Accelerated Aging and Contact with Food Simulants in Adhesion of Amorphous Hydrogenated Carbon Films Obtained by the PECVD Process from Recycled PET from Packaging

S. A. Cruz,[1] M. Zanin,[2] M. A. B. de Moraes[3]

[1]*Centro de Engenharia Modelagem e Ciências Sociais Aplicadas-CECS, Universidade Federal do ABC-UFABC, Rua Santa Adélia, CEP 09.210-170, Santo André-SP, Brasil*
[2]*Departamento de Engenharia de Materiais, Universidade Federal de São Carlos-UFSCar, Rod. Washington Luís, CEP 13565-905, São Carlos-SP, Brasil*
[3]*Instituto de Física, Universidade Estadual de Campinas-UNICAMP, Cidade Universitária Zeferino Vaz, CEP 13083-970, Campinas-SP, Brasil*

Received 3 April 2008; accepted 28 May 2008
DOI 10.1002/app.29037
Published online 3 October 2008 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: This work focuses principally on the influence of time, temperature, and contact with food simulants in adhesion of amorphous hydrogenated carbon (a-C:H) films obtained by the plasma enhanced chemical vapor deposition process in recycled PET from packaging. Shelf life of packaging used in soft drinks, fruit juice, etc. is known to be ~ 6 months, with possible variations. The a-C:H film, used in this study as a functional barrier against possible contaminants in recycled PET, was analyzed to determine possible alterations in its physical and chemical properties. The film underwent an accelerated aging test and was exposed to contact with food simulants listed by the FDA. In this case, adhesion is one of the properties most in need of conservation. This property was analyzed by means of the tape test and scanning electronic microscopy. Superficial chemical alterations resulting from both the accelerated aging test and contact with liquids were examined by the contact angle. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 111: 281–290, 2009

Key words: amorphous hydrogenated carbon films; PET; recycling; plasma etching; adhesion; accelerated aging

INTRODUCTION

One of the alternatives to using packaging made from recycled polymer is employing a protective virgin resin layer, which is not necessarily of the same material as the packaging. However, it should constitute a barrier sufficient to reduce possible contaminants, present in the recycled polymer, to quantities innocuous to human health, or incapable of altering organoleptic characteristics of foodstuffs. These layers make up functional barriers preventing direct contact between recycled polymer and foodstuff. Therefore, they must meet hygiene standards.[1]

In general, when considering the effectiveness of functional barriers in preventing or reducing contaminant migration, reference is made to models stipulated by the Food and Drug Administration (FDA).[2] Piringer et al.,[3] for example, examined the migration process in multilayered PET packaging produced by the coextrusion process, in which the intermediate layer was PET contaminated by toluene and chlorobenzene. The amount of migration into food simulants (water, 3% acetic acid, and isooctane) was measured at temperatures up to 60°C. The layer of virgin material was found to have been partially contaminated during processing owing to the high temperature used. Besides film effectiveness in preventing contamination, a crucial property to be considered is adhesion between polymer and the functional barrier, a reduction of which could damage the packaging and its shelf life. In spite of several studies[4–6] on adhesion between thin films and polymer samples, few of them have evaluated the effect of time, temperature, and contact with food simulants.

Amorphous hydrogenated carbon (a-C:H) has been widely used as protective coating in the variety materials in a lot of applications.[7] The films are usually applied by plasma enhanced chemical vapor deposition (PECVD). However, bulges and cracks may appear in the films as a consequence of the high internal stress of these materials. As flow formation benefits from poor adhesion, process leading to the strong adhesion of the barrier coating onto the

Correspondence to: S. A. Cruz (sandra.cruz@ufabc.edu.br).

Journal of Applied Polymer Science, Vol. 111, 281–290 (2009)

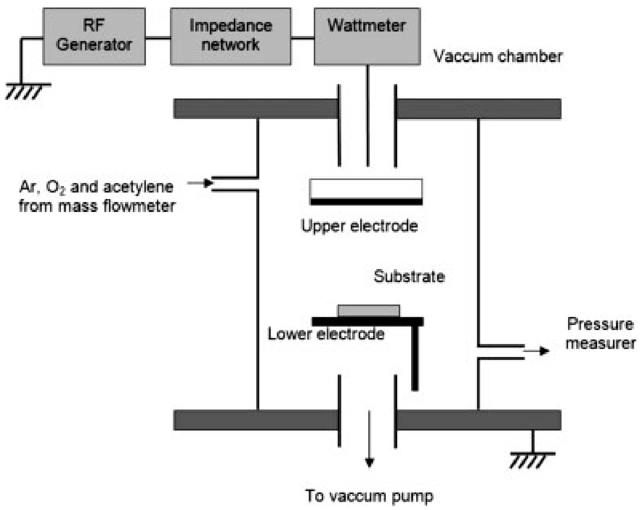


Figure 1 Schematic representation of PECVD system.

plastic packages surface is a major concern. Fortunately, increases in the adhesion of a film onto a substrate can be improved by previous treatments of the substrate.[8,9] In a polymer surface, the main modifications produced by plasma treatment are etching and addition of new functional groups, as verified by Cruz et al.[10]

This article aims at determining the influence of time, temperature, and food-simulant contact in adhesion between a-C:H thin film and polymer surfaces. Adhesion of prime importance if a-C:H-coated recycled PET is to be used for foodstuff packaging. Therefore, we treated PET packaging with oxygen plasma prior to depositing film. Adhesion modifications were evaluated by the tape test method and by scanning electronic microscopy (SEM). Resulting chemical alterations produced by both the accelerated aging test and exposure to food simulants were characterized by contact angle measurements.

EXPERIMENTAL

Materials

Packagings made from recycled PET were used for plasma modification and films deposition. The recycled PET was previously treated by solid state polymerization (SSP) to increase the molar mass and to make it suitable for the confection 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 $\sim$ 25 cm^2. Prior to surface modification experiments, the samples were cleaned with acetone, isopropyl alcohol, and water to remove the organic contamination and dried in a nitrogen flow.

Argon (99.999%), oxygen (99.8%), and acetylene (99.8%) supplied by White-Martins S/A, of Brazil, were used to plasma surface modification and the film deposition.

The food simulants acetic acid (3%) and ethanol (10%) were used according to FDA specifications.[12]

Methods

Plasma treatment and deposition apparatus

The equipment system used was essentially that describe previously.[10] In a few words, plasma treatment and film deposition were carried out in a stainless steel vacuum chamber schematically represented in Figure 1. A glow discharge plasma was generated in the chamber between two water-cooled parallel plate electrodes and was pumped by a 150 m^3/h Roots pump, backed by a rotary vane pump. The upper electrode was connected to an RF generator (40 MHz) through an impedance matching network and a through line wattmeter. The gases used (Ar, O_2, and acetylene) were introduced in the chamber using precision electronic mass flow meters (Datametrics 1500).

Oxygen plasma treatment and a-C:H film deposition

An oxygen mass flow rate of 49 sccm (F_{O2} = 49 sccm) (exposure times of 1.0, 2.5, 5.0, and 10.0 min) was used for oxygen plasma treatment. An acetylene and argon mass flow rate of 10 and 70 sccm (F_{C2H2} = 10 sccm and F_{Ar} = 70 sccm), respectively, for 5 min was used for film deposition.

Accelerated thermal aging

To determine the period in which properties of deposited films would be retained, an accelerated aging test based on UL 746 B norm was carried out.[13] Table I presents temperature and exposure time in hours of samples used.

The accelerated aging test used ovens to expose the samples to higher temperatures and for shorter periods than would be experienced in actual use. The time was extrapolated to 9 months and 25°C, as shown in Figure 2. The results were evaluated by a-C:H film adhesion time.

Immersion in liquid food simulants

The a-C:H film deposited in PET packaging, both with and without previous oxygen plasma

TABLE I
Time and Temperature in the Accelerated Aging Test

	Oven 1	Oven 2	Oven 3
Time (h)	1000	450	168
Temperature (°C)	45	55	65

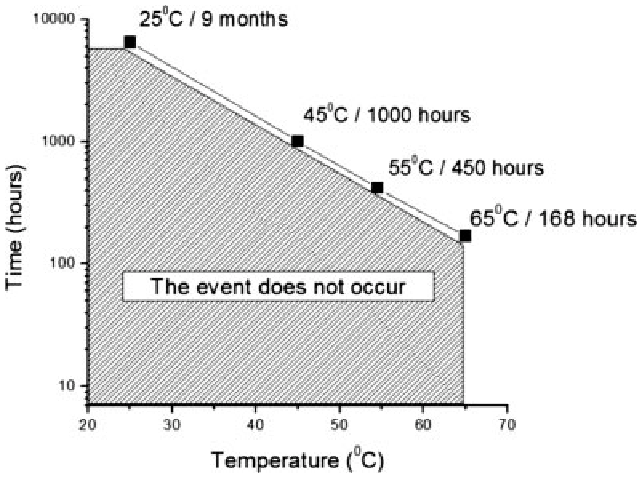


Figure 2 Time as a function of temperature in the accelerated aging test.

treatment, was immersed in the liquid food simulants acetic acid (3%) and ethanol (10%). The accelerated aging test followed.

Contact angle

Contact angle measurements were carried out using a distilled water drop. An optical microscope (Micronal Olympus G10X) attached 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, i.e., using three different samples. Table II shows frequency of contact angle measurements made in samples submitted to the accelerated aging test. Contact angle measurements were made to verify possible chemical superficial alterations that could occur when the samples were submitted to accelerated aging test and put in contact with liquid food simulants.

Scanning electronic microscopy

To identify points at which a-C:H film lost adhesion, it used a Stereoscan 440 SEM microscope (Leica) equipped with SE detector, working height varying between 20 and 25 mm and a 30° incidence angle. Table III shows exposure conditions and analysis frequency of samples.

TABLE II
Contact Angle Measurements Frequency for the Samples Submitted to the Accelerated Aging Test

	Contact-angle measurement frequency (h)			
Oven 1 (1000 h/45°C)	0	336	672	1000
Oven 2 (480 h/55°C)	0	240	480	–
Oven 3 (168 h/65°C)	0	168	–	–

TABLE III
Conditions and Frequency of SEM Measurements of Samples

	Contact-angle measurement frequency (h)		
Oven 1 (1000 h/45°C)	0	672	1000
Oven 2 (480 h/55°C)	0	480	–
Oven 3 (168 h/65°C)	0	168	–

Tape test measurements

The tape test measurements of the a-C:H films onto the PET surface were carried out according to the ASTM D 3359-90 norm. The test consisted in applying a 3M-810 adhesive tape on the film surface and removing it with a quick pull, after which the film removal was visually verified.

RESULTS AND DISCUSSION

Contact angle measurement

Figure 3 shows the contact angle measurements to a-C:H films deposited with $F_{C2H2} = 10$ sccm and $F_{Ar} = 70$ sccm during 5.0 min onto PET. The PET was previously submitted to oxygen plasma treatment ($F_{O2} = 49$ sccm) during 0, 1.0, 2.5, 5.0, and 10.0 min.

The results presented indicate contact angle decrease as a function of increased time of oxygen plasma treatment. This reduction, although less pronounced than that found for treated samples not coated with a-C:H film, as revealed in a previous work,[10] shows that oxygen plasma treatment prior to depositing promotes a polarity increase in a-C:H film. In spite of this treatment being carried out only in PET substrate, which should not alter film properties, generation of many reactive species containing oxygen that remained in the oven,

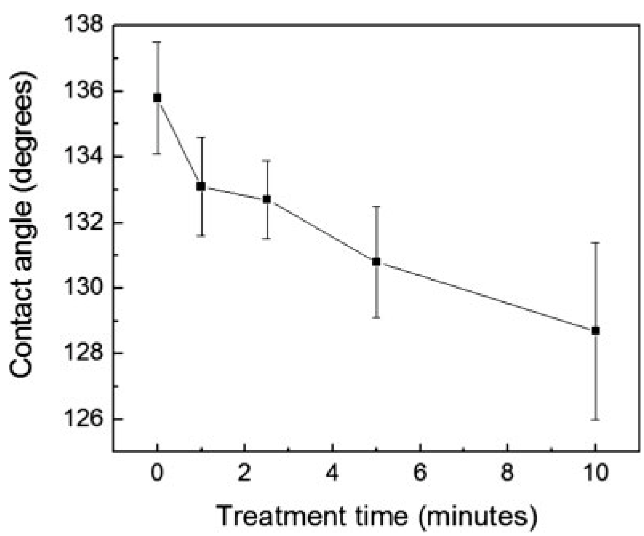


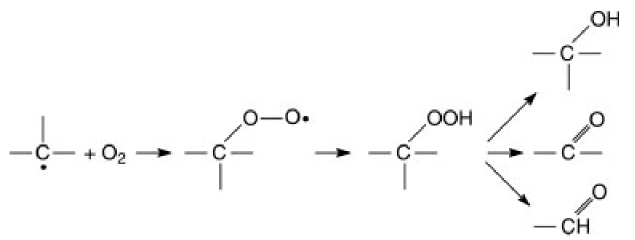
Figure 3 Contact angle measurements of a-C:H films as a function of oxygen plasma treatment time.

TABLE IV
Contact Angle (Standard Deviation-SD) for a-C:H Deposited on PET Samples as a Function of Exposure Time to Oxygen Plasma

Treatment time (min)	Contact angle (±SD) 10% Ethanol 45°C/672 h	45°C/1000 h	55°C/240 h	55°C/480 h	65°C/168 h
0	134.5 ± 1.9	133.2 ± 2.3	128.5 ± 2.7	126.8 ± 1.5	129.5 ± 2.4
1.0	129.2 ± 4.1	128.0 ± 3.9	126.3 ± 5.1	123.5 ± 2.6	128.1 ± 0.8
2.5	127.2 ± 2.3	126.8 ± 3.1	125.5 ± 1.4	120.3 ± 3.4	126.0 ± 3.4
5.0	123.7 ± 2.7	124.7 ± 2.7	125.1 ± 2.6	121.0 ± 3.0	122.0 ± 1.4
10.0	118.0 ± 1.7	116.3 ± 3.6	112.3 ± 3.7	115.0 ± 2.9	120.0 ± 2.4

Samples submitted to accelerated aging test and immersed in ethanol (10%).

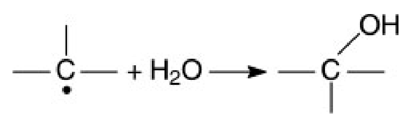
even after treatment termination, may have occurred. As this is immediately followed by film deposition, a new combination would happen between these species and those generated by acetylene/argon plasma according to the reaction[14]:



The result is oxygen incorporation in the film surface through the formation of carbonyl and hydroxyl groups. This was proven by gradual contact angle decrease with time of exposure to oxygen plasma, i.e., the greater the exposure time, the more the oxygen species generated, which favors recombination on the film. Some results show almost the same statistically significance, as can be observed from samples treated at time of 0, 1, and 2 min. In spite, of this behavior, all results suggest a decreasing of the contact angle.

Tables IV and V show the contact angle of samples submitted to accelerated aging in the liquid food simulants ethanol (10%) and acetic acid (3%). In every instance, increase in exposure time to oxygen plasma brought about contact angle decrease, as shown in Table IV.

The results showed that at both 45 and 55°C all samples showed a tendency to contact angle reduction over time (672–1000 h, 240–480 h). This is explained by the commonly observed presence of long-lived free radicals in plasma processes, which has been observed in plasma polymer 15 months following exposure to air, as reported by Yasuda.[14] Because the samples remained in contact in a strongly water-based liquid (10% ethanol), hydroxyl groups could have been incorporated by the following reaction:



Hydroxyl group incorporation would promote a contact angle reduction because of polarity increase in the a-C:H film. Table V presents the contact angle results for samples submitted to the accelerated aging test in acetic acid (3%) liquid simulant.

TABLE V
Contact Angle (Standard Deviation-SD) for a-C:H Film Deposited on PET Samples as a Function of Treatment Time with Oxygen Plasma

Treatment time (min)	Contact angle (±SD) 3% Acetic acid 45°C/672 h	45°C/1000 h	55°C/240 h	55°C/480 h	65°C/168 h
0	133.8 ± 2.5	129.3 ± 1.2	129.3 ± 2.1	127.8 ± 2.2	131.8 ± 1.8
1.0	131.2 ± 2.6	128.3 ± 2.5	126.5 ± 2.4	125.2 ± 3.9	130.1 ± 1.3
2.5	127.5 ± 1.9	126.0 ± 2.7	126.0 ± 1.1	124.0 ± 2.7	125.8 ± 2.6
5.0	126.2 ± 1.5	126.3 ± 1.7	122.0 ± 0.9	119.7 ± 2.6	123.1 ± 1.5
10.0	125.0 ± 1.5	122.7 ± 1.2	119.5 ± 3.2	121.7 ± 1.6	122.7 ± 1.6

Samples submitted to the accelerated aging test and immersed in 3% acetic acid.

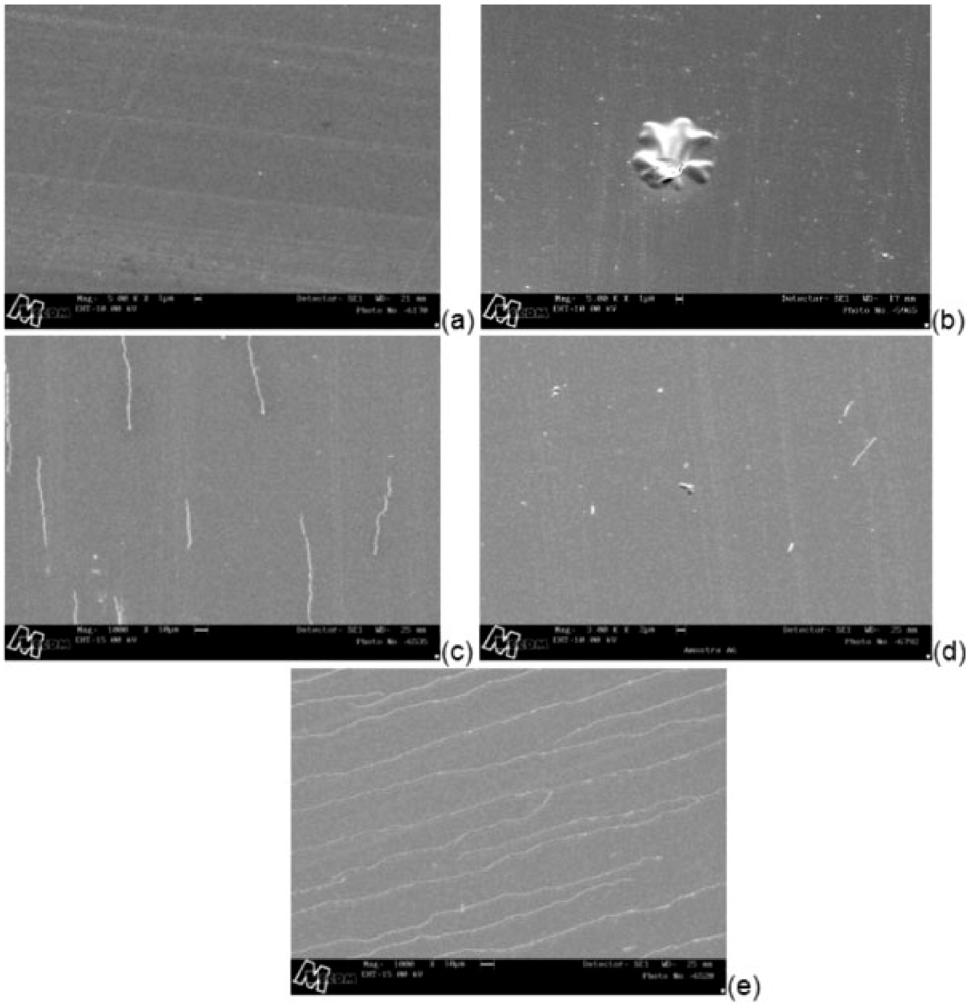


Figure 4 SEM micrographs representing five levels of adhesion loss: (a) level 1, no adhesion loss; (b) level 2, sample with few adhesion-loss points; (c) level 3, samples with few lines of adhesion loss; (d) level 4, samples with loss of adhesion points; and (e) level 5, sample with adhesion loss lines.

The results obtained for samples immersed in 3% acetic acid agree with those found for those immersed in 10% ethanol. A contact angle reduction was again observed with increased exposure time to oxygen plasma. This result, which corroborates those shown in Table IV, demonstrates that the greater the exposure time to liquid simulant, the greater the film polarity. In other words, in comparing the contact angle of samples exposed at 45°C for 672 h with that of those exposed at the same temperature for 1000 h, a contact angle reduction occurs regardless of prior oxygen plasma treatment. The same behavior was observed for samples tested at 55°C for both 240 and 480 h. Again, despite some results are not present statically significance, an evident behavior is established.

With either 10% ethanol or 3% acetic acid, no correlation was detected between temperature and contact angle.

Scanning electronic microscopy

Adhesion loss between a-C:H film and PET substrate was analyzed by SEM through visual comparison. Five levels were used to classify samples according to adhesion loss (Fig. 4).

Table VI presents SEM results of the accelerated aging test for a-C:H films deposited on PET.

For a period of 288 h/45°C, no adhesion loss was detected in 120-nm-thick films (level 1). Thereafter, adhesion loss ''bubbles'' occurred on film surfaces. Following this period, increases occurred in adhesion loss points culminating in branched structures appearing with increased frequency by test's end (1000 h), as shown in Figure 5. However, this structure appears in small amount being classified, as shown in Table VI at level 2.

Similar behavior occurred with 170-nm-thick films, except that the branched structures were less

TABLE VI
SEM Results Classified by Adhesion Level for a-C:H Film (Thickness: 120 and 170 nm) after Accelerated Aging

Temperature	45°C				55°C		65°C
Exposure time (h)	0	288	625	1000	96	480	168
120 nm	Level 1	Level 1	Level 2	Level 2	Level 1	Level 2	Level 1
170 nm	Level 1	Level 1	Level 3	Level 3	Level 1	Level 3	Level 1

frequent. On the other hand, beginning at 624 h, these films developed lines indicating adhesion loss (level 3). Because thicker film has a greater adhesion loss tendency, this behavior was expected.

Analysis detected no adhesion-loss points in 120-nm-thick deposited film after a 96-h period at 55°C (level 1). Thereafter, adhesion reduction occurs, as demonstrated by adhesion-loss points in 120-nm-thick samples (level 2), and some loss lines in 170-nm-thick samples (level 3). In spite of temperature increase from 45 to 55°C, no branched structures from adhesion loss appeared. As already described, thicker film presented higher residual tension, i.e., less adhesion than thinner film. This explains the greater tendency to adhesion loss that 170-nm-thick film presents at this temperature.

As shown by the micrographs, samples submitted to 65°C for 168 h presented virtually no adhesion loss (level 1) in spite of the relatively high temperature. Accelerated aging test results are determined by two factors: time and temperature. Increase in temperature promotes acceleration in either the process or the property being studied. The results obtained indicate that the determining factor in adhesion loss in the samples studied was time rather than temperature. This is seen by comparing 120 and 170 nm samples submitted for 1000 h to 45°C with those submitted for 168 h to 65°C.

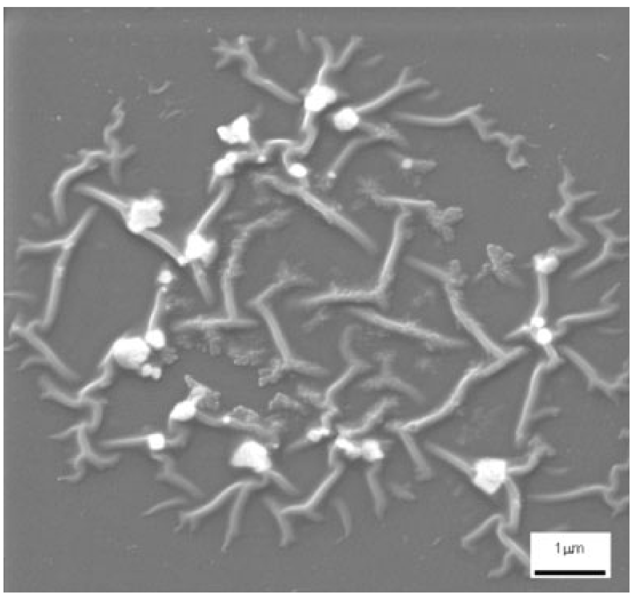


Figure 5 Micrograph of a-C:H film (thickness: 120 nm) following 1000 h at 45°C.

These results indicate the need to increase adhesion between the a-C:H film and the PET substrate. With the exception of samples submitted for 168 h at 65°C, the other samples, regardless of thickness, showed adhesion loss that excluding them from use as barrier layers in recycled-material packaging. It should be remembered that the samples used were not immersed in food simulants, which would increase adhesion loss.

Therefore, a-C:H film adhesion on PET samples, previously treated with oxygen plasma and submitted to the accelerated aging test, was analyzed by SEM. These samples had been immersed in two liquid food simulants specified by the FDA[12]: 10% ethanol and 3% acetic acid.

Adhesion analysis was evaluated for 120-nm-thick a-C:H film on PET substrate previously treated with oxygen plasma (F_{O2} = 49 sccm) for 0, 1.0, 2.5, 5.0, and 10.0 min. Samples were submitted to the accelerated aging test; contact with liquid food simulants was periodically analyzed by SEM. The results according to adhesion loss level are presented in Tables VII and VIII.

The results presented in Table VII show that untreated samples and those treated for 1.0 min with oxygen plasma showed levels 3 and 4 of adhesion loss. In contrast, for equal periods and those exceeding 2.5 min no adhesion-loss points were observed (level 1). For samples not treated with oxygen plasma and exposed to 45°C, an adhesion reduction accompanied time increase, as seen by an

TABLE VII
Adhesion Level Results by SEM for 120-nm-thick a-C:H Film as a Function of Treatment Time with Oxygen Plasma

Treatment time (min)	45°C		55°C	65°C
	627 h	1000 h	480 h	168 h
0	Level 3	Level 4	Level 3	Level 4
1.0	Level 2	–	Level 3	Level 4
2.5	Level 1	–	Level 1	Level 1
5.0	Level 1	Level 1	Level 1	Level 1
10.0	Level 1	Level 1	Level 1	Level 1

Samples immersed in 10% ethanol and submitted to accelerated aging test.

TABLE VIII
Adhesion Loss Levels Obtained by SEM for 120-nm-thick a-C:H Film as a Function of Oxygen Plasma Treatment Times

Treatment time (min)	45°C	55°C	65°C
	1000 h	480 h	168 h
0	Level 4	Level 3	Level 4
5.0	Level 1	Level 1	Level 1
10.0	Level 1	Level 1	Level 1

Samples immersed in 3% acetic acid and tested in the accelerated aging test.

increase in adhesion loss from level 3 at 627 h to level 4 at 1000 h.

For untreated samples and those treated at 65°C for 1.0 min with oxygen plasma, adhesion loss lines occurred. These were not observed with treatment times above 1.0 min.

Of the three experimental conditions analyzed, the samples submitted to the third (65°C/168 h) showed the greater influence of temperature with respect to adhesion. This result contradicts those presented previously, in which time was the most significant influence. The explanation could be the proximity of the test temperature (65°C) to that of PET glass transition temperature (T_g) PET (67°C), coupled with a variation, though slight, in the oven temperature during the test, which would have resulted in movement of the polymeric chains in the amorphous phase. Thus, film with loss adhesion would easily detach from the PET substrate. Furthermore, biorientation causes stretching, inducing axial and transverse orientation. Material so affected usually presents low thermal resistance. However, no alterations, e.g., warping or deformations, were detected

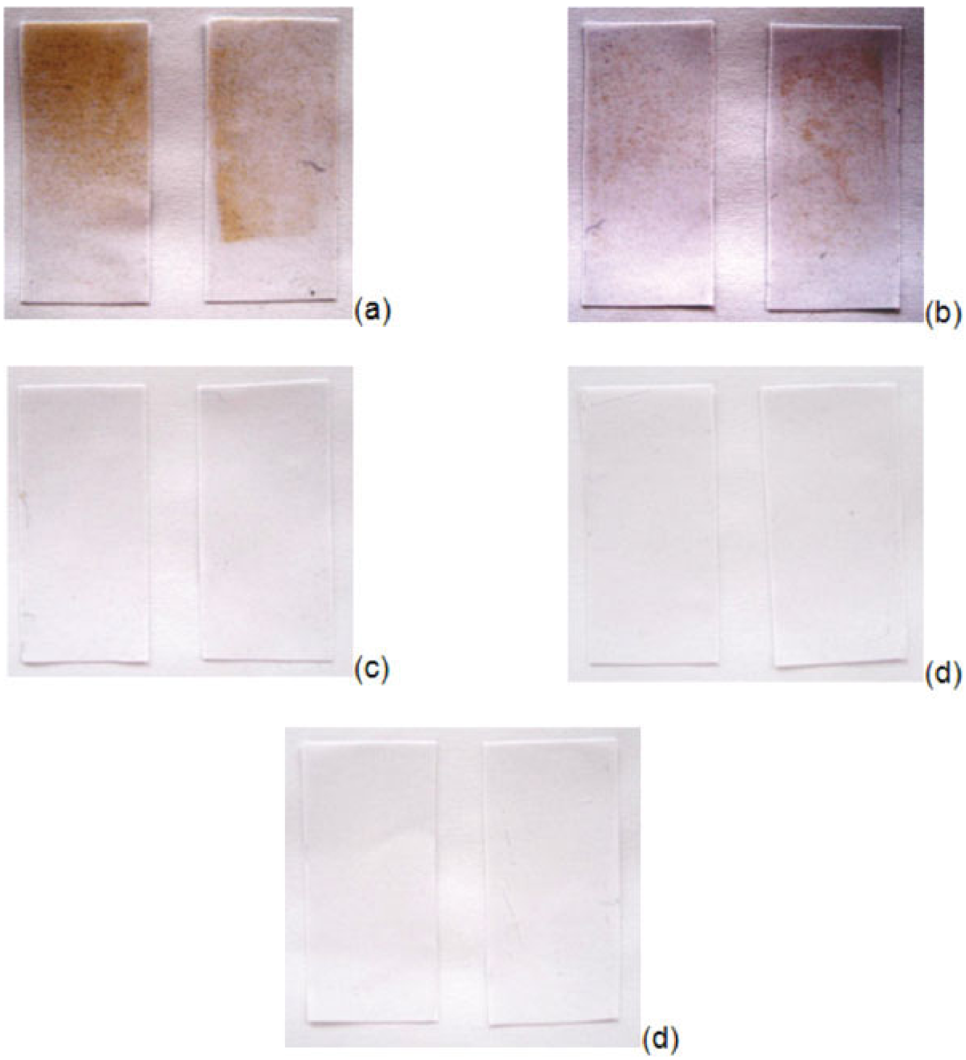


Figure 6 Adhesion test for untreated a-C:H film deposited on PET (a) and film previously treated with oxygen plasma for (b) 1.0 min, (c) 2.5 min, (d) 5.0 min, and (e) 10.0 min. Samples immersed in 10% ethanol and submitted for 1000 h at 45°C. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

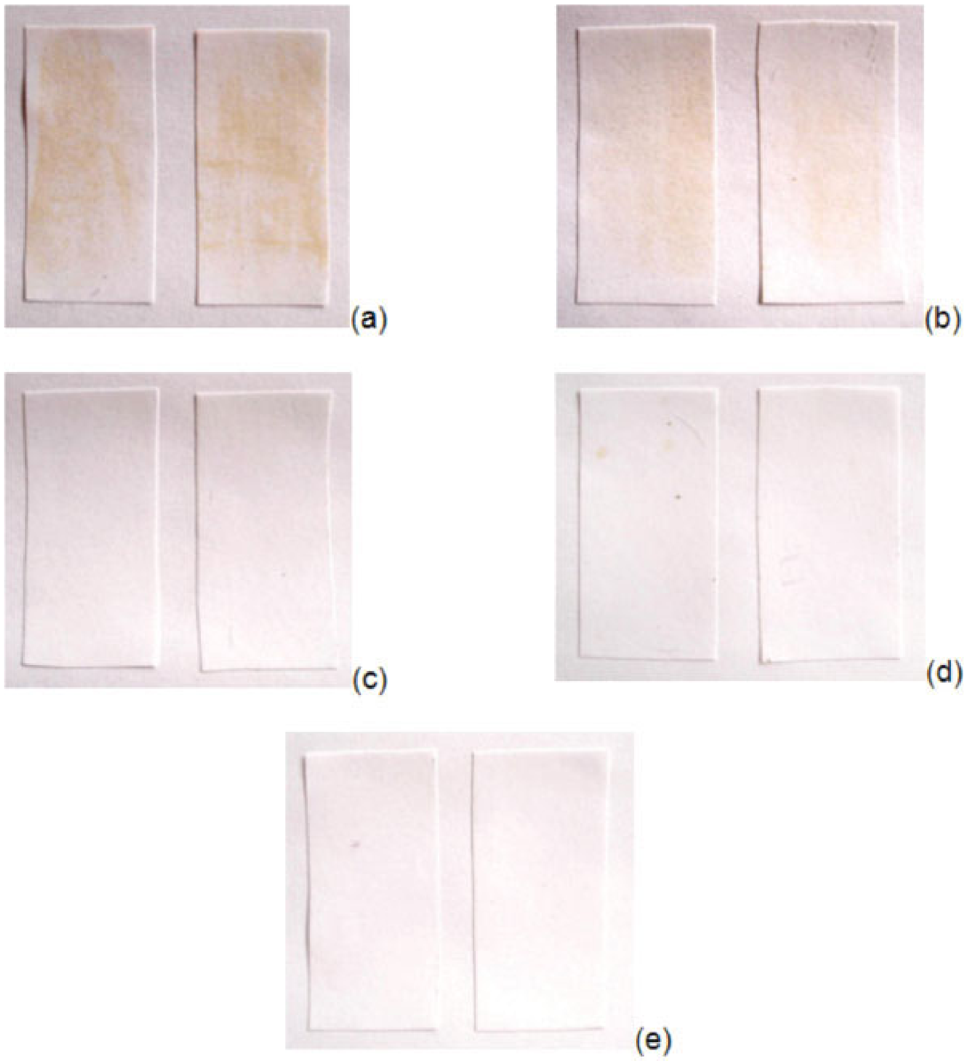


Figure 7 Adhesion test for untreated a-C:H film deposited on PET (a) and film previously treated with oxygen plasma for (b) 1.0 min, (c) 2.5 min, (d) 5.0 min, and (e) 10.0 min. Samples immersed in 10% ethanol and submitted for 450 h at 45°C. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

macroscopically, although chain movement producing adhesion loss in the film might have occurred microscopically. It should be pointed out that adhesion loss lines were observed throughout the samples.

Analysis of the SEM micrographs showed adhesion loss (level 4) points in samples untreated with oxygen plasma and submitted for 1000 h to 45°C. With oxygen plasma treatment these points decreased. Similar behavior happened with samples submitted to 55°C/480 h and 65°C/168 h. Film shifts occurring as lines, clearly visible and spread throughout some samples, are most likely explained by increased oven temperature approximating that of T_g. Again, after 5 min of oxygen plasma treatment, reduction of adhesion loss occurred.

Comparing dry samples tested with samples immersed in liquid food simulants (3% acetic acid and 10% ethanol) showed that immersed a-C:H film presented a greater tendency toward detachment from the PET substrate. This shows the importance of testing adhesion with samples exposed to food simulants.

Tape test measurements

Figures 6–8 present adhesion analyses by adhesive tape for a-C:H film deposited on PET previously treated with oxygen plasma for 0, 1.0, 2.5, 5.0, and 10.0 min. The samples were immersed in 10% ethanol and submitted to the accelerated aging test. All analyses were done in duplicated.

Figures 6–8 show that previous treatment with oxygen plasma promotes a substantial increase in amorphous carbon film adhesion. For samples submitted for 1000 h to 45°C and for 450 h to 55°C,

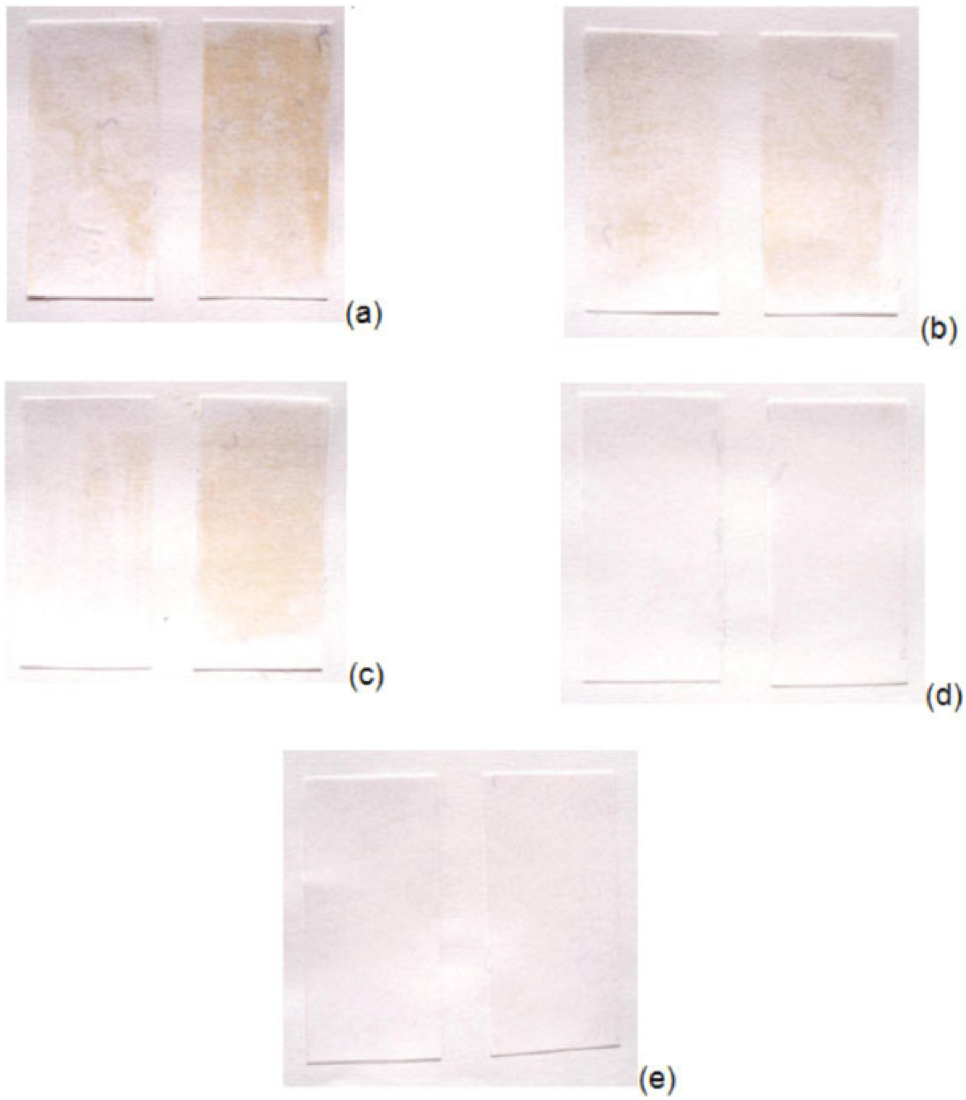


Figure 8 Adhesion test for untreated a-C:H film deposited on PET (a) and film previously treated with oxygen plasma for (b) 1.0 min, (c) 2.5 min, (d) 5.0 min, and (e) 10.0 min. Samples immersed in 10% ethanol and submitted for 168 h at 65°C. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

increased adhesion was observed after 2.5 min as no loss occurred. However, when the samples were exposed for 168 h to 65°C adhesion loss was noted after 2.5 min.

Similar SEM adhesion analysis results were found for the same samples. On the other hand, for the samples without oxygen plasma treatment and submitted for 1000 h to 45°C, numerous adhesion loss points were observed. Oxygen plasma treatment promoted increased adhesion, as demonstrated by unaltered adhesion from 5 min on. After 2.5 min, samples tested at 55 and 65°C showed no adhesion loss. Although SEM analyses on these samples were not carried out for 2.5 min treatments, at 55 and 65°C, from 2.5 min on, no adhesion loss was observed.

Adhesion analysis results, whether by SEM or adhesive tape, show that from 5.0 min on, under all time/temperature testing conditions, no adhesion loss occurred in a-C:H film on PET substrate. Furthermore, the close correlation between results indicates that the adhesive tape test, although an extremely simple technique, is suitable for measuring mechanical stability in fine films.

CONCLUSIONS

SEM, as well as adhesive tape, proved suitable tools for testing adhesion between a-C:H film and PET samples. Samples that were not treated by oxygen plasma presented relatively low adhesion when submitted to the accelerated aging test as both those of ~ 120 and of 170 nm in thickness showed adhesion loss points from 360 h on at 45°C. In lesser time periods, even at higher temperatures few adhesion loss points occurred. The accelerated aging test, carried out with samples immersed in FDA-specified liquid food simulants, showed that those untreated with oxygen plasma presented several adhesion loss points. For treated samples, however, from 5.0 min on, adhesion increased significantly, insofar as no loss was noted.

Contact angle analyses showed that increased time of oxygen plasma treatment promotes increased polarity in a-C:H film. These analyses also indicate that immersion in liquid together with increase in exposition time results in a tendency toward increasing polarity by incorporating oxygen atoms into film surfaces.

Finally, both the SEM and adhesive tape results demonstrate that oxygen plasma treatment promotes film adhesion increase in polymer film. They also indicate the importance of analysis following film contact with liquid food simulants, which generates the greatest tendency toward adhesion loss. Oxygen plasma treatment for 5.0 min proved extremely effective because within this period under all conditions analyzed, no adhesion loss was detected. Polarity increase in film immersed in liquid food simulants shows reaction throughout the period of contact, which increases incorporation of oxygen-based species, as verified by the contact angle measurements.

References

1. Catalá, R.; Gavara, R. Migración de Componentes y Residuos de Envases en Contacto con Alimentos; Instituto de Agroquímica y Tecnología de Alimentos: Valencia, 2002; p 329.
2. FDA. Points to Consider for the Use of Recycled Plastics in Food Packaging Chemistry Considerations; Center for Food Safety and Applied Nutrition: Washington, 1992; p 1.
3. Piringer, O.; Franz, R.; Huber, M.; Begley, T. H.; McNeal, T. P. J Agric Food Chem 1998, 46, 1532.
4. Quinn, J. P.; Lemoine, P.; Maguire, P.; McLaughlin, J. A. Diamond Relat Mater 2004, 13, 1385.
5. Martinez, E.; Polo, M. C.; Pascual, E.; Esteve, J. Diamond Relat Mater 1999, 8, 563.
6. Rochat, G.; Delachaux, A.; Letterrier, Y.; Manson, J. A. E.; Fayet, P. Surf Interface Anal 2003, 35, 948.
7. Chan, C. M.; Ko, T. M.; Hiraoka, H. Surf Sci Rep 1996, 24, 1.
8. Tsai, H.; Body, D. B. J Vaccum Sci Technol 1987, 5, 3287.
9. Zou, J. W.; Schimidt, K.; Reichelt, K.; Dischler, B. J Appl Phys 1990, 67, 487.
10. Cruz, S. A.; Nascente, P. A. P.; Zanin, M.; Moraes, M. A. B. J Appl Polym Sci, to appear.
11. Cruz, S. A.; Zanin, M. J Appl Polym Sci 2006, 99, 2117.
12. FDA. Available in: <http://www.fda.gov>.
13. Underwriters Laboratories-UL. UL 746B: Polymeric Materials—Long Term Property Evaluations; Underwriters Laboratories-UL: Northbrooks, Illinois, 1996.
14. Yasuda, H. Plasma Polymerization; Academic Press: Orlando, 1985; p 432.