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X-ray photoelectron spectroscopy studies of polymer surfaces

Part 1 *Chromic acid etching of polyolefins*

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X-ray photoelectron spectroscopy (XPS) has been used to study the chromic acid etching of polyethylene (low density) and polypropylene film surfaces. Both core and valence levels have been used to monitor changes in surface composition and these results correlated with contact angle measurements. Besides the expected observation of oxygenated species, the technique detects a sulphur containing species, identified as $-SO_3H$. Information about the depth of polymer attack has been obtained from two types of data (comparative core level intensities and angular variation of relative peak intensities) which provide depth resolution. Differences in behaviour of the two polyolefins are discussed in connection with previous non-surface specific data.

1. Introduction

X-ray photoelectron spectroscopy (XPS or ESCA) has already shown itself to be a valuable technique for studying the structure of polymers [1–3]. More particularly, the surface sensitivity of XPS is beginning to be applied to the study of chemical modification of polymer surfaces [4–6] in order to understand changes in surface properties such as adhesion and wettability. The great majority of previous work on polymers has concentrated on highly fluorinated materials especially PTFE because of the large C1s core level shifts induced by the presence of highly electronegative fluorine atoms.

The present work is the first in a systematic series of studies on the effects of polymer surface pretreatment methods used to increase adhesion. We chose chromic acid etching of polyolefin surfaces for the first study for two reasons. Firstly, to investigate the usefulness of XPS in the study of non-fluorinated polymer systems and, secondly, because discussion of the factors affecting this process in different polyolefins has reached the stage where an input of specific surface chemistry measurements is required to advance our understanding. In particular, XPS should prove extremely useful in determining whether surface pretreatments for non-polar polymers are effective by introducing polar groups or by eliminating weak boundary layers. [7, 8].

2. Experimental

2.1. XPS measurements

These were carried out on an AEI ES200B electron spectrometer equipped with a Mg*Kα* source (exciting energy 1253.6 eV) rated at 500 W, but normally run at 300 W. Radiation damage was not found to be significant, except in certain cases when exposure times were much longer than normal. In this spectrometer the angle of emission of photoelectrons from the polymer surface (θ) can be varied simply by rotation of the sample probe about its own axis. This is important since at low θ the intensity of signal from the surface layer relative to the sub-surface is enhanced markedly [9, 10]. This effect can be used to differentiate surface and bulk effects and ideally, to estimate the depth of surface modification within the XPS sampling depth (~300 Å) [11].

Binding energies (B.E.) are corrected to C1s = 285.0 eV for the untreated polyolefins. 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" WJG47 is a low density polyethylene with a melt flow index of 2. Blown film (thickness = 0.012 mm) containing no additives was used. "propathene" HF20 is a polypropylene with a melt flow index of 3. Polymer powder containing no additives was pressed into a film (thickness = 0.012 mm) between two films of poly(ethylene terephthalate) which had been extracted with trichloroethylene. The two polyolefins are products of Imperial Chemical Industries Ltd. "Araldite" AV100 is an epoxide resin made by Ciba-Geigy Ltd. "Araldite" HV100 is the appropriate curing agent which is used in the ratio 1:1.

2.3. Treatment with chromic acid

The films were immersed in chromic acid ($K_2Cr_2O_7:H_2O:H_2SO_4 = 7:12:150$ by weight) for the conditions detailed in the table; for the 6 h treatment the acid was changed every 2 h. The films were then washed with agitation in distilled water for 15 min or overnight. The films were dried under vacuum.

2.4. Determination of lap shear strength

Laminates similar to those described by Sharpe and Schonhorn [12] were used. The polyolefin films were bonded to aluminium strips with the epoxide adhesive under a pressure of 3000 $kg\,m^{-2}$. The adhesive was cured in an oven at 60° C for 3 h. The bonded structures were then removed from the oven and the joint strengths determined 1 h later using a Hounsfield Tensometer (type W) at a withdrawal rate of 6.25 mm min^{-1}. The results quoted are the mean of 10 determinations.

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

3.1. Core level spectra

X-ray photoelectron spectra of the pure polyolefin films revealed extremely clean surfaces. Small oxygen O1s peaks were detected but their magnitude is such (atomic C:O ratio $\simeq$ 400:1) that they can be neglected in the ensuing discussion. All the chromic acid etched samples gave pronounced oxygen (O1s) and sulphur (S2s and 2p) peaks but there was little evidence of Cr.* Variation of the angle of electron emission (θ) only revealed depth of sampling effects in the case of polypropylene etched for 1 min at 20° C, consistent with estimated rates of polymer attack [13] and the etching times used. Peak areas can be converted into elemental atomic ratios by means of the differential cross-sections for core-level excitation. Those of Wagner [14] have been found to be reasonably applicable to our instrument, but in this work we used internally generated values for C1s, O1s and S2p from studies of poly(ethylene terephthalate) and poly (phenylene sulphide). These quantitative data are shown in Tables I and II.

The most intense sulphur peak (S2p) was relatively sharp, and probably indicative of a single species, with a B.E. of 169.3 eV. This compares with 164 eV for the sulphur atoms in poly(phenylene sulphide) (measured under identical conditions) a relative shift of +5.3 eV which can be compared to +5.2 eV for the chemical shift between R-*S*-R and R-$\mathit{S}O_2$-OR determined by Siegbahn *et al.* [15]. (Our B.E. values are ~ 1.7 eV higher, presumably due to differences in calibration procedure). It seems likely, therefore, that $-SO_3H$ groups are introduced into the polyolefin surface during etching.

It can be clearly seen from Table I, that sulphur and oxygen are increasingly incorporated into the surface of polyethylene during etching. Polypropylene, on the other hand (Table II) is modified to a similar extent by etching for 1 min at 20° C or for 6 h at 70° C.

Let us consider in detail the data from a highly modified polyethylene surface (30 min at 70° C). The expected O:S atomic ratio for a surface modified only by incorporation of $-SO_3OH$ groups in 3:1. Obviously an excess of oxygen is introduced. From the C:S ratio, some 1.25% of the C

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*The most intensely treated polyethylene samples showed traces of Cr.

TABLE I XPS analytical data[a], contact angles and joint strength data for chromic acid etched polyethylene surfaces

Etching Conditions	C:S atomic ratio	O:S atomic ratio	% C atoms with SO_3H groups	% O (not in SO_3 groups) to total C	θ adv deg.	Lap shear strength ($MN\,m^{-2}$)	Failure type[b]
Untreated	–	–	–	0.25	98	0.55	I
1 min/20° C Normal wash	269	14.9	0.37	4.4	76	7.45	M
30 min/70° C Normal wash	80.0	12.2	1.25	11.5	66	7.58	M
6 h/70° C Normal wash	47.1	11.2	2.12	17.4	45	9.48	M
6 h/70° C Overnight wash	59.2	14.1	1.69	18.6	64	6.96	M

[a] All data refer to an electron emission angle (θ) of 75°

[b] I = Apparent interfacial failure
M = Failure of polyolefin film.

atoms in the polymer surface are attached to $-SO_3H$ groups. Assuming the remaining oxygen is involved in C-OH and C=0 groups (i.e. one 0 per C only) then the number of carbon atoms in these groups is calculated to be 11.5%. Hence, a total of ~ 13% of the carbon atoms in the surface should be "chemically shifted" out of the main C1s peak by virtue of their higher B.E.s. Published data [16] show that shifts relative to C1s (hydrocarbon) are ~ 3 eV for $C = O$, ~ 1.5 eV for C–OH and ~4.5 eV for COOH groups. Data for C-SO_3H are not available but the shift will probably be within 1 to 2 eV.

The core-level spectra from this sample are shown in Fig. 1. Note the obvious tail on the high B.E. side of the C1s peak (in the untreated polyethylene spectra the C1s peak in highly symmetrical). Deconvolution shows that this high B.E. tail accounts for 11 to 12% of the total C1s intensity, slightly lower than the calculated value. The spread of B.E.'s involved (out to ~+ 4.5 eV) suggests, however, that there are carboxyl groups present (two oxygens per carbon), which could explain this result. These data, and similar data for the other samples are collected in Tables I and II.

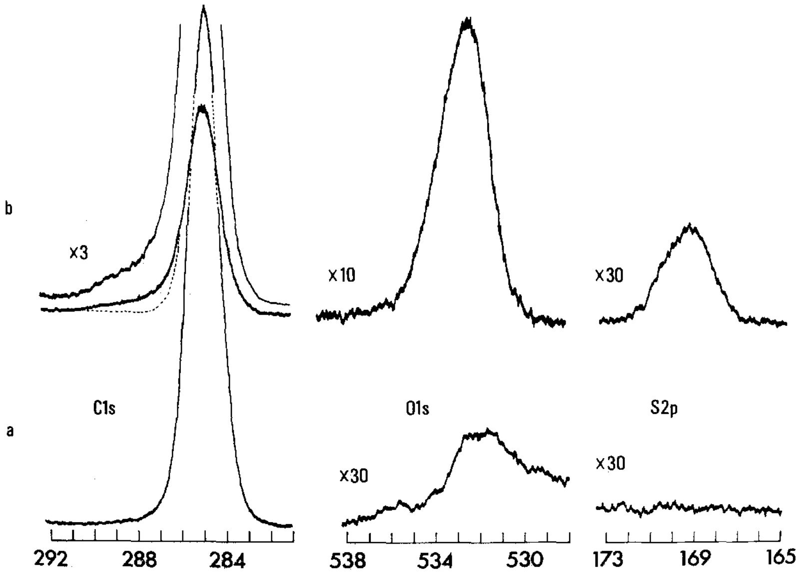

Figure 1 Binding energies (in eV) of core level peaks from samples of polyethylene: (a) untreated, (b) chromic acid etched for 30 mins at 70° C.

TABLE II XPS analytical data[a], contact angles and joint strength data for chromic acid etched polypropylene surfaces

Etching conditions	C:S atomic ratio	O:S atomic ratio	% C atoms with SO_3H groups	% O (not in SO_3H groups) to total C	θ adv. deg.	Lap shear strength ($MN\,m^{-2}$)	Failure type[b]
Untreated	–	–	–	0.25	92	0.28	I
1 min/20° C normal wash	283 (223)	19.1 (19.0)	0.35 (0.45)	5.9 (7.3)	73	4.69	I & M
1 min/20° C overnight wash	583 (307)	27.1 (19.4)	0.19 (0.33)	4.5 (5.3)	82	4.83	I & M
6 h/70° C normal wash	261	15.9	0.38	4.8	97	11.2	M

[a] Data refer to an electron emission angle (θ) of 75° C, bracketed values to θ = 15°

[b] I = apparent interfacial failure
M = failure of polyolefin film.

An interesting effect was noted when the surface of the etched polypropylene was wiped with an acetone soaked tissue. Both O1s and S2p signals decreased in intensity and the FWHM of the O1s peak decreased markedly. Data evaluation shows the loss of oxygen is largely due to removal of fragments containing $-SO_3H$ groups. The narrowing of the O1s signal shows that O atoms attached to S and C have different, but unresolved B.E's. Prolonged washing experiments produced a similar effect.

The question of whether weak boundary layers are important in determining adhesive strengths of untreated polyolefins was investigated by a

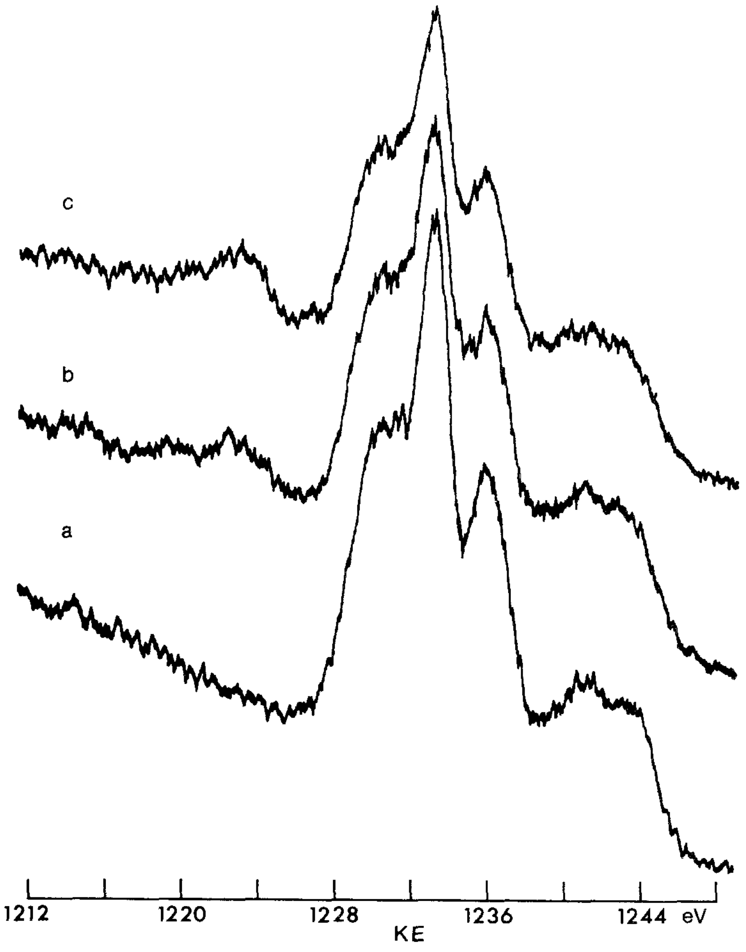

Figure 2 Valence band spectra of polypropylene: (a) untreated, (b) and (c) chromic acid etched for 1 min at 20° C and 6 h at 70° C respectively.

study of epoxy resin surfaces cured (a) in air and (b) in contact with polyethylene which was subsequently removed as in a lap shear test. XPS did not detect any residual polyethylene on the epoxide surface, the carbon spectra of both surfaces being identical. However, the O1s:N1s peak ratios differed sufficiently to indicate a somewhat different surface composition for the two surfaces.

3.2. Valence band spectra

The study of polymer valence band structures by XPS is still in its infancy, relying heavily on quantum mechanical calculations for interpretation. Again, most published data, [17, 18] relate to fluorinated homopolymers, although the valence band spectrum of polyethylene has been reported and assigned [19].

Figs. 2 and 3 show the valence band spectra of polypropylene and polyethylene before and after chromic acid etching. No attempt has been made to attach a B.E. scale, since this requires a precise knowledge of the valence band cut-off energy and the band gap to locate the Fermi level (B.E. = 0).

Incorporation of oxygen into the polymer surfaces is reflected in the growth of a band at ~1222 eV due to electrons in orbitals with strong O2s character. For polypropylene the overall spectrum is little affected in keeping with low degree of polymer modification. In the case of polyethylene, however, the valence band spectrum is increasingly perturbed as etching continues. In the spectrum of pure polyethylene, the doublet in the region 1226 to 1238 eV is assigned to C-C bonds and the band between 1238 to 1248 eV to C-H bonds [19]. Clearly the polypropylene valence band spectrum, which does not seem to have been studied previously, contains similar bands. The distinctly new peak at 1233 eV must be associated with the C-CH_3 bond.

As expected from these data, the major change on etching is perturbation of the C-H band region (Fig. 3c). The relative increase in intensity of the peak at ~ 1230 eV is probably due to the

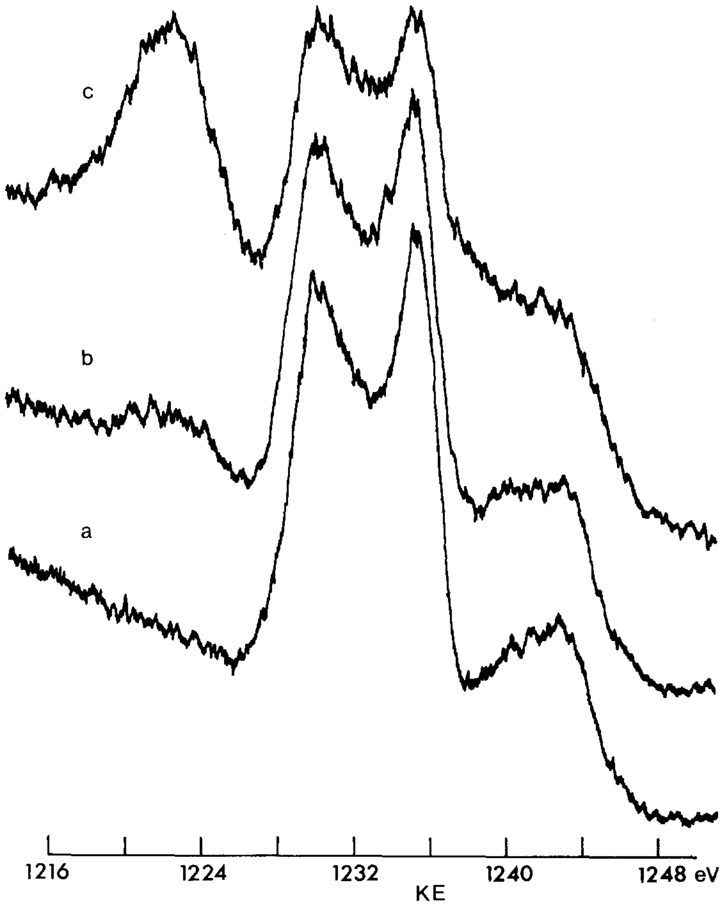

Figure 3 Valence band spectra of polyethylene: (a) untreated, (b) and (c) chromic acid etched for 1 min at 20° C and 30 min at 70° C respectively.

growth of an overlapping S3s band, expected in this region, with incorporation of $-SO_3H$ groups in the polymer surface.

3.3. Comparison of O1s and O2s intensities

In the range of electron kinetic energies covered in XPS using Mg$K\alpha$ radiation (from ~100 to 1250 eV) the escape depth* in metals increases in a roughly linear fashion from ~ 5 to 20 Å. Hence, a high K.E. core level will sample a greater depth than a low K.E. core level. In organic systems the escape depths are believed [15] to be higher by about × 5, but a similar situation should hold.†

In these spectra the O2s level in the valence band region is semi-core like (1222 eV K.E.) and samples a greater depth than the O1s level (717 eV K.E.). As the depth of polymer which has been etched increases the intensity ratio O1s: O2s should decrease to a limiting value when this depth reaches ~3λ(O2s). Since there is no guarantee that etching will take place uniformly (e.g. amorphous regions will probably be attacked more rapidly than crystalline regions) it would be dangerous to apply this model rigorously to calculate depths of etching. However the O1s: O2s ratio may reasonably be taken as a qualitative guide to relative degree of attack within the top ~300 Å of polymer.

Table III gives the O1s:O2s peak area ratios for several etched films. From these data the limiting O1s:O2s ratio (according to our instrumental parameters) appears to be ~ 19. Thus 1 min at 20°C etches polyethylene almost down to the sampling depth, 6h at 70°C etches polypropylene to a similar extent. However, 1 min at 20°C only etches polypropylene down to a fraction of this depth. These results agree nicely with the angular rotation experiments, which also show that only in the latter case is there evidence that etching has affected a layer significantly less deep than the sampling depth.

TABLE III Ols:O2s peak area ratio for etched films

Polymer	Etching conditions (normal wash)	O1s:O2s[a]
PP	1 min/20° C	45.4
PP	6 h/70° C	27.4
PE	1 min/20° C	25.9
PE	30min/70° C	18.3
PE	6 h/70° C	19.7

[a]Electron emission angle (θ) of 75°

A comparison of Tables II and III shows that the essential difference between etching polypropylene for 1 min at 20° C or 6 h at 70° C is in the degree of polymer modification on a depth scale rather than on the molecular scale. In the case of polyethylene, however, it can be seen from Table I and III that polymer modification on both these scales takes place as etching proceeds.

4. Discussion

There has been much controversy over the last 15 years regarding the reason for the poor adhesion of polyethylene, polytetrafluoroethylene and other non-polar polymers. Various authors [8, 12, 20] have supported the argument that inadequate contact is achieved between an adhesive and the non-polar polymer, while others [7, 21, 22] have argued that the poor adhesion is due to regions of low strength on the polymer surfaces. Most surface pretreatments probably introduce sustantial polarity into the polymers, but some treatments may be effective by eliminating weak boundary layers e.g. by cross-linking [7].

The most thorough investigation of the chromic acid treatment is that of Blais *et al.* [13] who investigated the topography, wettability and adhesion of etched low and high density polyethylene (LDPE and HDPE) and polypropylene (PP). Surface chemistry investigations were, however, limited to ATR-infra-red spectroscopy studies, which inevitably suffer from the relatively large sampling depth (~ 1 μm = 10^4 Å) compared with the modification depth (10^2 to 10^3 Å for typical etching times) of the polymer. Thus only

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*For our purposes, the escape depth, λ (equivalent to the electron mean free path in a solid) is best defined by the integrated intensity equation $I_d = I_\infty(1 - e^{-d/\lambda})$ where I_d is the elastic peak intensity from a layer of thickness d and I_∞ is the intensity from an infinitely thick layer from an electron with associated escape depth λ. Thus 95% of the elastic peak intensity originates from a layer 3λ thick and this can be taken as a useful guide to the depth of a solid actually sampled by XPS.

†More work needs to be done to determine escape depths in organics. For the present we will assume a rough value of 100 Å for λ. Since values of etched polymer depths are derived from d/λ values, any future change in the determined value of λ will alter all d values by this ratio effect.

LDPE sample etched for long periods (~ 1 h) gave spectra which revealed extensive chemical changes ($-OH$, $>C=0$ and possibly $-SO_3H$ groups were identified). HDPE and PP (the latter after 6h etching) gave unchanged spectra.

As the above results show, XPS with a sampling depth of <300 Å is a much more sensitive probe of polymer surface chemistry changes. Moreover, it can comment on changes which occur during short reaction times, which bear closer comparison with commercially treated surfaces that do those treated for periods long enough to give effects detectable by ATR-infra-red.

It is useful to consider the degree of polarity that is necessary to give good adhesion. Consider the polypropylene film that has been treated with chromic acid for 6h at 70° C followed by a normal wash. The lap shear strength is approximately 40x greater than that of the untreated film and similar to values obtained with poly(ethylene terephthalate) using the same adhesive [23]. Assuming the carbon is associated with oxygen in a 1 : 1 ratio, i.e. as C-OH or C = O, about 5% of the carbon atoms would have polar groups associated with them. For comparison, the O:C ratio in poly(ethylene terephthalate) is 0.4, i.e. about 5x greater than that of the polypropylene sample under discussion. Hence XPS shows that high adhesion levels can be obtained with a low degree of polarity in the polypropylene, assuming that the degree of oxidation does not vary significantly with depth. This means that either sufficient interaction between substrate and adhesive can be achieved with this low degree of polarity or that a weak boundary layer has been removed during the etching process.

The XPS examination of a fractured adhesive joint involving untreated polyethylene and the epoxide adhesive gave no evidence of transfer of polyethylene to the epoxide. This is evidence against the weak boundary layer concept and in favour of the idea of inadequate contact with untreated polyolefins. However, further work is required before a definite conclusion can be reached.

The exact significance of the contact angles is not yet clear. The contact angle for polypropylene treated for 1 min at 20° C and given a normal wash is 73°. The reduction of 19° from the untreated polymer seems large in view of the small increase in polarity as determined by XPS. It could possibly be due to a very thin layer (perhaps 20 Å) of more highly oxidized material and this is supported to some extent by the XPS and contact angle results for a sample washed overnight.

The more severe treatment of polypropylene gave higher contact angles than the mild treatment in agreement with Blais *et al.* [13]. However, they suggested that this increase was due to less oxidation for the more severe treatment, while XPS shows that the amount of oxidation for the two treatments is about the same. Also, scanning electron microscopy shows that the surface roughness is much greater with the more severe treatment [24] and we believe this is the reason for the increased contact angle. The effect of surface roughness on contact angles has been discussed elsewhere [25].

The treatment of polyethylene for 1 min at 20° C confirms that good adhesion can be achieved with little polarity in a polymer. XPS shows that polarity increases with longer treatment but these increases are not reflected in increased adhesion, the limiting factor being the strengths of the polyolefins.

5. Conclusions

(1) XPS has probably detected the presence of $-SO_3H$ and $-COOH$ as well as C = O and C $-$OH groups in the surfaces of chromic acid etched PE and PP, the latter reaching the maximum degree of oxidation more quickly.

(2) Only in the case of PP etched for 1 min at 20° C is the depth of oxidation less than about 300 Å.

(3) Assuming the degree of oxidation does not vary significantly with depth, high adhesion levels can be obtained with a relatively low degree of polarity in polyolefin surfaces; with about 5% oxidation, 13- and 16-fold increases in adhesion are achieved with PE and PP respectively.

(4) There was no direct evidence of weak boundary layers, i.e. XPS did not detect any polyethylene on the epoxide adhesive after an adhesive joint was broken; it is possible that there was a PE layer thinner than the detection limit of about 20 Å.

(5) Reductions in contact angles due to increased polarity can be more than offset by increased surface roughness.

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