



Study of the effect of atmospheric pressure air dielectric barrier discharge on nylon 6,6 foils



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ABSTRACT

Nylon 6,6 foils have been treated by an atmospheric pressure air dielectric barrier discharge. The action of plasma on nylon foils was determined by means of a wide range of techniques that enabled us to study changes in their surface as well as bulk properties. The plasma treatment was found to cause significant changes in morphology, surface chemical composition and wettability of the foils depending on the treatment time. On the other hand, optical, thermal and mechanical properties remained unaffected by plasma treatment even for prolonged treatment duration. In addition, independence of dielectric properties of nylon 6,6 foils of the plasma treatment was observed except for the high temperature region. These results clearly show that air atmospheric plasma treatment is suitable for applications in which modification of surface properties of nylon without alteration of their bulk properties is required.

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1. Introduction

Polymers are nowadays used in a wide range of applications including, for instance, food packaging, flexible electronics or biomedical field. The popularity of polymers is in general given mainly by their low cost and advantageous bulk properties such as optical transparency, relatively high thermal stability and resistance, high strength-to-weight ratio, flexibility or barrier properties. However, the use of common polymers is in many cases hampered by their poor chemical reactivity and low surface energy, which can lead, e.g. to bad printability, low adhesion to functional coatings, or to limited biocompatibility or possibility to bind various kinds of biomolecules needed for biomedical applications. Because of this, surface treatment of polymers is usually required to achieve satisfactory improvement of their surface properties (e.g. Refs. [1–3]). Among various strategies that were developed for surface modification of polymeric materials, plasma treatment represents a highly attractive option, as the technique is easy to implement, cost effective and in general environmentally friendly. Plasma based technologies are moreover typically low temperature processes and, since plasma affects only the outermost layers of a treated object, bulk properties of treated polymers remain unchanged during and after the treatment. Although the plasma

treatment was traditionally performed in low pressure discharges (e.g. Refs. [4–11]), in the last decade there is an evidently growing interest in plasmas operated at medium or atmospheric pressure. This is mainly due to the possible decrease of the costs of the process in terms of capital investments, since the operation of atmospheric plasma does not require expensive vacuum installations and equipment. Because of this, different kinds of atmospheric plasma sources were recently developed and their effect was tested on a wide range of polymeric materials (e.g. Refs. [12–19]). However, the demand to decrease further the running costs of plasma treatment led to increasing use of ambient air as a working gas. From this point of view, dielectric barrier discharges (DBD) in different configurations were found to be a highly advantageous option, since they allow the generation of stable air plasma at atmospheric pressure. Moreover, it was demonstrated by different groups that activation of a wide range of polymers may also be achieved in this case (e.g. polypropylene [20], poly(ethylene terephthalate) [21–23], polyurethane [22], polyimides [24], polyethylene [25,26], poly(ethylene naphthalate) [27], poly(methyl methacrylate) [28] or polyamides [29–31]).

Nevertheless, it has to be noted that in most of these studies the attention was devoted solely to the evaluation of the plasma effect on surface properties of polymers and it was assumed, without real experimental confirmation, that the bulk properties of the polymers remained unaffected by the plasma treatment. In this study, we therefore focus on a detailed determination of the influence of dielectric barrier discharge operated in air not only on surface

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chemical structure, surface energy and morphology, but also on mechanical, thermal, dynamic mechanical, dielectric and optical properties of nylon 6,6 foils.

2. Experimental

2.1. Treatment of nylon 6,6 foils

A schematic diagram of the DBD system used for the treatment of nylon 6,6 foils is depicted in Fig. 1. The plasma was operated in laboratory air between two parallel planar electrodes, one conductive and the other covered with dielectric. The rectangular top electrode, with dimensions $20 \times 20 \times 50$ mm, was made of stainless steel and enabled scanning along the length of the bottom electrode. The bottom electrode, which was 1.5 mm from the top electrode, was a grounded steel plate, with dimensions $72 \text{ mm} \times 160 \text{ mm}$, covered with 1 mm thick sintered alumina.

Semicyrystalline Nylon 6,6 foils (obtained from Goodfellow) with $50 \mu\text{m}$ thickness were cut into strips approximately 2.5 cm wide and about 7 cm long. The strips were placed on the bottom electrode. The upper powered electrode was driven by a high voltage low frequency (22.5 kHz) power supply operated at 30 W. Under these conditions the DBD plasma was in filamentary mode with number of detected current pulses approximately $5 \times 10^4 \text{ s}^{-1} \text{ cm}^{-2}$. In order to increase homogeneity of the treatment, the upper electrode was made to scan over the strips with constant scanning speed 40 mm/s. Taking into account the scanning speed and the dimensions of the electrode, during 1 scan the surface of the foil is exposed to plasma for 0.5 s. In order to evaluate the effect of treatment duration on the properties of nylon foils, the number of scans was varied from 1 up to 64 scans, which corresponds to treatment times up to 32 s.

2.2. Samples characterization

Morphology of the samples was evaluated by atomic force microscopy (AFM, Quesant Q-scope 350) in the semi-contact mode (scan rate 2 s, resolution 512×512 points) using NSC-16 silicon cantilevers (Schaefer Technologie, GmbH). Each reported value of surface root mean square (RMS) roughness represents an average over at least three $10 \mu\text{m} \times 10 \mu\text{m}$ scans performed on randomly selected positions on nylon foils. In addition, untreated nylon foil selected as reference was repeatedly scanned after each set of AFM measurements in order to ensure the same shape of AFM tip.

Chemical changes of nylon foils were determined by X-ray photoelectron spectroscopy (XPS) that was carried using an XPS spectrometer equipped with a hemispherical analyzer (Phoibos 100, Spec). The XPS scans were acquired at constant take-off angle of 90° using Al K α X-rays source (1486.6 eV, 200 W, Specs). Survey spectra were acquired for binding energies in the range of 0–1100 eV at a pass energy of 40 eV (dwell time 100 ms, step

0.5 eV). C1s, O1s, and N1s region spectra were acquired at a pass energy of 10 eV with 10 scans (dwell time 100 ms, step 0.05 eV) to obtain a higher spectral resolution and to lower the noise level. All the XPS spectra were referenced to the binding energy of aliphatic C–C bonds at 285.0 eV. The fitting of high resolution XPS spectra of C1s, N1s and O1s peaks was performed after Shirley background subtraction with mixed Gauss-Lorentzian lines (70% Gaussian and 30% Lorentzian) using the CasaXPS program.

The wettability and surface energy of the foils before and after the DBD treatment was determined by a goniometer of own construction by means of the sessile droplet method. Surface free energy and its polar and dispersive components were determined from the contact angles of deionized water and diodomethane (Sigma Aldrich) according to Fowkes' theory [32]. Each value represents average of three droplets (volume $3 \mu\text{l}$).

Optical properties of untreated and DBD treated nylon foils were measured by means of UV–Vis spectrophotometer (U-2900, Hitachi) in the spectral range 200–1100 nm.

The calorimetric measurements were performed using a DSC8500 apparatus (Perkin–Elmer). Purge gas (nitrogen) was let through the DSC cell with a flow rate of 20 mL/min. The temperature of the equipment was calibrated with water, indium, tin and lead. The melting heat of indium was used for calibrating the heat flow. The nylon samples were subjected to a heating scan from 0°C to 280°C , held at 280°C for 5 min and cooling scan to 100°C . Both heating and cooling scans were carried out at a rate of $10^\circ\text{C}/\text{min}$.

Mechanical properties of nylon foils were studied by the nano-indentation method, first. The complex Young's modulus of the surface layers of the foils was assessed via nano-DMA (Hysitron, Triboscope 75 with a nano-DMAIII module combined with an AFM microscope Ntegra Prima, NT-MDT) with a standard Berkovich-type indenter. Prior to each measurement, the indenter was brought to contact with the foil under the constant force of $0.4 \mu\text{N}$. Linearly increasing load function was applied immediately afterwards to indent the surface with superimposed dynamic load (with a variable amplitude and a frequency of 220 Hz) until the maximal quasi-static force reached 100 μN .

Dynamic mechanical measurements (DMA) were performed on the dynamic mechanical analyzer Tritec 2000 (Triton Technology Ltd., UK) under the tension mode. The measurement was carried out on a rectangular sample of $10 \text{ mm} \times 0.05 \text{ mm} \times 5 \text{ mm}$. The temperature dependence of the complex Young's modulus $E^* = E' + iE''$ (E' is the storage and E'' the loss modulus) was measured at a heating rate of $2^\circ\text{C}/\text{min}$ over the temperature range from 25°C to 180°C by using 10 Hz frequency. Deformation of the sample was 0.5%.

Dielectric measurements were realized by means of an Alpha-N High Resolution Dielectric analyzer (Novocontrol GmbH, Germany) in the frequency range from 10 mHz up to 10 MHz. The measured foils were placed into the dielectric sample cell BDS 1200 with upper electrode diameter of 20 mm and 0.05 mm thickness. The samples were cooled down from room temperature to -100°C with a cooling rate of approximately $10^\circ\text{C}/\text{min}$. After the cooling, the samples were measured at a constant temperature with a 10°C step up to 240°C . Acquired experimental data of complex permittivity $\epsilon^* = \epsilon' - i\epsilon''$ (ϵ' is real – storage and ϵ'' imaginary – loss part) were evaluated by the Cole–Cole distribution (position, magnitude and shape of obtained relaxation spectra).

3. Results

3.1. Surface morphology

The changes in surface morphology of nylon 6,6 foils induced by DBD plasma treatment were determined by AFM measurements. As

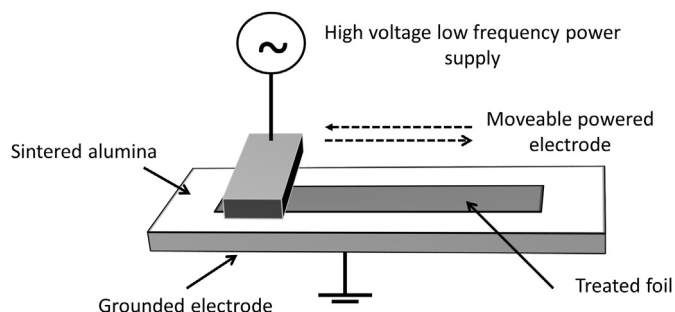


Fig. 1. Schematic of DBD system used for treatment of nylon 6,6 foils.

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