Influence of helium-dielectric barrier discharge treatments on the adhesion properties of polyamide-6 surfaces

G. Borcia*, N. Dumitrascu, G. Popa

Plasma Physics Department, A.I. Cuza University, 11, bd. Carol I, Iasi-700506, Romania

Received 5 April 2004; accepted in revised form 21 January 2005
Available online 10 March 2005

Abstract

Due to the poor adhesion properties of polymers, the immobilization of certain species onto the polymer surface requires a pretreatment in order to increase the surface reactivity. In our experiments, a diffuse dielectric barrier discharge (DBD) in helium at atmospheric pressure has been used to improve the wettability and the adhesion properties of polyamide-6 (PA-6) films. The surface characteristics are analyzed by atomic force microscopy (AFM), contact angle measurements and X-ray photoelectron spectroscopy (XPS). The treated surfaces present a modified morphology, with an increased area compared to the untreated ones, effect which is favorable for the physical adsorption at the surface. The strong increase of the adhesion work on the treated surfaces show that new functional (hydrophilic) groups are introduced onto the surface. The surface modification takes place in less than 10 s of treatment and presents only limited reversal to the untreated state over long ageing time. The DBD treatment markedly induces an important increase of the oxygen amount at the surface, which is due both to the “cleaning” of the surface by removal of the weak cohesive layer that makes barrier with the environment and to the surface oxidation by oxygen incorporation from atmospheric air. The physico-chemical surface modifications, related with a modified morphology, an increased polarity and a higher level of surface oxidation, may be favorable to the further linkage of selected biological species relevant in medical usages.

© 2005 Elsevier B.V. All rights reserved.

PACS: 52.50.Dg; 52.77.–j; 81.65.–b

Keywords: Dielectric barrier discharge; Helium; Surface treatment; Polyamide-6 films; Adhesion; Oxidation; Stability

1. Introduction

Nowadays, the polyamides are increasingly used for many applications, such as thermoplastic sheet composites, foils for protective and packaging purposes (foodstuffs, engineering components), coatings for corrosion protection or sealing applications, synthetic textile fibers, tapes and cable insulation, etc. The polyamide-6 (PA-6) is one of the most common polymer surfaces of interest in many biological and medical applications such as orthopedic implants, membranes for reverse osmosis, ultrafiltration and electrodealysis, biosensors or as nonabsorbable mono- and polyfilaments with minimal inflammation effects [1,2]. The PA-6 material is characterized by high toughness and tensile strength, low coefficient of friction, high melt point, good resistance to abrasion, water and chemicals, good thermal stability, low gas permeability and easiness to process. Although some of these properties may be desirable in several applications, including, for example, low friction films and seals, these become a disadvantage and have to be overcome for many other applications. Due to their low surface energy, poor chemical reactivity below melting point and the presence of a weak cohesion layer at the surface, the PA-6 surfaces have poor wettability and adhesion with other substrates. For this reason, a surface pre-treatment is required to reach satisfactory adhesion, such as for bonding, painting, stamping, metallizing and printing applications. For applications in the medical domain, a correlation of the bulk and the surface properties is necessary to achieve the requirements of biocompatibility and one of the solutions for improving the biocompatibility...
of materials is to cover the surface with selected biological layers, which is directly related to the adhesion properties of the material.

On account of these applications of PA-6, the methods used to treat a polymer surface are highly various. They can be mechanical, thermal, chemical, photochemical, various discharges and plasma. For example, physical and chemical methods used on the PA thermoplastic sheet composites can improve the hydrophilicity and the transport flux for dialysis, the permeability to NaCl and urea of PA-6 dialysis membrane [3,4]. The incorporation of inorganic salts in PA-6 films induces an increase in the glass transition temperature, the melting temperature and the index of crystallinity [5]. Other methods such as microwave plasma treatment in nitrogen/oxygen can improve the wettability and the adhesive properties of PA-6 films by introduction of oxygen [6] or nitrogen-containing groups on the surface [7].

Recently, the chemical processes occurring in dielectric barrier discharges (DBD) have many applications in various material processing technologies [8]. The major advantage of this technique is that it offers the possibility of inducing significant surface chemical modifications on a material exposed to the discharge at atmospheric pressure. Such plasma-based treatments using DBDs are obviously attractive to the industrial user who wants to avoid the high engineering costs usually associated with vacuum-based plasmas. Moreover, DBD can be used to treat large categories of substrates (metallic, dielectric, semiconductors) with various geometry and size and the surface modification takes place only on a few top monolayers of the surface keeping the bulk physical and chemical properties unaffected below a depth of about 100 Å. DBD is also able to improve the wettability and the adhesive properties of the surface by removing the weak cohesion layer present at the surface, introducing and/or generating new functional groups onto the surface, increasing the surface roughness, etc. [9]. These processes could be further used in enhancing the biocompatibility of the materials by controlling the properties of the surfaces at the contact with the biological environment, which are relevant for surface linkage of molecules intervening in medical usages (drugs, enzymes, proteins, etc.) [2–4,10].

Taking into account the above discussions, we present here the effects of a helium diffuse dielectric barrier discharge (DBD) on the surfaces of PA-6 films. Helium is well known for use in polymer surface treatments, with its low degradation effect and high properties of crosslinking and functionalization onto surface [11]. Moreover, helium allows stabilizing glow discharges at atmospheric pressure much easier compared to other gases, at lower sustaining voltages and inter-electrode gaps as high as a few centimeters [12].

The treatments of the PA-6 films were performed for various DBD exposure times up to 1 min. The influence of this parameter on the surface properties was investigated by atomic force microscopy (AFM), contact angle measur-
parameter on the surface properties was systematically investigated.

2.3. Morphology analysis

The atomic force microscopy (AFM) technique was used to visualize and compare the morphology of untreated and treated polymer surfaces. The AFM measurements were carried out in the tapping (non-contact) mode, with commercial standard silicon-nitride cantilever (NSC21) the force constant of 17.5 N/m, resonance frequency of 210 kHz and tips radii ≤10 nm. Topography and phase images were simultaneously recorded for each sample on various scanned areas between 70 μm×70 μm and 1 μm×1 μm. Each image consists of multiple scans laterally displaced from each other in the y direction, the surface being sampled with 256×256 pixels. Low-pass filtering was performed to remove the statistical noise without loss of information. AFM measurements were repeated on different sites of the sample, for the purpose of reproducibility, under the same conditions of room temperature and ambient atmosphere.

2.4. Contact angle measurement

Contact angle measurements were performed by the sessile drop technique (0.5 μl drops of bidistilled water). The values shown are averaged over 10 measurements per sample. The adhesion work of water on the PA-6 samples was evaluated. The stability of the modified samples was monitored for 2 months after treatment, with measurements repeated periodically within this interval.

2.5. Surface chemical characterization

The X-ray photoelectron spectra (XPS) were recorded on a HP 5950A spectrometer using monochromatic AlKα radiation (1486.6 eV) under a vacuum of about 10⁻⁹ Torr at electron take-off angle of 51.5°. Under these conditions, XPS probes the top 50 Å of the polymer films. An X-ray power of 600 W was used during analysis. The high-resolution spectra were taken in the constant analyzer energy mode with a 120 eV pass energy. The value of 285.0 eV of the hydrocarbon C1s core level was used as a calibration of the energy scale. The peak envelopes were curve-fitted using mixed Gaussian–Lorentzian component profiles, with linear-type background subtraction. Spectra were fitted based on standard measurement [14].

3. Results and discussion

3.1. Morphology analysis

The evaluation of the surface morphology and the surface roughness is relevant in our discussions on the adhesion properties of the samples. For example, in medical applications, the surface morphology, specifically the particles size and their distribution, could significantly enhance the human endothelial cell attachment at the surface of an implant [15].

In our experiments, the AFM images recorded on treated and untreated PA-6 samples showed that a new morphology was induced by DBD treatments (Fig. 2). 10 s exposure did show small changes on the surface of the polymer film, while visible change was observed for increased treatment time. On the surface treated for 60 s, small irregularly shaped grains are observed, which tend to become clearly distinguishable with increasing treatment time. This effect could be due to the “cleaning” of the surface by DBD. On the untreated surface, these grains could be hidden by the outermost amorphous regions, so they become more visible after the sputtering of the amorphous low cohesion surface layer, known to have high chemical inertness. The DBD treatments may thus produce such effects as removal of contaminants, oligomers and amorphous layers existing on the surface, allowing the “activation” of the material. This will be discussed later related to XPS results.

Obviously, the treated surfaces present an increased area (increased roughness) compared to the untreated ones. In this respect, the absolute roughness and the rms roughness are presented in Table 1. This effect could be favorable for the physical adsorption at the surface, as this “real” exposed area can subsequently undergo linkage to biological species of interest in medical usages.

Importantly, treatments with duration of a few tens of seconds do not lead to damage as a result of etching effects.

3.2. Contact angle measurement

The first step in the mechanisms taking place at the interface between a material and its environment is governed by the surface energy components, which are controlling the adsorption. The adhesion work \( W_a \) was chosen as a thermodynamic parameter relevant for the adsorption characteristics of the surface, while it controlled all physical interfacial events. \( W_a \) was calculated using the Dupré–Young equation:

\[
W_a = \gamma_{lv}(1 + \cos \theta)
\]

where \( \theta \) is the contact angle and \( \gamma_{lv} \) is the surface tension of the liquid used for measurements.

Fig. 3 presents the influence of the treatment time on the adhesion work of water on the DBD treated PA-6 films.

In the present case, the adhesion work is found to change from 100.8 mJ/m² for the untreated sample to the highest value of 136.9 mJ/m² associated with the 60 s treated sample, i.e. about 36% increase from the initial value.

The strong increase of \( W_a \) on the treated surfaces suggests that new functional (hydrophilic) groups be
introduced onto the surface. This behaviour can be attributed to surface oxidation. The molecular oxygen which is inherently entrained in the inter-electrode gap from the contacting air is activated, ionised and dissociated in the discharge to give extremely reactive oxygen species that react readily with the substrate surface. The details of this oxidation were assessed by XPS analyses and are given later.

The surface modification takes place in less than 10 s of treatment, as shown by the “saturation” of the \( W_a \) values for all treatment times up to 1 min. Thus, DBD treatments lead to the enhanced wettability and adhesion properties even after very short treatment times.

Referring to Fig. 3, the treated PA-6 film material partly recovers after treatment, as shown by the diminution of the adhesion work with ageing time. In fact, \( W_a \) reverted by 10–16% towards that of the untreated state over a period of 60 days. As expected, the material never fully returns to the untreated state. The modified surfaces tend to recover in the first 3 days after treatment and all further evolution is much slower.

### 3.3. Surface chemical characterization

The XPS technique was used to elaborate the results obtained by contact angle measurement, which suggested a strong oxidation level at the surface of the DBD treated samples, i.e. increased hydrophilicity after treatment.

The polyamide characteristic elements (C, O and N) were identified on the general spectra. High-resolution spectra of the polyamide surfaces for the C1s, O1s and N1s regions were

| Table 1 | Absolute roughness \(|R|\) and rms roughness \(R_{\text{rms}}\) (in nanometers) for PA-6 films vs. the treatment time |
|---------|----------------------------------|-----------------|-------------|-------------|
|          | Untreated | 10 s | 30 s | 60 s |
| \(|R|\) (nm) | 2.40     | 3.08 | 4.14 | 4.98 |
| \(R_{\text{rms}}\) (nm) | 3.07     | 3.88 | 5.09 | 5.91 |

Fig. 2. AFM images of treated and untreated PA-6 films (3 \( \mu \text{m} \times 3 \mu \text{m} \)): (a) untreated, (b) 10 s, (c) 30 s and (d) 60 s treated.

Fig. 3. Adhesion work of PA-6 films vs. treatment time and ageing time.
due to the formation of C–O bonds as shown by the strongly increased ratio of O2/O1 for the treated samples (Table 3c).

No major change in the surface elemental composition further occurs at treatment time between 10 s and 30 s. Obviously, one can expect that all sample surfaces reach a limiting level of oxidation as the surface equilibrates, under specific discharge conditions, by a combination of surface oxidation and/or loss of carbon through conversion to low weight volatile fragments, such as CO or CO2. After the treatment time of 60 s, a decrease of the oxygen content at the surface is measured, showing that more extended treatment eventually leads to a reversal of the balance between the functionalization and the degradation of the surface, i.e. a diminution of the level of oxidation arises due to etching, as chain scission dominates at high treatment times.

The nitrogen amount at the surface shows only a minor augmentation with prolonged DBD exposure (Table 3a). One source could be the nitrogen in atmospheric air, but the nitrogen amount is certainly too low to achieve nitrogen functionalization in a discharge with no nitrogen-containing gas deliberately added. It is very probable that the surface cleaning allows the fingerprint of the material bulk to appear on the spectra and the nitrogen percentage thus appears to increase. This interpretation is also consistent with the increase of the C2 component, which may be due not to the formation of C–N groups but to CO moieties, as carbon singly bonded to oxygen has a binding energy very close to carbon in CN groups.

In our experiments, the surface chemical functionalization and the enhanced adhesion properties are thus due to oxygen-related polar groups, not surprisingly for an atmospheric pressure discharge, where oxygen represents a very reactive species, present even under well controlled working environments.

4. Conclusion

We present in this paper the effects of a helium diffuse dielectric barrier discharge (DBD) on the modification of the surface characteristics of PA-6 films that are controlling the adhesion properties. The morphology and the roughness of the surface, the surface energy characteristics and the chemical structure, in particular the presence of specific functional groups, are all parameters with an important role in the adhesion properties of the material.

The treatments of the PA-6 films were performed for various DBD exposure times up to 1 min. The stability of the modified samples was monitored for 2 months after treatments.

The treated surfaces present a modified morphology, with an increased area (increased roughness) compared to the untreated ones, obtained by such effects as removal of contaminants, oligomers and amorphous layers existing on the surface, allowing the “activation” of the material. This effect is favorable for the physical adsorption at the surface. As this “real” exposed area can subsequently undergo linkage to biological species of interest in medical applications.

The strong increase of the adhesion work on the treated surfaces is correlated with the XPS results, which show that new functional (hydrophilic) groups are introduced onto the surface. The surface modification takes place in less than 10 s of treatment and presents only limited reversal (10–16%) to the untreated state over long ageing time. The DBD treatment markedly induces an important increase of the oxygen amount at the surface, which is due both to the “cleaning” of the surface by removal of the weak cohesive layer that makes barrier with the environment and to the surface oxidation by oxygen incorporation from atmospheric air.

The results bring further information to previous investigations, which showed that DBD treatments had the ability to create active and ionized sites on the polymer surface of PA-6 films, favoring interactions between the material and biological liquids (immunoglobulin G and heparin) of interest in medical applications [10]. The chemical surface analysis demonstrates that the polar sites created onto the surface are related to oxygen incorporation.

Thus, the DBD represents an attractive technique to improve the adhesion properties of PA-6 films by synergetic effects, i.e. the increase of adhesion work and surface area available for subsequent bonding and incorporation of oxygen-related functional groups. The efficiency of the DBD for very short treatment time and the stability with time of adhesion properties are demonstrated. In further studies, this technique will be optimized to link biological layers on the treated surfaces.

References

The surface oxidation of selected polymers using an atmospheric pressure air dielectric barrier discharge. Part I

G. Borcia*, C.A. Anderson, N.M.D. Brown

Surface Science Laboratory, School of Electrical and Mechanical Engineering, University of Ulster, Cromore Road, BT52 1SA Coleraine, Northern Ireland, UK

Received 9 June 2003; received in revised form 9 June 2003; accepted 1 July 2003

Abstract

In this paper, we report and discuss the results of the surface treatment, using an atmospheric pressure dielectric barrier discharge (DBD), of selected polymer films which have no bonded oxygen in their intrinsic structures. Contact angle, X-ray photoelectron spectroscopy (XPS) and scanning electron microscopy (SEM) data are presented with respect to post-treatment characterisation and the dependence of these outcomes on the salient processing variables: energy dissipated, exposure duration and inter-electrode gap. Under the treatment conditions used, remarkably uniform treatment and markedly stable modified surface properties result from the test surfaces exposed to the discharge, even at transit speeds simulating those associated with continuous on-line processing. The DBD system thus described, provides chemically mild and mechanically non-destructive means of altering surface properties, targeting improved surface characteristics and potentially better application performance.

2003 Elsevier B.V. All rights reserved.

PACS: 81.65.-b; 52.77.-j; 52.50.Dg

Keywords: Dielectric barrier discharge (DBD); Polymer films; Surface treatment; Surface characterisation; Oxidation; Ageing

1. Introduction

Polymers play an increasing role as structural materials, in films and foils for packaging applications, supporting substrates, protective coatings and sealing applications. Although known polymer properties such as thermal stability, chemical inertness, low surface energy and low friction may be desirable in several applications, for example, when used as low friction films, seals and in biomedical devices, for many industrial uses, these properties are a disadvantage and have to be overcome. Due to their low surface energy, their normally poor chemical reactivity and the presence of a weak cohesion layer at the surface, polymer surfaces are often difficult to wet and offer poor adhesion to other contiguous materials. Thus, surface pre-treatment is usually required to achieve satisfactory adhesion, for painting and printing, metalisation, etc. while retaining their advantageous bulk characteristics.

On account of the numerous applications of the common polymers, the methods used to treat and modify such polymer surfaces are many and varied. These include chemical-, mechanical-, thermal-, photo-chemical-, and plasma-based processing. Among these,
polymer types so treated. As expected, the modified surfaces tend to recover mostly in the first 2–3 days after treatment, all further evolution being much less important.

The stability of the PE films should be specially emphasised, with the contact angle reverting only by 5–10° towards that of the untreated state over a period of several days (Fig. 2a). The PTFE films also show very stable surface properties following the DBD treatment (Fig. 2d). On post-treatment, the PMP film recovers more, with contact angles reverting by up to 20°. Thus, 2 weeks after DBD processing, the 5 mJ, 5 s treated PMP film shows a reduced degree of modification, with a ~30% reduction in the contact angle compared to that of the untreated surface. The PS film shows the most accentuated effects of post-treatment ageing. The 5 mJ, 5 s treated sample, in this case, shows only a ~20% reduction in the contact angle after ageing, compared to that of the untreated material. However, as expected, the material never fully returns to the untreated state. Moreover, since the measured contact angles still have a similar low dispersion (3–4°) during the post-processing ageing survey, it can be concluded that the surface is not significantly degraded after such short treatments, with the result that the resultant modification of the surface properties is relatively stable with time.

Fig. 2. Contact angle of water ($\theta^\circ$) on various polymer films vs. treatment time and ageing (5 mJ energy, 1.8 mm gap): (a) HDPE, (b) PMP, (c) PS and (d) PTFE.