

Transverse Alignment of Liquid Crystalline Epoxy Resin on Carbon Fiber Surface

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ABSTRACT: Transverse alignment of liquid crystalline epoxy (LCE) resin was effectively induced on carbon fiber (CF) surface by amine treatment. Aliphatic and aromatic amines were grafted on oxidized CF surface, and anisotropic orientation of LCE network was identified with X-ray diffraction and it was correlated with mechanical properties of CF/LCE composites. Vertical alignment of LCE enhanced the transverse dynamic modulus of the composite. Espe-

cially, aromatic diamines were effective in promoting the interfacial adhesion as well as transverse composite modulus. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 684–689, 2006

Key words: transverse alignment; liquid crystalline epoxy; amine treatment; carbon fiber

INTRODUCTION

Anisotropic orientation of liquid crystalline networks has been major concern of many researchers in the field of crosslinkable liquid crystalline polymers.^{1–5} Anisotropically ordered network shows peculiar optical, mechanical, and thermal properties compared with the properties of isotropic networks.

Anisotropic orientation of liquid crystalline material can be accomplished on highly oriented substrates,^{6,7} on surface-modified substrates,¹ in magnetic field,^{2–4} and in electric field.⁵ Homogeneous or homeotropic orientation of liquid crystalline material can be induced by these methods. These methods can be applied in liquid crystalline networks and there have been several reports concerning the anisotropic alignment of liquid crystalline networks. Hikmat and Broer¹ aligned liquid crystalline epoxy (LCE) on rubbed polyimide surfaces, while Ober and coworkers^{4,5} oriented LCE in magnetic field and electric field. In their results, uniaxial homogeneous orientation of LCE was effectively induced, leading to anisotropically ordered LCE network. However, there was no work reporting the homeotropic orientation of LCE networks.

Homeotropic orientation of liquid crystalline material has been known to be achieved by surface treatment of inorganic substrate,⁸ deposition of amphiphilic material,⁹ and oblique evaporation of SiO.¹⁰ Therefore, homeotropic alignment of LCE network can also

be induced by modifying the substrate with long-chain molecule such as silane coupling agent and long-chain amines.

Transverse alignment of LCE network on various substrates can be advantageous in several applications such as optical materials or a matrix for advanced composites. In particular, vertical orientation of LCE network is of great importance in unidirectional composites as it can improve the transverse mechanical properties of the composite considerably. There has been an attempt to align liquid crystalline material in the vertical direction of CF; however, it was not successful.⁷

In this study, anisotropic alignment of LCE network perpendicular to CF long axis was induced by simple surface treatment. Aliphatic amine and aromatic amine were introduced on CF surface and their effect on the orientation of LCE network was investigated. In addition, the influence of anisotropic orientation on the dynamic mechanical properties and thermal expansion of CF/LCE composite was discussed.

EXPERIMENTAL SECTION

Materials

Carbon fiber (CF) was purchased from Torayca Co., Japan (T-300) and used after desizing in dichloromethane for 5 days and in distilled water for 2 days. The desized CF was dried in vacuum oven at 100°C for 2 days. Liquid crystalline epoxy resin (LCE) was synthesized according to the method proposed by our group in previous paper.¹¹ Nematic transition temperature of LCE was 158°C and isotropic transition temperature was 222°C. Diaminodiphenylester (DDE) was used as a curing agent for the curing of LCE.

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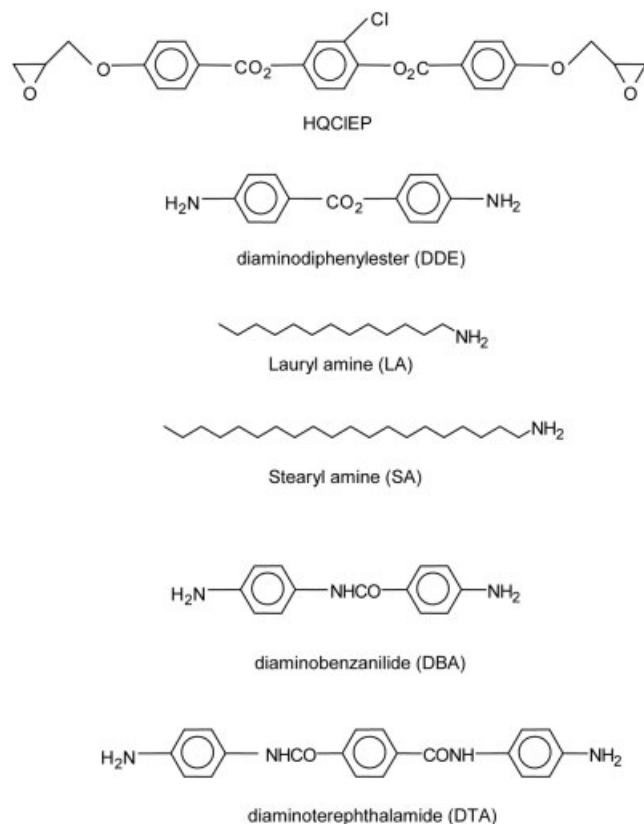


Figure 1 Chemical structures of LCE, DDE, and various amines.

Oxidizing agent, nitric acid (60–65%) was supplied from Dongyang Chemical Co., Korea. Lauryl amine (LA), stearyl amine (SA), and diaminobenzanilide (DBA) used for modification of CF were purchased from Aldrich, USA. Diaminophenylterephthalamide (DTA) was synthesized by reaction of *p*-phenylenediamine with terephthaloyl chloride. Thionylchloride and other solvents were obtained from Junsei Chemical Co., Japan and used without further purification. Chemical structures of LCE, DDE, and various amines are shown in Figure 1.

Surface treatment of cf

Oxidation of CF was performed in nitric acid solution (60–65%) at 100–110°C. CF was put into preheated nitric acid solution and oxidized for 120 min. Oxidized CF was refluxed with distilled water for 2 days and dried in vacuum oven at 100°C for 24 h.

CF oxidized for 120 min in nitric acid solution was modified with various amines. LA, SA, DBA, and DTA were used to modify CF surface. Oxidized CF (30 g) was put into boiling 1000 mL thionylchloride solution containing 1 mL of DMF. The reaction was carried out for 1 h in boiling thionylchloride solution and excess thionylchloride was evaporated perfectly in

vacuum. After reaction with thionylchloride, the CF (10 g) was put into 500 mL of dried dioxane solution containing 0.2 mol of pyridine and 0.1 mol of amine at room temperature. It reacted with amine for 24 h and was washed with boiled dioxane, dichloromethane, tetrahydrofuran, and acetone successively. It was dried in vacuum oven at 40°C for 24 h before use. In case of DBA and DTA, DMF was used as solvent.

Composite manufacturing

Unidirectional CF/LCE composite was manufactured by resin infusion process. It was cured at curing temperature for 2 h and postcured at 230°C for 2 h.

Physical measurements

Surface acidic function of oxidized and amine-modified CF was determined by NaOH uptake. NaOH solution ($2 \times 10^{-3}M$) was prepared and about 1 g of CF was immersed in NaOH solution for 12 h. The pH value of prepared NaOH solution and resulting NaOH solution was measured using a pH meter (Ion Analyzer 250, Corning). The amount of NaOH consumed was calculated from the pH value and acidic function of CF was also determined. Average of three samples was adopted as acidic function of CF surface.

Surface basic function of amine-modified CF surface was determined by HCl uptake. HCl solution ($2 \times 10^{-3}M$) was used to calculate the basic function of CF. It was immersed in HCl solution for 12 h and the basic function of it was calculated from pH value before and after immersion. Data of three samples were averaged.

Wide angle X-ray diffraction patterns of the composite were obtained with MAC science M18XHF. X-rays were produced by a generator operated at 45 kV and 20 mA and nickel filtered copper $K\alpha$ radiation was used.

Dynamic mechanical thermal analyzer (DMA, Rheometrics co. MK III) was used to measure the glass transition temperature and dynamic modulus of cured LCE networks. Data were collected in bending mode at a frequency of 1 Hz and heating rate was 5°C/min. Coefficient of thermal expansion (CTE) of cured CF/LCE composites was determined with DMA in tensile mode. Heating rate was fixed at 5°C/min and applied load was 100 mN.

RESULTS AND DISCUSSION

Several aliphatic and aromatic amines were grafted on CF surface to induce the alignment of LCE perpendicular to the fiber long axis. Chain length of amines was between 10 and 20Å. Amines were grafted on CF surface oxidized with nitric acid for 120 min as the amount of polar functional group and surface area were optimized at this reaction condition.

TABLE I
Grafting Efficiency of Amine-Grafted Carbon Fiber

	Acidic function (eq/g)	Grafting efficiency (%)	Basic function (eq/g)	Grafting efficiency (%)
LA	35.0	43.5	–	–
SA	36.4	41.3	–	–
DBA	27.5	55.7	34.2	55.1
DTA	27.9	55.0	33.8	54.5

Acidic function of oxidized carbon fiber: 62.0 eq/g.

Amine grafting efficiency was determined from HCl and NaOH titration to confirm the grafting of amines. Table I shows the titration results of amine-grafted CF. Aliphatic amines showed lower grafting efficiency than aromatic amines from NaOH titration. Low grafting efficiency in long aliphatic amines may be due to shielding effect of grafted amine group. Long and bulky molecule present on CF surface prevents the reaction of reactive site on CF surface with other molecule because of steric hindrance. The decrease of grafting efficiency of several polymers with high molecular weight was reported by many researchers.^{12,13} By comparing NaOH titration and HCl titration, the fraction of internal cyclization reaction may be estimated roughly. Basic function of CF surface only includes amine group grafted on CF surface without internal cyclization. Internal cyclized amine group is not active in HCl titration as amide group is known to be inert toward HCl. Therefore, large difference of grafting efficiency from NaOH and HCl titration indicates that internal cyclization reaction occurred extensively. In this case, both aliphatic and aromatic amines did not show internal cyclization. There may be some errors in NaOH titration results as bulky aliphatic amine protects carboxylic acid or phenol group because of steric hindrance. However, this effect is thought to be not so significant in NaOH titration as it can diffuse into small pores or crevices effectively.

To investigate the effect of amine treatment on the alignment of LCE, the LC phase of CF/LCE mixture was analyzed. There was some change of the LC phase of LCE after amine treatment; however, it could not be clearly analyzed with polarized optical microscope. Therefore, the orientation mode of LCE on amine-modified CF surface was identified with X-ray diffraction. Figure 2 represents the X-ray diffraction pattern of untreated CF/LCE composite. Unidirectional CF/LCE composite was analyzed in three directions to confirm the orientation of LCE. Intense diffraction peak at 25.2° observed in the direction of fiber long axis is attributed to the basal plane of CF, while shoulder around 18.6° is caused by LCE aligned along fiber long axis. However, there was no diffraction peak found in diagonal and meridional directions. This apparently demonstrates that LCE is anisotropically

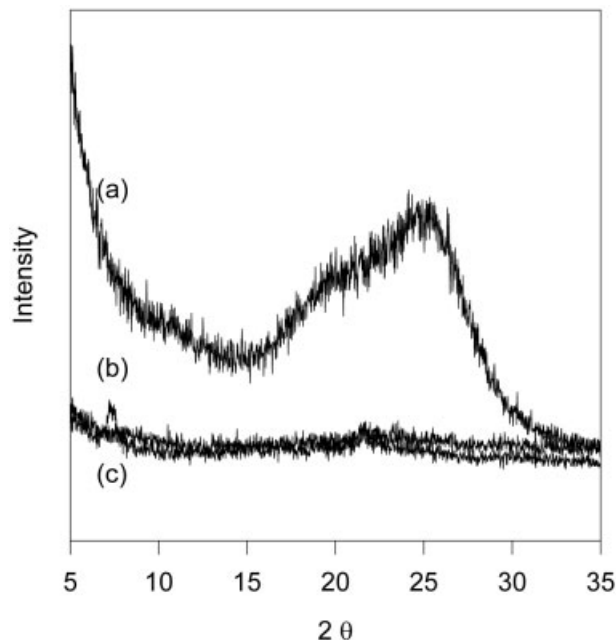


Figure 2 X-ray diffraction patterns of untreated CF/LCE composite (a) parallel to fiber long axis, (b) perpendicular to fiber long axis, and (c) 45° to fiber long axis.

aligned on untreated CF surface along fiber long axis. Parallel alignment of the cured network is due to highly oriented and microgrooved surface structure of CF.

Figure 3 shows X-ray diffraction pattern of DTA-treated CF/LCE composite. Strong diffraction peak at

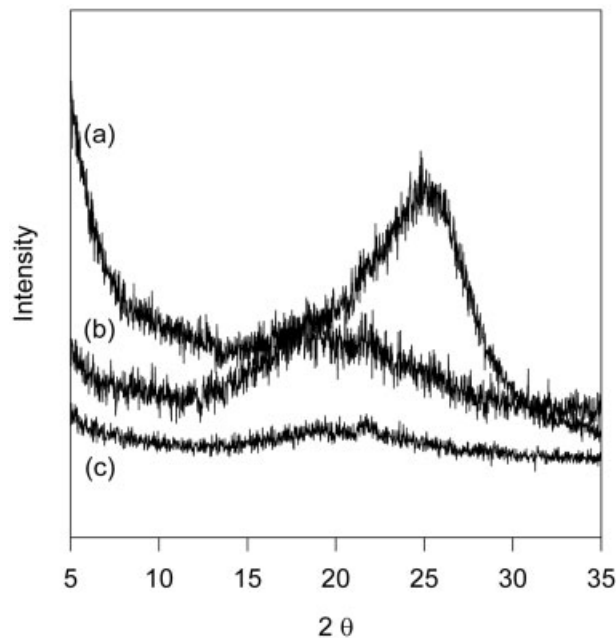


Figure 3 X-ray diffraction patterns of DTA-treated CF/LCE composite (a) parallel to fiber long axis, (b) perpendicular to fiber long axis, and (c) 45° to fiber long axis.

2θ of 25.2° and weak shoulder at 2θ of 18.6° are observed in fiber direction. Compared with the diffraction pattern in Figure 2, similar diffraction pattern was obtained in fiber direction except for the intensity decrease of the diffraction peak at 2θ of 18.6° . Diagonal diffraction pattern was also not changed by amine treatment. However, peculiar diffraction peak appeared in transverse direction at a diffraction angle of 18.6° in DTA-treated CF/LCE composite. In case of untreated CF/LCE composite, there was no peak observed in transverse direction. This indicates that transverse alignment of LCE is effectively induced by DTA treatment. However, weak shoulder in parallel direction implies that all LCE resins are not oriented perpendicular to fiber axis. That is, LCE resins are aligned perpendicular to fiber long axis in some regions and are oriented along fiber axis in other regions. Orientation mode of LCE network on CF surface is depicted in Figure 4 schematically. Amines are covalently bonded to CF surface perpendicularly and

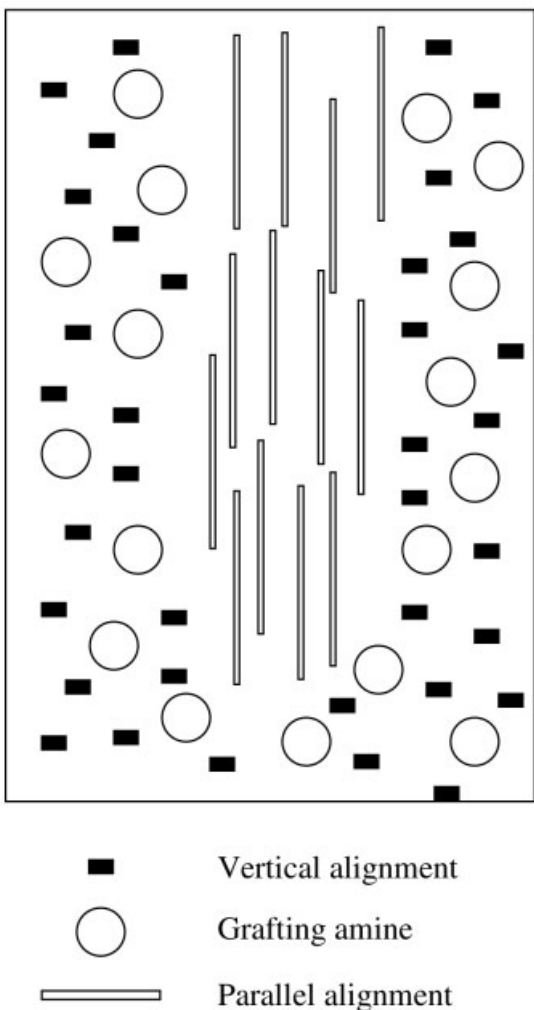


Figure 4 Schematic diagram of alignment of LCE on amine-treated CF surface.

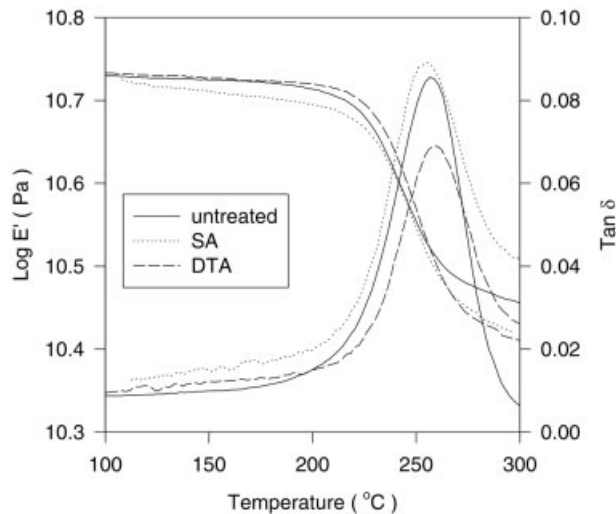


Figure 5 DMA thermograms of amine-treated CF/LCE composite in the direction of fiber.

LCE molecule aligns with respect to the amine on fiber surface. Parallel orientation of LCE is thought to be caused by the inhomogeneity of the amine treatment. In the region where amine group is dense, vertical alignment dominates, while in the region where amine group is coarse, parallel alignment is dominant. In DBA- and SA-treated composite, similar X-ray diffraction patterns were obtained. However, in case of LA-treated CF composites, clear meridional diffraction peak was not observed. Short chain length of LA is mainly responsible for this. Low grafting efficiency caused by steric hindrance is another reason for little vertical alignment in LA-treated composite.

Surface treatment of CF to improve interfacial adhesion between matrix and CF is known to affect the dynamic mechanical properties of composite. Especially, damping properties of composites are greatly affected by interfacial modification. In this section, the influence of various surface treatment methods on the ordering of LCE resins and damping at interface were evaluated.

To precisely study the influence of surface modification on mechanical properties of CF/LCE composites, mechanical properties of amine-grafted CF/LCE composites were examined. DMA thermograms of amine-treated CF/LCE composites in the direction of fiber alignment are shown in Figure 5. Glassy modulus was not altered much; however, rubbery modulus was little lowered by amine modification. That is, untreated CF/LCE composites showed higher rubbery modulus than that of amine-treated ones. These results can be understood in terms of the orientation of LCE molecules. In general, composite modulus is determined by the modulus of the reinforcement and matrix according to rule of mixture. Especially, long fiber reinforced composite obeys the rule over all vol-

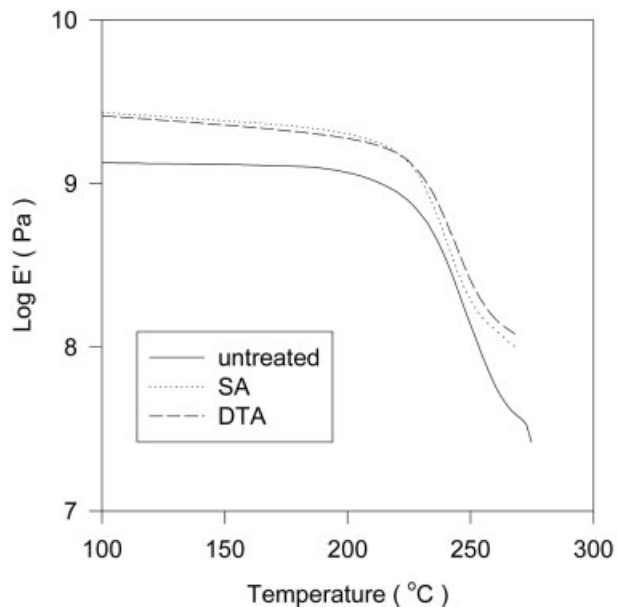


Figure 6 DMA thermograms of amine-treated CF/LCE composite in the vertical direction of fiber.

ume percent ranges reasonably. In other words, composite modulus is typically dependent on the reinforcement and matrix. Other factors like interfacial adhesion have little effect on the composite modulus. Therefore, the rubbery modulus of amine-grafted composite should be analyzed in view of the modulus of each component. Modulus of CF can be postulated to be constant irrespective of surface treatment condition as it is chemically modified with amines. On the other hand, matrix modulus can not be kept constant as the anisotropic orientation of LCE is dominated by the amine modification as shown previously. Judging from previous result, low rubbery modulus of DTA- or SA-treated composite in the direction of fiber axis is attributed to transverse alignment of LCE molecule. However, the decrease of rubbery modulus was not so significant. On the whole, the modulus of amine-treated composites was also lower than that of nitric acid-treated one because of the decrease of orientation parallel to long molecular axis of CF.

Mechanical damping of the amine-treated composites showed complicated tendency. $\tan \delta$ showed maximum value in SA-treated composite, while it showed minimum value in DTA-treated one. There are several factors influencing the energy dissipation of CF/LCE composite. Intrinsic damping of CF, orientation and degree of cure of LCE network, and interfacial adhesion are important factors determining the damping properties of CF/LCE composites. Among these, degree of orientation and interfacial adhesion can be regarded as the major factors affecting the energy dissipation of CF/LCE composites. In terms of the degree of order, SA- or DTA-treated composite

should have high $\tan \delta$, while in terms of interfacial adhesion, SA-treated one should have high $\tan \delta$ and DTA-treated one shows low $\tan \delta$ as interlayer surface strength of the composite is high in DTA-treated composite. Interfacial adhesion of diamine-treated composite was much higher than that of untreated or monoamine-treated composite. Comparing this prediction with experimental result, interfacial adhesion rather than degree of order is the principal factor controlling the damping properties of CF/LCE composites.

Transverse modulus of amine-treated CF/LCE composites is represented in Figure 6. Contrary to longitudinal modulus, SA- or DTA-treated composite displayed much higher transverse modulus than did the untreated one. Transverse alignment of LCE may improve the transverse properties of SA- or DTA-treated composite. Glassy modulus as well as rubbery modulus was enhanced by these amine modifications. This result is of significant importance as the disadvantage of unidirectional fiber-reinforced composite can be overcome by simple surface treatment with little drop of longitudinal modulus. Higher modulus of SA-treated composite compared with that of DTA-treated one implies that the degree of orientation of LCE in the vertical direction of CF is higher in SA-treated composite. Catalytic effect of aromatic amine group in DTA may be responsible for this behavior as it accelerates the curing of LCE. Fast curing hinders the orientation of LCE, diminishing the modulus of the composite. There was no acceleration of curing observed in SA-treated composite. $\tan \delta$ value in the transverse direction showed the same tendency as in longitudinal direction.

CTEs of amine-grafted CF/LCE composite were measured in longitudinal direction and transverse direction (Table II). Negative CTE value was obtained in longitudinal direction, while positive CTE value was observed in transverse direction. This difference is due to intrinsic CTE of CF. Amine treatment did not have considerable influence on the CTE in the direction of fiber alignment. However, transverse CTE was low in SA-, DBA-, or DTA-treated composite. As can be expected from dynamic modulus data, transverse align-

TABLE II
Coefficient of Thermal Expansion of Amine-Treated CF/LCEE7 Composites in Glassy Region

Amines	CTE ($\mu\text{m}/\text{m } ^\circ\text{C}$)	
	Longitudinal	Transverse
Untreated	-14	75
LA	-8	64
SA	-3	45
DBA	-5	46
DTA	-3	42

ment of LCE lowered the thermal expansion of the composite. From these results, it can be known that unidirectional CF/LCE composite with excellent longitudinal and transverse mechanical properties as well as dimensional stability can be prepared by modifying CF surface with long amine. Especially, rigid aromatic diamine treatment could enhance the elastic modulus and interfacial adhesion of the composite simultaneously.

CONCLUSIONS

Anisotropic alignment of LCE resin on CF surface was investigated. Amine grafting efficiency was high in case of aromatic amines and internal cyclization of amine was not observed. Transverse alignment of LCE resin was effectively induced on aromatic-amine-treated CF/LCE composite though LCE was oriented along fiber long axis in some regions. However, it was not apparent in composite treated with relatively short aliphatic amine. Longitudinal modulus of CF/LCE composite was not dependent upon the surface modification of CF. Transverse modulus of CF/LCE com-

posite aligned perpendicular to fiber long axis was greatly enhanced by amine treatment. Thermal expansion of the composite was also reduced considerably in the vertical direction of fiber by amine surface modification. Especially, aromatic diamine treatment improved the interfacial adhesion of CF/LCE composite as well as modulus.

References

1. Hikmat, R. A. M.; Broer, D. J. *Polymer* 1991, 32, 1627.
2. Jahromi, S.; Kuipers, W. A. G.; Norder, B.; Mijs, W. J. *Macromolecules* 1995, 28, 2201.
3. Jahromi, S.; Mijs, W. J. *Mol Cryst Liq Cryst* 1994, 250, 209.
4. Barclay, G. G.; McNamee, S. G.; Ober, C. K.; Papatomas, K.; Wang, D. *J Polym Sci Part A: Polym Chem* 1992, 30, 1845.
5. Korner, H.; Shiota, A.; Bunning, J. J.; Ober, C. K. *Science* 1996, 272, 252.
6. Mallon, J. J.; Adams, P. A. *Mol Cryst Liq Cryst* 1992, 213, 173.
7. Adams, P. A.; Mallon, J. J. *Mol Cryst Liq Cryst* 1991, 208, 65.
8. Taylor, G. N.; Kahn, F. J.; Schonhorn, H. *Proc IEEE* 1973, 61, 823.
9. Porte, G. *J de Physique* 1976, 37, 1245.
10. Hiroshima, K. *Jpn J Appl Phys* 1982, 21, L761.
11. Lee, J. Y.; Jang, J. *J Polym Sci Part A: Polym Chem* 1998, 36, 911.
12. Hughes, J. D. H. *Compos Sci Technol* 1991, 41, 13.
13. Wu, Z.; Pittman, C. U., Jr.; Gardner, S. D. *Carbon* 1995, 33, 597.