Improved adhesive properties of high-modulus polyethylene structures: 3. Air- and ammonia-plasma treatment

F. P. M. Mercx
TNO Plastics and Rubber Research Institute, PO Box 6031, 2600 JA Delft, The Netherlands
(Received 11 June 1993; revised 27 July 1993)

Air- and ammonia-plasma treatments markedly improve the adhesion of gel-spun high-modulus polyethylene (PE) tapes to epoxy resin, as measured by pull-out and evidenced by the change in failure mode from interface controlled to shear failure within the PE. By monitoring the changes in wetting, surface topography and surface composition, the factors responsible for the adhesion could be identified. These results suggest that for air-plasma-treated PE tapes the adhesion depends on (1) the physicochemical interaction between the various carbon–oxygen functionalities and the epoxy resin, (2) mechanical interlocking, and (3) non-polar dispersion forces. The pull-out strength is the sum of these three terms and their contributions in this specific system are about 76%, 12% and 12%, respectively. Physicochemical interactions of the amine groups, in addition to non-polar dispersion forces, determine the adhesion of ammonia-plasma-treated PE tapes to epoxy resin. Their contributions are 87% and 13%, respectively.

(Keywords: polyethylene; plasma treatment; adhesion)

INTRODUCTION

Oriented polyethylene (PE) structures with moduli in excess of 100 GPa and tensile strengths of 2–4 GPa can be produced by the so-called gel-spinning method[1,2]. The low density of these structures, compared to aramid or carbon fibres, offers the opportunity to develop composites with strength-to-weight ratios never before obtainable[3]. For most applications, an adequate adhesion between reinforcement and matrix is necessary to impart the properties of the reinforcement to the composite[4,5]. A low level of adhesion is mandatory only in composites for impact or ballistic applications. The adhesion between oriented PE structures and most matrices is poor, owing to the apolar nature and smooth surface, which prevent chemical as well as mechanical bonding. Several methods have been developed to overcome this problem. Among these are acid etching[6–9], corona treatment[10], and the surface grafting of acrylic acid after photoirradiation[11] or inert gas corona[12]. Plasma treatment has also been investigated[6,7,13–23]. In fact, it is the most widely used technique both commercially and scientifically to improve the adhesion of high-modulus PE structures. In a plasma process, gas molecules are dissociated into ions, electrons, free radicals and neutral species. The interaction of these species with the surface of the PE causes chemical and/or physical changes in a thin surface layer (1–100 nm). The type of plasma employed depends to a large extent on the chemistry of the resin used. For PE-reinforced epoxy and polyester composites, mainly air-[14,15,17], oxygen-[6,7,13,16,18–20] and ammonia-[19–23] plasma treatments are used to increase the level of adhesion.

Air or oxygen plasma contains a mixture of active oxygen species, mainly atomic oxygen[24], and leads to oxidation of the PE. As a result, a variety of functional groups are introduced onto the surface, including hydroxyl, carbonyl, ester and carboxylic acid groups[14–17,19]. Surface roughening of the PE fibres, after air- or oxygen-plasma treatment, was noted in some of the investigations[6,7,13,14,16,18]. Recently, Tissington *et al.*[16] reported the formation of a crosslinked skin, which was associated with the intense u.v. radiation of the oxygen plasma at higher input powers. Treatment of the high-modulus PE fibres with air or oxygen plasma markedly improved the adhesion to epoxy and polyester resins and resulted in a change in failure mode from interface controlled to internal shear within the PE fibre[6,7,13,18–20,25]. There exists much controversy over the importance of the changes brought about by these treatments and, consequently, over the mechanism responsible for the increased adhesion. The discussion focuses on the importance of weak boundary layers, wetting/wettability, surface topography and specific interactions.

The composition of an ammonia plasma has been investigated by d'Agostino *et al.*[26]. Several radicals exist in the plasma, including hydrogen, and primary and secondary amine radicals. Owing to the different reaction rates of the formation and disappearance of these radicals, the concentration of primary amine radicals is much larger than that of the other radicals. From this observation d'Agostino concluded that the primary amine radical is the species most likely to react with surface radicals, resulting in the incorporation of primary amine groups on the substrate. Amine functional groups have indeed been identified by dye exchange[19–22] and/or X-ray photoelectron spectroscopy measurements[19] on the surface of high-modulus PE fibres subjected to ammonia plasma. Scanning electron micrographs showed

0032-3861/94/10/2098–10

no change in the surface texture[21,23]. Fracture surface analysis revealed different failure modes for composites made of ammonia-plasma-treated PE fibres. Fibrilliation, which is indicative of shear failure within the PE fibres, is reported by several authors[19–21]. Contrary to this, clean interface failure was observed by Li *et al.*[23]. Although no conclusive evidence was gathered, improved wetting and covalent bonding[19,22] have been mentioned as the mechanisms responsible for the improvement in adhesion of the ammonia-plasma-treated fibres to epoxy resins. The increase in adhesion to vinylester resins has been attributed to non-covalent interactions[20].

In this study we investigate the effect of air- and ammonia-plasma treatment on gel-spun high-modulus PE structures by surface analytical techniques in addition to mechanical tests. Furthermore, the relationship between surface chemistry, surface topography and the adhesion is examined. The main purpose of the study is to assess the mechanisms responsible for the increased adhesion as a result of air- or ammonia-plasma treatment.

EXPERIMENTAL

Polyethylene tapes

Oriented PE tapes were employed in this study. These were obtained by ultradrawing cast films as described previously[27], except that decalin was replaced by xylene in the preparation procedure. The cast films were drawn on hot shoes ($T=125°C$) to $\lambda=60$. The PE used was Hostalen Gur 412 with a weight average molar mass (M_w) of about $1.5\times10^3\,kg\,mol^{-1}$. Stabilizer and 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 $10\%\,min^{-1}$). It should be noted here that the tapes obtained by this batchwise process are identical to those obtained by gel-spinning, precluding that the concentration of the PE solution and the draw ratio are the same.

Plasma treatment

Plasma treatment was performed using a plasma apparatus developed at the TNO laboratories in Delft. It consists basically of a reaction chamber (Pyrex glass, 146 mm long, 25 mm diameter), a radiofrequency generator and a vacuum system. The reaction chamber is fitted with a gas inlet, a pressure gauge, an externally placed inductive copper coil (10 turns, 90 mm long) and an exhaust valve. A 13.56 MHz radiofrequency generator (ENI ACG-3), coupled to a matching impedance network (Astech ATH-50) to minimize the reflected power, was employed for all the experiments. Pressure was measured continuously using a membrane pressure gauge (MKS Baratron 222B). Either dry air (Hoekloos, $\geqslant$99.9% pure) or ammonia (Hoekloos, $\geqslant$99.5% pure) was used as plasma gas.

The standard experimental procedure consisted of evacuation ($P_{min}=133.3\,mPa$) of the reactor for 5 min followed by bleeding in the plasma gas ($P=66.6\,Pa$) for 5 min before initiating the plasma. The flow rate (not measured) was adjusted in such a way that the pressure remained constant at the desired level. Following plasma treatment, the samples were kept in flowing gas for 5 min before the reactor was evacuated once again and air admitted to raise the pressure to environmental conditions. This was done to allow for the decay of residual free radicals. All treated samples were stored in a desiccator over P_2O_5.

Determination of adhesion

Pull-out tests were performed on specimens, as illustrated in *Figure 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, subsequently heated to 80°C at a rate of $2°C\,min^{-1}$ and kept at this temperature for 1.5 h. After curing, and prior to testing, the samples were stored in a conditioned room (23°C, 50% r.h.). 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 average value of the adhesion strength.

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 the calculation of Young's modulus and tensile strength, were obtained from the mass and the length of the tapes assuming a crystal density of $10^3\,kg\,m^{-3}$. The values given are the average of at least six measurements.

X-ray photoelectron spectroscopy

X-ray photoelectron spectroscopy (X.p.s.) 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 6.7×10^{-6} Pa, and the operating 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 at an angle of 50° to the analyser, giving a probing depth of about 4 nm for the electrons of the C_{1s} X.p.s. line.

Infra-red spectroscopy

Fourier transform reflection i.r. spectra were obtained using a Perkin Elmer 1750 spectrometer equipped with a 1 GE-TRG attenuated total reflection (a.t.r.) unit or a Nicolet 20 SXB spectrometer equipped with a Specac ATR unit. A germanium crystal (45° face angle) was used

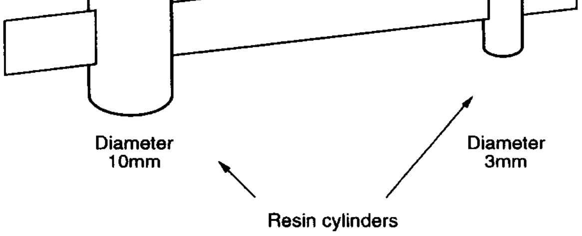

Figure 1 Pull-out specimen

at a nominal angle of incidence of 45°. Under these conditions the penetration depth was about 400 nm at a wavelength of 10 μm.

Scanning electron microscopy

Scanning electron microscopy (SEM) was carried out with a Camscan 4-DV. SEM micrographs of the air-plasma-treated PE tapes were taken at an angle of 45° to enhance the topological features. The samples were first coated with carbon using an Emscope TB-500 Carbonstring coater. Then a platina coating was applied in an Ion-Tech B50 ion-beam sputter coater. The coating thus applied had a total thickness of about 25 nm. A voltage of 20 kV or less was used, while the tapes were pressed in silver paint to ensure a good conductivity.

Direct observation of the groove resulting from pull-out was in some cases obstructed by the slow degradation of the epoxy by the electron beam. Therefore negative replicas were studied, made by the following procedure. First a layer of silver was applied on top of the epoxy, using a Leybold Hereaus EPA-100 sputter unit. The mechanical strength of the silver layer was increased by electrochemical treatment with a $CuSO_4/H_2SO_4$ solution (250 g $CuSO_4$, 40 ml conc. H_2SO_4, 960 ml H_2O, current density 0.06 A cm^{-2}). The resulting negative replica could then be lifted easily from the epoxy. These replicas were coated in the same way as described above for direct comparison with the corresponding PE tapes.

INFLUENCE OF PROCESS PARAMETERS

The plasma parameters that could be changed during the course of the experiments were residence time, pressure and input power. To study the influence of these variables, a wide range of air-plasma experiments was performed. Residence time was varied from 5 s to 5 min, with pressures ranging from 20.0 to 66.6 Pa. Input power could not be changed substantially. To initiate the plasma, a minimum input power of about 9 W was required. In practice, we therefore used a lower limit of 10 W. On the other hand, an excessive input power ($\geqslant$30 W) instantly melted the PE tape. This melting was not solely governed by power, but by residence time as well. At an input power of 25 W the residence time had to be kept below 120 s, and below 300 s for an input power of 10 W, in order to prevent melting. In contrast to this, no practical limits were found for the ammonia-plasma treatment.

All the air-plasma treatments markedly enhanced the adhesion to epoxy resin. Input power proved to be the only significant variable. With an increase in input power, the shear strength increased and reached a maximum at 25 W. Variations in residence time or pressure had no effect on the adhesion values obtained. SEM and X.p.s. examination of the treated and untreated PE tapes revealed the following. Air-plasma treatment produced a dramatic change in the appearance of the PE surface. Wereas the untreated PE tapes were relatively smooth, air-plasma-treated tapes showed a pitted surface. The size and shape of these pits appeared to be insensitive to changes in the process variables. A range of oxidation products was found at the surface of the PE tapes after air-plasma treatment. These included hydroxyl, carbonyl and carboxylic acid groups. The degree of oxidation was controlled by the input power and was independent of residence time and pressure. This indicates that oxidation of the surface was already complete within a few seconds, a feature reported by many other investigators[16,17]. Prolonged exposure only resulted in an increase in depth of oxidation, or alternatively a mechanism of simultaneous oxidation and ablation was operative.

No attempt was undertaken to investigate in detail the effect of the process variables on the adhesion of ammonia-plasma-treated PE tapes. As a result of the above experiments, input power was the only variable taken into account in the main experiments, the results of which are reported below. A fixed residence time of 30 s was employed. The pressure was kept constant at 66.6 Pa.

RESULTS AND DISCUSSION

Tape characterization

X.p.s., i.r. spectroscopy, SEM and mechanical tests were used to characterize the PE tapes before and after plasma treatment. *Table 1* shows the surface chemical composition of the untreated and plasma-treated PE tapes, as measured with X.p.s. The amount of oxidation is evident in the oxygen/carbon ratios and the amount of amination in the nitrogen/carbon ratios.

Detailed information about the nature of the incorporated groups can be derived from the high resolution C_{1s}, O_{1s} and N_{1s} spectra taken, of which the C_{1s} is the most informative. The binding energy of carbon (1s) in hydrocarbon is 285 eV. Introduction of oxygen induces a chemical shift to higher binding energies for those carbon atoms chemically bonded to oxygen. These shifts are 1.5 eV for hydroxyl/ether, 3.0 eV for carbonyl/aldehyde and 4–4.5 eV for carboxylic acid/ester groups[28–30]. The chemical shift of carbon bonded to nitrogen depends on the nature of the substituents and amounts to 0.6, 1.8 and 1.8 eV for $-NH_2$, $-NCO$ and $-NO_2$, respectively[28,29]. Oxygen spectra are less informative, because a similar binding energy is often observed for oxygen atoms in different chemical environments[28–30]. The binding energy of oxygen in carbon–oxygen functionalities is usually about 532 eV, with the exception of $O{=}C{-}\underline{O}{-}$. When carboxylic acid or ester groups are detected in carbon spectra, a second contribution is also seen in the oxygen spectra, some 1.8–2.0 eV higher in binding energy. The binding energy of nitrogen in carbon–nitrogen functionalities[28,29], i.e. amines and nitriles, is 399–400 eV. Neighbouring electron withdrawing groups, for instance as found in amides and isocyanates ($C{=}O$), cause a small shift of 0.5–1.0 eV to higher binding energy. A more distinctive shift (3–4 eV) is observed in oxidized nitrogen species (NO, NO_2)[28,29].

X.p.s., air plasma. The C_{1s} and O_{1s} spectra of untreated and air-plasma-treated PE are shown in *Figure 2.*

Table 1 Surface composition of plasma-treated PE tapes

		Surface composition (atomic %)			Atomic ratio	
Plasma	Power (W)	C	O	N	O/C	N/C
None		98.2	1.8		0.02	
Air	10	81.5	18.5		0.23	
Air	25	73.1	26.9		0.37	
Ammonia	10	88.9	2.9	8.2	0.03	0.09
Ammonia	25	88.9	3.0	8.1	0.03	0.09

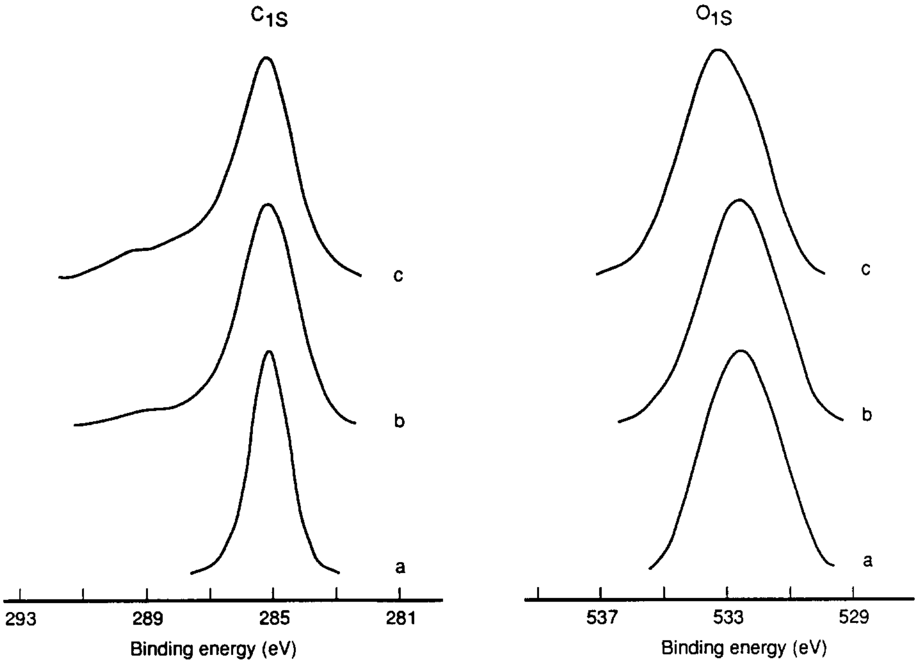

Figure 2 High-resolution C_{1s} and O_{1s} spectra of (a) untreated, (b) 10 W air-plasma-treated and (c) 25 W air-plasma-treated PE tapes (spectra are scaled to have the same peak height for comparison)

The sharp (1.5 eV at half height) and symmetrical C_{1s} peak for untreated PE indicates a single predominant species of carbon, as expected. Although no high binding energy shoulder is visually discernible in the C_{1s} peak, some minor oxidation is evidenced by the appearance of a small O_{1s} peak at 532.4 eV. Compared to untreated PE, tailing on the high energy side of the C_{1s} spectrum is observed upon 10 W air-plasma treatment. This tail extends up to 6 eV, indicating the presence of hydroxyl, carbonyl and carboxylic acid groups. The corresponding oxygen peak is located at 532.4 eV, which is consistent with carbonyl and/or hydroxyl groups. Closer examination shows that the O_{1s} curve is slightly asymmetric, with some tailing on the high energy side. Apparently a minor component with higher binding energy, assessed to carboxylic acid groups, is present. The amount of oxygen introduced increases with increasing power (*Table 1*). This is not surprising, since at a given pressure and frequency, an increase in field strength (i.e. a rise in input power) causes a correspondingly higher concentration of active species owing to the increased number of electron collisions. The resulting increase in flux of active species at the PE surface may enhance the rates of the oxidation reaction. A comparison of the C_{1s} spectra of 10 and 25 W air-plasma-treated PE tapes reveals that the extent of tailing is identical for both spectra. Hence the same type of functional groups are present at the surface, although the concentration of the different groups changes with input power. Lineshape analysis indicates an increased concentration of carbonyl and, especially, carboxylic acid groups at the surface of the 25 W treated sample. The corresponding oxygen curve is located at 533.1 eV, intermediate between the binding energy of oxygen in carbonyl (532.4 eV) and carboxyl ($O{=}C{-}\underline{O}$, 533.9 eV) groups. The shift of 0.7 eV, compared to the O_{1s} spectrum of a 10 W treated PE sample, tends to confirm the introduction of a substantial amount of carboxylic acid groups.

X.p.s., ammonia plasma. The nitrogen species observed after treatment in ammonia plasma have a binding energy of 399.9 eV, regardless of the input power used (*Figure 3*). Furthermore, as judged from the symmetry and sharpness of the N_{1s} peak, only one nitrogen functionality is present, which is most likely amine in nature[28–30]. The degree of amine attachment is independent of the input power (*Table 1*), as was also observed by Holmes and Schwartz[21]. Although amination prevails, some oxidation occurs, as evident from the small increase in oxygen concentration. The binding energy of 532.4 eV for oxygen, indicates that oxygen is present in the form of hydroxyl and carbonyl functionalities. A question remains regarding the source of oxygen giving rise to the observed oxidation. It may stem from system contamination by oxygen or oxygen-containing species. Another possibility is the reaction of surface free radicals with atmospheric oxygen.

Infra-red spectroscopy. In contrast to X.p.s., no traces of oxidation or amination products could be detected by reflection i.r. spectroscopy. The sensitivity of surface analysis is far better for X.p.s. with shallow penetration (4 nm) than for reflection i.r. spectroscopy (400 nm). The fact that reflection i.r. spectroscopy failed to detect any chemical changes indicates that oxidation and amination are confined to the outermost surface layers.

Scanning electron microscopy. The surface of an untreated PE tape, as shown in *Figure 4a*, is rather smooth except for the typical microfibrillar structure caused by the hot-drawing process. Air-plasma treatment resulted in severe etching of the fibres (*Figures 4b,c*), giving a pattern of short cracks on the surface, perpendicular to the drawing direction, which will be referred to as pits. This pattern is not exclusive to plasma treatment: similar, although larger, pitted structures are reported for shrinkable synthetic fibres (wool, polyamide 6.6, poly(ethylene terephthalamide) (PET)) exposed to

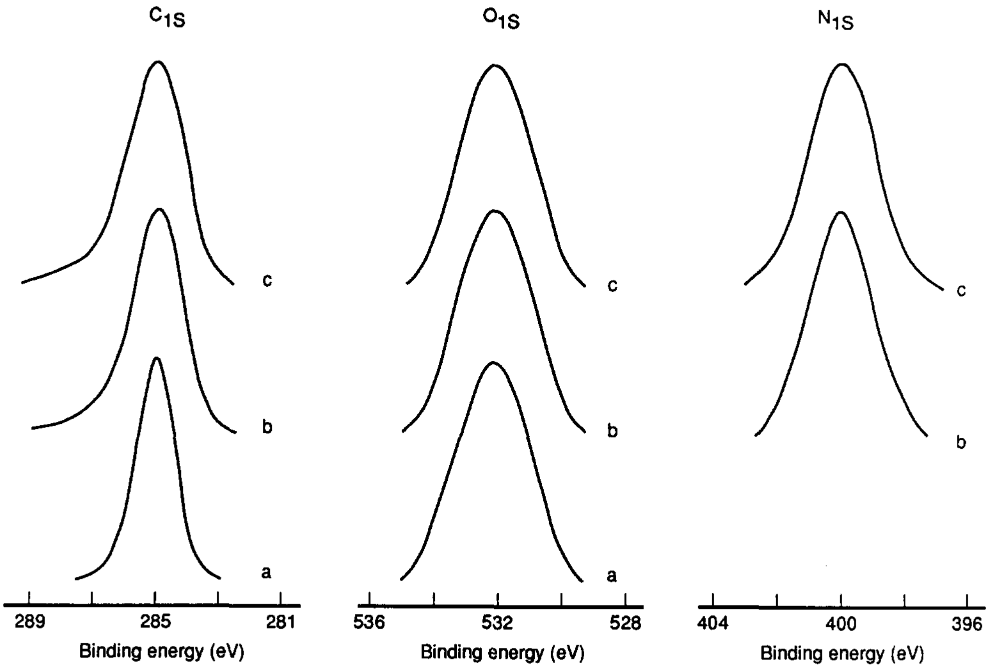

Figure 3 High-resolution C_{1s}, O_{1s} and N_{1s} spectra of (a) untreated, (b) 10 W ammonia-plasma-treated and (c) 25 W ammonia-plasma-treated PE tapes (spectra are scaled to have the same peak height for comparison)

laser excimer radiation[31,32]. A synergetic model based on thermal contributions and shrinkage behaviour was recently presented[32] to explain the development of these pitted structures. Although no conclusive evidence was gathered, our observations indicate that the conditions as found in air-plasma treatment of PE tapes and laser excimer radiation of wool, polyamide 6.6 or PET fibres are more or less identical. We therefore assume that a similar mechanism to that described by Bahners and Scholmeyer[32] is operative. In contrast to the above, no evidence of an increase in surface roughness was found after ammonia-plasma treatment (*Figures 4d,e*). Differences in topography as a function of plasma gas were also reported by Nardin and Ward[7]. They observed that upon exposure of melt-spun PE filaments to a water-vapour plasma, smaller pits were produced in comparison to exposure of similar filaments to an oxygen plasma, keeping the other conditions constant.

Crosslinking. Plasma treatment may produce crosslinking within the top surface layer[16,30,33]. To check this, we exposed the untreated and plasma-treated PE tapes to boiling xylene. For the 25 W air-plasma-treated PE tapes only, a small, initially insoluble, fraction remained ($<0.1\%$), which finally dissolved after prolonged exposure (± 1 h) to boiling xylene. This indicates that some crosslinking takes place, although the extent is not enough to produce an insoluble network. All other PE tapes instantly dissolved in the boiling xylene. The crosslinking is thought to be related to the u.v. radiation present in the plasma, which leads to chain scission and the formation of free radicals in the PE[16,24]. Owing to the competition between the recombination of the free radicals and the reaction with atomic oxygen, crosslinking can only occur when the u.v. intensity is high. Both the nature of the plasma gas and the input power have a strong influence on the u.v. intensity and may account for the differences described above.

Mechanical properties. The tensile strength of the PE tapes did not change significantly following ammonia- or 25 W air-plasma treatment (*Table 2*). A 10 W air-plasma treatment, on the other hand, caused a small decrease (10%) in tensile strength. This was attributed to the accompanying change in surface roughness. The surface pits produced are likely to act as flaws and hence reduce the tensile strength. Crosslinking of the upper surface layers increases the strength of these layers, thereby neutralizing the negative effects of the surface pits. As a result, higher values are found for the 25 W air-plasma-treated PE tapes, despite the similar surface topography of the 10 and 25 W air-plasma treated PE tapes. The Young's modulus is not affected by either air- or ammonia-plasma treatment.

Adhesion and failure mode

Plasma treatment markedly enhances the adhesion of oriented PE tapes to epoxy resin, as illustrated by *Table 2*. These results show more than a seven-fold increase in shear strength to 2.25 MPa after a 10 W air-plasma treatment. A further gain in adhesion to 2.68 MPa could be realized by raising the input power to 25 W. Ammonia-plasma-treated PE yielded shear strength values of about 2.45 MPa, independent of the input power used.

To establish the failure mode, fracture surfaces were examined by SEM and X.p.s. As shown in *Figures 4a* and *5a*, there appears to be little difference between the surface topography of the PE tapes before and after pull-out. Furthermore, X.p.s. analysis of the pulled PE tape and the groove left after pull-out showed a clean PE (*Table 3*) and epoxy surface, respectively. These results indicate that slippage along the interface is the primary mode of failure, as has been observed previously by others[6–10,13–23]. The debonded part of air-plasma-treated PE tapes exhibits a rather smooth surface with spots of drawn material (*Figure 5b*). No trace of the original pitted surface is visible. These results suggest that

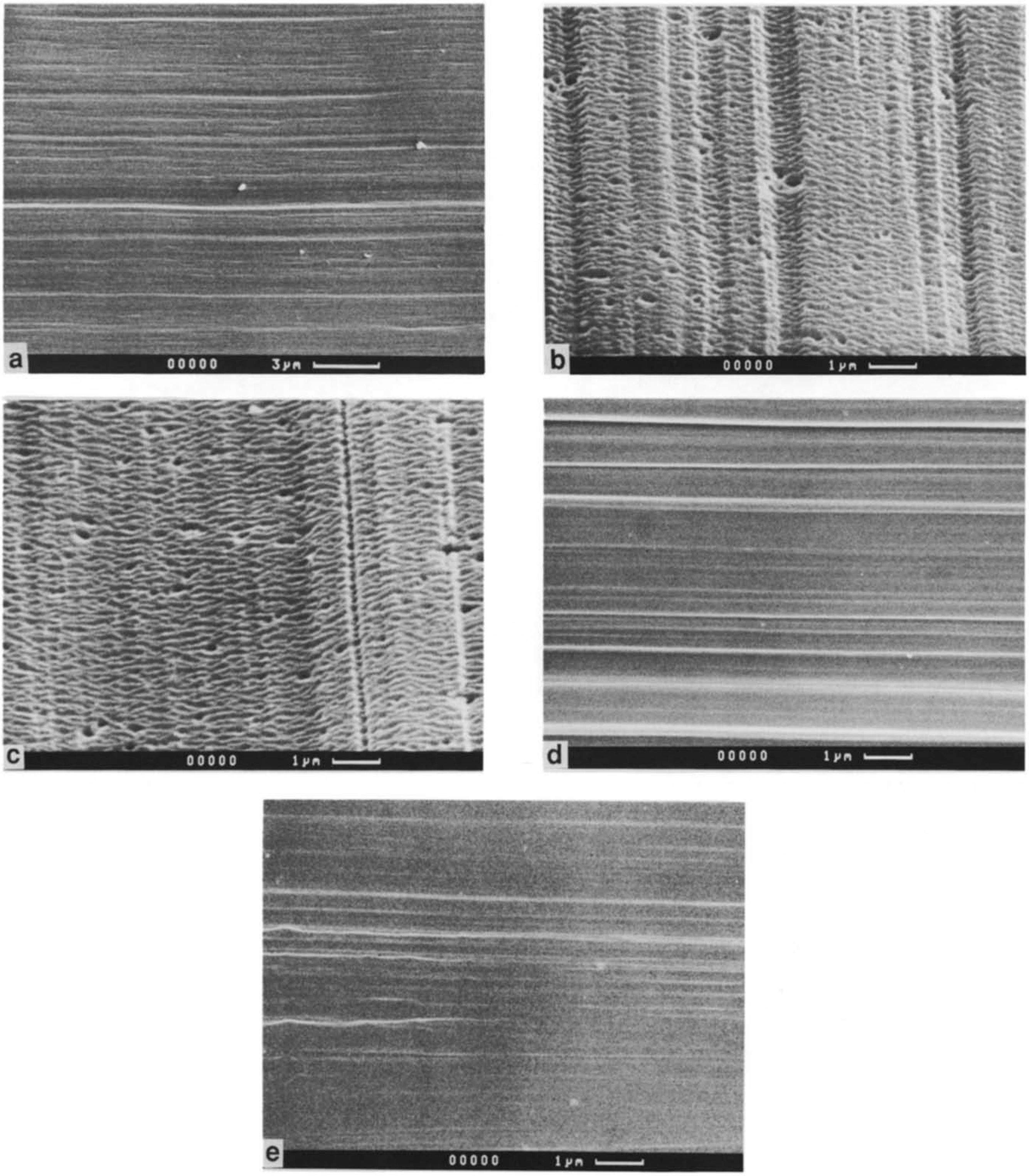

Figure 4 Scanning electron micrographs of (a) untreated, (b) 10 W air-plasma-treated, (c) 25 W air-plasma-treated, (d) 10 W ammonia-plasma-treated and (e) 25 W ammonia-plasma-treated PE tapes (drawing axis vertical for air-plasma-treated PE tapes, otherwise horizontal)

a layer of material has been removed owing to failure inside the PE tape. This is substantiated by the X.p.s. results (*Table 3*). No trace of nitrogen could be detected, indicating that epoxy resin is not present at the surface of the air-plasma-treated PE tapes after pull-out. Matrix failure can therefore be excluded and interfacial failure would not have altered the surface composition significantly. Consequently, the sharp decrease in oxygen concentration points to shear failure inside the PE removing the highly oxidized surface layer. X.p.s. was also used to unambiguously assess the failure mode of the ammonia-plasma-treated PE tapes. Following the same line of reasoning as above, the reduction in nitrogen content to virtually zero ($<0.1\%$) indicates shear failure within the PE tapes to be the primary mode of failure. The corresponding roughened fracture surface is shown in *Figure 5c*. Although all the plasma-treated PE tapes fail cohesively, failure occurs at different pull-out stresses,

Table 2 Adhesion, tensile strength and modulus of plasma-treated PE tapes

Plasma	Power (W)	Pull-out strength (MPa)[a]	Tensile strength (GPa)[a]	Modulus (GPa)[a]
None		0.32 (0.08)	2.41 (0.06)	140 (7)
Air	10	2.25 (0.09)	2.15 (0.10)	145 (4)
Air	25	2.68 (0.10)	2.29 (0.07)	138 (5)
Ammonia	10	2.44 (0.06)	2.32 (0.08)	141 (5)
Ammonia	25	2.47 (0.07)	2.37 (0.09)	136 (6)

[a] Standard deviation is given in parentheses

Table 3 Surface composition of pulled PE tapes

Plasma	Power (W)	Surface composition (atomic %)	
		C	O
None		97.9	2.1
Air	10	94.6	5.4
Air	25	93.4	6.6
Ammonia	10	94.5	5.5
Ammonia	25	95.6	4.4

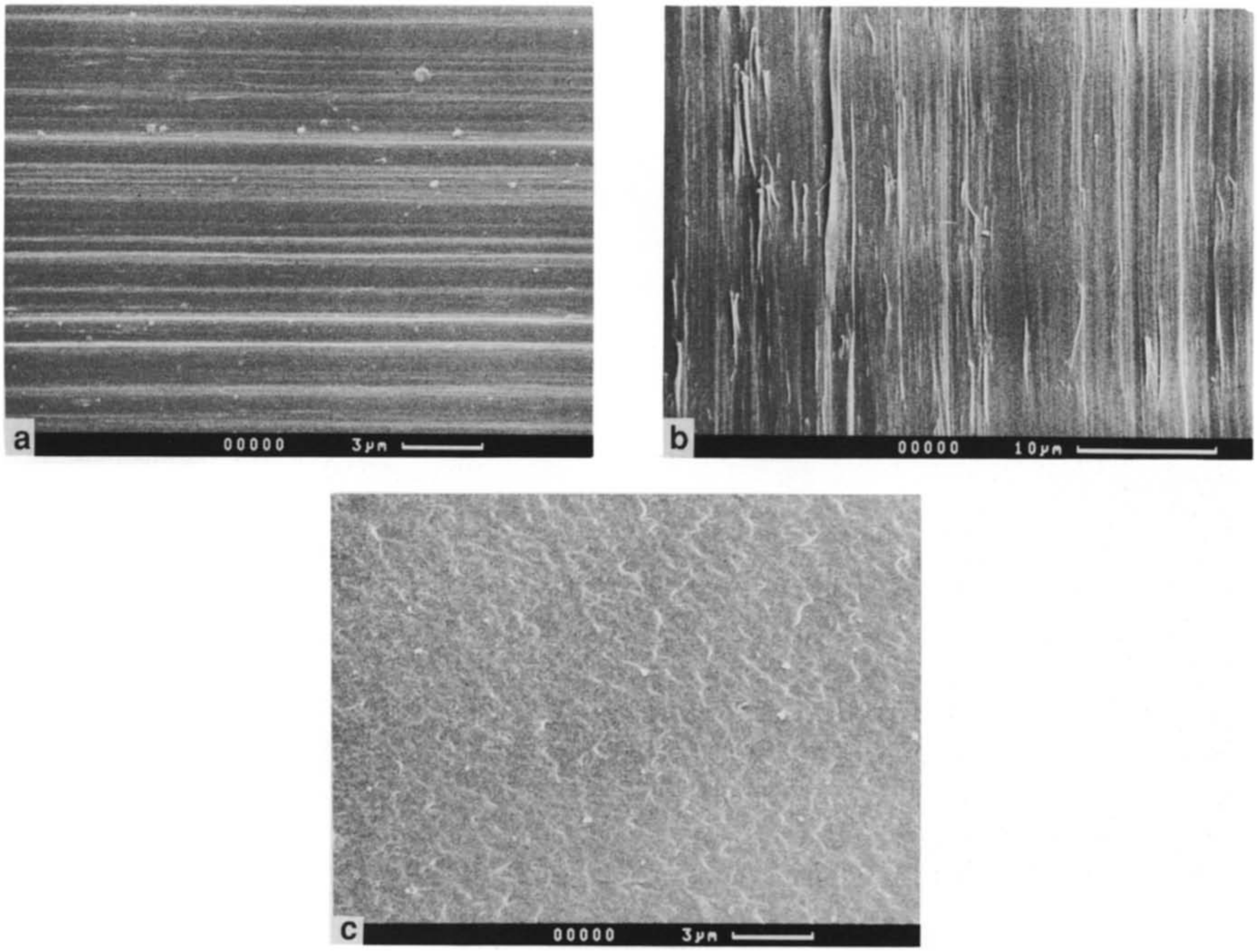

Figure 5 Typical examples of scanning electron micrographs of the pulled PE tapes: (a) untreated; (b) air-plasma-treated; (c) ammonia-plasma-treated (drawing axis vertical for air-plasma-treated PE tapes, otherwise horizontal)

indicating differences in shear strength of the upper surface layers following plasma treatment. These differences are thought to arise from topographical features (pits) in addition to crosslinking and/or chain scission caused by the plasma process.

Mechanism of adhesion

As mentioned in the Introduction, there exists much controversy about the nature of the changes brought about by plasma treatment and, consequently, the mechanism responsible for the increased adhesion. The discussion focuses on the importance of weak boundary layers, wetting/wettability, surface topography and specific interactions. The role of each factor has been investigated and will be discussed to some extent.

Impurities in polymers, such as lubricants, antistatics and antioxidants, are known to migrate to the film surface and to take part in weak boundary layer formation. It has been proposed that plasma treatment removes these impurities to a large extent (ablation), thereby increasing the adhesion. The removal of remaining solvent and stabilizer by extraction, prior to plasma treatment, should minimize the effect of weak boundary layer formation. In fact, X.p.s. analysis (*Table 1*) indicates a clean surface for the as-made and hence extracted PE tapes.

It is generally accepted that wetting of a substrate by the resin is a prerequisite, but is not necessarily sufficient, to obtain good adhesion. In other words, improper wetting always yields low adhesion values. In the case of PE, the wettability is low, owing to its non-polar surface. Plasma treatment might increase the wettability through the introduction of polar groups and/or surface roughening[34]. As such, it can be argued that differences in wetting reflect differences in these factors, and that wetting is not a separate factor. Nevertheless, we investigated the wetting of the PE tapes by the epoxy resin used in this study. SEM micrographs of negative replicas of the grooves left after pull-out and subsequent extraction with boiling xylene (to remove any adherend PE) are shown in *Figure 6*. A distinctive surface texture can be seen on the replicas of the grooves from air-plasma-treated PE tapes (*Figure 6b*). The resemblance between this micrograph and those shown in *Figures 4b* and *c* is remarkable. The same resemblance is found between the micrographs of the untreated and ammonia-plasma-treated PE tapes and the replicas of the corresponding grooves (*Figures 4a, d, e* and *Figures 6a, c*). Even the typical microfibrillar structure present at the surface of these tapes is faithfully replicated in the matrix. It thus appears that all, even the untreated, PE tapes are completely wetted by the epoxy resin, as observed by other investigators[6,7]. Hence, differences in wetting are an unlikely explanation for the differences in adhesion values.

SEM and X.p.s. examination, in addition to the foregoing discussion, reveal that three factors add to the adhesion following air-plasma treatment: the adhesion due to mechanical interlocking (τ_m); physicochemical binding due to the introduction of functional, oxygen-containing groups (τ_f); and non-polar dispersion forces (τ_d). The last factor is responsible for the adhesion of the untreated, non-polar PE tapes to epoxy resin. The pull-out strength is the sum of these three terms[7] and can be written as:

$$\tau = \tau_m + \tau_f + \tau_d$$

No significant changes in the non-polar dispersion component of the surface free energy of carbon surfaces is observed after oxidation or amination[35,36]. We therefore assume that the same is true for plasma-treated PE and that the contribution of the non-polar dispersion strength to the total shear strength is constant and equals 0.32 MPa. To clarify the contributions of τ_f and τ_m, air-plasma-treated PE tapes were subjected to non-constrained annealing in a nitrogen atmosphere (130°C, 45 h). Neither the surface chemical composition nor the amount of different chemical groups (C–O, C=O, O–C=O) were altered by this treatment (X.p.s.). It resulted, however, in a smoothing of the surface texture. In fact, no observable differences on an SEM scale could be detected between the surface roughness of the annealed (*Figure 7*) and the as-made PE tapes (*Figure 4a*). Consequently, by employing these PE tapes, pull-out

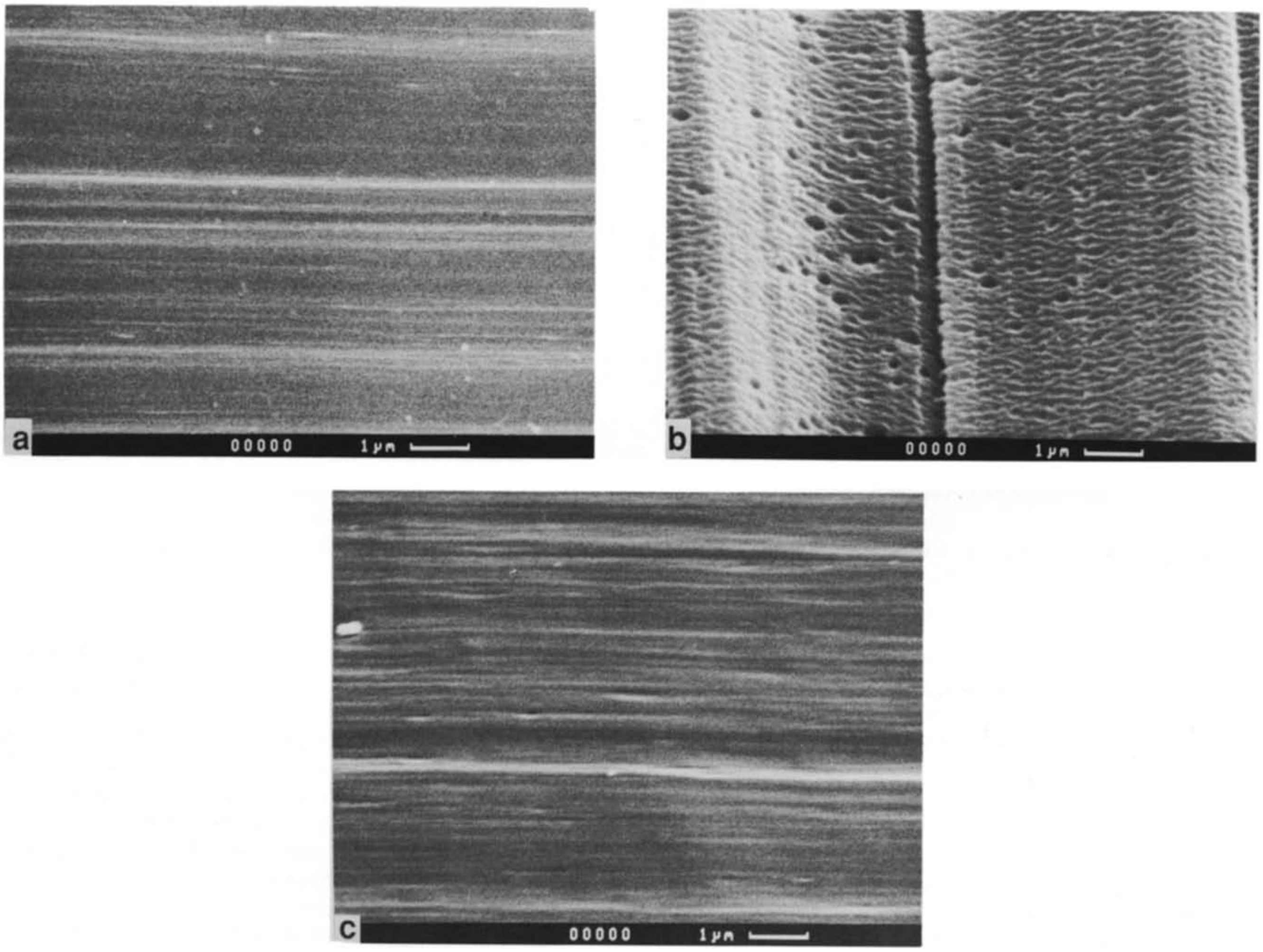

Figure 6 Typical examples of scanning electron micrographs of the xylene-extracted grooves left after pull-out of (a) untreated, (b) air-plasma-treated and (c) ammonia-plasma-treated PE tapes (drawing axis vertical for air-plasma-treated PE tapes, otherwise horizontal)

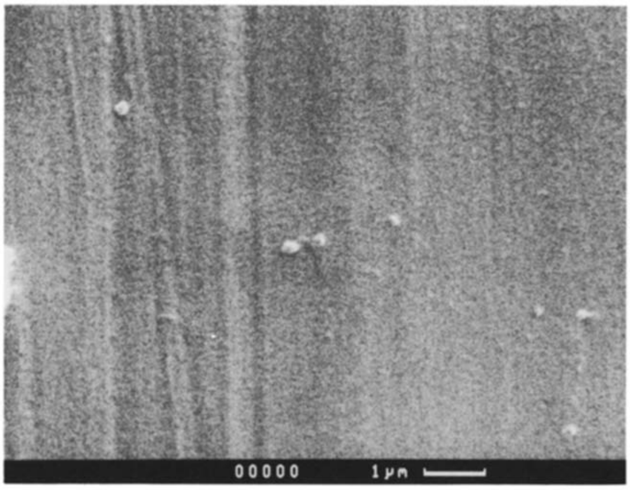

Figure 7 Scanning electron micrograph of an annealed air-plasma-treated PE tape (drawing axis vertical)

Table 4 Contribution of functional groups (τ_f), mechanical interlocking (τ_m) and non-polar dispersion forces (τ_d) to the adhesion (τ)

Plasma	Power (W)	τ (MPa)	$\tau_a{}^a$ (MPa)	$\tau_f{}^b$ (MPa)	$\tau_m{}^b$ (MPa)	$\tau_d{}^b$ (MPa)
None		0.32				0.32 (100)
Air	10	2.25	2.06	1.74 (77)	0.19 (9)	0.32 (14)
Air	25	2.68	2.35	2.03 (76)	0.33 (12)	0.32 (12)
Ammonia	10	2.44		2.12 (87)		0.32 (13)
Ammonia	25	2.47		2.15 (87)		0.32 (13)

[a] τ_a = pull-out strength of annealed air-plasma-treated PE tapes
[b] Contribution (in per cent) is given in parentheses

values are obtained free from the contribution of surface roughening. *Table 4* summarizes the results of these tests and the calculated values for τ_f and τ_m. The greatest contribution to the adhesion stems from the functional groups, which accounts for about 76%. Somewhat lower values, i.e. 56–62%, are found for the contribution of functional groups in the adhesion of oxygen-plasma-treated melt-spun PE fibres to epoxy resin[7] (calculated from the data given in ref. 7). Of the oxidation products, the carbonyl and carboxylic acid groups are among the most effective for improving the adhesion to epoxy resin[37]. Raising the input power increases the concentration of these groups, which explains the higher absolute value of τ_f for the 25 W air-plasma-treated PE tapes. The contribution of mechanical interlocking to the adhesion is much lower, with values of 9 and 12% for 10 and 25 W air-plasma-treated PE tapes, respectively. Despite a similar surface topography, higher absolute values of τ_m are found for the 25 W air-plasma-treated PE tapes. This, as well as the higher absolute value for τ, is ascribed to the greater shear strength of the 25 W treated PE tape, which is related to the crosslinking of the upper surface layer. The calculation presented above shows that the introduction of functional groups is the major factor contributing to the increase in adhesion following air-plasma treatment. It accounts for 90% (10 W) and 84% (25 W) of the measured increase in adhesion. For melt-spun highly drawn PE fibres, more research has been conducted to elucidate the factors influencing the adhesion to epoxy resin after oxygen-plasma treatment. Although mechanical interlocking was previously thought to be the major factor[6], recent research indicates that both improved wetting and crosslinking play a significant role[16]. There are some major differences with respect to structure and crystallinity between these melt-spun highly drawn low-molecular-weight PE fibres and the high-molecular-weight PE tapes used throughout this study. Little is known about the effect of molecular weight and structure on the different aspects of plasma treatment, i.e. crosslinking, oxidation, pitting, and thus a direct comparison of the results between these high-modulus PE structures is not possible. A somewhat different situation is encountered for the ammonia-plasma-treated PE tapes. The increase in adhesion is governed solely by the introduction of amine groups, as shown by SEM and X.p.s. examination. *Table 4* lists the values for τ_f.

The hydroxyl, carboxylic acid or amine groups introduced by air- and ammonia-plasma treatment may participate in subsequent covalent bonding with a curing resin network. But even if this is not the case, these groups, as well as the carbonyl groups, are capable of forming hydrogen bonds with the hydroxyl groups of the resin network. At present it is not clear whether covalent bonding takes place between the modified PE tapes and the epoxy resin or whether coulomb and/or hydrogen bonding forces prevail.

CONCLUSIONS

This study was aimed at investigating the changes brought about by air and ammonia-plasma treatment of gel-spun, high-strength, high-modulus PE tapes and relating these changes to the increased adhesion to epoxy resins. It was found that:

1. air-plasma treatment introduces hydroxyl, carbonyl and carboxylic acid groups at the surface of the PE tapes. It also results in severe etching of the surface, giving a pattern of short cracks perpendicular to the drawing direction
2. ammonia-plasma treatment results in the incorporation of amine groups but does not alter the surface topography
3. three factors are responsible for the adhesion of the air-plasma-treated PE tapes: (i) physicochemical interactions between the various carbon–oxygen functionalities and the epoxy resin; (ii) mechanical interlocking; and (iii) non-polar dispersion forces. The pull-out strength is the sum of these three terms and their contributions in this specific system are about 76%, 12% and 12%, respectively
4. the adhesion of ammonia-plasma-treated PE tapes is determined by physicochemical interactions in addition to non-polar dispersion forces. Their contributions to the adhesion in this specific system are 87% and 13%, respectively
5. the introduction of functional groups and the subsequent increase in physicochemical interactions is the major factor contributing to the increase in adhesion following air- and ammonia-plasma treatment
6. the marked increase in adhesion following plasma treatment is evidenced by a change in failure mode from interface controlled to cohesive failure inside the PE tape.

ACKNOWLEDGEMENTS

The author is indebted to Mr J. A. J. Goossen (M&E-TNO, Delft) for the scanning electron microscopy and to Dr P. H. de Haan (KRI-TNO) and Professor Dr P. J. Lemstra (Department of Polymer Technology, Eindhoven University of Technology) for carefully reading the manuscript.

REFERENCES

1 Smith, P. and Lemstra, P. J. *Makromol. Chem.* 1979, **180**, 2983
2 Smith, P. and Lemstra, P. J. *Colloid Polym. Sci.* 1980, **258**, 891
3 Nguyen, H. X. *Polym. News* 1992, **17**, 135
4 Plueddemann, E. P. 'Silane Coupling Agents', Plenum Press, New York, 1982, Ch. 1
5 Chamis, C. C. in 'Composite Materials-6' (Ed. E. P. Plueddemann), Academic Press, New York, 1974
6 Ladizesky, N. H. and Ward, I. M. *J. Mater. Sci.* 1983, **18**, 533
7 Nardin, M. and Ward, I. M., *Mater. Sci. Technol.* 1987, **3**, 814
8 Hsieh, Y.-L., Xu, S. and Hartzell, M. J. *Adhesion Sci. Technol.* 1991, **5**, 1023
9 Mercx, F. P. M., Benzina, A., Van Langeveld, A. D. and Lemstra, P. J. *J. Mater. Sci.* 1993, **28**, 753
10 Yuhas, D. E., Dolgin, B. P., Vorres, C. L., Nguyen, H. X. and Schriver, A. in 'Interfaces in Polymer, Ceramic and Metal Matrix Composites' (Ed. H. Ishida), Elsevier, London, 1984, p. 97
11 Feng, Z. and Ranby, B. *Angew. Makromol. Chem.* 1992, **195**, 17
12 Mercx, F. P. M. *Polymer* 1993, **34**, 1981
13 Ladizesky, N. H. and Ward, I. M. *Comp. Sci. Technol.* 1986, **26**, 129
14 Nguyen, H. X., Rinhi, G., Wood, G. and Poursartip, A. Proceedings of 33rd International SAMPE Symposium, Anaheim, 1988, p. 1721–1729
15 Kolluri, O. S., Kaplan, S. L. and Rose, P. W. *Eng. Plast.* 1992, **5**, 127
16 Tissington, B., Pollard, G. and Ward, I. M. *J. Mater. Sci.* 1991, **26**, 82
17 Biro, D. A., Pleizier, G. and Deslandes, Y. *J. Appl. Polym. Sci.* 1993, **47**, 883
18 Gao, S. L. and Zeng, L. *J. Appl. Polym. Sci.* 1993, **47**, 2065
19 Chappell, P. J. C., Brown, J. R., George, G. A. and Willis, H. A. *Surf. Interface Anal.* 1991, **17**, 143
20 Brown, J. R., Chappell, P. J. C. and Mathys, Z. *J. Mater. Sci.* 1992, **27**, 6475
21 Holmes, S. and Schwartz, P. *Comp. Sci. Technol.* 1990, **38**, 1
22 Brown, J. R., Chappell, P. J. C. and Mathys, Z. *J. Mater. Sci.* 1992, **27**, 3167
23 Li, Z.-F., Netravali, A. N. and Sachse, W. *J. Mater. Sci.* 1992, **27**, 4625
24 Hudis, M. in 'Techniques and Applications of Plasma Chemistry' (Eds J. R. Hollahan and A. T. Bell), John Wiley and Sons, New York, 1974, p. 113
25 Peijs, A. A. J. M., Rijsdijk, H. A. and Lemstra, P. J. in 'Composites, Design, Manufacture and Application' (Eds S. W. Tsai and G. S. Springer), SAMPE, Covina, 1991, p. 11-j-1
26 d'Agostino, R., Cramarossa, R., De Benedictis, S. and Ferraro, G. *Plasma Chem. Plasma Process.* 1981, **1**(1), 19
27 Lemstra, P. J., Van Aerle, N. A. J. M. and Bastiaansen, C. W. *Polym. J.* 1987, **19**, 85
28 Briggs, D. in 'Practical Surface Analysis' (Eds D. Briggs and M. P. Seah), Wiley, Chichester, 1983, p. 359
29 Wagner, C. D., Riggs, W. M., Davis, L. E. and Moulder, J. F. in 'Handbook of X-ray Photoelectron Spectroscopy' (Ed. G. E. Muilenberg), Perkin-Elmer, USA, 1979
30 Gerenser, L. J. *J. Adhes. Sci. Technol.* 1987, **1**, 303
31 Bahners, T. and Schollmeyer, E. *Angew. Makromol. Chem.* 1987, **151**, 19
32 Bahners, T. and Schollmeyer, E. *Angew. Makromol. Chem.* 1987, **151**, 39
33 Yao, Y., Liu, X. and Zhu, Y. *J. Adhesion Sci. Technol.* 1993, **7**, 63
34 Bascom, W. D. in 'Advances in Polymer Science-85' (Ed. K. Dusek), Springer Verlag, Berlin, 1988, p. 89
35 Wesson, S. P. and Allred, R. E. in 'Acid–Base Interactions: Relevance to Adhesion Science and Technology' (Eds K. L. Mittal and H. R. Anderson Jr), VSP, Utrecht, 1991, p. 145
36 Schreiber, H. P. and St. Germain, F. in 'Acid–Base Interactions: Relevance to Adhesion Science and Technology' (Eds K. L. Mittal and H. R. Anderson Jr), VSP, Utrecht, 1991, p. 273
37 Chew, A., Brewis, D. M., Briggs, D. and Dahm, R. H. in 'Adhesion 8' (Ed. K. W. Allen), Elsevier, London, 1984, p. 97