

# Graft Copolymerization of $\epsilon$ -Caprolactam onto Kevlar-49 Fiber Surface and Properties of Grafted Kevlar Fiber Reinforced Composite

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**ABSTRACT:** The anionic graft copolymerization of  $\epsilon$ -caprolactam onto a Kevlar-49 fiber surface was carried out by using a metalation reaction in a dimethyl sulfoxide solution of sodium hydride. The effects of reaction conditions on the graft yield and on the tensile strength of the fiber have been investigated. Graft yield significantly increased with increasing metalation time, NaH concentration, and monomer concentration. The graft yield varied from 6 to 32% with reaction conditions. The tensile strength of the fiber depended predominantly on NaH concentration. The retained tensile strength was over 93% when the concentration of NaH was below 2.1 mmol/L per 0.5 g of Kevlar. The discontinuous Kevlar fiber reinforced composites were prepared by a blending/melt-pressing method. In thermomechanical and dynamic mechanical analyses, the relaxation peak of grafted Kevlar fiber/Nylon 6 composite film moved to higher temperatures, compared with the original Kevlar fiber/Nylon 6 composite film. The grafted Kevlar fiber reinforced Nylon 6 composite film exhibited mechanical properties superior to those of the original Kevlar fiber reinforced composite film. The higher thermal and mechanical properties were due to the effect of higher interfacial interaction between the grafted Kevlar fiber and matrix. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **65**: 99–107, 1997

**Key words:** Kevlar-49;  $\epsilon$ -caprolactam; graft copolymerization

## INTRODUCTION

Kevlar is an aramid fiber with high modulus and high tensile strength. It has become very popular for a variety of applications ranging from body armor to aircraft structural parts. Kevlar-49 is very useful as a reinforcing fiber for composite materials.<sup>1–5</sup> In discontinuous fiber-reinforced composites, the performance and properties are generally functions of fiber type, fiber content, fiber aspect ratio, fiber orientation and dispersion, and fiber–matrix adhesion. Since loads are transferred from the matrix to the fiber at the interface,

the fiber–matrix interface plays an essential role in determining the mechanical properties.

The chemical stability of Kevlar-49 fiber prohibits strong interfacial interactions with matrix polymers such as epoxy resins. Therefore, surface treatment techniques for fibers have been widely studied with the aim of improving the interfacial bonding between the fiber and the resin matrix in composite materials. In practice, two main principles are recognized in treatment techniques. The first is to facilitate chemical bonding between the fiber and the matrix by forming a resin-compatible fiber surface through a chemical modification of fiber surfaces or through the intermediary of a suitable coupling agent. The second principle is to increase the physical contact and

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the friction between the fiber and matrix through roughening of fiber surfaces.

Eagles et al.<sup>6</sup> studied the adhesion of Kevlar-49 monofilaments to thermoplastic polymers, and Vaughan<sup>7</sup> investigated the interfacial adhesion between aramid fiber and epoxy or polyester matrix with a number of commercial coupling agents. Mai and Castino<sup>8</sup> compared two commercial vanishes as aramid fiber coatings and stated that the silicone-based coating was superior to the polyurethane coating. Breznic et al.<sup>9</sup> proposed a surface treatment technique which provided the attack of aramid fiber by surface roughening, which resulted in a fiber strength loss accompanied by a considerable improvement in the interlaminar shear strength.

Wu and Tesoro<sup>10</sup> reported that the presence of amino groups incorporated on Kevlar fabric could, remarkably, provide improved peel strength and apparent interlaminar shear strength to epoxy laminates and suggested a significant role of covalent bonding in improving adhesion in aramid-epoxy composites. Takayanagi et al.<sup>11-13</sup> reported that the reagent prepared by the reaction of sodium hydride with dimethyl sulfoxide (DMSO), giving a solution of sodium methylsulfinylcarbanion in DMSO, dissolved poly(*p*-phenylene terephthalamide) (PPTA) in inert gas atmosphere and that the polyanion of metalated PPTA dissolved in DMSO was able to react with various aliphatic and arylalkyl halides, giving *N*-substituted PPTA. The introduction of various substitutional groups into the amide groups of PPTA increased their solubilities, but decreased their thermal stabilities, compared with nonsubstituted PPTA. Polybutadiene was selected as polymer chain to graft/block copolymerization with PPTA.<sup>14</sup> In order to improve interfacial adhesion between the Kevlar fiber surface and epoxy resin, the functional groups such as alkyl halides and epoxy compounds were introduced to the surface of the Kevlar fiber by graft copolymerization.<sup>15</sup>

In this study, the graft copolymerization of  $\epsilon$ -caprolactam onto the Kevlar-49 fiber surface was carried out by anionic polymerization on the *N*-metalated Kevlar-49 fiber surface with the metalation reaction in a solution of sodium methylsulfinylcarbanion in DMSO. The effects of reaction conditions on the graft yield and on the tensile strength of the fiber have been studied. Also, the thermomechanical and dynamic mechanical properties of original Kevlar fiber/Nylon 6 and grafted

Kevlar fiber/Nylon 6 composite films were also investigated.

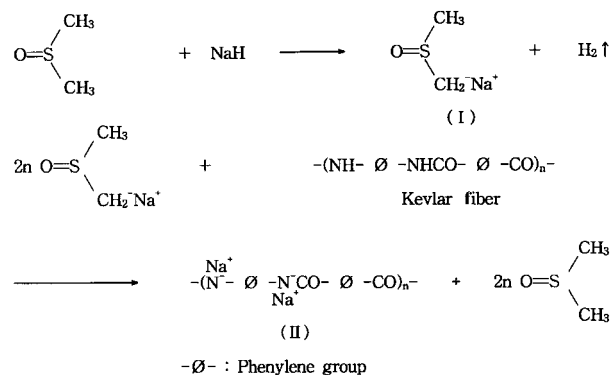
## EXPERIMENTAL

### Materials

Kevlar-49 filament (Du Pont Kevlar-49, 1000 denier/666 fils) was cleaned by Soxhlet extraction with carbon tetrachloride for about 24 h. The cleaned samples were then dried in a dry oven at 100°C for about 20 h. DMSO was fractionally vacuum distilled over calcium hydride and dried over 4-Å molecular sieves. Sodium hydride (60% mineral oil in suspension) and  $\epsilon$ -caprolactam were used as received. Matrix polymer Nylon 6 (Kolon Co. Ltd.) was obtained from industrial sources and used after drying at 70°C for 10 h under vacuum.

### Metalation

A solution of sodium hydride (0.008 ~ 0.16 mol/L) in DMSO (150 mL) was added to a 250-mL three-necked separable flask, equipped with a nitrogen gas inlet, dropping funnel, and mechanical stirrer, under nitrogen atmosphere at 30°C. The reaction temperature rose to 70°C after 30 min, and the solution was maintained at 70°C for 40 min under nitrogen atmosphere with stirring. The sodium methylsulfinylcarbanion (**I**) in DMSO was formed by the following reaction of sodium hydride with DMSO. The metalation reaction of Kevlar fiber was carried out by adding the Kevlar-49 fiber (0.5 g) to the DMSO solution of sodium methylsulfinylcarbanion at 30°C. The metalated Kevlar fiber (**II**) was obtained as follows:

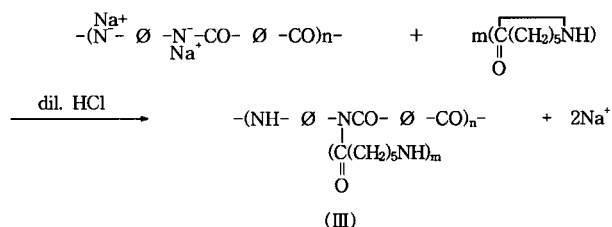


### Preparation of *N*-Grafted Kevlar Fiber

After the metalation reaction, the NaH solution was separated under a dried N<sub>2</sub> gas atmosphere.

The solution of ε-caprolactam in DMSO was added to an N-metalated Kevlar fiber under a dried N<sub>2</sub> gas atmosphere. The ε-caprolactam-grafted Kevlar-49 fiber was prepared by anionic polymerization of ε-caprolactam monomer onto the N-metalated Kevlar fiber under a variety of reaction conditions: different polymerization time, monomer concentration, and polymerization temperature. Finally, the polymerization reaction was stopped through neutralization with a dilute HCl solution.

The homopolymers were removed by Soxhlet extraction for 60 h with dimethyl formamide. However, the amount of homopolymers formed was negligible. The grafted polymer (III) was polymerized from the following reaction:



Graft yield (%) was determined by the following equation:

Graft yield (%)

$$= \frac{\text{Weight of grafted } \epsilon\text{-caprolactam (g)}}{\text{Weight of Kevlar fiber used (0.5 g)}} \times 100 \quad (1)$$

### Preparation of Composite Films

Nylon 6 and cut Kevlar-49 fibers (5 mm, 5 wt %) were mixed in a brabender plasticorder (Bench Kneader, twin screw, PBV-01, Irie Shokai Co.) at 220°C for sufficient time to disperse the fibers in the matrix. Then, the composite film was made by compression molding at 220°C for 10 min. The thickness of the composite film was about 0.2 mm.

### Characterization

An ultraviolet- (UV-) visible spectrometer was used to determine the active site formed on the Kevlar fiber surface from absorbances of NaH solution before and after metalation at 312 nm. The tensile strength was measured with an Instron UTM. Stress-strain curves were recorded with a crosshead speed of 100 mm/min and a chart speed of 20 mm/min. The values reported here were averages of at least 10 specimens. The surface of

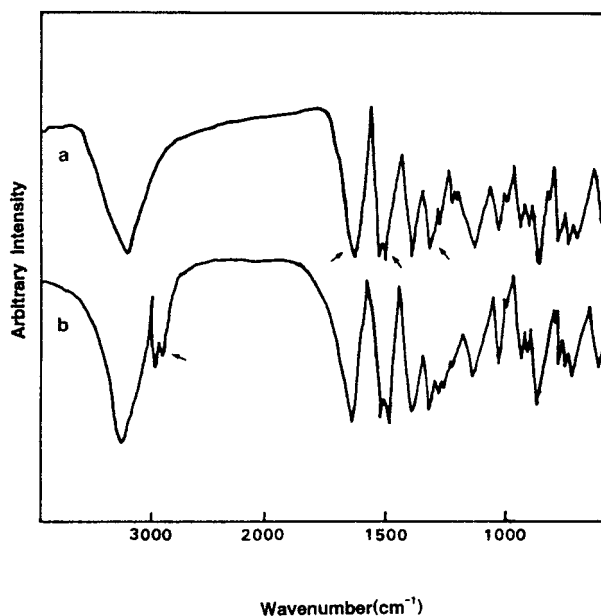


Figure 1 Infrared spectra of the Kevlar fiber: (a) original Kevlar; (b) grafted Kevlar (graft yield, 21.8%).

the Kevlar fiber was observed with a scanning electron microscope (JEOL JSM-5400). The thermomechanical properties of the composites were measured with a thermomechanical analyzer (Seiko, TMA 120C). Rheovibron (DDV, 01FP) was used to measure dynamic mechanical properties at 3°C/min and 11 Hz. A Fourier transform infrared (FTIR) spectrophotometer (Nicolet Impact 400D) was used to obtain absorption spectra of the samples by grinding the grafted Kevlar fiber and using a KBr pellet method.

## RESULTS AND DISCUSSION

### FTIR Spectra of Kevlar Fiber

Figure 1 shows the FTIR spectra of (a) original Kevlar fiber and (b) grafted Kevlar fiber. The characteristic peaks of the original Kevlar fiber, amide I at 1,650 cm<sup>-1</sup> (C=O stretching), amide II at 1,540 cm<sup>-1</sup> (N—H bond and C—N stretching), and amide III at 1,310 cm<sup>-1</sup> (C—N, N—H, and C—C vibration) were observed. The grafting of ε-caprolactam onto Kevlar fiber was identified by the characteristic peak around 2,800 ~ 2,900 cm<sup>-1</sup> (methylene group).

### Effects of Reaction Conditions on the Graft Yield

Table I shows the effect of reaction conditions on the graft yield (%). It can be seen that the graft yield (%) can be controlled by the NaH concentration and grafting conditions. The graft yield (%) was varied from 6.3 to 32% by controlling reaction conditions.

Figure 2 shows the relationship between graft yield (%) and grafting time for different NaH concentrations. The metalation was carried out with various NaH concentrations (0.9, 1.4, and 2.1 mmol/L per 0.5 g of Kevlar) at 30°C. The graft yield was found to increase with an increase in metalation time. For 20 min of metalation time, the graft yield was obtained up to 25%. The graft yield (%) increased sharply with the increase in NaH concentration. This is due to the increasing number of active anions on the Kevlar fiber surface with NaH concentration.

Figure 3 shows the relationship between graft yield (%) and grafting time for different monomer concentrations (1 ~ 11.34 mol/L per 0.5 g of Kevlar). The metalation of Kevlar fiber (0.5 g) was carried out in DMSO (150 mL) with an NaH concentration of 1.4 mmol/L per 0.5 g of Kevlar at 30°C for 10 min. Then, the grafting was carried out with  $\epsilon$ -caprolactam concentration at 50°C for 5 min. It could be seen that the graft yield increased with increasing monomer concentration and grafting time and then leveled off. The graft yield was increased with increasing monomer concentration and varied from 8 to 20%.

### Number of Active Sites and Grafted $\epsilon$ -Caprolactam per Active Site

Figure 4 shows the effect of NaH concentration on the number of active sites and the number of grafted  $\epsilon$ -caprolactam per active site at a constant monomer concentration (5.04 mol/L per 0.5 g of Kevlar). The active site formed on the fiber surfaces via metalation was calculated from absorbances of NaH solution before and after metalation with a UV-visible spectrometer at 312 nm. The number of grafted  $\epsilon$ -caprolactam units per 0.5 g of Kevlar (A, the weight of grafted  $\epsilon$ -caprolactam  $\times 6.02 \times 10^{23}$ /molecular weight of  $\epsilon$ -caprolactam), the number of active sites per 0.5 g of Kevlar fiber (B, the number of moles of the consumed NaH  $\times 6.02 \times 10^{23}$ ), and the number of grafted  $\epsilon$ -caprolactam units per active site ( $C = A/B$ ) are also

shown in Figure 4. The number of active sites depended on NaH concentration and metalation time, whereas the number of grafted  $\epsilon$ -caprolactam per active site depended on the grafting time and monomer concentration. With the increase of NaH concentration, the number of active sites increased; however, the number of grafted  $\epsilon$ -caprolactam per active site decreased. Thus, it was found that the number of grafting sites and the length of grafted polymer were mainly controlled by NaH concentrations and grafting conditions.

### Morphology of Kevlar Fiber

Figure 5 shows scanning electron micrographs of (a) original Kevlar-49 fiber and (b) grafted Kevlar fiber (grafting percentage, 21%). A comparison of the surface of original Kevlar with that of metalated Kevlar showed that the metalated fiber was rough, whereas the original Kevlar was very smooth. The rougher grafted poly( $\epsilon$ -caprolactam) layer of the Kevlar fiber surface might be a reason for enhancing interfacial adhesion between the fiber and the matrix resin.

### Effects of Reaction Conditions on the Tensile Strength of Fiber

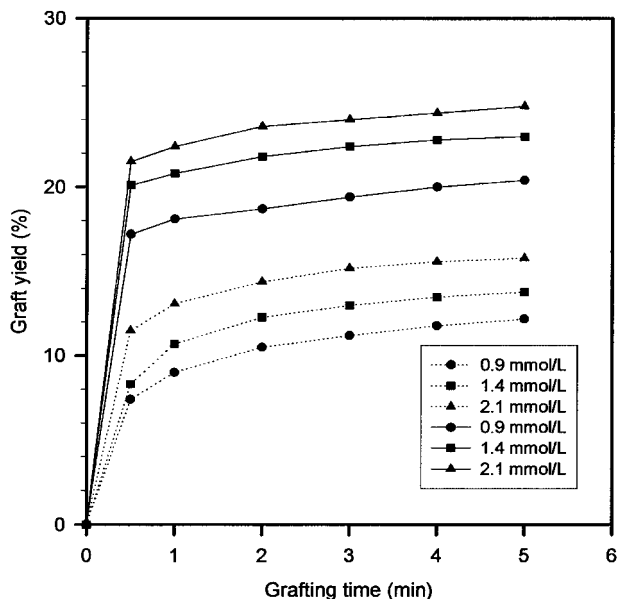
The typical stress-strain curves are shown in Figure 6. The filament was pulled in tension, at a rate of 100 mm/min, and the chart recording was carried out at a rate of 2000 mm/min. The remarkable feature of these curves was the reduction in the breaking stress, breaking strain, and modulus with metalation time and NaH concentration. With the increase of NaH concentration from 0.9 to 8.44 mmol/L per 0.5 g of Kevlar, the tensile strength of the fiber was reduced with 2.9, 6.2, 7.0, 13.0, 23.0, and 25.0%, respectively. It is generally accepted that 10% strength reduction is allowable with chemical treatment of reinforcements for composites. The increase in the metalation times from 10 to 30 min reduced the tensile strength of the fiber with 7, 15, and 45%, respectively (Fig. 7).

### Thermomechanical and Dynamic Mechanical Properties of Nylon Composites

On the other hand, significant information on the interaction between the grafted Kevlar fiber and the matrix polymer Nylon 6 could be obtained from Rheovibron analysis. The storage modulus

**Table I Grafting Conditions and Yields (%) of Graft Copolymerization of ε-Caprolactam onto Kevlar-49 Fiber**

Metalation Conditions		Grafting Conditions			Graft Yield (%)
NaH Concentration (mmol/L per 0.5 g of Kevlar)	Time (min)	Temperature (°C)	Time (min)	Monomer Concentration (mol/L per 0.5 g of Kevlar)	
0.9					7.1
1.4	10	50	2	2.24	8.7
2.1					9.3
			0.5		6.3
			1		7.8
1.4	10	50	2	2.24	8.7
			3		9.2
			4		9.7
			5		10.1
				1.00	6.3
1.4	10	50	2	1.49	7.8
				2.24	8.7
				3.36	9.5
0.9					12.6
1.4	10	50	2	5.04	14.2
2.1					15.5
			0.5		10.8
			1		12.5
1.4	10	50	2	5.04	14.2
			3		14.8
			4		15.4
			5		15.7
				3.36	12.5
1.4	10	50	2	5.04	14.2
				7.56	15.8
				11.34	17.2
2.50					20.2
3.75	10	50	2	5.04	24.6
5.63					27.3
8.44					28.5
			0.5		21.7
			1		23.6
3.75	10	50	2	5.04	24.6
			3		25.8
			4		26.2
			5		26.7
			0.5		25.1
			1		26.4
3.75	20	50	2	5.04	27.8
			3		29.1
			4		30.3
			5		31.2
			0.5		25.8
			1		26.9
3.75	30	50	2	5.04	28.2
			3		29.4
			4		30.6
			5		31.9

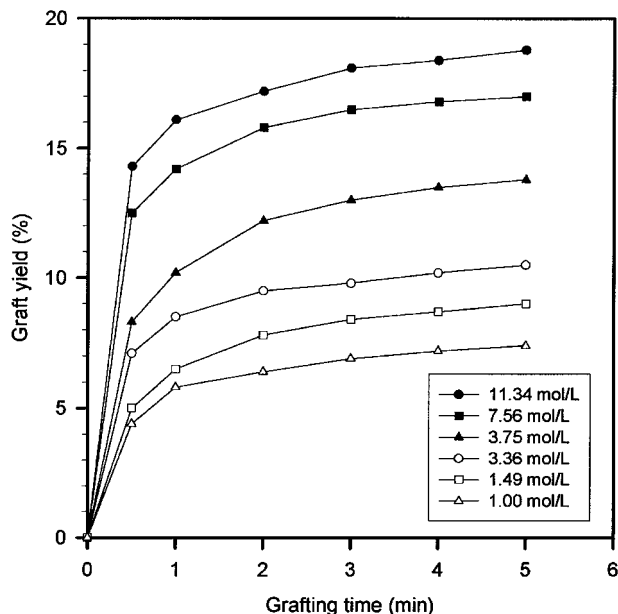


**Figure 2** Effect of grafting time on the graft yield with different NaH concentrations. Metalation time: (---) 10 min, (—) 20 min; grafting temperature, 50°C; monomer concentration, 5.04 mol/L per 0.5 g of Kevlar.

$E'$  was shown as a function of temperature in Figure 8. The storage modulus of the grafted Kevlar fiber reinforced composite (GK/Nylon) film showed a higher value than that of the original Kevlar fiber reinforced composite (OK/Nylon) film. However, the storage modulus of the OK/Nylon composite film showed a higher value than that of pure Nylon 6 film.

Figure 9 shows the temperature dependence of  $\tan \delta$  for Nylon 6, OK/Nylon, and GK/Nylon. The dispersion peaks were shown in Nylon 6 film at 45°C, OK/Nylon at 60°C, and GK/Nylon at 70°C. The  $\tan \delta$  peak temperature and the decreased temperature of the storage modulus of the GK/Nylon composite film showed the highest value among these three samples. These high values of storage modulus and relaxation temperature of the GK/Nylon composite film indicated the presence of a strong interaction between the grafted Kevlar fiber and matrix Nylon 6.

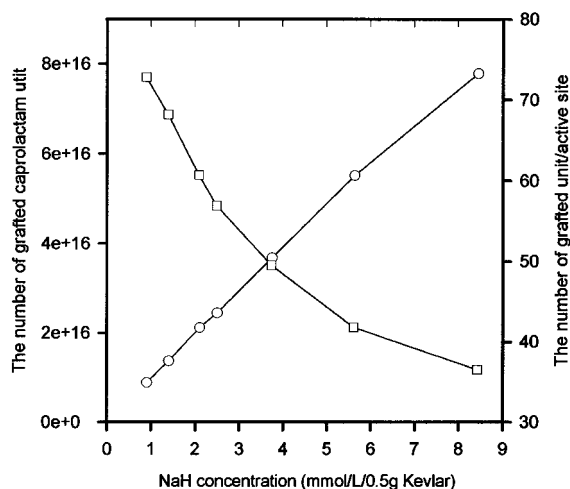
Figure 10 shows the thermomechanical analysis (TMA) displacement–temperature curves of Nylon 6, OK/Nylon, and GK/Nylon films. The GK/Nylon composite film was found to have a higher glass transition temperature than OK/Nylon composite film. The glass transition temperature can be influenced by the interaction between



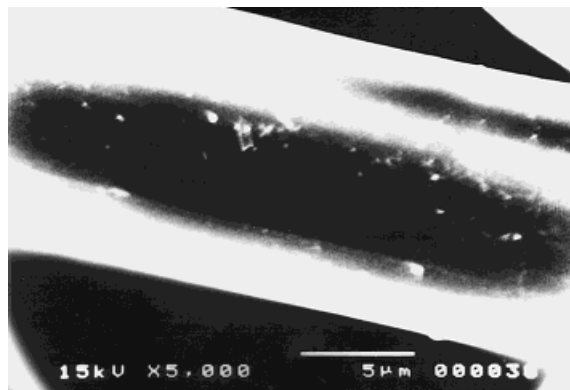
**Figure 3** Effect of grafting time on the graft yield with different monomer concentrations. NaH concentration, 1.4 mol/L per 0.5 g of Kevlar; metalation time, 10 min; grafting temperature, 50°C.

the fiber and the resin. By TMA, it was found that the grafted Kevlar fiber had a higher interaction with Nylon resin than the original Kevlar fiber.

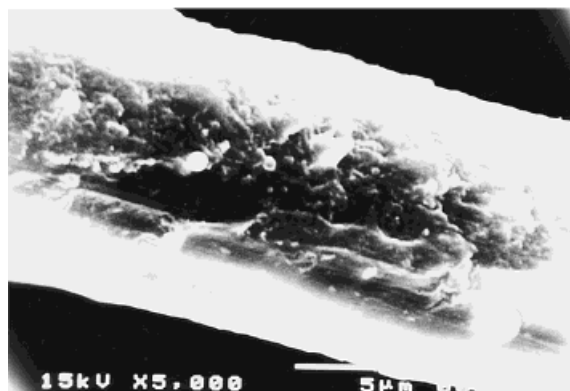
From scanning electron microscopy, Rheovibron, and TMA results, it was concluded that the stronger interaction between the Kevlar fiber and matrix of the GK/Nylon film, compared with the



**Figure 4** Effect of NaH concentration on the number of grafted  $\epsilon$ -caprolactam units and the number of grafted  $\epsilon$ -caprolactam units per active site.



(a)



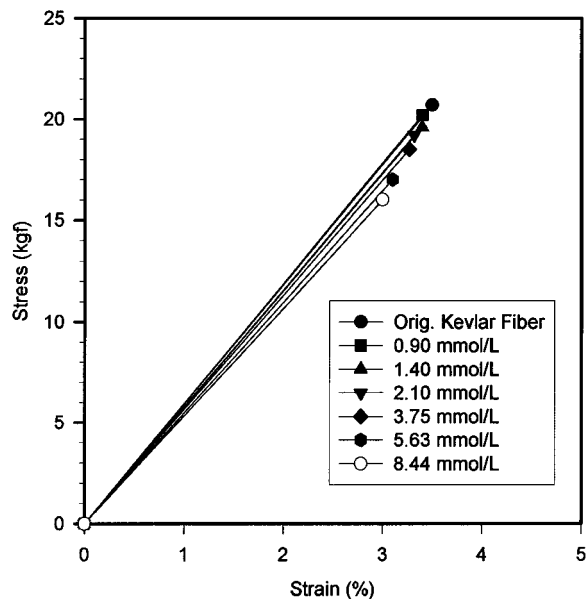
(b)

**Figure 5** Scanning electron micrographs of Kevlar fibers: (a) original Kevlar fiber; (b) grafted Kevlar fiber.

OK/Nylon film, was in part due to mechanical interlocking from the rougher grafted polycaprolactam layer and in part due to the compatibility between grafted polycaprolactam and Nylon 6. However, the origin of the strong interaction is not clear at present.

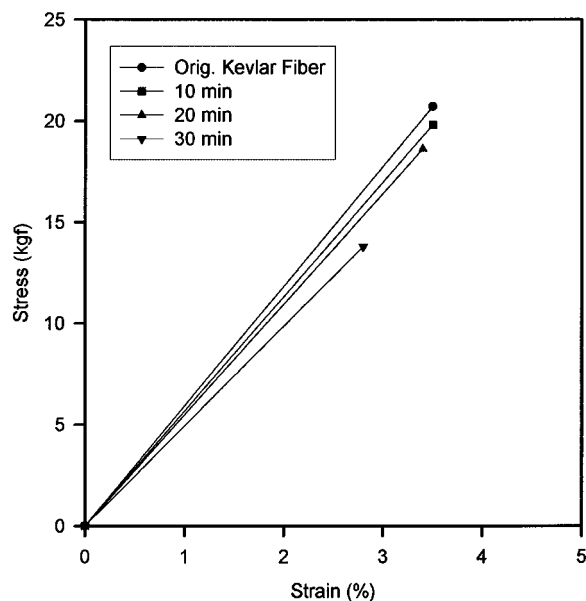
## CONCLUSIONS

The graft copolymerization of  $\epsilon$ -caprolactam onto the Kevlar-49 fiber surface was carried out by anionic polymerization onto *N*-metalated Kevlar fiber with the metalation reaction in a solution of sodium methylsulfinylcarbanion in DMSO. The effects of reaction conditions on the graft yield and on the tensile strength of the fiber have been investigated. The thermomechanical and dynamic

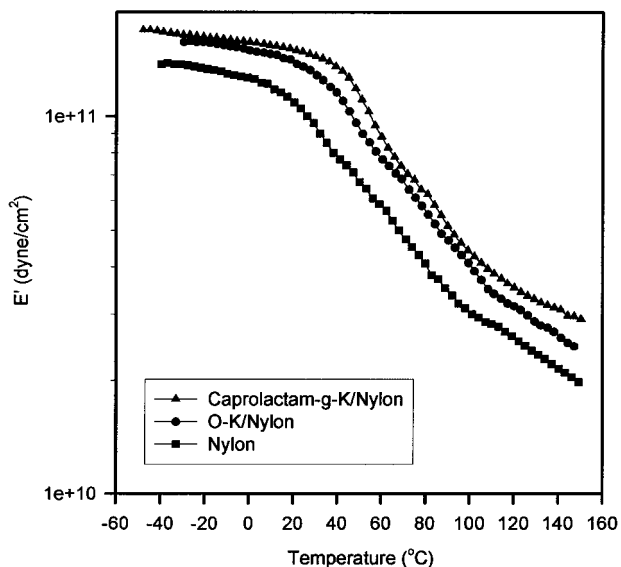


**Figure 6** Stress-strain curves with different NaH concentrations. Metalation time, 10 min; monomer concentration, 5.04 mol/L per 0.5 g of Kevlar; grafting temperature, 50°C; grafting time, 2 min.

mechanical properties of composite films, containing grafted and original Kevlar fibers, were also investigated. The results obtained were as follows:

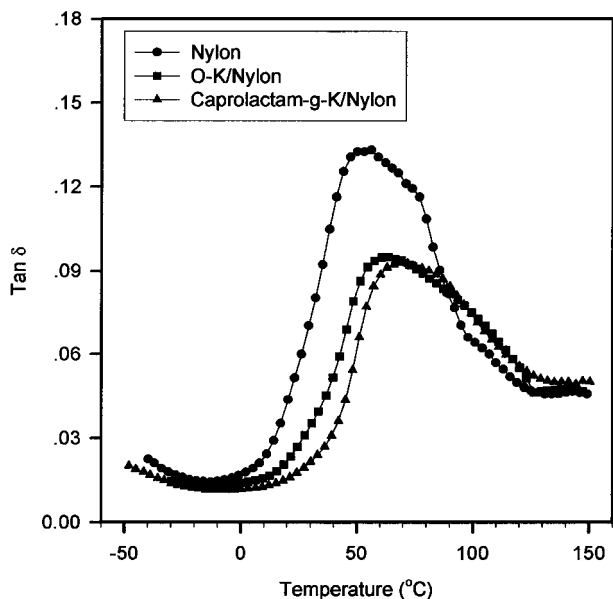


**Figure 7** Stress-strain curves with different metalation times. NaH concentration, 2.1 mol/L per 0.5 g of Kevlar; grafting temperature, 50°C; grafting time, 2 min.

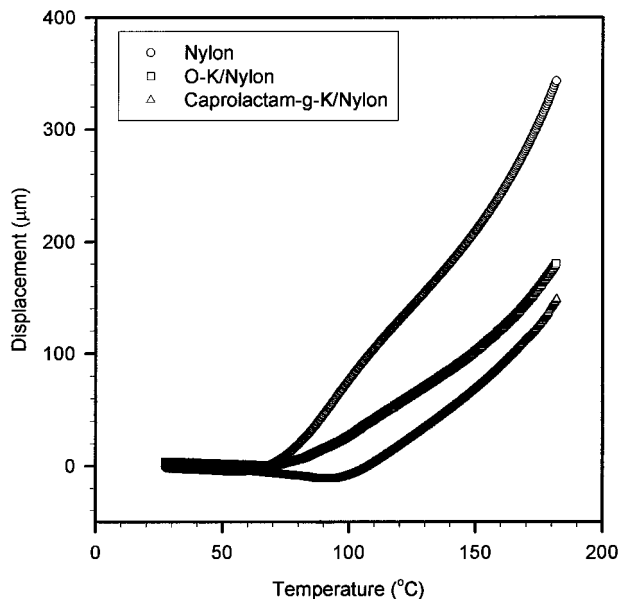


**Figure 8** The relationship between storage modulus and temperature for nylon composites. NaH concentration, 1.4 mmol/L per 0.5 g of Kevlar; monomer concentration, 5.04 mol/L per 0.5 g of Kevlar; grafting temperature, 50°C; grafting time, 2 min.

1. The graft yield significantly increased with the increase of NaH concentration, metalation time, grafting time, and monomer con-



**Figure 9** The relationship between  $\tan \delta$  and temperature for nylon composites. NaH concentration, 1.4 mmol/L per 0.5 g of Kevlar; monomer concentration, 5.04 mol/L per 0.5 g of Kevlar; grafting temperature, 50°C; grafting time, 2 min.



**Figure 10** The TMA curves for displacement and temperature for nylon composites. NaH concentration, 1.4 mol/L per 0.5 g of Kevlar; monomer concentration, 5.04 mol/L per 0.5 g of Kevlar; grafting temperature, 50°C; grafting time, 2 min.

- centration. With the increase of NaH concentration, the number of active sites increased, whereas the number of grafted  $\epsilon$ -caprolactam per active site decreased. The graft yield could be varied from 6.3 to 32% by controlling the reaction conditions.
2. The loss of tensile strength of the fiber depended predominantly on NaH concentration. Over 93% of the tensile strength was retained when the concentration of NaH was below 2.1 mmol/L per 0.5 g of Kevlar fiber.
3. By dynamic mechanical analysis, the storage modulus ( $E'$ ) and the declined temperature of  $E'$  of films increased in the order of GK/Nylon, OK/Nylon, and Nylon. The  $\tan \delta$  peak temperatures, related to glass transition temperature, increased in the same order.
4. By TMA, the glass transition temperature, determined from TMA displacement-temperature curves, also increased in the same order of GK/Nylon, OK/Nylon, and Nylon.

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