Stable surface modification of fluoropolymers by nitrogen discharge at atmospheric pressure

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Abstract: A new modification method to treat fluoropolymer films using atmospheric pressure nitrogen plasma was developed. It was found that the plasma provokes a change in roughness as well as the formation of nitrogen and oxygen functional groups on the surface of FEP. These modifications resulted in a drastic increase in the adhesion properties observed by peel test. Scrub-washing methods were used to evaluate the stability of the modifications. Results highlight that the modified surfaces remain stable after scrub-washing process.

Keywords: Atmospheric pressure nitrogen plasma, stable surface modification, FEP.

1.Introduction

Fluoropolymers (FPs) are used in many applications thanks to their non-sticky and waterproof surfaces, chemical and temperature resistance, and low friction coefficient [1]. Due to their non-adhesive properties, FPs must be modified if used as composites to ensure the best compatibility with the adhesives. Several methods already exist, including wet-chemical treatments [2], [3] and plasma treatments [4]. It is well known that wet-chemistry employs hazardous reagents based on sodium solutions (e.g., metallic sodium-ammonia or metallic sodium naphthalene tetrahydrofuran) and produce harmful residual products. These approaches are also quite expensive. Moreover, they present serious limitations such as loss of optical and mechanical properties due to strong etching [4], as well as the presence of residual solvent on the surface of the polymer or swelling of the substrate [5]. In the last decade, a vast array of low-pressure plasma systems has been used to change the surface properties of FPs [4]. The obtained results highlight the possibility to enhance their adhesion, wettability, and biocompatibility without affecting the bulk properties. However, low-pressure plasma has different drawbacks as substrate sizes are limited to the reactor chamber. In fact, specialized vacuum pumps are required, and a long waiting time is necessary because samples must be treated in batch. Therefore, there is a rapidly growing interest towards similar modifications using atmospheric pressure systems. This approach eliminates expensive vacuum equipment, avoids extended maintenance, and increases the amount/size of substrates that can be treated. All these advantages could help industries to move toward cleaner, safer and less expensive solutions to modify FPs. In this context, different works from the literature report the use of atmospheric pressure plasma systems to treat other FPs surfaces and obtain higher adhesion [6]-[8]. For cost-effective industrial processes, nitrogen or air plasma are the most common

plasma [9]. In this work, we study an atmospheric pressure nitrogen plasma system to modify fluorinated ethylene propylene (FEP) films. The polymers were treated in dielectric barrier discharge (DBD) in nitrogen [10], [11]. The samples were characterized by Atomic Force Microscopy (AFM), X-ray Photoelectron Spectroscopy (XPS), T-peel tests and wettability. To evaluate the stability of the modification, a scrub-washing method (ASTM D-2486 – 17) was also employed using different solvents.

2. Experimental

a. Materials

Fluorinated Ethylene Propylene (FEP) films of 0.127 mm (5 mil) of thickness were provided by Saint-Gobain Research North America (Northborough, MA, USA). To evaluate the effect of the modification over the adhesion, T-peel tests were carried out using commercially available adhesive tape 3M 853.

b. Methods

Figure 1 shows a schematic illustration of the discharge cell. The configuration employed consists of a plane-tocylinder system. The high-voltage electrodes consist of two bars of stainless steel (L: 15 cm × W: 1 cm x H: 6 cm) separated by a 0.4 mm slot through which N₂ (research grade UN1066, 99.9999% purity) is injected. The ground electrode is a 15 cm stainless-steel cylinder. FEP films were placed on top of the ground electrode acting as a dielectric barrier and are connected to a roll to-roll system that allows moving the sample up to 5 m/min through the discharge. The gas gap between the high-voltage electrodes and the polymer is 0.5 mm. The power is supplied consists of an AFG2021 function generator (Tektronix, ORE, USA) plugged into a PL380 audio amplifier (QSC). The low to high voltage conversion is done by a transformer manufactured by Raftabtronics (DeLand, FL, USA) and allows reaching 28 kV (peak-topeak) between 5 and 15 kHz. During the treatment, N₂ was injected between the two high-voltage electrodes. The N_2 flow was controlled by a flow controller (EL-Flow) from Bronkhorst High-Tech B.V. (Ruurko, Holland).



Fig. 1. Schematic illustration of the plasma system.

The breakdown of the gas was achieved by applying a sinusoidal voltage modulated by a duty cycle (DC). The DC depends on the frequency, the burst interval, and the number of cycles. Figure 2 shows a representation of the typical signal used. The frequency was set at 10 kHz (T = 0,1 ms, Eq. 1). The number of cycles (t_{on}) corresponded to the number of discharges created during a specific interval (called t_{total} , Eq. 2). Accordingly, the DC was calculated using equation 3.

$$T = \frac{1}{f} \tag{1}$$

$$t_{total} = t_{on} + t_{off} \tag{2}$$

$$DC = \frac{t_{on}}{t_{total}} x \ 100 \tag{3}$$

Thus, for an experiment at 10 kHz (T = 0.1 ms) and 10 ms of t_{total}, a 50% duty cycle means the signal is on 50% of the time (5 ms) and off 50% of the time (5 ms).



Fig. 2. Representation of the typical applied voltage in the dielectric barrier discharge.

The electrical signals were analyzed using a MDO3054 oscilloscope (Tektronix). The high voltage was measured at the secondary of the transformer by a P6015A high voltage probe (Tektronix). For the power measurement, the Lissajous method was used [12]. The voltage is measured across a 100 nF capacitor in series with the plasma reactor on the ground side with a TPP0500B passive probe (Tektronix). The charge is then calculated using Eq. 4. The power is determined from the area of the Lissajous figure using Eq. 5.

$$Q = C \cdot V \tag{4}$$
$$P = \frac{f}{S} \oint V(t) dQ(t) \tag{5}$$

It can be noticed that power can be calculated by Lissajous figures either over one period of the applied signal, or as an average value over one burst when the signal is modulated by duty cycle. Prior to all treatments, the chamber was pumped down to 0.6 Torr to remove impurities. The chamber was then filled with N2 to reach 760 Torr. FEP films were treated for 2 minutes keeping a constant N₂ flow of 4 standard litres per minute (slm). The frequency and the average power over one burst were constant at 10 kHz and 3.75 W/cm² (10 kV_{p-p}, and 50% of DC). The physical regime of the discharge in these conditions was filamentary. To evaluate the adhesion properties of the modification, three samples (2.54 cm x 16 cm) were taken. Adhesion strengths between FEP films and a tape were measured by a T-peel test (configuration illustrated in Figure 3). Samples were manually taped perpendicularly the treated zone, and then pressed using a cylinder (diameter: 10.1 cm, height: 3 cm, weight: 1.8 kg). T-Peel tests were carried out on a Instron universal testing machine 5565 (Instron, MA, USA) with a load cell of 50 N. The specimens were placed in pneumatic grips of 3.8 cm in width, and peeled under constant speed of 300 mm/min.



Fig. 3. T-peel test configuration.

The surface chemistry of FEP films was studied by XPS using a PHI 5600-ci (Physical Electronics, MN, USA) operated at a take-off angle of 45° for a detection area of 0.5 mm². Surveys spectra (1200-0 eV) were collected using a standard aluminum X-ray source (1486.6 eV) at 300 W with a charge neutralizer. Additionally, high resolution analysis of the C1s region were collected using standard magnesium X-ray source (1253.6 eV) at 300 W, without charge neutralization and with a pass energy of 5.85 eV. Curve fitting was performed by referencing each spectrum to CF₂ signal at 292.0 eV using Multipak software by Gauss-Lorentz peak fitting and Shirley baseline. To study the effect of the modification over the surface topography, samples were analyzed by AFM using an atomic force microscopy (AFM). Investigations were performed using a Dimension 3100 atomic force microscope (Digital Instruments, Santa Barbara, CA, USA) in tapping mode with an etched silicon tip (OTESPA, tip radius <10 nm, aspect ratio \approx 1.6/1). The topography was evaluated for areas covering 5 x 5 µm using the Nanoscope program. The surface roughness was determined by the root mean square roughness parameter R_{rms}. Finally, the stability of the modification was evaluated fallowing the ASTM D-2486 -17 procedure in an Abrasion & Washability Tester

(Elcometer 1720, USA). This test describes scrubbing resistance of wall paints. Two different abrasives were evaluated a nylon brush (reference: KT001720P030) and a sponge (reference: KT001720P073) from Elcometer. 100 g were added on top of the abrasive, and different number of cycles (3, 10 and 33) were evaluated using water or acetone as a solvent.

3. Results and Discussions

First, FEP wettability was studied by contact angle. After plasma treatment, water contact angles changed from 109.4 \pm 1.3 ° (untreated) to 102.1 \pm 1.3 °, and diiodomethane contact angle from 83.6 ± 0.5 ° (untreated) to 79.2 ± 1.4 °. These results lead to a higher surface energy after the discharge (from $16.5 \pm 1.1 \text{ mN/m}$ to $19.1 \pm 1.1 \text{ mN/m}$). To study the chemical changes that causes the increase of wettability after treatment, XPS analyses were carried out on FEP samples before and after plasma treatment. In FEP untreated, 37.4 ± 1.0 atomic % of carbon and 62.6 ± 1.0 of fluorine were detected, indicating a C/F ratio of 0.60. After plasma treatments, C/F ratio increased to \approx 0.7. Also, nitrogen and oxygen were detected in FEP surface, indicating a defluorination process and the creation of new functionalities by the plasma treatment. XPS HR of C1s region were also carried out. In FEP untreated, C1s region (Figure 4a) was fitted into 3 peaks: 293.4 eV, 292.0 eV and 290.7 eV, assigned to CF₃; CF₂; and CF respectively [13], [14]. After 1 m/min plasma treatment, C1s region highlighted 6 peaks (Figure 4b), including peaks from the FEP structure (CF₃, CF₂, CF); peaks at 287.1 eV and 285.8 eV assigned to \underline{C} -O and \underline{C} -C/ \underline{C} -N respectively, and peak at 289.0 eV assigned to C-CF_x/CO-CF_x [13].



Fig. 4. XPS HR of C1s region of: a) FEP untreated; b) FEP plasma treated.

To further investigate the changes on FEP upon plasma treatment, samples were analyzed by AFM and the results are shown in Figure 5a-b. Untreated FEP exhibited a surface with small protuberances and a root-mean-square roughness average (RMS-Ra) of 7.1 \pm 0.6 nm. Plasma treated FEP showed similar surface topology with a reduction of protuberances and a smoother surface (RMS-Ra at of 3.6 \pm 0.3 nm).



Fig. 5. AFM micrographies of: a) FEP untreated; b) FEP treated.

T-Peel tests were carried out in FEP samples (untreated and treated) before and after the scrubbing-washing process. Results are presented in Figure 6. It can be noticed that plasma treatment increases the peel strength of the samples from (40 ± 16) g/cm to (1360 ± 550) g/cm. In addition, the scrubbing-washing process does not change the peel strength on the untreated FEP, which remains around (60 ± 50) g/cm. Peel strength values for treated FEP after the scrubbing-washing test remain higher than the ones from the untreated surfaces. It is worth mentioning that two samples highlight an increased in adhesion after the scrubbing test (scrubbing-washing with acetone with 10 or 33 cycles). This means that aging processes could increase the roughness of surfaces and affect the adhesion mechanisms.



Fig. 6. Peel strength obtained by peel tests of samples.

At this stage, one can also affirm that discharge treatment affects the FEP surface roughness by cross-linking and/or removing contaminants from the surface [15]. Also, plasma treatment introduces oxygenated and nitrogenated species in the surface, causing defluorination. These modifications causes the increase in wettability and the peel strength. The resistance of the peel strength after the washing-scrubbing process also suggests that the energetic filaments present in the discharge produce a robust surface modification not removable by these methods.

4. Conclusions

Experiments were performed to study the modification of the samples and the variation of the adhesion after interaction of the surfaces with a nitrogen discharge at atmospheric pressure. After treatment, the roughness decreased and new chemical functionalities containing oxygen and nitrogen were observed on the surface. The modifications were not affected by the washing-scrubbing process. It is worth mentioning that by changing the exposition of the polymer to the discharge (*i.e.*, different scroll speed) it is possible to obtain a higher degree of modification was observed (not shown here).

5. References

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