Improved adhesive properties of high-modulus polyethylene structures:
2. Corona grafting of acrylic acid

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High-modulus polyethylene (PE) tapes were grafted with acrylic acid using a two-step procedure. The tapes were first subjected to He/Ar corona discharge, immediately followed by exposure of the corona-treated tapes to acrylic-acid-saturated He gas. Evidence for the grafting was provided by X-ray photoelectron spectroscopy, which showed the surface of the treated tapes to consist of 64% acrylic acid and 36% PE. The grafting of acrylic acid is confined to the outermost surface layers, as indicated by reflection infra-red spectroscopy. Pull-out tests showed that the corona grafting of acrylic acid improves adhesion to epoxy resins by a factor of eight. Moreover, the increased adhesion is not achieved at the expense of a decrease in mechanical properties of the high-modulus PE tapes.

(Keywords: high-modulus PE tapes; surface modification; corona grafting; acrylic acid; epoxy resin)

Introduction

The process of gel-spinning has enabled the production of oriented polyethylene (PE) structures with moduli in excess of 100 GPa and tensile strengths of 2–4 GPa[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 fibre and matrix is necessary to impart the properties of the fibre 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, due to their chemical inertness 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[6–8], plasma[6,9–11] and corona treatment[12]. These processes are generally oxidative and cause chemical and physical changes in a thin surface layer. For most treatments, the increase in adhesion is accompanied by a (small) decrease in mechanical properties.

The above-mentioned pretreatments all introduce a variety of functional groups onto the surface, including hydroxyl, hydroperoxide, carbonyl, ester and carboxylic acid groups[8,9,11]. Of these oxidation products, the carboxylic acid groups are among the most effective for improving the adhesion to epoxy resin[13]. In this communication we report on the corona grafting of oriented high-modulus PE structures with acrylic acid, and the effect on both the adhesion to epoxy resin and the mechanical properties.

Experimental

Polyethylene tapes. Oriented PE tapes were employed in this study. These were obtained by ultra-drawing cast films as described previously[14], 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 $1.5 \times 10^3\ \mathrm{kg\,mol^{-1}}$. Stabilizer and remaining xylene were removed by subsequent extraction with hexane (15 h) and methanol (5 h).

Surface grafting. The surface grafting was performed by first treating the PE tapes with He/Ar corona, followed by exposure to acrylic-acid-saturated He gas. The home-built corona apparatus basically consists of a reaction chamber, a Teflon-coated and ground aluminium plate and a ceramic-coated electrode. The standard experimental procedure consisted of evacuation of the reactor ($P \leqslant 1.3$ mPa), after which He/Ar gas (83/17 vol/vol, $P = 9.1 \times 10^4$ Pa) was introduced. This step was repeated twice before initiating the corona (2.9 kV, 50 Hz). The reactor was evacuated once again after the treatment, then acrylic-acid-saturated He gas was introduced. After a post-bleed of 15 min in this gas mixture ($P = 9.1 \times 10^4$ Pa) the reactor was evacuated again, then air was introduced to raise the pressure to environmental conditions. All treated samples were extracted with hot (50°C) water for 24 h, dried and stored in a desiccator over P_2O_5.

Characterization. X-ray photoelectron spectroscopy (X.p.s.), attenuated total reflection infra-red (a.t.r.-i.r.), contact angles and scanning electron microscopy (SEM) were used to evaluate the effect of the surface treatment described above. Under the conditions used, X.p.s. had a probing depth of about 4 nm for the electrons of the C_{1s}–X.p.s. line, whereas the penetration depth of the a.t.r.-i.r. is about 400 nm at a wavelength of 10 μm. The samples for SEM were coated with a gold/palladium layer approximately 15 nm thick. A voltage of 25 kV or less was used, while the tapes were pressed in silver paint to ensure good conductivity.

Testing. Pull-out tests were performed to measure the fibre–matrix adhesion. A medium viscosity resin

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(Schering, Europox 730) together with an aliphatic amine hardener (Schering, XE-278) in the ratio 100/15 wt/wt, were used throughout this study. They were 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 temperature for 1.5 h. After curing, and prior to testing, the samples were stored in a conditioned chamber (23°C, 50% r.h.). Tests were run on an Instron tensile testing machine at a crosshead speed of 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.

The mechanical properties of the PE tapes were determined by tensile tests. The strain rate was 10% min^{-1} and closed loop operation made accurate constant strain rate experiments possible. Initial cross-sectional area, used for the calculation of Young's modulus and tensile strength, was 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.

Results and discussion

As a result of the interaction of inert gas electric discharges with PE, free radicals are produced within the top surface layers[15], the number of which depends on the processing conditions. The parameters that could be changed during the course of the experiments were voltage and residence time. As the corona was only stable within a narrow range of voltages, residence time was the only variable taken into account. The optimum residence time was derived by measuring the contact angle with water after exposure of the corona-treated samples to air for 15 min. This leads to oxidation[15,16], the degree of which is linked to the number of radicals present. Contact angles are a convenient way to follow the degree of oxidation and are inversely related to it. It was found that the contact angle initially decreases with residence time, going from 68° for the virgin PE tape to 39° for a PE tape treated for 1 min, after which it remains constant. A residence time of 1 min presents an optimum and was employed in the surface grafting experiments described below.

X-ray photoelectron spectroscopy. The presence of oxygen can inhibit the grafting reaction[17], which is the reason for evacuating the corona reaction chamber twice before initiating the corona, and for degassing the acrylic acid before use. The surface composition of the PE tapes and surface-modified PE tapes, as measured with X.p.s. and expressed as the oxygen-to-carbon ratio, is given in *Table 1*. Detailed information about the nature of the incorporated groups can be obtained from the high resolution C_{1s} and O_{1s} spectra. The C_{1s} spectra, shown in *Figure 1*, are the most informative. The binding energy of carbon in hydrocarbons is 285 eV. Introduction of oxygen induces a shift, for those carbon atoms chemically bonded to oxygen, to higher binding energies. A shift of 4.5 eV, as found in the surface-modified PE tapes, is characteristic of carbon atoms in a carboxylate environment (–O–C=O), i.e. carboxylic acid or ester groups[17,18]. Peak-fitting the spectrum provides evidence for the existence of C–O (286.5 eV) and C=O (288 eV) functionalities, although they constitute less than 2% of the total amount of carbon–oxygen functionalities. Most likely these oxidation products are the result of the reaction of long-living radicals with oxygen. From the absence of a significant contribution at 286.5 eV (carbon singly bonded to oxygen), it was concluded that the majority of the intensity of the peak at 289.5 eV stems from carboxylic acid groups.

Table 1 Surface composition and mechanical properties of untreated and acrylic acid (AA)-grafted high-modulus PE tapes

Treatment	Surface composition (O/C)	Pull-out strength[a] (MPa)	Tensile modulus[a] (GPa)	Tensile strength[a] (GPa)
None	0.03	0.32 (0.04)	138 (6)	2.40 (0.06)
AA-grafted	0.35	2.52 (0.07)	141 (13)	2.43 (0.05)

[a] Standard deviation is given in parentheses

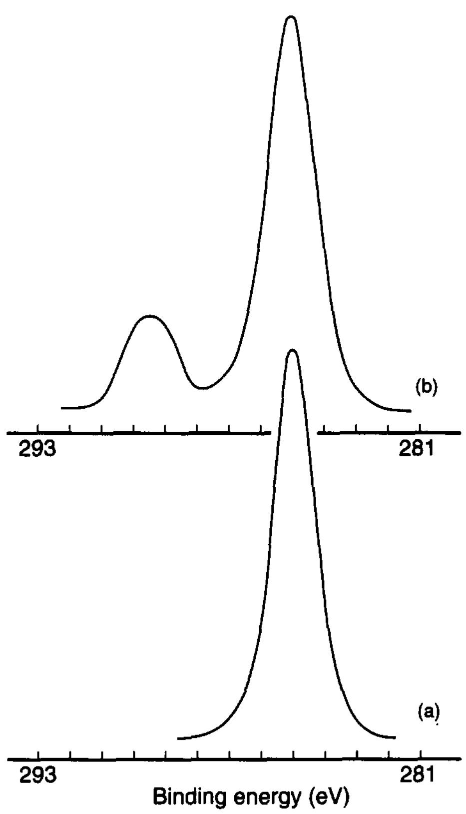

Figure 1 High resolution C_{1s} spectra of (a) untreated and (b) acrylic-acid-grafted high-modulus PE tapes

From the peak area at 289.5 eV, and allowing for the contribution to the hydrocarbon peak, the composition over the penetration depth was estimated to be 64% (poly)acrylic acid and 36% PE. This value is in good agreement with the composition calculated from the O_{1s}/C_{1s} ratio, i.e. 65% (poly)acrylic acid. Similar results were reported by Munro[17] for the irradiation grafting of low density PE in the presence of acrylic acid vapour. Photoinitiated surface grafting of acrylic acid onto high-modulus PE fibres (Spectra 900)[19] yielded lower values ($\leqslant 50\%$) for the acrylic acid content of the surface (calculated from the X.p.s. data given in ref. 19).

The C_{1s} peak for the virgin PE tape is a single sharp peak (1.5 eV at half height) centred at 285 eV as expected for a clean PE surface. The broadening of the hydrocarbon peak (1.8 eV at half height) after corona grafting is indicative of sample damage, probably in the form of chain scission.

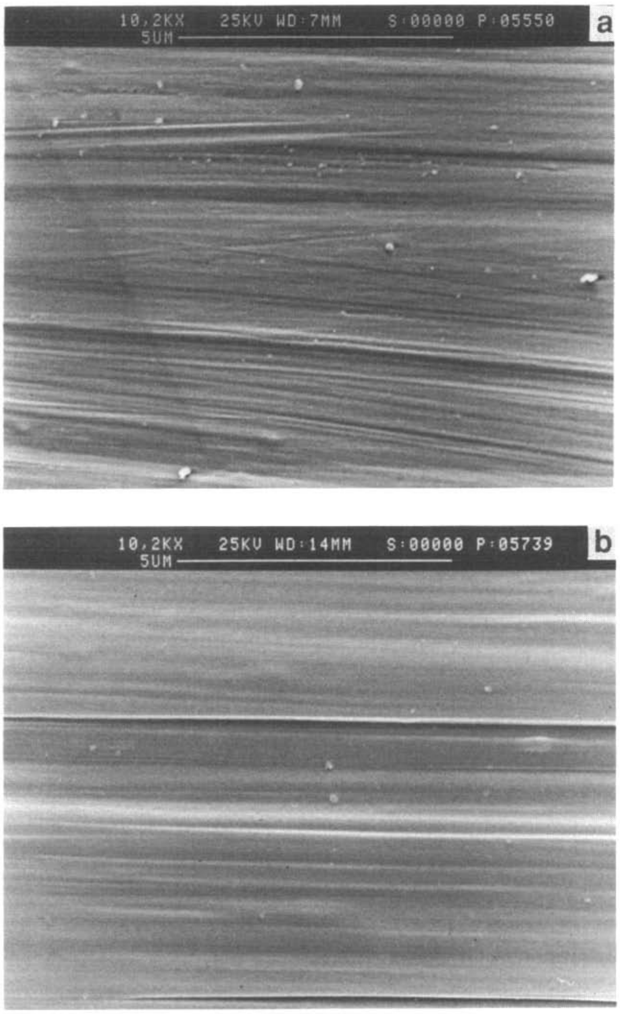

Figure 2 Scanning electron micrographs of (a) untreated and (b) acrylic-acid-grafted high-modulus PE tapes

Infra-red spectroscopy. The reflection infra-red spectrum of the surface-modified PE tapes shows two extra peaks compared to the reflection infra-red spectrum of PE. Most prominent is a small peak at $1720\,\mathrm{cm}^{-1}$, which is consistent with the stretching vibrations of C=O in acid groups[19,20]. The relative intensity of this C=O peak compared to the CH_2 ($1465\,\mathrm{cm}^{-1}$) peak is 1.2%. A broad and hardly discernible peak at $3100\,\mathrm{cm}^{-1}$ is ascribed to O–H stretching vibrations. The fact that reflection infra-red failed to detect the O–H deformation ($900–950\,\mathrm{cm}^{-1}$) and coupled C–O stretching and O–H deformation (near 1430 and $1300\,\mathrm{cm}^{-1}$) vibrations of carboxylic acids[20], indicates that the grafting of acrylic acid is confined to the outermost surface layers.

Scanning electron miscroscopy. The surface of the virgin PE tapes (*Figure 2a*) is rather smooth, except for the typical microfibrillar structure caused by the hot-drawing process. No change in surface texture was evident after the corona grafting of acrylic acid (*Figure 2b*).

Adhesion and mechanical properties. The introduced carboxylic acid groups may or may not participate in covalent bonding with the curing resin network. Even if this is not the case, these groups may form hydrogen bonds with the hydroxyl groups in the cured resin network. Although the exact mechanism of the improvement is not yet clear, the adhesion to epoxy resin is markedly enhanced (*Table 1*). The increase in adhesion by a factor of eight compares well with the improvement found after air–plasma treatment[6,9–11,21], the most effective treatment reported so far. Moreover, and contrary to the case of air–plasma treatment, the tensile strength of the acrylic-acid-grafted PE tapes is not affected. Feng and Ranby[19] found a three-fold increase in the adhesion of PE fibres grafted with acrylic acid by a photoirradiation method. As indicated before, the extent of acrylic acid grafting was far less for their procedure compared with corona grafting, and may account for the differences in adhesion observed.

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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 Hsieh, Y-L., Xu, S. and Hartzell, M. *J. Adhes. Sci. Technol.* 1991, **5**, 1023
8 Mercx, F. P. M., Benzina, A., Van Langeveld, A. D. and Lemstra, P. J. *J. Mater. Sci.* 1993, **28**, 753
9 Biro, D. A., Pleizier, G. and Deslandes, Y. *J. Mater. Sci. Lett.* 1992, **11**, 698
10 Tissington, B., Pollard, G. and Ward, I. M. *Comp. Sci. Technol.* 1992, **44**, 185
11 Kolluri, O. S., Kaplan, S. L. and Rose, P. W. *Eng. Plast.* 1992, **5**, 127
12 Yuhas, D. E., Dolgin, B. P., Vorres, C. L., Nguyen, H. and Schriver, A. in 'Interfaces in Polymer, Ceramic, and Metal Matrix Composites' (Ed. H. Ishida), Elsevier, New York, 1988, p. 595
13 Chew, A., Brewis, D. M., Briggs, D. and Dahm, R. H. in 'Adhesion 8' (Ed. K. W. Allen), Elsevier, London, 1984, p. 97
14 Lemstra, P. J., Van Aerle, N. A. J. M. and Bastiaansen, C. W. *Polym. J.* 1987, **19**, 85
15 Wu, S. 'Polymer Interface and Adhesion', Marcel Dekker, New York, 1982, p. 298
16 Bamford, C. H. and Ward, J. C. *Polymer* 1961, **2**, 277
17 Munro, H. S. *Polym. Commun.* 1987, **28**, 221
18 Briggs, D. in 'Practical Surface Analysis' (Eds D. Briggs and M. P. Seah), John Wiley, Chichester, 1983, p. 358
19 Feng, Z. and Ranby, B. *Angew. Makromol. Chem.* 1992, **195**, 17
20 Williams, D. H. and Fleming, I. 'Spektroskopische Methoden zur Strukturaufklärung', George Thieme Verlag, Stuttgart, 1979
21 Ladizesky, N. H. and Ward, I. M. *J. Mater. Sci.* 1989, **24**, 3763