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Factors affecting the interfacial adhesion of ultrahigh-modulus polyethylene fibre–vinylester composites using gas plasma treatment

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The interfacial adhesion of ultrahigh-modulus polyethylene (UHMPE) fibre–vinylester composites was improved by the oxygen plasma treatment of the UHMPE fibre. The chemical functional group formations on the UHMPE fibre surface by oxygen plasma treatment were analysed using diffuse reflectance Fourier transform infrared spectroscopy and the morphological changes of the UHMPE fibre surface by plasma etching were observed by scanning electron microscopy. The wettability enhancement by the chemical functional group formation and the mechanical interlocking due to the micropits were important factors in improving the interfacial adhesion of the UHMPE fibre–vinylester composites by oxygen plasma treatment. In order to investigate the relative importance of the two factors, wettability enhancement and mechanical interlocking, in the improved interfacial adhesion of the UHMPE fibre–vinylester composites, nitrogen plasma treatment was also performed. Nitrogen plasma treatment of the UHMPE fibre was proved to be effective in the formation of the micropittings and ineffective in the chemical functional group formation in comparison with the oxygen plasma treatment. The interlaminar shear strengths of the nitrogen-plasma-treated UHMPE fibre–vinylester composites showed almost the same value as those of the oxygen-plasma-treated UHMPE fibre–vinylester composites. The wettability enhancement and mechanical interlocking are important in the improvement of interfacial adhesion of UHMPE fibre–vinylester composites by plasma treatment and mechanical interlocking seems to be more important.

1. Introduction

Polyethylene has the simplest structure of all the olefin polymers. In extended conformation, polyethylene chains show high strength and high modulus and can be applied to high-performance fibre. Polyethylene fibres made from high-density polyethylene (HDPE) by solution or melt spinning and drawing show a high strength and a high modulus [1–4]. However, the mechanical properties of melt-spun polyethylene fibre are restricted by the intrinsic chain entanglements [2]. The spinning of ultrahigh-molecular-weight polyethylene gel induces ultrahigh-modulus polyethylene (UHMPE) fibre with much reduced chain entanglements. The UHMPE fibre made from ultrahigh molecular-weight polyethylene by the gel spinning method shows improved modulus and strength in comparison with the melt-spun polyethylene fibre [5].

However, the UHMPE fibre has a low surface energy and shows poor interfacial adhesion in composite applications. Therefore, surface modifications of the UHMPE fibre to improve the interfacial adhesion of UHMPE fibre composites have been important research subjects [6–20].

Of the various surface treatment methods, low-temperature plasma treatments have been one of the most effective treatment methods. Oxygen plasma treatment of the UHMPE fibre has been widely investigated and many papers reported that the interfacial adhesion of the UHMPE fibre composites increased considerably by the oxygen plasma treatment of the UHMPE fibre [13–20].

However, the reason for the improvement in the interfacial adhesion in the UHMPE fibre composites by the oxygen plasma treatment has not been known clearly although some papers reported the important factors for the interfacial adhesion of the UHMPE fibre composites [15–20]. Most of them focused on the UHMPE fibre–epoxy composites for structural applications. On the other hand the UHMPE fibre–vinylester system is widely used for ballistic applications. Therefore, improving the interfacial adhesion and investigating the factors affecting the interfacial adhesion of the UHMPE fibre–vinylester composites

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are very important for impact-resistance research fields.

The purpose of this study is to examine the important factors in the improved interfacial adhesion of the UHMPE fibre–vinylester composites. The interfacial adhesion of the UHMPE fibre–vinylester composites was improved by oxygen and nitrogen plasma treatment of the UHMPE fibre and the changes in the UHMPE fibre surface by the plasma treatments were investigated using diffuse reflectance infrared Fourier transform (DRIFT) spectroscopy and scanning electron microscopy (SEM). In addition, the relative importance of factors affecting the improvement of the interfacial adhesion of the UHMPE fibre–vinylester composites by the gas plasma treatments was also mentioned.

2. Experimental procedure

2.1. Material

The UHMPE fibre used in this experiment was Spectra 900 plain fabric from Allied Signal Inc. The cleaning of the fibre surface was carried out by refluxing for 2 days using *n*-hexane as a solvent for impurities. After the cleaning, the fabric was dried for 2 days at 60 °C in a drying oven.

The matrix resin used was XSR-10 vinylester resin from National Synthesis Co. in South Korea. This XSR-10 vinylester resin is a kind of vinylester resin modified with carboxyl-terminated butadiene acrylonitrile rubber and has very similar properties to Derakane 8084 vinylester resin from Dow Chemical Co.

Dibenzoyl peroxide (BPO) was used as an initiator for the curing reaction and diallyl phthalate (DAP) was used as a cross-linking agent.

2.2. Plasma treatment

The plasma treatment apparatus used was manufactured by Korea Vacuum Co. in South Korea. This plasma treatment reactor is parallel electrode type with 13.56 MHz radio frequency generator. The diameter of the powered electrode on which the sample is placed is 35 cm and the distance between the two electrodes is 8 cm. The chamber was evacuated below 30 mTorr and a carrier gas (oxygen or nitrogen) flow was introduced to make the chamber pressure of 100 mTorr at steady state. The plasma output power was 100 W; after the plasma treatment for the determined period the plasma chamber was re-evacuated below 30 mTorr and the chamber was purged with air.

2.3. Fourier transform infrared analysis of the ultrahigh-modulus polyethylene fibre surface

The Bomem MB-100 Fourier transform infrared (FTIR) spectrometer with a deuterated triglycine sulphate detector was used and dry nitrogen was purged to remove the interference from CO_2 and water vapour in atmosphere. The diffuse reflectance technique was used to observe the chemical changes in the UHMPE fibre surface after the plasma treatment. The resolution was fixed at 4 cm^{-1} and the total of 200 scans were coadded.

2.4. Scanning electron microscopy analysis of the ultrahigh-modulus polyethylene fibre surface

The JEOL JSM-35 microscope was used and gold coatings were applied to give the sample electronic conductivity. A magnification of 10 000 was used.

2.5. Prepreg preparation

The XSR-10 vinylester resin, DAP, BPO and acetone (solvent for the BPO and viscosity reducer) were mixed in the weight ratio of 100:20:1.2:10. The plasma-treated UHMPE fabrics were impregnated in this resin bath and dried for 2 days at room temperature in a drying hood.

2.6. Manufacturing of the composites

The UHMPE fibre–vinylester composites were manufactured by the open leaky mould method. The curing temperature was 113 °C and the total curing time was 2 h. The curing was performed under atmospheric pressure for the initial 10 min and under 4137 kPa (600 lbf in^{-2}) for the rest period. The composites consisted of eight plies of the UHMPE fabric and the thickness of the composites was 3.0 ($\pm$ 0.1) mm.

2.7. Interlaminar shear strengths measurement

The relative interfacial adhesions of the UHMPE fibre–vinylester composites were evaluated by interlaminar shear strengths. The interlaminar shear strengths of the UHMPE fibre–vinylester composites were measured by the three-point short beam test method according to ASTM D2344. An Instron 4201 universal testing machine was used; the diameter of the loading tip was 3 mm and the diameter of support tip was 2 mm. The dimensions of the test specimens were 1.8 × 1.0 ($L \times W$) cm and the thickness of the test specimens was 0.3 cm. The ratio of the span length to the sample thickness was adjusted to 4 and the crosshead speed was 2 mm min^{-1}.

3. Results and discussion

Fig. 1 shows the interlaminar shear strength values of the UHMPE fibre–vinylester composites as a function of the oxygen plasma treatment time. The oxygen plasma treatment of the UHMPE fibre increases the interlaminar shear strengths considerably and after treatment for 5 min the interlaminar shear strengths of the UHMPE fibre–vinylester composites show the maximum value. The slight decrease in the interlaminar shear strength after a 7 min oxygen plasma treatment is thought to be due to the deteriorative properties of the UHMPE fibre itself after a long plasma treatment time.

In the oxygen plasma treatment of the UHMPE fibre, two phenomena occur simultaneously and these

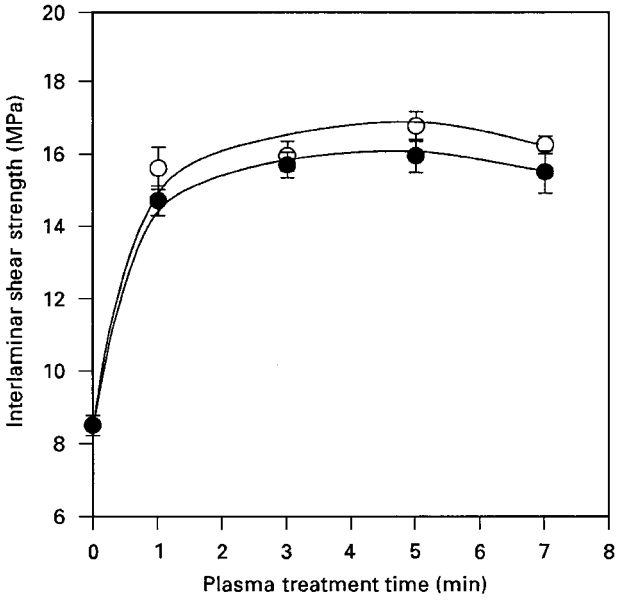

Figure 1 The variation in the interlaminar shear strengths of the UHMPE fibre–vinylester composites with the plasma treatment time. (○), oxygen plasma; (●), nitrogen plasma.

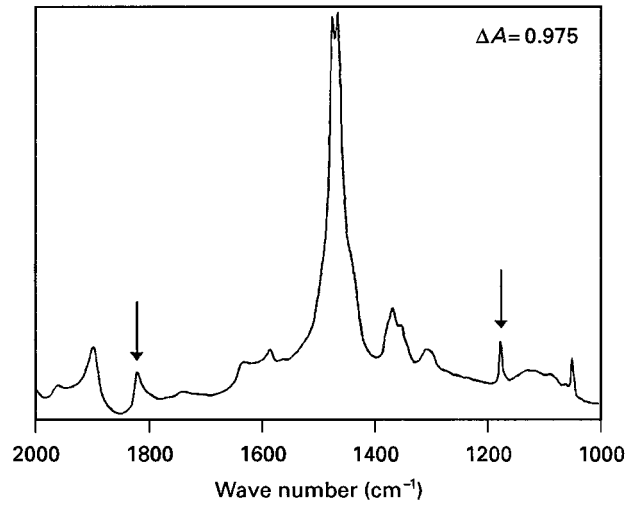

Figure 2 The DRIFT spectrum of the control UHMPE fibre (the arrows indicate the internal standard peaks).

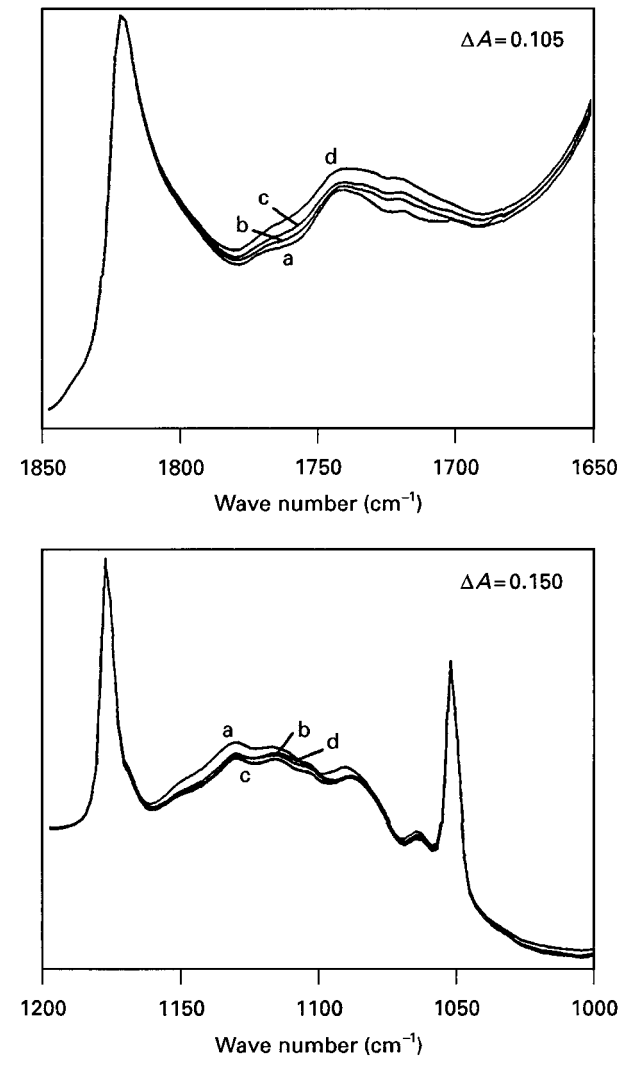

Figure 3 The DRIFT spectra of the UHMPE fibre treated with the oxygen plasma for the following times. Curves a, control; curves b, 3 min; curves c, 5 min; curves d, 7 min.

two phenomena contribute the improvement in the interfacial adhesion of the UHMPE fibre–vinylester composites. One is the formation of oxygen-containing chemical functional groups on the UHMPE fibre surface and the other is the formation of micropits on the UHMPE fibre surface by plasma etching. The oxygen-containing chemical functional groups formed by oxygen plasma increase the surface energy of the UHMPE fibre and enhance the wetting of the UHMPE fibre by the vinylester matrix resin. This enhanced wettability increases the interfacial adhesion and the interlaminar shear strengths of the UHMPE fibre–vinylester composites. The micropits formed by oxygen plasma treatment contribute to the interfacial adhesion of the UHMPE fibre–vinylester composites through the mechanical interlocking between the micropits and the impregnated vinylester resin. These two factors, wettability enhancement and mechanical interlocking, play important roles in improving the interfacial adhesion of the UHMPE fibre–vinylester composites.

The formation of the oxygen-containing chemical functional groups on the UHMPE fibre surface can be investigated using DRIFT spectroscopy by measuring the changes in the carbonyl peak and the C–O single-bond peak intensities. The diffuse reflectance method has been known to be suitable for the investigation of the UHMPE fibre surface [21]. Fig. 2 shows the DRIFT spectrum of the control UHMPE fibre. The most intense peak at 1464 cm^{-1} is assigned to CH_2 bending and other peaks arises from the crystalline region of the UHMPE fibre. The peak at 1819 cm^{-1} is thought to be a crystalline combination peak and the peak at 1176 cm^{-1} is assigned to crystalline methylene wagging mode of the UHMPE fibre [22].

These two peaks at 1819 cm^{-1} and 1176 cm^{-1} remain almost the same after the oxygen plasma treatment and can be used as internal standard peaks for the carbonyl band near 1740 cm^{-1} and C–O band near 1100 cm^{-1} respectively for the following reason.

The average diameter of the UHMPE fibre used in this research is about 36 μm and the thickness of the plasma-treated layer is less than 0.1 μm [14]. The

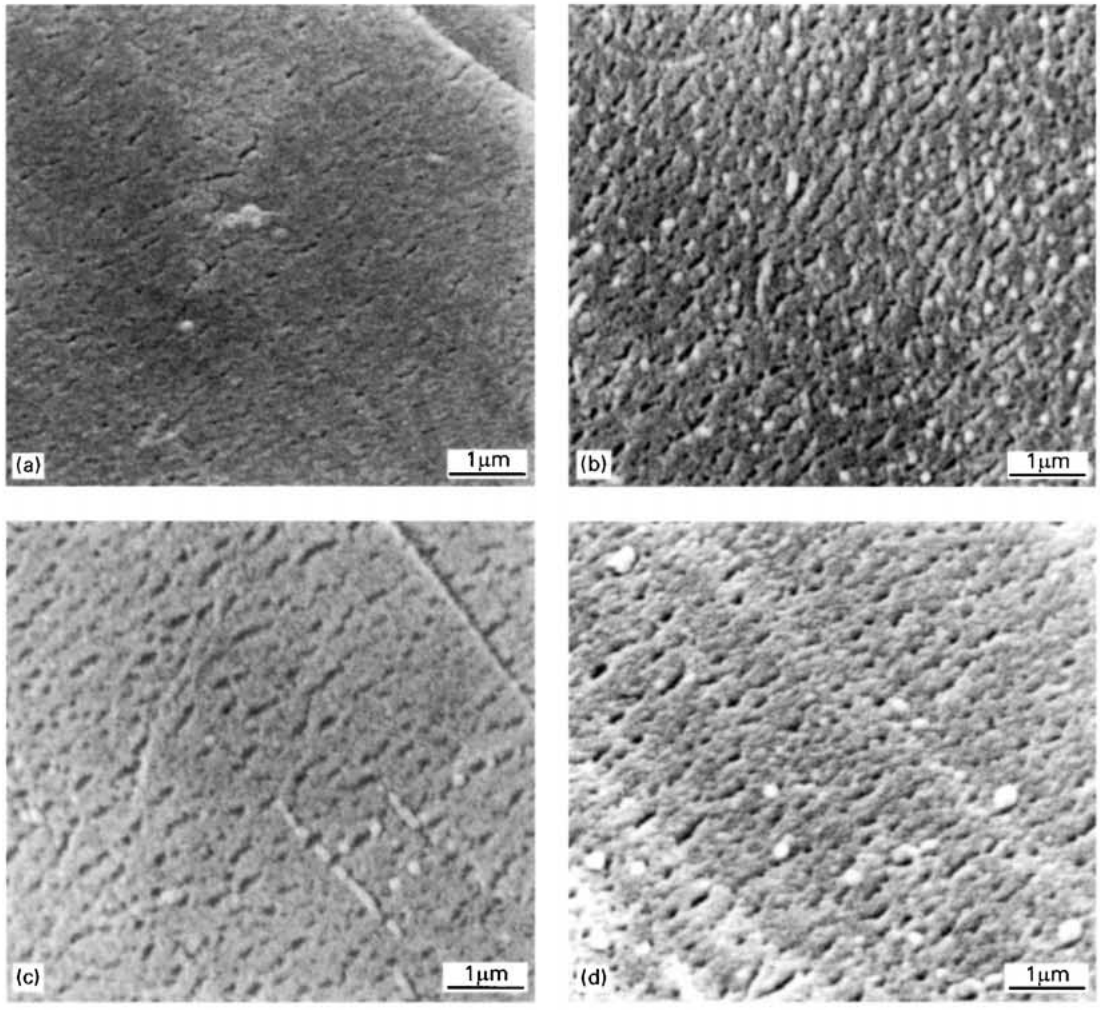

Figure 4 The SEM photographs of the UHMPE fibre treated with the oxygen plasma for the following times: (a) control; (b) 3 min; (c) 5 min; (d) 7 min.

penetration depth of the infrared ray in the diffuse reflectance technique is in the range of a few micrometres and the resultant DRIFT spectrum of the UHMPE fibre is mainly related to the information from the fibre bulk rather than from the fibre surface [21]. Therefore, the peaks from the crystalline region in the bulk remain almost the same and can be used as internal standard peaks for the changes in the peaks from the surface only if the plasma treatment does not change the bulk crystallinity of the UHMPE fibre.

Fig. 3 shows the changes in the carbonyl peak and the C–O single-bond peak of the UHMPE fibre normalized using internal standard peaks with the oxygen plasma treatment time. From this figure, it can be seen that the carbonyl peak increases with increasing oxygen plasma treatment time and that the C–O single-bond peak decreases and increases slightly after 5 min treatment. The control fibre shows the carbonyl peak and C–O single-bond peak although the control UHMPE fibre was expected to have no functional groups on its surface. This unexpected carbonyl peak and C–O single-bond peak of the control UHMPE fibre will be discussed later with SEM photographs of the fibre. Although it can be seen that the oxygen-containing chemical functional groups (especially carbonyl groups) are introduced onto the UHMPE fibre surface by the oxygen plasma treatment, it was difficult to determine the exact chemical nature or quantitative trend of the functional groups with oxygen plasma treatment time from these DRIFT spectra alone.

The changes in the surface morphology of the UHMPE fibre after the oxygen plasma treatment were investigated using SEM. Fig. 4 shows the SEM photographs of UHMPE fibre treated with oxygen plasma. The control fibre shows small pits although it was expected to have a clean smooth surface. Judging from this SEM photograph and DRIFT spectrum in Fig. 3, the control fibre might be thought to have been surface treated by the manufacturer. The formation of micropits by oxygen plasma treatment can be confirmed by the SEM photographs. The micropits on the UHMPE fibre surface become larger with increasing oxygen plasma treatment time and after 5 min treatment small micropits begin to form again. These small micropits are inefficient in improving the interfacial adhesion of the UHMPE fibre–vinylester composites because small pits are difficult to impregnated by the vinylester resin.

The formation of the chemical functional groups on the UHMPE fibre surface could be confirmed by the DRIFT spectroscopy and the formation of micropits by plasma etching could be confirmed by SEM. From

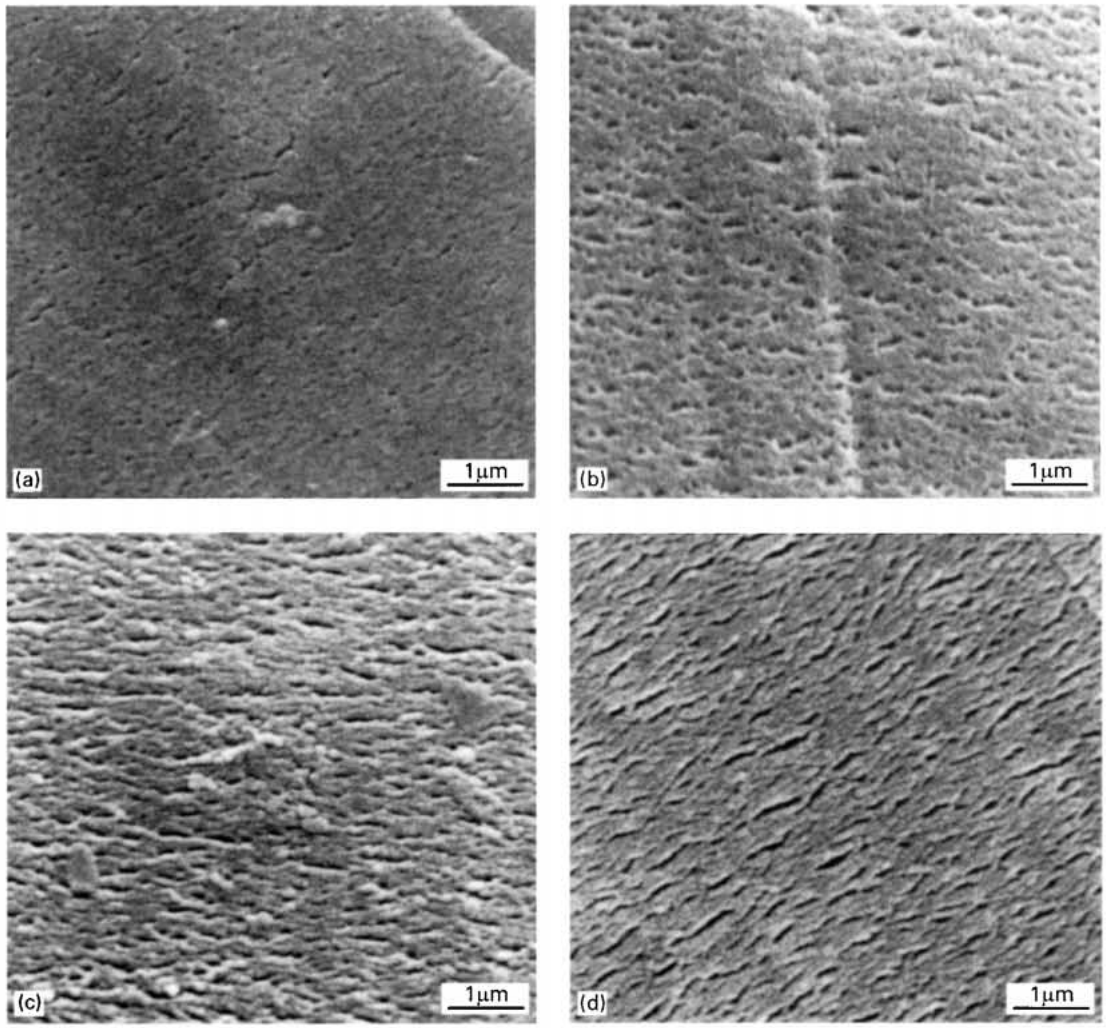

Figure 5 The SEM photographs of the UHMPE fibre treated with the nitrogen plasma for the following times: (a) control; (b) 3 min; (c) 5 min; (d) 7 min.

these results, it is known that the wettability enhancement by chemical functional groups and the mechanical interlocking due to micropits are important factors for improving the interfacial adhesion in the UHMPE fibre–vinylester composites by oxygen plasma treatment. However, it could not be determined which of these two factors, wettability enhancement and mechanical interlocking, is more important in the interfacial adhesion of the UHMPE fibre–vinylester composites. In order to investigate the relative importance of the factors affecting the improvement in the interfacial adhesion in the UHMPE fibre–vinylester composites, a nitrogen plasma treatment was performed.

Nitrogen is a chemically inert gas and nitrogen plasma is thought to be less efficient in the introduction of the chemical functional groups on the UHMPE fibre surface than is oxygen plasma although it is well known that oxygen-containing chemical functional groups are always formed during the nitrogen plasma treatment of polymers [23]. However, the formation of micropits by surface etching is expected to occur in the nitrogen plasma treatment although the extent of etching may be different from that of the oxygen plasma treatment.

Fig. 5 shows the SEM photographs of the UHMPE fibre treated with nitrogen plasma. The formation of micropits by nitrogen plasma can be observed in the SEM photographs and the extent of the etching is almost the same as that due to the oxygen plasma treatment although the shape of the micropits is slightly different from that of the micropits obtained in the oxygen plasma treatment. Judging from this figure, it can be seen that nitrogen plasma treatment of the UHMPE fibre is effective in the formation of micropits by surface etching.

The chemical changes of the UHMPE fibre surface by nitrogen plasma treatment was observed by DRIFT spectroscopy. Fig. 6 shows the DRIFT spectra of the UHMPE fibre treated with the nitrogen plasma. The carbonyl peak and the C–O single-bond peak decrease and then increase again with increasing nitrogen plasma treatment time. However, in the experimental conditions the nitrogen plasma treatment causes the carbonyl peak and the C–O single-bond peak to decrease in comparison with those of the control fibre and it can be deduced that the nitrogen plasma treatment is less efficient than the oxygen plasma treatment in the introduction of the oxygen-containing chemical functional groups onto the UHMPE fibre surface. No formation of nitrogen-containing chemical functional groups in detectable quantity was observed in the DRIFT spectra of the UHMPE fibre treated with the nitrogen plasma.

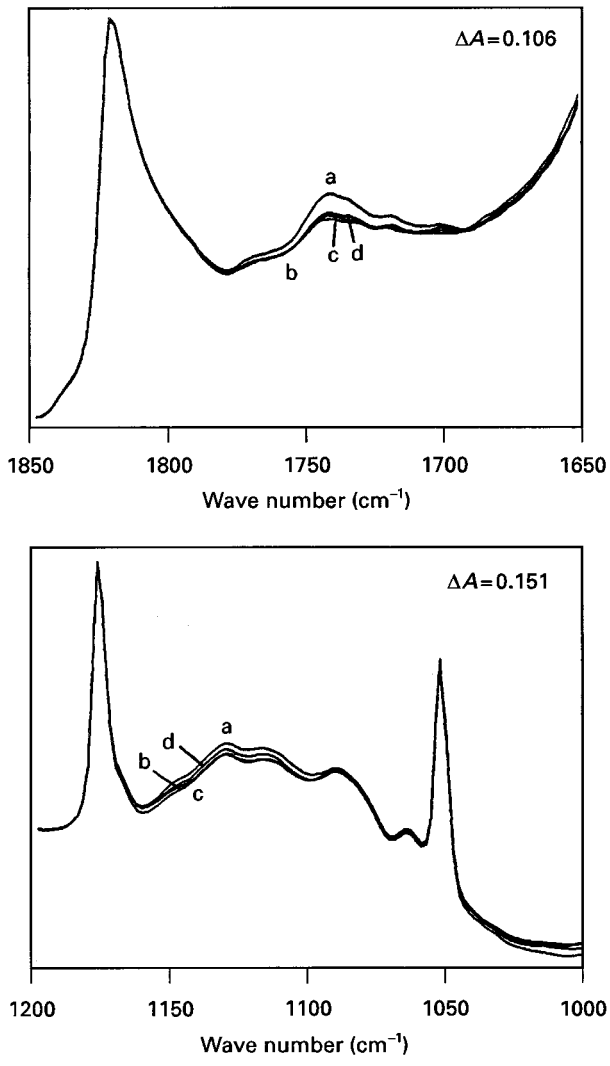

Figure 6 The DRIFT spectra of the UHMPE fibre treated with nitrogen plasma for the following times: Curves a, control; curves b, 3 min; curves c, 5 min; curves d, 7 min.

Judging from the FTIR spectra and the SEM photographs of the UHMPE fibre treated with the nitrogen plasma, the nitrogen plasma treatment of the UHMPE fibre is ineffective in the formation of chemical functional groups and effective in the formation of micropits in comparison with the oxygen plasma treatment.

The interlaminar shear strength values of the UHMPE fibre–vinylester composites with the nitrogen plasma treatment time are also shown in Fig. 1. From this figure, it can be seen that almost the same interlaminar shear strength values can be obtained by nitrogen plasma treatment of the UHMPE fibre. The slightly higher values obtained by the oxygen plasma treatment are thought to be due to the additional wettability enhancement effect. From these results, it can be concluded that the wettability enhancement and mechanical interlocking are important and that mechanical interlocking is more important in improving the interfacial adhesion of the UHMPE fibre–vinylester composites by oxygen and nitrogen plasma treatment.

4. Conclusions

The interfacial adhesion of the UHMPE fibre–vinylester composites was improved by oxygen and nitrogen plasma treatment of the UHMPE fibre and the following conclusions can be obtained from the results.

1. The oxygen plasma treatment of the UHMPE fibre introduced chemical function groups and micropits onto the fibre surface. The chemical functional groups increase the interfacial adhesion of the UHMPE fibre–vinylester composites owing to the wettability enhancement; the micropits increase the interfacial adhesion owing to mechanical interlocking.

2. The nitrogen plasma treatment of the UHMPE fibre was known to be effective in the formation of micropits by surface etching and ineffective in the formation of the chemical functional groups in comparison with the oxygen plasma treatment.

3. The interlaminar shear strengths of the UHMPE fibre–vinylester composites were increased considerably by the oxygen and nitrogen plasma treatment and showed almost the same values.

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