INVESTIGATION OF LOW PRESSURE RADIO FREQUENCY AMMONIA PLASMA TREATEMENT ON POLYPROPYLEN FILM AND FIBERS

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Abstract- TheseIn this study, ammonia plasma treated polypropylen films and fibers surfaces were investigated to find out the influence of polymer forming process during plasma modification. The findings show that higher amino functionalities quantity were incorporated on the surface of both film and fibers when the plasma treatment was longer (typically 200 s). In contrast, the selectivity of NH2/N was higher when using lower plasma treatment time. The statistical study demonstrated the factor of treatment time and both treatment time and materials type affect significantly the amino quantity.

Keywords- Plasma modification, polypropylene, surface morphology, amine grafting.

I. INTRODUCTION

Polypropylene (PP) has excellent properties, such as low specific weight, high strength, and good resistance to acids and alkalis, and it also possesses good thermal resistance and anti-bacterial properties [1-3]. Among many synthetic polymeric materials, polypropylene is used widely in biomedical applications such as disposable hypothermic syringes, blood oxygenerator membranes, packaging for devices, sutures, vascular grafts, etc. [1, 4-6]. The low pressure plasma technique is becoming popular as a versatile tool for modifying surface chemistries that improve the wettability and adhesion of medical devices and the biocompatibility of polymer surfaces by introducing functional groups or depositing thin films of defined composition on such devices [7]. Three major effects are normally observed in this case: a) functionalization, which can lead to covalent bonds suitable for attachment of other coatings; b) cross linking, which can cohesively strengthen the topmost surface layer; and c) surface ablation, which can also be used for surface cleaning [8]. The type of functional group introduced into the polymer depends on the type of gas used with the plasma [9]. The most frequently grafted groups are -NH2, -OH and –COOH by means of RF glow discharges fed with non-depositing gases such as NH_3, O_2, H2O, etc. The introduction of amino groups through Radio Frequency Glow Discharge (RFGD) treatment is particularly interesting for two reasons: first, amino groups are known to facilitate cellular spreading on a biomaterial surface; and second, amino groups may react fairly easily with other chemical functionalities, therefore allowing strong attachment of specific molecules and preventing their removal by blood flow [10]. Additionally, low discharge power favors the formation of NH_2 groups because there is less fragmentation of monomers in the plasma. Moreover, amino groups provide an excellent basis for subsequent surface modification techniques because they allow biomolecules to bond with high selectivity. The 2-3.5% amino group relative surface concentration corresponds to approximately 0.5 to 2% amine every 2 nm. This amino surface concentration is by far sufficient to conjugate biological molecules such as proteins, enzymes, or growth factors, considering that the surface plasma modification occurs on the first atomic layers of the polymer surface [11]. On the other hand, hydrophilic and hydrophobic surfaces can be created on polymers through interaction with gas plasma. Hydrophilic surfaces are typically known to adsorb less protein. Unlike hydrophilic surfaces, biomaterials with hydrophobic surfaces have been shown to strongly adsorb albumin and other proteins.Plasma treatments can greatly change the surface topography of PP without modifying its bulk properties [7, 12, 13]. This paper sought to compare the effect of two different surface geometries, PP film and PP fiber, on low pressure ammonia radio frequency plasma. The grafted amino groups were recognized for biomolecule conjugation. The chemical composition of the surface was analyzed with X-ray photoelectron spectroscopy (XPS), whereas the surface evolution was determined via atomic force microscopy (AFM) analyses. Moreover, the effects and the interactions of factors such as materials type and treatment times were statistically evaluated.

II. MATERIALS AND METHODS

2.1 Materials and sample preparation

The PP film sheets (biaxially oriented, 0.075 μm thickness) were obtained from Goodfellow

(Huntingdon, England), whereas the PP fiber (0.1 mm thickness, porosity of 80-90%, fiber diameter of 8-10 μm) was produced by the melt-blown method. Briefly, this process transforms polymer resins into a non-woven material by extruding polymer through a multi-hole die (230 –hole grid, nominal diameter 300 μm) in a single, integrated process. Both the PP film and PP fibers were cut (4 cm x 1.6 cm) into small pieces and were then ultrasonically and successively cleaned for 10 min in acetone, deionized water, and methanol. Afterward, they were dried under vacuum until use. The reagent 5-bromosalicylaldehyde, with a level of purity of 98%, was purchased from the Sigma Aldrich corporation (Milwaukee, WI, USA).

2.2 Surface modification

A home-made cylindrical plasma reactor with high purity ammonia gas (Matheson Tri-Gas Inc. Newark, CA, USA) was used for plasma treatment. The treatments were performed only in the inner surface of rolled PP film and PP fiber at 15 W, 13, 56 MHz and 300 mTorr for 1, 15, 60, 100, and 200 s. Each experiment was reproduced in triplicate. A vapor-phase chemical derivatization technique was used to quantify the amine surface concentration using 5-bromosalicylaldehyde. Briefly, a small quantity of reagent was added to the bottom of a glass tube and then soda-lime glass beads (a layer of ~ 1 cm) were added to separate the reagent from the sample. The chemical reaction was proceeded for 2 hours at 85 °C. Prior to analysis, the surface was vacuum-dried overnight at 40 °C. The aging test method was performed to quantify the amine surface concentration and surface reorganization. Plasma-treated PP film and PP fiber were washed ultrasonically at room temperature for 5 min in deionized water (pH 6) and then dried under vacuum overnight prior to further analysis.

2.3 Surface characterization

The wettability of the surface was measured using the static contact angle VCA 2500 XE system AST, Billerica, MA, USA. The test consisted of at least five drops of a 3 μL droplet of deionized water in different areas of the sample surface. The chemical composition with and without, as well as chemical derivated or/and aging PP film and PP fiber, was determined as previously described with an XPS-PHI 5600-ci spectrometer (Physical Electronics, Eden Prairie, MN, USA). Surface topography was performed byAFM using the tapping mode of a Dimension^{TM}3100 Atomic Force Microscope (Veeco, Woodbury, NY, USA) with a Supersharpsilicon^{TM} tip (NanoWorld Innovative Technologies, Neuchatel, Switzerland, tip radius < 2 nm). An area of 500 x 500 nm^2 was scanned and evaluated by a Nanoscope program. The surface roughness of samples was calculated with the Root Mean Square (R_{rms}) roughness parameter. ImageJ software (free version) was used for area measurement of the polymer nodules. All of the experiments cited above were repeated three times for each plasma condition.

III. RESULTS AND DISCUSSION

3.1 Contact angle analyses

The wettability behavior of PP film and PP fiber was evaluated via contact angle measurement. Figure 1 shows the contact angle change of PP film and PP fiber in ammonia plasma for a treatment time from 0 to 200 s. Untreated (0 s) PP film and PP fiber had contact angle values of 99° and 140°, respectively. This discrepancy is a result of the topographic consequence engendered by interconnected fibers and their porosity. After 1 s of plasma treatment, the contact angle value of both materials decreased significantly. For PP film, the contact angle decreased to 68° and thereafter remained constant at 53° (Fig. 1). Comparable findings were found for PP fiber; the contact angle value lowered from 140° to 5° after a plasma treatment of 1 s and thereafter remained essentially regular. This means that the surface of the PP fiber became hydrophilic instead of hydrophobic after plasma treatments. The common findings indicate that the introduction of hydrophilic groups onto both surfaces, which alters the surface roughness, is the main reason for the contact angle reduction.

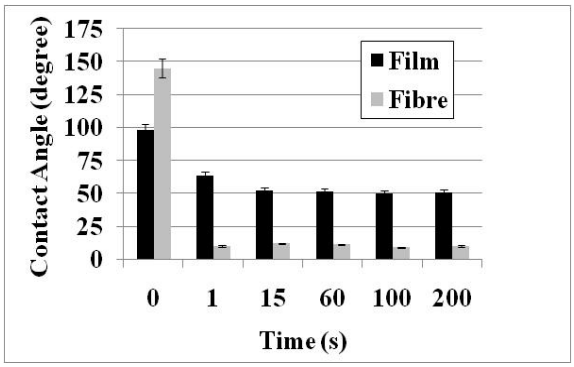


Figure 1. Contact angle variation of the PP films and PP fiber as a function of plasma treatment times.

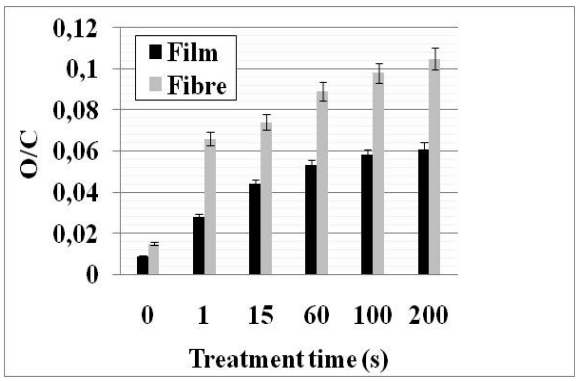
3.2 Chemical composition

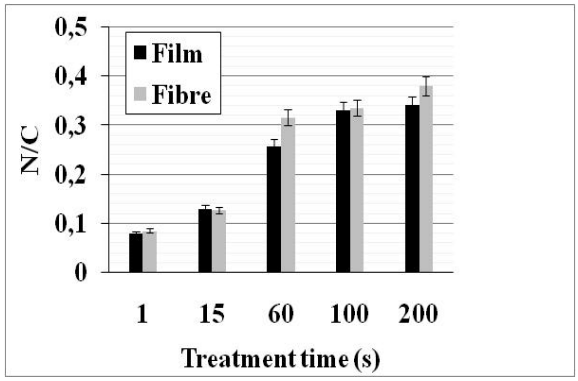
When a polymer surface is subjected to a high-energy particle bombardment from plasma, it causes polymer degradation and produces selectivity. To investigate the change in chemical composition after plasma modification, the XPS survey spectra of PP film and PP fiber were analyzed. The incorporation of nitrogen after the ammonia plasma treatment was observed for both materials. The relative atomic surface concentration percentages of oxygen, carbon and nitrogen recorded on the PP film and PP fiber before and after ammonia plasma treatment are given in Table 2. As presumed, the relative concentrations of O and C found on the untreated film and fiber matched the theoretical values: % O and % C. After 1 s of plasma treatment, XPS uncovered that approximately 8.5% of the nitrogen atomic concentration was grafted onto the surface of both

materials, which means that the polymer materials were successfully modified by the ammonia plasma (Table 2). Moreover, the nitrogen and oxygen concentration values increased in contrast with the carbon concentration value, which decreased with the treatment times for both materials. The study of Friedrich et al. [20] also showed a co-introduction of oxygen into polypropylene after nitrogen was discharged via radio-frequency for 10 min. This increase of oxygen after plasma treatment can be observed with any plasma treatment. In the absence of oxygen containing plasma gases, the plasma generates automatically metastable trapped radicals that always react with oxygen upon exposure to air. These surface concentration values were dependent on plasma treatment time. Longer exposure times resulted in N surface concentrations reaching approximately 25% after 200 s of treatment for both materials, which is approximately 3 (three) times compared to a 1 s treatment. Consequently, the relative loss of carbon with respect to untreated materials was 28-31% for both materials. Accordingly, the relative oxygen increased by approximately 4-6% for both materials with respect to untreated materials. However, the effect of plasma treatment on PP film and PP fiber was studied in more detail by calculating the surface atomic ratios (O/C, N/C) because the XPS values were relative data (Fig. 2). For both surfaces studied, the plasma treatment increased the O/C ratio from ~ 0.01 to 0.03 for PP film and 0.07 for PP fiber after 1 s of treatment and increased progressively with plasma time duration. It was also observed that the ratio O/C of PP fiber was higher than PP film for each treatment. The N/C ratio was not different for both surfaces up to 15 s, whereas PP fiber had a slightly higher N/C after 60 s than did PP film. As explained in previous work, amino groups quantification is essential for further molecule conjugation. Figure 2 shows the amine concentration and NH_2/N selectivity for both PP film and PP fiber. As observed in this figure, the highest amine concentrations were obtained after 200 s of treatment for PP film and PP fiber with 3.1% and 3.2% of amine (NH_2), respectively. A shorter treatment below 200 s was conducted to decrease the amines quantity. In contrast, the selectivity of amino groups (NH_2/N) was highest for a shorter treatment for PP film and PP fiber (Fig. 2).

Table 1. Chemical composition of PP film and PP fiber, both untreated and treated by ammonia, from the XPS survey spectra.

Treatment time	PP FILM			PP FİBER		
	O (%)	C (%)	N (%)	O (%)	C (%)	N (%)
Untreated	0.9±0.2	99.1±0.2	---	1.4±0.7	98.6±0.8	---
Plasma 1 s	2.6±0.7	89,8±0.8	7.6±0.6	5.7±0.7	85.9±0.9	8.4±0.7
Plasma 15 s	3.8±0.8	84.8±0.6	11.4±0.8	6.2±0.7	83.0±0.8	10.8±0.8
Plasma 60 s	4.1±0.8	76.5±0.7	19.4±0.4	6.4±0.7	71.7±0.6	21.9±0.8
Plasma 100 s	4.2±0.9	72.0±0.9	23.8±0.5	6.9±0.5	69.7±0.8	23.4±0.9
Plasma 200 s	4.4±0.6	71.3±0.6	24.3±0.6	7.1±0.6	67.1±0.7	25.8±0.8





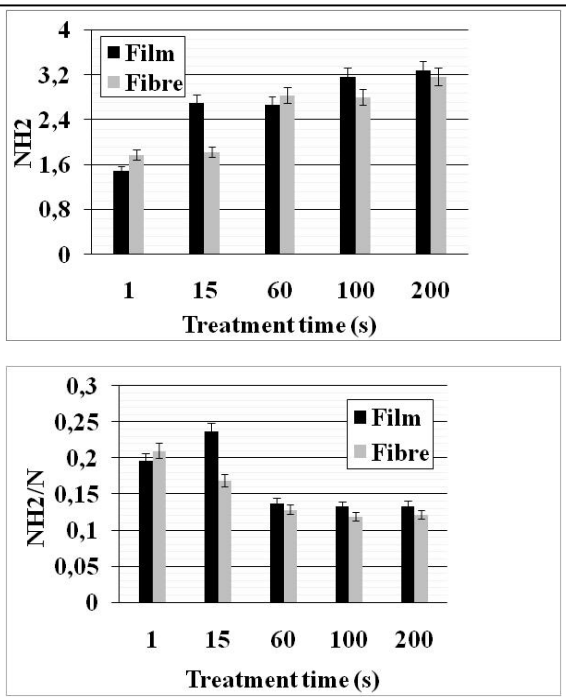


Figure 2.Chemical composition (O/C, N/C), amino concentration (%NH_2), and selectivity (NH2/N) variation for PP film and PP fiber after plasma treatments between 1-200 s.

Figure 3 shows the HR C1s spectra results before and after a plasma treatment of 200 s. The HR C1s spectra of the untreated PP film and PP fiber exhibit a hydrocarbon component (C-C/C-H) at 286.8 eV (100%). The surface of the untreated materials appears clean and comprises almost no oxygen. After 200 s of treatment, it was observed that the intensity of the main peak decreased for PP fiber to 68.8% and for PP film to 66.3%. This difference is mainly explained by the chain scission of C-C(H) and grafting of possible new functional groups such as C-N (amine), C-0 (alcohol, ether), C=0 (carbonyl) and N-C=0 groups. The new band at 287.7 eV for PP film and 288.9 eV for PP fiber formed after 200 s of treatment may also be attributed to the functional groups cited above.

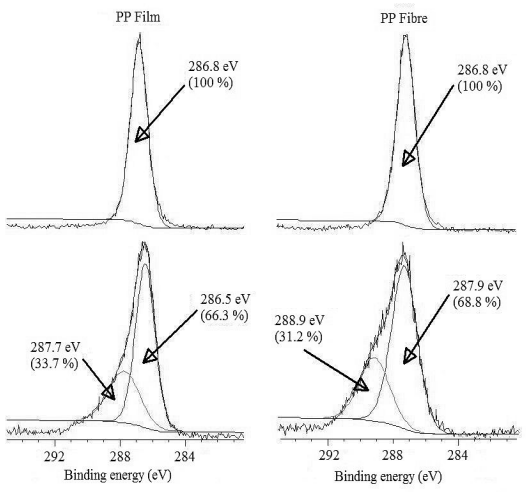


Figure 3. HR C1 s spectra of untreated and plasma treated PP film and PP fiber at 200 s.

3.4 Surface topography

After plasma treatment or high energy particle bombardment of the polymer surface, chain degradation always occurs and polymer fragment that are loosely bonded are created. The surface of the PP film was scanned using AFM for all of the plasma treatment times, as well as the aged PP film after 1 s of treatment, and they were presented tri-dimensionally in Figure 4. For PP fiber plasma-treated and PP fiber aged samples, the AFM images were not workable due to the small-scale dimensions of fibers; for this reason, they were not presented. However, the PP film images revealed topography modification after ammonia plasma treatment. Every observed surface was composed of round nodules of various sizes that were more pronounced for the 60 s and 200 s treatments. The number of nodules and the size were dependent on the plasma duration; when the treatment time increased, the number of nodules decreased and the nodule size increased. This feature, called agglomeration processes, was explained previously.

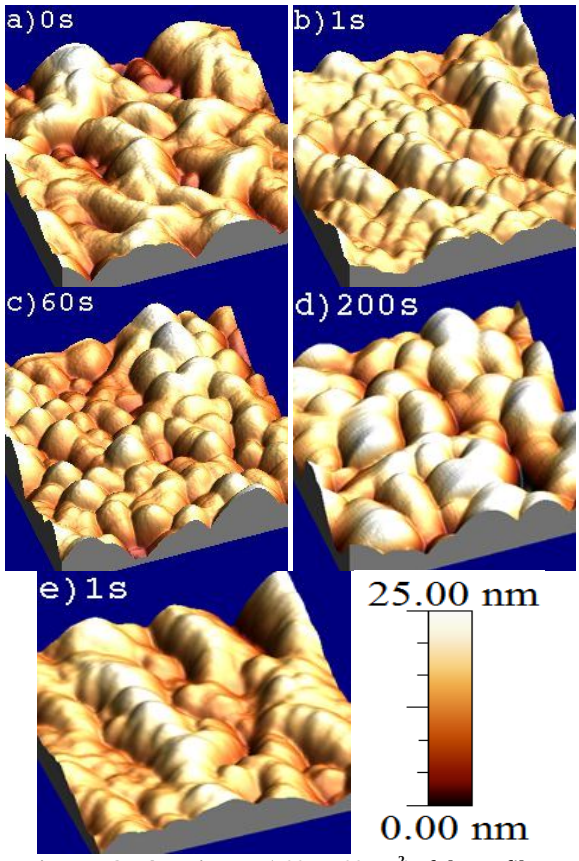


Figure 4. 3D AFM images (500 X 500 nm^2) of the PP films before and after treatment: a) untreated, b) 1 s, c) 60 s, d) 200 s and e) aging process after 1 s.

CONCLUSIONS

The results highlight the influence of the surface geometry when grafting functional groups using low pressure radio frequency ammonia plasma treatment. For this purpose, flat surface PP film and porous

scaffold made of PP fiber were evaluated. The ammonia plasma treatment of these samples produced new polar groups that increased the hydrophilicity of polymers. The unique surface formed is due to the new arrangement of the polymer chain into nodular shapes that was observed with AFM. On the other hand, XPS revealed the chain scission of C-C(H) with new functional groups, which can be associated with the amine groups. Moreover, the highest amino group surface concentration was obtained at a longer plasma treatment time (200 s); in contrast, the selectivity of NH2/N was higher at short treatment times (1-15 s).

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