

Superficial Modification in Recycled PET by Plasma Etching for Food Packaging

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ABSTRACT: An oxygen plasma treatment has been used to improve the adhesion of amorphous hydrogenated carbon (a-C:H) films onto surfaces of recycled poly(ethylene terephthalate) (PET). Modifications produced by the oxygen plasma on the PET surface in chemical bonds and morphology were investigated by X-ray photoelectron spectroscopy and atomic force microscopy, respectively. Contact angle measurements were used to study the changes in the surface wettability. Adhesion of the a-C:H film onto the PET surface was investigated by the tape test method. It was observed that the improvement in film adhesion is in good

correlation with the increase in surface roughness, due to plasma etching, and with the appearance of oxygen-related functional groups at the surface. The results of this study indicate that a-C:H-coated recycled PET can be used in food packaging. The a-C:H film could be used as a functional barrier to reduce or prevent migration of contaminants from the polymer to the package content. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 115: 2728–2733, 2010

Key words: PET; recycling; plasma; etching; adhesion; coating

INTRODUCTION

Amorphous hydrogenated carbon (a-C:H) films have been widely used as protective coatings in a variety of materials for applications such as gas barriers, gas separations membranes,^{1,2} and ultimately as a functional barrier to avoid or reduce the migration of possible residual contaminants in packaging made by recycled polymers.³

Poly(ethylene terephthalate) (PET) is one of the most applied materials used for bottle fabrication in the soft drinks market. The principal of PET application is in blow-molded packaging. Thus, it would be extremely useful if this material could be treated in such a way as to return it to a form suitable to its original purpose. However, restrictions still exist to the use of the recycled material in direct contact with food because of the possibility of contaminant migration.^{4,5} This problem can be avoided using a functional barrier, which can be a layer of virgin material placed between the recycled polymer and the food. This layer could reduce the migration of possible residual contaminants.⁶ In general, the ability of functional barriers to

prevent or reduce the migration of contaminants is discussed in terms of models stipulated by the Food and Drugs Administration (FDA) of USA.⁷ Cruz et al.³ verified the feasibility of the use of recycled PET for food packaging employing an internal coating made from a-C:H film deposited by plasma-enhanced chemical vapor deposition (PECVD) process. To verify the efficiency of the carbon layer as barrier for contaminants, PET samples were deliberately contaminated with a series of surrogates using a FDA protocol. They concluded that the carbon-coated material increases the chemical resistance to a series of surrogates (chloroform, toluene, benzophenone, and lindane), which represents the behavior of different chemical families. The samples were analyzed using a solid-phase micro-extraction coupled to GC-MS.

a-C:H films could be used as a functional barrier in food packaging. The films are usually applied by PECVD. However, bulges or cracks may appear in the films as a consequence of the high internal stress of these materials. As flaw formation benefits from poor adhesion, processes leading to the strong adhesion of the barrier coating onto the plastic package surface are a major concern. Fortunately, increases in the adhesion of a film onto a substrate can be improved by previous treatments of the substrate surface. In a polymer surface, the main modifications produced by plasma treatment are etching

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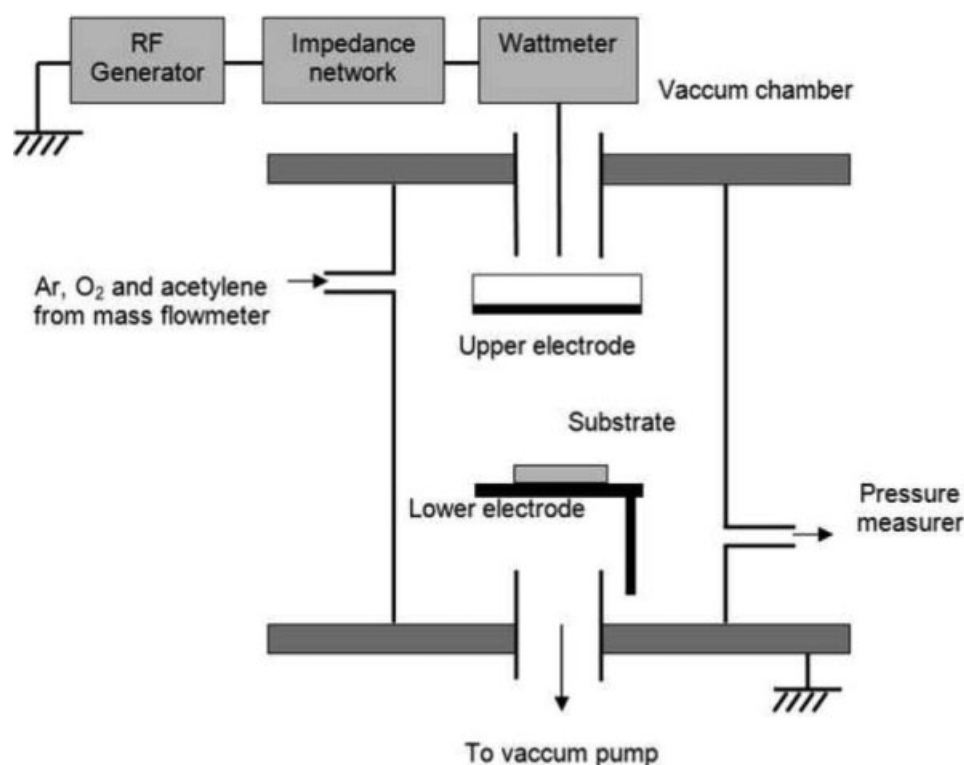


Figure 1 Schematic representation of PECVD system.

and the addition of new functional groups. The etching reactions are due to the degradation of the polymer chains at the surface. Usually, etching increases the surface roughness, thus increasing the substrate–film interaction and consequently the adhesive strength. On the other hand, the addition reactions are due to combinations between chemical species of the polymer surface with reactive species from the plasma, such as activated oxygen, nitrogen, and fluorine.^{8–10}

In this article, the superficial modifications by an oxygen plasma treatment in recycled PET for food packaging are described. The main goal of the investigation is the improvement of adhesion between the recycled polymer surface and an a-C:H thin film deposited by PECVD. Such an adhesion is utterly important if a-C:H-coated recycled PET is considered for food packaging. With this purpose, PET packaging were treated in a radiofrequency oxygen plasma at different times before film deposition. Chemical modifications were characterized by contact-angle measurements and X-ray photoelectron spectroscopy (XPS). Morphological alterations were observed by atomic force microscopy (AFM), and adhesion modifications were evaluated by the tape test method.

EXPERIMENTAL

Materials

Packagings made from recycled PET were used for plasma modification and film deposition. The

recycled PET was previously treated by solid-state polymerization (SSP) to increase the molar mass and to make it suitable for the fabrication of packagings by the blow-molding process. Details of the SSP and the blow-molding process can be found in another publication.¹¹ The PET packagings were cut into $\sim 50\text{-cm}^2$ squares. Prior to surface-modification experiments, the samples were cleaned with acetone, isopropyl alcohol, and water to remove the organic contamination, and then they were dried in a nitrogen flow.

Oxygen (99.8%), acetylene (99.8%), and argon (99.999%), supplied by White-Martins S/A, São Paulo, Brazil, were used for plasma surface modification and a-C:H film deposition.

Methods

Plasma treatment and deposition apparatus

Plasma treatment and film deposition were carried out in a stainless steel vacuum chamber described in detail in previous publications^{12,13} and schematically represented in Figure 1. The chamber was pumped by a 150 m³/h Roots pump, backed by a rotary vane pump. A glow discharge plasma was produced in the chamber between two water-cooled parallel-plate electrodes. The lower electrode was grounded, and the upper one (driving electrode) was connected to a rf generator (40 MHz) through an impedance-matching network and a throughline wattmeter. A

constant rf power of 18 W was used in all plasma treatments and film depositions. The gases used (O_2 for plasma treatment, and Ar and C_2H_2 for film deposition) were introduced in the chamber using precision electronic mass flowmeters. An O_2 mass flow rate of 49 sccm (exposure times of 1.0, 1.5, 2.0, 2.5, 5.0, and 10.0 min) was used in all oxygen plasma treatments; film depositions were performed at mass flow rates of 8 and 70 sccm for C_2H_2 and Ar, respectively, for 15 min. During plasma treatment and film deposition, the pumps were continuously pumping, keeping the chamber base pressure at about 5×10^{-4} mbar.

Atomic force microscopy

The surface morphology was analyzed by AFM using a Topometrix TMX 2010 Discoverer microscope, equipped with a silicon nitride cantilever of 100- μm length, 0.5- μm thick, and a needle tip diameter of 0.4 μm . This technique was also used to measure the film thicknesses. All measurements were carried out in the noncontact mode.

Contact angle

Contact angle measurements were performed using a distilled water drop. An optical microscope (Micronal Olympus G10X) attached to a video camera (Sony Hyper Had DXC-151 A) was used. The images obtained were captured and analyzed by the Image Pro Plus III software. Each contact angle was measured in triplicate.

X-ray photoelectron spectroscopy

A Kratos XSAM HS spectrometer was used to obtain the XPS spectra. The analyses were made in an ultrahigh vacuum environment (10^{-9} Torr). Al $K\alpha$ radiation (1487 eV) was used for photoelectron excitation. The binding energies (BEs) of the peaks in the spectra were referred to that of the 1s electrons in carbonaceous carbon (284.6 eV). To investigate the various binding states of C and O at the PET surface, the C1s and the O1s spectra were decomposed into Gaussian peaks, using a least-square computer-fit program. The atomic ratios of O to C atoms ($O^{(\text{tot})}/C^{(\text{tot})}$) and those of C and O atoms in different binding states were determined from their integrated peak areas corrected for electron escape depth, spectrometer transmittance, and photoelectron cross sections for the photon energy of 1487 eV.¹⁴

Adhesion measurements

The adhesion measurements of the a-C:H films onto the PET surfaces were made according to the ASTM

D-3359-90 norm. The test consisted in applying a 3M-810 adhesive tape to the film surface and removing it with a quick pull, after which the film removal was visually verified.

RESULTS AND DISCUSSION

Atomic force microscopy

The effect of the oxygen plasma treatment on the PET surface is shown in the AFM micrographs of Figure 2. A micrograph of an untreated sample is also shown. The latter reveals an uneven surface, with several imperfections, better identified in the two-dimensional picture. Such a morphology is probably due to the packaging production process. The blow-molding process causes biorientation. Since it is a crude process of chain stretching, the packaging topography tends to be less homogeneous. From a comparison of Figure 2(a–c), it can be seen that oxygen plasma treatment removes gross imperfections at the same time when it increases the

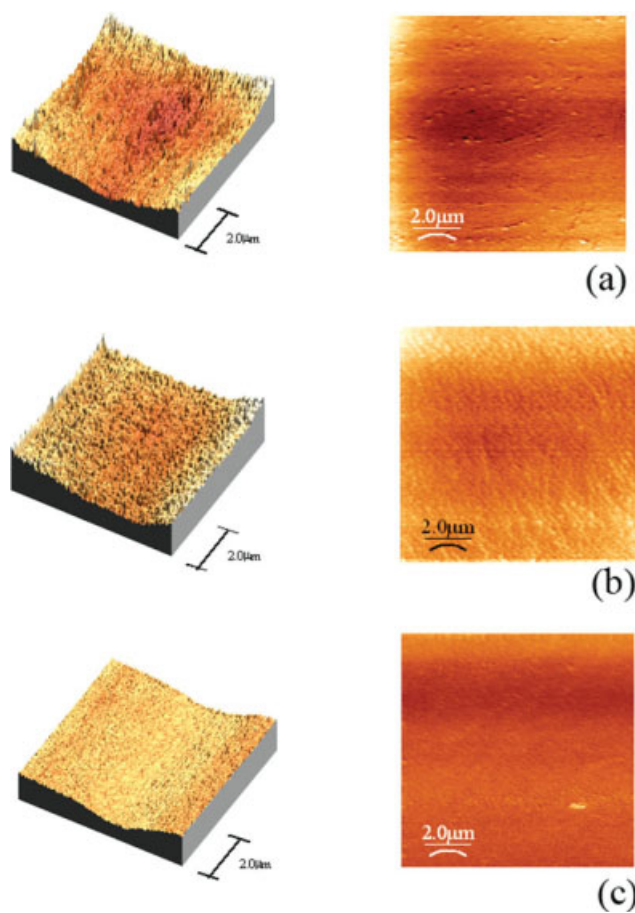


Figure 2 Atomic force microscopy micrographs of samples (a) without treatment and treated with oxygen plasma for (b) 2.5 and (c) 5.0 min. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

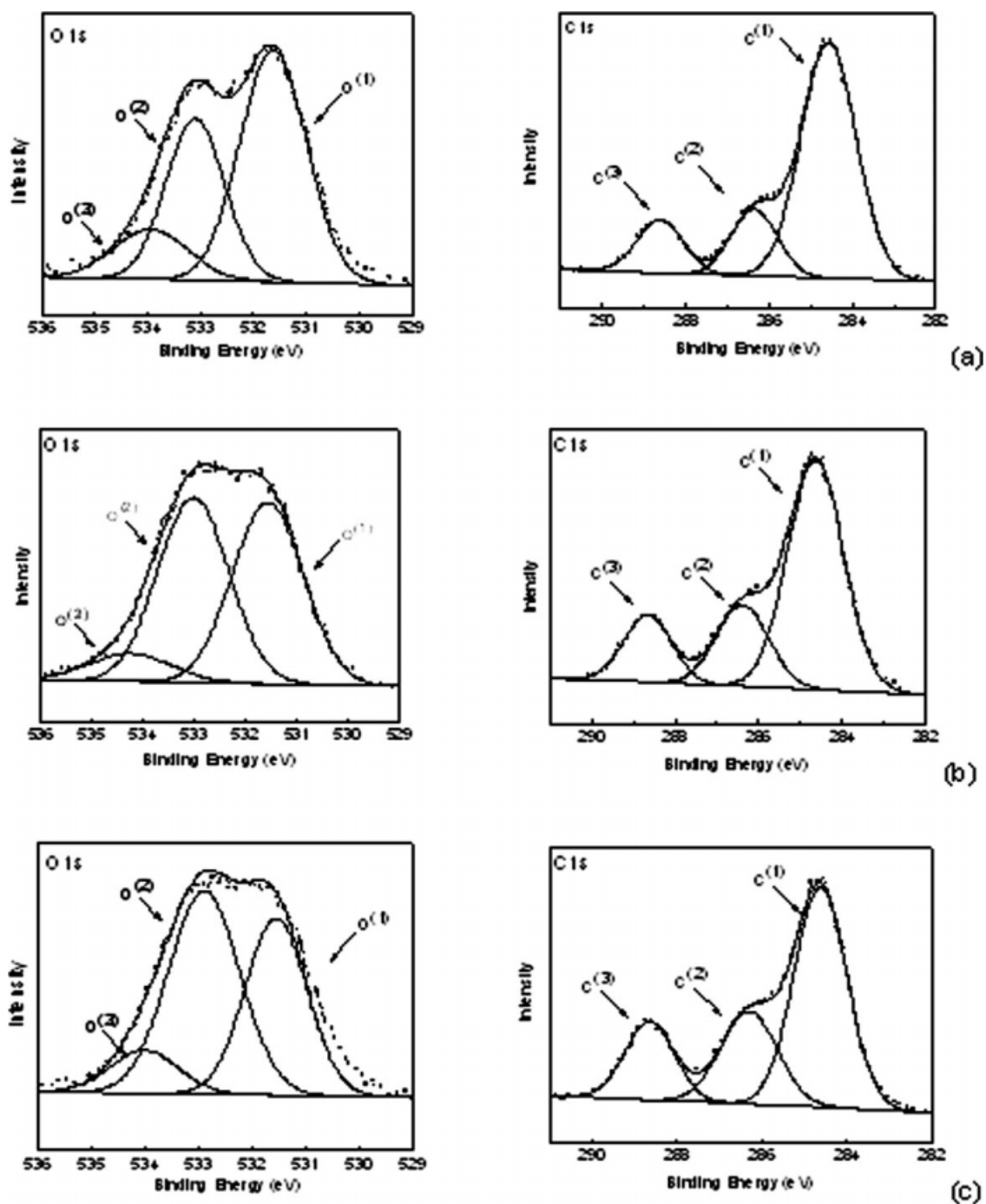


Figure 3 XPS spectra of the C1s and O1s peaks for PET samples without treatment (a) and plasma-treated during (b) 2.5 and (c) 10.0 min.

surface microroughness. No significant alterations were observed in the micrographs of other analyzed periods of oxygen plasma treatment.

X-ray photoelectron spectroscopy

Figure 3 shows the C1s and O1s spectra of PET surfaces of an untreated sample and of samples treated during 2.5 and 10.0 min with oxygen plasma. The high asymmetry and width of all spectra are due to

photoelectrons from C and O atoms in various chemical environments. The spectra are fitted by Gaussian functions corresponding to different bonding configurations. The three Gaussian peaks ($C^{(1)}$, $C^{(2)}$, and $C^{(3)}$) fitting the C1s spectrum for the untreated sample are at the energies of 284.6, 286.4, and 288.8 eV and correspond to carbon atoms in benzenic rings, carbon bound to O, and carbon in ester functional groups, respectively. As for the O1s peak, the three Gaussians ($O^{(1)}$, $O^{(2)}$, and $O^{(3)}$) are

TABLE I
Binding Energies (BE) and Corresponding Bond
Assignments for the XPS Spectrum of the
Untreated PET Surface

C1s		O1s	
BE (eV)	Assignment	BE (eV)	Assignment
284.8	C—C, C—H	531.8	C=O
286.4	C—O	533.3	C—O
288.8	COOH	534.9	OH

peaked at 531.8, 533.3, and 534.9 eV and are due to O in carbonyl, ester, and hydroxyl groups, respectively. The latter is not a very intense peak, as expected, as hydroxyl is only present at the end of the polymer chains similarly to carboxyl acidic groups. The BE values and bonding assignments for C and O peaks are given in Table I. They are according to literature results for XPS studies of PET surfaces.^{15,16}

From the XPS data for the three samples, some atomic ratios were calculated according to the procedure outlined in "X-ray photoelectron spectroscopy" section. Table II shows, for each sample, the ratios of C and O atoms in their various bonding states to the total C and O atoms, $C^{(tot)}$ and $O^{(tot)}$, respectively. The energies for the various bonding configurations of C and O do not significantly change with plasma treatment. However, their relative peak intensities are modified with plasma treatment. From Table II it can be seen that the oxygen plasma promotes a relative increase in the carbon–oxygen bond concentration, as indicated by the increase in the $C^{(2)}/C^{(tot)}$ and $C^{(3)}/C^{(tot)}$ ratios. Regarding the O ratios, an increase in the oxygen atoms in ester groups is evidenced by the increment in the $O^{(2)}/O^{(tot)}$. Oxygen plasma treatment promotes an increase in ester groups concentration. Its corresponding peak becomes predominant when compared with the peak of carbonyl group. This fact could be confirmed by proportions analysis, as presented in Table II. The relative increase in ester group peaks was also observed by Sandri and Sacher¹⁵ in a study of superficial treatment using corona discharge in PET samples. Furthermore, Deshmukh and Bhat¹⁷ studied adhesion mechanisms of paint and film in

TABLE II
Ratios of C and O Atoms in Different Binding States
and Ratio of the Total Oxygen to Carbon Ratio as a
Function of Plasma Treatment Time, *T*

<i>T</i> (min)	$C^{(2)}/C^{(tot)}$	$C^{(3)}/C^{(tot)}$	$C^{(2)}/C^{(3)}$	$O^{(1)}/O^{(tot)}$	$O^{(2)}/O^{(tot)}$	$O^{(1)}/O^{(2)}$	$O^{(tot)}/C^{(tot)}$
0	0.19	0.13	1.46	0.53	0.44	1.20	0.37
2.5	0.24	0.15	1.60	0.49	0.46	1.06	0.44
10.0	0.27	0.18	1.50	0.48	0.48	1.00	0.49

PET treated with air plasma. These investigators concluded that an increase in treatment time promotes an increase in absolute intensity of carbonyl and C—O bonding peaks. On the other hand, C—O peak's relative intensity gradually reduced when compared with carbonyl's, until the fusion of these two peaks.

The ratio of the total O to C atoms ($O^{(tot)}/C^{(tot)}$) is also given in Table II. Consistently with the evaluation of the oxygen-related peaks of the C1s spectra with plasma treatment, the increase in the $O^{(tot)}/C^{(tot)}$ ratio (from 0.37 to 0.49) reveals that the plasma treatment effectively incorporates oxygen onto the PET surface.

Contact angle measurement

Figure 4 shows the contact angle of the water drop on the PET surface as a function of plasma treatment time. According to this figure, there is a progressive decrease in contact angle as exposure time to oxygen plasma increases. These results are in accordance with those obtained by XPS, as there is an increase in oxygen incorporation on the sample surface with plasma treatment time. As the surface polarity is directly related to the contact angle, and as oxygen is a highly electronegative element, oxygen incorporation promotes an increase in the sample's surface polarity. Therefore, wettability increases if the liquid used (distillate water) is polar, which decreases the contact angle. As can be seen in Figure 4, the contact angle rapidly decreases with plasma treatment time up to about 2.5 min. Longer treatment times do not produce significant changes in contact angle.

Two distinct mechanisms can occur in oxygen plasma treatment: oxygen atoms incorporation to the polymer surface and etching. Therefore, there is a

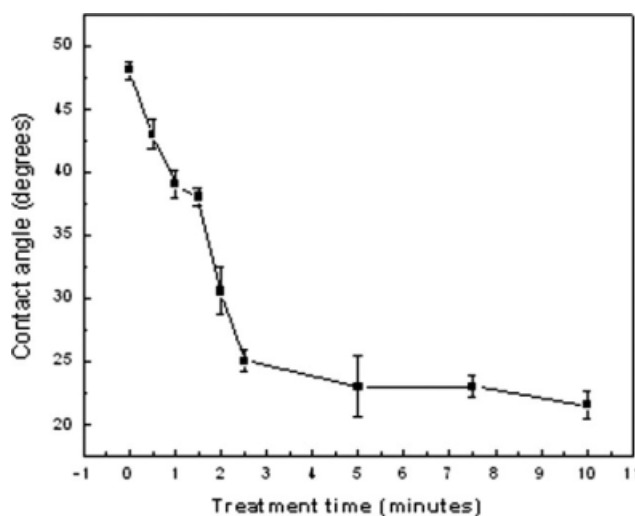


Figure 4 Contact angle measurements of PET samples as a function of oxygen plasma treatment time.



Figure 5 Photographs of the adhesive tapes after pull from a-C:H films deposited onto a PET surface without treatment (a) and with oxygen plasma treatment for (b) 1.5 and (c) 2.5 min. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

strong incorporation of oxygen atoms in the beginning of the treatment (up to 2.5 min), indicated by the quick decrease in contact angle, as shown in Figure 4. After this time, the oxygen incorporation rate decreases and etching effect is probably more significant, as observed from the AFM measurements of samples treated during 10 min.

Adhesion measurements

Adhesion analyses were carried out on the a-C:H films deposited onto PET samples plasma-treated during various times (1.5, 2.5, 5.0, 7.5, and 10.0 min). The thickness of all films was about 360 nm, and the adhesive tape method was used. Figure 5 shows the results, in duplicate, for tape removal from films deposited onto untreated substrates and treated during 1.5 and 2.5 min. Pictures of tapes used in the tests for films deposited onto substrates treated during 5.0, 7.5, and 10.0 min are identical to those of Figure 5(c) (data not shown). Dark (gray) regions on the tape indicate loosening of film parts; the lower the adhesion, the larger will be these regions.

Analysis of Figure 5 shows that oxygen plasma treatment promotes a substantial increase in a-C:H

film adhesion, even during relatively short time. For more than 2.5 min, there is no film loosening.

CONCLUSIONS

The changes in the surface of recycled PET by an oxygen plasma and its effect in the adhesion of a-C:H films were investigated. In oxygen plasma treatment, two processes can occur simultaneously: (i) surface etching through reactions of atomic oxygen with surface carbon atoms forming volatile CO and CO₂, resulting in an increase in the sample microroughness, and (ii) formation of oxygen-containing groups on the polymer surface through reactions between plasma-active species and surface atoms. The results indicated a balance between these two processes. The occurrence of etching is evidenced by the AFM micrographs. On the other hand, XPS data and contact angle measurements have clearly shown the occurrence and incorporation of functional groups containing oxygen on the polymer surface. As concluded from the tape test, oxygen plasma pretreatment, even for short times, promotes a substantial increase in the adhesion between the a-C:H film and the PET substrate.

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