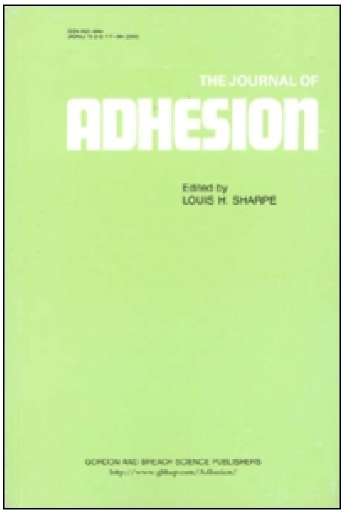

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Surface Analysis of Polymeric Joints*

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The stability of polymer-to-polymer joints was assessed using a thermodynamic method based on surface tension components, similar to that developed by Kinloch *et al.*,[1] showing that joint stability is improved in air by plasma treatments, while it is depressed in water. Shear strength tests showed qualitative agreements with these suggestions.

Surface analysis by contact angle measurements, SSIMS and XPS allowed the clarification of contributions which originated from phenomena unaccounted for by thermodynamic analysis. Plasma treatment was shown to form a weak boundary layer on polypropylene surfaces, possibly due to depolymerization. In the case of polycarbonate a water sensitive, possibly water soluble, layer is formed, therefore inducing a remarkable decrease in shear strength upon immersion in water.

KEY WORDS adhesion; polymer surfaces; plasma treatment; contact angle; surface free energy; epoxy adhesive; acrylic adhesive.

INTRODUCTION

Polymer-to-polymer joints have been studied much less than polymer-to-metal joints, mostly for technological reasons. While the latter assumed a big importance in aerospace and automotive applications, polymer-to-polymer joints are mostly present in industrial sectors less visible to academia, such as packaging.

As in the case of polymer-to-metal joints, most studies dealt with the identification of the locus of failure, in connection with either surface treatments or environmental effects (mostly water exposure).[2–5]

The main differences between failure analyses of polymer/polymer *vs.* polymer/metal joints lie in the characterization techniques which can be applied, since polymers are non-conductors and prone to degradation. Therefore, X-ray Photoelectron Spectroscopy (XPS) is used rather than Auger Electron Spectroscopy (AES) and Static Secondary Ions Mass Spectroscopy (SSIMS) rather than conventional, or dynamic, Secondary Ions Mass Spectroscopy (SIMS).

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EXPERIMENTAL

Isotactic polypropylene (PP) (Himont SP179 grade), high density polyethylene (HDPE) (Himont Moplen RO) and Bisphenol-A polycarbonate (PC) (Bayer) were used. Oxygen plasma treatments were performed using a parallel plate reactor, with the samples located on the water-cooled grounded electrode. 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.

Water (doubly distilled) and methylene iodide (Aldrich) contact angles were measured by the sessile drop technique, using a Ramé-Hart contact angle goniometer. From the measured advancing angles, the polar and dispersive components of the surface free energy were calculated, using the harmonic mean method.[3] From these data the fracture energy was calculated according to the Kaelble method, as follows (the polar and dispersive component of the surface free energy of air and water were taken from the literature):[2,3]

$$\sigma_c = \left(\frac{2\,E\,\Gamma_g}{\pi\,C}\right)^{1/2} \tag{1}$$

$$\Gamma_g = R^2 - R_o^2 \tag{2}$$

$$R_o = 0.25 \ast [(\alpha_1 - \alpha_3)^2 + (\beta_1 - \beta_3)^2] \tag{3}$$

$$R = (\alpha_2 - H)^2 + (\beta_2 - K)^2 \tag{4}$$

$$H = 0.5\,(\alpha_1 + \alpha_3) \tag{5}$$

$$K = 0.5\,(\beta_1 + \beta_3) \tag{6}$$

where:

σ_c = Critical crack propagation stress
Γ_g = Fracture energy
E = Young's modulus
C = Crack length
α, β = Square root of the dispersion and polar surface tension components of adhesive (1), environment (2) and adherend (3).

XPS spectra were obtained using a PHI model 548 XPS spectrometer. SSIMS studies were performed using a VG quadrupole-based SIMSLAB instrument.

PP, HDPE and PC joints for shear strength measurements were prepared using a commercial epoxy adhesive (Permabond E11) and an acrylic adhesive based on ethylmethacrylate and toughened with a Hypalon 20 chlorinated rubber. The joint preparation, geometry and testing were in agreement with the ASTM D1002-72 procedure.

To assess the effect of water or air aging, the joints were either immersed in distilled water at 363°K (below the T_g of the adhesive) for 3 d or aged in air at 293°K for the same time.

Shear strengths of adhesive joints were measured by an Instron TMSM electromechanical dynamometer.

RESULTS AND DISCUSSION

Thermodynamic Analysis

The stability of adhesive joints, *i.e.* the fracture energy, involves contributions due to work of adhesion (reversible) and plastic work (irreversible). Assuming the negligibility of mechanical interlocking and direct chemical bonding, fracture energy and work of adhesion can be related to polar and dispersion components of surface tension[1-3] or to the acid-base characteristics of polymers.[6] For this purpose we used the method suggested by Kaelble,[2,7-9] which is equivalent to the one reported by Kinloch.[1]

In Table I, results relative to plasma treated and untreated HDPE/epoxy/HDPE and PP/epoxy/PP adhesive joints are presented, while, in Table II, results relative to plasma treated and untreated PP/acrylic/PP and PC/acrylic/PC adhesive joints are compared with those relative to steel/acrylic/steel adhesive joints.

Two main points arise from the data; the first is that the higher the surface energy of adherends, the higher is fracture energy. Most polymers are surface treated before adhesion to improve wettability, therefore the net effect of these treatments is enhancing reversible contributions to fracture energy. The second point is that the stability of adhesive joints in humid environments is adversely affected by high surface energy adherends. In the case of steel, this leads to a strong instability in water, while for plasma-treated polymers only a drastic reduction in fracture energy is observed.

TABLE I
Calculated fracture energies of polymer/epoxy adhesive/polymer joints

Sample	Fracture energies (mJ/m^2)
Untreated PE	37.3
O_2 plasma tr. PE	59.7
Untreated PP	30.3
O_2 plasma tr. PP	44.6

TABLE II
Calculated fracture energies of polymer/acrylic adhesive/polymer and steel/acrylic adhesive/steel joints in air and water (taken from ref. 9)

	Fracture energies (mJ/m^2)	
Sample	Air	Water
Untreated PP	38.9	18.0
O_2 plasma tr. PP	59.1	4.3
Untreated PC	44.7	16.1
O_2 plasma tr. PC	59.4	4.0
Mild steel	150.3	−122.4

In Tables III and IV experimental shear strength values are reported. For epoxy adhesive, an increase in shear strength is observed upon treatment for both HDPE and PP, although more evident for HDPE. For acrylic adhesives, shear strengths in air of untreated samples follow again a surface energy order (PP<PC<steel) and indeed plasma treating polymer surfaces, thus increasing surface energy, resulted in higher shear strengths. In most cases aging in water reduced shear strengths. In Figure 1 the ratio between shear strengths relative to water and air aging are shown. Plasma treatment clearly resulted in reduction of water resistance for both PP and PC, yet the much higher loss in fracture energy of PC, along with the comparatively good resistance of high surface energy steel joints require explanations based on irreversible contributions, rather than on the data in Table I.

Effect of Surface Treatments on Fracture Loci

The effect of surface treatment, in particular oxygen plasma treatment, on the location of fracture loci was studied on HDPE/epoxy/HDPE and PP/epoxy/PP joints. The former tends to be crosslinked by plasma treatment, while for the latter molecular weight reductions are foreseen.[10]

In Table V contact angle and XPS results relative to fracture surfaces obtained by lap shear testing are presented. In the case of untreated HDPE and PP, as shown by the comparison with data relative to untreated samples, the fracture is adhesive. For plasma treated samples, contact angle data point to cohesive fracture within the adherend, as confirmed in the case of PP by SSIMS evidence (Figure 2). The positive

TABLE III
Results of lap shear testing of PP/epoxy/PP and HDPE/epoxy/HDPE bonds

Sample	Bond strength (N/mm^2)
Untreated PE	0.3±0.04
O_2 plasma tr. PE	3.4±0.7
Untreated PP	0.2±0.01
O_2 plasma tr. PP	1.4±0.5

TABLE IV
Experimental lap shear strengths of polymer/acrylic adhesive/polymer and steel/acrylic adhesive/steel joints aged in air and water

	Lap shear strengths (N/mm^2)	
Sample	Air	Water
Untreated PP	0.3±0.1	0.3±0.1
O_2 plasma tr. PP	0.9±0.1	0.7±0.1
Untreated PC	1.4±0.2	1.1±0.1
O_2 plasma tr. PC	2.2±0.2	0.4±0.1
Mild steel	22.6±0.7	17.9±0.5

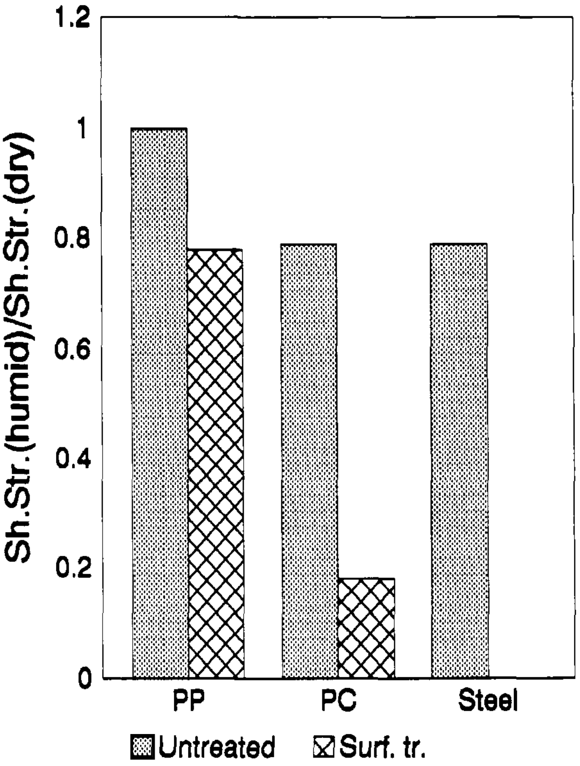

FIGURE 1 Ratio of lap shear strengths after aging in humid and dry environment for PP/acrylic/PP, PC/acrylic/PC and steel/acrylic/steel adhesive joints.

TABLE V
Water advancing (a.a.) and receding (r.a.) contact angles and XPS O/C ratios for PP and PE/epoxy fracture surfaces (from lap shear tests)*

Sample	Side	a.a.	r.a.	O/C
PE				
Untreated	PE	92	77	0.03
	Epoxy	90	22	0.12
O_2 plasma tr.	PE	94	82	0.03
	Epoxy	93	78	0.04
PP				
Untreated	PP	95	80	0.02
	Epoxy	91	20	0.12
O_2 plasma tr.	PP	95	79	0.02
	Epoxy	95	78	0.09

*Cured E11 adhesive : a.a. = 90°; r.a. = 18°; O/C = 0.15
Untreated PE : a.a. = 93°; r.a. = 78°; O/C = 0.04
Untreated PP : a.a. = 95°; r.a. = 80°; O/C = 0.02
O_2 plasma tr. PE : a.a. = 12°; r.a. = 7°; O/C = 0.32
O_2 plasma tr. PP : a.a. = 24°; r.a. = 10°; O/C = 0.19
Typical error on measured angles: ± 3°

ion spectra of both the adherend and the adhesive side of the broken joint, shown in Figure 2, exhibit the typical fragmentation pattern of PP,[11] with clusters based on one carbon atom (C_1, about 15 atomic mass units), C_2 (about 25 amu), C_3 etc. This result confirms that PP is found on the topmost layers of both sides of the fracture surfaces.

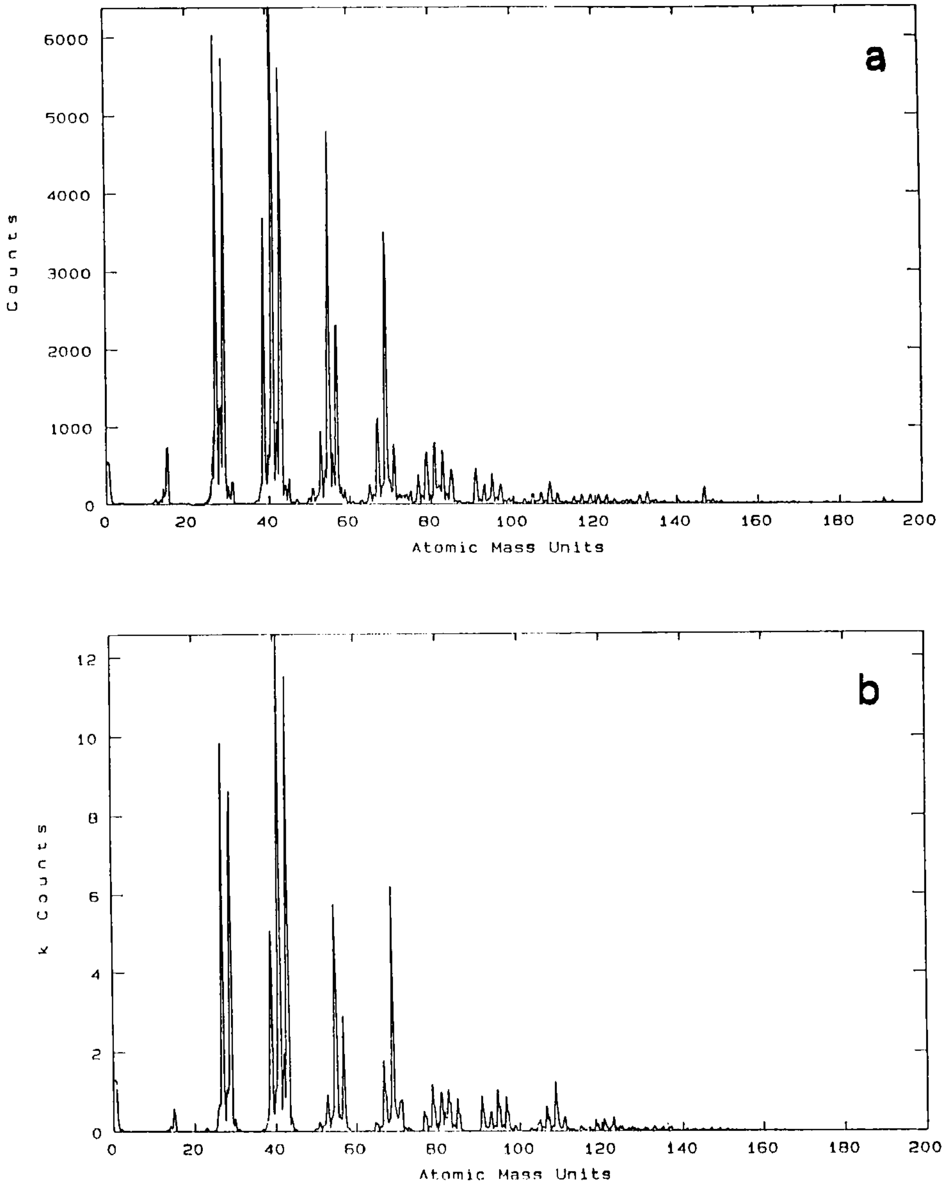

FIGURE 2 Static SIMS spectra of fracture surfaces of plasma treated PP/epoxy adhesive/PP joints: a) adhesive side; b) adherend side.

XPS, on the other hand, showed some differences between PP and HDPE. In the case of HDPE, very low O/C ratios have been observed at both surfaces of the locus of failure, suggesting failure within the bulk. For PP the O/C ratio on the adhesive side is higher, suggesting that the locus of failure is still within PP, but close to the modified layer, maybe due to the lowering of molecular weight close to the treated surface, leading to the formation of a weak boundary layer.

Effect of Aging in Water

The effects of aging in air and water on PP/acrylic/PP and PC/acrylic/PC joint fracture surfaces were studied by XPS. The results are presented in Table VI. For PP, both untreated and plasma treated, no effect of aging environment was observed, in agreement with the limited loss in mechanical properties (Table IV).

On the other hand, for PC, fracture surfaces of joints aged in air show an O/C ratio close to that of the acrylic adhesive, suggesting the positioning of the locus of failure quite close to the adherend/adhesive interface, with some adhesive on both sides. Aging of untreated PC joints in water resulted in a similar situation, while for the aging of treated joints significantly different results were observed. On one side the O/C ratio is close to that of the acrylic adhesive, on the other side to PC. One possible explanation is the plasma-induced formation of a water-soluble oxidized layer, whose mechanical strength is rapidly decreased in the presence of water. This explanation is strongly supported by contact angle measurements on plasma treated PC samples.[9]

TABLE VI
XPS O/C ratios of fracture surfaces of air and water aged PP/acrylic adhesive/PP and PC/acrylic adhesive/PC joints (from lap shear tests)*

		Aging	
Sample	Side	Air	Water
PP			
Untreated	PP	0.02	0.02
	Acryl.	0.09	0.10
O_2 plasma tr.	PP	0.03	0.02
	Acryl.	0.02	0.02
PC			
Untreated	PC	0.11	0.09
	Acryl.	0.11	0.11
O_2 plasma tr.	PC	0.11	0.21
	Acryl.	0.09	0.15

*Untreated PP : O/C = 0.02
Untreated PC : O/C = 0.19
O_2 plasma tr. PP : O/C = 0.19
O_2 plasma tr. PC : O/C = 0.19
Untreated acrylic adhesive : O/C = 0.13

CONCLUSION

Thermodynamic analysis is reasonably correct in predicting the response of adhesive joints to adherend surface treatment and aging in humid environments. The analysis of fracture surfaces help in the understanding of irreversible effects contributing to joint strength and degradation. Plasma treating PP and HDPE results, in both cases, in improvements in shear strength. Yet the formation of a weak boundary layer, due probably to depolymerization effects, lowers the ultimate mechanical strength for the PP case. On the other hand, plasma treatment of PP does not induce the formation of a water-sensitive surface layer, as it does for PC. Therefore, the water resistance of the latter is much lower.

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