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Highlights

UV treated polyamide films have antimicrobial properties owing to presence of amine groups.

Plasma-treated polyamide surface properties are similar to those of UV-treated samples.

Plasma treatments, followed by antimicrobial coatings, produce antimicrobial film surfaces.

Corona treatment of polyamide surfaces induces the formation of functional groups.

Corona and UV treatments should be fully explored for antimicrobial packaging manufacture.

Surface treatment methods for polyamide films for potential application in smart packaging materials: structure and antimicrobial properties

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Abstract

Background: Antimicrobial packaging is currently one of the emerging technologies being pursued to extend the shelf-life of food products. Polyamides (PA) are widely used in food packaging, principally in laminate constructions, where they are used alone or combined with other materials. PA can be surface-treated using UV, plasma and corona treatments to create active film surfaces for various industrial applications.

Scope and Approach: The objective was to investigate the potential application of various surface treatment methods for the potential manufacture of antimicrobial packaging and to identify the necessary spectral characteristics deemed necessary to achieve this.
Key Findings and Conclusions: XPS and AMF methods are useful tools in the identification of film surface analysis and can be industrially applied. For UV treatment, different light sources, including lasers, can be applied to create antimicrobially-active packaging materials. UV-treated PA films possess antimicrobial properties and offer potential for industrial and medical packaging applications, however, the application of such packaging materials to foods needs some special consideration.
Different plasma treatment methodologies can be used for modification of PA surfaces, followed by attachment of antimicrobial coatings. Surface studies have shown that plasma-treated PA surfaces possess spectral properties similar to those for UV-treated samples. Corona treatment, like UV and plasma treatments, induce the modification of functional groups on PA film surfaces. Corona treatment has the capacity to activate polymeric surfaces for adhesion of a variety of functional coatings and should be explored further in terms of creating special antimicrobial coatings.

Introduction

Prolonging the shelf-life of food products through the control of microbial and chemical processes, both within and upon product surfaces, is critically important to ensure that the quality, safety and nutritional status of products are maintained throughout the distribution chain for as long as possible; successfully reaching the consumer for final use and consumption. Packaging with high barrier properties, which render them impermeable to gases and water vapour, can keep food contained and fresh for a long time, thereby avoiding chemical oxidation and reducing microbial spoilage which is principally driven by the presence of aerobic microorganisms. The packaging materials that are typically employed for their barrier properties in food applications are as follows; aluminium (Al) foil (as sheeting for complete or partial barrier properties depending on foil thicknesses employed or foil coatings applied through vacuum metallisation), barrier polymers like polyamide (PA)and polyethylene-vinyl alcohol (Kenneth, 2008), polymers which have the capacity to be orientated like polypropylene (PP), polystyrene (PS), PET and PA, polymers comprised of exfoliated nanoclay-montmorrilonite composite blends additives (Duncan, 2011), applied nanocoatings containing

elements such as AlOx and SiOx (Amberg-Schwab, 2005) and its combinations (Amberg-Schwab, 2006) on oriented films.

Antimicrobial packaging is a form of smart packaging which resides within the active grouping of technologies. It is a commercially important and emerging market sector within the food packaging area, principally because it addresses the primary factor responsible for food spoilage, which is microbial food spoilage. Delivering high quality food products in a suitable, high-barrier flexible packaging format is essential in order to reduce packaging weight and food wastage (Clarke et al., 2017). The potential to enhance the characteristics of such packaging materials through the creation of active packaging surfaces, which are antimicrobial in nature, would allow the food industry to continue to use desirable, polymer-based packaging materials, but with the added advantage of increasing product storage stability and shelf-life extension. Transnational, overseas shipping of food and beverage products makes significant demands upon the robustness and durability of products, especially in relation to shelf-life stability. For food and beverage processors, the necessity to retail products in ever distant markets means that conventional packaging materials and formats used for standard product lines are inadequate to cope with additional environmental, handling, storage and transport stresses posed by the elongated distribution chain. Consequently, the availability of active packaging materials would assist food and beverage companies cope with these issues through the extension of product shelf-life, while potentially allowing packaging materials to be further light-weighted. Antimicrobial packaging can continuously present antimicrobial agents directly to the food surface, or indirectly by the presence of atmospheric modifiers. Antimicrobial packaging that functions through a direct approach is usually the most successful. Numerous reviews have been published in recent years outlining the plethora of potential substances that are available and could be employed in conventional packaging materials to create active packaging for potential commercial uptake (Appendini & Hotchkiss, 2002; Quantavalla & Vicini., 2002; Suppakul et al., 2003; Kerry et al., 2006; Sung et al., 2013; Malhotra et al., 2015; Sofi et al., 2018). Such agents can be applied within or upon packaging materials to continuously migrate to the food surface and beyond or remain immobilised at the package/product interface in order to avoid migration issues. In any case, the purpose is to ensure that these materials are antimicrobial in nature.

A far less studied approach towards creating antimicrobial packaging surfaces is through commonly used surface treatment methods employed by the packaging industry for selected polymeric materials, with or without subsequent chemical modification. This approach

involves the chemical or physical modification of particular polymeric surfaces, such that these modifications result in the creation of antimicrobial properties. This approach can also be combined with grafting technologies, whereby other antimicrobial materials can be attached to the modified active film surfaces. Such approaches could lead to the development of wide range of new materials with very novel properties.

There are currently three common approaches employed in industry for the creation of surface modified polymers, namely; corona treatment, which is widely used in gravure printing processes or in coating applications for increasing of adhesion to inks, varnishes and adhesives to packaging materials (Brewis & Mathieson, 2002); vacuum and atmospheric plasma treatment which is also used for improvement in the adhesion to adhesives, inks, antimicrobial coatings (Wolf & Sparavigna, 2010) and mostly for oxide nanocoatings such as SiOx or AlOx to biaxial oriented films (Moosheimer & Bichler, 1999) and ultra violet (UV) light surface treatment which widely used in label printing and applications for the UV curing of inks (Pappas, 1992), solvent-less adhesives and as a minor application in the activation of smart oxygen sensors (Lee et al., 2005) or antimicrobial nanoparticles coatings (Kong et al., 2010). Additionally, electron energy and pulsed-laser irradiation can also be applied in polymer surface treatments (Cohen et al., 1995). One polymeric material which has widespread use in food packaging applications, especially in vacuum packaging applications and has the capability of functionalization after, or during, treatment is polyamide (PA) or nylon. Surface activating technologies have been used in the development and manufacture of antimicrobially-active PA-based packaging materials, including antimicrobial flexible packaging. Film structure properties and atomic spectral characteristics for film surfaces need to be understood in order to be capable of designing new packaging materials with predetermined properties. Consequently, Atomic force microscopy (AFM) and X-ray photoelectron spectroscopy (XPS) are useful tools for film surface characterisation studies. This review focuses on the description of the surface structure of PA films and properties as compared by AFM and XPS data following different treatments methods for the creation of antimicrobial materials for potential applications.

Polyamide (PA)

The first PA (nylon 6,6) was developed in 1935 by Wallace Carothers at DuPont's research facility in the USA (DuPont) and was introduced as a fabric at the 1939 New York World's Fair (Audra, 2008). Nylon is made of repeating amide units linked together by peptide bonds

(Fig. 1). Nylon was the first commercially successful synthetic thermoplastic polymer introduced for industrial use.

Figure 1. Nylon 6,6 and molecular hydrogen bonds between chains.

Polyamide is widely used in food packaging, principally in laminate constructions where they are often combined with polyolfins, foils or applied as a co-extruded layer in packaging films. PA films possess: low to moderately low oxygen transmission rates (10–50 cc/m^2 day at STM), good puncture resistances and high tensile strengths. Films containing PA are particularly used for the packaging of muscle-based food products (especially bone-in or shell-possessing products), cheese and products which are hard and possess distinctive edging using packaging formats which include; vacuum pouches, thermoforming trays, vacuum and heat-shrinking bags, vacuum skin packaging, MAP, among others (Laurence & Massey, 2013).

Polyamide-based film surface treatments

UV treatment

The first application of UV for the purposes of antimicrobial surface activation of PA was patented by Cohen et al., (1995). UV irradiation was applied through the use of disclosed photon sources, including excimer lasers and ultra violet (UV) lamps. ArF excimer lasers can generate wavelengths of 193 nm and were used in the development of this patent (Cohen et al., 1995). Adrienne et al., (2000) reported that approximately 10% of the amide groups can be converted to amines or approximately 5×10^{12} amine groups per cm^2 of the film for UV treated PA yarn or fabric. It was demonstrated that UV-irradiated nylon yarn exhibited antimicrobial activity against 99% of *Klebsiella pneumonia* (Shake Flask test) after 12 J/cm^2 energy per pass radiation exposure (Cohen et al., 1995). Paik et al., (1998) suggested that upon the impact of applying UV irradiation for the purposes of surface activation of nylon 6,6 with respect to the development of antimicrobially-active packaging materials. These authors employed a Lambda LPX-325i excimer laser which produced a beam of UV light at 193nm to convert amide groups on the surface of nylon to antimicrobial amines. Treated film surfaces were studied by XPS method (Paik et al., 1998). The XPS spectra generated from these studies is shown here (Fig. 2a, b) and it is interesting to note that the C=O groups of PA were diminished following UV irradiation as indicated by the decrease in signal at 292 eV, which is associated with carbonyl groups (Paik et al., 1998). Similar XPS spectrum was produced by Adrienne et al., (2000). The

appearance of a low binding energy component in the nitrogen N 1s atoms was shown by Paik et al., (1998). This curving behaviour in spectra is consistent with the conversion of amide groups to amine groups by carbonyl elimination, as suggested by the authors (Paik et al., 1998).

Figure 2. XPS spectra of irradiated and non-irradiated nylon film (C1s atom spectra (2a) and N1s atom-spectra (2b), (adopted from Paik et al., 1998).

The presence of amine groups on the surface of irradiated nylon was identified by reaction with indicator dyes (Paik et al., 1998; Adrienne et al., (2000.

Adrienne et al., (2000) curried out surface studies of excimer laser-treated PA with the help of AFM (Fig. 3a, b).

Figure 3. (a) AFM image of untreated PA film surface and (b) PA film treated with 193nm LPX 325i excimer laser employing 45 pulses of 58 MJ cm^{-2} (adopted from Adrienne et al., 2000).

As it can be seen from Fig. 3, film surface roughness was different both before and after UV treatment as a consequence of irradiation. Authors reported the antibactericidal effect of UV-treated PA films on food-related bacterial strains such as *Staphylococcus aureus 25923* and *Escherichia coli TV1058* which were exposed to the antimicrobial surface-activated film (Adrienne et al., 2000). However, the UV-treated nylon film was ineffective against *Pseudomonas fluorescens 13525* and *Enterococcus faecalis 19433* under similar conditions (Adrienne et al., 12000). Adrienne et al., (2000) investigated the antimicrobial activity of treated PA films held at different storage temperatures. No antimicrobial activity was observed in treated PA films held between 4-15°C, however, film antimicrobial activity increased against *S. aureus 25923* as temperature increased up to 45 °C (Adrienne et al., 2000). But this can be caused not only higher penetration rate of amines inside cell but also the effect of peptides denaturation of bacteria cells at this temperature. It was reported that bacteria cell adsorption diminished the effectiveness of active film amine groups owing to the presence of microbial protein and salt which inhibits the antibacterial properties of UV-treated PA films (Adrienne et al., 2000).

UV activation of PA films seems like a promising technology for antimicrobial packaging applications, but limitations exist for practical application. Foods high in protein and salt, such as muscle-based food products, are not suitable for use with such technology, particularly where fresh foods need to be refrigerated. Critically, amines created on a film surface have an offensive odour, similar to that of spoiled fish (Adrienne et al., 2000) which can effect the sensory perception of the packaged food in question. Thus, UV activation of PA might be more useful for antimicrobial medical or industrial packaging applications, where amines will not affect the product directly e.g. surgical tools, prostheses, industrial equipment, building materials etc.

However, chemical-surface modification of PA with antimicrobial elastomers could potentially solve this issue for food packaging applications. Wintzer et al., (2015) investigated the effect of short wave ultraviolet C light (UVC) produced by low-pressure mercury lamps employing 185nm and 254nm emissions on PA fibres. The UVC pre-treatment of PA fibre leads to significantly increased adhesion strength between the fibres and the melt, processable, elastomers (Wintzer et al., 2015) which can be modified by the addition of antimicrobial compounds. Another example of surface nylon modification for increasing adhesion for further surface functionalization is the treatment by a KrF 248nm excimer laser. Waugh & Lawrence (2018) applied this laser wave to surface pattern nylon 6,6 film in an attempt to modify the wettability characteristics. Thus, UV laser treatment opens up a wide range of possibilities for surface modification of films by utilising different coatings for application within the food packaging industry.

Plasma treatment

It has been known for some time that plasma can be used for surface treatment of different materials in order to increase adhesion properties for hydrophilic coatings and inks (Wolf & Sparavigna, 2010; Thomas & Mittal, 2013; Pankaj et al., 2014). Dubreuil & Bongaers, (2008) and Kuzminova et al., (2014) studied the effect of atmospheric air pressure dielectric barrier discharge (DBD) plasma on PA surfaces. The changes in surface morphology of nylon 6,6 films induced by the DBD system were determined by AFM (Fig. 4).

Figure 4. Examples of 10 x 5μm AFM scans of untreated nylon foil and nylon foil exposed to DBD plasma for different treatment times from 0.5 to 32 sec (adopted from Kuzminova et al., (2014).

These authors reported that the root-mean square (RMS) surface roughness of films increased up to about 37nm after 32sec film exposure from an initial ~15nm before plasma treatment (Fig. 5) (Kuzminova et al., 2014).

Figure 5. RMS roughness modifications of nylon films (50 μm) exposed to DBD plasma after different treatment times (adopted from Kuzminova et al., (2014).

Such RMS surface roughness changes in films are similar to the surface roughness produced in films following UV laser irradiation (Fig. 3b) when RMS changed from 3.7nm to 15.6nm (Adrienne et al., 2000).

Similar to the UV treatment (Fig. 2), C1s atoms, XPS studies revealed a decrease in carbon atom content (Kuzminova et al., 2014). These authors reported that the C1 component decreased from 66% (untreated PA) to 50% (after 32 sec of PA treatment) (Fig. 6a). As a result of the decrease in the C1 component, a new C4 component peak appeared and was described as the result of a formation of O-C=O groups on the surface of PA films and reached a level of 13% following a 32sec treatment of DBD plasma (Fig. 6a, Kuzminova et al., 2014). These authors indicated that all C, O and N-components in PA films had been identified through XPS spectra.

Figure 6. High resolution XPS spectra of C1s (a) and N1s (b) component peaks of untreated and DBD-treated nylon films (adopted from Kuzminova et al., 2014).

O-atom XPS spectra studies suggested the formation of COOH groups on film surfaces (Kuzminova et al., 2014) which can be caused by PA surface oxidation by atmospheric oxygen during treatment. N-atom XPS spectra (Fig. 6b) for plasma-treated samples showed the appearance of a new peak for the N1 atom, with an energy of 407 eV (N3) and 401.5 eV (N2). It was proposed that the N3 atom could be identified as nitrate and the N2 atom proposed as hydroxyimide or H-atom bonded to amide nitrogen. N1 was proposed to be amide, as found in untreated PA (Fig. 6b, Kuzminova et al., 2014). This explanation needs to be considered

carefully, as if this spectrum is compared to that produced by Paik et al. (1998), who proposed the formation of amine groups on PA surface after UV treatment (Fig. 2b), it would appear that the N2 atom actually belongs to the amines. It would be interesting to identify amine groups through reactions involving dyes, as proposed by Adrienne et al., (2000). Following this form of plasma treatment, treated films could also be used in antimicrobial packaging applications similar to that of UV-treated PA.

Interestingly, Kuzminova et al., (2014) determined that DBD plasma exposure time influences the water contact angle and surface energy properties of PA films. Even after 6 days of storage, only slight changes in water contact angle were observed for plasma-treated PA films. This phenomenon is clearly demonstrated in Fig. 7.

Figure 7. Water contact angle measurements from DBD plasma-treated and untreated PA films following storage in ambient air over treatment and storage time (adopted from Kuzminova et. al., (2014).

As can be observed from Fig. 7, water contact angle for treated films is much lower (30^o after 0.5 sec of treatment) than untreated nylon (64^o) and remains so (within a range of 25^o to 36^o), only varying slightly with treatment within 100h of storage.

Borcia et al., (2003) investigated the impact of applying DBD plasma to different types of polyamide films upon water contact angle (Table 1).

Table 1. Water contact angle (θ°) measured upon PA films as a function of energy and treatment time (sec), 3.5 mJ, (adopted from Borcia et al., 2003), selected data presented.

Film	Untreated	0.1 sec	0.2 sec	0.5 sec	1.0 sec	5.0 sec
PA 6	69.4	33.6	33.6	29.9	29.7	26.5
PA 6,6	80.6	48.1	44.1	32.9	30.2	23.1
PA 12	101.7	66.7	61.8	55.7	50.4	42.8

These water contact angle findings are interesting as they suggest that surface treatments of polymers like PA must be controlled when applying coatings to films at an industrial level, as it establishes how functional and stable antimicrobial coatings will be on film surfaces over

time. From extensive review of the scientific literature, it can be stated that the surface energy of plasma-treated PA films remains high and relatively stable over a long period of time. This means that once a high surface energy is created upon films surfaces, it will be maintained from the point of manufacture through the distribution chain and on into storage up to the point of utilisation, whereupon coatings can then be applied.

Borcia et al., (2003) investigated DBD plasma treatment time using PA 6 and assessed the impact of surface modification of the film and the degree of oxygen uptake by the film (Tab. 2). These authors determined that effective treatment time occurred extremely quickly and that contact angles reached a steady state after a mere 0.1-0.2 sec of exposure.

Table 2. Oxygen content (%) determined for various forms of PA films as a function of energy and treatment time (sec), 3.5 mJ, (adopted from Borcia et al., (2003), selected data presented).

Film	Untreated	0.1 sec	0.2 sec	0.5 sec	1.0 sec	5.0 sec
PA 6	13.5	18.2	18.6	18.7	19.6	23.5
PA 6,6	11.7	18.5	18.7	21.5	22.5	24.3
PA 12	10.3	12.2	15.6	17.3	19.2	27.3

As can be observed from Table 2, oxygen content increased during treatment time and this observation is consistent with the XPS spectra generated and can explain the occurrence of surface oxidation by atmospheric oxygen during treatment application.

The employment of different gases during plasma treatment was shown to produce different surface effects on PA films. AFM analyses of He/CF_4 atmospheric pressure plasma jet - treated PA showed that the surface roughness of films increased after atmospheric plasma treatment (Gao et al., 2009) as outlined previously in this review for other treatments. XPS analyses revealed that surface modification of PA films had occurred following exposure to He/CF_4 plasma in the presence of fluorine, nitrogen and oxygen containing functional groups (Tab. 3, Gao et al., 2009).

298 **Table 3**. Deconvolution analysis of C1s peaks of Control and He/CF_4 plasma treated PA 6 film
299 (adopted from Gao et al., (2009).

Sample	Relative area corresponding to different chemical bonds (%)					
	C-C (284,6 eV)	C-N (285,4 eV)	C-O/C-F_2 (286,5 eV)	CONH/CF (287,9 eV)	O-C=O (288,5 eV)	CF_3 (293,0 eV)
Control	58.4	31.8	-	9.8 (no CF)	-	-
He/CF_4, 30 sec	48,2	30.1	9.4	12.4	-	-
He/CF_4, 60 sec	40.0	27.8	10.4	17.8	-	-
He/CF_4, 90 sec	37.3	24.7	12.9	19.0	4.5	1.6

300

301 Thus, PA film surfaces can be physically modified by plasma when used in the presence of
302 different gases. Table 3 shows that after a treatment time of 90 sec, the O-C=O group appeared
303 on the film surface, which was also accompanied by the appearance of some other functional
304 groups, such as; C-O/C-F_2, CONH/CF, CF_3 which are associated with, and indicate, surface
305 functionalization including fluorination.
306 Pappas et al., (2006) used N_2/He atmospheric glow discharge plasma to treat PA 6 films. These
307 authors measured the atomic concentration of oxygen by XPS on the film surfaces and they
308 showed that oxygen concentration increased from 9.9% for untreated PA 6,6 film to 13.5% for
309 the equivalent film exposed to N_2/He plasma for 4.8 sec and determined the presence of new
310 functional groups such as –COOH and $R_1(R_2)C=O$ on the treated film surface which enhance
311 the hydrophilicity of the polymer. As previously described for other PA-treated materials,
312 surface roughness for these N_2/He glow discharge plasma treated films increased from
313 0.876μm to 1.769μm (after 4.8 sec treatment), as determined by confocal microscopy (Pappas
314 et al., 2006). Similarly, these authors showed that water contact angle decreased from 76.13^0
315 to 58.22^0 following N_2/He plasma exposure for 9.6 sec treatment, thereby increasing wettability
316 properties.
317 The ability to add and influence different functional groups on PA films through the
318 employment of different gas types used in conjunction with plasma application can alter and
319 increase the wettability properties of films. Consequently, this approach can be applied in the
320 development of antimicrobial packaging for polymer grafting and functionalization as shown
321 by Sedlarik, (2013). This specific strategy was employed by Shahidi et al., (2009) who treated
322 PA fibers with magnetron-sputtering low pressure glow oxygen plasma at ambient temperature.
323 Following plasma surface oxygen functionalization, PA fiber samples were placed in 0.1M
324 solution of $AgNO_3$ for 72hr, which was followed by washing in water and drying (Shahidi et

al., 2009). Antimicrobial properties for these coated nylon fibers were tested against *S. aureus*. Control fiber samples were compared against those which were deposited by magnetron sputtering of Cu nanoparticles on Ar plasma treated PA fibers. Cu-coated nylon fibres had the highest antimicrobial activity to *S. aureus,* as determined by inhibition growth zones determined in inoculated agar plates (Tab. 4, Shahidi et al., 2009).

Table 4. Percentage (%) inhibition of *S. aureus* based on nylon treatment (adopted from Shahidi et al., 2009).

PA fiber treatments	Percentage growth reduction (%)
Untreated Nylon	22
Cu-coated on Ar plasma treated Nylon	100
$AgNO_3$ coated Nylon	85
O_2 plasma treated $AgNO_3$ coated Nylon	92

As can be observed from Table 4, significant antimicrobial activities were achieved through application of oxygen plasma treatment, which proved to possess even higher antimicrobial activities than untreated $AgNO_3$ coated samples. This may have resulted from even greater adhesion between the activated fiber surfaces and the antimicrobial coating applied owing to the presence of –COOH and –OH groups following the application of oxygen plasma treatment.

Atmospheric-pressure plasma jets can applied for PA surface modification. Zhao et al., (2013) conducted experiments involving the deposition of Cu onto polyimide sheets following their treatment with Ar/H_2 atmospheric-pressure plasma jets. Penkov et al., (2015) published a review which focussed on the application of atmospheric pressure plasma jets upon different polymeric materials.

Combining technological approaches can result in producing different coating effects upon polymer surfaces or in the enhancement of different properties. One such interesting approach is the combined application of plasma jet technology and microwave generation. Hnilica et al., (2014) conducted experiments applying atmospheric microwave plasma jet technology to PA 12 films. These authors reported that this technological approach resulted in faster polymeric surface treatment than employing DBD, because of microwave generation, microwave discharges have advantages upon DBD and plasma jets because it leads to higher power density

and more homogeneous and heterogeneous chemical reactions in plasma (Hnilica et. al., 2014). Hnilica et. el., (2014) assessed the application of this treatment to PA 12 films, and employing different gases (Ar, Ar+2%O_2, Ar+2%N_2) and time treatments to do so. These authors determined that film wettability properties increased and that this phenomenon resulted from both chemical and morphological changes upon the film surfaces. AFM analysis of the film surfaces showed increasing RMS roughness in all treated samples (Tab. 5), with O1 atoms % increasing in the composition comparable to a control PA 12 film which was proved by XPS.

Table 5. RMS roughness from AFM and chemical composition of PA 12 films from XPS data, selected data presented (Hnilica et. el., 2014).

Film samples	RMS roughness after 1 sec of treatment, nm	O1s atom, %	C1s atom, %
Untreated PA 12 film	26	24.2	70.8
Plasma treated PA 12 with Ar (AM)	90	31.1	63.1
Plasma treated PA 12 with Ar+2%N_2 (AM)	44	35.9	56.8
Plasma treated PA 12 with Ar+2%O_2 (AM)	34	34.2	60.9

* (AM) - Amplitude modulated mode

Similar results to these were presented by Borcia et al., (2003) who showed that oxygen content on film surfaces increased over the same time following the application of DBD plasma to PA 12 films (Tab. 2).

In some instances, for food packaging, it is necessary to have hydrophobic surfaces, instead of those with a hydrophilic nature, for example, in packaging used for Ketchup, plastic bottles possessing hydrophobic surfaces make it easier to remove product from the bottle. This is an example of where the application of plasma surface treatment could assist in this application. Low pressure CF_4 plasma can be applied to PA films, when low wettability (hydrophobicity) is required over high wettability. Dreux et al., (2002) applied CF_4 and CF_4+H_2 (50/50 v/v) low-pressure, microwave plasma for surface modification of PA 12 films. In contrast to DBD plasma treatment, water contact angle increased, while polymer surfaces became more

hydrophobic (Dreux et al., 2002). Contact angle measurements were found to remain the same following about 5 min post-treatment, which means that the functionalization of film surfaces became stabilised after this time period (Dreux et al., 2002). This method also can be applied for the increasing of barrier films properties (Dreux et al., 2002). XPS studies revealed the appearance of fluorine groups on the film surfaces after plasma treatment and this observation was coupled with the finding that the water barrier properties of these films were altered following plasma fluorination (Dreux et al., 2002).

The application of physical vapour deposition and plasma jets to create antimicrobially-active PA-based packaging films through the employment of Cu and other metals seems promising, however, their use in food packaging applications might be somewhat limited owing to potential safety concerns and legislation. Low pressure plasma treatment conditions can enhance plasma treatment time and make chemical reactions more stable due to absence of atmospheric oxygen and can be applied to reel-to-reel inline plasma fluorination of film rolls. This method seems promising for the creation of hydrophobic surfaces on other polyamides and may prove to be a very useful approach for the creation of new packaging materials for potential food application when hydrophobic properties are necessary.

Corona treatment

Corona is the most useful and commonly used technology for surface treatment of packaging materials, particularly plastics and plastic-based laminates, in the packaging industry (Brewis & Mathieson, 2002). It is used to assist packaging materials to adhere to inks, varnishes, lacquers, adhesives and a host of other coatings. The impact of corona treatment upon the formation of amine groups in polymeric materials has not been described previously in the literature. Application of corona treatment on the other hand leads to the increase in wettability of PA films and thus, the increase in adhesion properties (Ilic et al., 2009).

Corona treatment, like UV and plasma treatments, induces the modification of functional groups on PA fiber surfaces. Ilic et al., (2009) reported that corona treatment led to a significant increase in the content of C=O, O–C=O, C-N and C-O groups on the surface of PA fibers as it can be seen from Tab. 6, which is consistent with plasma-treated PA films.

400 **Table 6**. Relative intensity data for deconvoluted C1s spectra of untreated and corona-treated
401 PA fabric as atomic ratio (%) from XPS data (adopted from Ilic et al., 2009).

Sample	C_{charge} 283.5 eV	C–C, C–H 285.0 eV	C–N, C–O 286.6 eV	C=O 288.3 eV	O–C=O 289.1 eV
Untreated PA fibre surface	18.81[a]	65.33	7.86	6.04	1.96
Corona treated PA fibre surface	22.21[a]	48.42	14.41	10.51	4.46

402 [a] This peak is observed at 283.2eV on PA fibers

403 Similar to plasma treatment followed by antimicrobial coating, corona treatment can be applied
404 in exactly the same manner. Corona was used in PA fibres in an attempt to attach antimicrobials
405 to its surface. Increasing PA hydrophilicity (like that reported previously for plasma and UV
406 treatments) after corona treatment led to the enhanced deposition of Ag nanoparticles (NPS)
407 onto PA fibers, which was determined by scanning electron microscopy (Ilic et al., 2009).
408 Vesna et al., (2009) demonstrated the antifungal activity of corona-treated PA fabrics
409 containing Ag NPS on their surfaces against *Candida albicans*. Radetic et al., (2008) applied
410 electrical discharge at atmospheric pressure corona treatment which facilitated the loading of
411 Ag NPS from colloids onto PA fabric surfaces. These authors demonstrated the antimicrobial
412 properties of these treated materials against *Staphylococcus aureus* and *Escherichia coli*.
413 Similar results were reported by Rezaei et al., (2016) following the corona treatment of PA 6
414 fabric with imbuement of nano-ZnO. These authors also showed the UV-blocking
415 characteristic of PA samples containing zinc oxide. This latter finding supports another benefit
416 to active coatings applied to polymeric surfaces, following corona treatment, especially for
417 food and beverage packaging applications where the consumable element of the product is
418 photo-sensitive. Photo-sensitive products can deteriorate in a number of ways, but particularly
419 through oxidation-led reactions which produce off-colours and off-flavours in food and
420 beverage products.

421 Like many technologies which have been around for a while and often consequently dismissed,
422 the use of corona treatment for PA packaging films should be explored further to assess its
423 capacity to activate polymeric surfaces for adhesion of a wide variety of functional coatings

and specifically, the impact that such applications might have on amine groupings on PA-based plastics for food application.

Conclusion

The surface structure of PA films remains relatively stable, irrespective of processing treatments applied. Processing treatments such as UV light irradiation, plasma and corona treatments appear promising in a bid to improve PA-based plastics for potential food usage through improvement in their adhesion (coating or grafting) properties with antimicrobial substances of natural and synthetic origin. UV treated PA has antimicrobial effect to a number of bacteria but the material application for food packaging is limited.

UV and Plasma treatments produce similar RMS surface roughness modifications in PA films after short periods of sample exposure. XPS surface studies involving PA plasma-treated surfaces showed that spectral properties for these films were similar to those treated using UV and that the functional groups created upon film surfaces following both treatments were similar. Additionally, different gases can be applied during plasma treatment in order to generate required surface properties on PA films. The employment of plasma treatments opens different opportunities for inline functionalization of PA surface modification, both with and without functionalised coatings. UV laser irradiation has been shown to be a useful tool for creating amine groups on PA film surfaces for antimicrobial application, however, more research is required around the application of this technology, as well as corona treatment which appears to have been ignored as a technology for applications as described in this review. As shelf-life issues become ever more important in terms of minimising food wastage, extending the food chain and minimising the use of packaging materials to achieve same, the development and use of packaging materials such as functionalised, active, PA-based packaging materials and systems could prove to be an example of legislatively-acceptable food packaging materials which address such problems.

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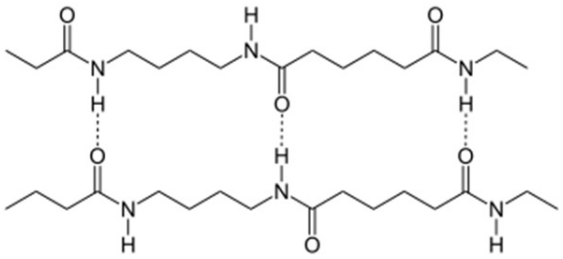
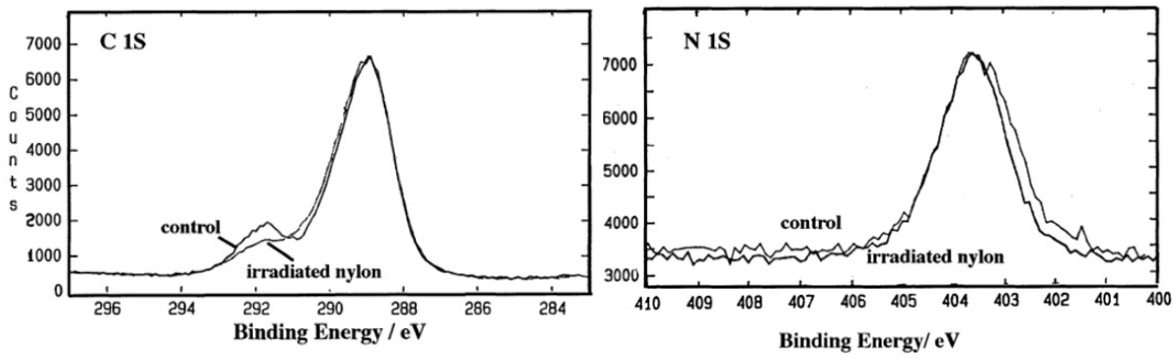


Figure 1. Nylon 6,6 and molecular hydrogen bonds between chains.



a b

Figure 2. XPS spectra of irradiated and non-irradiated nylon film (C1s atom spectra (2a) and N1s atom-spectra (2b), (adopted from Paik et al., 1998).

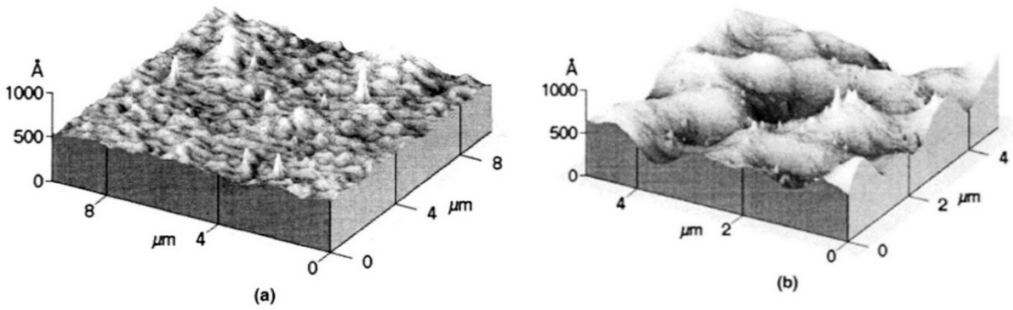


Figure 3. (a) AFM image of untreated PA film surface and (b) PA film treated with 193nm LPX 325i excimer laser employing 45 pulses of 58 MJ cm^{-2} (adopted from Adrienne et al., 2000).

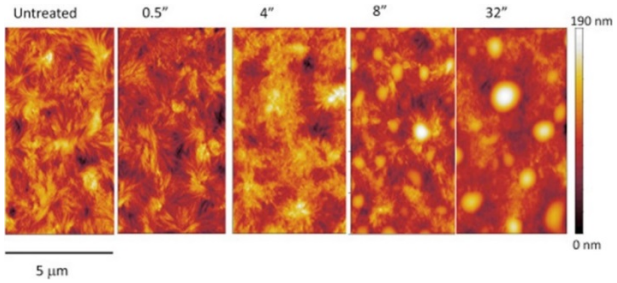


Figure 4. Examples of 10 x 5µm AFM scans of untreated nylon foil and nylon foil exposed to DBD plasma for different treatment times from 0.5 to 32 sec (adopted from Kuzminova et al., (2014).

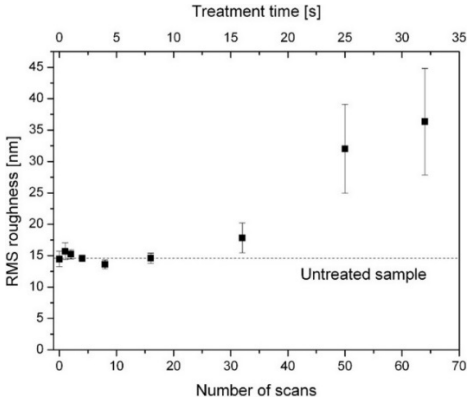
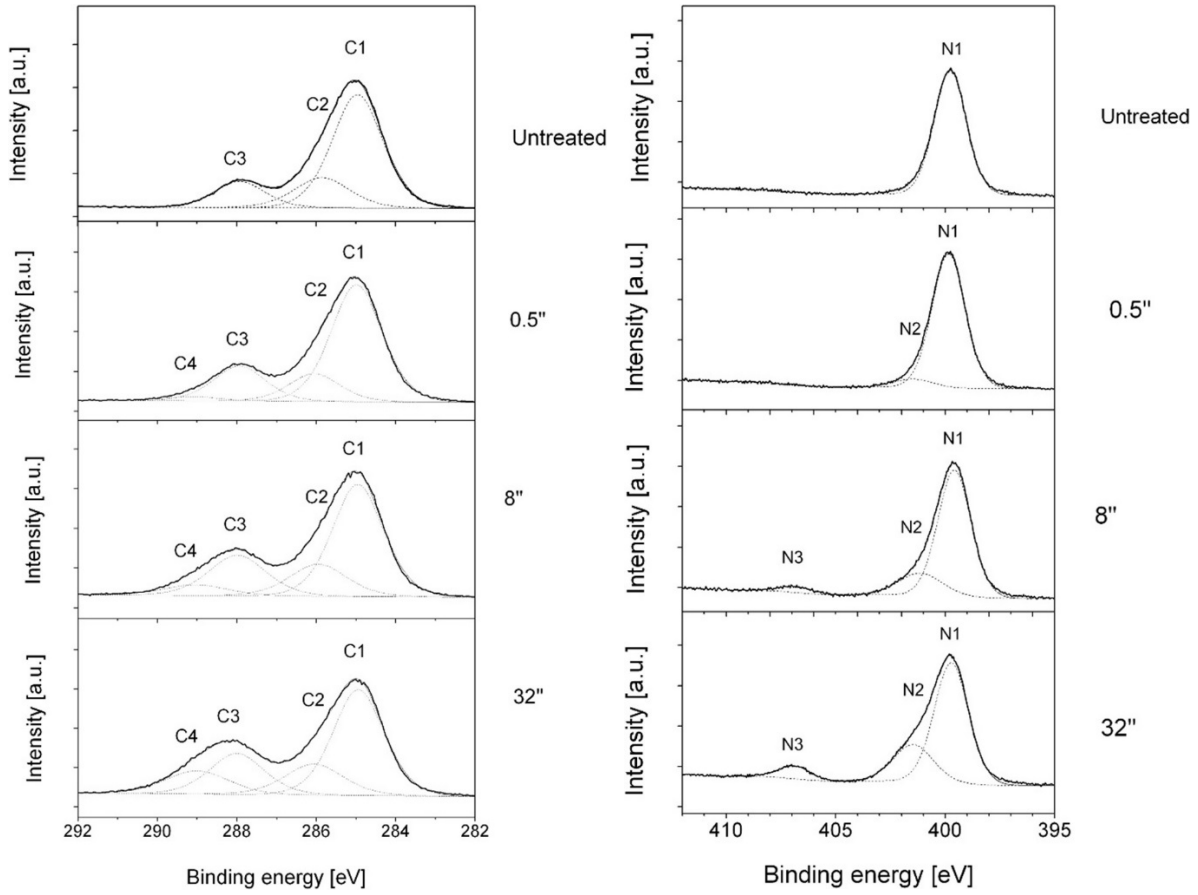


Figure 5. RMS roughness modifications of nylon films (50 μm) exposed to DBD plasma after different treatment times (adopted from Kuzminova et al., (2014).



a b

Figure 6. High resolution XPS spectra of C1s (a) and N1s (b) component peaks of untreated and DBD-treated nylon films (adopted from Kuzminova et al., 2014).

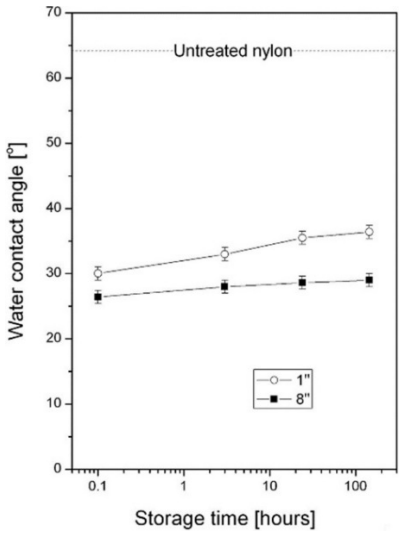


Figure 7. Water contact angle measurements from DBD plasma-treated and untreated PA films following storage in ambient air over treatment and storage time (adopted from Kuzminova et. al., (2014).