

Effects of Surface Treatments of Superdrawn Polyoxymethylene Fibers on Adhesion to Epoxy Resins

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SYNOPSIS

Strong adhesion in the superdrawn polyoxymethylene (POM) fiber/epoxy matrix system was achieved with surface treatments, 2H-hexafluoro-2-propanol (HFP) treatment, and surface phenolation of the fiber. HFP produced micropits for mechanical interlocking with the matrix. Surface phenolation formed active layers leading to interfacial miscibility.

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INTRODUCTION

Polyoxymethylene (POM) superdrawn fibers, which were invented by Clark and Scott¹ and Brew and Ward² and later improved by Japanese engineers,^{3,4} are now being applied to a fiber-reinforced material. Good adhesion between the fiber and matrix is indispensable to the high performance of the fiber-reinforced material. A fiber surface is usually pretreated to improve adhesion to the matrix. Surface treatments are usually a successive process: preparation of a clean surface (removal of surface contaminants by mechanical pretreatment or dissolution with solvents) followed by chemical modification (insertion of functional groups by chemical reaction or electric discharge). For high modulus polyethylene (PE) fibers, many studies reported on surface treatments for adhesion to an epoxy adhesive. Ladizesky and Ward^{5,6} reported that chemical etching with strong oxidizing agents, $K_2Cr_2O_7$ and $Ce(SO_4)$, and plasma etching with various gases, O_2 , He, Ar, CF_4 , improve the pull-out adhesion of PE fibers to epoxy resin, but lower the fiber strength inversely proportional to the adhesion. And the chemical etching method affords the pull-out failure of sliding along the monofilament/resin interface, whereas the plasma etching produces many pits on the fiber surface leading to a cohesive failure of the fiber. It has also been reported that ammonia plasma etching improves the pull-out adhesion to epoxy

resin fourfold but shows stick-slip debonding as well as the untreated fiber.⁷

Plasma etching has been shown to induce surface changes, oxidation of the fiber surface, and removal of the weak skin layers.⁸ Effects on adhesion have been shown to include three factors, chemical bonding, mechanical keying, and the nonpolar dispersion force.⁹

On the other hand, the studies on the chemical etching with oxidizing agents such as $K_2Cr_2O_7$, $KMnO_4$, CrO_3 , and H_2O_2 , have shown that the improvement in adhesion after etching results from the oxidative modification on the fiber surface; and the strength lowering of the etched fiber would be due to the destruction at the taut tie molecules of the fibers.¹⁰⁻¹²

A POM resin lacks chemical reactivity similar to PE and poly(tetrafluoroethylene). For the POM resin, some attempts have been made to improve adhesion: the use of an excellent solvent, 2H-hexafluoro-2-propanol¹³ (HFP), and a few etchants such as a satinizing solution¹⁴ and chromic acid.¹⁵ HFP is usually used as a primer; the method is therefore useful for coating of POM, adhesion between POM resins or between POM and nylon resins dissoluble with HFP. The method using the chemical etchants is based on elution of an amorphous phase of POM, for example, an anchor effect. However, the superdrawn POM fibers hardly dissolve in HFP and cannot be modified by those etchants because of the high crystallinity and high molecular orientation.

Recently, the author presented surface phenolation, a method for adhesion of the POM fibers to

rubbers.^{16,17} In this article, two methods are presented for adhesion with an epoxy resin matrix. One is the application of HFP to etch the fiber surface; the other is the application of surface phenolation to the epoxy adhesion. The differences between these methods are also discussed from the morphological viewpoint.

EXPERIMENTAL

A superdrawn POM fiber was prepared by the pressure-drawing method using an undrawn POM fiber of 6.0-mm outer diameter and 1.8-mm inner diameter, followed by a perfect removal of silicone oil adhering to the fiber surface. The fiber obtained had a 1.32-mm outer diameter. The details were previously given.⁴

Next, the fiber was sandpapered, treated with a chemical, embedded in an epoxy resin, and then a pull-out test was conducted to assess the adhesion to the resin.

The sandpapering was carefully carried out along the fiber circle using sandpapers of 40–320 mesh and controlled by a degree of ca. 1.5% fiber weight loss. Chemical treatment was performed by two methods. One was the HFP treatment: the sandpapered sample was immersed in HFP for 3 min at room temperature, washed with acetone, and air dried. The other was surface modification with resorcinol: the sandpapered sample was immersed in an aqueous solution of 40 wt % resorcinol for several minutes, put into an oven and cured at 160°C for 10 s, put out at room temperature, washed with methanol to remove the unreacted agent, and dried in air.

Tensile strength and Young's modulus of the samples along the fiber axis were measured using an Instron tensile testing machine. Tensile strength was measured using two stainless reel chucks of 160-mm diameter whose grooves were covered with a rubber sheet. The distance between the centers of the reels was 200 mm and crosshead speed was 100 mm min⁻¹. The modulus was determined from the slopes of the stress-strain curves at a strain of 0.2–0.3% using an extensometer. Sample gauge length was 150 mm, crosshead speed was 5 mm min⁻¹, and mark distance for strain measurement was 50 mm. Measurement was carried out five times and the results averaged. As a result, the tensile strength and Young's modulus, respectively, were 1.8 and 40 GPa for the original fiber, 1.5 and 40 GPa after the sandpaper/HFP treatment, and 1.5 and 36 GPa after the sandpaper/resorcinol treatment.

The fiber piece for the pull-out test was placed upright in the center of a Teflon cylinder 20-mm inner diameter and 20-mm height. The adhesive used was a room temperature curing epoxy resin (Ciba-Geigy Ltd., Araldite Rapid, which is a two step adhesive composed of a bisphenol type epoxy and a polyamide resin). This was used as a mixture of epoxy and polyamide in a 4/5 ratio by weight. The mixture was poured into the cylinder and cured for 24 h at room temperature.

The pull-out test was carried out using an Instron tensile-testing machine under the following conditions: sample gage length, 150 mm; embedding length, 20 mm; crosshead speed, 100 mm min⁻¹. The measurement was carried out using 10 composite bars per sample and the results were averaged. Fluctuation in the observed pull-out load was within about ±5%. The pull-out adhesive strength, T , was calculated from

$$T = F/\pi DL \quad (1)$$

where F is the maximum pull-out load, D is the diameter of the fiber piece embedded in the epoxy matrix ($D = 1.31$ mm), and L is the embedding length ($L = 20$ mm).

The sample surface was examined by scanning electron microscopy (SEM, Hitachi Seisakusyo Co., S-430, and JSM., T200-A).

RESULTS AND DISCUSSION

Effect of Mechanical Treatment

Table I shows the adhesive strength observed for each pull-out sample. The strength was increased appreciably by simple sandpapering. The effect of mechanical treatment on the strength tended to increase with the particle size of the sandpaper, in particular below 120 mesh, and was saturated at a value of 10.0 MPa. The larger sand scraped the fiber surface more deeply. Therefore, the depth of the scars related to the increase in adhesion as well as the appearance of the clean surface. The surface of the intact fiber is smooth as shown in Figure 1(a). In contrast, the surface sandpapered with a large particle size was extremely rugged as shown in Figure 1(b). The rugged surface seems to act as the macrobasin interlocking with the matrix. Figure 1(c), a higher magnification of Figure 1(b), displays micropores that were not found in the intact fiber. This kind of micropores are usually observed in the POM fiber when bent or stretched; most of the pores

Table I Pull-Out Strength for POM Fibers/Epoxy System.

Samples	Pretreatments	Pull-Out Load (N)	Pull-Out Strength (MPa)	Appearances of Pull-Out Regions
A	Without	49.9	1.6	Clean surface
B	Only HFP ^a	62.4	2.0	Clean surface
C	Polish (#320)	170.1	5.3	Clean surface
D	Polish (#120)	203.8	6.4	Clean surface
E	Polish (#100)	258.7	8.1	Clean surface
F	Polish (#80)	310.2	9.7	Clean surface
G	Polish (#40)	318.0	10.0	Clean surface
H	HFP/#320 ^b	383.9	12.1	Cohesive failure
I	HFP/#120	393.2	12.3	Cohesive failure
J	HFP/#80	396.4	12.4	Cohesive failure
K	HFP/#40	422.0	13.2	Cohesive failure
L	Resor./#320 ^c	407.6	12.8	Cohesive failure
M	Resor./#80	417.8	13.1	Cohesive failure
N	Resor./#40	423.6	13.3	Cohesive failure

In the system, the POM fibers were pretreated in different ways.

^a An original fiber was immersed in HFP for 7 days at room temperature.

^b HFP/#320 is the treatment with HFP after sandpapering using 320 mesh.

^c Resor./#320 is the treatment with resorcinol after sandpapering using 320 mesh.

in Figure 1(c) are, therefore, artifacts made by sandpapering.

Effect of HFP Treatment

The HFP treatment after sandpapering remarkably increased the adhesive strength. The strength was greater than the sum of the contributions of sandpapering and HFP, in particular when sandpapered above 120 mesh. After the pull-out test, most of the pieces displayed cohesive failure of the matrix. This means that the real interfacial shear strength (IFSS) may be much higher, at least higher than the cohesive failure strength of the matrix. As reported in the previous work,¹⁶ when an interfacial failure occurs in the fiber modified with the resorcinol-RFL adhesive-rubber system, the pull-out strength is 10% higher than the value of this epoxy resin adhesive system. Hence this value cannot be taken as the IFSS. In contrast, the fiber treated with HFP without sandpapering is pulled out gently with little resistance, similarly to the intact fiber, as given in Table I. HFP does not react with the POM molecules. HFP easily dissolves the POM resin at room temperature, but hardly dissolves the highly oriented crystalline POM fibers at ambient temperatures and only slightly at elevated temperatures. Therefore, the effect of HFP is not due to the dissolution of the POM, but probably due to the increase in surface roughness. The surface morphologies of these sam-

ples were then examined using SEM. The sample that was immersed in HFP without sandpapering showed almost the same surface morphology as that of the intact sample, although a few pores appeared in some places after the immersion [see Fig. 2(a)]. The pores are traces of the part etched by HFP. The morphology of pores running parallel to the fiber direction arises from the fibrillar structure of the highly oriented POM fiber, because the amorphous phase between fibrils are possibly less resistant to HFP than the crystalline fibrils (the bulk crystallinity determined by DSC was 73%).

Compared with the sandpapered sample (sample G) showing a typical surface that was roughened by sands [see Fig. 1(b)], the sample surface treated with HFP after sandpapering (sample K) showed a very porous morphology including many pits, most of which were submicron in size [see Fig. 2(c)]. Such a morphological change has been observed for high modulus PE fibers that were plasma treated.⁵ These characteristic observations were not found on etching with acid or alkali. Some of the mechanisms causing the morphological change can be explained as follows from the facts in Figures 1(b) and 2(a): many macroabrasions and micropores after sandpapering make the penetration of HFP easy into the inside of the POM fiber networks; the amorphous phase mechanically damaged by sandpapering is in the state liable to be eluted by HFP; as a result, the crystalline fibrillar networks insol-

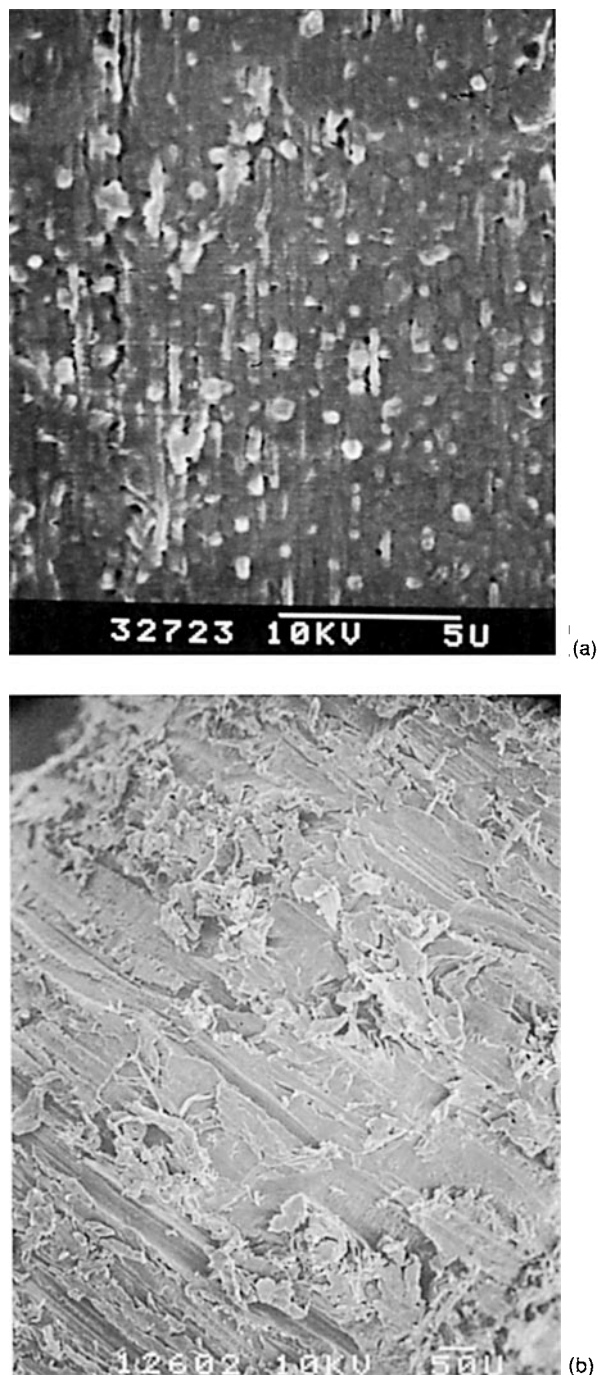


Figure 1 SEM micrographs of the POM fiber surfaces sandpapered: (a) the surface of the intact fiber, (b) the surface of the fiber sandpapered with 40 mesh, and (c) higher magnification of (b).

uble in HFP are left. The idea is supported by the finding of a characteristic fibrillar network previously reported.¹⁸ The morphology in Figure 2(c) makes us imagine an analogy to the “shishkebab” structure that is found for ultrahigh modulus PE

fibers¹⁹ and needlelike POM crystals.²⁰ However, the experimental confirmation is still not enough to assign the present networks to be the shishkebab.

The HFP treatment gives a microscopically porous surface, and the effect is presumed to be as follows: the adhesive penetrates the pores, hardens, and acts as microinterlocking wedges leading to the cohesive failure of the epoxy matrix. Figure 3 shows a SEM micrograph of the fiber surface after the pull-out test of sample k. A large part of the pull-out surface was covered with the epoxy resin; this demonstrates that a pull-out failure occurs at the epoxy matrix.

Effect of Chemical Modification

The surface-phenolated sample (sample N) exhibited the highest adhesive strength similar to sample K. The adhesive strength was little dependent on the particle size of the sandpapers. Figure 4 shows the SEM observation of sample N. The morphology was practically smooth in contrast to that of sample K. Such a surface is ineffective for interlocking with the epoxy matrix. This suggests that the improvement in the adhesion of sample N is based on another mechanism different from the case of scraping, for example, chemical activation of the fiber surface. As previously reported, the POM fiber that was treated with resorcinol at high temperatures above

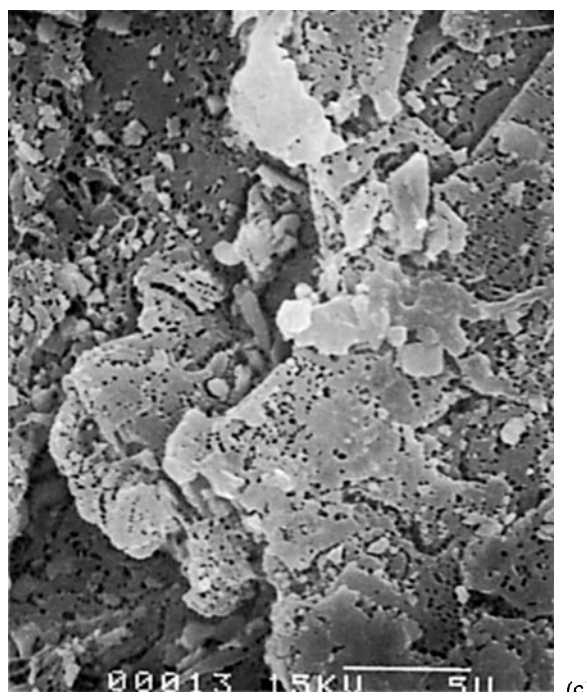
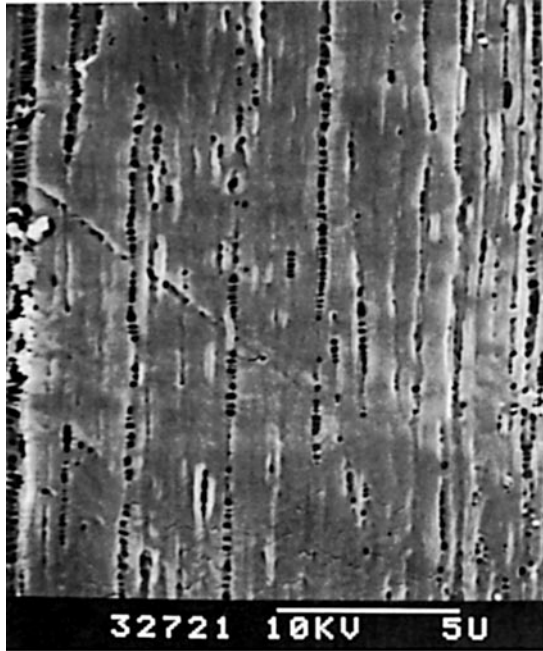


Figure 1 (Continued)



(a)



(b)

Figure 2 SEM micrographs of the POM fiber surfaces treated with HFP: (a) the fiber surface after the immersion of the intact fiber in HFP for 7 days at room temperature, (b) the surface of the fiber that was immersed in HFP for 3 min after sandpapering using 40 mesh, and (c) higher magnification of (b).

150°C, was chemically modified on the fiber surface.¹⁶ A mechanism leading to the high adhesion to the epoxy adhesive seems to relate to an inter-

facial miscibility, because the POM fiber treated with resorcinol is wetted with water much better than the intact fiber.

Thermodynamic Miscibility in POM Fiber/Epoxy System

The adhesive strength of sample K was recorded as 13.2 MPa. The value was nearly equal to the shear strength by tension loading, 12–14 MPa, of the used epoxy resin that was cured at 20°–25°C.

Adhesion between an adherend and adhesive has been explained on the following basic concepts. Perfect wetting is achieved when the surface tension, γ_{LU} , of the adhesive is smaller than the critical surface tension, γ_C , of the adherend.²¹ Complete miscibility is achieved when the thermodynamic solubility parameters, δ , of both materials are equal.²² The maximum interfacial adhesion is achieved when a system satisfies both conditions. The γ_C of the POM resin is $3.85 \times 10^{-2} \text{ (N m}^{-1}\text{)}$.²³ The γ_{LU} of the adhesive is $4.17 \times 10^{-2} \text{ (N m}^{-1}\text{)}$.²⁴ The δ of the POM resin is 20.9–22.5 $\text{(MPa)}^{1/2}$,²³ and that of the adhesive is 20.4 $\text{(MPa)}^{1/2}$.²⁵ The relation between γ_C and γ_{LU} in the POM/epoxy adhesive system is poor for complete wetting, although the δ relation in the system is satisfactory. Therefore, the high adhesion of sample K is due to the interlocking effect in addition to the thermodynamic miscibility.



(c)

Figure 2 (Continued)

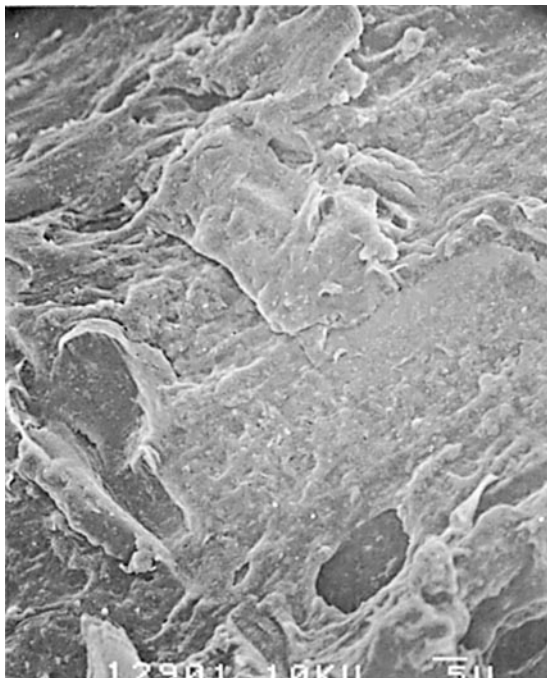


Figure 3 SEM micrograph of the pull-out region of sample K that was prepared by the HFP treatment after sandpapering with 40 mesh.

An adhesion mechanism of the modified POM/epoxy adhesive system is supposed to differ from the above system, because the modified POM surface is too smooth to have an interlocking effect. Before

discussing the mechanism, the chemical structure of the modified POM fiber needs to be explained. Resorcinol, which reacts with formaldehyde to afford a resorcinol resin, was found to swell the POM fiber above 120°C and to react with the POM fiber above 150°C. The surface layer of sample N is characteristic of a resorcinol–polyformaldehyde (RF) resin that is formed by the insertion of resorcinol into the POM molecular chains. These were previously confirmed by IR and NMR spectroscopies.¹⁶

Therefore, the chemical miscibility is noted between the epoxy adhesive and the modified layer including the resorcinol segments. The adhesive consists of bisphenol epoxy and polyamide. The functional groups on the modified POM surface are similar to the bisphenol epoxy on the chemical structure, and very polar similar to polyamide. The functional groups are then miscible with both components of the adhesive. Therefore, the good adhesion of the RF-modified POM fiber/epoxy system is probably due to the miscibility based on the diffusion of the adhesive into the substrate. The detection of the epoxy resin at the interface is a future subject.

Contributions of Pretreatments to Adhesive Strength

The effect of sandpapering on adhesive strength changed little in the region of 120–320 mesh, and re-

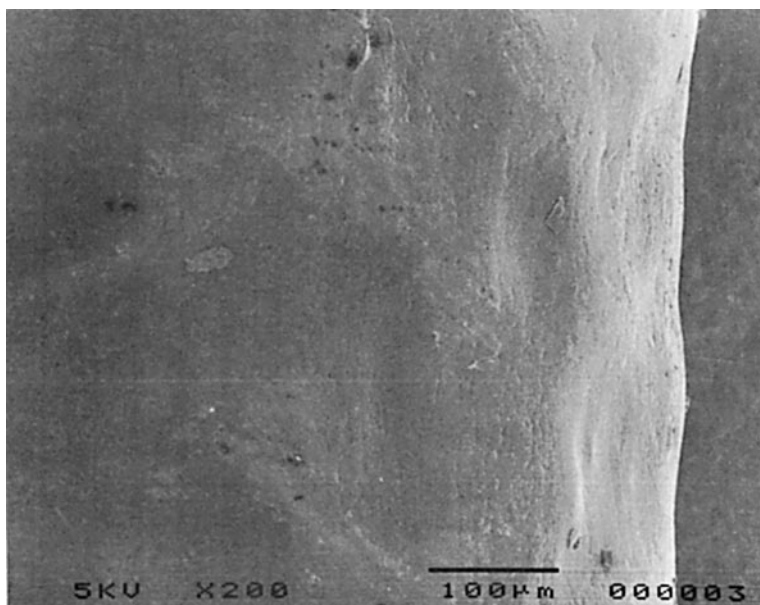


Figure 4 SEM micrograph of the POM fiber surface modified with resorcinol after sandpapering using 40 mesh.

markably increased below 120 mesh. The chemical modification gave the largest adhesion in spite of the smooth surface. The results mean that the effect of the surface treatment is a superposition of a clean surface effect, σ_C , an interlocking effect, σ_I , and a chemical modification effect, σ_M . A series of experimental conditions make it possible to estimate each effect in the following way. The control gives a background, σ_0 . Because the effect of the clean surface free from the remarkable interlocking effect appears on sandpapering above 120 mesh, the sandpapering with 320 mesh gives $\sigma_C + \sigma_0$. σ_I appears when sandpapered below 80 mesh and immersed in HFP; therefore, the treatment gives $\sigma_I + \sigma_C + \sigma_0$. The sandpapering/resorcinol treatment gives $\sigma_M + \sigma_C + \sigma_0$, because σ_M is given by the chemical modification. The result was $\sigma_C : \sigma_I : \sigma_M = 3.7 : (6.8-7.9) : (7.5-8.0)$. This means that the factors of surface roughness and polar groups are very important for epoxy adhesion.

CONCLUSIONS

Surface treatments of the superdrawn POM fiber, HFP treatment, and surface phenolation were presented for adhesion to the epoxy resin. The effects of the treatments on adhesion were discussed in terms of the surface morphology and thermodynamic compatibility. The adhesion was improved significantly by merely scraping the fiber surface. This was largely due to the mechanical interlocking with the matrix. HFP treatment and surface phenolation further improved the adhesion. The adhesion reached a level equivalent to the shear strength of the matrix. HFP was effective to form micropits on the fiber surface, leading to the increase in the interlocking effect with the epoxy matrix. Surface phenolation probably contributes to the interfacial miscibility that occurs through the diffusion of the epoxy adhesive into the modified layer.

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