FUNCTIONALIZATION OF POLYMERS USING N_2 PULSED DIELECTRIC BARRIER DISCHARGE*

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Abstract

Surface treatment of polymers using plasma has been widely used for purposes of enhancing the adhesion and wettability of the material through the inclusion of polar functional groups. Through the use of atmospheric pulsed-dielectric barrier discharges (DBD), ultra-high-molecular-weight polyethylene (UHMW-PE) films were treated with nitrogen gas to introduce nitrogen-containing groups on the surface for improved adhesion properties. To avoid the effect of oxidative degradation during plasma treatments, various treatment times and nitrogen gas flow-rates were used to achieve higher uptake of N-containing species over that of O-containing species.

Surface analysis techniques - attenuated total reflectance-Fourier Transform Infrared (ATR-FTIR) spectroscopy, X-ray Photoelectron Spectroscopy (XPS), and contact angle measurements were used to study variations in the surface energy and chemical composition. Optical emission spectroscopy (OES) has been applied to identify and characterize key chemical species present in the N_2-DBD plasma.

I. INTRODUCTION

Non-thermal plasma, more specifically dielectric barrier discharge (DBD) has become an attractive tool used for the surface treatment of polymers [1]. Typically, low-pressure plasmas [2] have been used but in the past decade atmospheric pressure plasmas have shown great promise owing to quick processing time, reduction in the use of wet-chemicals, and the absence of costly vacuum systems. Through the use of these non-thermal plasmas, several physiochemical processes can take place on the surface of the polymer – functionalization, etching, cleaning and crosslinking, while maintaining the overall bulk characteristics of the material [3-4]. In past work, many have used air and oxygen plasmas operating at atmospheric conditions to enhance the wettability of the polymer surface through the formation of polar groups on the polymer surface, mostly in the form of oxidized species [5-7]. By utilizing these particular plasma treatments, surface degradation in the form of low molecular weight oxidized materials (LMWOM) [8] in addition to physical defects such as micropits have been seen. An alternative method that has been explored to increase adhesion and wettability of these hydrophobic surfaces is the selective functionalization of nitrogen-containing groups. Massines *et. al.* have shown that further improvements in wettability can be achieved through the addition of nitrogen groups in polypropylene [9].

The aim of this work is to control the chemical functionalization imposed by the nitrogen plasma through the optimization of plasma processing parameters such as exposure time and gas flow-rate. Chemical groups – nitrogen and oxygen, formed by the plasma were identified using surface-sensitive spectroscopic techniques - attenuated total reflectance-Fourier Transform Infrared (ATR-FTIR) and X-ray Photoelectron Spectroscopy (XPS). Wettability studies were conducted to assess the effect of the nitrogen-containing groups in addition to that of the oxidized species on the surface of the polymer. Optical emission spectroscopy was used to study the gas phase reactions.

II. EXPERIMENTAL

A. Materials

To eliminate the complexities associated with the geometry of polymeric fibers, films of UHMW-PE were chosen for this study. UHMW-PE films with a sheet thickness of 75 μm were procured from Goodfellow Corporation (Devon, Pa). Prior to plasma treatment, UHMW-PE films were washed in ethanol and dried in air. Ultra-high purity (99.999%) nitrogen gas was supplied by Airgas, Inc.

B. Surface Treatments

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14. ABSTRACT

Surface treatment of polymers using plasma has been widely used for purposes of enhancing the adhesion and wettability of the material through the inclusion of polar functional groups. Through the use of atmospheric pulsed-dielectric barrier discharges (DBD), ultra-highmolecular- weight polyethylene (UHMW-PE) films were treated with nitrogen gas to introduce nitrogen-containing groups on the surface for improved adhesion properties. To avoid the effect of oxidative degradation during plasma treatments, various treatment times and nitrogen gas flow-rates were used to achieve higher uptake of Ncontaining species over that of O-containing species. Surface analysis techniques - attenuated total reflectance-Fourier Transform Infrared (ATR-FTIR) spectroscopy, X-ray Photoelectron Spectroscopy (XPS), and contact angle measurements were used to study variations in the surface energy and chemical composition. Optical emission spectroscopy (OES) has been applied to identify and characterize key chemical species present in the N2-DBD plasma

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Surface treatments were carried out by using various gas flow-rates and treatment times. Nitrogen gas flow-rate ranged from 0.01 to 10 LPM and exposure times as low as 30 seconds up to 7 minutes were implemented. The experimental DBD plasma reactor setup used to carry out the surface treatments is seen in Fig. 1. The system is comprised of a pulsed power supply and a planar configuration of stainless steel electrodes and quartz dielectric encapsulated within a plexiglass enclosure.

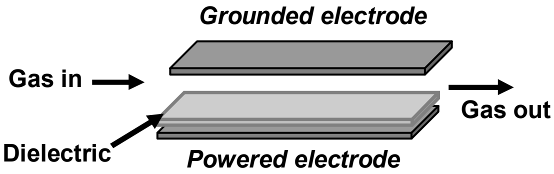

Figure 1. Pulsed-DBD Plasma Set-up

The pulsed power supply generates ~130 ns pulses and the power density was measured to be 0.1 W/cm^2. A constant gap of 2 mm in between the anode electrode and the quartz-covered cathode electrode was used for all treatments. Prior to plasma treatment of the UHMW-PE, the reactor was purged with flowing N_2 gas to ensure a nitrogen-rich environment.

C. Contact Angle Measurements

Static contact angles were measured using the sessile drop method. A standard goniometer equipped with a CCD camera was used to capture the contact angles created at the liquid/solid interface. A 5 μL drop dispensed by the microsyringe onto the substrate was allowed to reach equilibrium before recording contact angle measurements. Using LabView software, contact angles were determined from the captured images displaying the tangent angle formed on the film surface.

D. Attenuated Total Reflectance – Fourier Transform Infrared Spectroscopy (ATR-FTIR)

Attenuated total reflectance – Fourier Transform Infrared Spectroscopy was used to identify potential chemical functional groups. Absorbance spectra were generated using a Nicolet-Thermo 670 FTIR spectrometer equipped with a Specac® Silver-Gate single reflectance zinc selenide (ZnSe) ATR attachment with nitrogen as the purge gas. These spectra were recorded using a resolution setting of 4 cm^{-1} with a total of 32 scans.

E. X-ray Photoelectron Spectroscopy (XPS)

Qualitative and quantitative analysis of the chemically-functionalized surface of the plasma-treated UHMW-PE films were performed using the Kratos Axis Ultra 165 X-ray photoelectron spectroscopy (XPS) system, equipped with a hemispherical analyzer. A 100 W monochromatic Al K (1486.7 eV) beam irradiated a 1 mm x 0.5 mm sampling area with a take-off angle of 90°. Elemental high resolution spectra for the C1s, O1s, and N1s were taken at a pass energy of 20 eV. The C1s signals were curve-fitted for various nitrogen and oxygen-containing groups using the CasaXPS software. The hydrocarbon peak at 285.0 eV was used as the reference in all C1s curves to correct for sample charging.

F. Optical Emission Spectroscopy (OES)

Molecular and atomic species present in the N_2-DBD plasma were identified using optical emissions spectroscopy. An Acton Research SpectroPro 500i scanning monochromator with a fiber optic attachment was used. The entrance slit to the monochromator was set to 8μm. A RoperScientific model 7430 CCD camera was mounted onto the exit slit to digitally acquire the spectra. Typical acquisition times for the CCD images were 1-10 seconds. Background images with the discharge off were subtracted.

III. RESULTS AND DISCUSSION

In this subsection, physical and chemical changes imposed by the plasma on the UHMW-PE film will be discussed.

A. Wettability

From water contact angle measurements seen in Figure 2, angles formed at the film/liquid interface are significantly smaller than the angles formed on the untreated film. With increasing exposure time, from 1 minute to 5 minutes, the contact angle decreases from 60° to 45°.

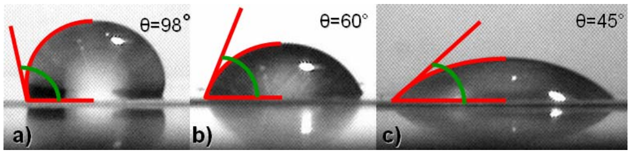

Figure 2. Water contact angles formed on (a) untreated UHMW-PE, plasma-treated UHMW-PE at 6 LPM for (b) 1 minute and (c) 5 minutes

The changes observed through water contact angles are a clear indication of hydrophilization brought about by the existence of polar functionalities created at the surface. Based on recorded values of water contact angles of films treated at different gas flow-rates and exposure times, no distinct relationship can be made.

B. ATR-FTIR Spectroscopy

Based on contact angle measurements, it is evident that polar groups are formed at the surface. Chemical groups that are likely to be identified from ATR-FTIR spectroscopy are hydroxyl, carbonyl, carboxyl, amine, imine, and/or amide groups based on what others have noted from literature [1, 8, 10]. The absorbance spectrum seen in Figure 3, characteristic of UHMW-PE films treated using low gas flow-rates of 0.01 up to 1.0 LPM,

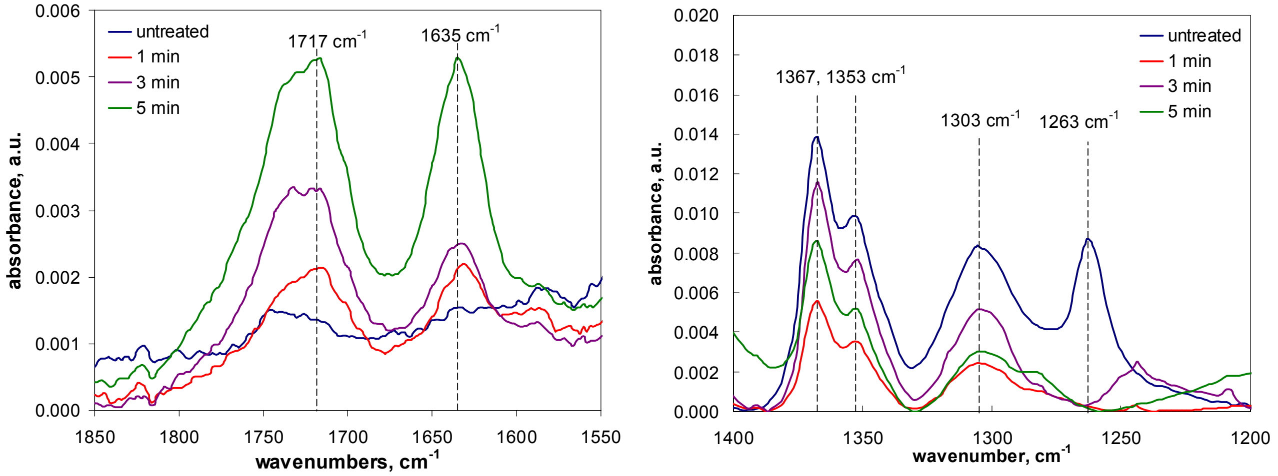

Figure 3. ATR-FTIR absorbance spectra of plasma-treated UHMW-PE films treated under low N_2 flow-rate of 0.01 LPM in the range of 1550-1850 (left) and 1200-1400 cm^{-1} (right)

show only the presence of carbonyl (C=O) and hydroxyl (C-OH) groups at 1717 and 1635 cm^{-1}, respectively. By increasing the N_2 gas flow-rate and treatment time up to 5 minutes, we see an additional peak at 1230 cm^{-1} (Fig. 4). This peak was assigned to the C-N single bond.

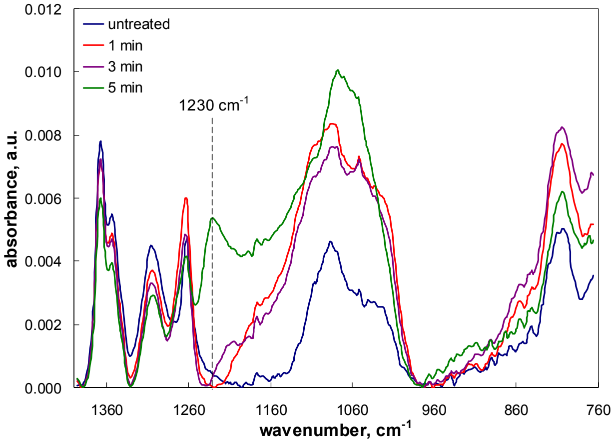

Figure 4. ATR-FTIR absorbance spectrum between 760 and 1410 cm^{-1} of plasma-treated UHMW-PE films treated under high N_2 flow-rate of 6.0 LPM.

In addition to the appearance of new peaks from the plasma treatments, the intensity of the main absorption peaks (Fig. 3) at 1303, 1353, and 1367 cm^{-1} decreases with increasing exposure time, signifying the breaking of C-H and C-C bonds by UV and plasma reactive species.

C. XPS

A correlation between the gas flow-rate and the nitrogen uptake from plasma treatments can be seen from XPS results. Quantitative analyses show that there is a significantly higher uptake of nitrogen-containing groups in the UHMW-PE films treated at higher flow-rates than that of samples treated under low flow-rates.

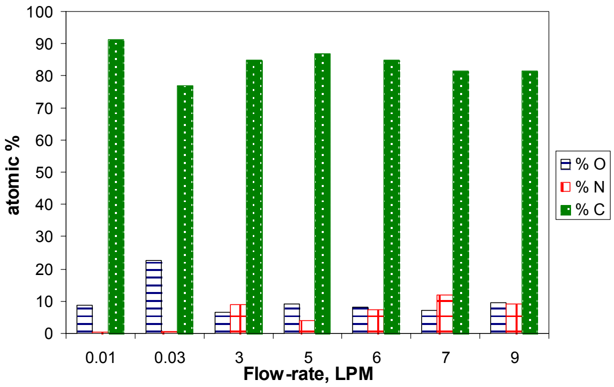

Figure 5. Atomic composition of UHMW-PE films treated for 5 minutes under different N_2 flow-rate.

At low flow-rates, the oxygen overtakes the nitrogen but once higher N_2 flow-rates are attained, a competing effect between O_2 and N_2 occur. As shown in Figure 5, at a flow-rate of 6.0 LPM the atomic percent of oxygen and nitrogen components are equal but at 7.0 LPM the nitrogen overtakes the oxygen. The role the gas flow-rate plays on the plasma and its influence in the surface chemistry is not fully understood.

The fitted peak for the untreated UHMW-PE C1s curve is a narrow peak at 285.0 eV whereas in the case of plasma-treated UHMW-PE, the curves are significantly broad. The broadening of the peak is attributed to the formation of complex chemical groups. From peak fitting of the C1s signal for both low and high gas flow-rates, it was found that the data complements the chemical groups identified from ATR-FTIR absorbance spectra.

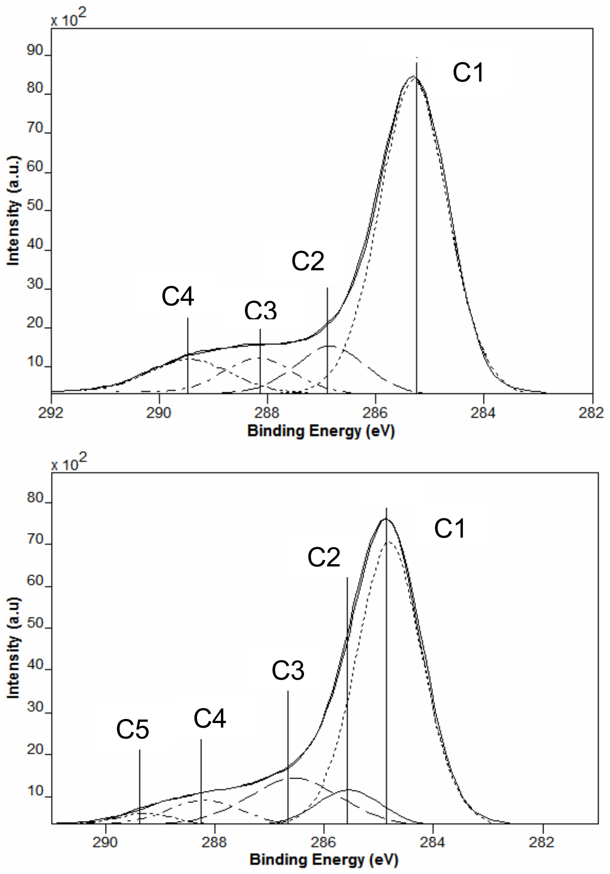

Figure 6. Deconvolution of the C 1s peak for UHMW-PE plasma treated for 5 minutes at 0.01 LPM (top) and 7.0 LPM (bottom).

The C1s peak for the UHMW-PE film plasma treated under the conditions of 0.01 LPM for 5 minutes was fitted with 4 curves (Fig. 6). The film treated with the same exposure time but at a flow-rate of 7.0 LPM was fitted with one additional curve, the C2 as seen in Figure 6. This C2 peak was assigned to the C-N group. Table 1 summarizes the assignment of chemical groups at specific binding energies of fitted peaks under the C 1s curve based on literature data [10-12].

Table 1. XPS high resolution C 1s Peak Deconvolution and their peak assignments for UHMW-PE films treated for 5 minutes

	Peak	**B.E. (eV)**	**Assignment**
0.01 LPM	C1	285.0	C-C, C-H
	C2	286.8	C-OH, C-O
	C3	288.6	C=O
	C4	289.4	COOH
6.0 LPM	C1	285.0	C-C, C-H
	C2	285.8	C-N
	C3	286.8	C-OH, C-O
	C4	288.6	C=O
	C5	289.4	COOH

D. OES

Results obtained from infrared and x-ray photoelectron spectroscopic analyses show that the surface bound oxygen-containing groups - hydroxyl and carbonyl are always present despite various treatment conditions used throughout this work. Surface treatments using a low-pressure plasma system such as the work performed by J.E. Klemberg-Sapieha et. al. [10] as well as others with atmospheric plasma systems [13-14] have documented this phenomenon. The source of oxygen has been speculated to come from residual air or water vapor trapped in the reactor, during treatment and/or from the reaction of the surface active sites with O_2 and water vapor upon exposure to the air after treatment.

Optical emission spectroscopy was used to detect if trace amount of oxygen is present in the nitrogen plasma. Spectra for the N_2 DBD plasma initiated under various gas flow-rates were taken from 290 nm to 390 nm (Fig. 7). The spectra in Figure 7 show no signs of O_2 present but a direct relationship between the intensity of the N_2 second positive bands and the N_2 flow-rate can be seen. The brightest lines between 300 and 400 nm are contributed from the nitrogen second positive electronic transition N_2 ($C\ ^3\Pi_u$-$B\ ^3\Pi_g$) and its family of vibrational and rotational sub-transitions.

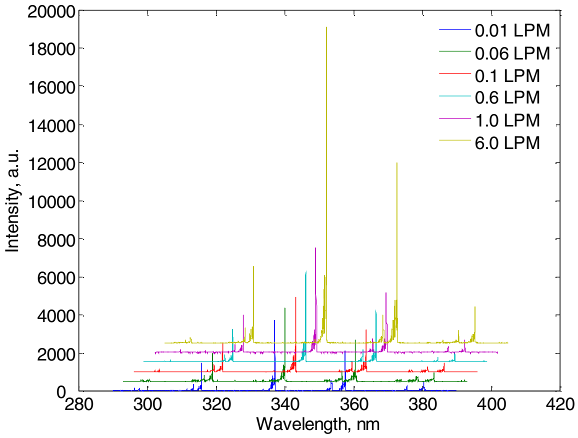

Figure 7. Spectra from N_2 DBD discharge between 290 and 390 nm at different gas flow-rates.

The emission spectrum for the gas flow-rate of 0.06 PM was taken to find bands of molecular oxygen in the plasma based on the observation that higher uptake of oxygen is associated with the low gas flow-rates used in this study. The strongest molecular O_2 band is known to exist at the wavelength of 759.37 nm. Spectra scanned within the visible and infrared range show no spectral lines of molecular oxygen. However, this does not exclude the existence of oxygenated species such as NO.

IV. CONCLUSION

It has been shown that utilizing an atmospheric pressure plasma system with a pulsed power source can functionalize polymers with specific chemical groups. By using high N_2 flow-rates and moderate exposure times, nitrogen groups as much as 14 at. % can be formed at the surface of UHMW-PE films. Optimum plasma conditions consists of high gas flow-rates of 6.0 LPM and higher with treatment times of 5-7 minutes. Results thus far show a correlation between gas flow-rate and the uptake of nitrogen functionalities as it plays a key role in functionalizing polymers.

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