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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.

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

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11
12 *Keywords:* Polyamide; Surface treatment; Film structure; Food packaging; Antimicrobial
13 packaging, surface analysis

14
15 **Highlights**

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22
23
24 ***Abstract***

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

30 *Scope and Approach:* The objective was to investigate the potential application of various
31 surface treatment methods for the potential manufacture of antimicrobial packaging and to
32 identify the necessary spectral characteristics deemed necessary to achieve this.

33 *Key Findings and Conclusions:* XPS and AMF methods are useful tools in the identification
34 of film surface analysis and can be industrially applied. For UV treatment, different light
35 sources, including lasers, can be applied to create antimicrobially-active packaging materials.
36 UV-treated PA films possess antimicrobial properties and offer potential for industrial and
37 medical packaging applications, however, the application of such packaging materials to foods
38 needs some special consideration.

39 Different plasma treatment methodologies can be used for modification of PA surfaces,
40 followed by attachment of antimicrobial coatings. Surface studies have shown that plasma-
41 treated PA surfaces possess spectral properties similar to those for UV-treated samples. Corona
42 treatment, like UV and plasma treatments, induce the modification of functional groups on PA
43 film surfaces. Corona treatment has the capacity to activate polymeric surfaces for adhesion of
44 a variety of functional coatings and should be explored further in terms of creating special
45 antimicrobial coatings.

46

47 **Introduction**

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

62 elements such as AlO_x and SiO_x (Amberg-Schwab, 2005) and its combinations (Amberg-
63 Schwab, 2006) on oriented films.

64 Antimicrobial packaging is a form of smart packaging which resides within the active grouping
65 of technologies. It is a commercially important and emerging market sector within the food
66 packaging area, principally because it addresses the primary factor responsible for food
67 spoilage, which is microbial food spoilage. Delivering high quality food products in a suitable,
68 high-barrier flexible packaging format is essential in order to reduce packaging weight and
69 food wastage (Clarke et al., 2017). The potential to enhance the characteristics of such
70 packaging materials through the creation of active packaging surfaces, which are antimicrobial
71 in nature, would allow the food industry to continue to use desirable, polymer-based packaging
72 materials, but with the added advantage of increasing product storage stability and shelf-life
73 extension. Transnational, overseas shipping of food and beverage products makes significant
74 demands upon the robustness and durability of products, especially in relation to shelf-life
75 stability. For food and beverage processors, the necessity to retail products in ever distant
76 markets means that conventional packaging materials and formats used for standard product
77 lines are inadequate to cope with additional environmental, handling, storage and transport
78 stresses posed by the elongated distribution chain. Consequently, the availability of active
79 packaging materials would assist food and beverage companies cope with these issues through
80 the extension of product shelf-life, while potentially allowing packaging materials to be further
81 light-weighted. Antimicrobial packaging can continuously present antimicrobial agents
82 directly to the food surface, or indirectly by the presence of atmospheric modifiers.
83 Antimicrobial packaging that functions through a direct approach is usually the most
84 successful. Numerous reviews have been published in recent years outlining the plethora of
85 potential substances that are available and could be employed in conventional packaging
86 materials to create active packaging for potential commercial uptake (Appendini & Hotchkiss,
87 2002; Quantavalla & Vicini., 2002; Suppakul et al., 2003; Kerry et al., 2006; Sung et al., 2013;
88 Malhotra et al., 2015; Sofi et al., 2018). Such agents can be applied within or upon packaging
89 materials to continuously migrate to the food surface and beyond or remain immobilised at the
90 package/product interface in order to avoid migration issues. In any case, the purpose is to
91 ensure that these materials are antimicrobial in nature.

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

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

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

123

124 **Polyamide (PA)**

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

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

130

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

132 Polyamide is widely used in food packaging, principally in laminate constructions where they
133 are often combined with polyolefins, foils or applied as a co-extruded layer in packaging films.
134 PA films possess: low to moderately low oxygen transmission rates (10–50 cc/m² day at STM),
135 good puncture resistances and high tensile strengths. Films containing PA are particularly used
136 for the packaging of muscle-based food products (especially bone-in or shell-possessing
137 products), cheese and products which are hard and possess distinctive edging using packaging
138 formats which include; vacuum pouches, thermoforming trays, vacuum and heat-shrinking
139 bags, vacuum skin packaging, MAP, among others (Laurence & Massey, 2013).

140

141 **Polyamide-based film surface treatments**

142 **UV treatment**

143 The first application of UV for the purposes of antimicrobial surface activation of PA was
144 patented by Cohen et al., (1995). UV irradiation was applied through the use of disclosed
145 photon sources, including excimer lasers and ultra violet (UV) lamps. ArF excimer lasers can
146 generate wavelengths of 193 nm and were used in the development of this patent (Cohen et al.,
147 1995). Adrienne et al., (2000) reported that approximately 10% of the amide groups can be
148 converted to amines or approximately 5×10^{12} amine groups per cm² of the film for UV treated
149 PA yarn or fabric. It was demonstrated that UV-irradiated nylon yarn exhibited antimicrobial
150 activity against 99% of *Klebsiella pneumonia* (Shake Flask test) after 12 J/cm² energy per pass
151 radiation exposure (Cohen et al., 1995). Paik et al., (1998) suggested that upon the impact of
152 applying UV irradiation for the purposes of surface activation of nylon 6,6 with respect to the
153 development of antimicrobially-active packaging materials. These authors employed a Lambda
154 LPX-325i excimer laser which produced a beam of UV light at 193nm to convert amide groups
155 on the surface of nylon to antimicrobial amines. Treated film surfaces were studied by XPS
156 method (Paik et al., 1998). The XPS spectra generated from these studies is shown here (Fig.
157 2a, b) and it is interesting to note that the C=O groups of PA were diminished following UV
158 irradiation as indicated by the decrease in signal at 292 eV, which is associated with carbonyl
159 groups (Paik et al., 1998). Similar XPS spectrum was produced by Adrienne et al., (2000). The

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

163

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

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

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

170

171 **Figure 3.** (a) AFM image of untreated PA film surface and (b) PA film treated with 193nm
172 LPX 325i excimer laser employing 45 pulses of 58 MJ cm^{-2} (adopted from Adrienne et al.,
173 2000).

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

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

198 However, chemical-surface modification of PA with antimicrobial elastomers could potentially
199 solve this issue for food packaging applications. Wintzer et al., (2015) investigated the effect
200 of short wave ultraviolet C light (UVC) produced by low-pressure mercury lamps employing
201 185nm and 254nm emissions on PA fibres. The UVC pre-treatment of PA fibre leads to
202 significantly increased adhesion strength between the fibres and the melt, processable,
203 elastomers (Wintzer et al., 2015) which can be modified by the addition of antimicrobial
204 compounds. Another example of surface nylon modification for increasing adhesion for further
205 surface functionalization is the treatment by a KrF 248nm excimer laser. Waugh & Lawrence
206 (2018) applied this laser wave to surface pattern nylon 6,6 film in an attempt to modify the
207 wettability characteristics. Thus, UV laser treatment opens up a wide range of possibilities for
208 surface modification of films by utilising different coatings for application within the food
209 packaging industry.

210 **Plasma treatment**

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

217

218 **Figure 4.** Examples of 10 x 5 μ m AFM scans of untreated nylon foil and nylon foil exposed to
219 DBD plasma for different treatment times from 0.5 to 32 sec (adopted from Kuzminova et al.,
220 (2014).

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

224

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

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

230 Similar to the UV treatment (Fig. 2), C1s atoms, XPS studies revealed a decrease in carbon
231 atom content (Kuzminova et al., 2014). These authors reported that the C1 component
232 decreased from 66% (untreated PA) to 50% (after 32 sec of PA treatment) (Fig. 6a). As a result
233 of the decrease in the C1 component, a new C4 component peak appeared and was described
234 as the result of a formation of O-C=O groups on the surface of PA films and reached a level of
235 13% following a 32sec treatment of DBD plasma (Fig. 6a, Kuzminova et al., 2014). These
236 authors indicated that all C, O and N-components in PA films had been identified through XPS
237 spectra.

238

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

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

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

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

258

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

262 As can be observed from Fig. 7, water contact angle for treated films is much lower (30° after
 263 0.5 sec of treatment) than untreated nylon (64°) and remains so (within a range of 25° to 36°),
 264 only varying slightly with treatment within 100h of storage.

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

267 **Table 1.** Water contact angle (θ°) measured upon PA films as a function of energy and
 268 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

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

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

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

281 **Table 2.** Oxygen content (%) determined for various forms of PA films as a function of energy
 282 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

283
 284 As can be observed from Table 2, oxygen content increased during treatment time and this
 285 observation is consistent with the XPS spectra generated and can explain the occurrence of
 286 surface oxidation by atmospheric oxygen during treatment application.

287 The employment of different gases during plasma treatment was shown to produce different
 288 surface effects on PA films. AFM analyses of He/CF₄ atmospheric pressure plasma jet - treated
 289 PA showed that the surface roughness of films increased after atmospheric plasma treatment
 290 (Gao et al., 2009) as outlined previously in this review for other treatments. XPS analyses
 291 revealed that surface modification of PA films had occurred following exposure to He/CF₄
 292 plasma in the presence of fluorine, nitrogen and oxygen containing functional groups (Tab. 3,
 293 Gao et al., 2009).

294
 295
 296
 297

298 **Table 3.** Deconvolution analysis of C1s peaks of Control and He/CF₄ 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-F₂, CONH/CF, CF₃ which are associated with, and indicate, surface
 305 functionalization including fluorination.

306 Pappas et al., (2006) used N₂/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 N₂/He plasma for 4.8 sec and determined the presence of new
 310 functional groups such as -COOH and R₁(R₂)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 N₂/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°
 315 to 58.22° following N₂/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 AgNO₃ for 72hr, which was followed by washing in water and drying (Shahidi et

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

330 **Table 4.** Percentage (%) inhibition of *S. aureus* based on nylon treatment (adopted from
 331 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

332 As can be observed from Table 4, significant antimicrobial activities were achieved through
 333 application of oxygen plasma treatment, which proved to possess even higher antimicrobial
 334 activities than untreated AgNO₃ coated samples. This may have resulted from even greater
 335 adhesion between the activated fiber surfaces and the antimicrobial coating applied owing to
 336 the presence of –COOH and –OH groups following the application of oxygen plasma
 337 treatment.

338 Atmospheric-pressure plasma jets can applied for PA surface modification. Zhao et al., (2013)
 339 conducted experiments involving the deposition of Cu onto polyimide sheets following their
 340 treatment with Ar/H₂ atmospheric-pressure plasma jets. Penkov et al., (2015) published a
 341 review which focussed on the application of atmospheric pressure plasma jets upon different
 342 polymeric materials.

343 Combining technological approaches can result in producing different coating effects upon
 344 polymer surfaces or in the enhancement of different properties. One such interesting approach
 345 is the combined application of plasma jet technology and microwave generation. Hnilica et al.,
 346 (2014) conducted experiments applying atmospheric microwave plasma jet technology to PA
 347 12 films. These authors reported that this technological approach resulted in faster polymeric
 348 surface treatment than employing DBD, because of microwave generation, microwave
 349 discharges have advantages upon DBD and plasma jets because it leads to higher power density

350 and more homogeneous and heterogeneous chemical reactions in plasma (Hnilica et. al., 2014).
 351 Hnilica et. el., (2014) assessed the application of this treatment to PA 12 films, and employing
 352 different gases (Ar, Ar+2%O₂, Ar+2%N₂) and time treatments to do so. These authors
 353 determined that film wettability properties increased and that this phenomenon resulted from
 354 both chemical and morphological changes upon the film surfaces. AFM analysis of the film
 355 surfaces showed increasing RMS roughness in all treated samples (Tab. 5), with O1 atoms %
 356 increasing in the composition comparable to a control PA 12 film which was proved by XPS.

357 **Table 5.** RMS roughness from AFM and chemical composition of PA 12 films from XPS data,
 358 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

359 * (AM) - Amplitude modulated mode

360 Similar results to these were presented by Borcia et al., (2003) who showed that oxygen content
 361 on film surfaces increased over the same time following the application of DBD plasma to PA
 362 12 films (Tab. 2).

363 In some instances, for food packaging, it is necessary to have hydrophobic surfaces, instead of
 364 those with a hydrophilic nature, for example, in packaging used for Ketchup, plastic bottles
 365 possessing hydrophobic surfaces make it easier to remove product from the bottle. This is an
 366 example of where the application of plasma surface treatment could assist in this application.
 367 Low pressure CF₄ plasma can be applied to PA films, when low wettability (hydrophobicity)
 368 is required over high wettability. Dreux et al., (2002) applied CF₄ and CF₄+H₂ (50/50 v/v) low-
 369 pressure, microwave plasma for surface modification of PA 12 films. In contrast to DBD
 370 plasma treatment, water contact angle increased, while polymer surfaces became more

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

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

387

388 **Corona treatment**

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

396 Corona treatment, like UV and plasma treatments, induces the modification of functional
397 groups on PA fiber surfaces. Ilic et al., (2009) reported that corona treatment led to a significant
398 increase in the content of C=O, O-C=O, C-N and C-O groups on the surface of PA fibers as it
399 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 ^aThis 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 imbueement 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

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

426 **Conclusion**

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

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

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452

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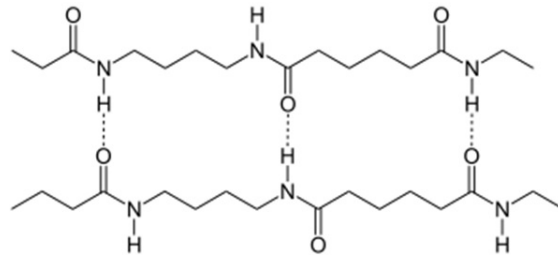


Figure 1. Nylon 6,6 and molecular hydrogen bonds between chains.

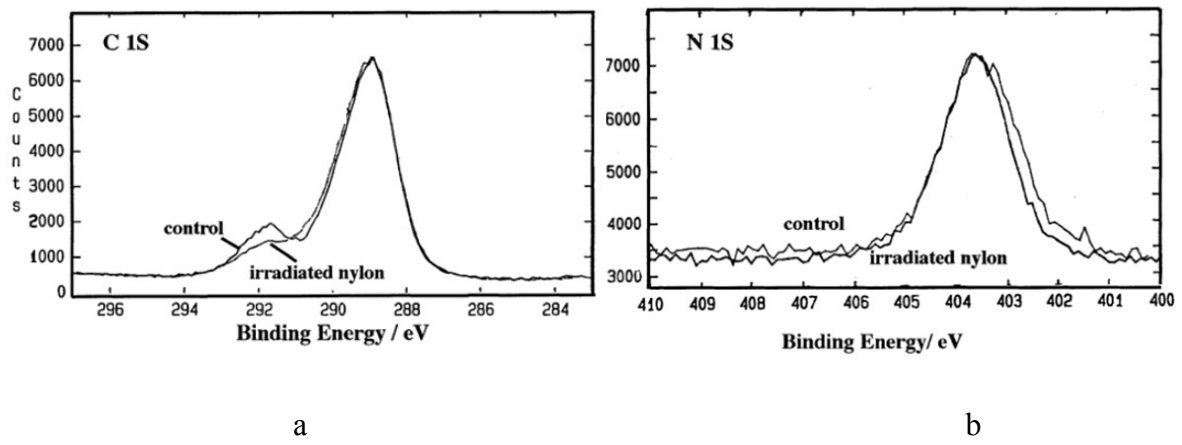


Figure 2. XPS spectra of irradiated and non-irradiated nylon film (C1s atom spectra (2a) and N1s atom-spectra (2b)), (adopted from Paik et al., 1998).

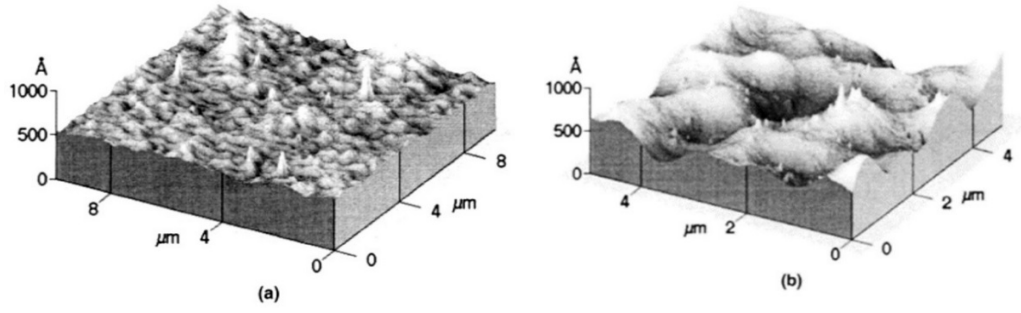


Figure 3. (a) AFM image of untreated PA film surface and (b) PA film treated with 193nm LPX 325i excimer laser employing 45 pulses of 58 MJ cm^{-2} (adopted from Adrienne et al., 2000).

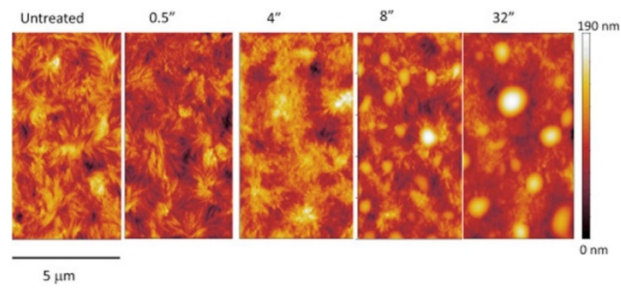


Figure 4. Examples of 10 x 5 μ m AFM scans of untreated nylon foil and nylon foil exposed to DBD plasma for different treatment times from 0.5 to 32 sec (adopted from Kuzminova et al., (2014).

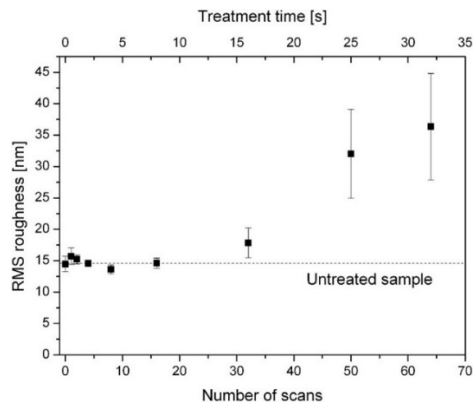


Figure 5. RMS roughness modifications of nylon films ($50\ \mu\text{m}$) exposed to DBD plasma after different treatment times (adopted from Kuzminova et al., (2014)).

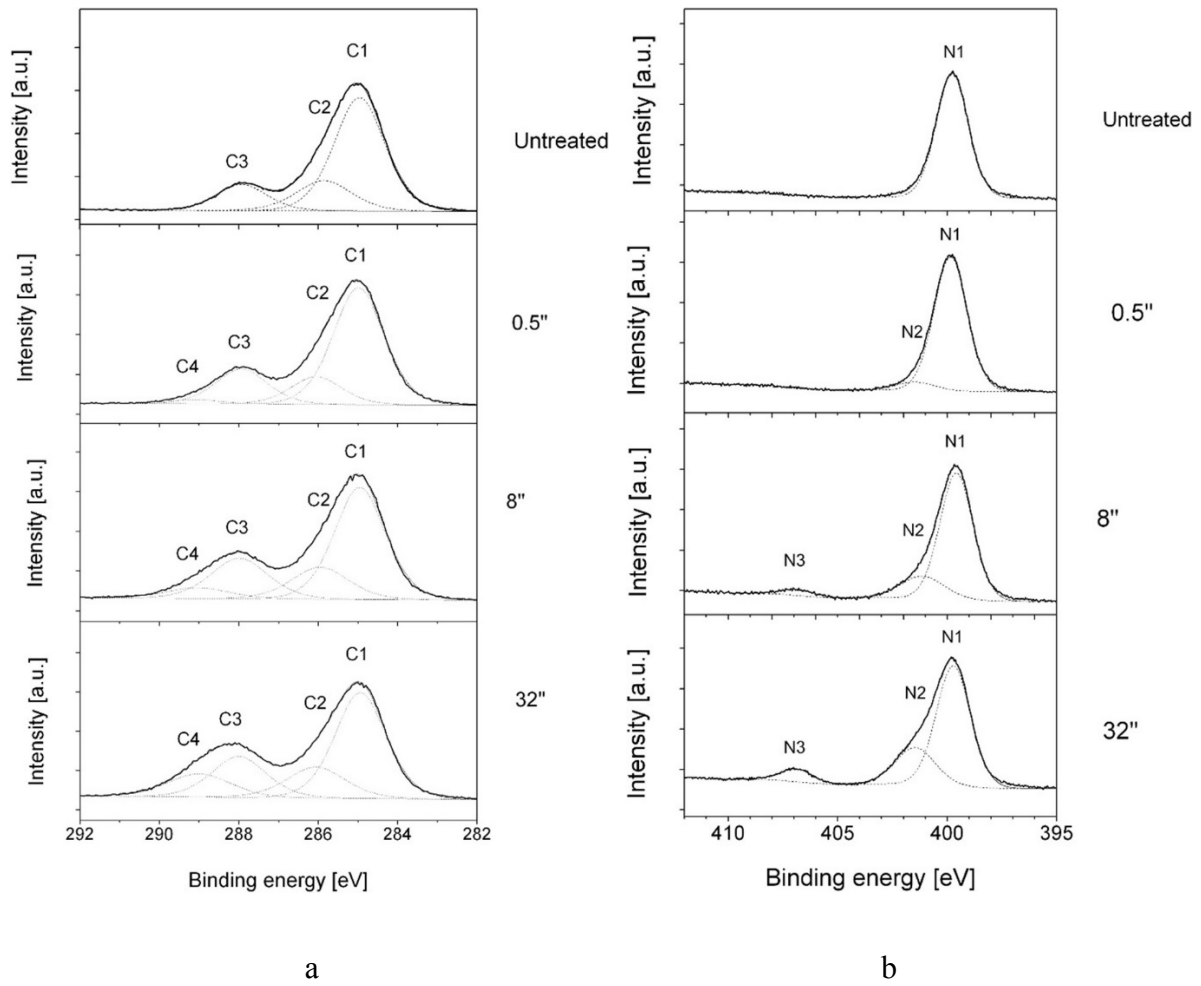


Figure 6. High resolution XPS spectra of C1s (a) and N1s (b) component peaks of untreated and DBD-treated nylon films (adopted from Kuzminova et al., 2014).

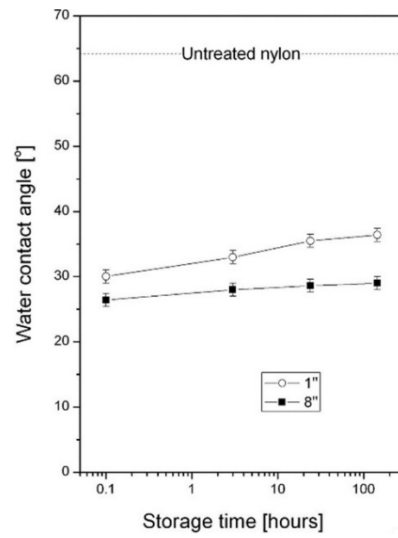


Figure 7. Water contact angle measurements from DBD plasma-treated and untreated PA films following storage in ambient air over treatment and storage time (adopted from Kuzminova et. al., (2014)).