

Improvement of Adhesion of Kevlar Fiber to Poly(methyl methacrylate)

Ming-Liang CHEN, Shigeyuki UETA, and Motowo TAKAYANAGI

*Department of Industrial Chemistry, Faculty of Engineering,
Kyushu Sangyo University, Matsukadai,
Fukuoka 813, Japan*

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ABSTRACT: The surface of Kevlar fibers can be modified by some chemicals through metalation reaction in a solution of methylsulfinylcarbanion and dimethylsulfoxide (DMSO) [Takayanagi *et al.*, *Rep. Prog. Polym. Phys. Jpn.*, **28**, 243 (1985)]. In this study, the functional groups introduced to the surface of Kevlar fibers were identified by means of ESCA, referring to the atomic ratios of unmodified Kevlar. The adhesion of the fibers to poly(methyl methacrylate) (PMMA) was evaluated by a single fiber pull-out test. The carboxymethylated and epoxy-reacted fibers showed the strongest affinity to PMMA compared with the untreated fiber and the one having a less-polar surface layer. After the pull-out test, the fiber was observed by SEM to survey the fracture mechanisms. It was observed by SEM that the fiber adhered to PMMA, resulting in both modes of fracture: one case was a strip of fiber skin torn out from the fiber surface and another case, the matrix resin of PMMA was fractured, the residue of which adhered to the fiber surface. Introduction of polar groups such as carboxy and hydroxy groups to the fiber surface layer was most effective in increasing pull out strength.

KEY WORDS Interfacial Adhesion / Poly(methyl methacrylate) / Kevlar / Pull-Out Test /

Kevlar fiber has low density, high tensile strength and high Young's modulus. Nowadays it is widely used in fiber-reinforced composites. Studies on the adhesion of Kevlar fibers to polymer resins have been reported in various papers.¹⁻³ Poly(methyl methacrylate) (PMMA) is light, strong in compression, but brittle in tensile deformation. Improved mechanical properties of PMMA should enhance application of its composites with Kevlar to tooth plates, for example. The properties of short fiber-reinforced composites are mainly determined by the properties of the matrix and fiber, the content of the fibers, fiber aspect ratio, fiber morphology and adhesive strength at the fiber-matrix interface. Among these factors, adhesion at fiber-matrix is one of the most important factors. In this study, the Kevlar fiber surface was treated by some

chemicals through polymer metalation reaction in a solution of methylsulfinylcarbanion and dimethylsulfoxide and a single fiber pull-out test was used to evaluate the adhesion of a fiber and PMMA.

EXPERIMENTAL

Evaluation of Interfacial Adhesion

The interfacial shear stress of fiber and matrix is calculated by the following formula:

$$\tau_i = \frac{\sigma R}{2L} \quad (1)$$

where σ is tensile stress for the pull-out of a single fiber, τ_i is the interfacial shear stress, R , the radius of the fiber and L , the immersion length of the fiber in matrix. When σ_f is the ultimate tensile strength of a fiber, the follow-

ing formula is obtained from eq 1:

$$L_c = \frac{\sigma_f R}{2\tau_i} \quad (2)$$

From eq 2, the critical immersion length of the fiber, L_c , can be calculated. In the pull-out test, if the fiber immersion length L is shorter than L_c , the fiber is pulled out. Otherwise, the fiber is broken. After being pulled out, the fiber was studied by scanning electron microscope to survey the fracture mechanism.

Treatment of Kevlar Fiber Surface by Chemicals

At first, the Kevlar fiber surface was washed with acetone. In a three neck flask being equipped with an N_2 inlet, drying tube, stirrer, and a thermometer, 150 ml of DMSO and 0.12 g of NaH were reacted at 30°C for 30 min and 70°C for 30 min. The surface cleaned fiber was placed in the flask and metalation was conducted at 30°C for 10 min. At this time, the

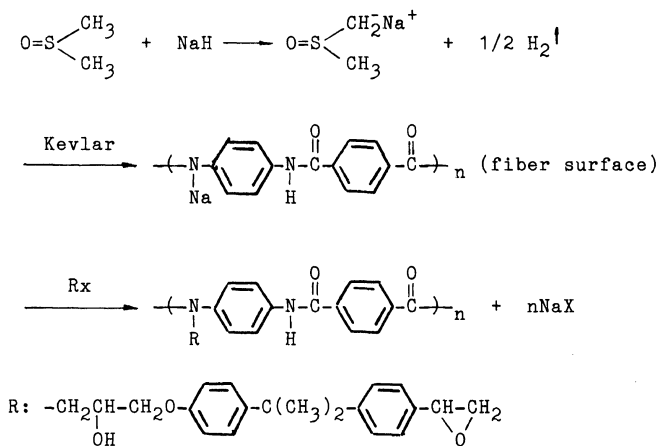
surface of the fiber was partially metalation-reacted and swollen by dimethyl sulfoxide (DMSO). The metalated fiber was rapidly soaked in a solution of reagent for introducing functional groups. The treated fiber was washed with acetone.

Epoxy reaction was conducted at 50°C for 1 h in the solution of 10 g of epoxy and 150 ml of DMSO. Liquid epoxy resin, DER 383 of Dow Chemical Co. with 176–186 of epoxy equivalent was used.

Allylation was conducted at 30°C for 2 h in a solution of 25 g of allylbromide in 300 ml of DMSO.

Ethoxycarbonylmethylation was conducted at 50°C for 50 min in a solution of 15 ml of ethyl monobromoacetate in 200 ml DMSO. The carboxymethylated fiber was obtained by deesterification of the ethoxycarbonylmethylated fiber with 1 N hydrochloric acid solution at room temperature for 1 h.

These reactions are represented as follows⁴:



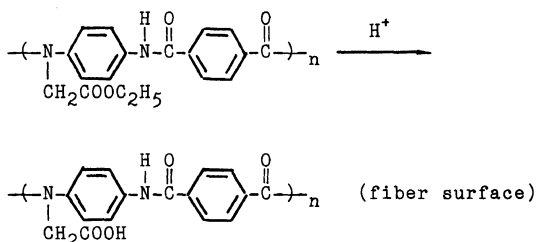
for epoxy reaction,

$-\text{CH}_2\text{CH}=\text{CH}_2$ for allylation reaction,

$-\text{CH}_2\text{COOC}_2\text{H}_5$ for

ethoxycarbonylmethylation,

and for carboxymethylation:



Preparation of a Single Fiber Pull-Out Samples

a) *Preparation of PMMA-MMA.* In a 200 ml three neck flask equipped with an N_2 inlet, stirrer, condenser with water circulation and a thermometer, 100 ml of methyl methacrylate (MMA) and 0.6 g of benzoylperoxide (BPO) were reacted for 25 min at 70–75°C, the content of PMMA being adjusted to about 25 wt%. To terminate the polymerization, PMMA-MMA was placed in a refrigerator until use.

b) *Preparation of a Single Fiber Pull-Out Samples.* A single fiber was placed along the axis of a small glass tube, one end sealed by tape. PMMA-MMA was injected into the tube and the fiber immersion length in PMMA was controlled to 0.1–1 mm. Then the tube was placed in a thermostat at 60°C for 8 h and at 85°C for 2 h for polymerization of remaining MMA. At room temperature, the single fiber pull-out test was conducted. The distance between the upper end of the fiber and horizontal upper surface of the PMMA resin was about 35 mm. The pull-out rate was 5 mm min^{-1} with a tensile tester, Tensilon. Figure 1 shows the preparation process of a single fiber

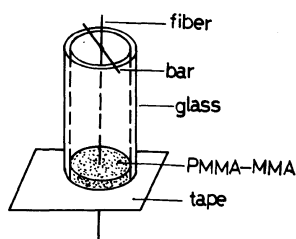


Figure 1. Preparation of a single fiber for a pull-out test.

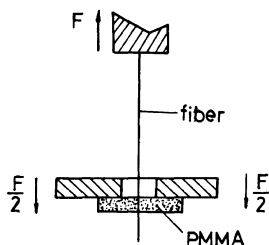


Figure 2. Layout of the pull-out test.

pull-out test sample, and Figure 2, the layout of the pull-out test.

An optical microscope was used to measure the diameter of the fiber before the pull-out test and the thickness of PMMA resin, that is, the immersion length of the fiber after the test.

RESULTS AND DISCUSSION

Table I shows the ratios of the number of carbon atoms to that of nitrogen atoms (C/N) and oxygen atoms to nitrogen atoms (O/N) for various fibers calculated from ESCA spectra. During the treatment of the surface of the fibers, the number of nitrogen atoms did not change. The fact that C/N and O/N values of treated fibers were greater than those of the untreated fiber indicates that the surface of the fiber reacted with the chemical reagents. The number of epoxy groups introduced into the surface layer of fiber was the most. C/N of carboxymethylated fiber was smaller than that of the ethoxycarbonylmethylated fiber, as the ethoxycarbonylmethyl groups were changed to carboxymethyl groups to some degree in the presence of protons.

Table I. Atom ratios of various fibers as calculated from ESCA

Treatment of Kevlar	C/N	O/N
Surface-cleaned	13.60	5.57
Allylated	15.22	6.30
Epoxy-reacted	37.38	16.42
Ethoxycarbonylmethylated	17.96	6.31
Carboxymethylated	15.25	7.67

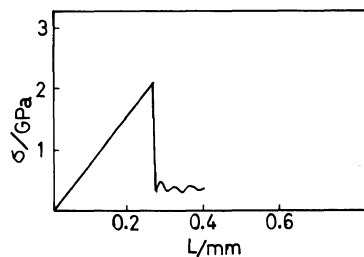


Figure 3. Typical curve of load-displacement of the pull-out test.

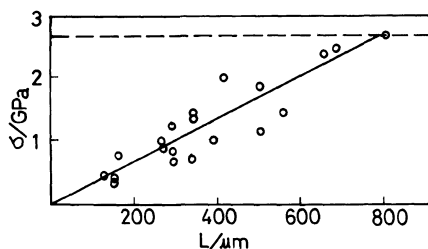


Figure 4. σ vs. L in the pull-out test for the cleaned Kevlar fiber.

Table II. Critical immersion length (L_c) and calculated interfacial shear stress (τ_i) for different Kevlar/PMMA

Treatment of Kevlar	$L_c/\mu\text{m}$	τ_i/MPa
Surface-cleaned	780	11.25
Metalation	660	13.30
Allylation	620	14.15
Epoxy-reacted	480	18.28
Ethoxycarbonylmethylated	590	14.87
Carboxymethylated	480	18.28

When fiber pull-out test was conducted, a load-displacement curve was recorded. Depending on the fibers whether being pulled out or broken, the load showed maximum tensile stress σ_m or tensile strength σ_f . Figure 3 shows a typical load-displacement curve of the pull-out test. Figure 4 shows the relation of tensile stress σ to immersion length L for the cleaned Kevlar fiber. Table II summarizes the critical immersion length L_c and calculated mean interfacial shear stress τ_i for the cleaned fiber and treated fibers. Adhesion of the fibers to PMMA can be evaluated by interfacial shear stress τ_i and critical immersion length L_c . The smaller the value of the immersion length L_c (the bigger the value of the interfacial shear stress τ_i), the greater the adhesion of the fiber to PMMA. For the cleaned fiber, L_c is $780\ \mu\text{m}$ and τ_i is $11.25\ \text{MPa}$; but for the surface metalation fiber, L_c is $660\ \mu\text{m}$ and τ_i is $13.3\ \text{MPa}$. Thus, the adhesion of the surface of metalation fiber to PMMA is stronger than that of the cleaned fiber. As the surface of cleaned fiber is highly oriented and crystalline,

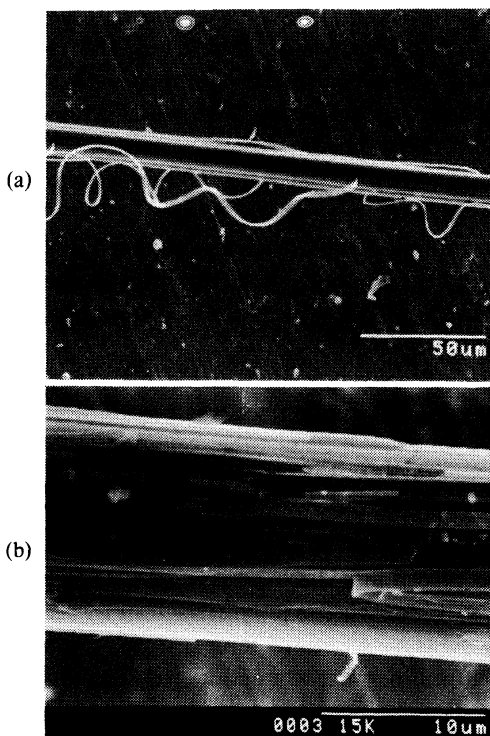


Figure 5. Scanning electron micrographs of untreated fibers pulled out from PMMA resin: (a) peeling off of the skin from a fiber; (b) remaining small amount of matrix resin on roughened surface of a fiber.

the metalation reaction acting to lower the high order of the fiber surface increases the affinity of the fiber to PMMA. In the case of the allylation fiber, L_c is $620\ \mu\text{m}$ and τ_i is $14.15\ \text{MPa}$. The allylation fiber is a little better than the metalation fiber in affinity to PMMA. Among these treatments of fibers, epoxy-reaction and carboxymethylation are the most effective for improving the adhesion of the fiber to PMMA. This is thought due to the formation of hydrogen bonds between hydroxy groups in epoxy-reacted fiber or acid groups in carboxymethylated fiber and carbonyl groups in PMMA, in addition to the effect of the roughened interfacial layer during metalation reaction.

After being pulled out, the fibers were observed by scanning electron microscope. In

general, when the fiber is pulled out, fracture occurs at the interface of the fiber and matrix or in matrix or at the surface of the fiber. In this study, observation of the fiber after being pulled out showed that the fracture mode was complex. Figure 5 shows typical SEM photographs of fibers after the pull-out test. Sometimes, the fracture of the fiber surface took place in the pull-out test. Figure 5(a) is such a case in which a thin fiber skin was stripped out of the fiber surface and formed a helical form. Figure 5(b) shows that the matrix was fractured so that some part of PMMA adhered to the surface of the fiber. As for the cleaned fiber, fracture often occurred on the surface of the fiber. When the fracture occurs in the matrix or at the surface of the fiber, the measured interfacial shear stress is lower than what it really is. Therefore, the above measured interfacial shear stress of various fibers and PMMA by the pull-out test may be lower in some cases than the actual values of in-

terfacial adhesion. Even in the case of carboxymethylated and epoxy-reacted fibers, both fracture modes were observed. The difference in apparent adhesive strength as seen in Table II may be ascribed to the strength of interfacial layer; the crack generated in the layer grows either in the bulk of matrix resin or at the intersurface.

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