

Synthesis and Characterization of Novel Epoxy-Modified Waterborne Polyurethanes and their Use in Carbon Fiber Sizing

Zhanqing Liu, Yanhong Tian, Sumei Kang, Xuejun Zhang

Key Laboratory of Carbon Fiber and Functional Polymers, Ministry of Education, Beijing University of Chemical Technology, Beijing 100029, China

Received 4 July 2011; accepted 24 October 2011

DOI 10.1002/app.36398

Published online in Wiley Online Library (wileyonlinelibrary.com).

ABSTRACT: Novel epoxy-modified waterborne polyurethanes (EPU) were synthesized from toluene 2,4-diisocyanate, poly(ethylene glycol) (PEG), dimethylolbutyric acid, and 2,3-epoxy-1-propanol (glycidol). The chemical structures of the EPU products were characterized by $^1\text{H-NMR}$ and Fourier transform infrared spectroscopy. The thermal properties of the EPUs were examined by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). TGA showed that the EPUs had good thermal stability, with an initial decomposition temperature higher than 250°C. DSC analysis showed that the glass-transition temperature of EPU1 was higher than that of EPU2. When the EPUs were heated above 150°C, the curing reaction took place. In this

study, the EPUs were used for carbon fiber sizing. The mechanical interfacial strength between the fibers and the matrix was evaluated by scanning electron microscopy (SEM) and interlaminar shear strength (ILSS) testing. The SEM images of the fracture sections of the composites proved that the interfacial adhesion between the fibers and the matrix improved after the EPU sizing treatment. The composites exhibited the highest value of ILSS after the EPU1 sizing treatment. The excellent properties of the EPUs confer it with potential applications in carbon fiber sizing. © 2012 Wiley Periodicals, Inc. *J Appl Polym Sci* 000: 000–000, 2012

Key words: composites; fibers; interfaces; polyurethanes

INTRODUCTION

Carbon fibers are widely used as reinforcements in composites, especially in advanced composites.^{1–4} Advanced polymer composites have been widely used in structural applications because of their high specific strength and stiffness, good corrosion resistance, and low thermal expansion relative to conventional metallic materials. However, composite materials also have certain drawbacks, such as poor interfacial adhesion between the reinforcement and the matrix resin, which is a critical factor in the properties of composite materials.^{5–7} To improve the wettability and adhesion of the carbon fibers to the matrices, much work has been done on the modification of the surface structure of the fiber to improve the interfacial bonding between the fiber and matrix;^{6,8} this has included surface treatment of the carbon fiber via various dry and wet oxidation methods,^{9–11} plasma treatment,⁵ electrochemical oxidation,¹² fiber sizing, and coating.^{13–15} Among these methods, fiber sizing is effective in improving the shear properties of carbon fiber/resin compo-

sites and is preferred because it allows the continuous processing of the carbon fibers. Because of safety, hygiene, and economy, the emulsion forms of sizing agents are widely used.^{8,16}

Various kinds of nonionic and ionic emulsifiers are used to disperse agents into aqueous emulsions. The emulsifying agent is a poor bonding agent and tends to inhibit the bonding of the dried emulsion finish to the carbon fibers. Furthermore, the presence of a substantial amount of emulsifying agent on the carbon fibers tends to present a problem with respect to water absorption of the eventual carbon fiber composite.⁴ Therefore, a feasible alternative to the emulsion forms of sizing agents is necessary.

In this study, two epoxy-modified waterborne polyurethanes (EPU) based on PEG were prepared, characterized, and chosen as sizing agents for carbon fiber. On the basis of the results, the EPUs could self-emulsify and self-crosslink.

EXPERIMENTAL

Materials

High-modulus carbon fibers (BHM3, 3K) with tensile strength and elastic modulus values of 3.2 and 420 GPa, respectively, were prepared. PEG (number-average molecular weights = 200 and 400) was

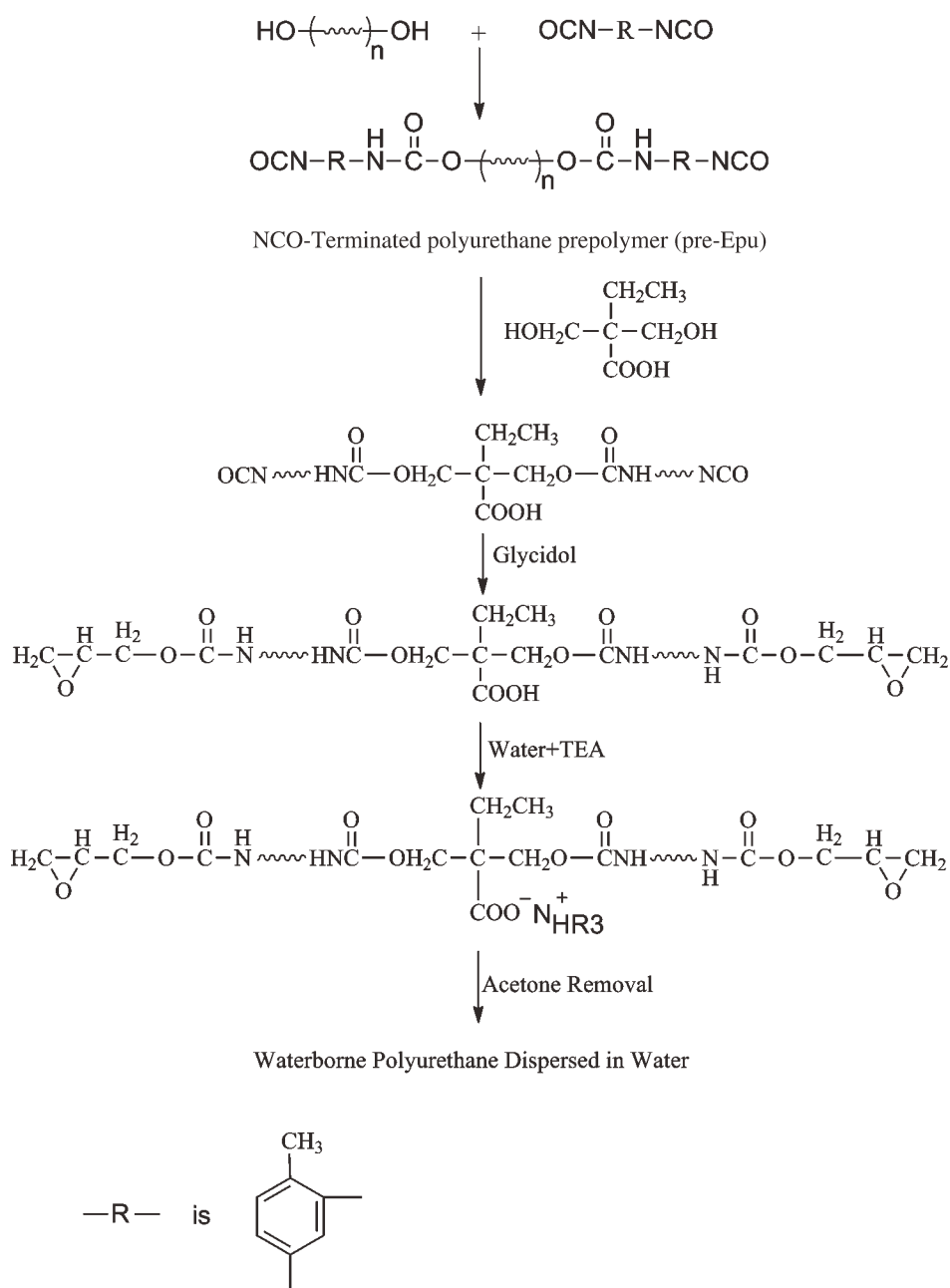
Correspondence to: Z. Liu (buct1985@126.com).

TABLE I
Reagent Amounts of All EPU Dispersions Prepared in this Study

Code	Polyol (number-average molecular weight)	Polyol/TDI/ glycidol molar ratio	DMBA (wt %)
EPU1	PEG200	4 : 2 : 3	5
EPU2	PEG400	6 : 3 : 4	5

dried for 2 h at 120°C *in vacuo* and were purchased from Beijing Yili Fine Chemicals Co., Ltd (China). Toluene 2,4-diisocyanate (TDI) from Bayer and 2,

3-epoxy-1-propanol (glycidol) from Aldrich were purified via vacuum distillation before use. Triethylamine, dibutyltin diacetate, and dimethylolbutyric acid (DMBA) were from Sinopharm Chemical Reagent Beijing Co., Ltd. Butanone (Beijing Yili Fine Chemicals Co.) was dried and passed through 4-Å molecular sieves before use. The water was deionized, whereas the other materials and solvents were used as received. The epoxy resin (F-48) and curing agent BF₃-monoethylamine complex (BF₃-400) were supplied by Sinopharm Chemical Reagent Beijing Co.



Scheme 1 Schematic diagram of the preparation of the EPU emulsions.

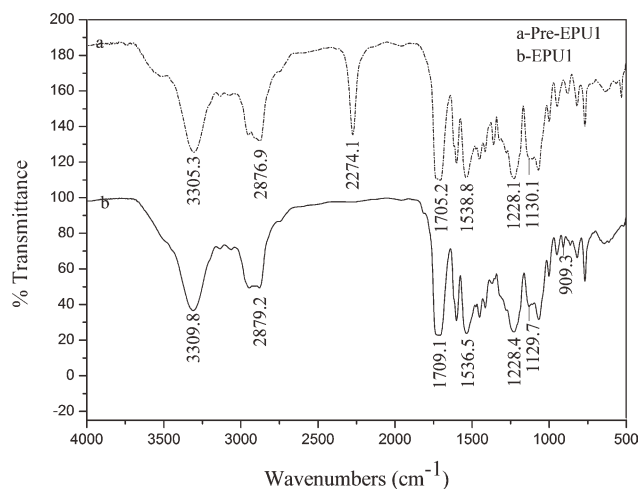


Figure 1 FTIR spectra of (a) EPU1 and (b) Pre-EPU1.

Preparation of the EPU dispersions

Two EPU dispersions were prepared in two major steps. The polymer was synthesized, and then, the dispersion process was carried out.

Synthesis of the EPUs

Appropriate amounts of TDI and dry butanone were placed into a four-necked reaction kettle equipped with a mechanical stirrer, an oil bath, a reflux condenser, a dropping funnel, and an N_2 inlet and outlet. The reaction mixture was heated to 50°C . A stoichiometric amount of PEG was added dropwise to the reactor at such a rate that the reaction temperature would not surpass 70°C . The temperature was maintained at the appropriate range, and the reaction was continued until the free isocyanate (NCO) content reached the theoretical value determined by dibutyl amine titration. Afterward, the solution of DMBA in *N*-methyl-2-pyrrolidone was added and stirred continuously for 2 h. The reaction kettle was then cooled to 40°C . The glycidol and the catalyst dibutyltin diacetate were then added dropwise and mixed. The temperature was increased slowly and maintained at about 70°C to allow the termination reaction to take place. The reaction was continued until the NCO peak at 2270 cm^{-1} disappeared totally in the Fourier transform infrared (FTIR) spectroscopy. The reagent amounts are summarized in Table I.

Dispersion process

The reaction mixture was cooled to 40°C . The triethylamine was added to neutralize the free carboxyl groups and then stirred for 0.5 h. The butanone was used to adjust the viscosity. At high-speed shear conditions, the deionized water was added gradually to the reaction mixture, and the mixture was stirred for

0.5 h. EPUs with a solid content of about 22% were obtained after the removal of methyl ethyl ketone by distillation. The synthetic route for the preparation of functional polyurethane with average two-end epoxy groups (EPUs) is outlined in Scheme 1.

Preparation of the emulsion sizing

The EPU emulsion with a solid content of about 22% was diluted with water to 2 wt % emulsions. The EPU was applied to carbon fiber sizing.

Sizing treatment of the carbon fibers

Carbon fibers tows were pulled off a spool at a speed of 0.3 m/min. The fibers were placed under tension by a nip roller and then passed through sizing at a 2 wt % concentration. The carbon fibers containing emulsion sizing were dried immediately in a hot gas oven.

Composite preparation

The carbon fibers were impregnated with an acetone solution of epoxy resin F-48 and 3 wt % BF3-400 to manufacture prepregs. The carbon/epoxy composites were manufactured by a compression-molding technique.^{5,14}

Measurements and apparatus

The FTIR spectra were recorded with a Nicolet 8700 instrument (Thermo Electron Corp., WI, USA) with KBr pellets. The background spectrum of the KBr pellet was subtracted from the sample spectrum.

$^1\text{H-NMR}$ spectra were recorded with a Bruker model AV600 MHz (Germany) with CDCl_3 as the solvent.

The colloidal stability of the waterborne dispersions is a vital characteristic, which determines their

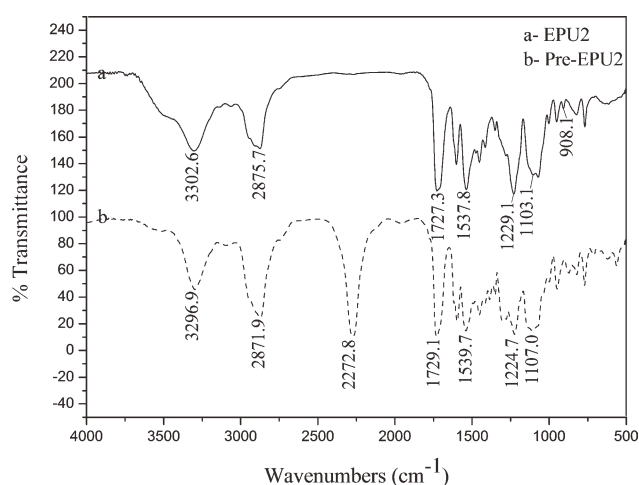


Figure 2 FTIR spectra of (a) EPU2 and (b) Pre-EPU2.

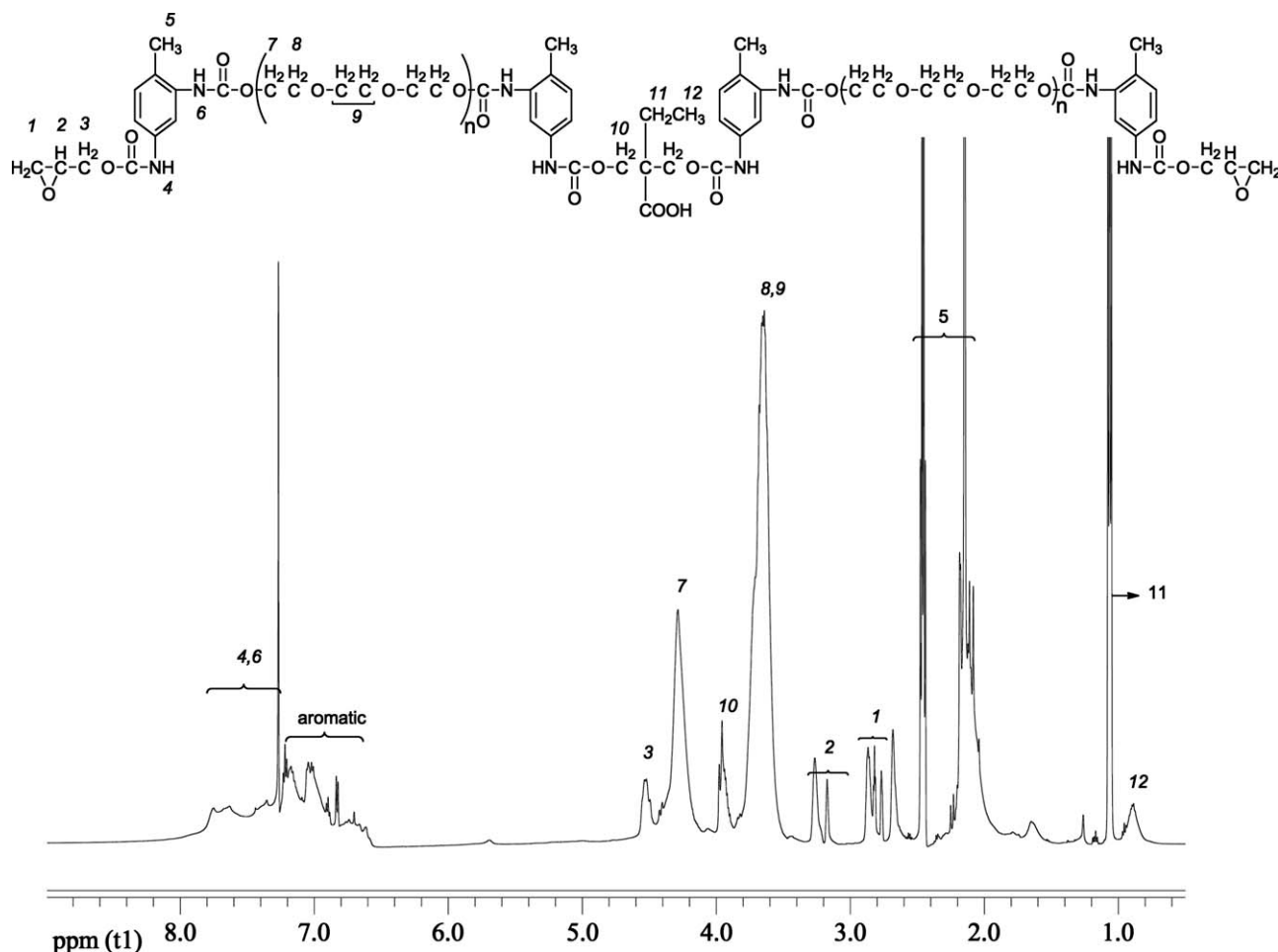


Figure 3 $^1\text{H-NMR}$ spectra of EPU1.

safe storage period. The measurements were carried out in a sealed container upon storage of the newly synthesized EPUs at room temperature (30–36°C). They were then observed for any kind of phase separation.¹⁷

Differential scanning calorimetry (DSC; Netzsch Instruments model DSC 204 F1, Germany) was used to examine the thermal properties of the EPUs at a heating rate of 10°C/min under a nitrogen purge of 20 mL/min. The temperature ranges of the DSC tests were from 20 to 180°C and from –40 to 100°C.

The thermogravimetric analysis (TGA) data were recorded on a Perkin Elmer TGS-2 (USA) under an N_2 atmosphere from room temperature up to 700°C at a heating rate of 10°C/min.

The interlaminar shear strength (ILSS) of the resulting composites was measured by the three-point short-beam shear test according to ASTM D 2344. The apparatus used was an Instron 5567 (USA). The specimen was 6 mm wide and 2 mm thick. Ten data points were collected and then averaged.

The surfaces of the sized and unsized carbon fibers and the fracture surfaces of the samples were examined with scanning electron microscopy (SEM; Zeiss

Supra 55, Germany). The scanned surfaces were coated with a thin layer of gold to eliminate the charging effects, particularly at high magnifications.

RESULTS AND DISCUSSION

Chemical characterization

The FTIR spectra of prepolymer of PU1 (pre-EPU1) and EPU1 and prepolymer of PU2 (pre-EPU2) and EPU2, are shown in Figures 1 and 2, respectively. The FTIR analysis was used to check the completion of the polymerization reaction. The disappearance of $-\text{NCO}$ at 2274.1 cm^{-1} and the appearance of $-\text{N-H}$ at $3000\text{--}3400\text{ cm}^{-1}$ implied that the reaction was completed and that the predesigned polyurethane was formed. The IR spectra also provided all the information relating to the primary structure of the final polymer. An absorption band was observed for N-H stretching at $3291\text{--}3310\text{ cm}^{-1}$, aliphatic C-H stretching at $2795\text{--}2938\text{ cm}^{-1}$, carbonyl (C=O) stretching at $1705\text{--}1729\text{ cm}^{-1}$, N-H bending vibration at $1536\text{--}1539\text{ cm}^{-1}$, and C-O-C stretching at $1000\text{--}1150\text{ cm}^{-1}$. The sharp absorption peaks of the $-\text{CH}_2-$

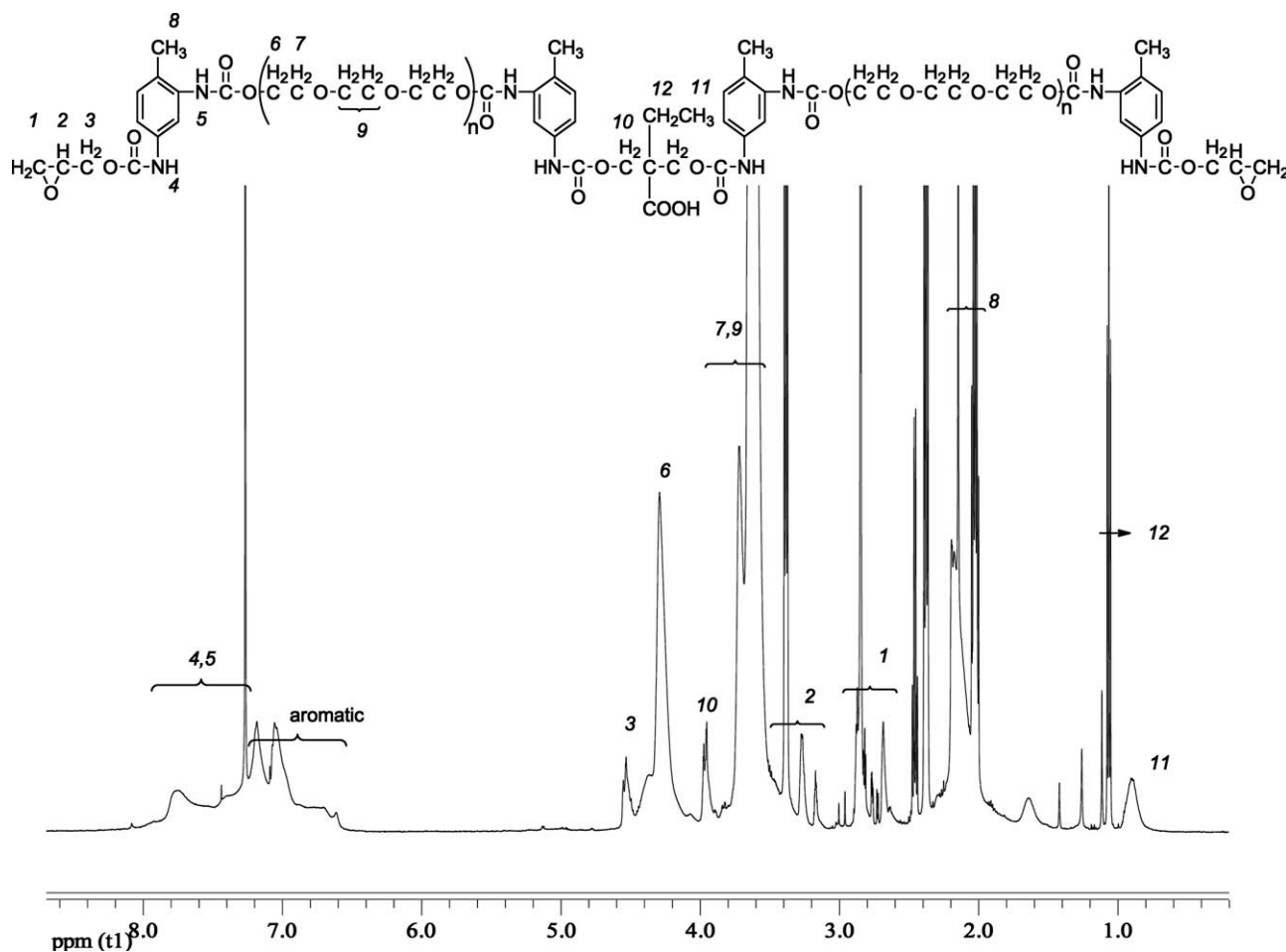


Figure 4 $^1\text{H-NMR}$ spectra of EPU2.

groups were around $2850\text{--}2930\text{ cm}^{-1}$, and the absorption peaks became relatively stronger with increasing molecular weight of PEG. The peak of the epoxy group appeared at $908.1\text{--}909.3\text{ cm}^{-1}$. These vibrations confirmed the formation of EPU1 and EPU2. Furthermore, the absorption peaks of the $\text{C}=\text{O}$ group in EPU1 shifted to lower frequencies because the hydrogen bonding in the $\text{C}=\text{O}$ group of the ether-based EPU1 occurred between the soft and hard segments. Therefore, hydrogen bonding in EPU1 was stronger than that in EPU2.

The $^1\text{H-NMR}$ spectra of the EPUs were also in accordance with the proposed structures. The $^1\text{H-NMR}$ spectra of EPU1 and EPU2 are shown in Figures 3 and 4, respectively. The chemical shift signals were assigned to their corresponding proton atoms. Peaks due to the epoxy groups were observed at about $2.61\text{--}3.25\text{ ppm}$. The signal of the aromatic protons was centered at 7.10 ppm . The urethane NH groups were present at about 7.2 ppm , and the methylene groups attached to the epoxy and urethane oxygen groups were observed at about $4.3\text{--}4.5\text{ ppm}$.

The $^1\text{H-NMR}$ and FTIR analyses confirmed the formation of the EPUs.

Colloidal stability

The colloidal stability measurements (Table II) revealed that the EPU2 was stable for more than 6 months. The EPU dispersion with ionic and nonionic emulsifiers built into the same polymer produced stable dispersions. The ionomer dispersion could be stabilized because of the formation of electrical double layers. At the interface between the ionomer particle and water, an electrical double layer was formed by the dissociation of the salt groups. The ionic constituents of the salt group chemically bound to the polyurethane remained fixed to the particle surface, whereas their counterions migrated into the water phase as far as the attractive forces of the oppositely charged particle surface allowed. This phenomenon formed a layer of decreasing electrical

TABLE II
Colloidal Stability of the EPUs

Code	pH	Colloidal stability	Solids (wt %)
EPU1	8.70	<6 months	22
EPU2	8.41	>6 months	22

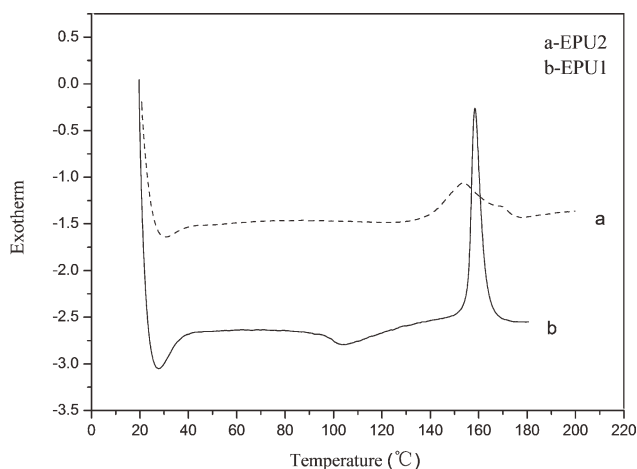


Figure 5 DSC curves of the EPU.

charge. The interference of the electrical double layers of the different particles resulted in particle repulsion, which in turn, was responsible for the overall stabilization of the dispersion.

Additionally, the hydration of the polyoxyethylene chains played an important role in the stabilization of the dispersion. A particle approaching close enough for coagulation required the desorption of water molecules and, thereby, resulted in considerable short-range repulsions.¹⁸

DSC analysis

The curing reactions were studied by DSC. Figure 5 shows the DSC thermograms of EPU1 and EPU2. The DSC curve of EPU2 showed a broad and flat exotherm between 139 and 163°C, whereas the DSC curve of EPU1 showed a sharp exotherm between 156 and 163°C. The appearance of the two exothermic peaks between 139 and 163°C was caused by

the self-crosslinked reaction of the EPU, which occurred at a specific temperature.

A crosslinking reaction between the carboxylic acid and epoxy groups was suggested by the IR spectroscopy data. The EPU and cured EPU were characterized by FTIR spectroscopic analysis. Figures 6(b) and 7(d) show the representative spectra of the two peaks in the carbonyl region: one at 1710 cm^{-1} and the other at 1735 cm^{-1} . The former peak was attributed to the carboxylic acid group, and the latter was attributed to the urethane carbonyl (C=O) group. From Figures 6(a) and 7(c), the infrared spectra of the 1732.8 and 1728.0- cm^{-1} ester carbonyl peak shrunk, and the 1709.1 and 1713.9- cm^{-1} carboxylic absorption peak disappeared. The absence of free epoxy group peaks at 909 cm^{-1} confirmed the complete conversion of the epoxy groups. When the EPU were heated at temperatures above 150°C, the curing reaction of a single-pack EPU system took place. This self-curing involved the ring-opening reaction of the epoxy group with the carboxylic group of the EPU and resulted in a crosslinked polymeric network formation. Accordingly, the self-crosslinking reaction of the copolymers of EPU is described in Scheme 2.

Glass temperature after curing

The fiber sized with the rubbery coating material was softer and more elastic than that sized with the glassy material. Generally, carbon fiber is used at room temperature during composite processing or textile processing into a woven or braided form. Therefore, a lower glass-transition temperature (T_g) of the coating material is more desirable.

Figure 8 shows the DSC curves of the crosslinked EPU1 and EPU2. The T_g values obtained from the DSC measurement are listed in Table III. A large

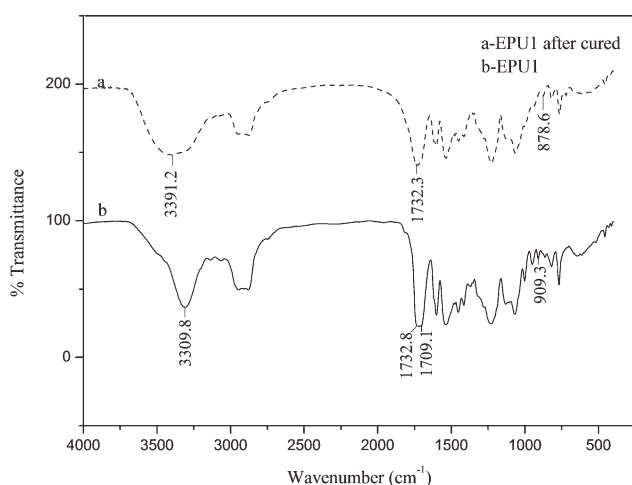


Figure 6 FTIR spectra of (a) EPU1 after curing and (b) EPU1.

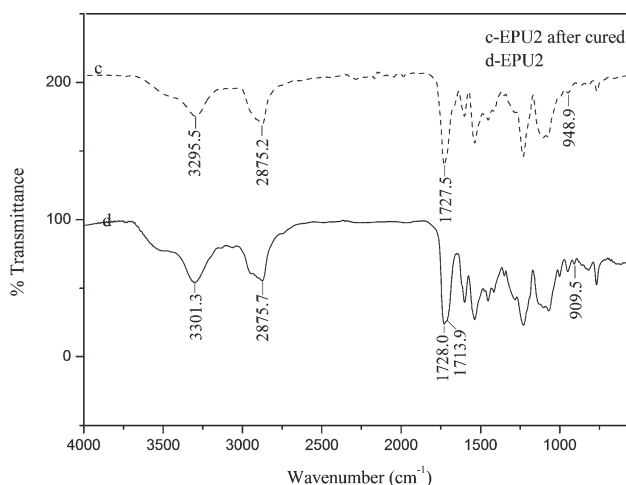
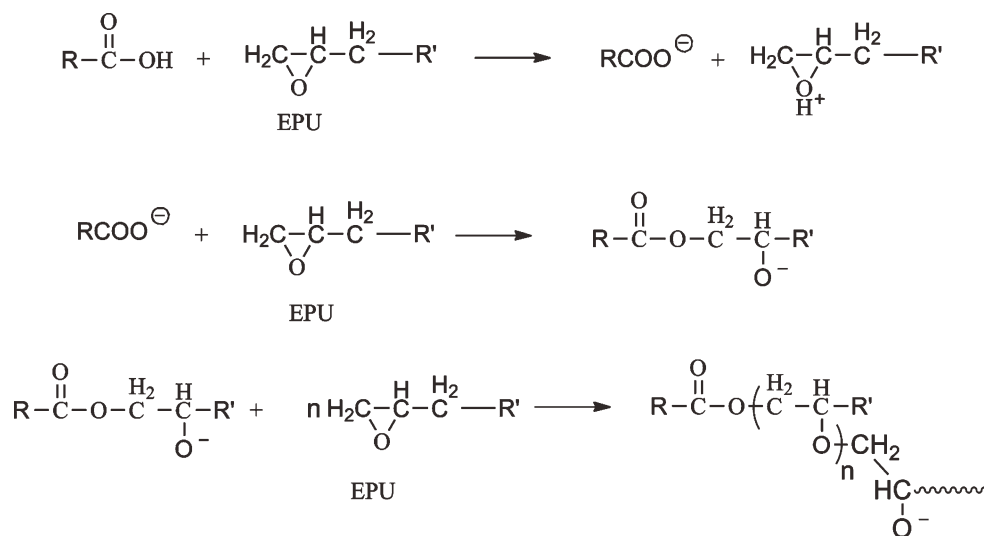


Figure 7 FTIR spectra of (c) EPU2 after curing and (d) EPU2.



Scheme 2 Crosslinking reaction of the EPUs.

variation between the T_g 's of the two EPU samples was found; this indicated that the carbon fiber sized with EPU2 had a softer handle and is suitable for applications at room temperature. EPU1 had a lower T_g compared with EPU2 because of the lesser number of alkylene groups on the shorter chain of the EPU1 in the polyester polyol backbone. The alkylene groups increased the crosslinking density and, thereby, offered more resistance to the rotatable bonds. This finding was in good agreement with the results from TGA.

TGA

The thermal stability of the EPUs was also studied. The epoxy sizing decomposed at about 250°C, as reported in the literature.¹⁹ The thermal resistances of the samples were analyzed by TGA in a nitrogen atmosphere. The TGA curves of the various EPUs are shown in Figure 9, and the thermal decomposi-

tion data are given as the initial decomposition temperature ($^{\circ}T_d$) and maximum rate decomposition temperature ($^{\text{max}}T_d$) in Table III. The thermograms revealed that for both EPUs, there was hardly any weight loss before 250°C. The TGA curves showed two distinct stages of degradation. The first stage of decomposition was due to the degradation of hard segments, started above 250°C, and ended at about 380–400°C. The second stage was due to the degradation of the soft segment and ended above 480°C with a less carbonaceous mass.

EPU2 appeared to be more stable than EPU1, showing higher onset and maximum rate decomposition temperatures. This may have been due to the presence of a lesser number of alkylene moieties on the shorter chain of the polyester polyol backbone in EPU1. This phenomenon increased the crosslinking density and, thereby, offered more resistance to rotatable bonds. This trend of degradation showed that a linear relationship existed between the thermal stability of the EPUs and the molecular weight of PEG. Thus, the higher stability of EPU2 was attributed to the higher molecular weight of its polyester backbone (PEG400), whereas the lower stability of EPU1 was ascribed to the lower molecular weight of PEG200. In synthesizing polyurethane dispersions, the same types of TDI and hydrophilic monomer DMBA were used, and the same NCO index

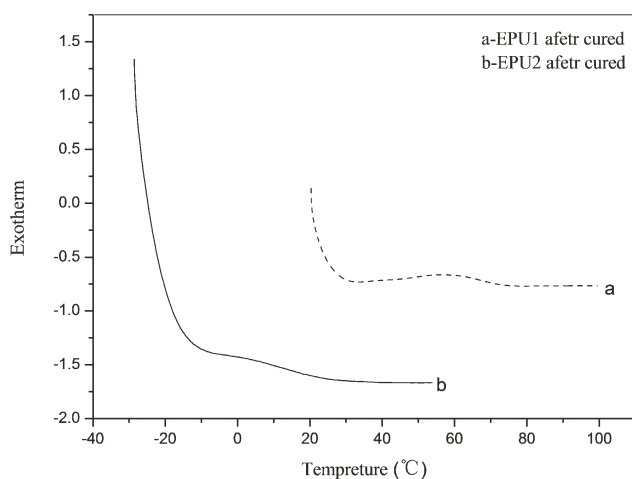


Figure 8 DSC curves of the crosslinked EPU1 and EPU2.

TABLE III
Characteristics of the EPU Dispersions

EPU	T_g from DSC (°C)	TGA weight loss temperature	
		$^{\circ}T_d$ (°C)	$^{\text{max}}T_d$ (°C)
EPU1	9.3	254.0	274.3
EPU2	60.3	305.5	340.8

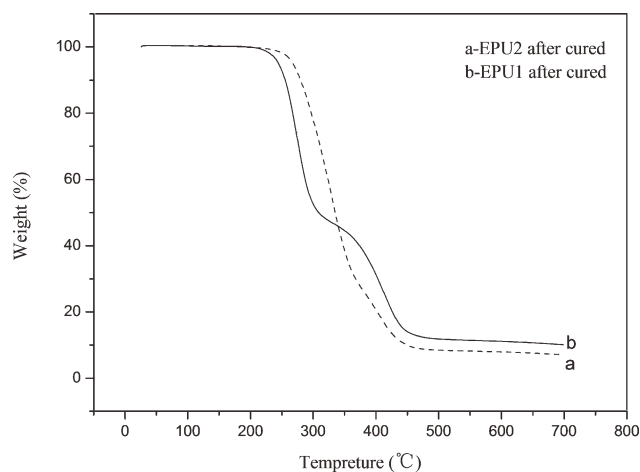


Figure 9 TGA curves of the different crosslinked EPU dispersions.

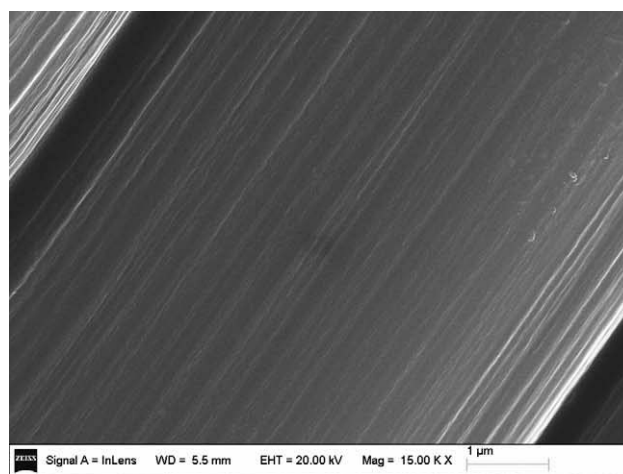
(NCO/OH) was maintained. Therefore, the difference in the thermograms could be attributed only to the difference in polyol structure resulting from the variation in the number of alkylene groups in the main polyester backbone of the EPUs. Thus, the molecular weights of PEG had a pronounced effect on the degradation behavior of the EPUs.

SEM

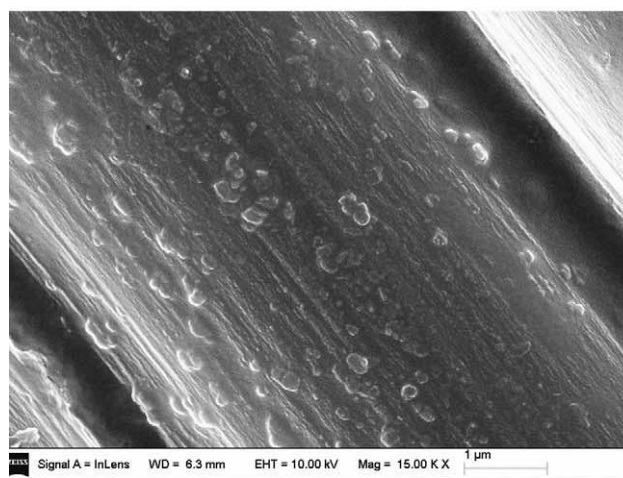
The SEM images of the untreated and sized carbon fibers are shown in Figure 10. Remarkable differences in the micrographs could be observed between the untreated and sized carbon fibers. The surface of the untreated carbon fiber was relatively smooth, and a few narrow parallel grooves or channels were distributed along the longitudinal direction of the fiber. After sizing, some concave and convex hills on the fiber surface were observed; this showed a significant increase in roughness compared with the unsized fiber. This change in the surface topography may have resulted from the self-crosslinking of the carbon fiber sizing. The increase in the surface roughness of the fibers could have led to an intimate interfacial adhesion between the fibers and the matrix by mechanical interlocking.

The fracture section topographies of the composites are shown in Figure 11. As shown in Figure 11(a), some carbon fibers were pulling out, and holes were observed on the fracture section of the unsized composites. These observations explained the poor interfacial bonding of the untreated carbon fibers with the epoxy matrix. That is, fiber debonding happened at the interfaces between the fibers and the matrix. However, as shown in Figure 11(b,c), the sizing treatment clearly improved the interfacial bonding of the composites. Each carbon fiber was embedded in the epoxy resin, and no fiber pullout was

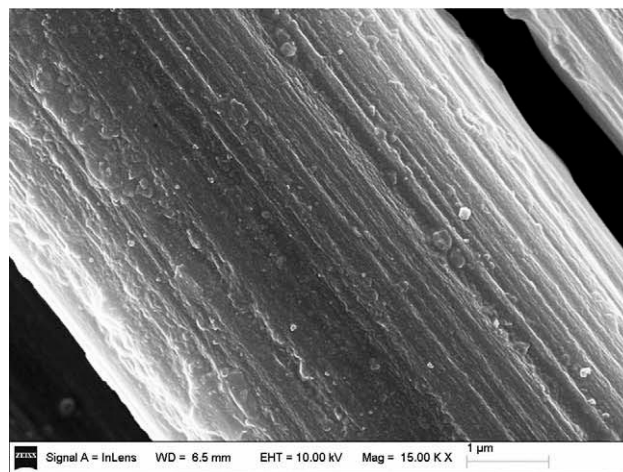
observed; this meant that the adhesion between the carbon fiber and the resin was very strong. Therefore, the sizing treatment was an effective method for improving the interfacial adhesion of the carbon fiber/epoxy composites.



(a)

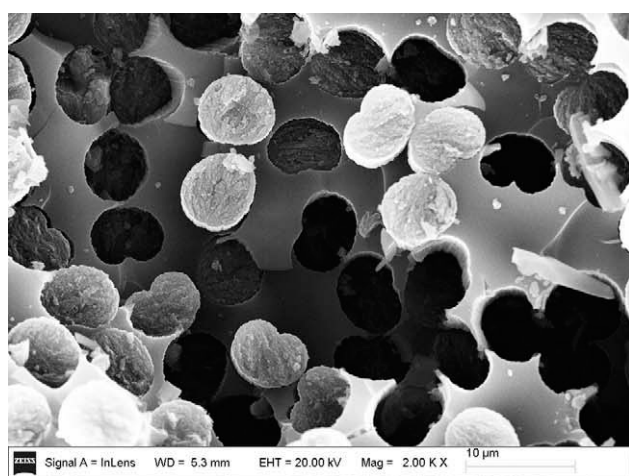


(b)

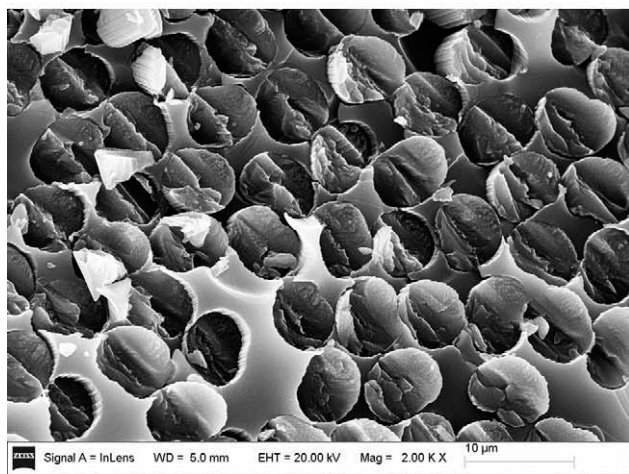


(c)

Figure 10 SEM micrographs of the carbon fiber surface: (a) untreated, (b) EPU1-sized, and (c) EPU2-sized.



(a)



(b)



(c)

Figure 11 SEM micrographs of the fractured surface of the composites: (a) untreated, (b) EPU1-sized, and (c) EPU2-sized.

ILSS

Figure 12 shows the ILSS test results of the composites. The figure indicates that the interfacial adhesion strengths between the fibers and the matrix

increased after the sizing treatment. After the EPU1 sizing treatment, the ILSS of the composites reached a maximum of 75.5 MPa, which was 17% higher than that of the untreated fibers. These results were in fairly good agreement with the SEM images of the fractured composite surface, shown in Figure 11.

For the fiber surface with EPU sizing, the surface characteristics of the carbon fibers changed via the increase in surface area and the addition of many active functional groups. That is, the surface roughness and the wettability of the carbon fibers by the matrix were enhanced further. In addition, the cross-linking site acted as a stress concentrator at the interfaces to improve the mechanical interfacial strength; this helped to hold back excessive stress from spreading in the flaw and changing the crack propagation paths.

CONCLUSIONS

1. Self-curing EPUs with expected chemical structures were prepared. When the EPUs were heated above 150°C, the curing reaction of a single-pack EPU system took place. The thermal storage stability and the flexibility properties of EPU2 were better compared with those of EPU1. TGA showed that the onset temperatures of thermal degradation of the EPUs were higher than 250°C; this indicated that the thermal stability of the EPU sizing was higher than that of the epoxy sizing. The storage stability test at room temperature showed that EPU2 was stable for more than 6 months. The thermal analysis indicated that the T_g values from the EPU sizing were about 60.3 and 9.3°C for EPU1 and EPU2, respectively. These findings indicated that the carbon fiber sized with EPU2

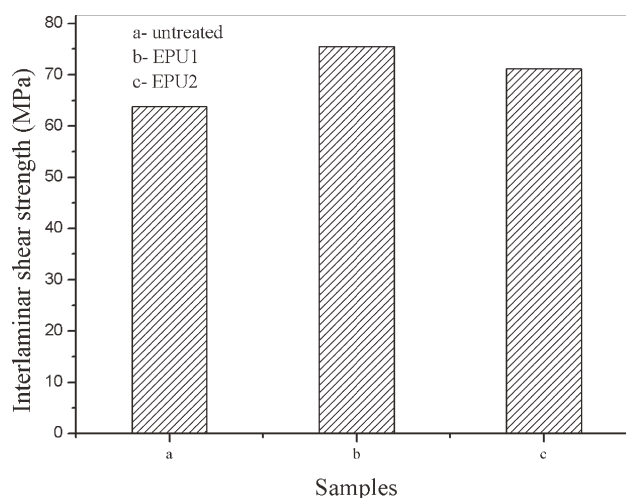


Figure 12 ILSS of the composites.

had a softer handle and is suitable for applications at room temperature.

2. The ILSS of the composites increased after the sizing treatment. After the EPU1 sizing treatment, the ILSS of the composites reached a maximum of 75.5 MPa; this value was 17% higher than that of the untreated fibers.
3. From the SEM analysis, the EPU sizing changed the surface roughness values on a microscopic scale. The interfacial bonding of the composites clearly improved.
4. The EPU2 sizing agent was better than the EPU1 sizing agent for use in carbon fibers.

References

1. Liu, R. M.; Liang, D. K. *Mater Des* 2010, 31, 994.
2. Guo, H.; Huang, Y. D.; Liu, L.; Shi, X. H. *Mater Des* 2010, 31, 1186.
3. Rezaei, F.; Yunus, R.; Ibrahim, N. A. *Mater Des* 2009, 30, 260.
4. Bai, Y. P.; Wang, Z.; Feng, L. Q. *Mater Des* 2010, 31, 1613.
5. Ma, K. M.; Chen, P.; Wang, B. C.; Cui, G. L.; Xu, X. M. *J Appl Polym Sci* 2010, 3, 1606.
6. Xu, Z. W.; Wu, X. Q.; Sun, Y.; Jiao, Y. N.; Li, J. L.; Chen, L.; Lu, L. S. *J Appl Polym Sci* 2007, 108, 1887.
7. Lindsay, B.; Abel, M. L.; Watts, J. F. *Carbon* 2007, 45, 2433.
8. Tang, L. G.; Kardos, J. L. *Polym Compos* 1997, 18, 100.
9. Varelidis, P. C.; Skourlis, T. P.; Bletsos, J. V.; McCullough, R. L.; Papaspyrides, C. D. *J Appl Polym Sci* 1995, 55, 1101.
10. Fukunaga, A.; Ueda, S. *Compos Sci Technol* 2000, 60, 249.
11. Sanchez-Adsuar, M. S.; Linares-Solano, A.; Cazorla-Amoros, D. *J Appl Polym Sci* 2003, 90, 2676.
12. Basova, Y. V.; Hatori, H.; Yamada, Y.; Miyashita, K. *Electrochem Commun* 1999, 1, 540.
13. Hung, K. B.; Li, J.; Fan, Q.; Chen, Z. H. *Compos A* 2008, 39, 1133.
14. Yang, Y.; Lu, C. X.; Su, X. L.; Wu, G. P.; Wang, X. K. *J Mater Sci* 2007, 42, 6347.
15. Tian, Y. H.; Liu, Z. Q.; Kang, S. M.; Zhang, X. J. *Adv Mater Res* 2011, 217–218, 728.
16. Hou, Y. P.; Sun, T. Q.; Wang, H. J. *J Appl Polym Sci* 2011, 121, 1059.
17. Athawale, V. D.; Kulkarni, M. A. *J Appl Polym Sci* 2010, 117, 572.
18. Satguru, R.; McMahon, J.; Padget, J. C.; Coogan, R. G. *J Coat Technol* 1994, 66, 45.
19. Chung, D. D. L. *Carbon Fiber Composites*; Butterworth-Heinemann: Newton, MA, 1994.