The Preparation of Emulsion Type Sizing Agent for Carbon Fiber and the Properties of Carbon Fiber/Vinyl Ester Resin Composites

Jianye Liu, Heyi Ge, Juan Chen, Dongzhi Wang, Huashi Liu

School of Material Science and Engineering, University of Jinan, Jinan 250022, China

Received 4 August 2010; accepted 17 June 2011 DOI 10.1002/app.35126 Published online 10 October 2011 in Wiley Online Library (wileyonlinelibrary.com).

ABSTRACT: Vinyl ester resin emulsion type sizing agent (HMSA-1) was synthesized by phase inversion emulsification method. Centrifugal sedimentation analysis, particle size analysis, Fourier transforms infrared spectroscopy (FTIR), and gel permeation chromatography were used to characterize HMSA-1 and Japanese commercial sizing agents (JSA-1 and JSA-2). Meanwhile, abrasion resistance, fluffs and breakage, stiffness, scanning electron microscope (SEM) were used to analyze the workability in later process of carbon fiber and surface morphology. The results showed that HMSA-1 could significantly improve han-

dling characteristics of carbon fiber. SEM micrographs demonstrated that the sized carbon fiber had smooth surface. HMSA-1 had better compatibility with vinyl ester resin. The interlaminar shear strength (ILSS) of HMSA-1 sized carbon fiber/vinyl ester resin composite reached the maximum value of 45.96 MPa. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 124: 864–872, 2012

Key words: carbon fiber; sizing agent; workability in later process; ILSS

INTRODUCTION

Due to the superior strength and fatigue resistance of carbon fibers, carbon fiber-reinforced polymer matrix composites have been widely used in motor cars, aerospace, sports goods, etc.¹ As carbon fibers are basically brittle, there tend to arise many problems of filament breakages and fluffs due to mechanical friction against guides and rollers during the manufacturing process.^{2–4} Therefore, carbon fibers are generally sized or coated with a thin polymer layer.⁵ Good sizing agents can significantly improve the subsequent processing of carbon fibers and improve the interfacial properties between carbon fibers and matrices.^{6–8}

The adhesive property of the carbon fiber to the matrix resin mainly depends on the sizing agent used for carbon fibers. According to "similar dissolve mutually theory," the main components of sizing agents are normally similar to the matrix resins. Thus, different matrix resins usually require compatible sizing agents. Epoxy resin is widely used as the

Contract grant sponsor: Fund of the Science and Technology Program of the Higher Education Institutions of Shandong Province; contract grant number: J09LD06. matrix resin in fiber-reinforced composites. Thus, previous work was mainly focused on epoxy emulsion or aqueous epoxy type sizing agents.^{9–15} To meet the wide requirements of composites, the application of vinyl ester resin matrix has been gradually increased. The development of sizing agents tends to be diversified.

Makoto Saito¹⁶ invented a solution or a self-emulsifying type sizing agent for carbon fiber which mainly comprised an unsaturated urethane compound produced by a reaction of unsaturated alcohol and isocyanate. This sizing agent could significantly improve ILSS of fiber-reinforced vinyl ester and unsaturated polyester resin matrix composites. However, the polymerization process of the unsaturated urethane compound was complicated and difficult to control. The sizing agent for carbon fiber reported by Hiroshi Minami¹⁷ could not only improve the property of handling characteristics of carbon fiber but also combine with epoxy and unsaturated polyester resin. The sizing agent had three constituents: an epoxy compound, a copolymer having within its molecule one oxyalkylene derivative of a polycyclic phenol segment (B1), and one or two monoester or polyester segments (B2) connected through an ester linkage, and oxyalkylene derivative of substituted phenol. Desired characteristics could be obtained by selecting the molecular weights of B1 and B2, their ratio, structures, and compositions to adapt to epoxy and unsaturated polyester resin. However, it was difficult to synthesize B1 and B2 and the carcinogenic

Correspondence to: H. Ge (mse_gehy@ujn.edu.cn).

Contract grant sponsor: Scientific Research Fund of University of Jinan; contract grant number: XKY0901.

Journal of Applied Polymer Science, Vol. 124, 864–872 (2012) © 2011 Wiley Periodicals, Inc.



Figure 1 The chemical structures of resin: (a) V-3200 and (b) ETBN.

intermediate products might cause security and health hazards. Hiroshi Minami et al.¹⁸ synthesized a bisphenol-polyalkylene glycol ether ester copolymer from polyoxyalkylene bisphenol ether, maleic acid anhydride or phthalic acid anhydride, and alkylene oxide. The emulsion type sizing agent prepared by this copolymer, lubricant, and emulsifier could increase the ILSS of epoxy and vinyl resin matrix composites. But the water resistance of composites would be influenced due to long polyoxyethylene polyoxypropylene block segments and many hydrophilic groups of the copolymer such as carboxyl.

Normally, vinyl ester resin was rigid because of its rigid-benzene structure. Carbon fiber sized with pure vinyl ester resin was stiff and lacked flexibility, which would lead to poor handling characteristics of carbon fiber. In this article, the epoxy terminated butadiene-acrylonitrile oligomer (ETBN) was used to ameliorate rigidity and stiffness of vinyl ester resin. A stable emulsion type sizing agent was prepared by adding surfactant, diluent, penetrant, and other additives. The preparation of the sizing agent was simple and easy to control. Additionally, the properties of the sizing agent and carbon fiber/vinyl ester resin composite were compared to Japanese commercial sizing agents JSA-1 and JSA-2 by centrifugal sedimentation analysis, particle size analysis, Fourier transforms infrared spectroscopy, and gel permeation chromatography. Meanwhile, abrasion resistance, fluffs and breakage, stiffness, and scanning electron microscope (SEM) were used to analyze the workability in later process and surface morphology of carbon fiber. Interfacial adhesion property was evaluated by ILSS measurement.

EXPERIMENTAL

Materials

Vinyl ester resin V-3200 was supplied by Yisheng Resin Factory, China (viscosity of 0.3–0.5 Pa s at 25 °C, styrene content of 30%, molecular weight about 400). ETBN was supplied by Beijing devote chemical company (molecular weight between 3000

and 4000, viscosity of 500 Pa s at 25°C, epoxy value of 0.0625). The chemical structures of V-3200 and ETBN are shown in Figure 1. Acetone and styrene were bought from Tianjin Guangcheng Chemical Reagent Corp., China. T700 SC carbon fibers were obtained from Toray Company, Japan (3k, diameter about 7–8 μ m, a tensile strength of 4.9 GPa, modulus of 230 GPa, and an elongation of 2.1%). Nonylphenol ethoxylate phosphate (NP-10P) was purchased from Shuangyi Fine Chemical Factory, China. Ammonia was supplied by Sanhe Chemical Reagent Corp., China (NH₃ content of 25–28%).

Polyoxyethylene nonylphenol phosphoric ammonium (NP-10A) was homemade using chemical precursor NP-10P. A calculated amount of NP-10P was placed in a flask and stirred at the rate of 150–200 r/ min at 50°C. Next, ammonia was gradually added with a separatory funnel, and pH value was measured. When pH value was 8, adding ammonia was stopped and stirring was continued for an hour. Then NP-10A was obtained. Polyoxyethylene castor oil (EL-40) was obtained from Venture Grease Chemical Plant, China. The penetrant selected from Jinan Chuanglong Chemical Company, China, was 2-octanol polyoxyethylene ether (JFC-2). Japanese commercial sizing agents JSA-1 and JSA-2 were produced by Takemoto Oil and Fat Co. Ltd. and Matsumoto Yushi Seiyaku Co. Ltd.

Preparation of emulsion type sizing agents

The sizing agents were prepared by phase inversion emulsification method.¹⁹ The formulas of the sizing agents were listed in Table I. First, a calculated amount of NP-10A (3.3–10.0 g), EL-40 (0–4.0 g), and JFC-2 (0–3.0 g) were mixed by constant stirring until the mixture (M1) was homogeneously blended. A certain percentage of ETBN (40–100 g), V-3200 (0–60 g), and diluent (0–150 g) were added into a flask and mixed uniformly, then M2 was obtained. Next, M1 to M2 were added, the mixture was heated and dispersed at 60° C under a constant stirring rate. Thereafter, a quantity of deionized water was dripped. The system changed phase (from water-in-

The Formulas of Sizing Agents										
Material/sizing	V-3200 (g)	ETBN (g)	NP-10A (g)	EL-40 (g)	Diluent (g)		IFC-2	Stirring rate		
agents					Styrene	Acetone	(g)	(r/min)		
HMSA-1	60	40	6.6	3.4	50	0	2.0	10,000		
HMSA-2	50	50	4.0	4.0	0	50	0	10,000		
HMSA-3	40	60	3.3	1.7	0	0	3.0	10,000		
HMSA-4	0	100	10.0	0	150	0	0	8000		
HMSA-5	60	40	6.6	3.4	50	0	2.0	6000		

TABLE I

oil to oil-in-water) with the increasing of water. After passing the phase inversion point, the amount of water dripped in was increased. An emulsion containing about 20% by weight of the solid component was obtained.

Sizing treatment of carbon fiber

The commercial sized carbon fiber T700 SC was refluxed in boiling acetone for 36 h using a Soxhlet apparatus, then washed repeatedly with deionized water and dried under vacuum at 100°C for 12 h, so as to remove the sizing agent coated in carbon fiber surface.

Sizing agents were diluted with deionized water to obtain an emulsion with 0.5% solid component. The dipping method was used in the sizing process. The carbon fibers were immersed in the emulsion for 30 s by use of a dip tank in conjunction with automatic processing equipment for continuous running of the carbon fibers through the dip tank. Then the carbon fiber was dried at 100°C for 20 min.

Characterization

- (1). Centrifugal stability of the sizing agents was tested by 800B type desk centrifuge (Shanghai Anting Scientific Instrument Factory, China). The sizing agent was diluted to 4% by weight of the solid component; 10 mL sizing agent was placed into a centrifuge tube and centrifuged 20 min at a rotation speed of 3500 r/ min. Next, the sediment was dried and measured. The SEDIMENT weight of every sizing agent was measured five times, and the average value was recorded.
- (2). Particle size and distribution of sizing agents were analyzed by LS-13320 laser particle size analyzer (Beckman Coulter, United States).
- (3). The chemical structure and composition of sizing agents were analyzed by the Nicolet 380 infrared spectrometer (Thermo Electron Corp., United States).
- (4). Molecular weights of the sizing agents were measured by Waters gel permeation chromatography analyzer (Waters Corp., United States).

- (5). Fluffs and breakage: Fluffs and breakage was measured according to Japanese patent.²⁰ Fiber bundle passed through two polyurethane sponges (40 \times 10 \times 5 mm) at rate of 1 m/min, load of sponge was 200 g, and after 10 min fluffs attached to sponges was calculated. Five carbon fiber bundles were measured and the average fluffs and breakage weight were recorded.
- (6). Abrasion resistance: Abrasion resistance equipment was shown in Figure 2. Diameters of guide rollers and stainless rod were 10 and 15 mm, respectively. Frictional angle of a stainless rod and two guide rollers was 120°, with a load of 50 g. Carbon fiber bundle reciprocatingly abrased with a stainless steel roll at a rate of 120 times/min until all fiber fractured. Five carbon fiber bundles were measured and the average abrasion resistance numbers were recorded.
- Unwinding carbon fiber (7). Stiffness: was obtained according to ISO standard.²¹ The carbon fiber stiffness tester was shown in Figure 3. The stainless steel hook (radius of 10 mm) was made of a stick (radius of 5 mm). There was a sliding scale at standard distance of 60 mm below the suspension point. First, the carbon fiber bundle (500 mm) was suspended. Its center was hung on the stainless steel hook. The distance of the two hanging ends of carbon fiber was measured by the



Figure 2 Diagram of abrasion resistance equipment: (1) guide rollers, (2) stainless rod, (3) fiber bundle, and (4) reciprocating apparatus.



Figure 3 Diagram of carbon fiber stiffness tester: (a) front view, (b) left view; (1) stainless steel hook, (2) carbon fiber, and (3) sliding scale.

sliding scale after 30 s. Five carbon fiber bundles were measured and the average stiffness value was recorded.

- (8). The surface morphology of the sized and unsized carbon fibers was observed by HITA-CHIS-2500 SEM (Hitachi Company, Japan).
- (9). ILSS: Vacuum bag molding technology was used in the preparation of carbon fiber/vinyl ester resin composites. After the lay-up was fabricated on a mold from precut plies of unidirectional carbon fibers, the release bag and resin flow were placed over the lay-up. Then the vacuum bagging film was placed over the resin flow and sealed at the mold flange. The vinyl ester resin/methyl ethyl ketone peroxide/cobaltous naphthenate mixture was mixed uniformly with a weight ratio of 100 : 2 : 2. Then a vacuum was drawn on the bag formed by the film and resin was infused. The composite was cured at room temperature for 3 h and postcured at 100°C for 1 h.

ILSS of carbon fiber/vinyl ester resin composites was measured by the three-point short-beam shear test according to ASTM D-2344 at WDW-30 type universal testing machine (Shanghai Shenli Testing Machine Company, China). Specimens were unidirectional carbon fiber/vinyl ester resin composites laminates with 60% volume content of carbon fibers with dimensions of $20 \times 6 \times 2$ mm and a span-to-depth ratio of 6/1; the crosshead speed was 2 mm/min. Five specimens were measured and the average ILSS was recorded.

The fracture surfaces of the ILSS samples were examined by HITACHIS-2500 SEM (Hitachi Company, Japan).

RESULTS AND DISCUSSION

Centrifugal stability of sizing agents

Table II shows the centrifugal stability of sizing agents. Table II represents JSA-1, which shows optimal centrifugal stability. HMSA-1 comes second. Their deposition weight is 0.0302 and 0.0355 g, respectively. A stable emulsion is prepared by means of dispersing the resin in the form of particles or droplets into the dispersion medium based on water as a continuous phase through high stirring rate.²² Under low stirring rate, the system is not prone to the change phase, which leads to poor stability of the emulsion. Generally, the higher the stirring rate, the more uniform the system, the higher the stability of the emulsion.²³ Styrene was added to decrease the viscosity of ETBN and make the stirring process easy to handle for HMSA-1. The ratio of emulsifier and resin was by weight of 10%. The emulsifier was enough to form a dense interfacial film at the interface of two phases (water and oil), and interfacial tension was decreased significantly. On the other hand, adsorption and friction made the dispersed phase droplets charged, an electric double layer structure was formed on both sides of the interface by charged droplets, which enhanced the stability of emulsion.²⁴ Carbon fiber is hydrophobic and there exists air in fiber gaps, which makes it difficult for sizing. Therefore penetrant JFC-2 was added to improve the wettability and hygroscopicity of the carbon fiber. Penetrant as surfactant could further enhance the stability of the emulsion.¹ This led to the highest stability of HMSA-1.

The stability of HMSA-2 was also higher due to the presence of acetone, appropriate stirring rate, and emulsifier dosage. The viscosity of ETBN in HMSA-3 was too high as a consequence of the absence of diluent. The stirring process was difficult to

TABLE II Centrifugal Stability of Sizing Agents

-	
Sizing agents	Deposition weight (g)
JSA-1 JSA-2 HMSA-1 HMSA-2 HMSA-3 HMSA-4 HMSA-5	$\begin{array}{r} 0.0302 \pm 0.0025 \\ 0.0371 \pm 0.0030 \\ 0.0355 \pm 0.0029 \\ 0.0482 \pm 0.0042 \\ 0.2056 \pm 0.0185 \\ 0.1714 \pm 0.0121 \\ 0.1856 \pm 0.0120 \end{array}$

Journal of Applied Polymer Science DOI 10.1002/app



Figure 4 Particle size and distribution of sizing agents: (a) JSA-1, (b) JSA-2, and (c) HMSA-1.

operate, causing poor stability for HMSA-3. A large quality of styrene was added in HMSA-4 to dilute the single component ETBN and high stirring rate and enough emulsifier was used. But excessive diluent might have bad effects on the properties of the sizing agent. Worse still, the organic solvent was volatile and toxic, which would bring the problems of safety and hygiene. HMSA-5 was less stable because the low stirring rate (6000 r/min) was not high enough to make water droplets disperse uniformly in the resin continuous phase before phase inversion, which led to uneven phase inversion. In brief, the stability of HMSA-1 could better meet the requirement of the sizing agent.

Particle size and distribution of sizing agents

Particle size and distribution shown in Figure 4 demonstrating the average particle size of JSA-1, JSA-2, and HMSA-1 are 0.058, 0.148, and 0.065 μ m, respectively. The distribution of particles is narrow and uniform. This result is consistent with aforementioned centrifugal stability experimental results. JSA-1 has the optimal centrifugal stability and the smallest particle size. HMSA-1 comes second. Generally, the stability of emulsion with small particle size and uniform distribution is usually high. Stable sizing agent with small particle size and narrow distribution can adhere firmly to the carbon fiber surface.⁷

Chemical structure of sizing agents

FTIR spectra of JSA-1, JSA-2, and HMSA-1 are shown in Figure 5. FTIR spectra display that functional groups of JSA-1 and JSA-2 are mainly similar. They are all bisphenol A type epoxy resin evidenced by the peaks at 913 and 766 cm^{-1} due to epoxy ring vibration. The 1607, 1508, and 833 cm⁻¹ absorption are caused by a para-substituted benzene ring. The strong absorption peak at 1246 cm⁻¹ is an aliphatic aromatic ether bond asymmetric stretching vibration. In addition, JSA-1 is likely to contain glycidyl ether type epoxy resin or modified compound attributed to peak in the 1738 cm⁻¹ (-C=O) and 3340 cm⁻¹ (-OH). The biggest difference among HMSA-1, JSA-1, and JSA-2 is the spectra of HMSA-1 containing 2238 cm⁻¹ cyano ($-C \equiv N$) peak and 1646 cm⁻¹ double bond (-C=C) peak.

At the same time, the results of gel permeation chromatography indicate that the molecular weights of JSA-1 and JSA-2 are 3860 and 3572, respectively.



Figure 5 FTIR spectra of JSA-1, JSA-2, and HMSA-1.

Workability in Later Process of Unsized and Sized Carbon Fibers							
Carbon fibers	Abrasion resistance times (times)	Fluffs and breakage (mg)	Stiffness value (mm)				
Unsized JSA-1 sized JSA-2 sized HMSA-1 sized	302 ± 20 1331 ± 110 1131 ± 104 1156 ± 102	$\begin{array}{c} 26.8 \pm 2.0 \\ 1.1 \pm 0.1 \\ 1.8 \pm 0.1 \\ 1.3 \pm 0.1 \end{array}$	60 ± 4 76 \pm 7 73 \pm 6 63 \pm 4				

TABLE III

Therefore, JSA-1 and JSA-2 are not merely bisphenol A type epoxy resins (such as E-51, molecular weight about 400). They might be bisphenol A type epoxy resin modified compounds. Meanwhile, the dried films of JSA-1 and JSA-2 could dissolve in water easily. Thus, it can be concluded JSA-1 and JSA-2 are water-based or self-emulsifying epoxy resin emulsions. Hydroxyl, ester group, or other long chain hydrophilic groups are grafted into their molecular chain to improve the hydrophilicity of the resin, which leads to the significant increase of molecular weight.

Workability in later process of carbon fibers

The results in Table III clearly demonstrate that three sizing agents cannot only greatly reduce fluffs and breakage of carbon fiber but also improve abrasion resistance. JSA-1 has the maximum abrasion resistance and the lowest fluffs and breakage. HMSA-1 is second, with abrasion resistance times being 1156, and the weight of fluffs and breakage is 1.3 mg. The sizing film attached on the fiber surface is flexible and smooth, which can improve the strand integrity of carbon fiber. In this way, fiber fluffs and breakage is reduced and handing processing is facilitated.²⁵



Figure 6 SEM micrographs of different carbon fibers: (a) unsized, (b) JSA-1 sized, (c) JSA-2 sized, and (d) HMSA-1 sized.

Journal of Applied Polymer Science DOI 10.1002/app

30 20 10 0

Figure 7 ILSS data of the composites based on the carbon fibers with different sizing agents.

The stiffness value of JSA-1 sized carbon fiber, whose flexibility is slightly worse, reaches to 76 mm. The stiffness value of HMSA-1 sized carbon fiber is 63 mm. Carbon fiber will bend frequently during the process of weaving the tows to fabrics. Thus, for carbon fiber appropriate flexibility is required. Stiffness may reflect the flexibility of the carbon fiber. Generally, the higher the stiffness, the lower the flexibility. HMSA-1 sized carbon fiber is more flexible because of the additive of flexible ETBN. Simultaneously, as there is long carbon chain in the main-chain structure of ETBN, it can greatly improve the flexibility of the carbon fiber. Moreover, there are a lot of double bonds in the molecular chain of ETBN. They can participate in the curing reaction of the vinyl ester resin matrix. Interfacial adhesion of the carbon fiber to vinyl ester resin matrix is promoted. The application range of sizing agents is also widened.

Carbon fiber surface morphology

SEM micrographs of unsized and sized carbon fibers are shown in Figure 6. During the preparation of carbon fiber, various internal and surface defects are unavoidable, such as radial cracks, center hole, wool yarn, etc. As seen in Figure 6(a), the surface of the carbon fiber is uneven. There are deep grooves and other defects. Figure 6(b-d) show that the surfaces of carbon fibers sized with JSA-1, JSA-2, and HMSA-1 become smooth due to grooves and flaws filled with sizing agents. The surface of the carbon fiber is a uniform layer of sizing agent, which can absorb some stress, scatter external stress, and change the propagation paths of crack from the matrix when the carbon fiber suffers external force.²⁶ Meanwhile, the load transfers effectively through the interface to carbon fiber. The sizing agent layer on the defective parts plays a role of inhibiting internal stress. In addition, interfacial bonds between carbon fiber and resin owing to a large number of reactive coupling groups in HMSA-1 can further strengthen the interfacial adhesion.

Interfacial adhesion analysis

Interfacial adhesion of composites has been evaluated by means of ILSS measurement. A comparison of ILSS data of composites based on the carbon fibers with different sizing agents is shown in Figure 7.

Figure 7 indicates that the sized carbon fiber/vinyl ester resin composites have higher ILSS than unsized carbon fiber/vinyl ester resin composites. Compared with the unsized carbon fiber/vinyl ester resin composite ILSS of HMSA-1 sized carbon fiber/ vinyl ester resin composite reaches the maximum value of 45.96 MPa, increasing by 20.7%. ILSS of the unsized carbon fiber/vinyl ester resin composite has the lowest value of 38.09 MPa, owing to fluffs and breakage of unsized carbon fiber and poor wetting characteristics relative to the matrix resin.

As above the FTIR analysis, JSA-1 and JSA-2 are mainly based on epoxy resin. The curing mechanism of epoxy resin is epoxy groups ring-opening polymerization. However, the curing mechanism of vinyl ester resin is free radical polymerization. When carbon fiber sized by epoxy resin is used to reinforce vinyl ester resin, the film of the epoxy sizing agent coated on the carbon fiber surface cannot be initiated by polymerization initiator of vinyl ester resin. On the contrary, the film plays a role of a interface separation layer. Thus JSA-1 and JSA-2 sized carbon fiber composites have relatively lower ILSS values of 41.42 and 40.53 MPa, increasing by 8.7% and 6.4%, respectively.

According to "similar dissolve mutually theory," the main components of HMSA-1 are similar to the vinyl ester resin matrix. The chemical reactions

(a)
$$\downarrow$$
 COOH + \cdots CH \cdots \downarrow COO-CH \cdots ξ

Carbon fiber surface HMSA-1 sizing agent

(b)
$$CH = CH$$
 + $CH_2 = CH \cdots CH = CH_2$
HMSA-1 sizing agent Vinyl ester resin matrix
Initiator
 $CH - CH - CH_2 - CH \cdots$
 ξ ξ ξ

Figure 8 The chemical reactions of the interface: (a) carbon fiber surface/HMSA-1 sizing agent; (b) HMSA-1 sizing agent/vinyl ester resin matrix.

Journal of Applied Polymer Science DOI 10.1002/app





Figure 9 SEM images of the fracture surfaces of composites with different carbon fibers: (a) unsized; (b) HMSA-1 sized.

between carbon fiber surface/HMSA-1 sizing agent/ vinyl ester resin system are shown in Figure 8. It can be seen from Figure 8(a) that the —COOH functional groups existing on the carbon fiber surface may react with —OH existing in HMSA-1 sizing agent, which makes strong bonding between the carbon fiber surface and HMSA-1 sizing agent coating. Meanwhile, it can be concluded from Figure 8(b) that the double bonds existed in vinyl ester resin and ETBN for HMSA-1 sizing agent may permit a crosslinking reaction with double bonds existing in vinyl ester resin matrix to form strong bonds.¹⁶ So HMSA-1 sizing agent has good interaction with carbon fibers and vinyl ester resin matrix.

SEM images of the fracture surface of composites with unsized carbon fibers and HMSA-1 sized carbon fibers are shown in Figure 9. It can be seen from Figure 9(a) that some carbon fibers are pulled out from the vinyl ester resin matrix, which illustrates the weak layers in the fiber/resin interface region. Strong interlocking of fiber/matrix could be observed in Figure 9(b), and a large amount of the resin matrix is covered on the fibers' surface, which indicates strong interfacial adhesion between HMSA-1 sized carbon fibers and the matrix.

CONCLUSIONS

By adding a calculated amount of NP-10A, EL-40, styrene, and other additives, V-3200 and ETBN were used to prepare the stable emulsion type sizing agent HMSA-1. The average particle size of JSA-1, JSA-2, and HMSA-1 were 0.058, 0.148, and 0.065 μ m, respectively. The distribution of emulsion particles was narrow and uniform. JSA-1 and JSA-2 whose

molecular weights were 3860 and 3572, respectively, might be water-based or self-emulsifying bisphenol A epoxy resin, including hydroxyl, ester, and other long chain hydrophilic groups in their molecular chains. SEM images demonstrated that the surface of sized carbon fiber became smooth and grooves, holes, and other flaws were reduced. HMSA-1 could significantly improve the handling characteristics of carbon fibers due to the increase of abrasion resistance and flexibility of carbon fiber and the decrease of fluffs and breakage. Compared with the unsized carbon fiber/vinyl ester resin composite, JSA-1 sized carbon fiber/vinyl ester resin composite showed 8.7% increase in ILSS and JSA-2 sized carbon fiber/ vinyl ester resin composite showed 6.4% increase. HMSA-1 with a large number of reactive coupling groups had better compatibility with vinyl ester resin. The interfacial adhesion between carbon fiber and vinyl ester resin could be further strengthened due to chemical bonding. ILSS of HMSA-1 sized carbon fiber/vinyl ester resin composite reached the maximum value of 45.96 MPa, increasing by 20.7%.

References

- 1. Minami, H. U.S. Pat. 4751258 (1988).
- Fernandez, B.; Arbelaiz, A.; Valea, A. Polym Comp 2004, 25, 319.
- 3. Chen, W. M.; Yu, Y. H.; Li, P. Comp Sci Technol 2007, 67, 2261.
- 4. Paipetis, A.; Galiotis, C. Comp Mater 1996, 27, 755.
- 5. Dilsiz, N.; Wightman, J. P. Carbon 1999, 37, 1105.
- 6. Dilsiz, N.; Wightman, J. P. Colloids Surf A 2000, 164, 325.
- 7. Yang, Y.; Lu, C. X.; Su, X. L. J Mater Sci 2007, 42, 6347.
- 8. Upadhyaya, D.; Tsakiropoulos, P. Mater Proc Technol 1995, 54, 17.

- 9. Taniguchi, I.; Itoh, R. U.S. Pat. 4167538 (1979).
- 10. Liang, G. Z.; Zhang, Z. P. Polym Comp 2006, 27, 591.
- 11. Nakaoka, Y.; Makino, O. U.S. Pat. 5688554 (1997).
- 12. Ogawa, H.; Shima, M. U.S. Pat. 4420512 (1983).
- 13. Raymond, G. U.S. Pat. 4517245 (1985).
- 14. Sugiura, N.; Taguchi, M. U.S. Pat. 7150913 (2006).
- 15. Broyles, N. S.; Chan, R.; Davis, R. M. Polymer 1998, 39, 2607.
- 16. Saito, M.; Toki, H. U.S. Pat. 4781947 (1988).
- 17. Minami, H. U.S. Pat. 4880881 (1989).
- 18. Minami, H.; Inoue, K. U.S. Pat. 4904818 (1990).

- 19. Sugiuro, N.; Taguchi, M. U.S. Pat. 7094468 (2006).
- 20. Isao, N. Jpn. Pat. 10-266076 (1998).
- 21. ISO 3375-2009.
- 22. Zhang, R. H.; He, Y. H. J Math Mod Meth Appl 2007, 4, 232.
- 23. Binks, B. P.; Cho, W. G.; Petsev, D. N. Langmuir 2000, 16, 1025.
- 24. Yang, X. G.; Tan, W.; Bu, Y. Energy Fuels 2009, 23, 481.
- 25. Sugiuro, N.; Maki, N. U.S. Pat. 7135516 (2006).
- 26. Yang, Y.; Lu, C. X. Mater Lett 2007, 61, 3601.