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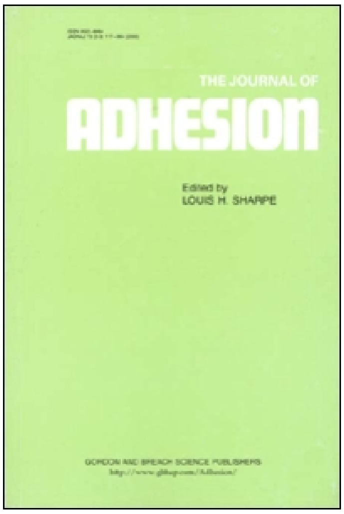

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R. Cueff[a]; G. Baud[a]; J. P. Besse[a]; M. Jacquet[a]; M. Benmalek[b]
[a] Laboratoire de Physico-Chimie des Matériaux—U.R.A. 444, Université Blaise Pascal, AUBIERE CEDEX, France [b] Centre de Recherches de Voreppe (Groupe Pechiney), VOREPPE, France

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Surface Free Energy Modification of PET by Plasma Treatment—Influence on Adhesion*

R. CUEFF, G. BAUD, J. P. BESSE and M. JACQUET**

Laboratoire de Physico-Chimie des Matériaux—U.R.A. 444, Université Blaise Pascal, 63177 AUBIERE CEDEX (France)

M. BENMALEK

Centre de Recherches de Voreppe (Groupe Pechiney), BP 27, 38340 VOREPPE (France)

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Different cold plasmas have been used to treat the surface of polyethylene terephtalate (PET) in order to improve the adhesion of alumina thin films deposited by RF sputtering. The influence of these treatments on the surface free energy of the polymer is shown by a study of wettability. ESCA analysis of the PET surface suggests that chemical changes occur as the polymer is plasma treated.

The adhesion of alumina films on PET is studied by using tensile testing. The results show that the surface treatment of the PET by a slightly oxidizing plasma, such as carbon dioxide, increases by a factor of 1.7 the adhesion of alumina coatings.

KEY WORDS polyethylene terephtalate; plasma treatment; surface free energy; adhesion; physical vapor deposition; alumina; wettability.

INTRODUCTION

The utilization of polymer surfaces in adhesion applications requires a preliminary activation since the chemical reactivity of these materials is low and since the surface layers may have low cohesion.

Among the different techniques used for activation, treatment by plasmas makes it possible to maintain the mechanical properties of the polymers and gives the surfaces the required qualities that optimize their adhesion.[1]

In the present work, plasma treatments are used in order to improve the adhesion of the alumina coatings produced by Physical Vapor Deposition on polyethylene terephtalate (PET).

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**Corresponding author.

EXPERIMENTAL DETAILS

The studied PET is a bi-stretched film (Terphane RP) 13 μm thick. Treatments by plasma and alumina deposition are performed in a cathodic sputtering unit (Alcatel SCM450) equipped with an RF generator (13.56 MHz). The PET film is fixed on a cooled substrate holder; the different plasma treatments are made at a pressure of 1 Pa with an RF power of 0.2 W/cm^2. The alumina target (99.9% purity 100 mm diameter) fixed to a magnetron-effect cathode is situated at 90 mm from the PET film. The alumina is sputtered using pure argon plasma (pressure 1 Pa) at a deposition rate of 0.07 μm/h. The thickness of the coatings is measured by interferometry using a glass-substrate standard.

The PET surface analysis is performed by ESCA using a SSI M probe (AlKα monochromatic radiation, spectral resolution 0.65 eV on Ag 3d 5/2). The spectrometer energy scale is calibrated for Au 4f 7/2 (84.0 eV) and charging compensation is applied assuming C(1s) hydrocarbon peak (285 eV). The studied section has a surface of 2 mm^2 and a depth of 4 nm.

The surface free energies of the PET and the alumina are measured by a study of wettability, using the two-liquid method developed by Schultz.[2] It consists of measuring the contact angle of a liquid (water) on a given solid (PET or alumina) in the presence of a second, non-miscible liquid (hydrocarbon). The contact angle measurement is performed immediately after the sample is taken out of the vacuum chamber, to minimize surface contamination by atmosphere.[3] For that measurement, the solid is placed in a cell filled with hydrocarbon and the second liquid is put on the sample (a small drop: 2 mm^3). The contact angle is measured on a graduated disk mounted in the viewing microscope.

Tensile tests are carried out with the help of a traction machine (Jobin & Yvon, model D495) on polymer samples (15 mm × 90 mm) coated with an alumina deposit 0.15 μm thick and 50 mm long in their central part. The samples are subjected to elongations (70% of the plastic deformation) in order to produce the brittle cracking and subsequent debonding of alumina films. The interfacial shear strength, τ_0, which characterizes the adhesion of the film-substrate system is evaluated from the measurement (performed with a microscope) of l_f, the largest debonded segment length of the coating when debonding occurs. Five replicates have been carried out for each measurement.

RESULTS AND DISCUSSION

First of all, we have determined the surface free energy of each solid: PET and alumina. The surface free energy, γ_S, of a solid is the sum of the dispersion component, γ_S^D, and the non-dispersion component, γ_S^P. These values are obtained by measuring the contact angle between the polar liquid (water) and the solid, operating in various non-polar liquids (alkanes: pentane, hexane, octane, decane, dodecane). The influence of the roughness has been corrected measuring the Wenzel factor in comparison with the glass-substrate reference.[4] The values obtained for PET and alumina surface free energies are given in Table I.

TABLE I
Surface free energy components of untreated PET and alumina (mJ·m^{-2})

Solid	γ_S^D	γ_S^P	γ_S
PET	40 ± 2	3 ± 1	43 ± 3
Alumina	158 ± 36	27 ± 3	185 ± 39

Similar surface free energy values have been reported by several authors[5–7] for PET films (from 39 to 47 mJ·m^{-2}). The surface free energy of alumina appears to be 185 ± 39 mJ·m^{-2}. This value is in good agreement with Kinloch's[8] (169 mJ·m^{-2}).

We have subjected the PET to various plasma treatments in order to increase its surface free energy and to improve its adherence capacity. In order to optimize the sought effect, we varied the nature of the plasma gas: argon, argon-oxygen (2.5%–5%–20%), air, and carbon dioxide. We also examined the influence of the treatment time.

The results given in Table II show the modifications of γ_S^D and γ_S^P for treatments with different gases and times. The different treatments do not improve, in a significant way, the dispersion component of the surface free energy of the PET. On the other hand, they modify considerably the non-dispersion component. We notice that the content of oxygen in the plasma seems to be the predominant factor in the activation phenomenon of the PET surface. The best results are obtained with short time treatments (less than one minute) using low oxidizing plasmas such as air and carbon dioxide.

The surface of the PET samples subjected to plasma treatments have been studied by ESCA. Atomic composition of the PET surface appears to be 70.4% and 29.6% for carbon and oxygen, respectively (71.4% and 28.6% for the required theoretical values); no contaminant is detected.

Figure 1 shows the spectra relative to the C(1s) photoelectrons for the reference sample (untreated PET) and treated samples during 10 s using argon, air, and carbon dioxide plasmas. The C(1s) spectra of the untreated PET is the result of three contributions: C_1 calibrated at the binding energy of 284.6 eV and corresponding to the C—C and C—H bonds of the benzene ring, C_2 at 286.2 eV for the C—O bonds and C_3 at 288.5 eV for the O—C=O bonds. A low C(1s) shake-up satel-

TABLE II
Modification of PET γ_S^D and γ_S^P *versus* gas nature and treatment time

Treatment time (s)		10		60		360	
Surface free energy components (mJ·m^{-2})		γ_S^D	γ_S^P	γ_S^D	γ_S^P	γ_S^D	γ_S^P
Plasma treatments	Ar	43 ± 5	9 ± 2	48 ± 5	11 ± 2	37 ± 7	1 ± 1
	Ar + O_2 (2.5%)	46 ± 6	11 ± 2	41 ± 7	13 ± 2	42 ± 6	1 ± 1
	Ar + O_2 (5%)	48 ± 7	14 ± 3	39 ± 5	7 ± 2	43 ± 4	1 ± 1
	Ar + O_2 (20%)	45 ± 6	25 ± 3	43 ± 4	16 ± 3	41 ± 5	6 ± 2
	air	47 ± 7	31 ± 4	45 ± 6	31 ± 4	43 ± 6	28 ± 4
	CO_2	46 ± 6	38 ± 4	43 ± 6	31 ± 4	41 ± 5	27 ± 4

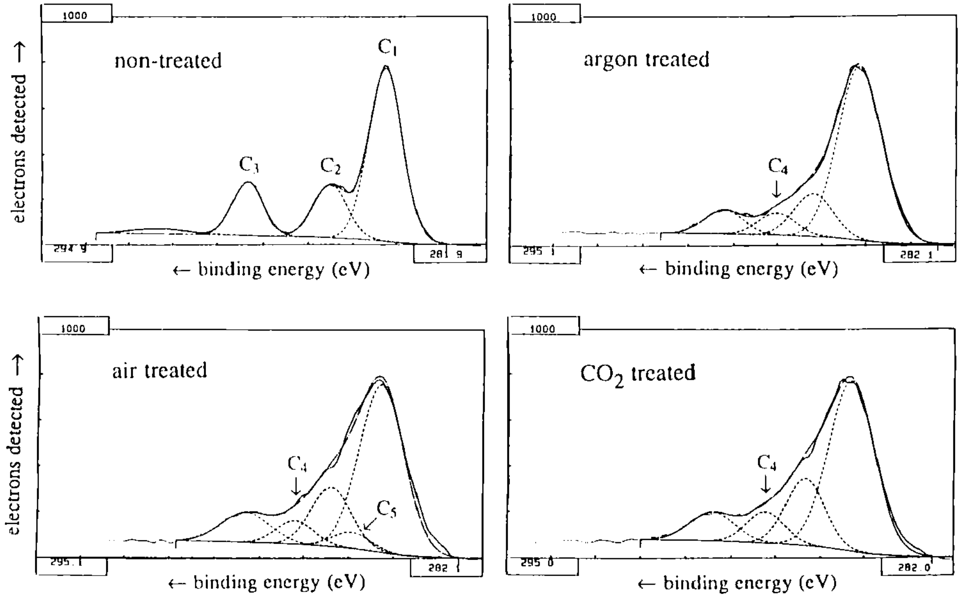

FIGURE 1 Decomposition of the C(1s) ESCA spectra for the PET.

lite associated with the benzene ring appears at 291 eV.[9] The O(1s) peak of the untreated PET has two contributions at 531.5 eV (O_1) and 533 eV (O_2), corresponding to C=O and C—O bonds, respectively.

Table III shows the effect of the different plasma treatments on the components of the C(1s) spectra. The values obtained for the untreated PET sample are similar to the required theoretical values for the stoichiometric PET: 60, 20, 20% for C_1, C_2, C_3, respectively.

Chemical changes occur as the polymer is plasma treated. Isolated carbonyl groups (C_4) appear at 287.5 eV with a decrease in the number of ester groups. The surface density of the carbonyl groups is maximum for a CO_2 plasma (slightly oxidizing). Only for the air treatment, a peak is observed at 285.9 eV (C_5), corresponding to CN bonds. This assignment is supported by the N(1s) peak appearing at 399.5 eV.[10]

Table IV shows the effect of the plasma treatments on the two components of O(1s) spectra. The chemical composition of the untreated PET agrees well with the theoretical values: 50, 50% for O_1, O_2. The O_1 contribution to the total O(1s) peak increases relative to that of O_2 as the polymer is plasma treated.

The presence of new chemical species generated by plasma treatments on the polymer surface is related to the activation process observed before. The increased concentration of isolated carbonyl groups is responsible for the increase in the non-dispersion component of the surface free energy. Similar results have been reported by Kinloch *et al.*[11,12] for a corona surface treatment on thermoplastic fibre composites and by Liston[13,14] for a water-vapor plasma on a polystyrene surface. The increase in the C(1s) peak for argon treatment suggests the surface is carburized by

TABLE III
Experimental values of the C(1s) spectra contributions
(% of the total C(1s) peak)

		C_1	C_2	C_3	C_4	C_5
Untreated		63.4	19.5	17.1	0.0	0.0
Plasma treatments	air	58.6	18.3	11.3	7.0	4.8
	argon	68.8	15.4	8.4	7.4	0.0
	CO_2	60.9	20.0	9.9	9.2	0.0

TABLE IV
Experimental values of the O(1s) spectra contributions
(% of the total O(1s) peak)

		O_1	O_2
Untreated		49.5	50.5
Plasma treatments	air	56.1	43.9
	argon	52.7	47.3
	CO_2	54.2	45.8

argon treatment, indicative of a crosslinking process,[15] with improvement of the cohesion between PET surface and bulk.[16,17]

The reversible energy of the adhesion W^{adh} between PET (S_1 solid) alumina (S_2 solid) can be calculated from the following relation:[18]

$$W^{adh} = 2\,(\gamma^D_{S1}\,\gamma^D_{S2})^{1/2} + 2\,(\gamma^P_{S1}\,\gamma^P_{S2})^{1/2}$$

The results given in Table V show the increase of W^{adh} obtained with the short time plasma treatments used in this study. This increase is essentially due to the alteration of the non-dispersion component caused by the plasma treatments. It reaches 30% with the plasmas obtained from air and carbon dioxide.

In order to verify experimentally the previous results, the PET samples coated with alumina (0.15 μm thick) were subjected to a tensile test.[19-22] The capacity of the interface to transfer stress from the substrate to the coating is evaluated from the shear strength of the interface, τ_0, which characterizes the adhesion.

Under tensile strain, a shear stress is produced at the interface. When an alumina film is bonded to the PET, the shear stress induces a tensile stress in the coating.

TABLE V
Influence of the plasma treatments (t = 10s) on W^{adh}, l_f, τ_0/σ_0

		W^{adh} ($mJ{\cdot}m^{-2}$)	l_f (μm)	$10^2\ \tau_0/\sigma_0$
Untreated		177.1 ± 13.1	21 ± 2	2.8 ± 0.3
Plasma treatments	Ar	196.1 ± 16.5	18 ± 2	3.3 ± 0.4
	Ar + O_2 (2.5%)	204.9 ± 17.2	—	—
	Ar + O_2 (5%)	209.5 ± 18.6	15 ± 1	4.0 ± 0.3
	Ar + O_2 (20%)	220.6 ± 17.7	14 ± 1	4.3 ± 0.3
	air	230.3 ± 18.9	12 ± 1	5.0 ± 0.4
	CO_2	234.7 ± 18.1	12 ± 1	5.0 ± 0.4

The film fails by brittle fractures; it develops straight parallel cracks transverse to the direction of strain until the shear stress of the interface is reached. Then debonding of segments occurs and the interfacial shear strength, τ_0, may be calculated from the length, l_f, of the largest debonded alumina film segment, and the tensile strength, σ_0, and the thickness, h, of the coating:[23]

$$\tau_0 = 4\,\sigma_0 \cdot h \cdot l_f^{-1}$$

However, no precise knowledge of the film and substrate physical properties is needed to compare the relative effects of the different surface treatments of the polymer on the intrinsic bond strength of alumina films on PET.

The results given in Table V show that the largest debonded alumina film segment, l_f, decreases when the PET surface is treated, as would be expected if the interfacial strength were increased by plasma treatments. The surface treatment of PET by the plasmas obtained from air and carbon dioxide increases by a factor of 1.7 the adhesion of alumina coatings.

CONCLUSION

The plasma treatment of PET leads to an alteration of the chemical structure of its surface, thus leading to an increase in the non-dispersion component of the surface free energy. The increase in the adhesion energy has been verified using tensile testing.

The adhesion of alumina coatings on PET is increased by a factor of 1.7 when a short time carbon dioxide plasma treatment is applied prior to deposition.

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