



Reactive-ion etching of nylon fabric meshes using oxygen plasma for creating surface nanostructures



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ABSTRACT

A facile one-step oxygen plasma irradiation in reactive ion etching (RIE) configuration is employed to nylon 6,6 fabrics with different mesh sizes to achieve surface nanostructures and improved wettability for textile and filtration applications. To observe the effects of power and irradiation time on the samples, the experiments were performed using constant irradiation time in varying power and using constant power in varying irradiation times. Results showed improved wettability after the plasma treatment. The FTIR spectra of all the treated samples exhibited decreased transmittance of the amide and carboxylic acid groups due to surface etching. The changes in the surface chemistry are supported by the SEM data wherein etching and surface nanostructures were observed for the plasma-treated samples. The etching of the surfaces is enhanced for higher power plasma treatments. The thermal analysis showed that the plasma treatment resulted in decreased crystallinity. Surface chemistry showed that the effects of the plasma treatment on the samples have no significant difference for all the mesh sizes. However, surface morphology showed that the sizes of the surface cracks are the same for all the mesh sizes but samples with larger mesh sizes exhibited enhanced etching as compared to the samples with smaller mesh sizes. Higher power induced higher negative DC self-bias voltage on the samples that favored anisotropic and aggressive etching.

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1. Introduction

Nylon 6,6 (polyhexamethylene adipamide) fabrics are semi-crystalline polyamides that possess outstanding versatile properties that are used in textile, automobile, military, electronics, and medical industries. Although the fibers possess excellent mechanical, chemical, and thermal properties, there are still some limitations on its uses and applications [1–10]. In general, to extend the use and applications of polymers, several treatments are employed and some of them uses atmospheric pressure plasma to improve the dye uptake of nylon 6 fibers with different absorbed moisture [1] and to enhance the antibacterial activity and natural dyeing properties of nylon 6 fabrics [6]; direct low-pressure and low-temperature plasma to enhance the adhesion of carbon nanotubes on nylon 6,6 fabrics [3], to improve the mechanical properties of nylon 6 plain woven fabrics [5], to correlate the crystallinity and plasma

susceptibility of poly(ethylene terephthalate) (PET) and nylon 6,6 fibers [10], and to achieve superhydrophilic or superhydrophobic properties for lignocellulosic seagrass, PET, and poly(tetrafluoroethylene) (PTFE) materials [11–14]; gas discharges in improving the wettability, superhydrophobicity and antibacterial properties of PTFE [15–18]; laser to improve the dyeability of poly(amide) 6,6 knitted fabrics [19]; and microwave jet plasma for the functionalization of electrospun poly(amide) 6 nanofibers to improve the adhesion properties during the production of composites in tissue engineering [7].

In this study, RF oxygen plasma in reactive-ion etching (RIE) configuration was used to modify the chemistry and morphology of the nylon 6,6 samples. This technique has some advantages over the other techniques since it is an extreme form of direct plasma treatment and it has an increased DC bias level that favors anisotropic and aggressive etching on the samples [20,21]. The plasma configuration under vacuum is favorable in the processing of materials since the integrity of the plasma and the materials are maintained throughout the irradiation process [11–13,15–18]. Plasma treatments were found to be favorable over non-plasma techniques since the plasma may contain different species such as electrons,

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neutral species, charged species, and excited species that can interact with the material's surface [22].

2. Experimental procedures

2.1. Materials and plasma treatment

Sefar Nitex® nylon 6,6 fabrics (Sefar AG, Switzerland) of different mesh sizes ranging from 25 μm to 1550 μm were used in the experiments. Different mesh sizes were used because the pressure that a fabric can support is highly dependent on the mesh size. Before plasma treatment, the nylon 6,6 fabrics were soaked in acetone for 10 min followed by air-drying for 2 h at room temperature in order to remove any impurities on the surface. The cleaned and dried samples were then irradiated using oxygen plasma produced in reactive ion etching configuration of a BSET EQ NT-1 plasma device (Digit Concept Microelectronics and High Tech Equipment, France) operating at an excitation frequency of 13.56 MHz. The plasma device operates on the principle of a capacitive coupled plasma (CCP) reactor where the RF current through the oxygen gas maintains a steady state discharge by heating the electrons. The samples were placed on the power electrode, which is parallel to the ground electrode at 50 mm distance from each other. A 20 m^3/h rotary pump evacuated the system, and the base pressure was kept at 100 mTorr. Oxygen gas was fed into the chamber at a flow rate of 20 sccm. The plasma sheath produced between the power and ground electrodes induced negative DC self-bias voltage on the samples that was measured using a voltmeter with a low-pass filter.

In order to determine the effects of power and irradiation time on the treatment of the fabrics, two sets of plasma parameters were used. The first experiment was done with constant irradiation time of 600 s but with varying powers of 100 W, 200 W, and 300 W, and the second experiment was done with constant power of 600 W but with varying irradiation times of 100 s, 200 s, and 300 s. The experimental parameters used in the first set have the same incident energy as the second set ranging from 60 kJ to 180 kJ.

2.2. Characterizations

2.2.1. Contact angle measurements

A DSA-30 goniometer (Krüss GmbH) equipped with a drop shape analysis (DSA4) software was used to study the changes in the wettability of the samples. Sessile drop method was used to determine the apparent contact angles. 2 μL of Milli-Q deionized water was dropped vertically onto the samples using a motorized syringe mechanism. For each samples, contact angle measurements were performed at three different sites.

2.2.2. Fourier transform infrared spectroscopy

The changes in the sample's chemical functionalities were obtained using a Spectrum 100 FT-IR spectrometer (Perkin Elmer, USA) with a diamond attenuated total reflectance (ATR) top plate accessory. The samples were scanned 5 times at 4 cm^{-1} spectral resolutions over the range of 450 cm^{-1} to 4000 cm^{-1} . The spectra reported in this paper were obtained by subtracting the background spectra from the measured spectra.

2.2.3. Differential scanning calorimetry

Melting and crystallization profiles were determined for each sample using a Jade Differential Scanning Calorimeter (DSC) (Perkin Elmer, USA). Samples were filled in a measurement cell of the DSC and the temperature was first heated from 25 $^{\circ}\text{C}$ to 300 $^{\circ}\text{C}$ at the rate of 20 $^{\circ}\text{C}/\text{min}$ and held for 3 min. The samples were then quenched to 25 $^{\circ}\text{C}$ from 300 $^{\circ}\text{C}$ at the rate 100 $^{\circ}\text{C}/\text{min}$. The glass transition temperature (T_g), melting temperature (T_m), and enthalpy of melting

(ΔH_m) were extracted from the melting profile and the crystallization temperature (T_c), and enthalpy of crystallization (ΔH_c) were extracted from the crystallization profile. The crystallinity of the fabric samples were then calculated using the following equation:

$$\% \text{Crystallinity} = \frac{\Delta H_m - \Delta H_c}{\Delta H_m^0} \times 100\%$$

where ΔH_m^0 is a reference value and represents the heat of melting if nylon 6,6 were 100% crystalline [23].

2.2.4. Scanning electron microscopy

A JSM 6700F NT (JEOL Ltd., Japan) scanning electron microscope was used to determine the morphology of the surface of the material. The samples were scanned at 250 \times , 10,000 \times , and 25,000 \times magnifications.

3. Results and discussion

Control nylon 6,6 fabrics of mesh sizes 25 μm , 100 μm , 200 μm , and 400 μm exhibited high wettability since the water contact angles are less than 10 $^{\circ}$ and the water droplet spread on the surface within 1 s of contact. This was expected since the nylon 6,6 fabrics used in this study are usually used for filtration applications. For the control nylon 6,6 fabrics of 700 μm and 1550 μm mesh sizes, the contact angle is 84 $^{\circ}$ and 43 $^{\circ}$, respectively, since the volume of the water droplet used in the measurement is 2 μL . This means that the fiber spacing is an important factor when studying wettability, for example, when the material is used for filtration, the selection of an appropriate filter is necessary for different types of filtrates. After the plasma treatment, all the nylon 6,6 fabric samples exhibited improved wettability, especially for samples of mesh sizes 700 μm and 1550 μm . This improvement in the wettability is favorable when dealing with filtration using different types of filtrates.

For the FTIR, DSC, and SEM data, only the nylon 6,6 fabric with mesh size of 100 μm will be shown, since it was found in the study that the effects of the plasma treatment on the samples have no significant difference for all the mesh sizes (i.e., the same trend and behavior on the surface chemistry, surface morphologies, thermal properties, and crystallinity were observed for samples of mesh sizes 25 μm , 100 μm , 200 μm , 400 μm , 700 μm and 1550 μm).

Fig. 1 shows the superimposed view of FTIR spectra of the control and plasma-treated nylon 6,6 fabric samples with 100 μm mesh size. For spectra b, c, and d, the plasma treatment was performed with constant irradiation time (600 s) of varying power (100 W, 200 W, and 300 W). The spectrum of the control sample verifies that the material is nylon 6,6 since it contains the following chemical functionalities: N–H stretching (3264 cm^{-1}), C–H asymmetric stretching (3085 cm^{-1}), asymmetric and symmetric stretching (2962 cm^{-1} and 2851 cm^{-1} , respectively), C=O stretching from carboxylic acid groups (1734 cm^{-1}), amide I band and amide II and CH₂ asymmetric deformation groups (1650 cm^{-1} and 1539 cm^{-1} , respectively), N–H deformation and CH₂ scissoring (1452 cm^{-1}), amide III band and CH₂ wagging (1347 cm^{-1}), CCH symmetric bending and CH₂ twisting (1145 cm^{-1} and 1130 cm^{-1}), C–C stretching (962 cm^{-1}), N–H wagging and CH₂ rocking (742 cm^{-1}), C–C bending (600 cm^{-1}), and O=C–N bending (548 cm^{-1}).

For all the peaks except the C–C stretching, it was found that the transmittance intensities decreased which are proportional to the values of the incident energy. The existence of the amide I, amide II, and carboxylic acid groups which are polar and hydrophilic supports the over-all hydrophilic properties of the nylon 6,6 fabrics. The decrease in the transmittance peaks can be associated with the breakage of some amide linkage in the nylon 6,6 fabrics which creates free amino groups, this change in the chemistry of the material

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