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# INFLUENCE OF DIELECTRIC BARRIER DISCHARGE TREATMENTS ON THE SURFACE PROPERTIES OF POLYAMIDE-6 FILMS

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A dielectric barrier discharge (DBD) in helium at atmospheric pressure was used to obtain physico-chemical modifications of polyamide-6 (PA-6) films, focussing on the surface properties that are controlling the adhesion, particularly the degree of surface oxidation. The polymer surface is analyzed by AFM, contact angle measurements, XPS and ATR-FTIR. It is found that the adhesion properties of PA-6 (expressed by the adhesion work, the morphology and the oxygen-related functional groups introduced onto the surface) are enhanced by DBD treatment. No degradation effects with ageing time were observed, emphasizing the stability of the oxidised surface layer, in equilibrium with the bulk of the material.

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## 1. Introduction

Polyamides are used for many applications, such as thermoplastic sheet composites, synthetic textile fibres, in the field of packaging, for tapes and cable insulation and also in medical applications, such as orthopedic implants, membranes for reverse osmosis, ultrafiltration and electrodialysis, biosensors or nonabsorbable mono and polyfilaments with minimal inflammation effects [1, 2].

Due to their low surface energy, their poor chemical reactivity below the melting point and the presence of a weak cohesion layer at the surface, polymer surfaces, and in particular polyamide-6 (PA-6), are often difficult to wet and have poor adhesion with other substrates. For this reason a surface pre-treatment is usually required to achieve satisfactory adhesion. The methods used to treat a polymer surface are highly varied such as chemical, mechanical, thermal, photochemical or plasma. A plasma processing technique presenting increased interest nowadays is the DBD, due to specific advantages [3-5]. This method offers the possibility of inducing significant surface chemical modifications by development of functional groups on the polymer matrix, favorable to further linkage to other molecules.

The first step in the complex study of the adhesion properties of polymer surfaces is the control of the oxidation state of the material. This takes into account that any surface treatment of polymers is inherently followed by post-treatment modification in atmospheric air, including chemisorption of ambient particles and reactive species from the surrounding.

In our experiments the effects of the DBD treatment on the modification of the surface characteristics of PA-6 films, that are controlling the adhesion properties, particularly the degree of surface oxidation, in competition with other processes like the rearrangement of active sites and the possible surface degradation. The surface analysis is performed using atomic force microscopy (AFM), contact angle measurements, X-ray photoelectron spectroscopy (XPS) and atenuated total reflexion Fourier transform infrared spectroscopy (ATR-FTIR).

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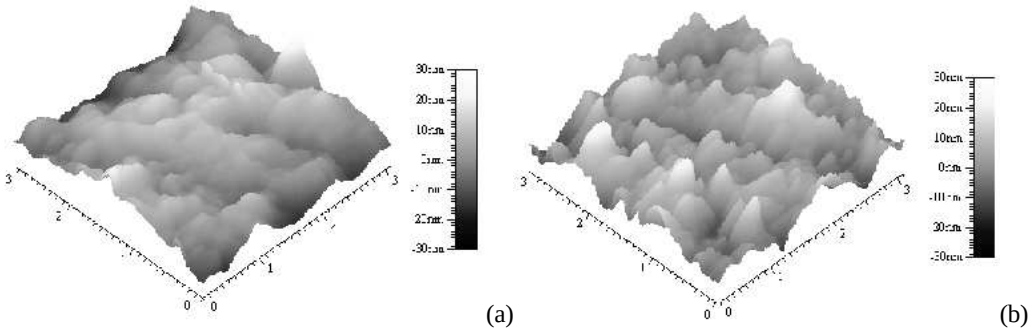
## 2. Experimental

The treatments were performed on commercial films of polyamide-6 (PA-6), thickness 0.25 mm (Goodfellow Ltd.). The in-house designed DBD system is described in detail elsewhere [6, 7]. The discharge is generated in a disc-to-plan geometry, with adjustable inter-electrode gap, using a pulsed high-voltage supply (peak-to-peak 28 kV, frequency 13.5 KHz). Helium is introduced into the inter-electrode gap at 100 $cm^3$/min flow rate, at atmospheric pressure, by a gas shower placed near the disc electrode.

The treatments of the PA-6 films were performed for various DBD exposure times up to one minute and the influence of this parameter on the surface properties was investigated by AFM, contact angle, XPS and ATR-FTIR. The stability of the modified samples was monitored for two months after the treatments.

## 3. Results and discussions

The morphological modification of the PA-6 films was investigated by AFM. The AFM images recorded on treated and untreated samples showed that DBD treatments are modifying the morphology, in that the treated surfaces present an increased area (increased roughness) compared to the pristine ones (Fig. 1).



(a) (b)

Fig. 1. AFM images of PA-6 films (3μm × 3μm): (a) untreated, (b) 60s treated.

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 by chemisorption of ambient particles and reactive species from the surrounding.

Table 1. Absolute roughness $|R|$ and rms roughness $R_{rms}$ for PA-6 films vs. treatment time.

| | untreated | 10s | 30s | 60s |
|---|---|---|---|---|
| $\|R\|$ (nm) | 2.40 | 3.08 | 4.14 | 4.98 |
| $R_{rms}$ (nm) | 3.07 | 3.88 | 5.09 | 5.91 |

This first step in the mechanisms taking place at the interface between a material and its environment is governed by the surface energy characteristics, which are controlling the adsorption. The adhesion work ($W_a$) was chosen as a thermodynamic parameter relevant for the adsorption characteristics of the surface and was calculated using the contact angle measurements. The adhesion work is found to change from 100.8 mJ/$m^2$ for the untreated sample to the highest value of 136.9 mJ/$m^2$ associated with the 60s treated sample, i.e. about 36% increase from the initial value. The results in terms of relative variation of the adhesion work compared to the untreated sample ($\Delta W_a/W_{ao}$, in %) are presented in Fig. 2.

The strong increase of $W_a$ on the treated surfaces suggests that new functional (hydrophilic) groups be introduced onto the surface, due to the extremely reactive oxygen species formed in the inter-electrode gap from the atmospheric air. The surface modification takes place in less than 10s of treatment, as shown by the "saturation" of the $W_a$ values for longer treatment times up to 1min. Thus DBD treatments lead to the enhanced wettability and adhesion properties even after very short treatment times.

The treated PA-6 samples partly recover after treatment, as shown by the diminution of $W_a$. As expected, the material never fully returns to the untreated state.

The ATR-FTIR analysis gave qualitative indication on the oxidation of the surface. The stability of the functionalized surface layer is confirmed by the ATR-FTIR ageing survey. The spectra showed no degradation of the oxidised layer created onto the surface, emphasising thus that the oxidation reaction does not continue post-treatment in the bulk of the material.

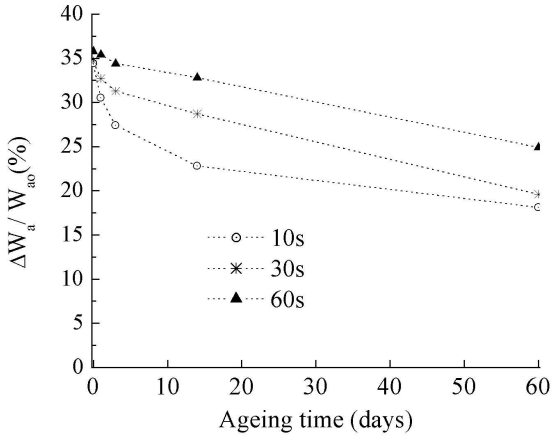



Fig. 2. Variation of the adhesion work of PA-6 film vs. treatment time and ageing time.

The details of the strong surface oxidation are given by XPS.

The high-resolution XPS spectra of the PA-6 treated and untreated samples for the carbon $C_{1s}$, oxygen $O_{1s}$ and nitrogen $N_{1s}$ regions were recorded.

The reconstructed $C_{1s}$ spectrum for the untreated sample consists mainly of three peaks, accordingly to the PA-6 stoechiometric formula:

$$[\text{— NH —CH}_2\text{ — (CH}_2)_3\text{ —CH}_2\text{ —CO —}]_n$$

aliphatic carbon atoms (C1), carbon atoms bonded to the -NH- group in nylon (C2) and carbonyl carbon atoms (C3). The reconstructed $O_{1s}$ and $N_{1s}$ spectra show each only one peak.

Table 2 summarizes the elemental surface composition for untreated and treated samples, expressed as atomic concentration percentages of C, O and N, as a function of the treatment time.

The DBD treatment markedly induces an important increase of the oxygen amount at the surface within the first few seconds of treatment (Table 2a). This effect is certainly 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 oxidation of the surface takes place mainly by formation of C-O (Table 2b).

The nitrogen amount at the surface shows only a minor augmentation with prolonged DBD exposure (Table 2a). 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.

Table 2. Elemental surface composition of the PA-6 samples vs. the treatment time: (a) total composition and (b) carbon components.

| (a) | 0s | 10s | 30s | 60s |
|---|---|---|---|---|
| C (at. %) | 78.2 | 67.0 | 65.8 | 69.4 |
| O (at. %) | 14.2 | 24.3 | 24.8 | 20.6 |
| N (at. %) | 7.6 | 8.7 | 9.4 | 10.0 |

| (b) | 0s | 10s | 30s | 60s |
|---|---|---|---|---|
| C1 (at. %) | 69.8 | 60.7 | 56.4 | 59.2 |
| C2 (at. %) | 13.9 | 19.2 | 21.7 | 20.3 |
| C3 (at. %) | 16.3 | 20.1 | 21.9 | 20.5 |

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. No major modification in the surface elemental composition further occurs between 10s and 30s of treatment. Obviously, it is to be expected that all sample surfaces reach a limiting level of oxidation as the surface equilibrates, under specified discharge conditions, by a combination of surface oxidation and/or loss of carbon by conversion to low weight volatile fragments, such as CO or $CO_2$. For 60s of treatment a decrease of the oxygen content at the surface is now measured, demonstrating thus that after more extended treatment a diminution of the level of oxidation arises due to etching, as chain scission dominates at high treatment times.

## 4. Conclusions

We present in this paper the effects of a helium diffuse glow-like 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 oxidation state of the surface are 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 one minute. The stability of the modified samples was monitored for two months after the 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 by chemisorption of ambient particles and reactive species from the surrounding. The strong increase of the adhesion work on the treated surfaces is correlated with the XPS results that show that new functional (hydrophilic) groups are introduced onto the surface. The surface modification takes place in less than 10s 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, effect 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 oxidation reaction does not continue post-treatment in the depth of the material, as shown by the ATR-FTIR ageing survey. No degradation effects with ageing time were observed, emphasizing the stability of the oxidised surface layer, in equilibrium with the bulk of the material.

The DBD represents thus an attractive technique to improve the adhesion properties of PA-6 films by synergetic effects, i.e. increase of the adhesion work and the 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.

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