

Solid-State Hydrolysis of Postconsumer Polyethylene Terephthalate After Plasma Treatment

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ABSTRACT: Plasma treatments were applied on the surface of postconsumer polyethylene terephthalate (PET) bottles to increase their wettability and hasten the subsequent hydrolysis process. Sixty-four treatments were tested by varying plasma composition (oxygen and air), power (25–130 W), pressure (50–200 mTorr), and time (1 and 5 min). The best treatment was the one applied in air plasma at 130 W and 50 mTorr for 5 min, as it provided the lowest contact angle, 9.4°. Samples of PET before and after the optimized plasma condition were subjected to hydrolysis at 205°C. Although the treatment changed only a thin surface layer, its influence was evident up to relatively high conversion rates, as the treated samples presented more than 40% higher conversion rates than the untreated ones after 2 h of reaction. Infrared spectroscopy showed that the terephthalic acid obtained from 99% of depolymerization was similar to the commercial product used in PET synthesis. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2012

KEYWORDS: recycling; surface modification; polyesters; plasma treatment

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INTRODUCTION

According to the Brazilian polyethylene terephthalate (PET) Industry Association, Brazil consumed 471,000 tons of virgin resin in 2009, mainly to manufacture bottles for soft drinks, oils, isotonic beverages, etc. In the same year, 262,000 tons of these bottles (55.6% of the total) were recycled.¹

One of the obstacles to the expansion of these numbers is the quality of the end products obtained through mechanical recycling, which accounts for 81% of PET recycling in Brazil.¹ This quality is generally considered inferior to that of products made of virgin resin^{2–4} and even to that of products obtained through chemical recycling, which is used to recycle the remaining 19% of PET wastes in Brazil.¹ Among the products obtained by chemical recycling are alkyd and unsaturated polyester resins, which are obtained from the glycolysis of polymer.⁵

Although hydrolysis is a harmful form of PET degradation (and therefore extensively studied) because it occurs mainly in the processing stages of polymer (and obviously also in reprocessing), it is the form least applied in chemical recycling. Recent studies, however, confirm its ability to cleave the main chain and obtain products of highly added value, such as terephthalic acid (TPA) and ethylene glycol, which are used in PET polymerization.^{6–12}

Biotechnological routes have been tested, as in the case of experiments that have resulted in the production of TPA after

surface hydrolysis of PET fibers and films by enzymes produced by microorganisms that used the polymer as substrate.^{6,7}

The chemical reaction of PET in aqueous solution of sodium hydroxide is one of the most widely studied hydrolytic reactions, with or without the aid of specific catalysts such as hexadecyl tributyl phosphonium bromide.⁸ In the latter case, there are studies that used alkaline hydrolysis for the surface treatment of fibers⁹ or the removal of the original surface to expose a new one with fewer impurities.¹⁰

In addition to catalysts, surface modifications have proved to be efficient in increasing the reactivity of PET with water. When the polymer is in the solid state, its surface plays a fundamental role in reactivity, as it is the first target for attack by reagents and/or catalysts. Previous studies on hydrolysis concluded that concentrated solutions of sulfuric acid cause irregularities on the surface of the PET particle, increasing the area of the polymer exposed to hydrolytic attack. Scanning electron microscope images of particles remaining after different reaction times enabled this surface modification to be correlated with the abrupt increase observed in the reaction rate.^{13,14}

Significant surface changes were also reported by Liebminger et al. after subjecting samples of PET fibers to enzymatic hydrolysis. The authors observed a considerable increase in the

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polymer's hydrophilicity, which favored subsequent hydrolytic attacks.⁶

Thus, plasma surface treatments may be an interesting alternative to increase the rate of hydrolysis, because they can increase both surface area and hydrophilicity. In this context, oxygen plasma has been tested successfully on PET fibers to increase the interaction with a composite matrix.¹⁵

Yang et al. studied the effect of air plasma on PET films and, similar to oxygen plasma-treated samples, observed an increase in the number of oxygen-containing chemical groups on the surface, thus increasing the films' affinity for water. Moreover, atomic force microscopy data revealed a clear increase in surface roughness, which also tends to increase the wettability. This increase in roughness is explained by the preferential removal of surface layers of the polymer by the impact of energetic plasma species on the surface.¹⁶

Oxygenated groups have also been incorporated by oxygen plasma treatments on the surface of recycled postconsumer PET bottles, which augmented the adhesion of subsequently deposited hydrogenated amorphous carbon films.¹⁷

The objective of this work was to investigate the benefits of an optimized plasma treatment on the productivity of chemical recycling of PET by hydrolysis. The plasma treatments were optimized by varying the pressure, power, and chemical composition (oxygen and air).

EXPERIMENTAL

To reduce interferences typically originating from postconsumer wastes, only colorless 2-L Coca-Cola® PET bottles were used in this study. Samples of ~ 1 cm in width and 6 cm in length were washed for 20 min in an aqueous detergent solution, rinsed with distilled water, washed twice more for 20 min (first in distilled water and then in isopropyl alcohol), and air-dried in a desiccator. All the washes were performed in an ultrasonic bath.

Clean samples were placed in the bottom electrode of a stainless steel plasma reactor fully described elsewhere.¹⁸ The pressure of the system was reduced to 15 mTorr and oxygen or air was fed into the reactor until the pressure reached the values predetermined for each treatment, i.e., 50, 100, 150, or 200 mTorr. Plasma ignition was then promoted by the application of radiofrequency power (13.56 MHz) to the sample holder. In addition to plasma pressure, the effect of the plasma excitation power (25, 50, 100, or 130 W) and exposure time (1 or 5 min) on the surface properties of the polymer were investigated.

The water contact angle and surface energy of the samples were examined immediately after the treatment, using the sessile drop method.¹⁹ Droplets of deionized water and diiodomethane were measured using a Ramé Hart 100-00 goniometer. The harmonic method was used to evaluate the surface energy from the polar and dispersive components of the contact angle. The contact angle of each treated sample (three) was measured 40 times, making a total of 120 values for each treatment condition and for each probe liquid. The temporal

evolution of the contact angle in atmospheric air was also assessed for the plasma-treated samples that exhibited the highest hydrophilicity.

For the hydrolysis experiments, untreated and plasma-treated samples were first ground into particles of about 5 mm in diameter. Based on previous studies,^{10,20,21} polymer-to-water molar ratios of 1 : 91 were used in a 160-mL cylindrical austenitic stainless steel pressure vessel (to allow for magnetic shaking) equipped with internal temperature and pressure meters. The pressure and temperature in the reactor were 12×10^6 mTorr and 205°C, respectively. For the two sets of experiments (i.e., samples with and without surface treatment), the reaction times were 1.0, 1.5, 2.0, 2.5, 3.0, and 4.0 h, the latter defined by the attainment of more than 99% of depolymerization. The reactions were carried out in duplicate at all the aforementioned times.

The extent of the hydrolytic reaction was determined by gravimetric assays, considering the mass of the samples before and after the reactions. The product of the reaction was filtered through membranes with a pore diameter of 1.0 μm to separate the liquid from the solid phase, the former containing principally ethylene glycol and water and the latter possibly containing unreacted PET and TPA, plus possible oligomers formed by depolymerization. For the gravimetric calculation, the TPA was isolated by mixing the solid phase with 15 mL of concentrated ammonium hydroxide (NH_4OH) and shaking the mixture for 5 min. This procedure, adapted from Yoshioka et al.,¹³ enabled all the TPA formed to be solubilized.^{11,20,21} Therefore, when 100% of depolymerization (or 100% of TPA) is attained in a reaction, it can be inferred that no other components are present in the solid phase.

After 5 min of shaking, the resulting mixture was vacuum-filtered through preweighed membranes, which were then dried in a desiccator at room temperature for 12 h and in an oven at no more than 74°C for 5 h. After cooling, they were weighed on an analytical scale to determine the quantity of remaining material and, from its ratio to the initial mass, the quantity of hydrolyzed polymeric material.

Purified TPA was produced by precipitating it through the acidification (with sulfuric acid up to $\text{pH} = 1$) of filtered diammonium terephthalate solution, followed by washing, drying, grinding, and sieving. This procedure was the same as that performed in previous studies.^{10,11,20,21} The resulting material, as well as commercial TPA (provided by Rhodiaco) were then characterized by infrared transmission spectroscopy (in KBr pellets), using a Perkin-Elmer 1000 FTIR spectrometer. The untreated PET samples and PET samples treated in the optimized condition were also characterized by infrared spectroscopy, but now using the attenuated total reflectance mode in a Jasco Analytical Instruments FTIR410 spectrometer.

RESULTS AND DISCUSSION

Contact Angle, Surface Energy, and Chemical Structure

The water contact angle for the outer and inner surfaces of the bottles measured before the plasma treatment were 82° ($\pm 7.5^\circ$) and 57° ($\pm 3.6^\circ$), respectively. This difference may be due to

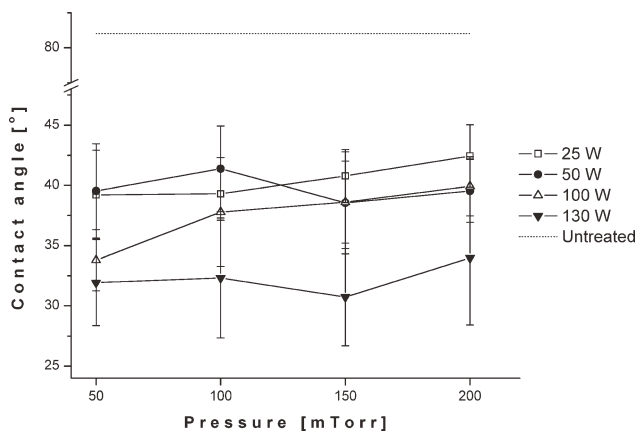


Figure 1. Contact angle of PET surfaces as a function of pressure and power applied in oxygen plasma treatments conducted for 1 min. Data acquired using deionized water.

one of the following factors: the residual stress generated in the bottle fabrication process or the degradation process acting differently on the inner and outer surfaces during the bottle's service life. In this work, the optimization of the plasma treatment focused on the outer part, which is the most hydrophobic part of the bottle.

Figures 1 and 2 illustrate the tendencies of the contact angle as a function of the pressure applied in oxygen plasma treatments of 1 and 5 min, respectively. The different curves in these graphs represent data acquired from treatments performed with different powers. The general tendency is for the contact angle of PET to be reduced during plasma treatment in any condition of plasma excitation. Independently of the treatment time, varying the plasma excitation power was found to be more effective in reducing the contact angle than changing the pressure. The only exception was observed for the sample treated for 10 min at 50 W. An analysis of the results depicted in Figures 1 and 2 clearly indicates that the oxygen plasma treatment that yielded the best result was the one conducted with 50 mTorr for 5 min using 50, 100, or 150 W.

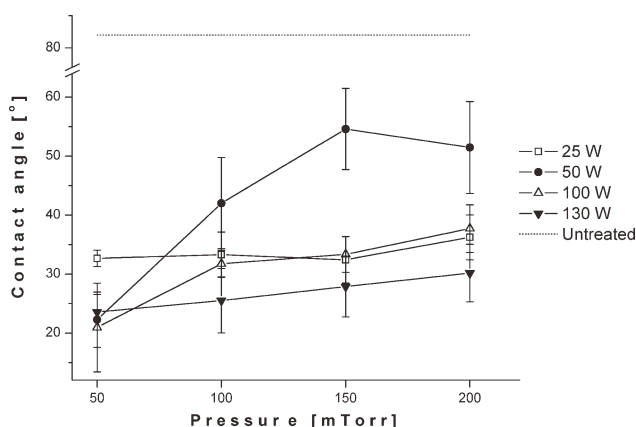


Figure 2. Contact angle of PET surfaces as a function of pressure and power applied in oxygen plasma treatments conducted for 5 min. Data acquired using deionized water.

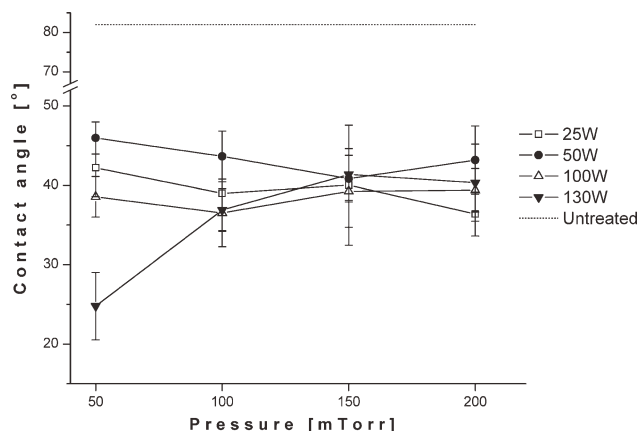


Figure 3. Contact angle of PET surfaces as a function of pressure and power applied in air plasma treatments conducted for 1 min. Data acquired using deionized water.

Figures 3 and 4 depict the PET surface contact angles as a function of pressure in the air plasma treatments conducted for 1 and 5 min, respectively. The different curves in these graphs show how the contact angle varies as a function of the plasma power condition. Again, the polymer was sensitive to the plasma treatment, independently of the excitation condition used, i.e., water receptivity increased on all the surfaces. In the shortest exposure time (Figure 3), changes in the power did not substantially alter the contact angle. The most visible variation was observed only in the curve corresponding to the treatment performed at 130 W and 50 mTorr. On the other hand, at the longest exposure time, there is a clear difference between the low-pressure (25 and 50 W) and high-pressure (100 and 150 W) treatments. Pressure did not affect the surface contact angle in the lowest power regime but was decisive at the highest power. Considering now the treatments in air plasmas (Figures 3 and 4), the highest wettability was obtained in the condition of lowest pressure (50 mTorr), highest power (100 or 130 W), and longest exposure time.

To understand these tendencies, one must consider the effect of power and pressure on the intrinsic properties of plasma. When

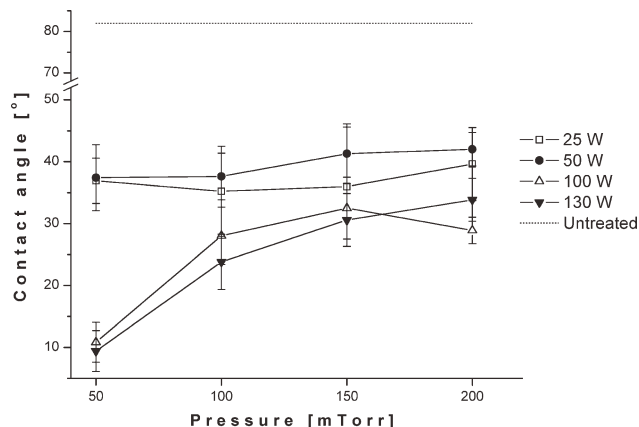


Figure 4. Contact angle of PET surfaces as a function of pressure and power applied in air plasma treatments conducted for 5 min. Data acquired using deionized water.

Table I. Surface Energy of the Samples Treated with Oxygen Plasma for 1 min, as a Function of Power and Pressure

Power (W)	Component (dynes/cm)	Pressure (mTorr)							
		50		100		150		200	
		Mean	SD	Mean	SD	Mean	SD	Mean	SD
25	Polar	27.3	1.6	27.4	0.5	26.6	0.2	26.0	0.3
	Dispersive	43.5	1.5	42.8	1.1	43.1	1.2	42.4	0.5
	Total	70.7	3.1	70.3	1.4	69.8	1.2	68.4	0.8
50	Polar	27.0	1.2	26.6	1.0	27.7	1.6	27.5	0.6
	Dispersive	43.4	1.8	41.9	1.9	42.9	1.1	42.2	0.8
	Total	70.4	2.6	68.6	2.8	70.6	2.7	69.7	1.1
100	Polar	29.6	0.3	28.0	2.2	27.5	1.4	26.7	0.9
	Dispersive	44.0	0.7	43.4	1.5	43.8	1.3	44.3	1.2
	Total	73.6	1.0	71.4	2.1	71.3	0.2	71.1	2.1
130	Polar	30.0	0.0	29.9	1.5	30.7	1.1	29.2	3.1
	Dispersive	45.3	2.2	45.3	0.5	45.1	0.7	45.8	1.3
	Total	75.3	2.2	75.3	2.0	75.8	1.1	75.0	2.4

SD: standard deviation of the measurements.

the pressure is reduced while the other parameters are kept constant, the average energy of plasma species increases. An increase in the power of the excitation signal causes the same effect as that of a reduction in pressure: the average energy of the species increases. The plasma becomes more reactive and energetic, thus augmenting its effectiveness in incorporating oxygen-containing groups on the surface. As a result, surface polarity, and hence wettability, increase. On the other hand, when the treatment time is increased, the plasma remains unaltered but the probability of species becoming incorporated into the material increases, altering its chemical composition and therefore its receptivity to other media such as water. Although it was not proven in this study, the incorporation of oxygenated groups has been reported in studies on air plasma-treated PET films¹⁶ and on oxygen plasma-treated postconsumer PET bottles.¹⁷

Based on Figures 1–4, it can be stated that all the 64 treatment conditions used in this study contributed significantly to reduce the contact angle between the deionized water and the surface of the samples. The lowest reduction (33%) was attained in the treatment conducted at 50 W, 150 mTorr oxygen plasmas for 5 min (Figure 2), whereas highest reduction (88%) was obtained at 130 W, 50 mTorr air plasmas for 5 min (Figure 4). This improvement in hydrophilicity is also reported in the literature for oxygen plasma treatments of PET fibers¹⁵ and bottles,¹⁷ and for air plasma treatment of PET films.¹⁶

Further information concerning the thermodynamic properties of PET was obtained from the surface energy of the samples. Tables I–IV list the results obtained from samples treated in oxygen plasma for 1 and 5 min and in air plasma for 1 and 5 min. The standard deviations (SD) of the surface energy are also given in these tables. For untreated surfaces, the mean results were 7 dynes/cm (± 1.1 dynes/cm) and 41.8 dynes/cm (± 2.1 dynes/cm) for polar and dispersive surface energies, respectively.

The surface energy provides information about the receptivity of a surface toward other materials and media. While surfaces with low energies have a greater tendency to remain unaltered, surfaces with high energies tend to interact readily with the surrounding medium to reduce their free energies. This is an aspect that enables a series of possible interactions with other media, such as water.

An analysis of the results presented in Tables I–IV indicates that the behavior of surface energy varies inversely to that of the contact angle, i.e., it increases on plasma treatment, enhancing the surface reactivity to the external medium. It is interesting to point out, in these results, the distribution of the values of the dispersive fraction of the surface energy, which were generally very similar to each other and also close to that of the untreated samples.

In general, Tables I–IV indicate that all the treatments applied in this study induced modifications in the surface energy of the PET samples. However, the most significant changes were those observed in the polar fraction of the surface energy. This was expected, up to a point, as the types of gases used for the generation of plasmas are known to promote the incorporation of polar groups on the surface of interest.^{15–17} It was found that the polar surface energy varied from about 7 dynes/cm in untreated surfaces to, at least, 21.4 dynes/cm (150 mTorr, 50 W oxygen plasma for 5 min). The highest polar surface energy recorded was 36.2 dynes/cm for the samples treated at 50 mTorr, 130 W air plasma for 5 min. This corroborated the contact angle results (Figures 1–4) and defined what was considered the best treatment, which was therefore repeated in the subsequent experiments.

The results of the polar surface energy also indicated that as in the contact angle results, by maintaining the parameters of gas (air), time (5 min), and pressure (50 mTorr), the powers of 100 and 130 W yielded very similar results: 36.0 and 36.2 dynes/cm,

Table II. Surface Energy of the Samples Treated with Oxygen Plasma for 5 min, as a Function of Power and Pressure

Power (W)	Component (dynes/cm)	Pressure (mTorr)							
		50		100		150		200	
		Mean	SD	Mean	SD	Mean	SD	Mean	SD
25	Polar	29.7	1.0	28.7	1.1	29.76	1.8	28.3	0.6
	Dispersive	45.7	1.9	45.0	1.5	45.3	0.3	44.8	1.0
	Total	75.4	0.9	73.7	2.3	75.0	2.1	73.1	1.0
50	Polar	33.6	1.8	23.6	0.9	21.4	1.4	23.4	2.2
	Dispersive	47.7	0.5	42.9	0.0	35.0	2.1	35.7	5.5
	Total	81.3	1.4	66.5	0.9	56.4	3.2	59.1	3.2
100	Polar	33.6	2.1	29.7	0.3	29.4	0.5	28.8	0.9
	Dispersive	47.2	0.2	47.1	0.4	45.6	0.1	42.4	0.7
	Total	80.8	2.3	76.8	0.5	75.0	0.5	71.1	1.6
130	Polar	32.7	0.1	32.0	2.1	30.6	2.3	29.8	1.9
	Dispersive	47.8	0.2	47.7	0.0	47.4	0.7	47.5	0.4
	Total	80.4	0.2	79.7	2.0	78.0	2.1	77.3	2.3

SD: standard deviation of the measurements.

respectively (with contact angles of 10.9° and 9.4°, respectively). Despite this similarity in mean values, it was determined that the best treatment was the one that applied the highest power since it caused the lowest SD (Figure 4 and Table IV), favoring reproducibility.

Effect of Aging on the Contact Angle

Figure 5 illustrates the temporal evolution of the contact angle of samples treated for 5 min in 50 mTorr, 130 W air plasma. This angle increases over time, reaching 33.5° 5 h after the treatment. For this set of assays, the repetition of the previously optimized treatment yielded samples with a mean contact angle of 11.7° (±1.9°), which is more than 2° higher than that

obtained when the treatment was optimized (item 3.1). However, this value still lies within the interval of confidence established for the SD of the measurements taken on that occasion.

The behavior of the contact angle of the plasma-treated samples was adjusted satisfactorily ($R^2 = 0.978$) according to the second-order exponential model presented in eq. (1):

$$\theta = 161.33 - 135.56 \cdot e^{-\frac{t}{5047.49}} - 16.36 \cdot e^{-\frac{t}{38.38}} \quad (1)$$

Figure 5 also indicates that after 20 min of aging, the contact angle was 16.3°. This value is important because 20 min was the average time elapsed from the end of the plasma treatment until the treated material reached a suitable condition for

Table III. Surface Energy of the Samples Treated with Air Plasma for 1 min, as a Function of Power and Pressure

Power (W)	Component (dynes/cm)	Pressure (mTorr)							
		50		100		150		200	
		Mean	SD	Mean	SD	Mean	SD	Mean	SD
25	Polar	26.4	0.6	27.5	1.7	27.6	3.2	28.6	1.0
	Dispersive	41.2	1.0	43.0	1.5	41.9	2.0	43.5	1.8
	Total	67.7	1.4	70.5	2.5	69.4	5.2	72.1	2.6
50	Polar	25.5	0.9	26.5	2.1	26.7	0.1	25.2	2.2
	Dispersive	39.4	0.8	43.0	1.9	42.8	1.0	43.0	1.0
	Total	64.9	1.1	69.5	3.8	69.5	1.1	68.2	3.2
100	Polar	27.8	0.5	28.0	2.2	27.5	1.6	27.6	0.8
	Dispersive	43.9	0.2	44.2	0.4	42.3	1.5	42.6	2.4
	Total	71.7	0.6	72.2	2.6	69.8	3.0	70.1	3.1
130	Polar	32.5	0.6	28.0	1.0	26.7	0.4	27.3	2.0
	Dispersive	46.6	1.2	44.5	1.8	41.6	1.3	41.0	0.4
	Total	79.1	1.7	72.4	2.8	68.3	1.2	68.2	2.3

SD: standard deviation of the measurements.

Table IV. Surface Energy of the Samples Treated with Air Plasma for 5 min, as a Function of Power and Pressure

Power (W)	Component (dynes/cm)	Pressure (mTorr)							
		50		100		150		200	
		Mean	SD	Mean	SD	Mean	SD	Mean	SD
25	Polar	28.5	0.1	28.2	0.7	28.9	2.8	27.1	2.3
	Dispersive	43.0	1.3	46.85	0.8	43.0	2.1	43.5	1.3
	Total	71.6	1.2	75.0	0.2	71.9	2.1	70.5	3.1
50	Polar	27.1	2.4	27.0	1.0	26.6	1.8	26.3	0.3
	Dispersive	47.5	0.4	46.8	1.6	42.0	0.2	42.0	1.4
	Total	74.6	2.0	73.8	0.6	68.5	2.00	68.4	1.6
100	Polar	36.0	0.6	31.8	1.8	29.1	2.3	31.1	0.7
	Dispersive	47.7	0.3	47.7	0.1	48.0	0.0	47.6	0.5
	Total	83.6	0.9	79.5	1.9	77.1	2.3	78.6	1.2
130	Polar	36.2	0.2	32.7	0.7	30.0	1.3	29.1	0.8
	Dispersive	47.6	0.2	47.8	0.3	47.6	0.4	46.3	1.5
	Total	83.8	0.4	80.5	0.5	77.6	1.7	75.4	2.2

SD: standard-deviation of the measurements.

reaction. In other words, after the polymer was removed from the plasma reactor, it took 20 min to grind it, mix it with water, place it in the pressure vessel, close the vessel, and place the reactor in the preheated oil bath. After 50 min, i.e., the time required to reach the hydrolysis temperature of 205°C, the contact angle was 22°.

Even after 20 or 50 min, the hydrophilicity of the treated material was still considerably higher than that of the untreated material (whose contact angle was 82°). This validates the procedure adopted in this work, which would have to be altered if the loss in hydrophilicity were much faster. Even the 5-h wait left the treated polymer with a much higher hydrophilicity (33°) than that of the untreated polymer.

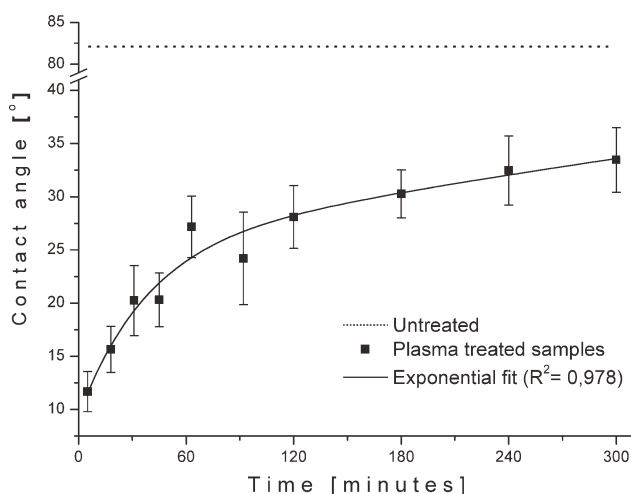


Figure 5. Temporal evolution of the contact angle of samples treated at 50 mTorr, 130 W air plasma for 5 min. Data acquired using deionized water.

Neutral Hydrolysis of PET Samples with and Without Plasma Treatment

Figure 6 shows the percentage of hydrolyzed PET during the neutral hydrolysis of the plasma-treated and untreated PET. Table V presents the mean values and the respective SD obtained for each sample. The sigmoidal adjustments of the results obtained from the degradation of untreated and treated PET samples are given, respectively, by eqs. (2) ($R^2 = 0.994$) and (3) ($R^2 = 0.999$). Both equations proved to be suitable for their respective cases and confirm that better results are indeed obtained from the treated samples, since the inflection point is reached earlier in eq. (3) (2.07 h) than in eq. (2) (2.36 h), yielding, for any time of reaction (x), values of hydrolyzed PET closer to 100%.

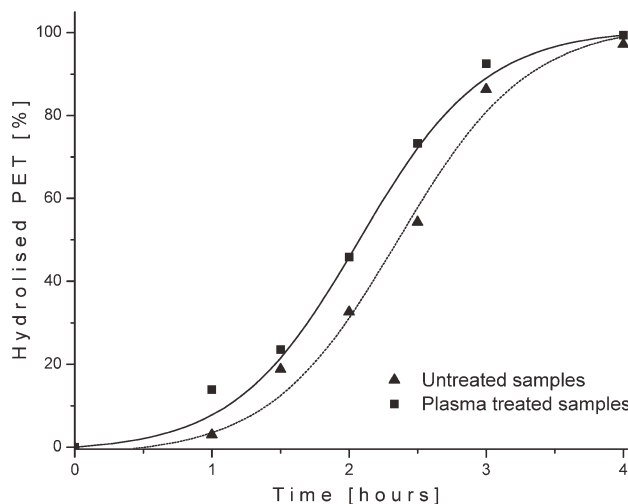


Figure 6. Percentage of hydrolyzed PET with (■, curve on left) and without (▲, curve on right) plasma treatment as a function of reaction time.

Table V. Mean Values and Standard Deviation of the Percentage of PET Hydrolyzed with and Without Plasma Treatment as a Function of Time

Time (h)	Without treatment		With treatment	
	Mean	SD	Mean	SD
0.0	0.0	0.0	0.0	0.0
1.0	3.0	1.1	13.9	13.2
1.5	18.7	3.9	23.5	5.8
2.0	32.6	5.6	45.8	0.2
2.5	54.3	3.0	73.3	14.8
3.0	86.3	3.8	92.5	6.7
4.0	97.1	3.8	99.4	0.3

SD: standard-deviation of the measurements.

$$\text{PET hydrolyzed}(\%) = 102.09 - \frac{104.14}{1 + e^{\frac{x-2.36}{0.47}}} \quad (2)$$

$$\text{PET hydrolyzed}(\%) = 100.84 - \frac{101.90}{1 + e^{\frac{x-2.07}{0.46}}} \quad (3)$$

Figure 6 and Table V show a behavior very similar to that reported for acid hydrolysis,^{11,13,14} i.e., a period of low reactivity (up to ~ 1 h of reaction), a period of exponential growth in the conversion rate, and another period of low reaction productivity (starting from about 90% of hydrolyzed PET). The results in Figure 6 and Table V also indicate that, on average, the neutral hydrolysis of plasma-treated PET showed consistently higher conversion rates than untreated polymer, at any reaction time. This suggests that the intensification of the water attack is indeed related to the plasma treatment, whether by causing an increase in surface area and/or by introducing hydrophilic groups on the surface.^{15–17}

The most important difference in the results of the treated and untreated samples lies in the region of high reactivity, ranging approximately from 1.5 to 2.5 h, between the upper and lower thresholds. For example, at a reaction time of 2 h, i.e., at the mid-point between the beginning and end of the reactions, the treated samples presented more than 40% higher conversion rates than the untreated samples (average values of 45.8 and 32.6%, respectively).

Especially at the beginning, a good part of the reaction involves the destruction of the surface polymer chains. Even at the minimum conversion rates obtained in the region of high reactivity, i.e., 18.7 and 23.5% (1.5 h), the original surface and, when treatment is applied, the treated surface, are expected to be destroyed. The behavior presented in this region indicates how the hydrolysis was affected by the plasma treatment, as it represents the only difference between the tested samples. As indicated in the central region of the graph in Figure 6, the curve corresponding to reactions with the treated polymer shifted about 15 min toward the left in relation to the curve of the untreated polymer. Moreover, 4 h of reaction was the time elapsed to achieve almost complete depolymerization of the untreated and treated PET. This was also expected since, as the reaction approaches the upper threshold region shown in Fig-

ure 6, the original surface (treated or untreated) probably no longer exists and the limiting factor becomes the ever smaller quantity of material available for the reaction.

Characterization of the TPA

Figure 7 shows the infrared spectrum of the TPA obtained in this study by chemical recycling of the plasma-treated PET. For comparison, the infrared spectrum of the commercial TPA is also presented, as well as the infrared spectra of PET before and after the optimized treatment.

In the spectrum of the untreated PET (a), the absorptions ascribed to C–H stretching vibrations are visible in the region of 2960–2850 cm^{-1} . The most intense band in the spectrum, at around 1715 cm^{-1} , is associated with the presence of the carbonyl group of saturated esters. Contributions at around 1100 cm^{-1} are characteristic of the stretching vibration of ester bonds. In the low-wavenumber region, another sharp and intense band arising at 723 cm^{-1} reveals the presence of two carbonyl groups in the aromatic ring. The spectrum of the sample exposed to the plasma treatment (b) shows no marked differences as all the main absorptions detected in the spectrum of the untreated material remained in the same wavelength, presenting no widening or shifting. This invariance is explained by the fact that infrared spectroscopy probes deep regions in the polymer ($\sim 1 \mu\text{m}$) while plasma treatment changes only the first monoatomic layers.

It is interesting to note in Figure 7 the similarity of the spectra of the commercial TPA (c) and the TPA obtained by chemical recycling (d), which are typical of carboxylic acids. The peak corresponding to carbonyl is located at 1680 cm^{-1} and no longer at 1715 cm^{-1} , as recorded for the PET. The bands around 1100 cm^{-1} , which are characteristic of the ester bond, are absent in Figure 7(d) [as well as in Figure 7(c)], indicating its break during the hydrolytic reaction. In contrast, spectra (c) and (d) show a broad band between 3400 and 2200 cm^{-1} , which is characteristic of –OH chain terminations of carbonyls in carboxylic acids.

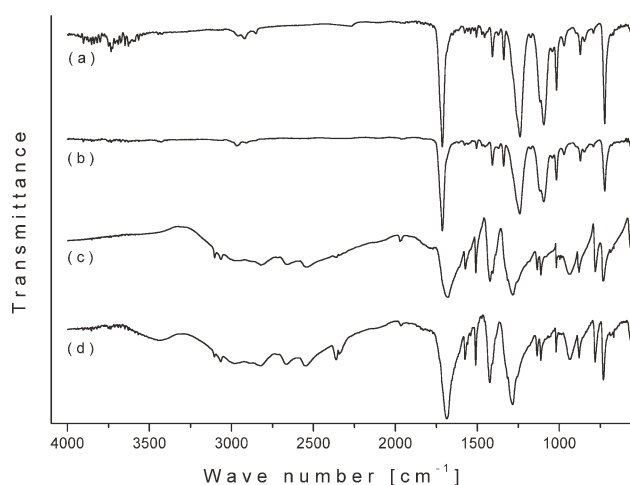


Figure 7. Infrared spectra of (a) PET before the optimized treatment, (b) PET after the optimized treatment, (c) commercial TPA, and (d) TPA obtained by chemical recycling of PET (neutral hydrolysis of plasma-treated polymer).

In other words, the TPA obtained by hydrolysis of the plasma-treated PET is very similar to the commercial purified TPA obtained from petrochemicals (via *para*-xylene oxidation) and to the TPA obtained via hydrolytic reactions of PET without treatment.^{10,11,20,21} This indicates that the procedures used here, particularly the surface treatment, were adequate in accelerating the depolymerization of postconsumer PET bottles and did not impair the quality of the resulting TPA. This result thus reveals the advantages of plasma treatment in modifying a thin surface layer of material while maintaining its internal integrity.

CONCLUSIONS

A total of 64 plasma treatment conditions were tested on the surfaces of postconsumer PET bottles to determine which condition rendered the material most hydrophilic to aid the subsequent hydrolysis. The results of this phase indicated that all the treatments to which the samples were subjected contributed to increase their wettability. The best condition was considered the one performed with air plasma for 5 min at 130 W and 50 mTorr, which yielded the highest polar surface energy, 36.2 dynes/cm (about fivefold higher than that of untreated samples), and the lowest contact angle, 9.4°, (representing a reduction of ~ 88% of the value observed initially).

The contact angle of the material after 20 min of air aging was 16.3°. This value ensured a high hydrophilic condition at the beginning of the hydrolytic attack, as 20 min was the average time elapsed between the removal of treated material from the plasma reactor and the beginning of heating of the depolymerization system.

Samples of treated and untreated PET were then subjected to hydrolysis, and in both cases, a lower threshold followed by a region of high productivity and an upper threshold were observed in the conversion curves. The curve of the plasma-treated samples was shifted to the left in relation to the curve of the untreated samples, indicating the higher reactivity rates of the treated samples. Although this treatment involved only a thin surface layer, its influence was evident even when depolymerization reached sufficiently high conversion levels, destroying the original surface and the treatment applied on it. For instance, 2 h of reaction led to conversion rates that were, on average, 40% higher in the treated than in the untreated samples. The limiting factor for the reaction when it was close to the end was associated to the ever diminishing quantity of available material to react.

The TPA obtained by depolymerization was considered similar to the commercial product obtained by petrochemical routes. This indicates that the procedures adopted here, including the plasma treatment, were adequate to accelerate depolymerization (the objective of the treatment) and did not impair the quality of the final product.

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