. *Surface and Interface Analysis*, 40(9), 1299-1303. doi: 10.1002/sia.2890
- Wang, R. H., Xin, J. H., & Tao, X. M. (2005). UV-Blocking Property of Dumbbell-Shaped ZnO Crystallites on Cotton Fabrics. *Inorganic Chemistry*, 44(11), 3926-3930. doi: 10.1021/ic0503176
- . World Health Organization: WHO Model of Essential Medicines. [<http://www.who.int/medicines/publications/essentialmedicines/en/index.html>].
- Xingping, Z., Siyu, N., Xiao, Z., Xiaqin, W., Xuhua, H., & Yong, Z. (2008). Controlling Shape and Size of TiO<sub>2</sub> Nanoparticles with Sodium Acetate. *Current Nanoscience*, 4(4), 397-401. doi: <http://dx.doi.org/10.2174/157341308786306125>
- Yameen, B. (2008). *Novel Polymer systems and surface modifications of planar and porous substrates for advanced applications*. Johannes Gutenberg Universität Mainz.
- Yang, Y., He, Q., Duan, L., Cui, Y., & Li, J. (2007). Assembled alginate/chitosan nanotubes for biological application. *Biomaterials*, 28(20), 3083-3090. doi: 10.1016/j.biomaterials.2007.03.019
- Ye, S., Wang, C., Liu, X., & Tong, Z. (2005). Multilayer nanocapsules of polysaccharide chitosan and alginate through layer-by-layer assembly directly on PS nanoparticles for release. *J Biomater Sci Polym Ed*, 16(7), 909-923.
- Yeo, S. Y., & Jeong, S. H. (2003). Preparation and characterization of polypropylene/silver nanocomposite fibers. *Polymer International*, 52(7), 1053-1057. doi: 10.1002/pi.1215
- Zhang, C.-L., & Yu, S.-H. (2014). Nanoparticles meet electrospinning: recent advances and future prospects. [10.1039/C3CS60426H]. *Chemical Society Reviews*, 43(13), 4423-4448. doi: 10.1039/C3CS60426H
- Znaidi, L., Chhor, K., & Pommier, C. (1996). Batch and semi-continuous synthesis of magnesium oxide powders from hydrolysis and supercritical treatment of Mg(OCH<sub>3</sub>)<sub>2</sub>. *Materials Research Bulletin*, 31(12), 1527-1535. doi: [http://dx.doi.org/10.1016/S0025-5408\(96\)00145-6](http://dx.doi.org/10.1016/S0025-5408(96)00145-6)



### Figure captions

Fig. 1: Schematic showing the sequential reactions occurring on a plastic. Step 1: plasma reaction forming -COOH functionality, step 2: reaction of -COOH functionality with diamine molecules forming urethane linkage and step 3: binding of silver to the amine group.

Fig. 2: Schematic showing the alternate LBL deposition process of chitosan and alginate solutions to create multilayer coating on polymer substrate.

Fig. 3: Typical reactions involved in the sol-gel process (Marini et al., 2007).

Fig. 4: Schematic showing (a) the cylindrical pattern (red) formed from PS-*b*-PEO phase separation and (b) silver NPs incorporated into the cylinders formed (blue).

Fig. 5: *Principle of gravure printing*. [Reproduced with permission from DTU Energy].

Fig. 6: *Principle of flexo printing*. [Reproduced with permission from DTU Energy].

Fig. 7: *Principle of flexo printing*. [Reproduced with permission from DTU Energy].

Fig. 8. *Principle of slot-die coating.* [Reproduced with permission from DTU Energy].

Fig. 9: Microbiological counts of chicken breast fillets during chilled storage under MAP condition using (*circle*) PVC control films or (*black triangle*) Ag/PVC nanocomposite films (a) total viable count, (b) *Pseudomonas* spp. and (c) lactic acid bacteria. *Error bars* represent standard deviation of analysis from eight readings (Azlin-Hasim, Cruz-Romero, Morris, et al., 2016). [Reproduced with permission from the authors].

Fig. 10. AFM (a, c and e) and SEM (b, d and f) images of PS-*b*-PEO template after ethanol treatment for Mn 32–11(a) and (b); Mn 42–11.5 (c) and (d) and Mn 102–34 (e) and (f) of BCP, respectively. AFM lighter regions indicated the presence of PS and darker region PEO domains. Scale bar: 200 nm (Azlin-Hasim, Cruz-Romero, Ghoshal, et al., 2015). [Reproduced with permission from the authors].

Fig. 11. SEM images of Ag nanodots for Mn 42–11.5 PS-*b*-PEO coated once with (a) 0.6 % or (b) 2 % Ag precursor and Ag nanodots coated twice with (c) 2 % Ag precursor. Inset of (a) shows a higher magnification. The schematic diagrams of (B) and (C) show how continuous films are formed after overfills and repeated deposition of Ag precursor. Scale bars: 200 nm (Azlin-Hasim, Cruz-Romero, Ghoshal, et al., 2015). [Reproduced with permission from the authors].

Fig 1

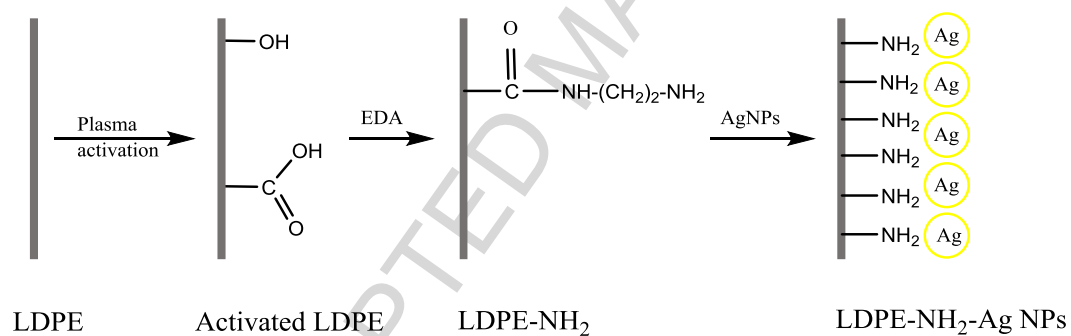


Fig 2

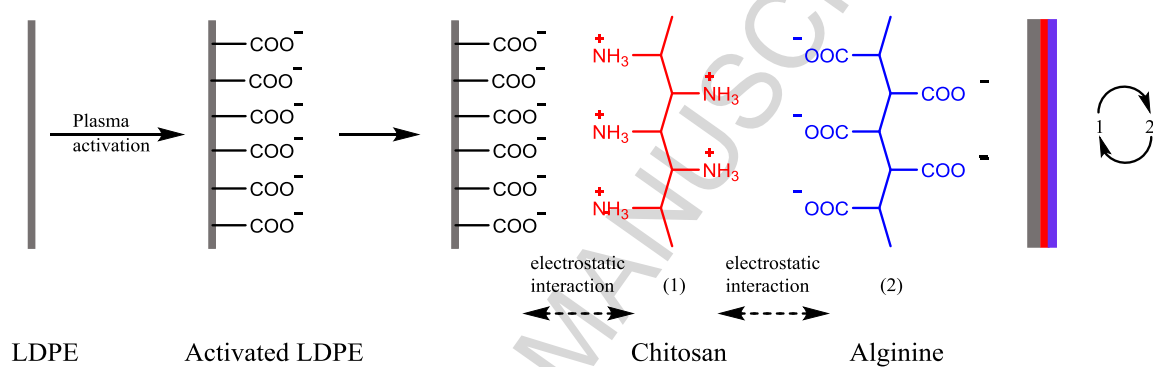
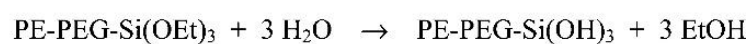
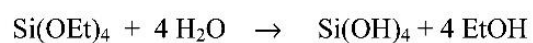


Fig 3

*Step 1. Hydrolysis*



*Step 2. Condensation*

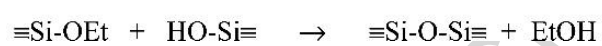
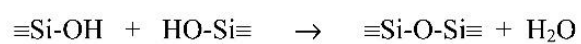


Fig 4

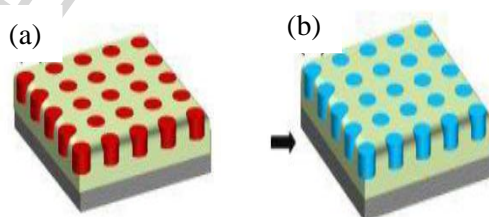


Fig 5

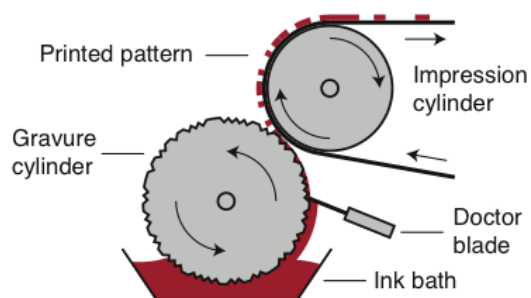


Fig 6

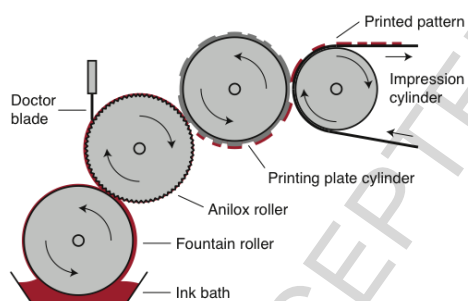


Fig 7

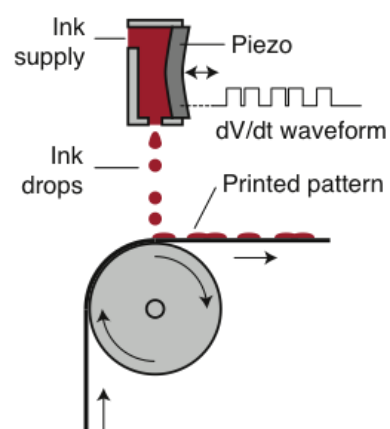


Fig 8

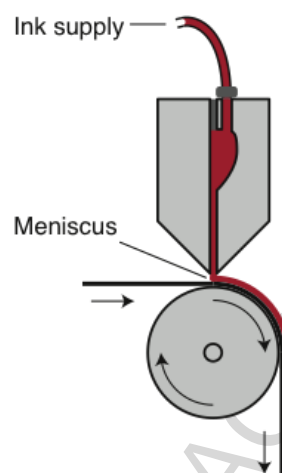


Fig 9

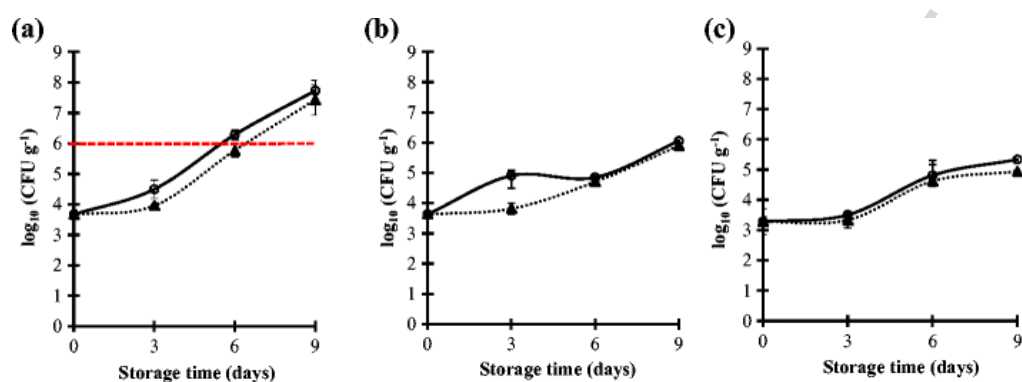




Fig 10

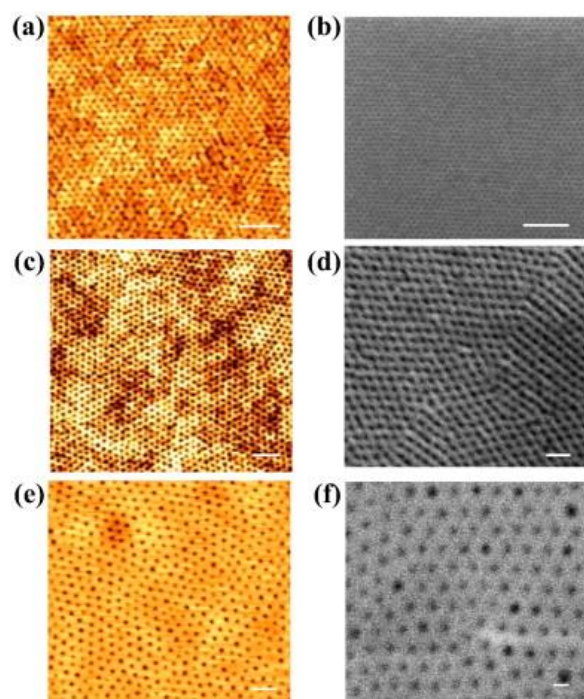


Fig 11

