

Kevlar-49 섬유표면에 대한 Acrolein의 그라프트 공중합에 관한 연구

김 은 영 · 김 한 도†

부산대학교 공과대학 섬유공학과

(1995년 7월 28일 접수)

Graft Copolymerization of Acrolein onto Kevlar-49 Fiber Surface

Eun-Young Kim and Han-Do Kim†

Dept. of Textile Eng., Pusan National Univ., Pusan, Korea

(Received July 28, 1995)

요 약 : Sodium methylsulfinylcarbanion을 Kevlar 49 섬유 표면의 PPTA와 반응시켜 음이온 중합법으로 acrolein을 Kevlar 49 섬유표면에 그라프트 공중합하였다. 반응 조건이 그라프트율 및 Kevlar 섬유의 인장강도에 미치는 영향을 조사하였다. 그라프트율은 NaH 농도, 그라프트 시간 그리고 단량체의 농도에 따라 증가하였으며, 그라프트율은 반응 조건을 조절함으로써 2~43%로 조절할 수 있었다. Kevlar 섬유의 인장강도의 손실은 NaH 농도가 0.04 mol/L/0.5g Kevlar 이하의 경우에는 약 8% 이하였다. NaH 농도가 증가함에 따라 활성 좌석수는 증가하였으나 활성 좌석수당 그라프트된 acrolein의 수는 감소하였다. 열, 기계적 및 동적 점탄성 거동에서, relaxation 피크가 original-Kevlar/SAN 복합재료 필름에 비하여 grafted-Kevlar/SAN 복합재료 필름의 피크가 더 높은 쪽으로 이동하였다.

Abstract : The graft copolymerization of acrolein onto Kevlar 49 fiber surface was carried out by using sodium methylsulfinylcarbanion in DMSO as an initiator through anionic polymerization under a variety of reaction conditions. The effects of reaction conditions on the grafting and on the tensile strength of the fiber have been investigated. The graft yield significantly increased with increasing NaH concentration, grafting time and monomer concentration. The graft yield varied from 2.0 to 43% with reaction conditions. The tensile strength loss of the fiber predominantly depended on NaH concentration. The tensile strength retained was over 92% when the concentration of NaH was below 0.04 mol/L/0.5g Kevlar fiber. On increasing the NaH concentration, the number of active sites increased, however, the number of grafted acrolein per active site decreased. In thermomechanical and dynamic mechanical analyses, the relaxation peak of grafted-Kevlar fiber/SAN composite film moved to higher temperatures, compared with the original-Kevlar fiber/SAN composite film.

Keywords : sodium methylsulfinylcarbanion, acrolein, anionic graft copolymerization, composite film.

INTRODUCTION

Kevlar 49 (poly(p-phenylene terephthalamide) : PPTA) fiber has already been noted for its good thermal stability, high tensile strength and modulus and chemical resistance. Therefore, the importance of Kevlar 49 fiber in the development of high strength light weight composites for aircraft and other advanced applications has been recognized. The mechanical properties of the fiber-reinforced composite depend critically on the behavior of the interface. The chemical stability (inertness) of the reinforcement fiber result in weak interfacial interactions with matrix polymers. So, surface modification of fibers is studied with the aim of improving the interfacial bonding between the fiber and the resin matrix in composite materials. These efforts have been made to increase the tensile strength and fracture toughness of composites by increasing the adhesion of the fiber/matrix interface. Covalent bonding of fiber surface and resin matrix is currently accepted as one valid mechanism for enhancing interfacial adhesion in epoxy composites reinforced with glass or graphite fibers. In the case of Kevlar fibers with no reactive functional groups, many approaches have been suggested, for example, pretreatment of the fibers with a polymeric sizing or coating prior to preparation of the epoxy composite, and chemical modifications of Kevlar fiber surface.¹ Many attempts have already been made to promote adhesion by modifying the aramid fiber surface. Vaugham² applied a number of commercial coupling agents and obtained some improvement. Mai et al.³ compared two commercial varnishes as aramid fiber coatings and stated that the silicone-based

material is superior to the polyurethane coating.

Many studies deal with the mechanical behavior and fiber-matrix interactions⁴⁻⁶ and enough data are reported on the physicochemical properties and structure of aramid fibers.⁷⁻¹⁰

Promising results have been reported on the chemical modification of PPTA fiber surfaces by plasma treatments designed to provide functional groups for covalent bonding with epoxy resin in composites. For example, Wertheimer and Schreiber¹¹ investigated effects of several types of microwave plasma, and Allred and co-workers¹² reported the results of an extensive study of surface chemistry and bonding of plasma-aminated aramid filaments. Wu and Tesoro¹³ have reported that the presence of amino groups incorporated on Kevlar fabrics can result in remarkably improved peel strength and apparent interlaminar shear strength of epoxy laminates, suggesting a significant role of covalent bonding in improving adhesion in aramid-epoxy composites. Keller et al.¹⁴ have attempted to produce amine sites on Kevlar 49 fiber surface by hydrolytic scission of amide groups. Decrease in fiber strength upon treatment with strong base or with acid and adsorption of acid dye by hydrolyzed samples showed that hydrolysis was not limited to the surface, and approaches based on selective cleavage of surface macromolecules do not seem promising.

Kashani et al.¹⁵ reported the method of synthesis of graft copolymers of poly(m-phenylene isophthalamide) via metalation in a solution of sodium in liquid ammonia. Takayanagi et al.¹⁶ found that sodium methylsulfinylcarbanion prepared by the reaction of sodium hydride and DMSO converts PPTA to PPTA-polyanion, and reported the preparation of N-substituted

PPTA's from the reaction of PPTA and corresponding halides via metalation reaction of a solution of sodium methylsulfinylcarbanion in DMSO. Takayanagi et al.¹⁷ also synthesized N-grafted PPTAs from PPTA and propylene oxide or acrylonitrile by this method.

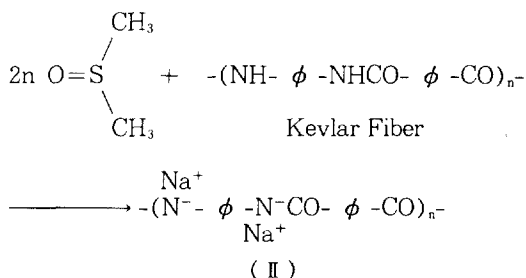
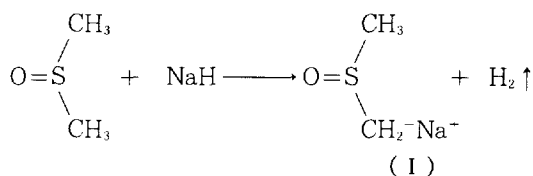
In this study, the graft copolymerization of acrolein onto Kevlar 49 fiber surface was carried out by the anionic polymerization of acrolein onto the N-metalated Kevlar. The chemical reaction must be controlled to avoid an excessive strength loss of the fiber. Studies have been made on the effects of reaction conditions on the graft yield and on the tensile strength of the fiber. The thermomechanical and dynamic mechanical properties of composite films containing grafted Kevlar were also investigated.

EXPERIMENTAL

Materials. Kevlar 49 filament (DuPont Kevlar 49, 1000 denier/ 666 fils) was cleaned by Soxhlet extraction with carbon tetrachloride for about 24 hours. The cleaned samples were then dried in a dry oven at 100°C for about 2 hours. Dimethyl sulfoxide(DMSO) was fractionally vacuum distilled over calcium hydride and dried over 4 Å molecular sieves. Sodium hydride (10% mineral oil in suspension) and acrolein were used as received. SAN(95HC, AN 25%, Lucky) are used on the matrix.

Metalation. A solution of sodium hydride(0.008~0.16 mole/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.



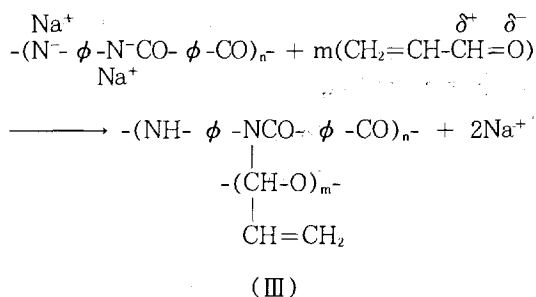
- ϕ - : Phenylene group

Preparation of N-grafted Kevlar Fiber.

After the metalation reaction, the N-metalated Kevlar fiber was added to a solution of acrolein in DMSO. The acrolein grafted Kevlar 49 fiber were prepared by anionic polymerization of acrolein monomer onto the N-metalated Kevlar fiber under a variety of reaction conditions of different polymerization time, monomer concentration and polymerization temperature.

The homopolymers were removed by Soxhlet extraction for 60h using dimethyl formamide (DMF). However, the amount of homopolymer formed was negligible. The grafted poly-

mer(III) was polymerized from the following reaction :



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

Graft yield(%) =

$$\frac{\text{Weight of grafted acrolein(g)}}{\text{Weight of Kevlar fiber used(0.5g)}} \times 100$$

Preparation of Composite Films. The matrix polymer(SAN) was dissolved in dichloromethane, and the cut fiber (content : 5 wt%, fiber length : 5 mm) was added to this solution and dispersed uniformly by stirring. This reinforcement-matrix mixture was cast on a glass plate. The composite film were obtained by evaporating the solvent in a vacuum oven at 100°C. For measurement of mechanical properties, composite specimens (composite film, about 0.15 mm) were made by compressing at 200°C. The composite film prepared in this study was discontinuous fiber-reinforced composite of random-in-plane fiber orientation.

Characterization. The extent of metalation reaction was measured using a UV-visible spectrophotometer(Hitachi 220). FTIR spectrophotometer(JASCO, IR-700) was used to obtain absorption spectra of samples in KBr pellets. The tensile strength were measured using an

Instron UTM. Stress-strain curves were recorded with cross head speed of 100 mm/min and chart speed of 20 mm/min. Each of the values reported here is an average of at least 10 specimens. The surface of Kevlar fiber was observed by using a SEM(JEOL JSM-5400). Thermomechanical properties of composites were measured using a thermomechanical analyzer (Seiko, TMA 120C). Rheovibron (DDV, 01FP) was used to measure dynamic mechanical properties at 3°C/min and 11 Hz.

RESULTS AND DISCUSSION

Fig. 1 is the IR spectra of the original Kevlar fiber(a), polyacrolein homopolymer(b), and grafted Kevlar fiber(c). In the case of original Kevlar fiber, hydrogen-bonded NH group appears as a wide absorption peak at 3,300 cm⁻¹. And the characteristic peaks of Kevlar fiber, amide I at 1,650 cm⁻¹ (C=O stretching), amide II at 1,540 cm⁻¹ (N-H bond, C-N stretching) and amide III at 1,310 cm⁻¹ (C-N, N-H and C-C

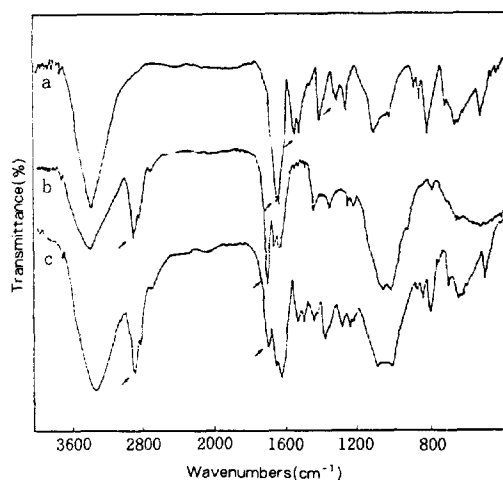


Fig. 1. IR spectra of (a) original Kevlar fiber, (b) polyacrolein, and (c) polyacrolein-g-Kevlar.

vibration) were observed.

R. C. Schulz¹⁸ found that the polyacrolein homopolymer synthesized by anionic polymerization resulted from the addition reaction of the carbonyl repeating unit exclusively. Therefore, carbonyl bands are not expected in the grafted samples. The polyacrolein homopolymer and polyacrolein grafted Kevlar prepared in this study have a C=C stretching at $1,680\text{ cm}^{-1}$ and a CH bond vibration at $3,100\text{ cm}^{-1}$. The grafting of acrolein onto Kevlar fiber was identified by these characteristic peaks around $1,680\text{ cm}^{-1}$ (vinyl group) and $3,100\text{ cm}^{-1}$ (CH group).

Table 1 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, grafting time and monomer concentrations. The graft yield(%) was varied from 2.0 to 43% by controlling reaction conditions.

The effects of monomer concentration on the graft yield(%) are shown in Figs. 2 to 4. The graft yield(%) increased with increasing grafting time and monomer concentration. The graft yield(%) increased markedly as the concentration of NaH increased from 0.008 to 0.027 mol/L/0.5 g Kevlar(see Figs. 2 to 4). Figs. 5 and 6 show the effect of NaH concentration on the grafting(%). The graft yield(%) increased sharply with the increase in NaH concentrations. This is due to the increase in the number of active anions with NaH concentrations. With increasing the NaH concentration up to 0.16 mol/L/0.5 g Kevlar, the graft yield(%) increases to over 40%.

Fig. 7 shows typical stress-strain curves of samples of the S' series. The remarkable feature of these curves is the reduction in the

Table 1. Effect of Reaction Conditions on the Graft Yield (%)

Sample Designation	Metalation		Grafting conditions	
	NaH conc. (mol/L/0.5g Kevlar)	Time (min)	Monomer conc. (mol/L/0.5g Kevlar)	Graft Yield (%)
S ₁	0.008			4.9
S ₂	0.012	10	0.84	6.0
S ₃	0.018			7.0
S ₄	0.027			8.8
T ₁		2		2.1
T ₂		4		4.2
T ₃	0.018	6	0.84	5.9
T ₄		8		6.5
T ₅		10		6.9
M ₁			0.42	4.8
M ₂	0.018	10	0.84	7.0
M ₃			1.68	8.0
M ₄			3.36	11.9
M' ₁			1.5	9.8
M' ₂			3.0	12.5
M' ₃	0.018	10	7.5	21.7
M' ₄			15.0	24.7
M' ₅			30.0	27.9
S' ₁	0.02			22.6
S' ₂	0.04	10	7.5	32.5
S' ₃	0.08			38.2
S' ₄	0.16			42.7
T' ₁		2		18.9
T' ₂		4		24.4
T' ₃	0.08	6	7.5	31.1
T' ₄		8		34.8
T' ₅		10		38.2
M'' ₁			1.5	16.1
M'' ₂			3.0	25.1
M'' ₃	0.08	10	7.5	38.2
M'' ₄			15.0	40.3
M'' ₅			30.0	42.6

Metalation time : 10min.

Metalation temp : 30°C.

breaking stress, breaking strain and modulus when the concentration of NaH is increased. When the concentration of NaH was below 0.04 mol/L/0.5 g Kevlar fiber, over 92% of the

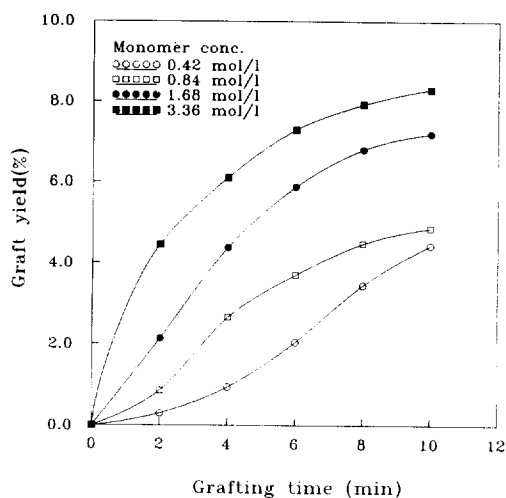


Fig. 2. Effect of monomer concentration on the graft yield(%). (NaH conc.: 0.008 mol/L/0.5 g Kevlar).

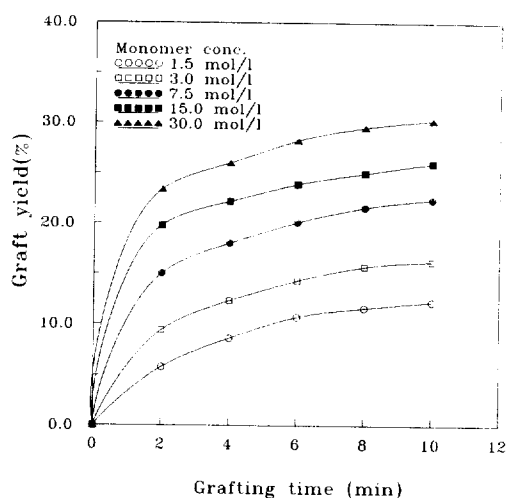


Fig. 4. Effect of monomer concentration on the graft yield(%). (NaH conc.: 0.027 mol/L/0.5 g Kevlar).

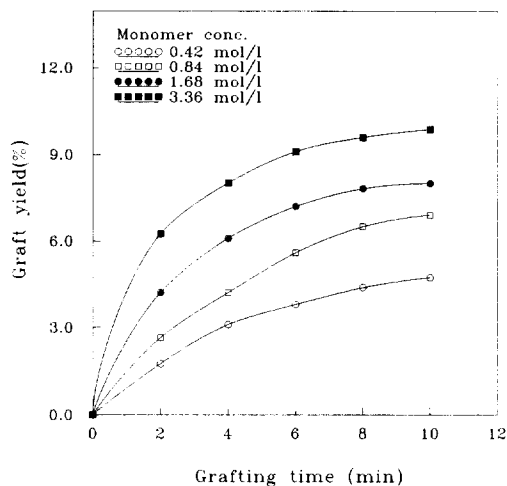


Fig. 3. Effect of monomer concentration on the graft yield(%). (NaH conc.: 0.018 mol/L/0.5 g Kevlar).

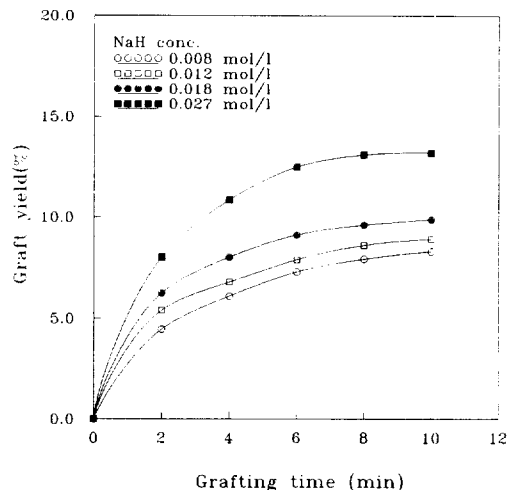


Fig. 5. Effect of NaH concentration on the graft yield(%). (Monomer conc.: 3.36 mol/L/0.5 g Kevlar).

tensile strength was retained. However, the tensile strength loss of other fibers are about 17 and 23% for the NaH concentration of 0.08 and 0.16 mol/L/0.5 g Kevlar, respectively. It is concluded that the concentration of NaH below 0.04 mol/L/0.5 g Kevlar fiber is desirable to maintain over 90 % of the tensile strength of the

fiber.

Table 2 shows the effect of NaH concentration on the number of active sites and the number of grafted acrolein per active site at a constant monomer concentration (0.84 mol/L/0.5 g Kevlar). The number of acrolein per active site on the fiber surfaces was calculated from

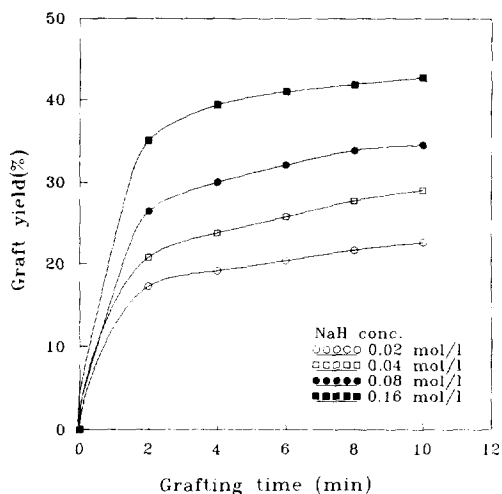


Fig. 6. Effect of NaH concentration on the graft yield(%). (Monomer conc. : 7.5 mol/L/0.5 g Kevlar).

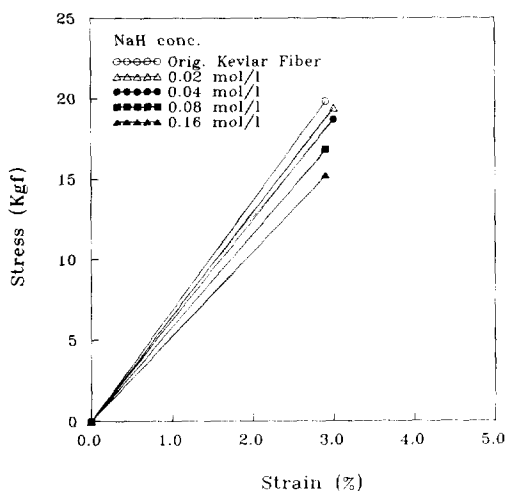


Fig. 7. Stress-strain curves of sample S' series.

absorbances of NaH solution before and after metalation using a UV-visible spectrometer at 312 nm. The number of grafted acrolein unit/0.5 g Kevlar (the weight of grafted acrolein $\times 6.02 \times 10^{23}$ / molecular weight of acrolein, A), the number of active sites/0.5 g Kevlar fiber (the number of moles of the consumed NaH $\times 6.02 \times 10^{23}$, B) and the number of grafted acrolein

Table 2. Effect of NaH Concentration on the Number of Active Sites and the Number of Grafted Acrolein Unit per Active Site

NaH concentration (mol/L)	A ^{a)}	B ^{b)}	C ^{c)}
0.008	8.16×10^{20}	9.81×10^{18}	83.18
0.012	1.10×10^{21}	1.45×10^{19}	74.83
0.018	1.21×10^{21}	1.86×10^{19}	65.20
0.020	1.21×10^{21}	2.30×10^{19}	52.61
0.040	1.75×10^{21}	3.53×10^{19}	49.58
0.080	2.05×10^{21}	4.60×10^{19}	44.57
0.160	2.29×10^{21}	5.54×10^{19}	41.34

Monomer concentration : 0.94 mol/L/0.5 g Kevlar.

Grafting time and temperature : 4 min and 10°C.

^{a)} The number of grafted acrolein unit/0.5 g Kevlar fiber.

^{b)} The number of active site/0.5 g Kevlar fiber.

^{c)} The number of grafted acrolein unit/active site.

unit/active site(A/B) are shown in Table 2. The number of active sites depended on NaH concentration and metalation time, however, the number of grafted acrolein per active site depended on the grafting time and monomer concentration. On increasing the NaH concentration, the number of active sites increased, however, the number of grafted acrolein per active site decreased. Thus, it is found that the number of grafting site and the length of grafted polymer are mainly controlled by NaH concentrations.

Fig. 8 shows scanning electron micrographs of original Kevlar 49 fiber (a) and grafted Kevlar fiber (b). A comparison of the surface of original Kevlar fiber with that of grafted Kevlar fiber shows that the grafted Kevlar fiber is much rougher, whereas the original Kevlar fiber is very smooth. The rougher grafted polyacrolein layer of Kevlar fiber surface may be responsible for the improvement of interfacial adhesion between the fiber and the matrix resin.

Fig. 11 shows the TMA displacement-temper-

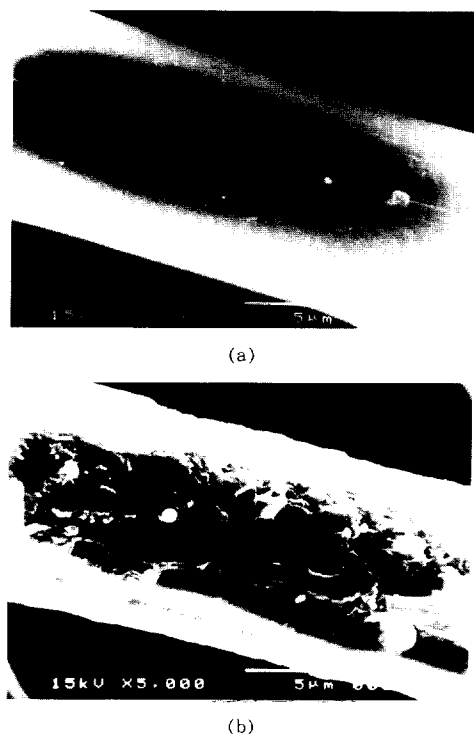


Fig. 8. Scanning electron micrographs of Kevlar fibers. (a : original Kevlar fiber and b : grafted-Kevlar fiber[Sample M₄]).

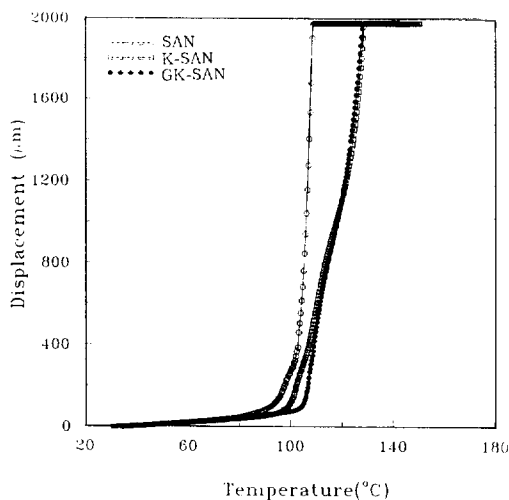


Fig. 9. The relationship between displacement and temperature for SAN, original Kevlar(K)/SAN, and grafted-Kevlar(GK, sample M₄)/SAN composite.

ature curves of SAN, original-Kevlar(K)/SAN and grafted-Kevlar(GK)/SAN films. The GK/SAN composite film was found to have a higher glass transition temperature than K/SAN composite film. The glass transition temperature can be influenced by the interaction between the fiber and the resin. By the TMA analysis, it was found that the grafted Kevlar fiber has higher interaction with SAN resin than original Kevlar fiber.

On the other hand, a significant information on the interaction between the grafted-Kevlar fiber and the matrix polymer SAN can be obtained from Rheovibron analysis. To compare the interaction of GK/SAN composite film with pure SAN film and K/SAN composite film, the dynamic mechanical properties of these films, were also measured(see Figs. 10 and 11). The storage modulus of the GK/SAN composite film showed higher values than did the K/SAN composite film. However, the storage modulus of K/SAN composite film showed higher value than that of pure SAN film. The $\tan\delta$ peak temperature and the declined temperature of storage modulus of GK/SAN composite film showed the highest value among these three samples. These high values of storage modulus and relaxation temperature of GK/SAN composite film indicate the presence of strong interaction between the grafted Kevlar fiber and SAN. The strong interaction is in part due to the rough surface of grafted Kevlar fiber. However, the compatibility between polyacrolein and SAN was not studied in this study. So the distinct origin of the strong interaction of grafted Kevlar fiber with SAN is not clear at the present moment. More detailed studies should be made.

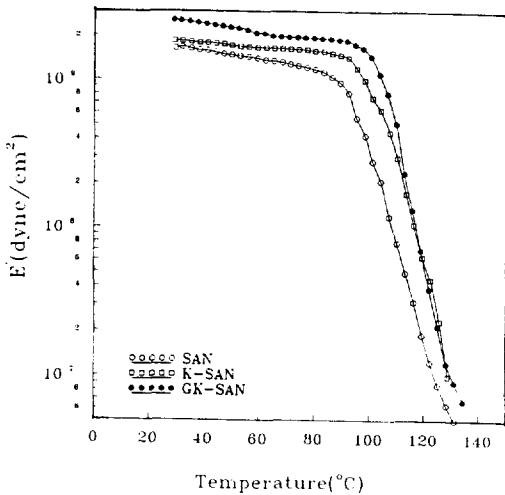


Fig. 10. The relationship between storage modulus and temperature for SAN, K/SAN, and GK(sample M_n)/SAN films.

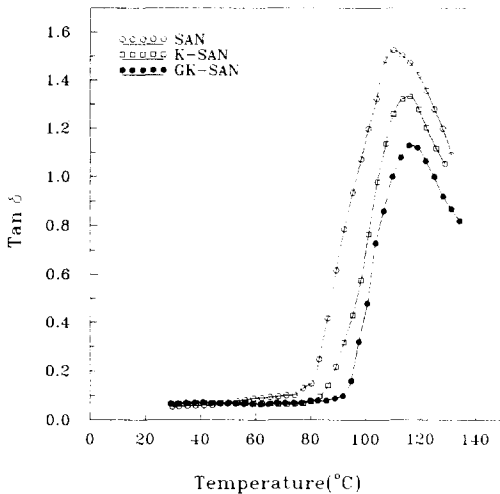


Fig. 11. The relationship between $\tan \delta$ and temperature for SAN, K/SAN, and GK(sample M_n)/SAN films.

CONCLUSION

The graft copolymerization of acrolein onto Kevlar 49 fiber surface was carried out by the anionic polymerization onto N-metalated Kevlar fiber formed via the metalation reaction in a so-

lution 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 mechanical properties of composite film containing grafted Kevlar were also investigated. The results obtained were as follows :

1. The graft yield significantly increased with increasing NaH concentration, grafting time and monomer concentration. The graft yield could be varied from 2.0 to 43% by controlling the reaction conditions.

2. The tensile strength loss of the fiber depends predominantly on NaH concentration. Over 92% of the tensile strength was retained when the concentration of NaH was below 0.04 mol/L/0.5 g Kevlar fiber.

3. On increasing the NaH concentration, the number of active sites increased, however, the number of grafted acrolein per active site decreased.

4. By thermomechanical and dynamic mechanical analyses, the relaxation peak of grafted Kevlar fiber/SAN composite film move to a higher temperature, compared to the original Kevlar fiber/ SAN composite film.

감사의 글 : 본 연구는 1994년도 교육부 신소재 분야 연구지원에 의해 이루어졌으며 이에 깊은 감사를 드립니다.

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