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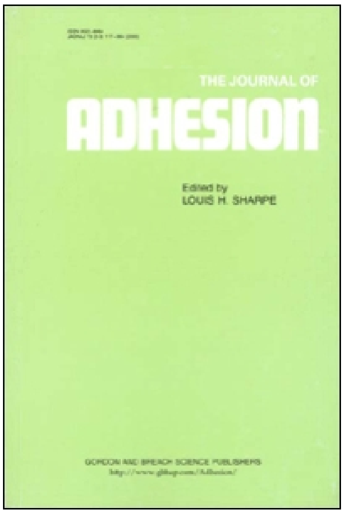

The Journal of Adhesion

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713453635

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To cite this Article Morra, M. , Occhiello, E. , Gila, L. and Garbassi, F.(1990) 'Surface Dynamics vs. Adhesion in Oxygen Plasma Treated Polyolefins', The Journal of Adhesion, 33: 1, 77 — 88
To link to this Article: DOI: 10.1080/00218469008030418
URL: http://dx.doi.org/10.1080/00218469008030418

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J. Adhesion, 1990, Vol. 33, pp. 77–88
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Printed in the United Kingdom

Surface Dynamics vs. Adhesion in Oxygen Plasma Treated Polyolefins†

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(Received February 19, 1990; in final form July 17, 1990)

Polyethylene (PE) and polypropylene (PP) were oxygen plasma treated and aged in carefully reproducible conditions. The effect of aging on the surface chemistry, wettability and adhesion were studied using a combination of techniques: contact angle measurements, XPS, SSIMS, adhesion tests (shear and pull).

PE was found to be relatively insensitive to aging both in terms of wettability and adhesion, due to crosslinking during plasma treatment, which is likely to reduce macromolecular mobility within the surface layer.

In the case of PP, dramatic decreases of wettability occur with time, due to macromolecular motions leading to minimization of oxygen-containing functions at the surface. This behavior was shown to affect the adhesion performance of treated PP.

KEY WORDS Wettability; surface rearrangement; plasma treatment; polyethylene; polypropylene; surface analysis.

INTRODUCTION

Plasma treatments are known to increase wettability and adhesion of polyolefin surfaces.[1,9] Well known also is the fact that treated surfaces tend to lose these properties with time.[1,10,11] The understanding of these phenomena, known as "hydrophobic recovery", recently benefited from studies aiming at a more detailed knowledge of polymer surface and interface dynamics.[1,12–17]

In this work a single and reproducible oxygen plasma treatment condition was chosen, focussing on the behaviour with time of the treated surface in contact with air. Polypropylene (PP) and polyethylene (PE) were chosen because of their opposite behavior when placed in high energy density media, such as plasmas, since the dominant phenomenon is crosslinking for PE, chain scission for PP.[18]

Both the behavior of treated surfaces with time and fracture surfaces were studied by a combination of surface-sensitive techniques. Water contact angle measurements and SSIMS (Static Secondary Ion Mass Spectroscopy) accounted

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† Presented at the Thirteenth Annual Meeting of The Adhesion Society, Inc., Savannah, Georgia, U.S.A., February 19–21, 1990.

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for a layer less than 1 nm thick,[19,20] XPS for a layer 3–5 nm thick.[21] Adhesion with epoxy resins was checked by pull and shear tests.

EXPERIMENTAL

Isotactic PP (Himont SP179 grade) and HDPE (Himont Moplen RO) 25 × 100 × 3 mm samples were used, as suggested by the ASTMD1002-72 procedure.

Oxygen plasma treatments were performed using a parallel plate reactor, with the samples located on the water-cooled grounded electrode.[15–17] The plasma parameters were the following: excitation frequency 13.56 MHz, power 100 W, pressure 2 Pa, gas flow 8 cc(STP)/min, treatment time 20 s. Oxygen from lecture bottles supplied by Carlo Erba was used.

Plasma-treated samples were aged at 293, 333, 363, 393 and 413 K both in atmosphere and at reduced pressure (500 Pa). Contact angle measurements were performed after allowing the sample to reach room temperature in air. The time between extraction from the oven and contact angle measurement never exceded 8 mins, therefore we can safely assume that the surfaces probed by contact angles are representative of the aging temperature. We always measured, besides the treated sample, untreated PP and PE subjected to the same thermal treatment, checking in this way that sample surface had reached room temperature. To assess the importance of thermal oxidation events we aged, at the same temperature, untreated and treated PP and PE samples and performed aging at normal and reduced pressure. No alteration was observed on untreated samples and no difference was found between contact angles measured after aging at different pressure, thereby excluding thermal oxidation effects.

Water contact angles were obtained by both the sessile drop and the Wilhelmy plate techniques,[1] in both cases the averages of 10 different measurements are reported. In the former case, advancing and receding angles were obtained using a Ramé-Hart contact angle goniometer by increasing or decreasing the drop volume until the three phase boundary moved over the surface. We kept the capillary pipette of the microsyringe immersed in the drop during the entire measurement.[1]

In the second case a Cahn DCA 322 dynamic contact angle analyzer was used. The stage speed was held at 40 μm/s. The contact angles were determined using the advancing and receding buoyancy slopes to determine the force at zero depth of immersion, at which point the measured force is linked to the contact angle by the following equation:[22]

$$\cos\theta = F/(\sigma_1 P) \qquad (1)$$

where F is the wetting force at zero depth immersion (advancing angle) and withdrawal (receding angle),[22] σ_1 is the surface tension of carefully deionized and doubly-distilled water (72.8 mJ/m^2), which we checked with the same instrument using a glow discharge cleaned glass slide, and P is the sample perimeter. The relevant software is provided by Cahn.

XPS spectra were obtained using a PHI model 548 XPS spectrometer, with the experimental procedures extensively described in Ref. 23.

SSIMS studies were performed using a VG quadrupole-based SIMSLAB instrument, with the procedures described elsewhere.[24] For SSIMS studies the samples were treated with $^{18}O_2$ plasma (provided by Merck Sharp and Dohme, 99% purity) to assess unambiguously the amount of oxygen introduced by the plasma.[17]

PP-epoxy and PE-epoxy joints for shear strength measurements were prepared using a commercial epoxy adhesive (Permabond E11) following manufacturer's instructions (cure cycle: 1 hour at 353 K). The joint preparation, geometry and testing were made in agreement with ASTM D1002-72 procedure. An Instron TMSM electro-mechanical dynamometer was used.

Pull tests were performed using a Sebastian II instrument, produced by Quad Group. Epoxy-coated pull studs were provided by the manufacturer. They were adhered to PP and PE samples following procedures suggested by the manufacturer (cure cycle: 1 hour at 373 K) and then tested.

For both shear and pull tests reported values are averaged over 10 measurements.

RESULTS AND DISCUSSION

Water contact angles

The behavior of advancing and receding angles of water as a function of aging time is a very good indication of hydrophobic recovery. In systems where the surface is morphologically smooth (as in our case, as checked by SEM), the advancing angle can be considered as representative of the least wettable portion of the surface, while receding angles represent the most wettable part.[25–27]

To assess the effect of aging in air on oxygen plasma treated PP and PE, we measured their contact angles as a function of aging time. In Table I advancing and receding angles as a function of time at room temperatures are presented. The effect of aging temperature has been reported elsewhere[15,16] and results essentially in faster recovery rates at higher aging temperatures.

In both cases, the untreated surface is hydrophobic, with contact angles in full agreement with literature values[1] and relatively low hysteresis. With the treatment, a sharp drop is observed reaching advancing angles of about 10° for PE and about 25° for PP. During aging, PE shows some hydrophobic recovery, reaching advancing contact angles close to 20–25° and receding angles close to 15°. PP shows a rather different behavior. A steep hydrophobic recovery is observed, within 1 day a 60° angle is observed, and in 10 days a limiting value of 95° is obtained, the same as the value for untreated PP. The receding angle reaches a value of 40°, lower than that of untreated PP, showing that some oxygen-containing functions remain close to the surface.

TABLE I

Water advancing (a.a.) and receding (r.a.) contact angles (both in degrees, measured by the sessile drop technique, typical error is ± 2°) for oxygen plasma treated PP and PE as a function of aging time

	PE		PP	
Time (hrs)	a.a.	r.a.	a.a.	r.a.
0.08	12	0	24	10
0.33	13	5	33	10
1.00	13	6	41	13
5.00	15	6	50	11
24.00	16	8	59	13
86.50	19	8	72	12
182.00	22	10	88	15
230.00	23	11	92	32
375.00	24	11	94	41
540.00	23	12	95	40
720.00	23	12	94	40
990.00	24	11	95	41

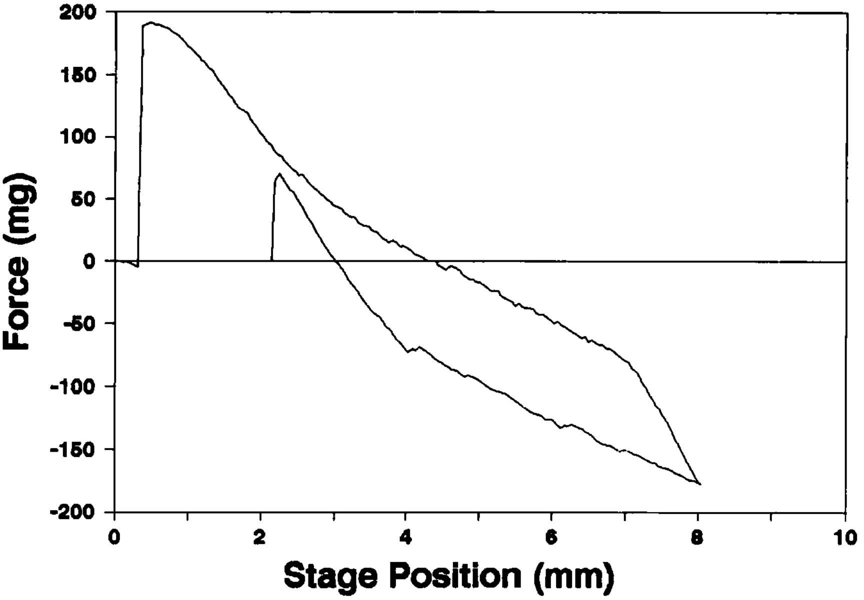
Untreated PE: a.a. = 93, r.a. = 78
Untreated PP: a.a. = 95, r.a. = 80

In Figures 1–3 hysteresis loops obtained by the Wilhelmy technique are presented. Those on the top are relative to PE, those on bottom to PP. In Figure 1 the loops relative to untreated samples are presented, showing characteristically hydrophobic surfaces. In Figure 2 there are results relative to just-treated specimens, in both PE and PP a drastic increase in wettabilty is evident. Finally, in Figure 3 loops relative to surfaces which reached limiting contact angles are presented. While the PE loop is still very much similar to that of the treated sample (Figure 2, top loop), a drastic change is observed for PP. The advancing angle returns to the value of the untreated sample (see Figure 1, bottom loop), while the receding angle increases drastically with respect to the just-treated specimen, even if it does not reach the value of the untreated sample.

A combination of sessile drop and Wilhelmy techniques also allowed us to exclude significant formation of low molecular weight, water-soluble species as a consequence of plasma treatment. When using the sessile drop technique, aqueous extraction experiments were performed according to the procedure described in Reference 22. No change in the drop behavior of both the untreated and treated samples was observed. Repeated hysteresis loops on just-treated samples did not show meaningful changes from the behaviour in Figure 2, supporting the evidence obtained by the sessile drop technique.

Surface spectroscopies

Further evidence on hydrophobic recovery is provided in Table II. SSIMS $CH^-/^{18}O^-$ ratios (about 1 nm observed layer) and XPS O/C ratios (abour 5 nm observed layer) are compared for selected aging conditions. Water advancing and receding angles are included for comparison.



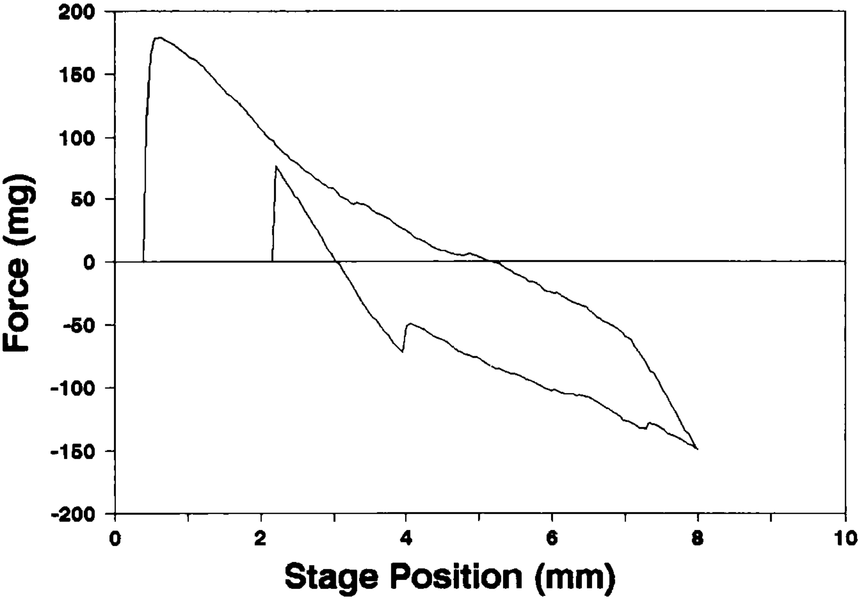
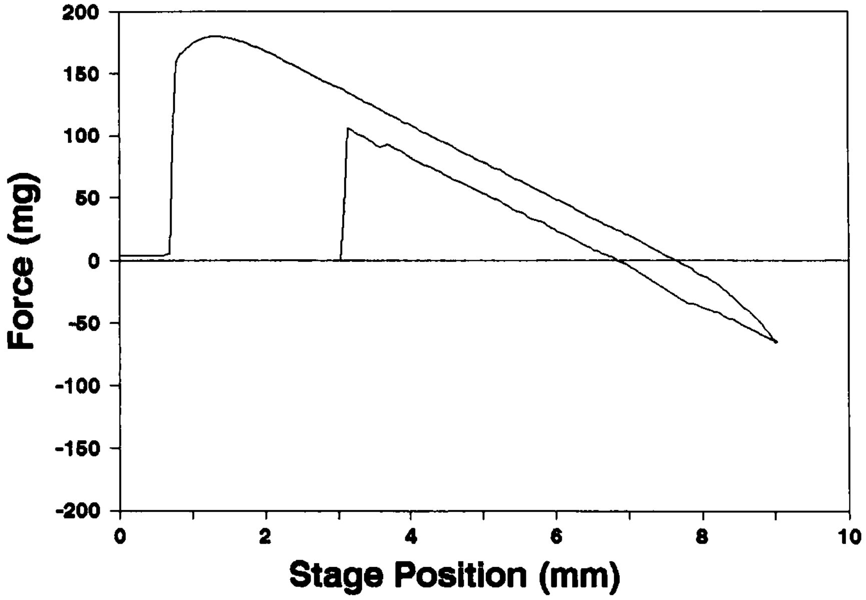


FIGURE 1 Wilhelmy plate technique hysteresis loops for untreated PE (top) and PP (bottom) in water.



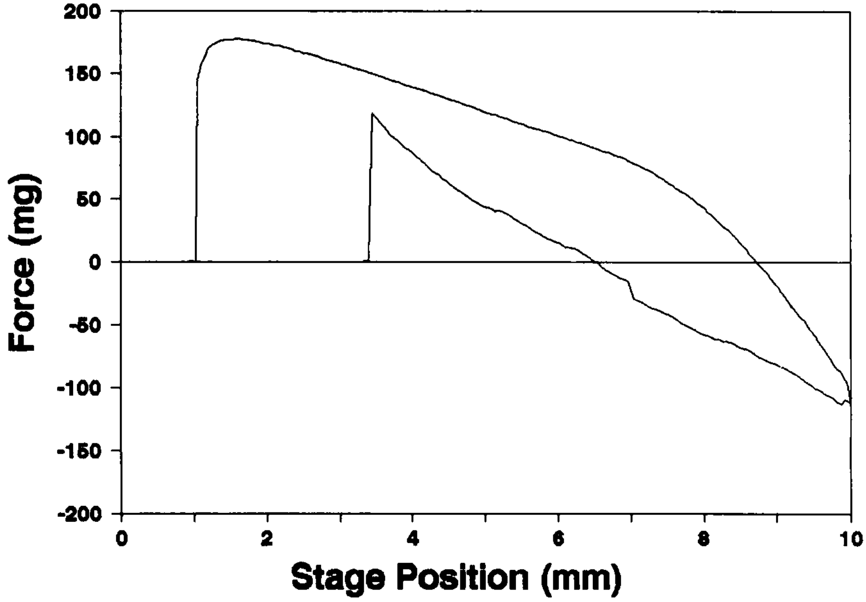
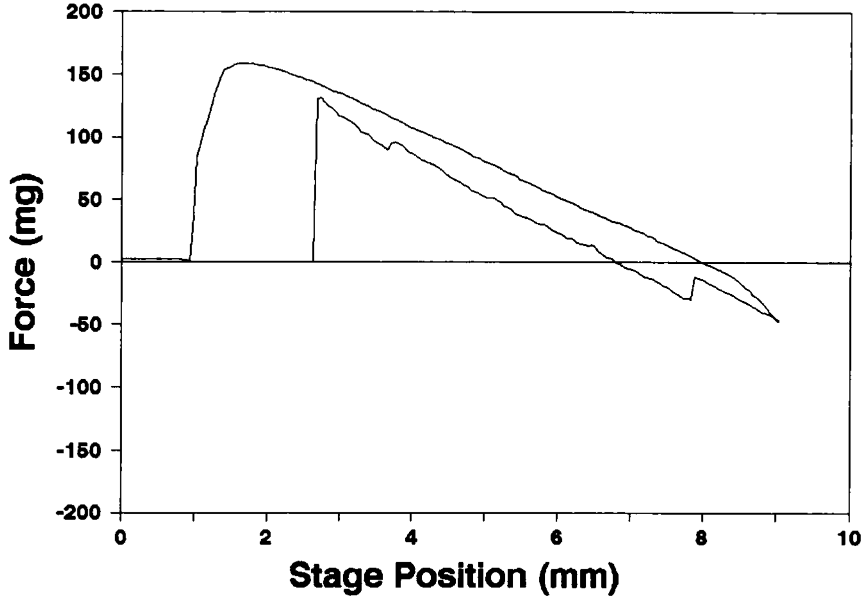


FIGURE 2 Wilhelmy plate technique hysteresis loops for just-treated PE (top) and PP (bottom) in water.



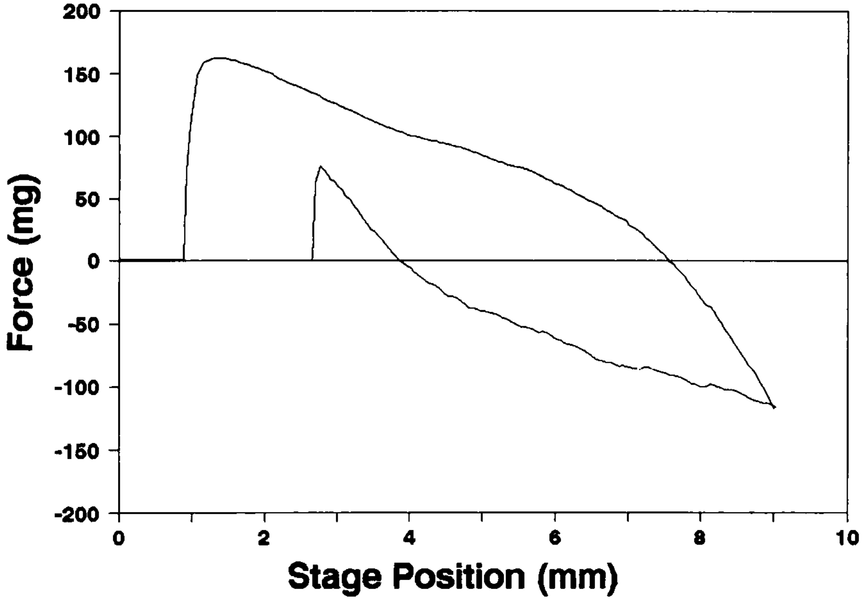


FIGURE 3 Wilhelmy plate technique hysteresis loops for treated PE (top) and PP (bottom) which reached limiting water contact angles.

TABLE II
Water advancing (a.a.) and receding (r.a.) angles (both in degrees), SSIMS $CH^-/^{18}O^-$ ratios and XPS O/C ratios for selected aging conditions

Aging conditions	a.a.	r.a.	SSIMS $CH^-/^{18}O^-$	XPS O/C
PE				
Untreated	93	78		0.04
Just-treated	12	7		0.32
24 hrs, 293 K	16	7		0.33
375 hrs, 293 K	24	12		0.30
8 hrs, 393 K	24	13		0.30
PP				
Untreated	95	80	—	0.02
Just-treated	24	10		0.19
16 hrs, 293 K	54	11	0.7	0.18
148 hrs, 293 K	81	13	1.3	
175 hrs, 293 K	86	15	1.7	0.19
3 hrs, 333 K, 44 hrs, 293 K	92	30	2.9	0.18
2 hrs, 393 K, 23 hrs, 293 K	94	50	4.5	
8 hrs, 393 K	94	49		0.19

In the case of PE, hydrophobic recovery is far less effective, due probably to crosslinking induced by plasma treatment.[2,3] XPS and contact angle evidence are parallel in showing no dramatic change upon aging.

In PP, aging induces effective depletion in oxygen-containing functions at the surface but this effect is not reflected by XPS O/C ratios. To make sure that the increase of contact angles is accompanied by a change in chemistry, we used SSIMS, a less penetrating chemical probe. The treatment with $^{18}O_2$ plasma provided an unambiguous estimate of the behavior of oxygen functions introduced by the plasma with aging. SSIMS $CH^-/^{18}O^-$ ratios do, indeed, show a dependence on aging paralleling that of contact angles. The SSIMS $CH^-/^{18}O^-$ ratio corresponding to limiting contact angles (Table II) still shows the presence of some ^{18}O, confirming that a complete recovery to the original PP surface does not occur, in good agreement with receding angle data.

The combination of contact angle, SSIMS and XPS information allows sensible hypotheses about the mechanism of hydrophobic recovery. In both PP and PE the XPS composition of treated samples is not affected by aging, which excludes outdiffusion of untreated bulk polymer as a cause of hydrophobic recovery. Adsorption of contaminants from the atmosphere is excluded by XPS itself and by temperature dependent studies, which showed strong enhancement in hydrophobic recovery rates by increasing the aging temperature.[15] The only remaining cause is polymer dynamics, *i.e.* motions of macromolecules within the plasma-modified layer to minimize the amount of polar functions at the surface,[16] as shown by the parallel increase of water contact angles and SSIMS $CH^-/^{18}O^-$ ratios.

TABLE III
Results of shear testing of PP and PE/epoxy bonds

Sample	Bond strength (N/mm^2)
PE	
Untreated	0.3 ± 0.04
Just-treated	3.4 ± 0.7
Aged (8 hrs, 393 K)	3.2 ± 0.6
PP	
Untreated	0.2 ± 0.01
Just-treated	1.4 ± 0.5
Aged (8 hrs, 393 K)	1.3 ± 0.2

Strength of adhesive joints

In Tables III and IV, respectively, the results of lap shear and pull testing of adhesive joints are presented. In both cases, joints made with just-treated polymer surfaces are compared with sample adherends which aged while reaching limiting water contact angles.

In the case of shear tests (Table III), the improvement by plasma treatment is most apparent for PE. In both PP and PE no significant variation in shear strength is observed after aging the polyolefin sample, meaning that the number of polar groups left at the surface after aging is sufficient to guarantee good adhesion.

In the case of pull tests the situation is different. Again the improvement due to plasma treatment is better in the case of PE, a value close to the tensile strength of PE, as reported in Reference 28, is reached. Furthermore, while PE pull strengths are unaffected by aging, in the case of PP a clear decrease was observed for the sample which had reached limiting water contact angles.

Pull and shear tests result in different evidence. In shear tests no important difference between just-treated and aged samples was observed, while in pull tests a clear decrease with aging was observed for PP. The reason is probably related to the different experimental arrangements. Adhesives are different, in one case

TABLE IV
Results of pull testing of PP and PE/epoxy bonds

Sample	Bond strength (kg/cm^2)
PE	
Untreated	not measurable
Just-treated	180 ± 20
Aged (8 hrs, 393 K)	178 ± 17
PP	
Untreated	not measurable
Just-treated	40 ± 10
Aged (8 hrs, 393 K)	7 ± 4

TABLE V
Water contact angles and XPS O/C ratios for PP and PE/epoxy fracture surfaces (from shear tests)[a]

Sample	Side	a.a.	r.a.	O/C
PE				
Just-treated	PE	94	82	0.03
	Epoxy	93	78	0.04
Aged (8 hrs, 393 K)	PE	94	80	0.05
	Epoxy	94	80	0.03
PP				
Just-treated	PP	95	79	0.02
	Epoxy	95	78	0.09
Aged (8 hrs, 393 K)	PP	95	80	0.01
	Epoxy	95	81	0.10

[a] Cured Permabond E11 adhesive a.a. = 90°; r.a. = 18°; O/C = 0.15

Permabond E11, in the other an epoxy-based adhesive coated on the pull studs provided by Quad Group. In addition, the cure cycles are different. Therefore, a different treated polymer-adhesive interaction is most likely.

Loci of failure

In both PP and PE cases, fracture surfaces obtained by lap shear testing were analyzed by XPS and contact angle measurement. The corresponding data are summarized in Table V.

The evidence from contact angle measurement points in both cases to fracture in the bulk of the material, in fact all measured contact angles are very similar to those of untreated PE and PP (Table I).

XPS showed some difference between PE and PP. In the case of PE, values typical of untreated PE have been observed, confirming contact angle evidence and suggesting that the locus of failure is in both cases within bulk PE.

In the case of PP XPS O/C relative to the two sides are different. On one side the value is typical of bulk PP, on the other side the amount of oxygen is significantly higher, suggesting the proximity of the plasma-modified layer. The combination of this evidence with that from contact angle measurements, suggests a locus of failure still within bulk PP, but very close to the modified PP layer. Actually, this might indicate a cause for the comparatively lower shear strengths in the case of PP, namely the lowering of molecular weight close to the treated surface, leading to the formation of a weak side.

In both cases, as expected on the basis of shear strength values (Table III), no significant difference was observed between just-treated and aged samples in terms of both water contact angles and O/C ratio.

CONCLUSIONS

After oxygen plasma treatment, for both PP and PE the top layer underwent rearrangement within itself by thermally activated macromolecular motions. In the case of PP, a nearly complete hydrophobic recovery occurs, while in PE only a slight increase in water advancing and receding angles occurs. The reason for this behavior lies probably in the fact PE is crosslinked by plasma treatment, while PP undergoes chain scission, even if the molecular weight is not reduced to the point of forming water-soluble species. A corollary of crosslinking is reduction of the mobility of macromolecular chains.

Shear and pull experiments showed a higher efficiency in improving adhesion for PE. In this case, the locus of failure was found to be within bulk PE, while in the case of PP it is again within the bulk polymer, but close to the interface with the plasma-modified layer. Surface dynamics and corresponding hydrophobic recovery do not affect shear strengths and corresponding loci of failure.

A reduction in pull strength was observed for PP, which undergoes strong hydrophobic recovery, while no effect was noted for PE. So, whenever the adhesive strength is strongly dependent on the number of polar groups on the surface, as seems indeed to be the case in the conditions used for pull testing, surface dynamics is a very important phenomenon in determining adhesion.

Acknowledgements

We wish to thank Drs. P. Humphrey and D. Johnson (UMIST) for assistance with SSIMS spectra and Mr. L. Pozzi for recording XPS spectra.. We wish also to acknowledge the assistance of Dr. A. Savoini for computer assistance.

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