Effects of Functional Groups and Surface Roughness on Interfacial Shear Strength in Ultrahigh Molecular Weight Polyethylene Fiber/Polyethylene System

TOSHIO OGAWA, HIROAKI MUKAI, SATOSHI OSAWA

Laboratory for Material Design Engineering, Graduate School of Engineering, Kanazawa Institute of Technology, 7-1, Ohgigaoka, Nonoichi, Ishikawa, 921-8501 Japan

Received 20 March 1998; accepted 27 June 1998

ABSTRACT: Corona discharge treatment was conducted for ultrahigh molecular weight polyethylene (UHMWPE) fiber. The functional groups and surface roughness of the polyethylene fiber surface were determined by an X-ray photoelectron spectroscopy (XPS) and atomic force microscopy (AFM). The interfacial shear strength of UHMWPE fiber with HDPE film was determined by microbond pullout method. The interfacial shear strength increased by corona treatment. Then, the effect of the chemical and physical factors on the interfacial shear strength was discussed based on the results of multivariate regression analysis. The results indicated that the contribution of functional groups and surface roughness to the interfacial shear strength was expressed as 50 and 50%, respectively. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 71: 243–249, 1999

Key words: UHMWPE fiber; interfacial shear strength; corona discharge; surface roughness; multivariate regression analysis

INTRODUCTION

High performance polymer sheets have been developed to use in various industrial fields.[1] However, it is difficult to improve drastically the mechanical properties of the sheet only by controlling the molding condition. Thus, the tensile strength of polyethylene (PE) sheet is ordinarily < 100 MPa.

Ultrahigh molecular weight polyethylene (UHMWPE) fiber was developed in the 1980s and applied to various fields, such as a nautical sea.[2–5] The highly drawn fiber has the tensile strength of 2.8 and a modulus of 100 GPa. If we can keep high molecular orientation of the fibers in PE sheets, it will be possible to have tough and flexible sheets originating from fiber. Higher strength and modulus will be necessary to expand such markets[6] as ballistic–resistant garments[7,8] and electromagnetic window applications.[9] However, the fiber is nonpolar in surface and is expected to have very weak compatibility with resins unless any treatment is conducted.[10] Many studies were already carried out on various treatments. Tissington et al.[11] and Chaoting et al.[12] determined the interfacial shear strength (IFSS) between oxygen plasma[13–20] or acid-treated[21–23] polyethylene fibers and epoxy resin. The IFSS increased with the extent of treatment. Two reasons for such improvement are considered: oxygen-containing groups produced in fiber surface and pits spread in fiber surface.

Polyethylene fiber-reinforced plastics with high-density polyethylene (HDPE) matrix have been prepared by compression molding in the vicinity of the melting point of the fiber.[10,24–28] However, the mechanical properties were about half of the predicted theoretical ones.[10,24,25] It

Correspondence to: T. Ogawa.

Journal of Applied Polymer Science, Vol. 71, 243–249 (1999)
 CCC 0021-8995/99/020243-07

Table I Mechanical and Thermal Properties of PE Fiber and HDPE Matrix

	UHMW-PE Fiber	HDPE Matrix
Density (g/cm^3)	0.96[a]	0.94
Tensile strength (MPa)	2800	211[b]
Elastic modulus (GPa)	100	2.8[b]
Elongation at break (%)	4	31[b]
Melting point[c] (°C)	152	135
Heat of fusion (J/g)	270	210

[a] Quoted from TEKMILON® catalog prepared by Mitsui Petrochemical Industries, Co., Ltd., Tokyo, Japan.
[b] HDPE is uniaxially oriented. These values were obtained by using a tensile tester.
[c] This value means endothermic peak temperature which was determined by us.

was concluded that the IFSS between PE fiber and HDPE matrix was important to improve the mechanical properties of PE/PE composites. In this study, corona discharge treatment was conducted for the PE fiber. Corona discharge treatment is perhaps one of the most popular methods for modifying polymer surface.[29–31] This treatment is simpler and more practical than the plasma treatment because samples are treated in air at atmospheric pressure. Many studies have already been reported on the functional groups determined by X-ray photoelectron spectroscopy (XPS). Most authors noticed only the contributions of chemical bonding to PE fiber/epoxy resin adhesion.[11,12,32,33] However, the quantitative contributions of surface roughness on interfacial shear strength were not reported yet. In this paper, the effects of the functional group and surface roughness on the IFSS were discussed based on the results of multivariate regression analysis.

EXPERIMENTAL

Materials

TEKMILON® fiber (Mitsui Chemical Industries, Ltd., Tokyo, Japan) was used in this study. Commercially available HDPE films (H.P.D., Ltd., Aichi, Japan) were used as the matrix of composites. This film is uniaxially oriented. Some properties of these materials are shown in Table I. For removing dirt and coating material from the fiber surface, the fibers were treated by following steps[17]:

1. Immersed in nonpolar solvent (benzene) for 1 h at room temperature;
2. Immersed in polar solvent (ethanol) for 1 h at room temperature;
3. Immersed in distilled water for 1 h at room temperature;
4. Dried in an oven for 4 h at 60°C.

Corona Treatment

Corona discharge treatment was performed using a commercially available apparatus (produced by Nippon Static Co., Ltd., Tokyo, Japan; Model HPS-10; discharge frequency: 20 kHz). In this study, the distance between the surface of PE fiber and electrode is 1 mm. The radiation energy E was calculated from the net power and the fiber velocity

$$E = \frac{P}{LV} \tag{1}$$

where P is the net power, L is the electrode width, and V is the fiber velocity. Radiation energy for PE fiber was applied in the range of $\sim$ 0–4.4 $\times$ 10^4 J/m^2, and that for PE film was treated at constant radiation energy of 2.2 $\times$ 10^4 J/m^2.

Surface Analysis

The spectra of PE fibers were obtained with an XPS ESCA-850 (Shimadzu Co., Ltd., Kyoto, Japan). XPS with MgKα X-ray source was used under the conditions of 8 kV in voltage and 30 mA in current. The monofilaments were placed on the etched Au plate to avoid the effect of oxygen on the sample holder. The broad shoulder in the high energy region of C_{1s} peak is evidence of oxygen bonded to carbon. These peaks were assigned to hydroxyl group (—OH), carbonyl group (>C═O), and carboxyl group (—COOH) at 286.5, 288.0, and 289.5 eV, respectively.

Surface Roughness

The PE fiber surface was examined by an atomic force microscopy (AFM) TMX-2100 (Topo Metrix Co., Ltd., CA, USA) in order to confirm the change of roughness due to the corona discharge. AFM was used under the condition of 10 μm in scan width for fiber direction. The electric charge on PE fiber surface generated by corona treatment was eliminated by a static eliminator. A sample was placed on double-coated carbon tape (Ohken Co., Ltd., Tokyo, Japan). Surface roughness can

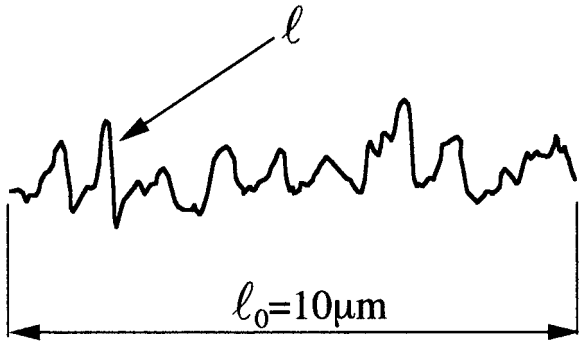

Figure 1 Definition of surface roughness.

be defined by various ways, i.e., arithmetic mean of roughness (R_a), maximum roughness (R_y), and ten point average roughness (R_z). In this study, another definition, i.e., the ratio of length in roughness curve (R_c), was adopted

$$R_c = \frac{l}{l_0} \tag{2}$$

where l_0 is the adopted linear distance in roughness curve, and l the real length along with roughness curve, shown in Figure 1. The results were evaluated using the average of six measured values.

Interfacial Shear Test

IFSS was determined by microbond pullout method,[34] which was described in detail previously.[10] Radiation energy of PE fiber was applied in the range of $\sim 0-4.4 \times 10^4$ J/m^2. HDPE film was treated in the constant radiation energy of 2.2×10^4 J/m^2.

Multivariate Regression Analysis

This method of multivariate regression analysis is very useful for describing the characteristics of the subject as a function of many factors. The amount of glass[35] and talc[36] in polypropylene was controlled by multivariate regression analysis. The injection molding model was also developed by multivariate regression analysis.[37] Also, not only the chemical surface activities but also the surface roughness must be taken into account[34,38,39] when considering the surface effect on IFSS. Therefore, we applied this method to the relationship between surface characteristic and IFSS. The basic equation for multivariate regression analysis is

$$Y = \beta_0 + \sum_j \beta_j X_j \tag{3}$$

where Y is a criterion variable, X_1, $X_2 \cdots X_j$ are the explanatory variables, β_0 is a constant, and β_1, $\beta_2 \cdots \beta_j$ are the regression coefficients or the rate of contribution for each variable.

To discuss the contribution of the explanatory variable, Y and X were normalized as Y' and X', respectively; and

$$Y'_j = \frac{Y_j - \bar{Y}_j}{\sqrt{Syy}} \tag{4}$$

$$X'_j = \frac{X_j - \bar{X}_j}{\sqrt{Sxx}} \tag{5}$$

where Y_j and X_j are the value of each variable, and $\bar{Y}_j$ and $\bar{X}_j$ are the average of Y_j and X_j, respectively. Syy and Sxx are a variance of Y_j and X_j, respectively.

In this study, Y corresponds to IFSS, $X_1 \cdots X_j$ functional groups, and surface roughness.

RESULTS AND DISCUSSION

XPS wide spectra of polyethylene fiber are shown in Figure 2. For the untreated sample, strong C_{1s} and a weak O_{1s} peak are observed at 285 and 532 eV, respectively. The weak $Au_{4f7/2}$ peak is observed at 84 eV because X-ray happened to pass between PE fibers. The oxygen peak is due to the oxidation of PE during fiber processing or unknown material coated on the fiber, which could not be removed with solvents. Figure 3 shows oxygen content on PE fiber surface which was generated by corona discharge treatment. The oxygen content increased with radiation energy. The maximum value of the oxygen content was 23 atom % (O/(C + O)) in the treatment of 4.4×10^4 J/m^2 in this study. Chaoting et al. discussed[12] the PE/epoxy interfacial adhesion where the oxygen content was 16.5 atom % by plasma treatment. The magnified peaks due to C_{1s} are shown in Figure 4. The broad shoulder in higher binding energy region is due to the existence of oxygen bonded to carbon. The corona discharge treatment of the polymer surface may produce carbon radicals from the hydrocarbon backbone, followed by the final formation of oxygen-based functional groups by reaction with oxygen.[30] The content of

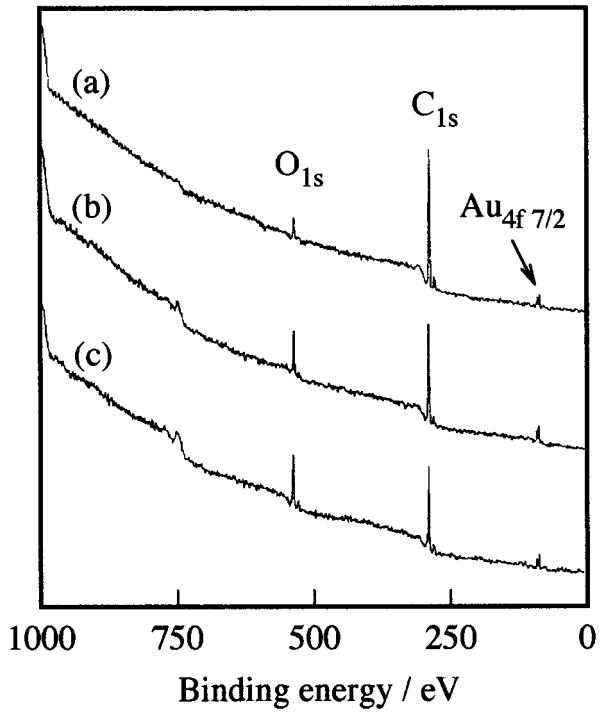

Figure 2 XPS wide spectra of corona-treated PE fiber: (a) untreated; (b) treated at 2.2×10^4 J/m^2; (c) treated at 4.4×10^4 J/m^2.

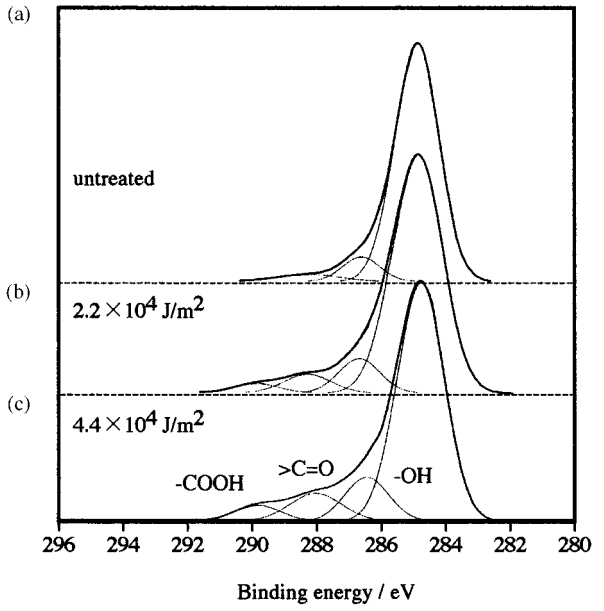

Figure 4 XPS C_{1s} spectra for corona-treated PE fiber surface. The broad shoulder in higher binding energy region means the existence of oxygen bonded to carbon such as —OH (286.5 eV), >C═O (288.0 eV), and —COOH (289.5 eV): (a) untreated; (b) treated at 2.2×10^4 J/m^2; (c) treated at 4.4×10^4 J/m^2.

functional groups is shown in Figure 5. The functional groups increased with radiation energy. It is expected that the adhesive properties of the fiber increases with the content of these groups on the surface.

The IFSS of PE fiber with HDPE matrix was determined by the microbond pullout method.

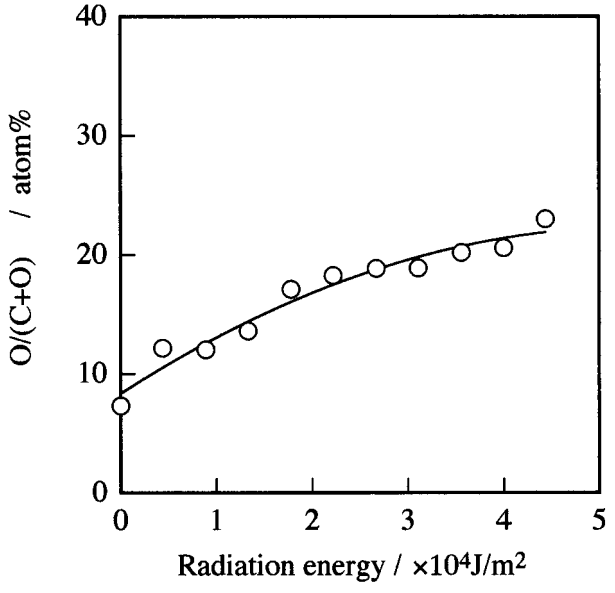

Figure 3 Oxygen content (atom%) on PE fiber surface as a function of corona radiation energy.

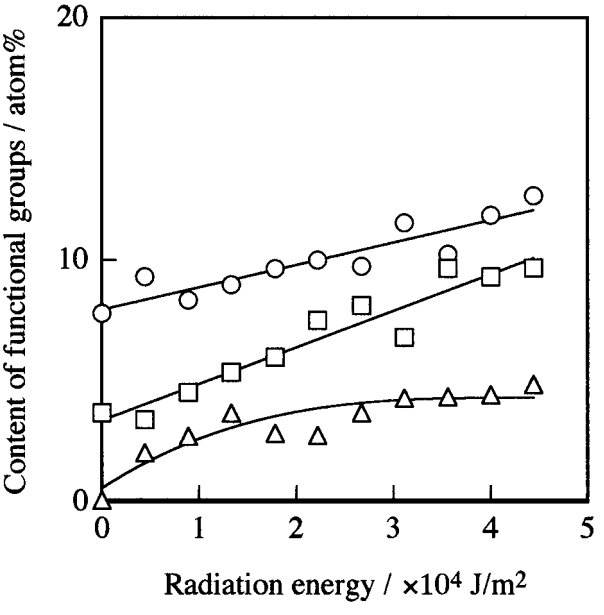

Figure 5 Content of functional groups (atom%) as a function of corona radiation energy: (○) —OH; (□) >C═O; (△) —COOH.

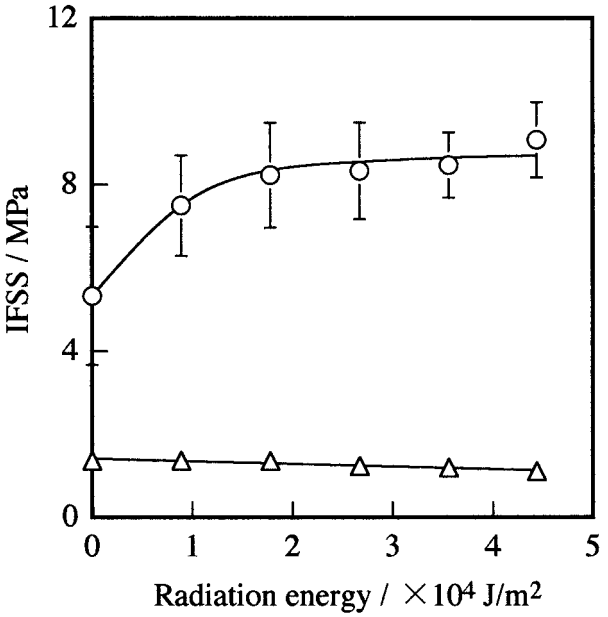

Figure 6 IFSS of UHMW–PE/HDPE composites as a function of corona radiation energy: (△) untreated HDPE film; (○) corona treated HDPE film at 2.2 × 10^4 J/m^2.

When the test specimen was prepared with treated PE fiber and untreated HDPE film, IFSS was < 1.5 MPa, as shown in Figure 6. Next, the test specimen was prepared from PE fiber treated in various degrees with treated HDPE film that was carried out in the radiation energy of 2.2 × 10^4 J/m^2. IFSS increased with radiation energy and leveled off at around about 2.0 × 10^4 J/m^2, as shown in Figure 6. The maximum value of 9.1 MPa was attained in 4.4 × 10^4 J/m^2. In this case, IFSS was improved by about 70% as compared with that of untreated fiber.

The effect of the functional groups on IFSS was analyzed by multivariate regression analysis. The calculated result for IFSS was obtained as follows:

$$\text{IFSS} = 5.34 + 0.0919 \times (\text{—OH}) - 0.165 \times (\text{>C═O}) + 0.906 \times (\text{—COOH}) \quad (6)$$

where —OH is the hydroxyl group, >C═O is the carbonyl group, and —COOH is the carboxyl group. The adjusted R^2 for the calculation is 0.893. Here, if adjusted R^2 was 1.0, the criterion variable was completely expressed by the contribution of explanatory variables. Therefore, the IFSS can be well described by the sum of contributions of the three variables. The contribution of carboxyl group to IFSS is about 80%.

The contribution of —COOH on IFSS was highest among the functional groups. Not only the functional groups, but also the surface roughness must be taken into account when considering the surface effect of the PE fiber. The surface roughness profile in fiber direction was examined by AFM and the results shown in Figures 7 and 8. There is a large difference in surface roughness between untreated and treated fibers. In this study, we determined R_a, R_y, and R_z according to Japanese Industrial Standard B 0601. However, it was difficult to find the relationship between surface roughness and radiation energy. On the other hand, the surface roughness R_c defined by eq. (2) showed good correlation with radiation energy, as shown in Figure 9.

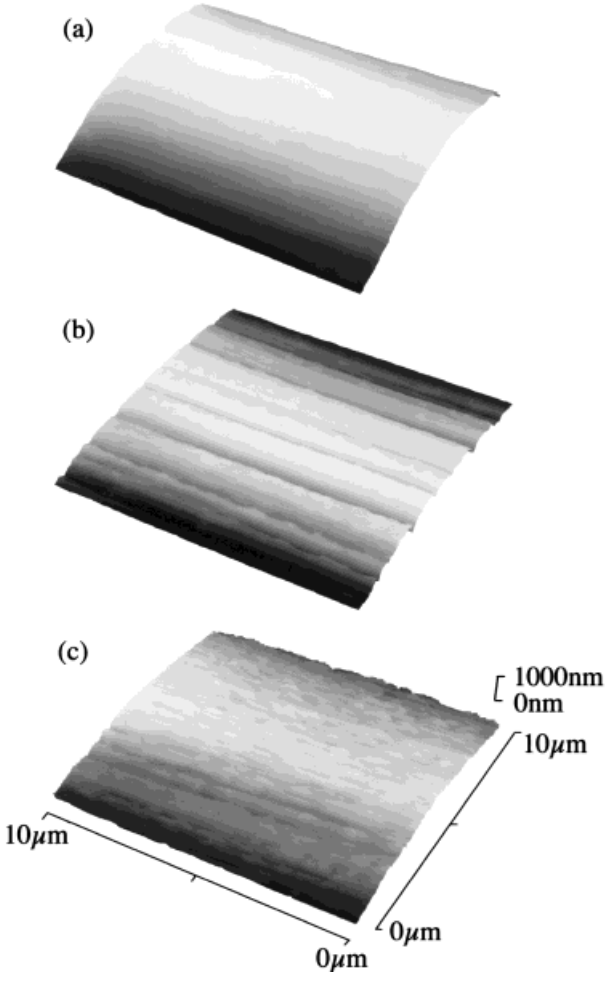

Figure 7 Diagrams of AFM for PE fiber surface: (a) untreated; (b) treated at 2.2 × 10^4 J/m^2; (c) treated at 4.4 × 10^4 J/m^2.

The effects of the functional groups and surface roughness were analyzed after normalization by eqs. (4) and (5). Because of a small number of experimental points, only the carboxyl group was adopted, which was the highest among the functional groups for eq. (6). Therefore, we also estimated the effects of surface roughness R_c on the IFSS by separating into two regions in radiation energy, i.e., ~ 0–2.2 and ~ 2.2–4.4 × 10^4 J/m^2. The results are shown by eqs. (7) and (8).

$$\mathrm{IFSS}_{0\text{–}2.2} = -0.00664 + 1.340 \times (\text{—COOH}) - 0.362 \times R_c \quad (7)$$

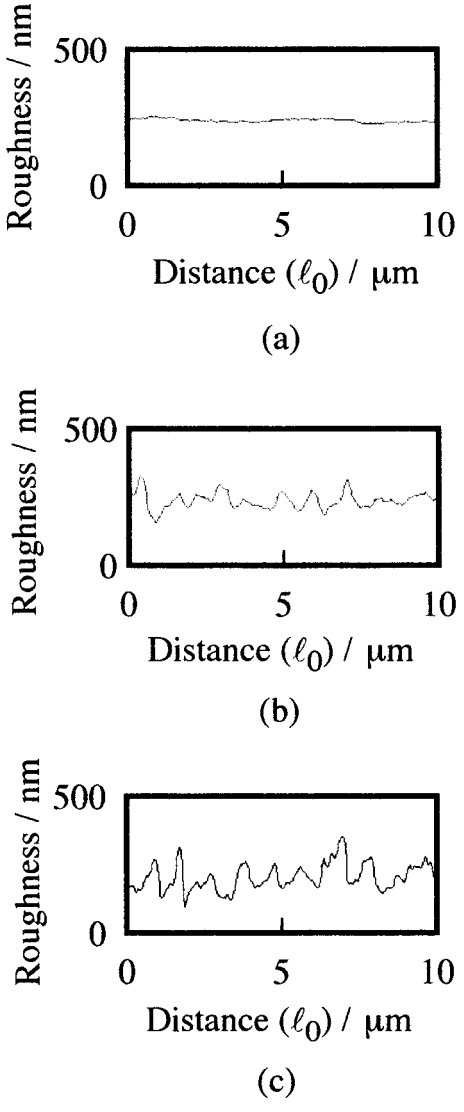

Figure 8 Surface roughness profile of the PE fiber in the fiber direction which was obtained by AFM: (a) untreated; (b) treated at 2.2 × 10^4 J/m^2; (c) treated at 4.4 × 10^4 J/m^2.

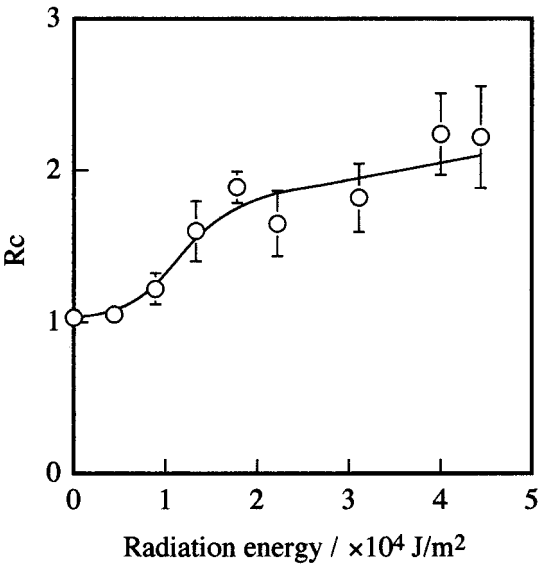

Figure 9 Surface roughness R_c of PE fiber in the direction as a function of corona radiation energy.

$$\mathrm{IFSS}_{2.2\text{–}4.4} = -0.0672 + 0.528 \times (\text{—COOH}) + 0.492 \times R_c \quad (8)$$

R_c is an index of surface roughness, which is already defined in this paper. The adjusted R^2 for this calculation is 0.998, indicating that IFSS can be well described by the R_c. The result demonstrates that the effect of the functional group on IFSS is larger than that of surface roughness in the region of 0–2.2 × 10^4 J/m^2. However, the contribution of —COOH and R_c on IFSS is about 50 and 50%, respectively, in the region of ~ 2.2–4.4 × 10^4 J/m^2. Tissington et al. reported[11] that the interlaminar shear strength of PE fiber (TEKMILON) composite reached the maximum within 5 s of plasma treatment, due to rapid surface oxidation, and showed no increase after 5 s. In principle, almost the same behavior as that by Tissington et al. was observed in this study.

CONCLUSION

Interfacial shear strength between PE fiber and HDPE matrix was six times improved by corona discharge treatment for both materials. The contribution of —COOH on IFSS was the highest among functional groups. The contribution of functional groups and surface roughness varied depending upon the degree of corona discharge treatment.

REFERENCES

1. Deng, M.; Shealaby, S. W. J Appl Polym Sci 1995, 58, 2111.
2. Porter, R. S.; Kanamoto, T. Polym Eng Sci 1994, 34, 266.
3. Yamashita, A. Shinsozai Jpn 1993, 4, 38.
4. Werff, H.; Pennings, A. J. Colloid Polym Sci 1991, 269, 747.
5. Payer, W. Kunststoffe 1993, 83, 775.
6. Segal, C. L. SAMPE J 1996, 32, 12.
7. Kirkland, K. M.; Tam, T. Y.; Weedon, G. C. ACS Symp Ser 1991, 457, 214.
8. Wilson, L.; Lin, L.; Mullaney, K.; Weedon, G. Polyolefin 8 1993, 174.
9. Cordova, D. S.; Collier, L. S. Int SAMPE Symp 1992, 37, 1406.
10. Ogawa, T.; Mukai, H.; Osawa, S. J Appl Polym Sci 1998, 68, 1431.
11. Tissington, B.; Pollard, G.; Ward, I. M. J Mater Sci 1991, 26, 82.
12. Chaoting, Y.; Gao, S.; Mu, Q. J Mater Sci 1993, 28, 4883.
13. Ladizesky, N. H.; Ward, I. M. J Mater Sci 1983, 18, 533.
14. Ladizesky, N. H.; Ward, I. M. Comp Sci Tech 1986, 26, 129.
15. Tissington, B.; Pollard, G.; Ward, I. M. Comp Sci Tech 1992, 44, 197.
16. Nguyen, H. X.; Weedon, G. C.; Chang, H. W. Int SAMPE Symp 1989, 34, 1603.
17. Bettge, D. J.; Hinrichsen, G. Comp Sci Tech 1993, 47, 131.
18. Li, Z.-F.; Grubb, T. J Mater Sci 1994, 29, 189.
19. Grubb, D. T.; Li, Z.-F. J Mater Sci 1994, 29, 203.
20. Peijs, T.; Rijsdijk, H. A.; Kok, J. M. M.; Lemstra, P. J. Comp Sci Tech 1994, 52, 449.
21. Vaykhansky, L. E.; Cohen, Y. J Polym Sci: Part B 1995, 33, 1031.
22. Mercx, F. P. M.; Benzina, A.; Langeveld, A. D. V.; Lemstra, P. J. J Mater Sci 1993, 28, 753.
23. Rarichandran, V.; Obendorf, S. K. Polym Adv Tech 1994, 5, 818.
24. Teishev, A.; Incadona, S.; Migliaresi, C.; Marom, G. J Appl Polym Sci 1993, 50, 503.
25. Teishev, A.; Incadona, S.; Migliaresi, C.; Marom, G. Ceram Matrix Comp Other Syst 1993, 870.
26. Marais, C. Eur Conf Compos Mater 1990, 4, 1057.
27. Arnold, J. J.; Zamora, M. P.; Brennan, A. B. Polym Comp 1996, 17, 332.
28. Teishev, A.; Marom, G. J Appl Polym Sci 1995, 56, 959.
29. Strobel, J. M.; Strobel, M.; Lyons, C. S.; Dunatov, C.; Perron, S. J. J Adhesion Sci Tech 1991, 5, 119.
30. Lee, J. H.; Kim, H. G.; Khang, G. S.; Lee, H. B.; Jhon, M. S. J Colloid Interface Sci 1992, 151, 563.
31. Lanauze, J. A.; Myers, D. L. J Appl Polym Sci 1990, 40, 595.
32. Gao, G.; Zeng, Y. J Appl Polym Sci 1993, 47, 2093.
33. Andreopoulos, A. G.; Liolios, K.; Patrikis, A. J Mater Sci 1993, 28, 5002.
34. Ogawa, T.; Uchibori, H. J Adhesion 1995, 47, 245.
35. Weil, R. C.; Mangararo, C. R.; Parrinello, L. M.; Subramanian, R. ANTEC 94′ 1994, 2770.
36. Borden, K. A.; Weil, R. C.; Mangararo, C. R. ANTEC 94′ 1994, 2761.
37. Potente, W. H. ANTEC 95′ 1995, 659.
38. Chawla, K. K.; Xu, Z. R. High Perfor Comp 1994, 207.
39. Drzal, L. T.; Rich, M.; Lloyd, P. J Adhesion 1983, 16, 1.