Surface Characterization Method of Oxygen Plasma-Treated UHMPE Fiber Using DRIFT Spectroscopy

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ABSTRACT: The surface treatment and characterization of ultrahigh modulus polyethylene (UHMPE) fiber has been an important research subject. In this study, in order to investigate the oxygen plasma-treated UHMPE fiber according to the treatment time, diffuse reflectance Fourier transform infrared (DRIFT) spectroscopy was used as an analysis tool. The UHMPE fiber in a plain fabric was used for the surface analysis. The KBr overlay technique was efficient for enhancing the characteristic peaks from the UHMPE fiber surface. However, the KBr overlay made the comparison of the spectra among the UHMPE fiber samples difficult due to the different KBr overlay amount of each sample. In order to compare the relative peak areas of the oxygen plasma-treated UHMPE fiber according to the treatment time, DRIFT analysis was performed without KBr overlay under constant fiber orientation to remove the fiber orientation effect. The spectral subtraction was useful for investigating the minute change of the UHMPE fiber after the oxygen plasma treatment under the constant fiber orientation. The peak at 1896 cm^{-1} was assigned to the crystalline combination mode of the UHMPE fiber and remained almost the same after the oxygen plasma treatment. This peak was used as an internal standard peak for the spectral subtraction and the peak area normalization. The relative peak areas in the DRIFT spectra of the UHMPE fiber were compared according to the oxygen plasma treatment time. The C=O group increases and the C—O group decreases as the oxygen plasma treatment time increases. The DRIFT analysis data of the oxygen plasma-treated UHMPE fiber correlated well with the electron spectroscopy for chemical analysis data and DRIFT spectroscopy is known to be useful for investigating the UHMPE fiber surface. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 68: 1117–1124, 1998

Key words: DRIFT spectroscopy; UHMPE fiber; oxygen plasma treatment; KBr overlay; spectral subtraction

INTRODUCTION

Ultrahigh modulus polyethylene (UHMPE) fiber is a high-performance organic fiber with excellent modulus and strength. Its high strength and high modulus combine with low density to give it the best specific mechanical properties of all the commercial reinforcing fibers.[1–4]

However, UHMPE fiber has low surface energy and a chemically inert surface, and shows poor interfacial adhesion in composites applications. Therefore surface modification of UHMPE fiber has been an important research subject.[5–14] Many surface treatment methods of UHMPE fiber have been reported and, especially, low-temperature oxygen plasma treatment has been known to be

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effective for improving the interfacial adhesion of the UHMPE fiber composites.[9–14]

Much research on the oxygen plasma treatment of UHMPE fiber has been performed.[9–14] However, the major view of such studies was improvement of the interfacial adhesion and mechanical properties of the UHMPE fiber composites. In performing oxygen plasma treatment of the UHMPE fiber efficiently, the analysis of the oxygen plasma-treated UHMPE fiber surface becomes an important subject. The surface analysis of the oxygen plasma-treated UHMPE fiber has not been performed intensively, although some articles mentioned surface analysis of the UHMPE fiber.[7,15,16]

There are many surface analysis techniques, and different surface analysis techniques supply different and often complementary information.[17,18] Several factors, such as sampling depth, surface information, and sample suitability, should be considered in choosing a surface analysis technique.[17]

Of the various surface analysis techniques, Fourier transform infrared (FTIR) spectroscopy gives sensitive and detailed chemical information on the sample, although the sampling depth of the FTIR is longer than those of other surface analysis techniques.[17,19]

Of the various FTIR analysis techniques, diffuse reflectance FTIR (DRIFT) spectroscopy was used in this study for investigating the oxygen plasma-treated UHMPE fiber surface. DRIFT spectroscopy is not a surface-sensitive technique in itself. However, DRIFT spectroscopy has been applied to the analysis of scattering surfaces; the KBr overlay technique makes it a relatively useful surface-sensitive analysis technique; and semi-quantitative analysis is also possible if properly used.[19,20] The KBr overlay technique has several advantages, such as the removal of sample orientation effect, the enhancement of characteristic peaks due to surface species, and the removal of the specular reflectance component. However, the KBr overlay technique has some limitations when applied to quantitative analysis because the DRIFT spectra are dependent on the KBr overlay amount, particle size, and packing conditions, and this fact makes quantitative analysis using DRIFT spectroscopy difficult.[20]

In this study, the KBr overlay technique is applied to the DRIFT analysis of the UHMPE fiber surface, and the problems of KBr overlay technique in applying to the UHMPE fiber surface analysis are discussed. The other object of this study is to develop a method of applying DRIFT spectroscopy to the analysis of oxygen plasma-treated UHMPE fiber according to the treatment time. The DRIFT analysis data are also correlated with the results of electron spectroscopy for chemical analysis (ESCA).

EXPERIMENTAL

Materials

The UHMPE fiber we used was Spectra 900 plain fabric from Allied Signal, Inc. (Morristown, NJ). The UHMPE fiber surface was washed by refluxing in *n*-hexane for 2 days. The cleaned UHMPE fabric was dried for 1 day at 60°C in a vacuum oven. The dried UHMPE fabric was kept in a sealed container until used for oxygen plasma treatment and the surface analysis.

Oxygen Plasma Treatment

The plasma treatment apparatus used in this experiment was manufactured by Korea Vacuum Co. (Seoul, Korea). This plasma-treatment apparatus is a parallel electrode type with 13.56 MHz RF 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 plasma chamber was evacuated below 4×10^3 Pa ($\approx$ 30 mmHg) and the oxygen gas was flowed into the chamber at the flow rate of 10 standard cc per min. The plasma output power was 100 W and the plasma treatment time was varied from 0 to 7 min.

FTIR Analysis

A Bomem MB-100 FTIR spectrometer with a deuterated triglycine sulfate detector was used. The diffuse reflectance accessory from Graseby-Specac, Inc. (Fairfield, CN), was used. DRIFT spectroscopy is an FTIR technique that has been used for the study of fiber surfaces.[19] Dry nitrogen was used as a purge to prevent the interference of atmospheric CO_2 and water. The resolution was fixed at 4 cm^{-1} and 200 scans total were combined. UHMPE fabric cut into 2 × 2 cm was used for DRIFT analysis and a plain instead of cup-type sample holder was used in order to accommodate the fabric sample in undeformed shape. The KBr overlay technique was used in the case of enhanc-

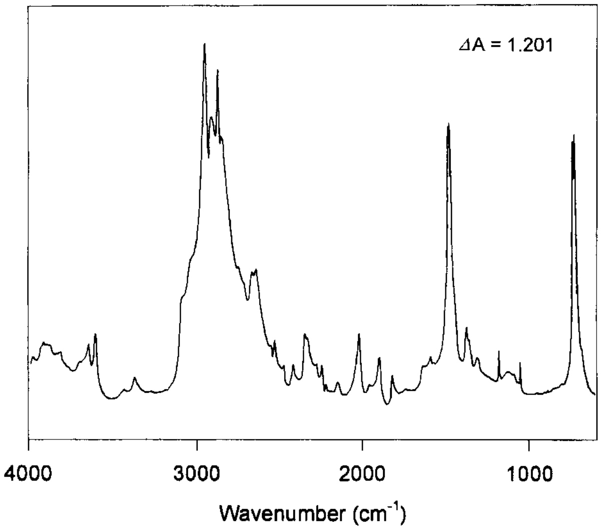

Figure 1 DRIFT spectrum of the control UHMPE fiber.

ing the characteristic peaks from the surface species to investigate the control UHMPE fiber surface. In the case where the KBr overlay technique was not used, every spectrum of the UHMPE fabric was obtained at the same fiber orientation to exclude the fiber orientation effect of the DRIFT spectra.

ESCA Analysis

ESCA analysis was performed with a 2830-S S probe surface spectrometer from SSI Co., (Mountain View, CA) An Al anode X-ray source and a concentric hemispherical analyzer detector were used.

RESULTS AND DISCUSSION

Surface Analysis of the Control UHMPE Fiber Using the KBr Overlay Technique

UHMPE fiber is composed mainly of methylene units and is expected to show a simple IR spectrum. However, the DRIFT spectrum of the UHMPE fiber shows many complex peaks. Figure 1 shows the DRIFT spectrum of the control UHMPE fiber in the range from 600 to 4,000 cm^{-1}. The axis of ordinates in the figure is represented in an arbitary scale. The UHMPE fiber shows a relatively strong absorbing character in DRIFT spectra; the DRIFT spectra could not be converted to Kubelka–Munk units because the Kubelka–Munk function is valid only for a limited range.[21] In general, the DRIFT spectrum of a polymer shows strong combination and overtone peaks in principle[22] and the peaks in the range from 1800 to 2800 cm^{-1} and above 300 cm^{-1} are mainly from combination modes and overtone modes of the UHMPE fiber. The high crystallinity of the UHMPE fiber makes the fiber's DRIFT spectrum more complex due to crystalline modes.[23] The IR peak assignment of the UHMPE fiber is represented in Table I.

Table I Peak Assignment of DRIFT Spectrum of the UHMPE Fiber

Wavenumber (cm^{-1})	Description of Mode
720, 730	CH_2 rocking
1464, 1472	CH_2 bending
2840, 2855	CH symmetric stretching
2897, 2932	CH antisymmetric stretching
1896	Crystalline combination

The KBr overlay technique is known to be a useful tool for surface analysis using DRIFT spectroscopy.[19] Figure 2 shows DRIFT spectra of the control UHMPE fiber with the different KBr overlay amounts. As the amount of the KBr overlay on the UHMPE fiber surface changes, the relative intensities of the peaks in the DRIFT spectra of the UHMPE fiber vary. The C—H stretching peaks and the C—H bending peaks of the UH-

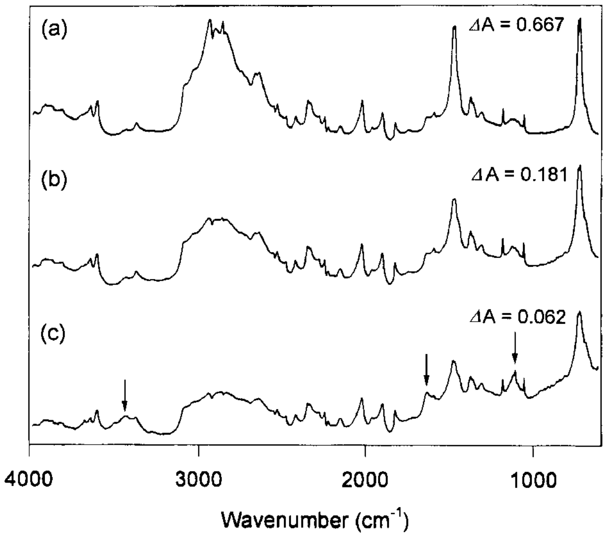

Figure 2 DRIFT spectra of the control UHMPE fiber in the order of increasing amounts of the KBr overlay: (a) < (b) < (c).

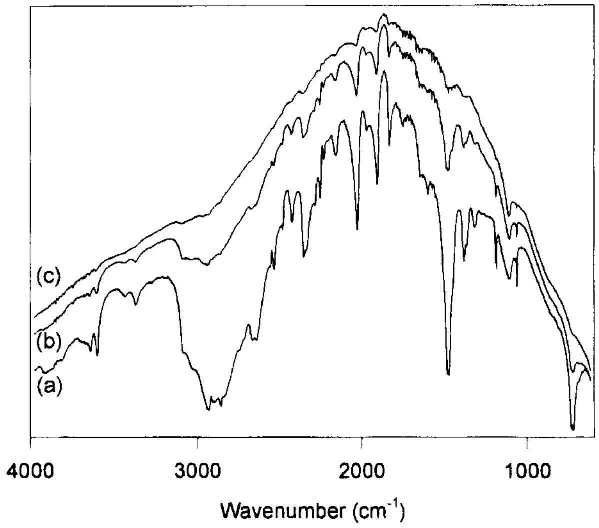

Figure 3 Raw spectra of the control UHMPE fiber in the order of increasing amounts of the KBr overlay: (a) < (b) < (c).

MPE fiber decrease as the amount of the KBr overlay increases, and the peaks at 1129, 1640, and 3434 cm^{-1} increase as the amount of the KBr overlay increases. It is known that as the amount of the KBr overlay increases, the relative intensities of the characteristic peaks from the surface species increase in a polymer's DRIFT spectra.[19] This phenomenon is obvious in the case of the UHMPE fiber from the raw spectra in Figure 3. "Raw spectra" means that the spectra were not normalized using the reference spectrum. As the amount of KBr overlay on the UHMPE fiber increases, the intensities of all peaks decrease in proportion to the KBr amount. However, after normalization using the reference spectrum, the relative intensities of peaks from the surface species increase with increasing the amount of the KBr overlay. The control UHMPE fiber is not expected to have any functional groups on the fiber surface or to show any functional group peak in the DRIFT spectrum. However, the relative intensities of the peaks from 1129, 1640, and 3434 cm^{-1} increase with the KBr overlay amount and these peaks are thought to arise mainly from the control UHMPE fiber surface. From this fact, we know that the UHMPE fiber used in this study has a chemically different surface from the bulk, or that the UHMPE fiber has been surface-treated by the manufacturer, and that the KBr overlay technique is effective for investigating the surface of the UHMPE fiber. The peak at 1129 cm^{-1} is thought to be due to C=O stretching vibration, the peak at 1640 cm^{-1} due to C=C stretching vibration, and the peak at 3434 cm^{-1} due to O—H stretching vibration.

DRIFT Analysis of the UHMPE Fiber Without KBr Overlay

Although the KBr overlay technique is a very efficient method for enhancing the characteristic peaks due to fiber surface in DRIFT analysis, there is some limitation in using the KBr overlay technique for the UHMPE fiber surface analysis. The UHMPE fiber fabric has a rough surface due to fabric structure, and it is very hard to obtain uniform thickness of the KBr overlay in a sample. It is also very hard to adjust the thickness of the KBr overlay to the same level in each UHMPE fabric sample. This fact makes it very difficult to compare the relative peak intensities between the DRIFT spectra when using the KBr overlay technique for UHMPE fiber surface analysis. In this study, the KBr overlay technique was not used so we could semiquantitatively compare the relative peak intensities of the UHMPE fiber DRIFT spectra among the samples.

However, when fiber samples are analyzed using DRIFT spectroscopy without KBr overlay, fiber orientation influences the DRIFT spectra and

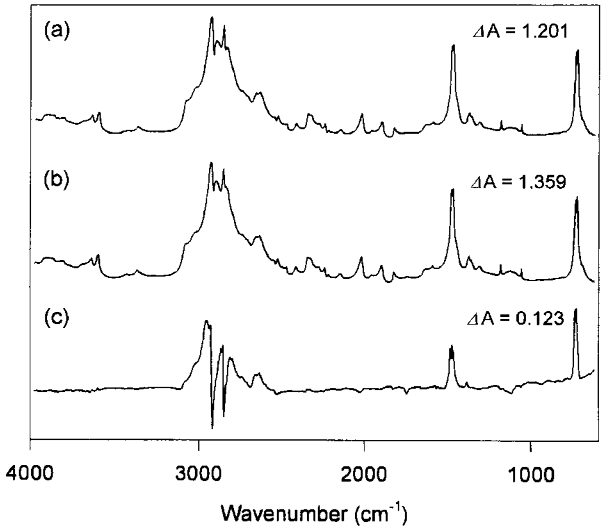

Figure 4 DRIFT spectra of the control UHMPE fiber with different fiber orientations: (a) initial spectrum; (b) spectrum obtained after rotating the sample 45 degrees with respect to the initial position; (c) difference spectrum: (a) − (b).

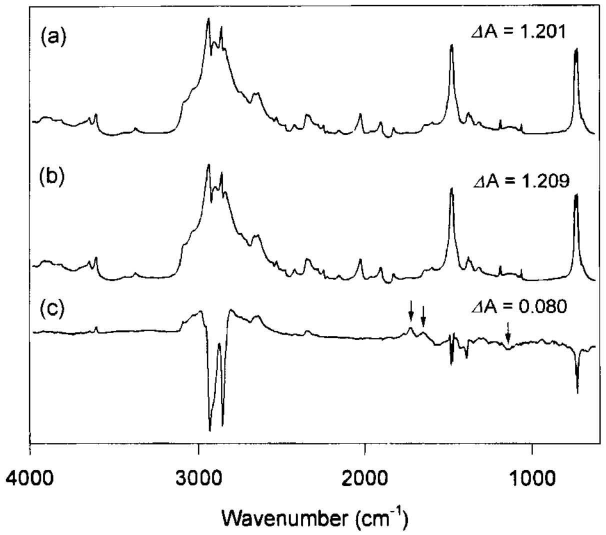

Figure 5 DRIFT spectra of the control and oxygen plasma-treated UHMPE fiber: (a) spectrum of the control UHMPE fiber; (b) spectrum of oxygen plasma-treated UHMPE fiber (100 W, 5 min); (c) difference spectrum: (b) − (a).

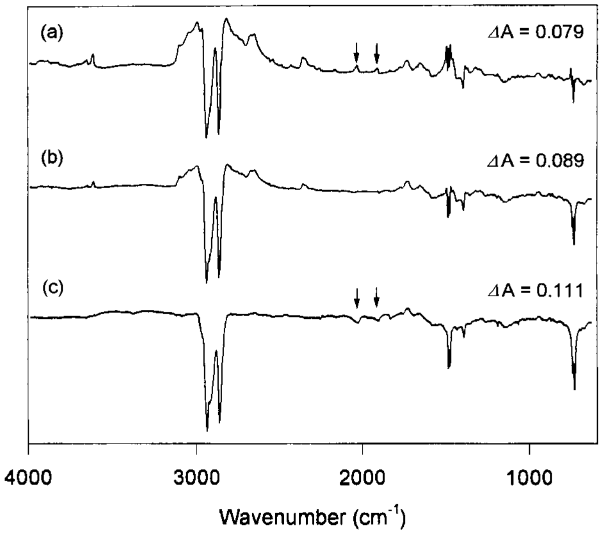

Figure 6 Difference spectra between the DRIFT spectra of the oxygen plasma-treated and control UHMPE fibers with different multiplying factors: (a) 1.028; (b) 1.052; (c) 1.082.

the fiber orientation becomes an important variable.[19,22] Figure 4 shows the DRIFT spectra of the control UHMPE fiber with different fiber orientations. Spectrum (a) represents the initial spectrum of the control UHMPE fiber, and spectrum (b) was obtained after the UHMPE fabric sample was rotated 45 degrees from initial position. Although the two spectra seem very similar, the differences between them are obvious in the difference spectrum (c). If fiber orientation does not affect the DRIFT spectrum of the UHMPE fiber, the difference spectrum shows zero intensities over the whole range. However, the difference spectrum in Figure 4(c) does not show zero intensities over the whole range due to the fiber orientation effect. Therefore, it is important to keep the fiber orientation constant when the relative peak intensities are compared in the DRIFT spectra of the UHMPE fiber samples without KBr overlay. In this experiment, the sample orientation with respect to the spectrometer was kept constant to obtain the constant fiber-orientation effect.

Figure 5 shows the DRIFT spectra of control and oxygen plasma-treated UHMPE fiber. Spectrum (c) is the difference spectrum of (b) − (a). Spectral subtraction has frequently been used to investigate minute differences between two spectra.[7,19,22] When spectrum (a) is subtracted from spectrum (b), difference spectrum (c) is obtained from (b) − $k \times$ (a). The constant k is a multiplying factor that adjusts the different absorbance scale of the two spectra to the same level. To obtain a good difference spectrum, the appropriate choice of the multiplying factor is an important process. Figure 6 represents the difference spectrum from Figure 5(c) obtained using different

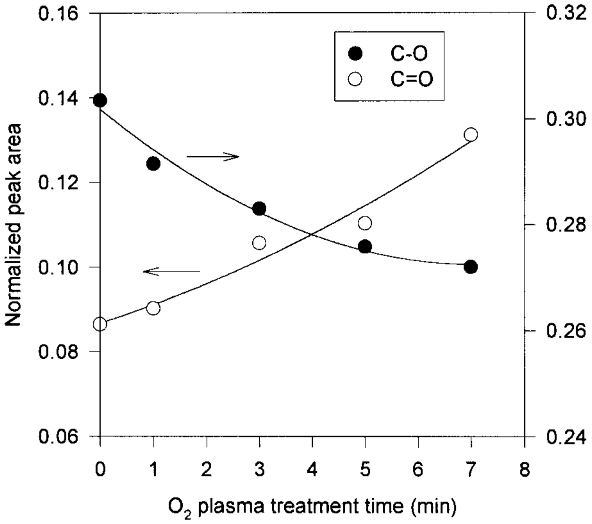

Figure 7 Variation of the relative areas of the carbonyl peak and C—O stretching peak in the DRIFT spectra of the UHMPE fiber with the oxygen plasma treatment time.

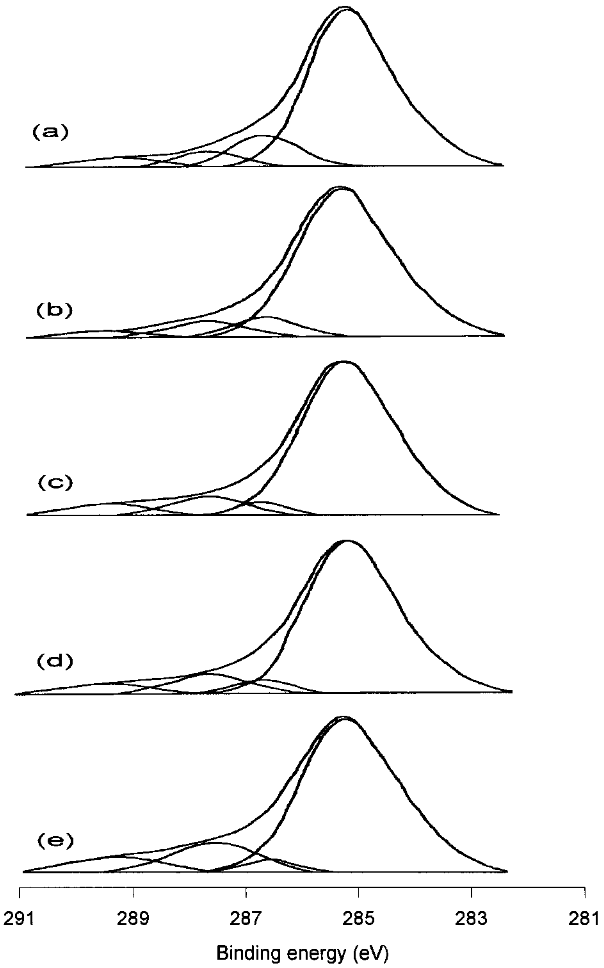

Figure 8 ESCA C_{1S} spectra of the UHMPE fiber with different oxygen plasma treatment times: (a) control; (b) 1 min; (c) 3 min; (d) 5 min; (e) 7 min.

multiplying factors. As the multiplying factor increases, the small peaks are changed from positive peaks to negative peaks. In general, negative peaks in a difference spectrum are known to mean a decrease in the chemical groups giving the peaks.[7,19,22] Therefore, appropriate selection of the multiplying factor is very important in the interpretation of difference spectra. A good multiplying factor is obtained using an internal standard peak, a peak for which the intensity and shape remain the same among the spectra. The multiplying factor is adjusted until the intensity of the internal standard peak becomes zero in the difference spectrum. The internal standard peak is selected from chemical and physical knowledge about the samples. In the case of the UHMPE fiber, the peak at 1896 cm^{-1} is assigned to the crystalline combination mode[23] and remains almost the same after the surface etching treatment.[7] The thickness of the plasma-treated layer was much shallower than the penetration depth of the IR ray in DRIFT spectroscopy and this crystalline peak was used as an internal standard peak of the UHMPE fiber. The difference spectrum in Figure 5(c) is adjusted to make the peak at 1896 cm^{-1} show zero intensity. From this difference spectrum, we see that the peaks at 1713 and 1640 cm^{-1} are increased and the peak at 1129 cm^{-1} is decreased by the oxygen plasma treatment of the UHMPE fiber. The peak at 1713 cm^{-1} is assigned to the carbonyl stretching mode and the peak at 1640 cm^{-1} is from the C=C stretching mode on the UHMPE fiber surface. The broad peak at 1129 cm^{-1} is assigned to C—O stretching vibration. The difference spectrum is useful for investigating the chemical changes in the UHMPE fiber caused by the oxygen plasma treatment. However, it is difficult to examine the variation of the peak intensities with the oxygen plasma treatment time from the difference spectra. The normalized peak area, using an internal standard peak, is a good parameter which indicates the variation of the peak with the oxygen plasma treatment time in the DRIFT spectra of the UHMPE fiber.

Figure 7 shows the variation of the normalized

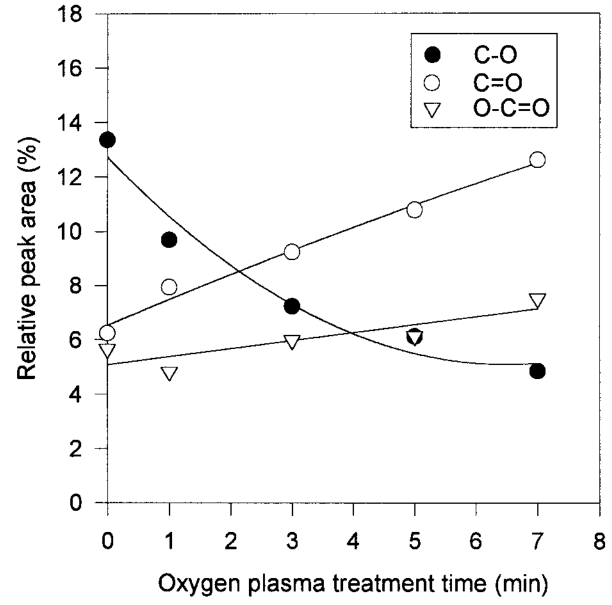

Figure 9 Variation of the contents of the C=O peak, C—O peak, and O—C=O peak in the ESCA C_{1S} spectra of the UHMPE fiber with the oxygen plasma treatment time.

carbonyl and C—O peak area with the oxygen plasma treatment time of the UHMPE fiber. The normalized area means that the carbonyl stretching peak and the C—O stretching peak areas are divided by the area of the internal standard peak at 1896 cm^{-1}. As the oxygen plasma treatment time increases, the carbonyl peak increases and the C—O peak decreases.

Correlation of the DRIFT Spectra with the ESCA Results

DRIFT spectroscopy is an efficient tool for investigating the UHMPE fiber surface if the KBr overlay technique, spectral subtraction, and normalized peak area are properly used. To examine the validity of the DRIFT analysis results, ESCA analysis of the oxygen plasma-treated UHMPE fiber was performed. Figure 8 represents the C_{1S} peaks of the ESCA spectra of the control and oxygen plasma-treated UHMPE fiber. The tails of the C_{1S} peaks arise from the carbon atoms attached to oxygen atom and can be separated into the component peaks. Many researchers have used several curve-fitting methods for the analysis of the surface-treated polyethylene and there are some differences among the curve-fitting methods and peak assignments.[15,16,24–26] In this study, the C_{1S} peaks of the UHMPE fiber are separated into four peaks[26]: CH and C=C peak at 285.0 eV; C—O peak at 286.5 eV; C=O peak at 287.6 eV; and O—C=O peak at 289.2 eV. Figure 9 shows the variation of the C—O peak, C=O peak, and O—C=O peak contents of the UHMPE fiber surface with the oxygen plasma treatment time. The exact correlation between the two sets of data is very difficult because the DRIFT spectra of the UHMPE fiber could not be shown in Kubelka–Munk units and the peak area of the DRIFT spectra is not linearly proportional to the concentration. However, the trends in the DRIFT spectra are well correlated with the trends of the ESCA data of the UHMPE fiber. From this result it is proved that DRIFT spectroscopy is a useful tool for the investigation of the UHMPE fiber surface.

CONCLUSIONS

The surface of the oxygen plasma-treated UHMPE fiber was analyzed using DRIFT spectroscopy and the following conclusions were obtained:

1. The KBr overlay technique is useful for enhancing the characteristic peaks from the surface of the UHMPE fiber. However, different KBr overlay amounts among the samples make comparison of the relative peak areas between the samples very difficult.
2. Without KBr overlay, DRIFT spectroscopy is a useful tool for the investigation of the oxygen plasma-treated UHMPE fiber according to the treatment time under constant fiber-orientation conditions. The carbonyl peak increases and the C—O stretching vibration peak decreases as the oxygen plasma treatment time increases.
3. The DRIFT analysis data are well correlated with the ESCA results, and DRIFT spectroscopy is a useful tool for investigating the UHMPE fiber surface.

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