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Surface characteristics analysis of polypropylene treated by dielectric barrier discharge at atmospheric pressure

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Abstract. Polypropylene (PP) samples were treated by Dielectric Barrier Discharge (DBD) in order to modify their surface characteristics. The XPS analysis reveals that the DBD treatment added oxygen atoms to the PP surface. These polar groups cause increase in the wettability as shown by water contact angle measurements. The formation of low-molecular-weight oxidized materials (LMWOMs) in the form of small nodules on the PP surface was observed by atomic force microscopy (AFM). The presence of oxygen polar groups on the PP surface was also confirmed by infrared spectroscopy (FTIR). All analysis were performed before and after rinsing the treated samples in water and showed that the LMWOM can be removed from the surface by polar solvents.

1. Introduction

The polypropylene (PP) is a common engineering polymer widely employed in industry because of its good mechanical properties and low processing costs. It is used in several industrial fields, such as food packaging, protective films, conventional adhesives, printing, coating, etc. Many of these industrial applications require good adhesion properties [1,2]. However, due to its non-polar nature and low surface energy the PP exhibits poor adhesion and wetting [3]. Thus, in order to improve these characteristics many processes using different kind of plasmas have been applied. One type of discharge that is broadly investigated is so-called dielectric barrier discharge (DBD) [4].

DBD is a kind of electrical discharge, which occurs between two metal electrodes, providing that the space between them is partially filled with a dielectric material. It generates large amount of ions, energetic electrons, and exited reactive species under low temperature and high-pressure conditions [5]. Unlike other plasma reactors, DBD can treat materials in air without costly vacuum systems. This discharge demonstrates a remarkable flexibility with respect to its geometrical shape, operation parameters and working gas [6].

When polymers are treated by DBD, the samples are placed in the discharge gap where are exposed to the reactive species of the plasma. The ultraviolet (UV) photons and energetic electrons collide with the material surface breaking covalent bonds [2,3]. Afterwards, the free radicals created on the polymers surface can combine with oxygen atoms in the air thus increasing the polymer surface energy. However, the incorporation of new functional groups onto the materials surface has some limitations, one of them is the polymer surface degradation which results in the production of low-

molecular-weight oxidized materials (LMWOMs) [7]. LMWOMs are short highly oxidized oligomers weakly bonded to the polymers surface that agglomerate into globular features on the polymer surface and can be easily removed by washing with polar solvents [3,8].

This work reports the effect of DBD on polypropylene samples focusing on the surface modification and production of LMWOM during the treatment. The surface chemistry and structural modification of PP were analyzed with contact angle measurements, atomic force microscopy (AFM), x-ray photoelectron spectroscopy (XPS) and infrared spectroscopy (FTIR) before and after rinsing the treated films with water.

2. Experimental setup

2.1. Material

A transparent 0.3-mm-thick PP film, provided by Goodfellow, Brazil, was cut into small pieces with 1.0x1.5 cm² size. Before plasma treatment the samples were cleaned using an ultrasonic cleaner with distilled water and isopropyl alcohol. After treatment some samples were rinsed 1 minute in distilled water, air dried for 1 hour and then subjected to further analysis.

2.2. Plasma treatment

The treatments were performed in a 11.5-cm-diam parallel plate reactor. Both reactor electrodes were covered by 0.5-mm-thick polyester film and the distance between them was fixed at 3 mm. The upper electrode was grounded while the lower one was employed as high-voltage electrode. The high-voltage power supply is consisted of a step-up high-voltage transformer driven by a variac autotransformer. A load resistor of 1 k Ω protected the transformer in case of DBD to arc transition. All plasma treatments were carried out in air at atmospheric pressure and ambient temperature. The experimental arrangement is sketched in figure 1.

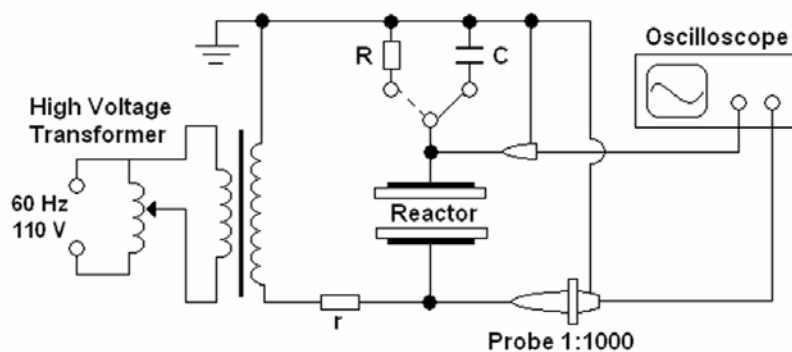


Figure 1. Schematic view of the DBD experimental setup.

The applied AC voltage was fixed at 35 kV peak to peak and was measured by a 1000:1 high-voltage probe (Tektronix – P6015A) and monitored on a digital oscilloscope (Tektronix – TDS 2024B). The treatments were performed at the line frequency of 60Hz. For displaying the waveform of the discharge current on the oscilloscope the reactor upper plate was grounded through a current measuring resistor of 68 Ω . The charge Q on the reactor plates was obtained from the voltage drop across a serial capacitor of 0.91 μ F.

To obtain the mean electric power we employed the so-called Lissajous figure. It is obtained when plotting the transported electric charge as a function of the applied periodical voltage. In most cases the Lissajous figure is almost a parallelogram, whose area is equal to the electric energy consumed per voltage cycle. The power of DBD reactor is obtained by multiplying the consumed electric energy to the discharge frequency [5].

Treatments of PP films were performed for different time intervals to analyze the effects of plasma exposure on polymer surface.

2.3. Characterization techniques

The treated samples were later analyzed with contact angle measurements, x-ray photoelectron spectroscopy (XPS), infrared spectroscopy (FTIR) and atomic force microscopy (AFM) to verify the changes on the PP surface. Some treated and washed (with distilled water) PP films were also analyzed to compare their structural modification with that of unwashed ones.

The contact angle between a test liquid and the polymer surface was obtained by the sessile drop method on a standard Rame-Hart goniometer, model 300-F1 using the DROPIImage software. The measurements were carried out in controlled environment with 60% relative humidity and temperature of 21 °C. The volume of distilled water drop was 2 μl . At least five different drops were deposited on the polymer surface to obtain the average value of the contact angles.

Surface chemical characterization was carried out by x-ray photoelectron spectroscopy by a Kratos XSAM 800 spectrometer, using Mg K α radiation and fixed analyzer transmission mode (80 and 40 eV pass energies for the wide scan and detailed spectra, respectively). The spectra were referenced to the C 1s line (binding energy, BE=285.0 eV) of the hydrocarbon type carbon.

AFM, was used to analyze surface morphology of the polymer samples. The AFM analysis was performed in air with a Shimadzu, model spm9600-j3 equipment. During the analysis, the microscope was operated in tapping mode with a scanning rate of 0.5 Hz for all scanning sizes using etched silicon probe ($k = 50 \text{ N/m}$). From the AFM images on $10.0 \times 10.0 \mu\text{m}^2$ areas the root mean square roughness (r_{rms}) of the topographic profiles was evaluated. For each sample several images on different spots were acquired and after that the average value of the roughness was calculated.

To analyze the changes of the surface chemical composition and the kind of chemical bonding Fourier transform infrared spectrometer PerkinElmer, model spectrum 100 was used. The spectrometer is equipped with a universal ATR accessory. The internal reflection element is a diamond crystal. The FTIR spectra were recorded using a resolution of 4 cm^{-1} and 16 scans were taken for each measurement.

3. Results and discussion

3.1. XPS analysis

The untreated PP sample exhibited a relatively narrow and symmetric C 1s peaks. In addition, a low intensity O1s peak was also detected at about 532.3 eV, probably due to slight surface oxidation, resulting in surface O-content of about 2 at%. XPS surface analysis performed on the DBD-treated PP samples revealed an elevated surface oxidation – intense O 1s photoelectron and O KLL Auger peaks could be detected in addition to the C 1s and C KLL peaks of carbon. Quantification of the detailed spectra showed a surface composition: C 80.4 at% and O 19.6 at%, resulting in an O/C ratio = 0.244.

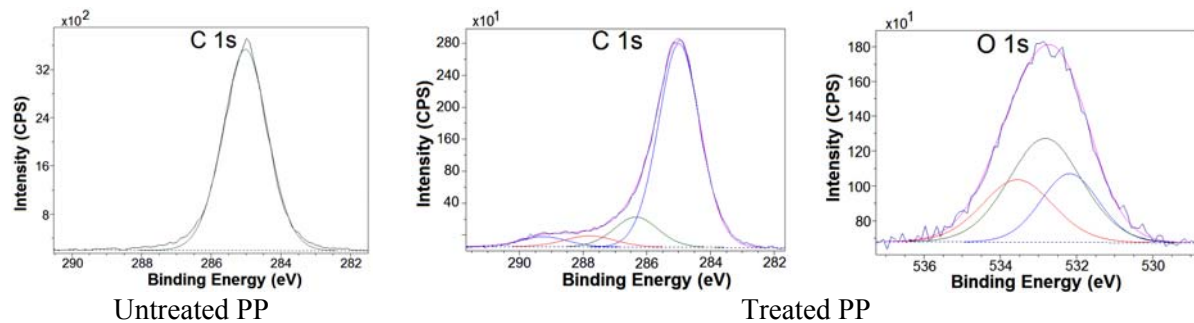
Figure 2 presents details of C 1s and O 1s peaks of the PP sample treated for 10 min. The C 1s peak of the untreated PP is also shown for comparison. Synthesis of XPS C 1s and O 1s peak deconvolution is listed in table 1.

The XPS reveals that the DBD treatment added oxygen atoms to the PP surface in the form of single, double and triple oxidized carbon bonding.

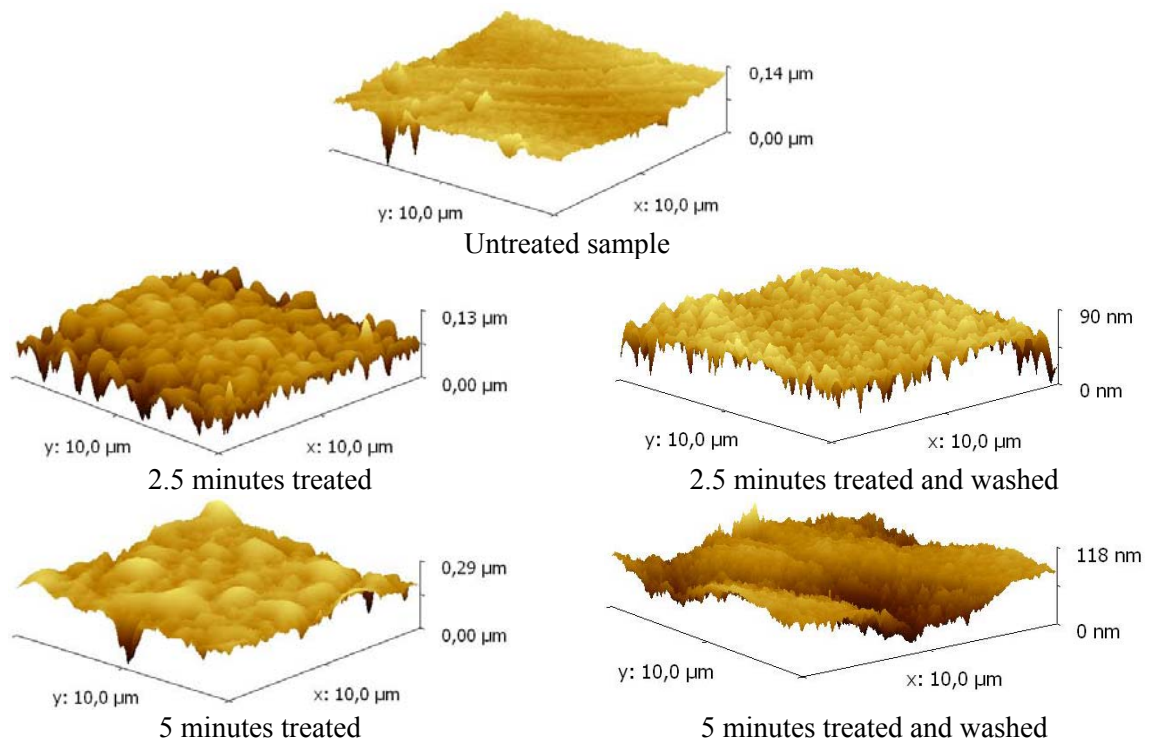
3.2. AFM analysis

The AFM images of PP surface, shown in figure 3, indicate the formation of globular structures whose size increases with the treatment time. The nodules are constituted by highly oxidized short polymer fragments, called in the literature LMWOMs [3]. These structures can be easily removed by washing in water, resulting in changes in the surface morphology and roughness.

In table 2 is presented the PP roughness before and after water rinsing the treated samples.

**Figure 2.** C 1s and O 1s peaks of DBD treated and untreated PP.**Table 1.** Results from peaks synthesis for air DBD-treated PP.

Peak	Component	Bonding mode	BE applied eV	Percentage at%
C 1s	C1	C-C, CH	285.0	62
	C2	C-OH, C-O-C	286.4	10
	C3	C=O, O-C-O	287.8	4
	C4	C(=O)OH	289.3	4
O 1s	O1	C=O	532.2	5
	O2	C-O-C, C-OH	532.8	9
	O3	C(=O)OH	533.6	5

**Figure 3.** AFM images of polypropylene samples.**Table 2.** Comparison of the PP roughness between washed and unwashed samples.

		Untreated	2.5 minutes	5 minutes
Rms (nm)	Unwashed	5,1±0,9	13±0,4	20±0,6
	Washed		10±0,2	6,1±0,4

3.3. Contact angle measurements

The figure 4 shows that plasma treatment enhanced the PP hydrophilicity due to the introduction of polar oxygen-containing groups to the surface as evidenced by XPS analysis. Couple of minutes DBD treatment converted the initially hydrophobic PP surface into hydrophilic with contact angle around 65°. Further increase of the treatment time did not lead to significant changes in the PP wetting properties. This finding can be explained by the accumulation of LMWOMs on the surface that prevents the oxidation of deeper atomic layers. However, after washing the samples, the LMWOM was removed which resulted in smaller oxygen content on the surface and correspondingly higher water contact angle.

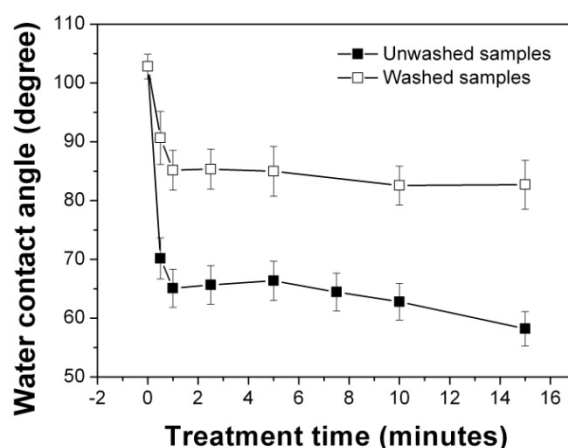


Figure 4. Reduction of the contact angle as a function of the treatment time.

3.4. Infrared analysis – FTIR

The ATR-FTIR spectra of DBD-treated PP samples shown in figure 5 clearly show the appearance of some new features [9]. A very broad band between 3100 and 3650 cm^{-1} is attributed to the OH stretching vibration. A broad pick at 1750 cm^{-1} appears owing to the presence of the carbonyl groups (C=O). The peak at 1280 cm^{-1} is associated with COOH groups. After the surface washing in water these new features disappear turning the FTIR spectrum of the washed sample identical to the one of the untreated PP. These changes are corroborated by the AFM analysis, which showed the existence of nodular structures on the surface that were removed by washing. The spectrum of washed samples in figure 5 exhibits lost of oxygen containing chemical groups, which confirms the presence of LMWOM in these structures.

4. Conclusion

The DBD treatment of PP modifies both the surface chemical composition (shown by XPS and FTIR) and the surface morphology (AFM). When working in air, the DBD produces oxygen-containing functional groups, which are introduced in the PP chain turning the material more hydrophilic and increasing its roughness.

The AFM analysis of PP samples reveals an increase of the surface roughness with increasing the time of plasma exposure. This is caused by the formation of short highly oxidized polymer fragments (LMWOMs) that tend to agglomerate into nodule-like structures. However, the PP samples washed in water did not fully recover their original wetting properties. This suggests that oxidation also occurred at deeper and more permanent levels of the samples.

There was also observed that after washing the treated samples in water they lost part of their hydrophobicity because the LMWOMs were dissolved, which also affected the surface roughness.

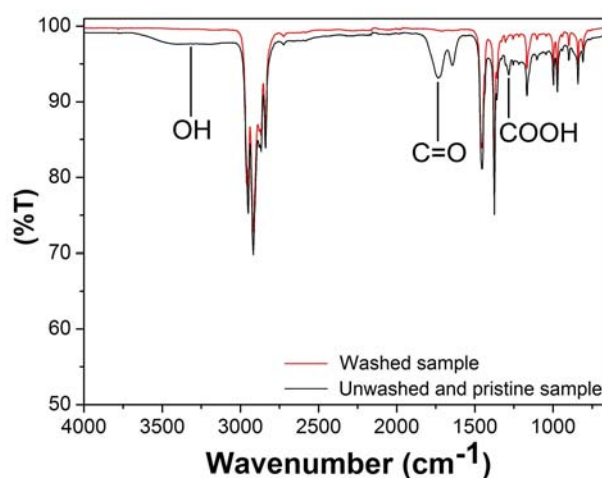


Figure 5. Comparison of the PP infrared spectra.

Acknowledgements

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