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X-ray photoelectron spectroscopy studies of polymer surfaces

Part 2 *Melting polyethylene against aluminium*

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The effect of melting polyethylene on aluminium has been re-examined using X-ray photoelectron spectroscopy. Even at 150° C, low and high density polyethylenes show degrees of oxidation similar to that observed with conventional pretreatments; large increases in adhesion are also observed. The results are discussed in relation to transcrystalline regions and weak boundary layers.

1. Introduction

To achieve satisfactory adhesion with polyethylene it is normally necessary to pretreat the polymer surface. However, there is much controversy as to whether the pretreatments are effective by increasing the surface energy [1–3] or by eliminating weak boundary layers [4, 5]. In Part 1, the effect of chromic acid on polyolefins was studied [6]. In the present paper, another pretreatment is re-examined using X-ray photoelectron spectroscopy (XPS or ESCA). The treatment, discovered by Schonhorn and Ryan [7], involves melting polyethylene onto aluminium followed by dissolution of the metal. These workers proposed that the treatment is effective by eliminating weak boundary layers. While the treatment is not commercially important, a study of the technique is highly relevant to the extrusion coating of aluminium with polyethylene.

Schonhorn and Ryan [7] pressed a high density polyethylene between etched aluminium foil at 150 or 175° C. The aluminium was then dissolved using dilute sodium hydroxide solution. They noted that the adhesion levels achieved, using an epoxide adhesive, usually increased by three- to five-fold as compared with the untreated polyethylene. The authors concluded that a transcrystalline region is formed at the aluminium polyethylene interface due to extensive nucleation. When the aluminium is dissolved, the transcrystalline region, which is of similar strength to the bulk polymer, remains thereby eliminating a weak boundary layer.

Schonhorn and Ryan, using ATR-infra-red spectroscopy, found no evidence of any chemical changes in the polyethylene surface. However, the sampling depth of ATR is such that any chemical changes in the first 100 Å of the surface would not normally be detected. In the present communication, results are presented using XPS to examine the surfaces of a low density and a high density polyethylene; this technique can readily detect changes in the first 100 Å of a surface. Joint strength and contact angles are also given for the two polyethylenes.

2. Experimental

2.1. XPS measurements

XPS data were obtained using an AEI ES200B electron spectrometer employing Mg$K\alpha$ exciting radiation (1253.6 eV). Samples were examined in the form of rectangles (~ 20 mm × 6 mm) cut from untouched sheet and mounted with double-sided Sellotape onto the probe tip. The working pressure in the spectrometer chamber was 10^{-8} Torr.

Binding energies are corrected to Cls = 285.0 eV for the untreated polyethylenes. The instrument was calibrated so that the $Au4f_{7/2}$ peak had B.E. = 84.0 eV relative to the Fermi level. Binding energies are considered to be accurate to ± 0.2 eV.

2.2. Materials

"Alkathene" WJG 47 is a low density polyethylene with a melt flow index of 2; it is a product of Imperial Chemical Industries Ltd. "Rigidex" 50 is a high density polyethylene with a melt flow index of 5; it is a product of BP (Chemicals) Ltd. "Araldite" AV100 and HV100 are products of Ciba-Geigy Ltd.

2.3. Treatment and bonding

Aluminium foil was etched in chromic acid ($Na_2Cr_2O_7.2H_2O:H_2O:H_2SO_4 = 1:30:10$ by weight) and then thoroughly rinsed in distilled water and dried [7]. The polyethylene was pressed between two sheets of this aluminium foil at 150 or 175° C for 10 min and then cooled rapidly by passing cold water through the press platens. The aluminium was then dissolved in sodium hydroxide (2 M) keeping the temperature below 5° C. The polyethylene film was washed thoroughly in distilled water and dried.

Composite lap joints were made of aluminium (127 mm x 25.4 mm x 3 mm)–epoxide adhesive–polyethylene film (0.125 mm)–epoxide adhesive–aluminium (127 mm x 25.4 mm x 3 mm) with a resultant 25.4 mm x 25.4 mm overlap [7]. The epoxide adhesive system was "Araldite" AV100 plus "Araldite" HV100 used in the ratio of 1:1, the adhesive was cured for 3 h at 60° C. The lap joints were tested at 6.25 mm min^{-1}, the values quoted being the mean of ten results. Control samples were prepared by pressing the polyethylenes between poly(ethylene terephthalate) film under the same conditions as with the aluminium and then peeling away the polyethylenes; the latter operation required a very low force.

2.4. Bromination of polyethylenes

The polyethylene films were immersed in a dilute solution of bromine in carbon tetrachloride for a few seconds and then rinsed in carbon tetrachloride. The films were then examined by XPS.

2.5. Contact angle measurements

The advancing contact angles (θ_{adv}) were determined using a telescope goniometer. They are the mean of six determinations and have an accuracy of ± 2°.

3. Results

Relative peak intensities in the XPS spectra from repeat experiments showed the reproducibility to be good (± 5%). The surface sensitivity of XPS is enhanced by using low "take-off" angles (θ) for the photoelectrons. For the samples considered, no difference in relative peak intensities was observed for $\theta = 15°$ or 75°. Hence, within the depth of polymer sampled (95% of the observed signal emanates from a depth of 3λ* where λ is the electron mean free path in the polymer) the element distribution is homogeneous.

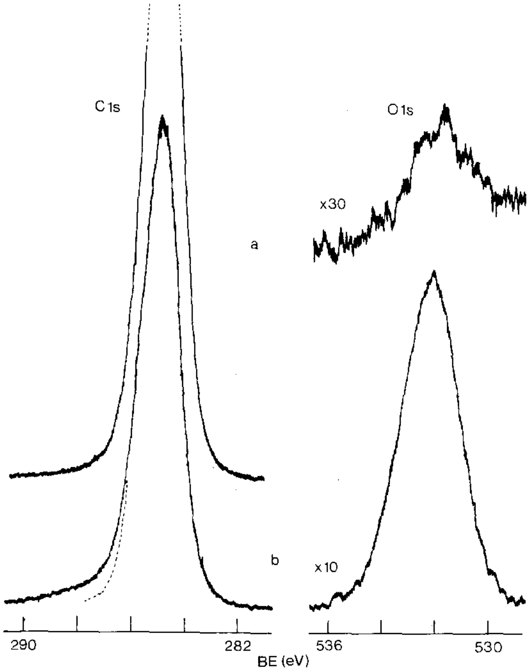

Figure 1 Cls and Ols peaks from low density polyethylene: (a) untreated, (b) melted against aluminium foil at 175° C followed by dissolution of Al with dilute NaOH. Count rate = 3×10^4 counts/sec f.s.d.

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* The correct value of λ for organic systems is a subject of controversy. A value of ~ 12 Å for Cls electrons has been claimed recently [10], which clashes with previously held values, almost an order of magnitude higher. It can safely be assumed, however, that $3\lambda < 300$ Å.

TABLE I XPS data, joint strengths and advancing contact angles for polyethylenes that have been melted against aluminium or poly(ethylene terephthalate)

Polymer*	Substrate	Temperature (°C)	O:C (at.%)	Lap shear strength ($\mathrm{MN\,m^{-2}}$)	Type of failure	θ_{adv} (deg)
"Rigidex" 50	poly(ethylene terephthalate)	150	0.52	0.38	I	96
"Rigidex" 50	aluminium	150	6.20	1.43	I	85
"Rigidex" 50	aluminium	175	†	2.19	I	93
"Rigidex" 50 Peeled	aluminium	150	0.92	–	--	–
"Alkathene" WJG47	poly(ethylene terephthalate)	150	0.25	0.55	I	98
"Alkathene" WJG47	aluminium	150	3.75	5.65	M	78
"Alkathene" WJG47	aluminium	175	6.88	6.38	M	80

* The polymers were pressed against the substrate for 10 minutes at the temperatures stated.
† Not available, see text.
I Apparent interfacial failure.
M Failure of the polyethylene.

XPS spectra of the untreated polyethylene surfaces reveal very low levels of contamination, oxygen being the only other detectable element in concentrations substantially less than 1 at.%; XPS showed that no polyethylene was transferred to the poly(ethylene terephthalate). Melting against aluminium produced markedly increased levels of oxygen and the Cls spectrum shows the growth of a weak peak to higher binding energy indicative of oxidized carbon atoms (probably $> C = O$), as shown in Fig. 1. Values of atomic O:C ratios are included in Table I. These were derived from Ols and Cls peak areas corrected for their differing X-ray photoemission cross-sections (determined *in situ* from poly(ethylene terephthalate)). The additional Cls peak can completely account for all the Ols intensity assuming a one oxygen per carbon situation.

Small Nls peaks were sometimes observed in the spectra for the treated samples, while peaks characteristic of SiO_2 also appeared strongly in samples of "Rigidex" melted at 175° C and for this reason, meaningful O:C data could not be included in the table. The spectra gave no evidence of Al or Na which might conceivably be present on the treated sample surfaces.

In a rather different experiment, a "sandwich" of "Rigidex" melted between aluminium foil at 150° C was prepared as above. When cool, one foil was peeled off and both the resulting surfaces analysed. The polyethylene surface showed an O:C ratio of 0.92% while the aluminium foil surface revealed the characteristic oxide on metal spectrum together with an intense Cls peak. Fig. 2 contrasts the Cls and Al2p spectra from this surface and from aluminium foil after subjection to the routine cleaning and etching procedure used before polymer melting experiments. Not only is the Cls/Al2p intensity ratio much higher for the former (indicating a much thicker carbon overlayer*) but also there are strong indications of oxidation of this carbon layer from the high B.E.

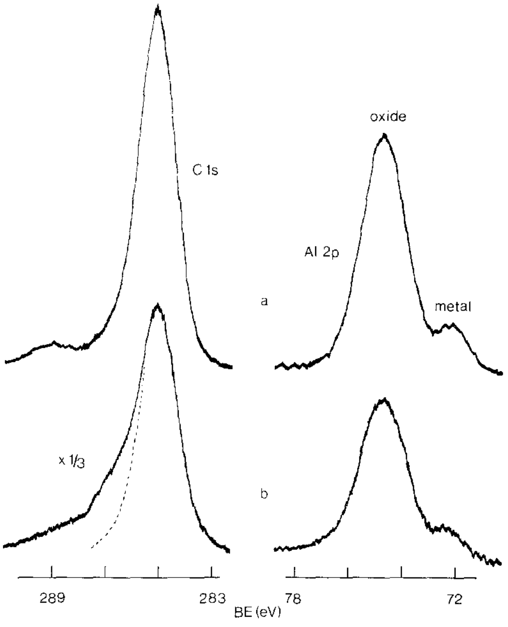

Figure 2 Cls and Al2p peaks from: (a) "clean" aluminium foil (b) the foil surface resulting from peeling at the aluminium foil/high density polyethylene interface (see text). Count rate = 3 × 10^4 counts/sec f.s.d.

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* Aluminium foil surfaces are contaminated with a tenaciously held hydrocarbon layer resulting from the rolling process [9].

TABLE II Estimate of unsaturation from XPS data on bromine uptake

Polymer	Substrate	Temperature (° C)	Cls(I_{CH_2})*	Br3d†	$I_{C=C}$‡	$I_{C=C}$:I_{CH_2} (%)
"Alkathene" WJG47	poly(ethylene terephthalate)	150	22.3	0.31	0.16	0.7
"Alkathene" WJG47	aluminium	150	21.0	0.80	0.40	1.9
"Rigidex" 50	poly(ethylene terephthalate)	150	22.3	0.04	0.02	0.01
"Rigidex" 50	aluminium	150	20.1	0.38	0.19	0.9

* Peak height (arbitrary units).

† Corrected for relative photoemission cross-section (twice that of Cls [11]).

‡ $I_{C=C}$ = Br3d/2 since $> C = C < + Br_2 \rightarrow > CBr - CBr <$.

components. Clearly, the oxidized layer observed on the polymer surface when the aluminium is chemically removed, remains on the aluminium surface when the polymer film is peeled away from the foil.

The XPS results show a higher level of oxidation for high density polyethylene. The bromination results in Table II show some interesting differences. Assuming only bromination of double bonds, the relative Br3d and Cls peak intensities show the unsaturation level of "untreated" low density polyethylene is approximately 0.7% (cf. 0.2 to 0.3% by standard infra-red techniques). After melting against aluminium foil at 150° C for 10 min, this figure increased to about 2%. The high density polyethylene sample melted against aluminium under the same conditions gave an unsaturation level of 0.9%, but the "untreated" sample took up a negligible amount of bromine. Crystallinity effects will be marked and this method of bromination can over-estimate the unsaturation level by causing side-chain bromination. However, these preliminary results indicate a significant increase in unsaturation following melting against aluminium especially in the case of low density polyethylene.

4. Discussion

There can be no doubt from the data in Table I that melting polyethylene against "aluminium" surfaces does produce substantial chemical modification of the surface. In the case of the low density polyethylene, the adhesion level increases with the degree of oxidation as measured by XPS. The degree of oxidation is greater in the case of high density polyethylene under identical conditions. However, the results in Table II show that melting against aluminium at 150° C results in a higher degree of unsaturation with low density polyethlylene.

Melting against aluminium produced large increases in adhesion with both low and high density polyethylenes compared with "untreated" polyethylenes. After treatment at 150° C, the adhesion level was considerably higher in the case of the low density polymer despite a lower degree of oxidation; no convincing explanation is apparent. Our studies of other pretreatments which result in surface oxidation, e.g. chromic acid etching [6], show that percentage increases in adhesion levels similar to those described here, are accompanied by similar degrees of surface oxidation. Also, there is no need to invoke the effect of a transcrystalline region at the aluminium–polyethylene interface to explain the increased surface energy because melting against aluminium introduces polar groups. Dwight and Riggs [8], came to a similar conclusion regarding the results of Schonhorn and Ryan for a fluorinated ethylene–propylene co-polymer (FEP) melted against gold. However, it is still possible that the poor adhesion of untreated polyethylene (and FEP) is due to a weak boundary layer and the increased oxidation is purely incidental. However, in some other XPS work [6], we found no evidence of the transfer of polyethylene to the adhesive as would be expected if a region of low strength existed on the polymer surface. The balance of evidence is hence strongly against the idea of a weak boundary layer in these cases.

A further consequence of the present results is that the use of contact angle measurements to infer surface structure (especially the degree of crystallinity) is not valid in the absence of reliable surface chemical composition data.

It is interesting to consider the origin of the oxidizing species in this treatment of polyethylene. Pressing against aluminium gave levels of surface oxidation 12 to 15 times greater than polyethylenes pressed against poly(ethylene terephthalate);

these results are given in Table I. This could be due to a specific catalytic effect or due to trapped air in the aluminium surface which is much rougher than the poly(ethylene terephthalate) film.

It is also worth noting that the assumption that oxidation is confined to the top monolayer, made by Clark *et al.* [9], is disproved by the absence of angular (θ) variation effects noted above.

5. Conclusions

(1) Melting polyethylenes against aluminium at 150 or 175° C for 10 min results in substantial oxidation and also some unsaturation. There are large increases in adhesion.

(2) Oxidation is not limited to a monolayer as has been previously claimed [9]. The increase in surface energy and adhesion are probably due to the introduction of polar groups and not due to a transcrystalline region.

(3) The use of contact angles to infer surface structure is not valid in the absence of strong supporting evidence, e.g. XPS data.

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