

Mechanical Properties of Ultrahigh-Molecular-Weight Polyethylene Fiber-Reinforced PE Composites

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ABSTRACT: Three types of high-strength polyethylene (PE) fiber-reinforced composite sheets were made by compression molding at the vicinity of melting point of the fiber. Sheet I was molded from only PE fibers. Sheets II and III were prepared by the compression molding of PE fiber with conventional high- and low-density polyethylene films, respectively. The mechanical properties, thermal behavior, and morphologies of the sheets have been investigated and compared with each other. The tensile strength and elastic modulus of sheet III are 660 MPa and 14 GPa, respectively, which were 60 and 30 times higher than those of typical low-density PE film. Although the elastic modulus of sheet III is 6 GPa less than that of sheet II, the tensile strength of 660 MPa is highest in the three types of sheets prepared in this study. The mechanical properties of sheets II and III were about half of predicted theoretical ones. It was concluded that the interfacial adhesion between PE fiber and PE matrix was an important factor to improve the mechanical properties of this PE sheet. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 68: 1431–1439, 1998

Key words: compression molding; polyethylene fiber; mechanical properties; thermal analysis; composite

INTRODUCTION

High-performance polymer sheets have been developed in order to satisfy the use in various industrial fields, such as wrapping, building, automobiles, and aircrafts as well as aerospace devices.^{1–6} Polyethylene (PE) has been one of widely used thermoplastics as a sheet in the fields since PE exhibits high tenacity, chemical resistance, good thermal property, and easy process control. Major efforts have been made to achieve high mechanical properties of PE sheet by means of molding conditions, such as cooling rate, molding temperature, and pressure via molecular orientation and crystallization.^{7–13} However, it is difficult to

improve drastically the mechanical properties of the sheet by only controlling the molding conditions. Thus, the tensile strength of PE film is in general less than 100 MPa.

Ultrahigh-molecular-weight polyethylene (UHMW-PE) fibers have been developed by melt-spinning and gel-spinning.^{14–16} The tensile strength and modulus of highly oriented UHMW-PE fibers are of their theoretical values.¹⁷ These values are over twice that of any other fiber on a weight basis, that is, normalized with respect to fiber density. Further, UHMW-PE fiber has the high abrasion, cut resistance, and impact resistance.^{18–20} The last one is in contrast to the stiff and brittle carbon or glass fibers usually used in the composite materials. If we can keep high molecular orientation of the fiber in a composite sheet, it will be possible to have tough and flexible sheets having such excellent properties originated from the fiber. Higher strength and modulus of PE fiber reinforced plastics

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will be necessary to expand markets as ballistic-resistant garment and electromagnetic window application.²¹ Although the UHMW-PE/PE composite materials are highly important in many applications, only a little information on the mechanical properties as a function of the time of compaction has been studied.²²⁻²⁸ The important process variables were the compaction temperature, pressure, and time.

On improving the mechanical properties of the composite materials, interfacial adhesion between fiber and matrix is one of important factors. Teishev et al. have studied PE/PE composites. The introduction of cocrystallization at the interface promotes an increase in adhesion.²³ Hine et al. developed a hot compaction technique to prepare large-section products from high-modulus polyethylene fibers. They reported that high strength is achieved by selective surface melting of the fibers via a suitable choice of compaction temperature. On cooling, the molten material recrystallizes to form a glue to bind the structure together.²⁴ Alternative ways to improve the interfacial adhesion have been studied by using plasma treatments on the fibers.²⁹ The degree of adhesion between fibers or between fiber and matrix is also correlated to the molding process.

In this article, three different types of polyethylene sheets have been prepared by a compression molding. Namely, sheet I was molded only from the UHMW-PE fiber, sheets II and III were from the fiber with high- and low-density polyethylene films, respectively. The resultant mechanical properties are discussed in terms of the compaction conditions and morphologies of the sheets. The interfacial share strength between the fiber and matrix is also discussed.

EXPERIMENTAL

Materials

TEKMILON fiber (Mitsui Petrochemical Industries, Ltd., Japan) was used in this study. Commercially available high- and low-density polyethylene (HDPE and LDPE) films were used as the matrix of composites. Some properties of these materials are shown in Table I.

Preparation of Composites

Three types of composite sheets (I, II, and III) were prepared by compression molding at a con-

stant temperature and a pressure. Sheet I was molded from only PE fiber. Sheets II and III were molded from PE fiber with HDPE and LDPE films, respectively. For preparation of sheet I, fibers were wound around a stainless reel, then pressed using a Test Press SA-303-II-S (Tester Sangyo Co., Ltd., Japan). In the case of sheet II or III, PE films were placed on both sides of wound fibers, then the material was pressed. The schematic illustration of the molding method is shown in Figure 1. The molding temperature was recorded from the mercury thermometer installed in steel blocks.

Tensile Test

Tensile tests were carried out using a AGS-1000B tensile tester (Simadzu Co., Ltd., Japan) with a load cell of 1 ton at the test speed of 2 mm/min. The composite pieces for the tests were prepared in a half-size of type II regulated in JIS K 7113. The test for fiber was performed according to JIS L 1069.

Thermal Analysis

Thermal analysis was carried out using a differential scanning calorimeter, DSC 8230B (Rigaku Co., Ltd., Japan). The heat of fusion and the temperature were calibrated by using standard indium. Sheet samples of approximately 5.0 mg were placed in a aluminum pan and heated at the rate of 10°C/min from 30°C to 200°C under nitrogen atmosphere. Table I lists the endothermic peak temperatures and heat of fusion of materials used in this study.

Fiber Volume Fraction

The fiber weight fraction (W_f) of the composites for sheets II and III were $W_f = 0.74$ and 0.70 , respectively. The fiber volume fraction (V_f) was calculated by the following equation:

$$V_f = \frac{W_f \rho_m}{\rho_f + W_f(\rho_m - \rho_f)} \quad (1)$$

where ρ_f and ρ_m are the density of the polyethylene fiber and film, respectively.

Interfacial Shear Test

Corona discharge treatment was performed using a commercial machine (produced by Nippon

Table I Properties of PE Fiber and PE Films

	UHMW-PE Fiber	HDPE Film	LDPE Film
Density (g/cm ³)	0.96	0.94	0.91
Tensile strength (MPa)	2800	211	11.2
Elastic modulus (GPa)	100	2.8	0.42
Elongation at break (%)	4	31	259
Melting point (°C)	152	135	118
Heat of fusion (J/g)	270	210	130

Static Co. Ltd., Japan; Model HPS-10; discharge frequency, 20 kHz). In this study, distance between the surface of PE fiber and electrode is 1 mm. A useful concept in corona treatment was the radiation energy E , calculated from the net power and the fiber velocity, as follows:

$$E = \frac{P}{Lv} \tag{2}$$

where P is the net power, L is the electrode width,

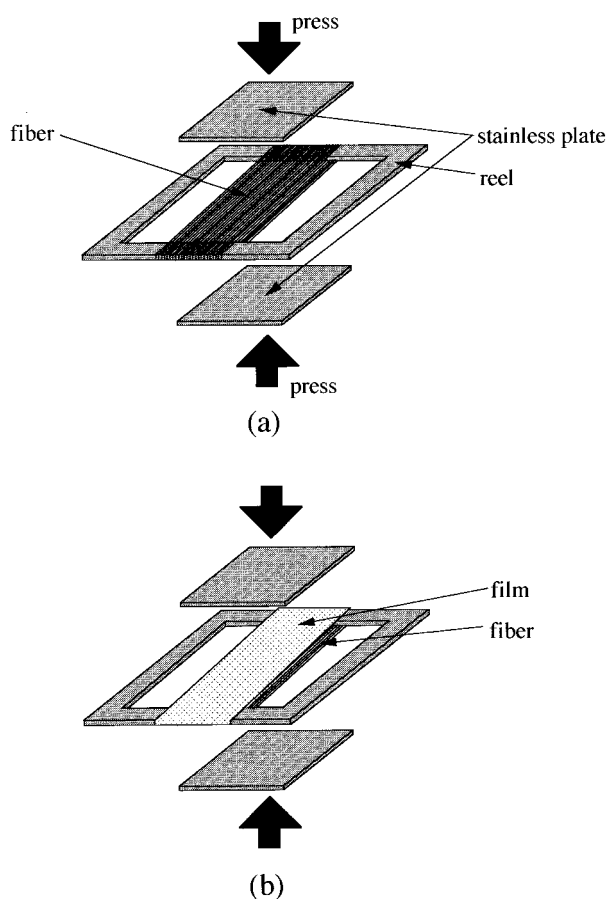


Figure 1 Schematic illustration of the molding method for (a) sheet I and (b) sheets II and III.

and v is the fiber velocity. Radiation energy of PE fiber was applied in the range of $0-4.4 \times 10^4$ J/m². HDPE film was treated at constant radiation energy of 2.2×10^4 J/m².

Interfacial shear strength was determined by pull-out method. The specimen was prepared with PE fiber and HDPE film by compression molding at 135°C, 10 min, as shown in Figure 2. The length covered with the HDPE matrix was adjusted to about 1 mm. Interfacial shear strength (τ) was calculated from

$$\tau = \frac{F}{\pi DL} \tag{3}$$

where F is the pull-out load, D is the fiber diameter, and L is the covered length. The adopted values is shear debonding, and the average of 20 to 30 measured values.

RESULTS AND DISCUSSION

Molding conditions, such as temperature and time, are very important to obtain sufficient

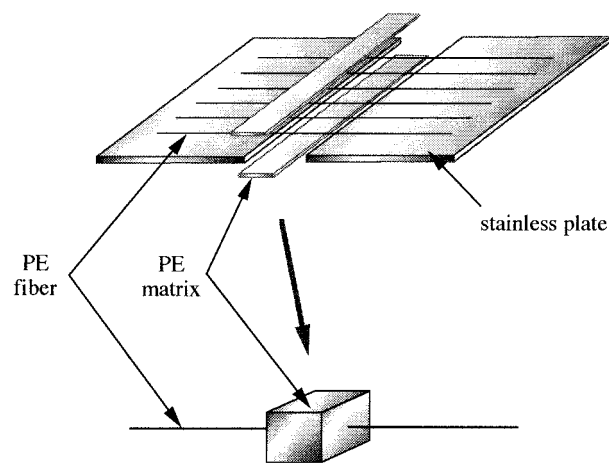


Figure 2 Schematic illustration of interfacial shear test specimen.

molded species without wrinkle, void, sink mark, and breaking of fiber. The macroscopically homogeneous sheets without such defects could be obtained under the following molding conditions: the molding temperatures of 150°C for sheet I, and 145°C for sheets II and III; and the molding time in the range of 170–240, 220–340, 180–1140 s for sheets I, II, and III, respectively. Figure 3 shows polarizing optical microphotographs of typical cross sections of sheets I, II, and III. These sheets were cut along perpendicular to the fiber axis direction. For sheet I, fibers changed from circular shape to hexagonal one and adhered to each other. Some small voids are seen along the boundary of fibers. Usually, fiber will lose its fiber structure during its melting. However, the hexagonal shape in Figure 3 indicates that the fibers were not completely melted at the molding temperature and the time (210 s). As will be shown in the differential scanning calorimetry (DSC) thermogram (see Fig. 8), the original fibers begin to melt at 145°C. Then they melt completely at 165°C. The molding temperature of 150°C is between 145 and 165°C and $\sim 2^\circ\text{C}$ lower than the peak melting point. Therefore, the fibers partially melt and contact each other in this molding condition. At a molding temperature of 160°C, the fibers lost their fiber structure. For sheets II and III, the shape of fibers are unchanged. The HDPE and LDPE matrices (their peak melting temperatures are 135 and 118°C, respectively) are filled between fibers at a molding temperature of 145°C. They also have minor voids; however, marked fiber agglomerations cannot be seen in any of these sheets.

Figure 4 shows a typical stress–strain curves for the three types of composite sheets. Each curve has stress maximum at the strain ranging from 2–4%, followed by large strain to break. The strength for sheets II and III are higher than that for sheet I. This might be related to degree of adhesion between fibers. For sheets II and III, fibers are bonded by HDPE and LDPE because these matrixes completely melt and filled between fibers, which leads to higher modulus. On the other hand, adhesion of fibers in sheet I was not complete because of partial melt of fibers, resulting in a lower tensile strength. For modulus, sheet III is lowest. This is due to the low modulus of LDPE, as shown in Table I. There are no significant catastrophic shape in stress–strain curves. The ultimate stress values are used as the tensile strength of the sheets hereafter. Figures 5–7 show the tensile strength and elastic modu-

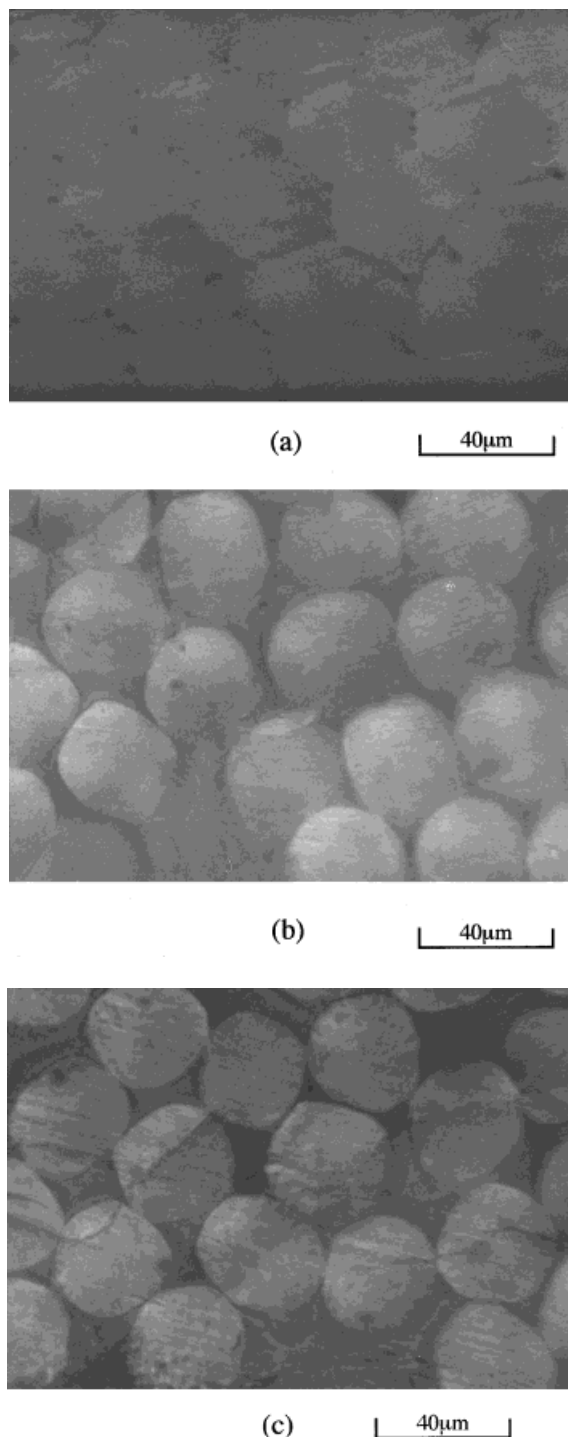


Figure 3 Polarizing optical microphotographs of typical cross sections of (a) sheets I, (b) II, and (c) III. The sheets were cut along perpendicular to the fiber axis direction.

lus of sheets I–III as a function of molding time, respectively. The tensile strength and modulus of sheet I give a maximum around 210 s. With

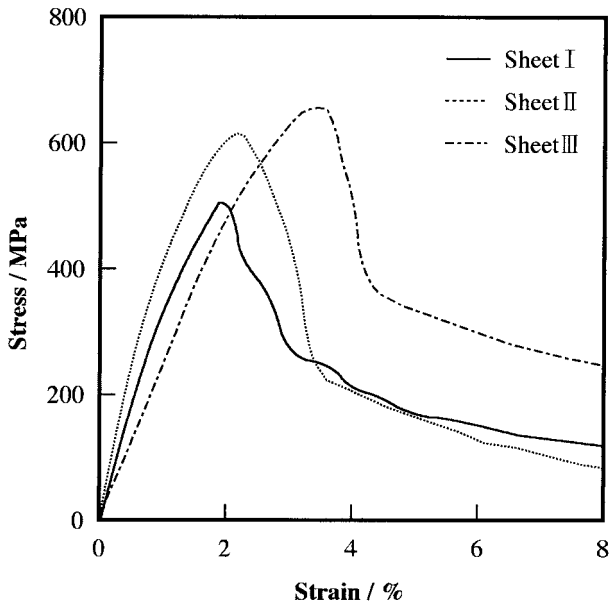


Figure 4 Typical stress-strain curves for sheets I, II, and III.

increasing molding time, fibers gradually lose their original structure (molding temperature is 5°C higher than the onset melting temperature), which lowered the mechanical properties. On the other hand, the partial melting of fibers might increase adhesion between fibers with increasing molding time. The opposite factors may provide a maximum of mechanical properties at an optimum molding time of ~ 210 s. The tensile strength and elastic modulus in sheet II are 600

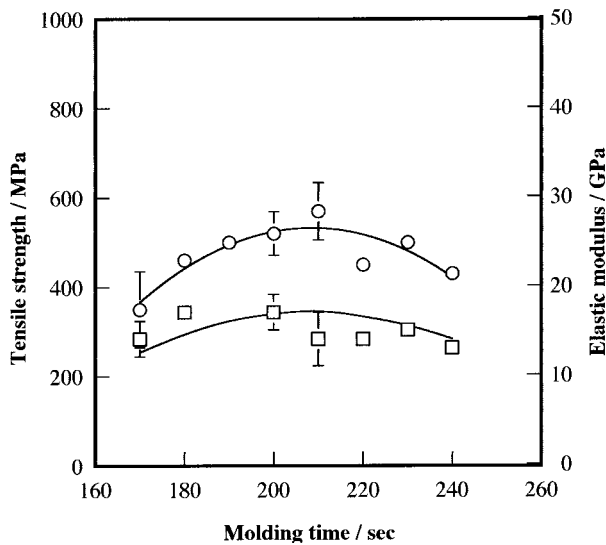


Figure 5 (○) Tensile strength and (□) modulus of sheet I as a function of molding time.

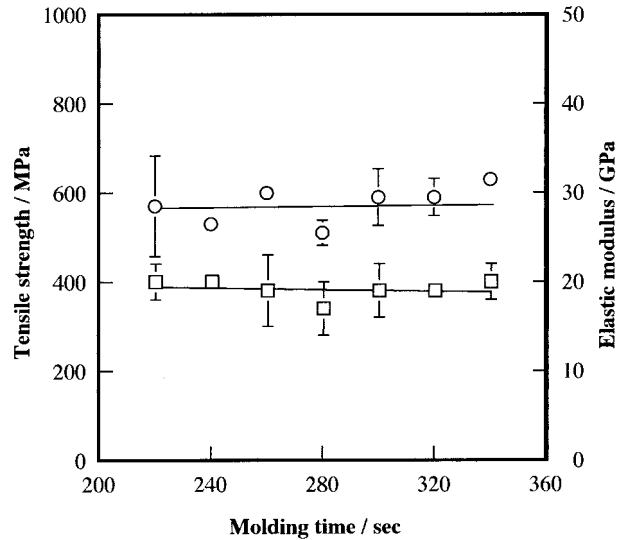


Figure 6 (○) Tensile strength and (□) modulus of sheet II as a function of molding time.

MPa and 20 GPa, respectively, which are almost independent of the molding time. These values are larger than those in sheet I and demonstrate that the mechanical properties can be improved by the presence of matrix resin. The tensile strength and elastic modulus of sheet III are 660 MPa and 14 GPa, respectively. Although the elastic modulus of sheet III is 6 GPa less than that of sheet II, the tensile strength of 660 MPa is highest in the three types of sheets prepared in this study.

It is well known that predicted theoretical values for tensile strength (σ_c) and elastic modulus

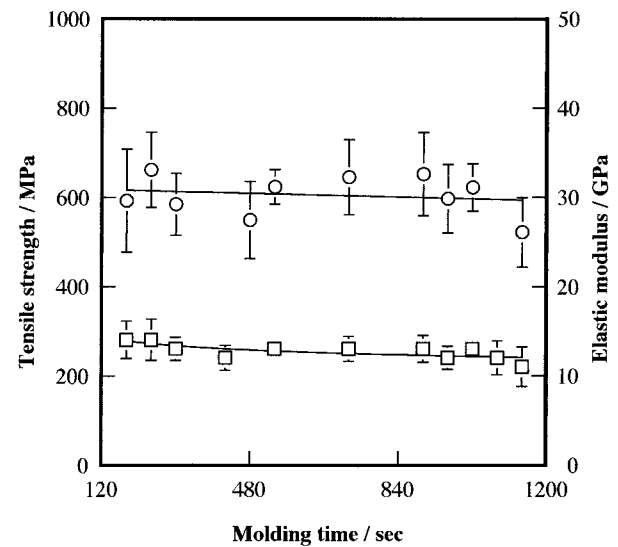


Figure 7 (○) Tensile strength and (□) modulus of sheet III as a function of molding time.

Table II Mechanical Properties of Fiber and Films Treated Separately Under the Same Conditions as Those in Preparing Sheets II and III

	UHMW-PE Fiber	HDPE Film	LDPE Film
Tensile strength (MPa)	1500	35	8.8
Elastic modulus (GPa)	44	1.0	0.49

(E_c) of fiber-reinforced composite were calculated by the following linear mixture rule³⁰:

$$\sigma_c = \sigma_f^* V_f + \sigma'_m (1 - V_f) \quad (4)$$

$$E_c = E_f V_f + E_m (1 - V_f) \quad (5)$$

where σ_f^* and σ'_m are the tensile strength of fiber and film, respectively, and E_f and E_m are elastic modulus of fiber and film, respectively. For the measurements of σ_f^* , σ'_m , E_f , and E_m , the fiber and the film were treated separately under the same conditions as those in preparing sheets II and III. The volume fraction of fiber V_f for sheets II and III used in this study are 0.74 and 0.69, respectively. The expected values for σ_c and E_c are calculated using the values listed in Table II. As listed in Table III, the experimental values both of tensile strength and modulus for sheets II and III are only around one-half of the calculated ones (see σ_e/σ_c , E_e/E_c). Hine et al. have discussed²⁴ the structure of hot compacted high-modulus melt-spun PE fiber in relation to bending strength. The results suggested that the crystallinity and orientation of compacted fiber were strongly affected by the molding temperature. For example, at a compaction temperature of 142°C, there was a significant drop in sample crystallinity; however, at 140°C, the crystallinity remained roughly similar to that of the original fiber.

In order to investigate such damage of fibers during the molding in our experiment, thermal

analyses by DSC were performed for original fiber and for sheets I, II, and III. The results are shown in Figure 8. Melting of original fiber begins at 140°C and appears as a doublet. The low-temperature endotherm observed at about 152°C is the main melting peak. It is followed by a small peak at about 159°C. The high-temperature peak has been assigned to melting of the hexagonal crystalline structure and possibly from randomization of chains to the gauche state in the melt.²⁰ The DSC

Table III Comparison of Expected Mechanical Properties with Experimental Ones

	Sheet II	Sheet III
σ_c (GPa)	1.1	1.0
E_c (GPa)	33	30
σ_e^a (GPa)	0.60	0.66
E_e^a (GPa)	20	14
σ_e/σ_c	0.55	0.66
E_e/E_c	0.61	0.47

^a Maximum values in this study.

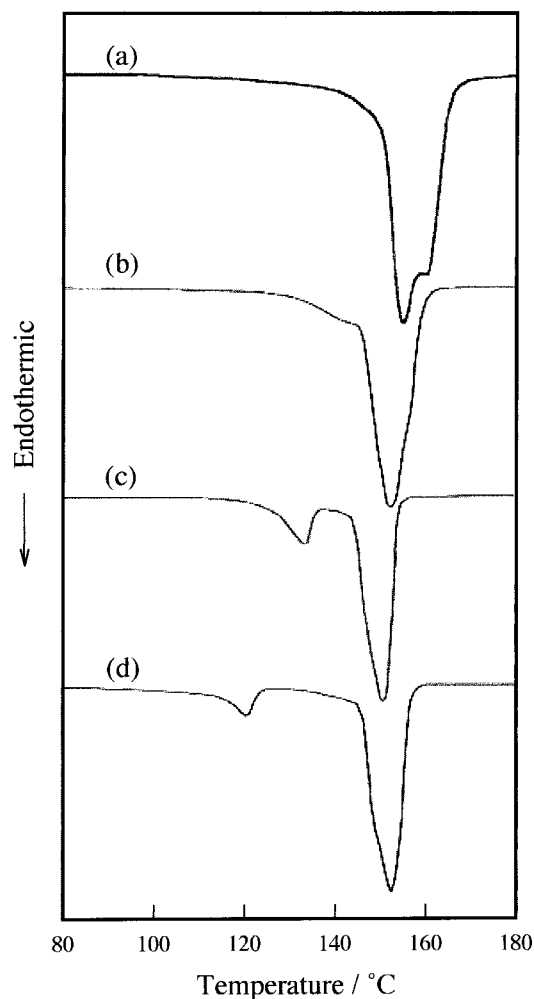
**Figure 8** DSC thermograms of (a) original fiber and (b) sheets I, (c) II, and (d) III.

Table IV Thermal Properties of Films Treated Separately Under the Same Conditions as Those in Preparing Sheets II and III

	HDPE Film	LDPE Film
Heat of fusion (J/g)	210	130
Melting point (°C)	132	118

trace of sheet I (consist of only fibers) exhibits a small shoulder at 138°C and appears the main peak at 148°C (~ 4°C lower than that for original fiber), indicating that the main peak of the fiber shifts to lower temperature by the compression molding. For each sheet II and III, two endothermic peaks are observed. The endotherm at higher temperature is from the fiber, and the lower one is from PE matrix. Since the molding temperature is between the melting points of fiber and PE matrix, LDPE and HDPE matrices melt during the compression molding, filling between the fibers. The endothermic peaks of fibers for sheets II and III are also recognized to be slightly lower temperature than that for original fiber.

The heat of fusion of fibers in sheets I–III seems to be decreased by the molding processes. Similar results of hot compacted PE fibers, that is, the drop of crystallinity of samples with compaction has been reported by Hine et al.²⁴ The endotherms from the fiber and PE matrix are unlikely overlapped in Figure 8. The heat of fusion only from the fiber in the composite ΔH_f can be estimated by eq. (6). Then a decrystallization rate of fiber K_f can be calculated by eq. (7) in this study,

$$\Delta H_f = \frac{\Delta H - \Delta H_m(1 - W_f)}{W_f} \quad (6)$$

$$K_f = 1 - \frac{\Delta H_f}{\Delta H_{pf}} \quad (7)$$

where ΔH_m is the heat of fusion of film in composite. For the measurement of ΔH_m , the LDPE and HDPE films were treated without fiber under the same conditions as those in preparing sheets II and III. The results are shown in Table IV. ΔH and W_f are the heat of fusion of the composites and the fiber weight fraction, respectively. ΔH_{pf} is the heat of fusion for single fiber, which is already shown in Table I. The obtained heat of fusion only from the fiber in the composite ΔH_f and the decry-

stallization rate K_f are summarized in Table V, together with the values of ΔH and W_f . K_f values reveal that the decrystallization of fiber occurs fairly. The results also show reasonable relation between K_f and elastic modulus; that is, sheet II showing the lowest K_f has the highest elastic modulus. For tensile strength, however, sheet III is stronger than sheet II; although the K_f for sheet III is higher than that for sheet II. Further, the value of $K_f = 0.07$ – 0.15 estimated for the sheets seems to be minor to compare with 40–50% drops of mechanical properties of composite sheet from their predicted theoretical values (see Table III). Therefore, the low values of mechanical properties in composite cannot be explained only by the decrystallization rate of fiber. The possible reason for such significant drop of mechanical properties is weak adhesion between fibers and matrix (for sheets II and III). To investigate the adhesion, interfacial shear strength between PE fiber and HDPE matrix has been tested by pull-out method. The strength between untreated fiber and matrix was 1.5 MPa, which was 1/10 and 1/50 in comparison with PE/epoxy³¹ and carbon fiber/epoxy³² composites, respectively. The interfacial strength were 4–6 times improved by corona treatment of PE fiber and HDPE; functional groups were introduced on the surfaces of fiber and matrix by the treatment. The tensile strength and modulus of a composite prepared from the treated fiber and matrix were ~ 30 and ~ 15% improved, respectively, in comparison with those for untreated composite. These results suggest that the interfacial shear strength is an important factor to improve the mechanical properties, especially in the tensile strength. The details will be reported separately.

Figure 9 shows scanning electron microphotographs of the longitudinal fracture surfaces in tensile tests for the sheets I, II, and III. For all sheets, fiber agglomerations with the diameter of approximately 250 μm can be seen. The agglomeration could not seen in the composite sheet before tensile test. For sheets I and II, fibers in the ag-

Table V Values of Decrystallization Rate for Fibers

	Sheet I	Sheet II	Sheet III
ΔH (J/g)	230	240	200
W_f	1	0.74	0.70
ΔH_f (J/g)	230	251	230
K_f	0.15	0.07	0.15

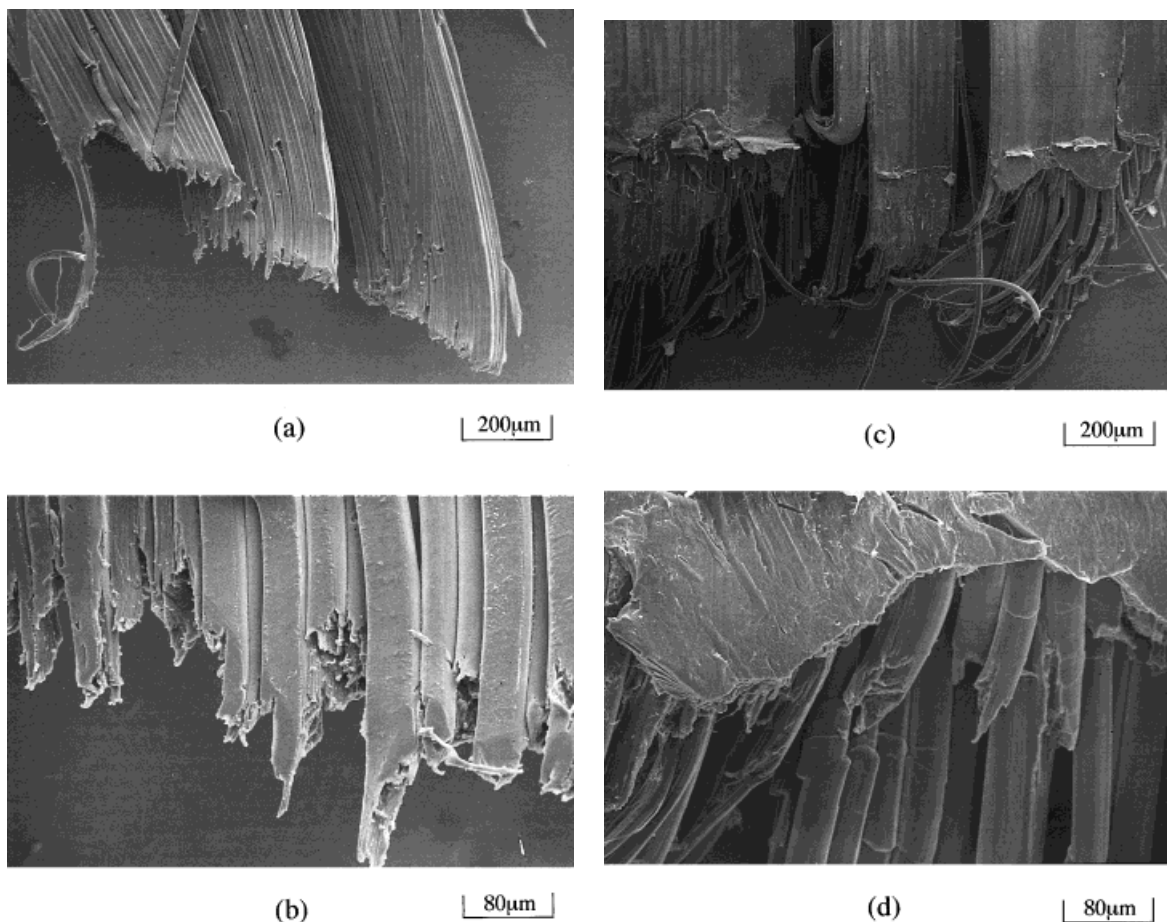


Figure 9 Scanning electron micrographs of longitudinal fracture section of the composite sheets in tensile tests: (a) and (b) for sheet I, (c) and (d) for sheet II, and (e) and (f) for sheet III.

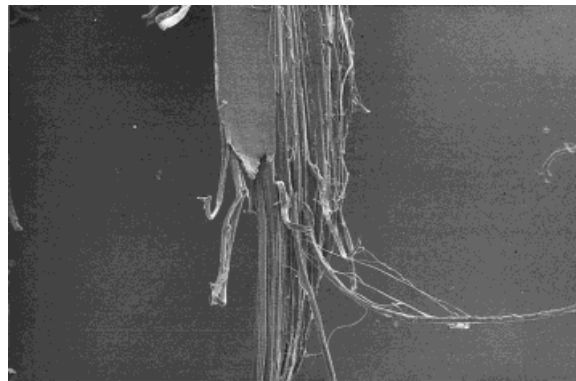
glomerate split each other at break, suggesting weak adhesive strength. For sheet III, on the other hand, most fibers in the agglomerate still adhered each other, even after the fiber break, indicating better adhesion between fibers and matrix, which would arise from the sufficient packing and contacting of matrix to fibers in the sheet III because of the lower viscosity of LDPE than that of HDPE in the melt. The tensile strength of sheet III recorded in this study is the highest value of 660 MPa. This fact combined with the results in Figure 9 indicate that interfacial adhesion between fiber and matrix is an important factor to achieve high mechanical property, especially for the tensile strength.

CONCLUSIONS

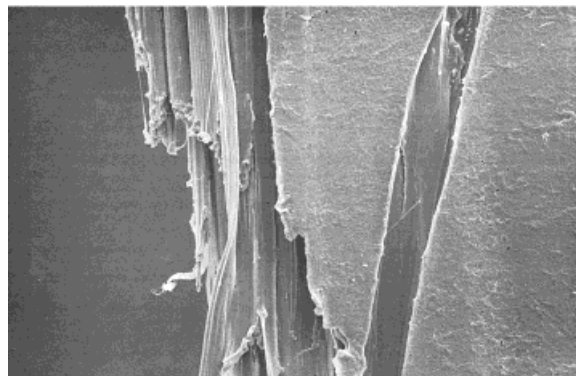
The tensile strength of sheet III (PE/LDPE) and elastic modulus of sheet II (PE/HDPE) reached

660 MPa and 20 GPa, respectively, which were 60 and 30 times higher than those of typical LDPE film. The mechanical properties of sheets II and III leveled off as a function of molding time. The tensile strength and modulus of sheet I (only PE fibers) was influenced by the time of compaction.

The mechanical properties of sheets II and III were about half of the predicted theoretical ones. To explain the low values of mechanical properties, a decrystallization rate K_f was defined by using drop of crystallinity of PE fibers in the composite (using DSC data) during the molding. The low values of elastic modulus in composites were closely correlated to K_f . However, tensile strength in composites cannot be explained only by that of PE fiber. The interfacial strength between PE fiber and LDPE was only 1.5 MPa. The strength was ~ 5 times improved by corona treatment on the surface of the fiber and matrix. The tensile strength and modulus of a composite prepared



(e) 200µm



(f) 80µm

Figure 9 (Continued from the previous page)

from the treated fiber and matrix were ~ 30 and $\sim 15\%$ improved, respectively. Thus, adhesion between PE fiber and HDPE matrix was very important to improve the mechanical properties especially in tensile strength.

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