

Effect of Diameter and Surface Treatment of Fiber on Interfacial Shear Strength in Glass Fiber/Epoxy and HDPE

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SYNOPSIS

The effect of fiber diameter and the surface treatment of fiber on the interfacial shear strength between glass fiber and matrix (epoxy and high-density polyethylene) has been investigated. Pullout experiments for measuring the interfacial shear strength have been carried out through use of microbonding and the solution microbond test methods for the epoxy and HDPE composite systems, respectively. From this study, it has been found that the interfacial shear strength decreased with the increasing fiber diameter regardless of the type of fiber surface treatment for both resin systems.

INTRODUCTION

The interfacial property between fiber and matrix, as well as the fiber length and orientation distributions, plays a critically important role in the mechanical properties of fiber-reinforced composites.^{1,2} Therefore, the appropriate control of the interfacial characteristics is required to achieve the optimum performance of the final products.

Actually, the interfacial bonding strength between fiber and matrix can be controlled to a great extent by the use of suitable coupling agents in conjunction with the surface modification of fiber itself, such as chemical oxidation, plasma etching, etc. Moreover, the correct evaluation of the interfacial shear strength for the composite system specified will also be of great help for the manufacturing of composite materials of supreme performance. However, there arise several problems associated with the sample preparation and the meniscus effect in measuring the interfacial shear strength, in particular for the case of fibers with small diameter ($< 10 \mu\text{m}$) like a glass fiber or carbon fiber. To date, various methods³⁻⁷ such as the three-fiber pullout test³ and the microdebonding test^{4,5} have been proposed to overcome these problems; among them, the "microbonding test" due to Miller⁸ is considered to be one

of the most versatile methods. However, the above-mentioned methods are applicable only to the thermosetting resin system, not to the thermoplastic resin system, usually present in a solid form at room temperature.

Although several approaches^{9,10} have been introduced for this purpose so far, they are still unsatisfactory for the small-diameter-fiber system. Recently, the "solution microbond method"¹¹ developed at our laboratory has been proved to be easily applicable to sample preparation of the pullout test based on thermoplastic resins provided a suitable solvent for the matrix polymer is available.

The objective of this study is to investigate the effect of the fiber diameter and the surface treatment condition of fiber on the interfacial shear strength for both the thermosetting and thermoplastic resin system. Hence, we used three grades of glass fiber of different diameters as fiber and epoxy resin and high-density polyethylene (HDPE) resin as matrix. The pullout tests for measuring the interfacial shear strength were carried out by using the glass fibers surface treated in three different ways with the aid of the microbonding and the solution microbond methods for the epoxy and the HDPE composite systems, respectively. In addition, the mutual comparison of the interfacial bonding strengths between fiber and both resins was made at the same status of fiber surface together with qualitative consideration.

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EXPERIMENTAL

Materials

The materials used in this study are as follows. The glass fibers, supplied by Han Kuk Fiber Glass Co., Ltd., Korea, and graded as the "E-type," had a density of 2.54 g/cm³, and the specifications on fiber diameter and tensile strength of three grades of the fibers with different diameters are given in Table I.

The fiber averaged diameter has been estimated from the measurement of the length and weight of the fiber with use of the value of fiber density. The tensile strength was (the number of strands weighed being 600) measured on single fiber at a crosshead speed of 1.5 mm/min using a tensile tester equipped with a load cell of 200 g. The respective values listed in Table I refer to the averaged values over 100 samples. The matrix resins chosen are epoxy (Seoul Epoxy, Model SEC #MF) and commercial HDPE (Han Nam Chem., *MW* = 200,000). The curing agent of the epoxy resin was BF₃ and, the curing condition was 130°C and 2 h.

Surface Treatment of Glass Fibers

The treated glass fibers used in the analysis have been classified into three types according to the condition of surface treatment as follows. The first is the as-received state coated with a coupling agent of the silane type, the second is obtained by washing the raw material in acetone for 1 h at room temperature, then drying in a vacuum oven at 80°C for 3 h, and further treated to give the third type in 0.5 wt % toluene solution of HDPE for 1 s, then vacuum dried at 120°C for 1 h to remove the residual toluene, hereinafter designated as the types "ST", "AW", and "AP", respectively.

Forming Resin Droplet to Glass Fibers

The surface-treated fiber thus obtained was embedded in resin to the required length of 50 to 500 μm for the pullout test by the microbonding⁸ and the

solution microbond methods¹¹ for epoxy and HDPE, respectively. In case of the epoxy resin, first the resin was heated to 80°C to drop the viscosity significantly to about the same extent as that for water, then made to form a resin droplet on a glass fiber using amorphous metallic fiber of about 40 μm diameter, and finally molded to complete microdroplet by heat curing. On the other hand, for the HDPE resin, usually present in solid form, the microdroplet was formed on the fiber using toluene as solvent, and finally subjected to enough heating in a vacuum oven at 150°C for 2 h to remove the residual solvent within the resin droplet.

The scanning electron micrograph (SEM) results presented in Figures 1 (a) and (b) illustrate the typical shapes of microresin droplets thus prepared before and after the pullout test. From this figure, we can realize that the shape of a microdroplet remains nearly unchanged even after the pullout test, reflecting the validity of the present methods used for the preparation of the pullout test specimen.

Pullout Test

The pullout test for measuring the interfacial shear strength between matrix and surface-treated fiber consists in applying the load to the fiber embedded in the resin fixed by the microvise in the direction of fiber axis and measuring the shear force developed at the interface between fiber and matrix, equated to the force required to pullout the fiber from the embedded resin. The pullout tests were carried out at a crosshead speed of 1.5 mm/min using an own-made tensile tester equipped with a load cell of 200 g on 50 to 60 samples prepared for both polyethylene (PE) and epoxy resins.

Figure 2 shows the typical load-displacement curve for the pullout test made on a single fiber embedded in the resin droplet to a given length, where F_d and F_s represent the force required for debonding and the purely frictional force between fiber and matrix occurring after debonding, respectively. Then, the interfacial shear strength (τ_d) and the frictional shear strength (τ_s) can be derived from the measured pullout forces (as given in Fig. 2) by the following expressions,¹² assuming the linear relationship between pullout force and embedded length of fiber:

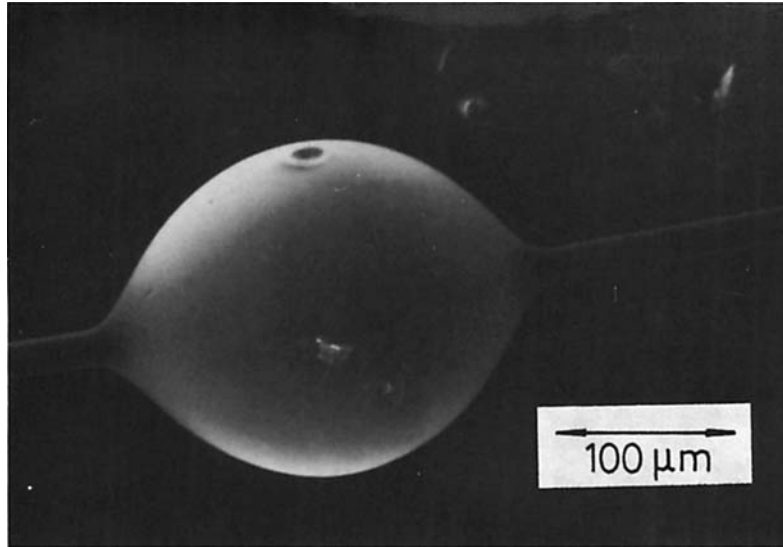
$$\tau_d = F_d / \pi D_f L \quad (1)$$

$$\tau_s = F_s / \pi D_f L \quad (2)$$

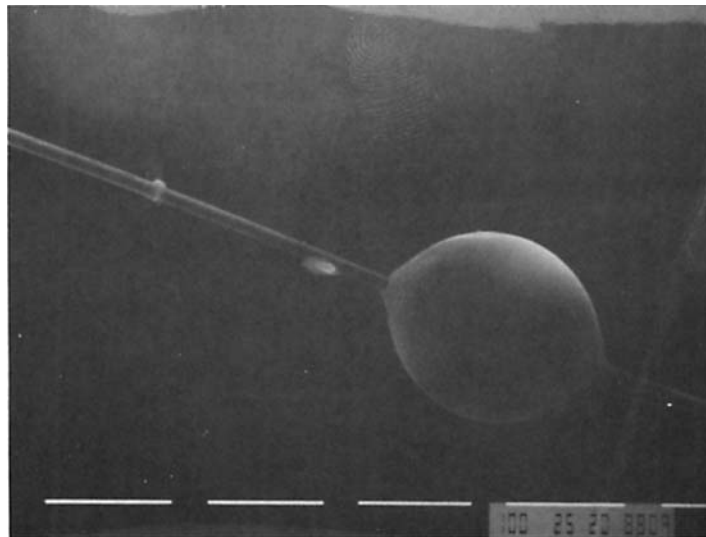
where D_f and L are fiber diameter and length of fiber embedded in the resin, respectively. The τ_d thus ob-

Table I Diameter and Tensile Strength of Glass Fiber

Fiber Diameter (μm)	9.6	12.1	19.5
Tensile strength (GPa) (SD)	2.20 ± 0.40	1.99 ± 0.42	1.66 ± 0.41



(a)



(b)

Figure 1 Typical resin droplet. (a), before pullout test; (b), after pullout test.

tained can be used to estimate the critical embedment length (L_c) of fiber, i.e., the maximum embedded length the fiber can be pulled out from the resin without breakage; hence, the critical fiber length (l_c), equated to $2L_c$, frequently used in fracture mechanics of composites. Similarly, τ_s is also widely used in the calculation of “pullout work”¹³ constituting an important part of the fracture work in fiber-reinforced composites. In addition, it should be pointed

out that the critical fiber length¹⁴ can be obtained by means of the following relationship in the case where the experiment has not been carried out until the embedded length reached L_c :

$$l_c = \sigma_{fu} D_f / 2\tau_d, \quad (3)$$

where σ_{fu} represents the tensile strength of fiber.

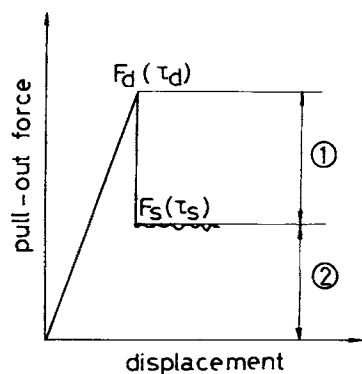


Figure 2 Pullout force vs. displacement. ①, physical and chemical bond force; ②, frictional force.

Interfacial Microstructure

The interfacial morphology, or the microstructure, for the composite system of crystallizable polyethylene with surface-treated glass fiber has been examined using a cross-polar optical microscope. A sketch of the specimen preparation is given in Figure 3. As shown in Figure 3, a small amount of PE was placed onto a cover glass preheated to 150°C on a hot plate, then a single filament of glass fiber was put on the melted PE, and finally another cover glass preheated was placed over the sample and pressed down using a weight of ~ 500 g to ensure complete melting and constant thickness. After the sample was subjected to the same heat-treatment condition (150°C, 2 h) as the specimen preparation of pullout test, it was allowed to remain a long time at room temperature for natural crystallization to occur. Then, the crystallized sample was used for the optical observation of the microstructure of the fiber-matrix interface.

RESULTS AND DISCUSSION

The pullout test results made on the single fiber for the epoxy/glass fiber ($D_f = 19.5 \mu\text{m}$, surface-treatment type = ST) are illustrated in Figure 4. In this figure, the pullout force is plotted against the length of the fiber embedded in the resin, where \circ and \bullet represent the tensile force at debonding and the pure

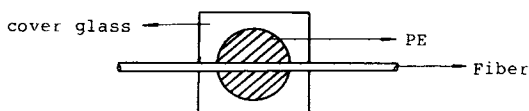


Figure 3 Specimen of cross-polar optical microscope.

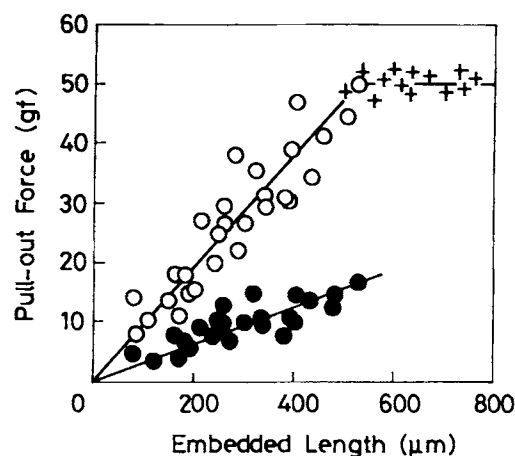


Figure 4 Pullout force vs. fiber-embedded length (glass fiber in epoxy resin droplet).

frictional force between fiber and matrix after debonding, respectively, and + refers to the breaking force of fiber, beyond which the fiber itself has been broken out before the fiber can be pulled out from the embedded resin. From Figure 4, we can easily understand that a relatively good relationship exists between pullout force (F_d) and fiber-embedded-length (L) and that the critical embedment length (L_c), corresponding to the initial fiber break point is about 500 μm . Because the frictional force (F_s) after debonding also has a linear relationship with the fiber-embedded length, we can estimate the (mean) interfacial shear strength (τ_d) and the (mean) frictional shear strength (τ_s) for the specific type of surface treatment and fiber diameter from the slopes of two straight lines in Figure 4 with the aid of eqs. (1) and (2); thus, τ_d and τ_s being treated to be independent of the fiber-embedded length.

Similarly, the pullout test results for the HDPE/glass fiber (the same fiber condition as above) are illustrated in Figure 5, where F_d and F_s are also found to be proportional to L , and hence τ_d and τ_s can be obtained from the slopes of the figure again. From the fracture-mechanical point of view, the present systems representing the linear relationship between pullout force and embedded length are judged to belong to the composite system, which fails by shear yield¹⁵ at the interface. In addition, the critical fiber or embedded length can be easily obtained in the case of Figure 4; however, in the case of Figure 5, without data on fiber breakage available the l_c should be evaluated with resort to eq. (3).

The pullout test results thus obtained for glass fibers of different diameters and different surface-treatment conditions embedded in epoxy resin are

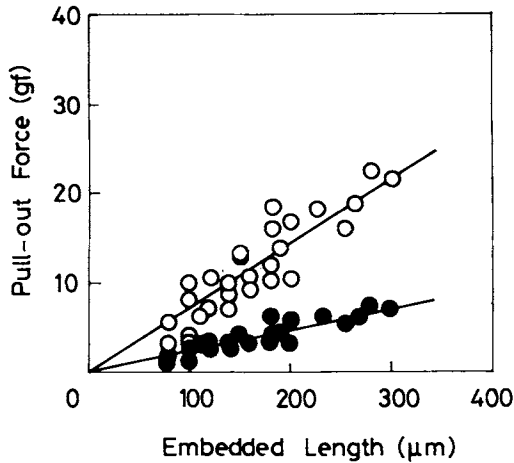


Figure 5 Pullout force vs. fiber-embedded length (glass fiber in PE resin droplet).

summarized in Table II. Inspection of the table reveals that as the fiber diameter increases the interfacial shear strength decreases, whereas the critical fiber length increases for both ST and AW surface-treatment conditions. This behaviour may be attributable to the fact that the shrinkage force on the fiber surface occurring during the process of epoxy resin curing increases as the fiber diameter decreases. Hence, it will be helpful to the understanding of the results obtained in this study to discuss the effect of fiber diameter on the bonding strength between treated fiber and matrix in more detail.

As sketched in Figure 2, the debonding force F_d for a given system consists of two terms: one, the

physical and chemical bonding force ($F_d - F_s$ or $\tau_d - \tau_s$); the other, the frictional force (F_s or τ_s). In principle, the first term is expected to mainly depend on the chemical nature of fiber and matrix and on the type of fiber surface treatment, whereas the second term should be largely dependent on fiber diameter, as evident from Table II. In fact, the frictional force between fiber and matrix can be represented by the shrinkage force multiplied by the frictional coefficient. While the coefficient term may be little affected by the extent of fiber diameter at a given fiber status, the shrinkage force, and hence the frictional force, will be greatly affected by the fiber diameter.

A possible, though qualitative, explanation for the reason the interfacial bonding strength decreases with the increasing fiber diameter would be made based on the concept of surface or interfacial phenomenon as follows. If we could assume the fiber embedded in the matrix fluid as "bubble" or "capillary," as in microbonding the molten resin to fiber, the pressure difference between inside and outside the bubble or the capillary-rising force would be proportional to surface tension of the matrix fluid, but inversely proportional to fiber diameter; thus, the smaller diameter promotes the shrinkage force against the fiber surface at a given type of matrix resin. Accordingly, the change in fiber diameter will make greater contribution to the extent of the interfacial shear strength through the frictional (or shrinkage) force rather than the physical and chemical bonding force.

In addition, Table II reveals that the difference in interfacial shear strength between the ST and the AW surface-treatment types seems to be not so

Table II Effect of Fiber Diameter and Surface Treatment on Interfacial Strength for Glass Fiber/Epoxy Resin

	D_f (μm)		
	9.6	12.1	19.5
ST			
τ_d (MPa) (SD)	26.8 ± 4.6	19.8 ± 3.3	17.3 ± 2.2
τ_s (MPa) (SD)	12.6 ± 2.1	6.8 ± 2.2	5.0 ± 1.3
$\tau_d - \tau_s$ (MPa)	14.2	13.0	12.3
l_c (μm)	394	606	926
AW			
τ_d (MPa) (SD)	23.5 ± 3.5	17.8 ± 3.2	15.6 ± 2.5
τ_s (MPa) (SD)	10.6 ± 2.2	5.5 ± 1.8	4.0 ± 1.4
$\tau_d - \tau_s$ (MPa)	12.9	12.3	11.6
l_c (μm)	448	673	1030

ST, silane treated; AW, acetone washing.

large, which may be due to the fact that the coupling agent of the silane type has not been completely removed yet by acetone washing for only 1 h.

The pullout test results for the HDPE/glass fiber system, as obtained from the pullout curve like Figure 5, are summarized in Table III, revealing the effect of fiber diameter and surface treatment on the interfacial bonding strength between fiber and matrix. Similar to the case of Table II, the interfacial shear strength decreases with increasing fiber diameter. However, the tendency seems to be small compared to the case of epoxy resin, which may be ascribed to the difference in surface tension between epoxy and HDPE resins [in fact, about 47.0 and 27.3 dyne/cm for epoxy and HDPE (at 150°C), respectively]. That is, the HDPE system with smaller surface tension will have the lower diameter dependence of the interfacial shear strength relative to the epoxy case for the reason discussed above.

On the other hand, in the case of fiber-reinforced composites based on crystallizable thermoplastic resin like HDPE, it is generally known that a columnar growth of crystals along the fiber axis, referred to as "transcrystallinity,"¹⁶⁻¹⁸ is caused by the presence of fiber, thereby resulting in a considerable volume change upon crystallization relative to the amorphous part of the matrix resin, and hence leading to the large shrinkage force yielding better adhesion between fiber and matrix. Moreover, the tendency to improve the interfacial bonding strength owing to the transcrystallinity is expected to be more pronounced in the case of fibers with smaller diameters due to the result of the increased nucleating ability.

In addition, we can see from Table III that the surface-treated glass fiber system of the AP type exhibits relatively high interfacial shear strength compared to that of the AW type at the same fiber diameter. This might be also qualitatively accounted for by considering the surface tension effect on the wettability at the interface between oil and water. Namely, a drop of oil on water will spread well; however, a drop of water on oil will remain as a drop, for water has much higher surface tension than oil. A similar argument may be applied to the HDPE/treated glass fiber system, where glass fiber has a critical surface tension of ~ 72.8 dyne/cm and PE has a molten surface tension of ~ 27.3 dyne/cm. Hence, the interfacial shear strength for the case where PE resin is thinly coated over the fiber surface (i.e., of the AP type) will be higher than that for the case where PE resin occupies a large volume then glass fiber (i.e., of the AW type) because of

good wettability arising from the difference in surface tension between fiber and matrix.

Meanwhile, comparison of Tables II and III reveals that the interfacial shear strength and its two components for the epoxy system are much higher when compared to the HDPE system at the same surface-treatment condition, more specifically, of the type ST. The reasoning for this would be as follows. As has been previously stated, the interfacial shear strength consists of the contributions from two terms, $\tau_d - \tau_s$ (physical and chemical) and τ_s (frictional). Here, a coupling agent of the silane type coated on glass fiber has two functional groups per molecule (organic and inorganic) and hence more affinity for epoxy than PE, thus increasing the value of $\tau_d - \tau_s$ for the epoxy system.

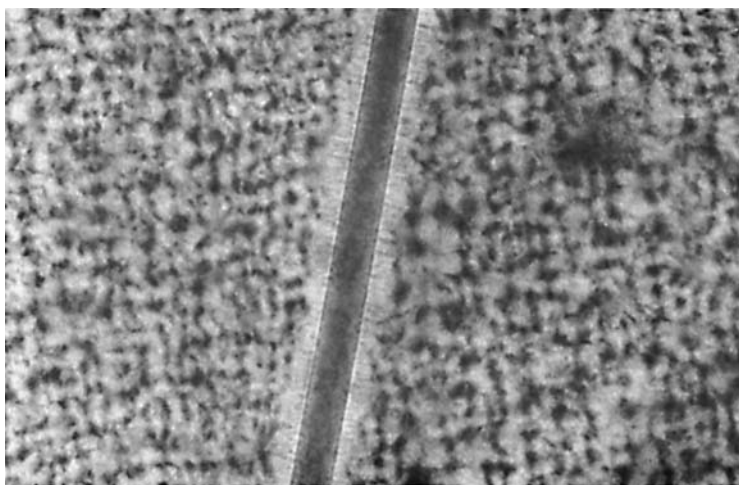
In addition, the shrinkage force for the epoxy system is also higher than that for the HDPE system at the same fiber diameter because of the difference in surface tension between two resins, thus increasing the value of τ_s .

Finally, polarized optical microphotographs of the interfacial microstructure for the composite system of crystallizable PE with the type ST glass fiber are shown in Figure 6. From this figure, we can see that the transcrystallinity is well developed along the fiber axis and that the lateral extent of the transcryst-

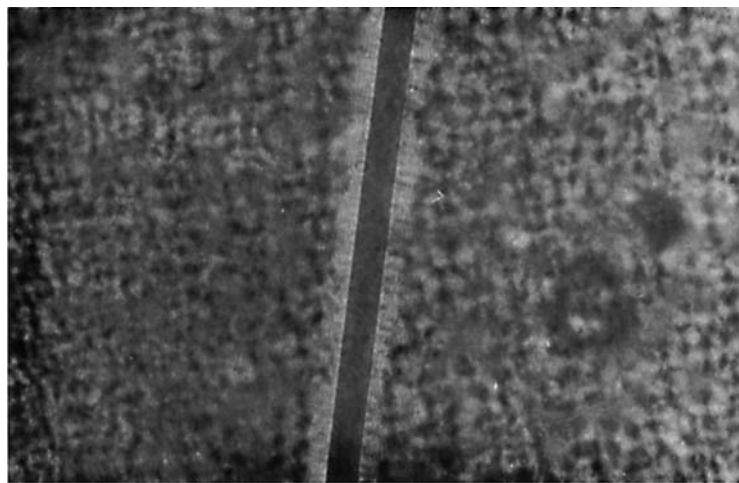
Table III Effect of Fiber Diameter and Surface Treatment on Interfacial Strength of Fiber/Polyethylene Resin

	D_f (μm)		
	9.6	12.1	19.5
ST			
τ_d (MPa) (SD)	15.1 ± 2.4	13.2 ± 2.1	12.1 ± 2.0
τ_s (MPa) (SD)	5.7 ± 1.2	4.3 ± 1.1	3.4 ± 0.1
$\tau_d - \tau_s$ (MPa)	9.4	8.9	8.7
l_c (μm)	698	908	1332
AW			
τ_d (MPa) (SD)	11.7 ± 2.0	9.5 ± 1.8	8.4 ± 2.2
τ_s (MPa) (SD)	4.8 ± 1.2	3.2 ± 1.0	2.7 ± 0.9
$\tau_d - \tau_s$ (MPa)	6.9	6.3	5.7
l_c (μm)	904	1276	1905
AP			
τ_d (MPa) (SD)	13.7 ± 1.5	11.5 ± 1.2	10.0 ± 1.3
τ_s (MPa) (SD)	5.1 ± 1.0	3.5 ± 1.0	2.9 ± 0.8
$\tau_d - \tau_s$ (MPa)	8.6	8.0	7.1
l_c (μm)	768	1038	1606

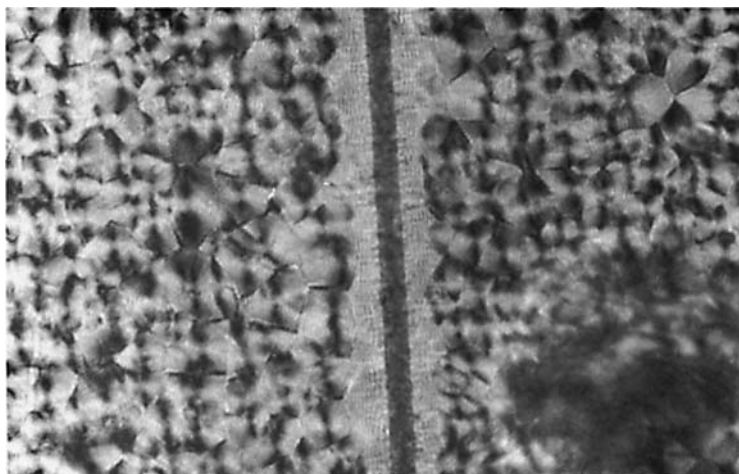
ST, silane treated; AW, acetone washing; AP, 0.5 wt % toluene solution of HDPE treated for 1 s after acetone washing.



(a) $D_f = 9.6 \mu\text{m}$



(b) $D_f = 12.1 \mu\text{m}$



(c) $D_f = 19.5 \mu\text{m}$

Figure 6 Cross-polar optical microphotographs showing interfacial microstructure for PE with glass fiber.

talline layer is more considerable in case of the fibers with smaller diameters, as expected. On account of this, the interfacial shear strength for the HDPE/treated glass fiber system increased with decreasing fiber diameter at the same treatment condition.

CONCLUSION

From the investigation regarding the effect of fiber diameter and surface treatment of fiber on the interfacial shear strength between glass fiber and matrix (epoxy and HDPE), the following results were revealed.

The interfacial shear strength for both epoxy and HDPE resin systems, as evaluated according to the microbonding and the solution microbond methods, respectively, were found to decrease with the increasing fiber diameter, which has been explained in terms of the frictional force rather than the physical and chemical force constituting the interfacial bonding strength. For the epoxy resin, the effect of fiber diameter on the frictional force was ascribed to the surface effect, whereas for the HDPE resin with relatively small surface tension the effect of fiber diameter on the frictional force was attributed to the transcrystallinity effect rather than to the surface tension effect.

In addition, the interfacial shear strength between HDPE and silane-treated glass fiber with PE thinly coated on it was higher than the case of glass fiber without coated PE layer, which was considered to

be due to the difference in wettability at the interface between fiber and matrix for both liquid states.

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