Improved adhesive properties of high-modulus polyethylene structures

Part I Oxidative acid etching

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The adhesion of oriented, high-modulus polyethylene-structures to epoxy resins is greatly enhanced by pretreatment with oxidizing acids. For $KMnO_4/H_2O/H_2SO_4$ treatment a maximum increase in adhesion, as determined by pull-out tests, of 600% was found. Chromic and chlorosulphonic acid treatment improves the adhesion with 550% and 300% respectively. Moreover, this improvement was obtained without substantially affecting the mechanical properties. The modulus remained the same, whereas tensile strength decreased by less than 10% after this treatment. By monitoring the changes in surface topography (SEM) and surface composition (X-ray photoelectron spectroscopy) the improvement in adhesion could be related to the introduction of functional oxygen-containing groups, i.e. hydroxyl, carbonyl, carboxyl. Furthermore, at the highest level of adhesion obtained the failure mode changed from interface controlled to shear failure within the polyethylene structure.

1. Introduction

Melt-spinning/drawing and solution(gel) spinning produce chain-extended polyethylene (PE) structures possessing excellent mechanical properties [1-3]. In fact, the specific moduli and strength of aramid and carbon fibres are surpassed, making these PE structures a potential candidate for composite applications.

Whether the properties of a fibre can effectively be imparted to the composite depends on the adhesion between reinforcement and matrix. However, for these high-strength high-modulus PE structures the adhesion with most materials is poor, due to the chemical inertness and a smooth surface preventing chemical as well as mechanical adhesion.

Over the last 30 years several methods to modify polyolefin surfaces have been developed, most of them with the aim to improve metal plating and/or printability. Examples are acid etching [4], plasma [5, 6], corona and ozone treatment [7, 8]. It is assumed that these treatments improve the adhesion in a two-fold manner [9]: firstly the surface free-energy is increased, improving wettability, and secondly and most importantly functional groups are introduced at the surface, giving rise to a large increase in the chemical interaction at the interface.

However, there is a great difference in the surface morphology of the polyolefins used in the studies mentioned above, which were mostly isotropic films or films of low draw ratio, with the high-strength high-modulus PE structures produced by gel-spinning or melt-spinning/drawing. These differences are, for instance, reflected in the extremely high crystallinity of the gel-spun/drawn PE structures exceeding 80%-90%, compared to 20%-60% for conventional low-density (LD)PE-high-density (HD)PE. Hence, the question arises whether the above-mentioned treatments are also effective in improving the adhesion of high-strength high-modulus PE structures.

The first attempt to improve the adhesion of ultra-drawn PE structures was undertaken by Ladizesky and Ward [10, 11], who investigated the effect of plasma and chromic acid treatment on the adhesion of melt-spun/drawn PE fibres to an epoxy matrix. Both treatments markedly improved the adhesion, although plasma treatment was far more effective. This was attributed to the pitted surface produced by the plasma treatment, providing excellent mechanical interlocking. Similar results following air or oxygen plasma treatment were reported by Nguygen et al. [12], Nardin and Ward [13] and Kaplan et al. [14]. A marked increase in wettability and adhesion was observed after ammonia plasma treatment, although scanning electron microscopy showed no changes in surface structure [15]. Recently, Postema et al. [16] reported a five-fold increase in the adhesion of gel-spun PE fibres to gypsum plaster after chlorosulphonation. According to the authors this improvement could be related to surface roughening of the fibres. Although some remarks concerning the introduction of functional groups were made in the above articles,

no attempts were undertaken to monitor the changes in surface chemical composition, nor to reveal the nature of the functional groups incorporated.

The purpose of the present study was to explore whether acid treatment could improve the adhesion of oriented PE structures to epoxy resin in relation to the chemical composition of the surface and the surface topography.

2. Experimental procedure

2.1. Preparation of tapes

Oriented PE tapes, obtained by ultra-drawing cast films as described previously [17], were employed in this study. However, a difference in the preparation procedure was that decaline was replaced by xylene. The cast films were drawn on hot shoes ($T = 125\,°C$) to $\lambda = 60$. The PE used was Hostalen Gur 412 with a molar mass, M_w, of about $1.5 \times 10^3\,kg\,mol^{-1}$. Stabilizer and any remaining xylene were removed by subsequent extraction with hexane (15 h) and methanol (5 h). The tapes prepared possessed a Young's modulus of 140 GPa, and a tensile strength of 2.4 GPa at room temperature (measured at a strain rate of $10\%\,min^{-1}$).

2.2. Acid treatment

PE tapes were immersed in chlorosulphonic acid, chromic acid, i.e. $K_2Cr_2O_7/H_2O/H_2SO_4$ (7:12:150 by weight) or $KMnO_4/H_2O/H_2SO_4$ (1:12:150 by weight) at room temperature for different exposure times. The chlorosulphonic acid-treated tapes were rinsed with concentrated sulphuric acid, whereas the $KMnO_4/H_2O/H_2SO_4$-treated tapes were rinsed with concentrated HCl. Next, all tapes were rinsed with distilled water. Finally, the PE tapes were rinsed with acetone, dried and stored in a desiccator.

2.3. Determination of adhesion

Pull-out tests were performed on specimens as illustrated in Fig. 1. A medium-viscosity resin, Europox 730, together with an aliphatic amine hardener XE-278 (both obtained from Schering) in the ratio 100/15 wt/wt were used throughout this study. The resin was cured for 1 h at room temperature followed by heating to 80 °C at a rate of $2\,°C\,min^{-1}$ and kept at this
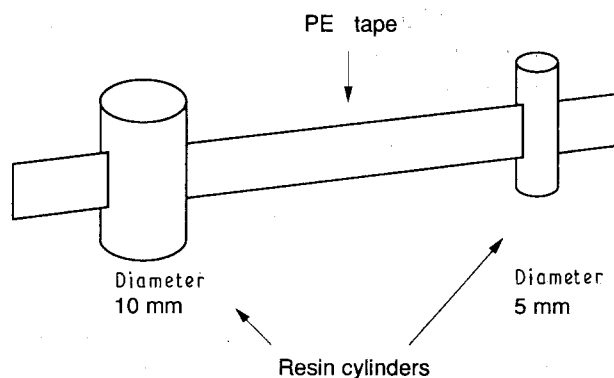

Figure 1 Pull-out specimen.

temperature for 1.5 h. After curing, and prior to testing, the samples were stored in a conditioned chamber (23 °C, 50% RH). Tests were run on an Instron tensile testing machine using specially designed grips. The crosshead speed was $10\,mm\,min^{-1}$. The adhesion was defined as the failure load divided by the interface area. At least six measurements were made for each value of adhesion strength and average values were taken.

2.4. Determination of mechanical properties

Tensile tests were performed on a Zwick Rel tensile machine. Closed-loop operation made accurate constant strain-rate experiments possible. The PE tapes were tested at a strain rate of $10\%\,min^{-1}$ in accordance with ASTM D-76. Initial cross-sectional areas, used for calculating Young's modulus and tensile strength, were obtained from the mass and the length of the tapes assuming a crystal density of $10^3\,kg\,cm^{-3}$. The values given are the average of at least six experiments.

2.5. X-ray photoelectron spectroscopy

X-ray photoelectron spectroscopy (XPS) spectra were recorded on a Physical Electronics 550 XPS/AES spectrometer equipped with a magnesium X-ray source and a double pass cylindrical analyser. Spectra were recorded in steps of 0.05 eV. The pressure did not exceed 5×10^{-8} torr (1 torr = 133.322 Pa), and the temperature was approximately 293 K. Operating conditions of the X-ray source were 10 kV and 40 mA. A sweeptime of 10 min was used for complete spectral scans, while for detailed recordings a sweeptime of 20 min per element was used. The sample was placed under an angle of 50° towards the analyser, giving a probing depth of about 4 nm for the electrons of the c_{1s} XPS line.

2.6. Infrared spectroscopy

Fourier transform reflection infrared spectra were obtained using either a Perkin–Elmer 1750 equipped with a 1 GE-TRG attenuated total reflection (ATR) unit or a Nicolet 20 SXB equipped with a Specac ATR unit. A germanium crystal (45° face angle) was used at a nominal angle of incidence of 45°. Under these conditions the penetration depth was about 400 nm at a wavelength of 10 μm.

2.7. Scanning electron microscopy

Scanning electron micrographs were taken with a Camscan 4-DV. A voltage of 20 kV was used, while the tapes were pressed in silver paint to ensure a good conductivity. The samples were first coated with carbon using an Emscope TB-500 Carbonstring coater. Secondly a gold/palladium (80/20 wt/wt) coating was applied in a Polaron E-5000 diode sputtercoater. The coating thus applied had a total thickness of about 50 nm.

3. Results

3.1. Adhesion versus mechanical properties

The effect of exposure time to acids on the adhesion and tensile strength is shown in Figs 2 and 3, and Table I. The time of exposure had no influence on the Young's modulus of 140 GPa. Chlorosulphonic acid
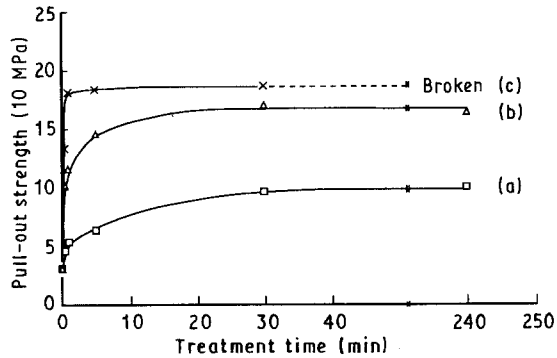

Figure 2 Pull-out strength as a function of treatment time for (a) chlorosulphonic acid, (b) chromic acid, and (c) $KMnO_4/H_2O/H_2SO_4$.
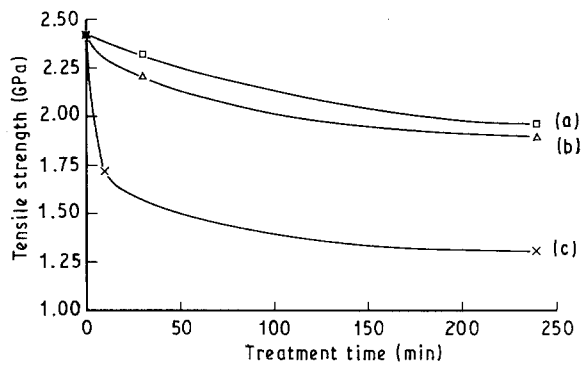

Figure 3 Tensile strength of the PE tapes as a function of treatment time for (a) chlorosulphonic acid, (b) chromic acid, and (c) $KMnO_4/H_2O/H_2SO_4$.

and chromic acid only slightly affects the tensile strength of PE even after prolonged exposure. Postema *et al.* [16] reported a greater decrease in tensile strength after exposure of gel-spun PE fibres to chlorosulphonic acid. This difference can be explained by the more severe conditions, i.e. higher temperatures, used in these studies. The system $KMnO_4/H_2O/$ H_2SO_4 had a marked influence on the tensile strength of the PE tapes. Consequently, tensile failure rather than pull-out occurred for the PE sample exposed to $KMnO_4/H_2O/H_2SO_4$ for 240 min (Fig. 2, Table I). Fig. 2 also shows that the levelling off of the adhesion value increases in the order chlorosulphonic acid, chromic acid, $KMnO_4/H_2O/H_2SO_4$, i.e. with the oxidation power of the acids applied [18]. The opposite order was found for the time required to reach this levelling off value.

3.2. Scanning electron microscopy

The surface of an untreated PE tape, as shown in Fig. 4a, is rather smooth except for the typical microfibrillar structure caused by the hot-drawing process. No change in surface roughness was observed up to 10 min exposure to $KMnO_4/H_2O/H_2SO_4$ (Fig. 4d). Upon further exposure a distinct texture developed, the result of degradation and dissolution of material (Fig. 4e). Prolonged exposure (240 min) is accompanied by an extensive loss of material producing a highly irregular surface (Fig. 4f). In contrast, no evidence of an increase in surface roughness was found after prolonged exposure to chlorosulphonic or chromic acid (Fig. 4b, c).

The regions of the PE tapes embedded in the epoxy resin and subjected to the pull-out test were also examined. Apparently, there was no difference in the appearance of the chlorosulphonic and chromic acid-treated PE surfaces before and after pull-out, suggesting that failure occurred at the interface. A typical

TABLE I Adhesion, tensile strength and surface composition of acid-etched oriented PE tapes

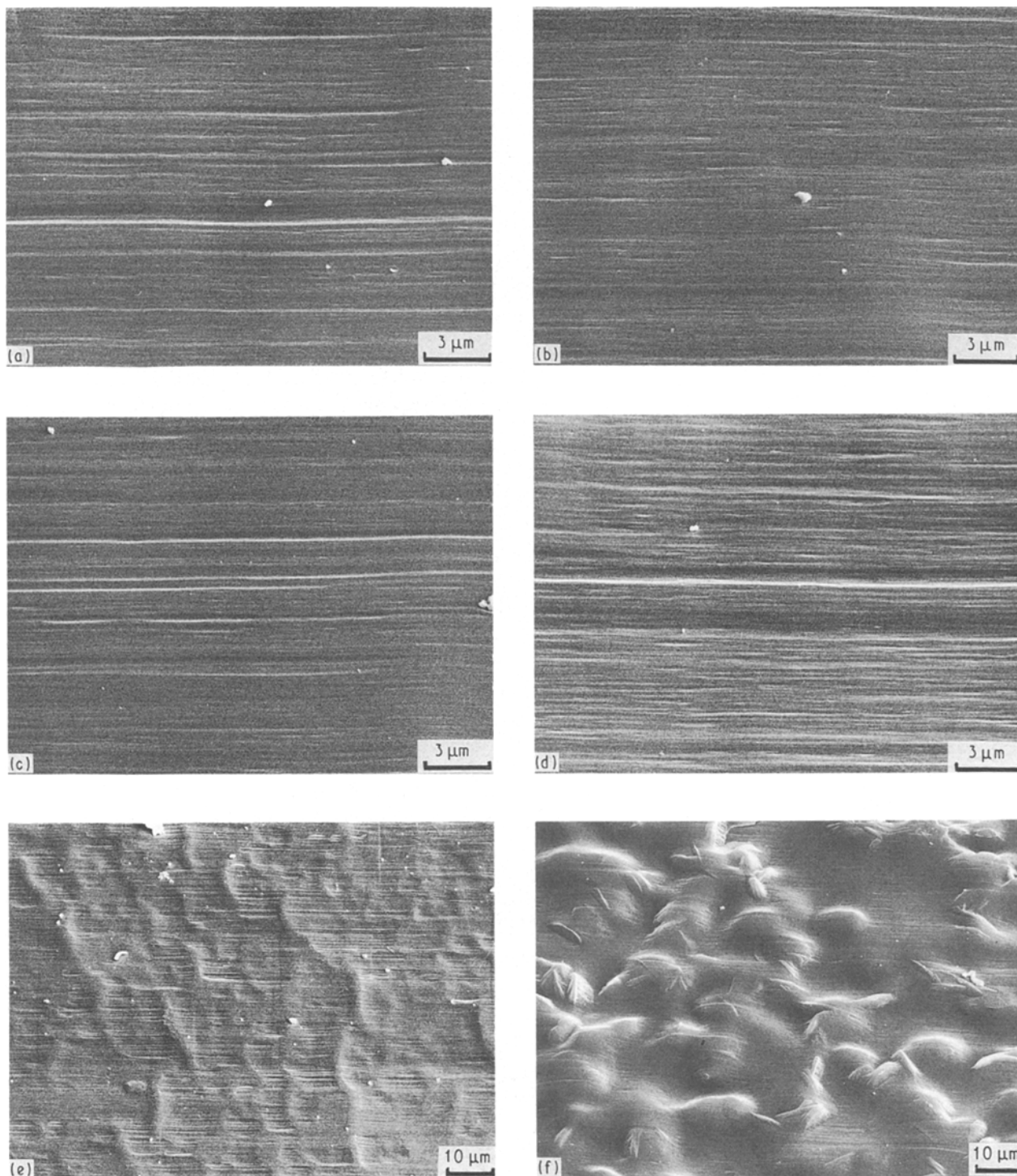| Treatment	Time (min)	Pull-out strength (MPa)	Tensile strength (GPa)	Surface composition atomic %			O/C atomic ratio. ($\times 10^2$)
				C	O	S	
None	–	0.31	2.42	97.5	2.5	–	2.6
Chlorosulphonic acid	0.5	0.45		95.0	4.6	0.4	4.8
	1	0.54		92.9	6.8	0.3	7.3
	5	0.65		93.2	6.4	0.4	6.9
	30	1.00	2.33	90.3	8.7	1.0	9.6
	240	1.07	1.98	91.3	7.4	1.3	8.1
Chromic acid	0.5	1.02		87.7	11.5	0.8	13.1
	1	1.16		87.3	12.2	0.5	14.0
	5	1.46		83.6	15.3	1.1	18.3
	30	1.73	2.21	88.6	10.6	0.8	12.0
	240	1.70	1.91	90.9	8.3	0.8	9.1
$KMnO_4/H_2O/$ H_2SO_4	0.5	1.33		86.1	13.9	–	16.1
	1	1.84		87.7	12.0	0.3	13.7
	5	1.86		89.0	10.9	0.1	12.2
	10		1.72				
	30	1.90					
	240	Tape broken	1.32				

Figure 4 Scanning electron micrographs of acid-etched PE tapes: (a) untreated; (b) chlorosulphonic acid, 240 min; (c) chromic acid, 240 min; (d) $KMnO_4/H_2O/H_2SO_4$, 10 min; (e) $KMnO_4/H_2O/H_2SO_4$, 30 min; (f) $KMnO_4/H_2O/H_2SO_4$, 240 min.

example of the groove in the epoxy matrix, left after pull-out of untreated, chromic or chlorosulphonic acid-treated PE tapes is seen in Fig. 5a. Note that even the typical microfibrillar structure present at the surfaces of these tapes are faithfully replicated in the matrix. It thus appears that even untreated PE tapes are completely wetted by the liquid resin. In the case of $KMnO_4/H_2O/H_2SO_4$ (5 min)-treated PE the situation is quite different. Localized spots of drawn material are visible at the surface of the pulled tapes as well as on the surface of the groove left after pull-out (Fig. 5b), suggesting the forcible removal of the top surface layer during pull-out. Further evidence for this

is obtained by treating the groove left after pull-out of a $KMnO_4/H_2O/H_2SO_4$ (5 min)-treated PE tape with hot (120 °C) xylene, a known solvent for PE (Fig. 5c). Clearly the adhering PE has dissolved, leaving a surface that shows a quite good resemblance to the original $KMnO_4/H_2O/H_2SO_4$ (5 min)-treated PE surface.

3.3. Weight loss

No weight loss was detectable for chromic or chlorosulphonic acid-treated PE samples, not even after prolonged exposure (18 h). Prolonged exposure to
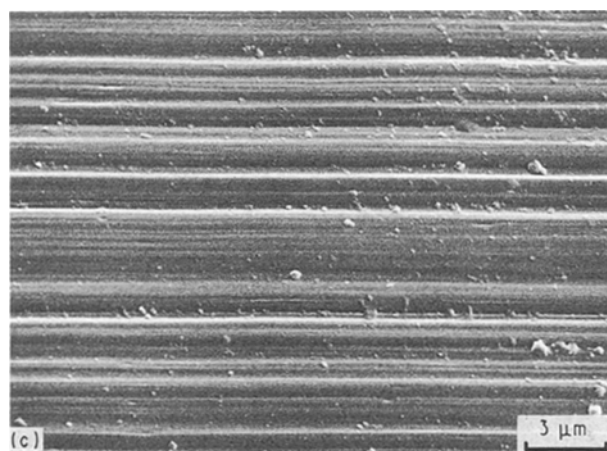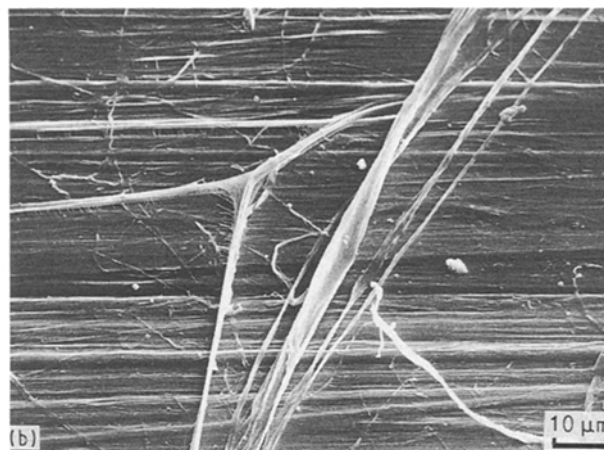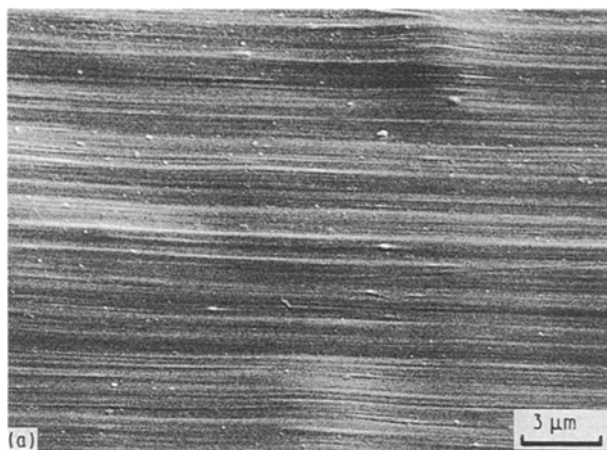
Figure 5 Typical examples of scanning electron micrographs of the grooves left after pull-out of (a) untreated, chromic or chlorosulphonic acid-treated PE tapes, (b) $KMnO_4/H_2O/H_2SO_4$ (5 min) -treated PE tapes, and (c) as (b) followed by treatment with hot (120 °C) xylene.

$KMnO_4/H_2O/H_2SO_4$, however, resulted in the partial degradation and dissolution of the PE tape (up to 67% weight loss).

3.4. Infrared spectroscopy

The reflection infrared spectra of treated and untreated PE tapes were identical in all cases, i.e. no oxidation products could be detected. Contrary to reflection infrared spectroscopy, X-ray photo electron spectroscopy (XPS) showed oxidation to have taken place (see Section 3.5). The sensitivity of surface analysis is far better for XPS with shallow penetration (4 nm) than for reflection infrared spectroscopy, because of its deep penetration (400 nm). The fact that reflection infrared spectroscopy failed to detect any chemical changes, indicates that the etching/oxidation is confined to the outermost surface layers.

3.5. X-ray photoelectron spectroscopy

The amount of carbon, oxygen and sulphur as detected by XPS is shown in Table I. In some cases (chlorosulphonic acid treatment), we also found traces of chlorine ($\ll 1\%$). The amount of oxygen incorporated at the surface initially increases with time of treatment. It seems that the gradient of this initial increase is proportional to the oxidation power of the acids applied. For longer treatment times the oxygen content reaches a maximum, after which it slowly levels off in all cases.

The surface chemical composition of three differently treated PE samples prior to, and after pull-out were determined. The samples investigated were chosen in such a way that a stepwise increase in adhesion level was obtained. No traces of nitrogen were detected, indicating that epoxy, i.e. amine hardener, was not present at the surface of the pulled samples. Consequently, matrix failure during pull-out can be ruled out. The O_{1s}:C_{1s} peak intensity ratios for these samples are shown in Table II. Comparison of the two columns shows that the degree of oxidation before and after pull-out is within the experimental error (12%), for both the chlorosulphonic and chromic acid-treated samples. This suggests that failure occurs at the interface. The $KMnO_4/H_2O/H_2SO_4$ treated sample, on the other hand, showed a significant decrease in oxygen content. This is attributed to failure inside the PE tape, removing the highly oxidized surface layer, in agreement with the results obtained by SEM.

The binding energy of carbon (1s) in hydrocarbons is 285 eV. Introduction of oxygen induces a chemical shift, only for those carbon atoms chemically bonded to oxygen, to higher binding energies. These shifts are 1.5 eV for hydroxyl, 3.0 eV for carbonyl and 4–4.5 eV for carboxyl groups [19]. The presence of SO_3H groups was concluded from the position of the S_{2p} peak and tabulated data [20, 21]. The C_{1s} spectra of several treated PE tapes as well as untreated PE tape are shown in Fig. 6. Note the tailing of the C_{1s} peak on the high-energy side of the treated samples. In almost all cases shown this tail extends up to 5 eV, indicating the presence of hydroxyl, carbonyl and carboxyl groups. The time of exposure had no influence on the general shape of the C_{1s} spectra of chromic acid and $KMnO_4/H_2O/H_2SO_4$-treated samples. Hence, it is concluded, that the same functional groups are present in all samples. This does not imply that the number of individual functional groups present are not subject to change. Differences were encountered

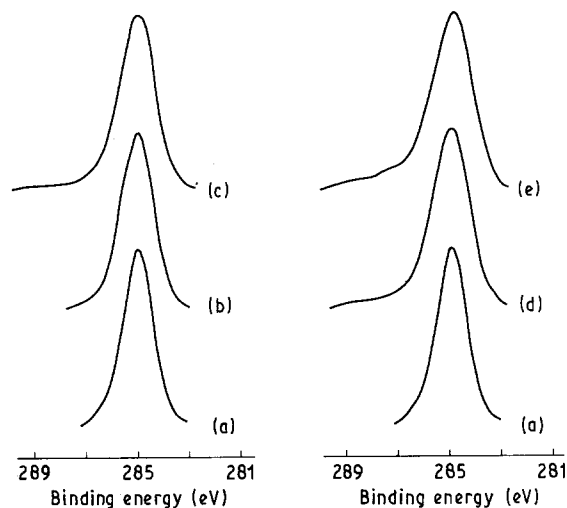| Treatment	Time (min)	Pull-out strength (MPa)	O/C atomic ratio ($\times 10^2$)	
			Before pull-out	After pull-out
Chlorosulphonic acid	30	1.00	9.6	8.5
Chromic acid	5	1.46	18.3	16.2
$KMnO_4/H_2O/H_2SO_4$	5	1.86	12.2	5.8

Figure 6 High-resolution C_{1s} spectra of acid-etched PE tapes: (both a) untreated; (b) chlorosulphonic acid, 5 min; (c) chlorosulphonic acid, 30 min; (d) chromic acid, 5 min; (e) $KMnO_4/H_2O/H_2SO_4$, 5 min.

when the C_{1s} spectra of PE tapes exposed to chlorosulphonic acid for less than 30 min were examined; in this case the tailing was limited to 3.5 eV, indicating that carboxyl groups were not present.

4. Discussion

As can be inferred from Table I and Fig. 2, adhesion of PE to epoxy resin is greatly enhanced by pretreatment of PE with oxidizing acids. The maximum increase in adhesion, as determined by pull-out, is 600% for $KMnO_4/H_2O/H_2SO_4$ treatment. Chlorosulphonic and chromic acid treatment improves the adhesion by 300% and 550%, respectively. Of course, these values are only valid for the reaction conditions used. It is interesting to note that this improvement in adhesion can be achieved without a severe loss in tensile strength and modulus. This is illustrated by Table III, which gives the etching time necessary to reach maximum adhesion as well as the corresponding tensile strength of the PE tapes. The remaining tensile strength was, regardless of type of treatment, 2.2–2.3 GPa, a drop of 10% or less compared to the initial value of 2.4 GPa. Prolonged exposures resulted in a further loss in tensile strength without further improvement in adhesion.

The etching of polyolefins and model compounds by chromic acid is well documented [22–25]. According to the literature, hydroxyl groups are the first species formed, and further oxidation causes chain scission to give carbonyl/aldehyde or carboxyl groups.

TABLE III The etching time required to reach maximum adhesion (Fig. 2) and the corresponding tensile strength (Fig. 3) of the PE tapes

Treatment	Time (min)	Tensile strength (GPa)
Chlorosulphonic acid	30	2.3
Chromic acid	30	2.2
$KMnO_4/H_2O/H_2SO_4$	1	2.2

It is likely that the other two acids follow the same scheme, although no comprehensive information is available. The presence of carbonyl and carboxyl groups, at the surface of the treated tapes, as detected by XPS, indicates that chain scission has taken place. Consequently, these broken chain ends act as flaws, initiating failure of the PE tape. This explains the observed decrease in tensile strength of the PE tapes upon exposure to chlorosulphonic acid, chromic acid, $KMnO_4/H_2O/H_2SO_4$.

The improved adhesion of polyolefins to epoxy resin after acid etching can, in general, be related to:

1. surface roughening;
2. an increase in the surface free energy, and consequently the wettability of the surface is improved, and the interfacial energy increases;
3. the introduction of specific functional groups, giving rise to an increase in the chemical/physical interaction at the interface; or
4. a combination of these [4, 9, 23]. However, it should be noted here that these factors are mutually dependent. This makes it difficult to distinguish the influence of one specific factor from the others.

SEM observations showed that chlorosulphonic and chromic acid treatment do not produce significant changes in surface topography. Consequently, surface roughening can be ruled out as a reason for the improved adhesion. A somewhat different situation is encountered for the $KMnO_4/H_2O/H_2SO_4$-treated tapes. The surface of a 1 or 5 min etched tape is quite smooth and comparable to an untreated tape, whereas a 30 or 240 min-treated tape is visibly etched. These differences are not reflected in the adhesion values which are equal within experimental error (Fig. 2, Table I). Examination by SEM and XPS of the 5 min $KMnO_4/H_2O/H_2SO_4$-treated tapes after pull-out, revealed that failure occurred inside the tape and not at the interface. Consequently, the increase in adhesion is not brought about by surface roughening. All the PE surfaces, treated as well as untreated, were completely
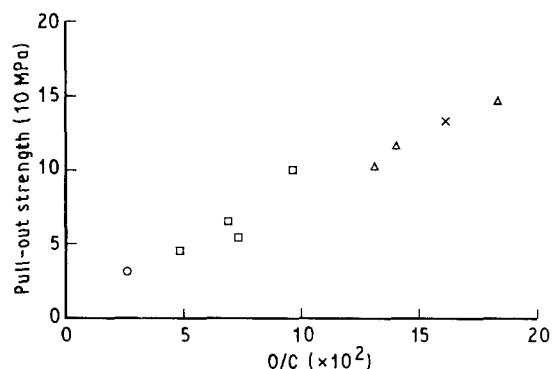
Figure 7 Pull-out strength as a function of the O/C ratio; data taken from Table I. ($\bigcirc$) control; ($\square$) chlorosulphonic acid, 0–30 min; ($\triangle$) chromic acid, 0–5 min; ($\times$) $KMnO_4/H_2O/H_2SO_4$, 0–0.5 min.

wetted by the epoxy resin as shown by SEM examination of the groove left after pull-out. Hence, differences in wetting as an explanation can be ruled out too. The increase in adhesion is solely caused by the introduction of functional groups. XPS showed these groups to be hydroxyl, carbonyl, carboxyl and sulphonic acid. They are the result from oxidation of the PE by the various acid treatments. As a first approximation we tried to relate the improved adhesion to the amount of oxygen, relative to carbon, i.e. the O/C ratio. Fig. 7 shows that a linear correlation exists during the initial stages of oxidation. No such correlation is observed when the overall O/C adhesion data are plotted in the same figure. This is not surprising. With increasing oxidation the type and number of functional groups are subjected to changes. Furthermore, the various groups differ in their efficiency to improve the adhesion to epoxy resins [9]. Consequently, an exact knowledge of the type and number of the different groups present at the surface is required, to relate the differences in adhesion to time or type of treatment, rather than the amount of oxygen introduced.

In conclusion, SEM and XPS studies showed that the improved adhesion to epoxy resin after pretreatment with chlorosulphonic acid, chromic acid or $KMnO_4/H_2O/H_2SO_4$ is brought about by the introduction of functional groups. Furthermore, at the highest level of adhesion obtained (1.8–1.9 MPa), the limiting factor is no longer adhesion, but the transverse and shear strength of the PE tapes.

Acknowledgements

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