

# Electrically Conductive Composites Based on Epoxy Resin Containing Polyaniline–DBSA- and Polyaniline–DBSA-Coated Glass Fibers

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**ABSTRACT:** Four kinds of polyaniline (PANI)-coated glass fibers (GF-PANI) combined with bulk PANI particles were synthesized. GF-PANI fillers containing different PANI contents were incorporated into an epoxy-anhydride system. The best conductivity behavior of the epoxy/GF-PANI composites was obtained with a GF-PANI filler containing 80% PANI. Such a composite shows the lowest percolation threshold at about 20% GF-PANI or 16% PANI (glass fiber-free basis). The PANI-coated glass fibers act as conductive bridges, interconnecting PANI particles in the

epoxy matrix, thus contributing to the improvement of the conductivity of the composite and the lower percolation threshold, compared with that of a epoxy/PANI-powder composite. Particularly, the presence of glass fibers significantly improves the mechanical properties, for example, the modulus and strength of the conductive epoxy composites. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 91: 1329–1334, 2004

**Key words:** composites; conducting polymers; thermosets

## INTRODUCTION

Polyaniline (PANI), one of the most promising electrically conducting polymers owing to its high polymerization yield and good environmental stability combined with moderate electrical conductivity and relatively low cost, still remains a subject of intense investigation of many research groups. Numerous potential applications have been demonstrated ranging from optical and electronic devices to antistatic packaging and coatings.

In the past decade, conducting polymers have received some attention in thermosetting antistatic and adhesive applications<sup>1–3</sup> as alternative conductive fillers to metallic particles and carbon black. Our recent studies have shown that composites of epoxy resin filled with PANI particles achieved volume resistivity values in the range of  $10^4$ – $10^8$  ohm cm, at over 40 wt % PANI loadings.<sup>4</sup> In addition, almost all epoxy/PANI composites were relatively brittle. To improve the mechanical properties of epoxy/PANI composites and reduce PANI loading at the same time, PANI-coated glass fibers were presently developed by *in situ* polymerization of aniline with dodecylbenzenesulfonic acid (DBSA) as a dopant in the presence of the glass fibers and thus used as a conductive fibrous filler in epoxy resin.

Glass fibers were selected since they offer several advantages over other materials when used as a reinforcement, such as high tensile strength, high Young's modulus, high heat resistance, production from readily available raw materials, availability in a variety of forms to suit particular end uses, and low cost.<sup>5</sup> The method of fiber coating with PANI can yield new composite materials having potential use in various fields. The research activities of coating conducting polymers onto various materials, such as polymers, glass, fiber, and textiles, were recently reviewed by Malinauskas.<sup>6</sup>

## EXPERIMENTAL

### Materials

The matrix polymer consists of bisphenol A epoxy resin (Araldite LY556), anhydride hardener (HY917), and an accelerator (heterocyclic amine, DY070), all from Ciba-Geigy Ltd. (Basel, Switzerland). The conductive fillers used were glass fibers coated with PANI (GF-PANI) combined with bulk PANI. Aniline (Aldrich, 99.5%) and ammonium peroxydisulfate (APS) were A.R. grades. Chopped glass fiber strands with an average length of ~3 mm were received from Vetrotex (Germany).

### Preparation of GF-PANI

To separate the as-received glass fiber strand, about 15 g glass fiber was immersed in 300 mL ethyl acetate

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and stirred for 5 h. The separated glass fibers were thoroughly washed with acetone and water and dried. The separated glass fibers have an average fiber diameter of  $\sim 8 \mu\text{m}$ , determined by scanning electron microscopy.

The synthesis procedure of PANI-DBSA in the emeraldine salt form was previously described in our articles.<sup>7,8</sup> For the preparation of GF-PANI, aniline, DBSA (at the stoichiometric ratio to form an anilinium-DBSA complex), and a desired amount of separated glass fibers were mixed in water at room temperature for 2 h. The dispersion was then cooled ( $0^\circ\text{C}$ ), and a solution of APS was added dropwise to initiate the polymerization. During the polymerization process, a color change from white through blue to dark green was observed. After polymerization, methanol was added to the dispersion to precipitate the doped PANI. The precipitate, containing PANI-coated glass fiber as well as bulk PANI, was collected on a Buchner funnel and washed by deionized water until the filtrate was clear and free of foam, indicative of the elimination of excess-free DBSA. The sample was dried at room temperature and subsequently in a vacuum at  $60^\circ\text{C}$  overnight.

### Preparation of composites

The anhydride hardener was premixed with the accelerator at a ratio of 180/1 (a double accelerator amount, i.e., anhydride to accelerator 90/1, was also studied), and then the epoxy resin was mixed with the hardener/accelerator mixture. The mixing ratio of the epoxy to the hardener was kept constant at 10/9. Different amounts of GF-PANI were added and thoroughly hand-mixed to attain different filler content composites. The conductive filler content (fiber plus PANI) is described by weight percent. The mixture was cast into a Teflon disc mold (2-cm diameter, 2.5-mm thickness) and cured at  $80^\circ\text{C}$  for 4 h, followed by an additional curing at  $140^\circ\text{C}$  for 2 h.

### Characterization

A two-probe technique was used for the electrical measurements. Electrical measurements were conducted using a Keithley 175A autoranging multimeter when the resistance of the sample was less than  $2 \times 10^8$  ohm. For resistance levels exceeding  $2 \times 10^8$  ohm, samples were measured using a Keithley 240A high-voltage supply and a Keithley 6514 electrometer. A dc voltage of 100 V was applied across the sample thickness. The two surfaces of the sample were coated with silver paint to reduce contact resistance. Neat fillers were measured as compressed pellets.

Thermal analysis of the composites was performed using a Mettler DSC30 differential scanning calorimeter under a nitrogen purge. A cured sample was

placed in a DSC cell and heated from 25 to  $250^\circ\text{C}$  at a rate of  $10^\circ\text{C}/\text{min}$ .

The filler morphology and filler distribution in the epoxy matrix was studied by scanning electron microscopy (SEM) with a Philips XL20 Model D816. Samples were fractured at room temperature. The fractured samples were gold-sputtered prior to observation.

The mechanical properties of the samples were measured using a dynamic mechanical thermal analyzer (DMTA; Perkin-Elmer 7e), in the three-point bending mode. The experiments were performed in the stress scan mode to produce stress-strain curves. The temperature was held at  $25^\circ\text{C}$ . Specimen dimensions were  $10 \times 2.5 \times 1$  mm. To determine the PANI content in the GF-PANI materials, samples (about 1 g) were placed in crucibles and heated in a furnace at  $600^\circ\text{C}$  for 18 h. The PANI content was calculated by the weight loss after heating.

## RESULTS AND DISCUSSION

### Electrical conductivity

All commercial inorganic fibers are sized, that is, coated with a thin organic layer, to protect the fiber surface and to improve handling of the brittle fiber material.<sup>9</sup> This organophilic characteristic enhances polymers, in this case, PANI, to deposit on the surface of glass fibers, when polymerized in a solution.

Through polymerization of anilinium-DBSA in the presence of different amounts of glass fiber, four kinds of GF-PANI materials were obtained, containing 20, 57, 80, and 90% PANI, respectively (determined by combustion experiments). Their resistivities along with the neat PANI powder are listed in Table I. The resistivity of GF-PANI#1 containing 20% PANI is one order of magnitude lower than that of neat PANI powder. It indicates that most PANI was deposited on the surface of the glass fibers and in the beginning of the formation of a continuous conductive phase also throughout the bulk sample. The resistivities of GF-PANI at higher PANI contents are slightly higher than that of the neat PANI powder. The conductivity behavior of GF-PANI is similar to that of PANI-mica composite, which has a core-shell structure with PANI encapsulating the mica particles. The conductivity mechanism of PANI-mica composites was discussed in our previous article.<sup>8</sup> SEM micrographs of GF-PANI materials containing 20 and 80% PANI are shown in Figure 1(a,b) and (c,d), respectively, clearly showing that at the lower PANI content most PANI adheres to the glass fiber surface. At higher PANI content, both PANI-coated glass fibers and bulk PANI are present, and PANI-coated glass fibers are located within PANI layers or on their surfaces, generating a matlike structure.

TABLE I  
Epoxy/GF-PANI Composites

Polymer matrix	Fillers	Resistivity of neat fillers (ohm cm)	Maximum filler content in epoxy	PANI and glass-fiber percentage in the composite at maximum filler content	Resistivity of epoxy/filler composites at maximum filler content (ohm cm)
Epoxy/hardener	GF-PANI#1 (20% PANI)	$3.3 \times 10^2$	11.6%	2.3% PANI, 9.3% GF	$4.3 \times 10^{14}$
	GF-PANI#2 (57% PANI)	$8.9 \times 10^1$	20%	11.4% PANI, 8.6% GF	$8.9 \times 10^{11}$
	GF-PANI#3 (80% PANI)	$4.1 \times 10^1$	30%	24% PANI, 6% GF	$5.5 \times 10^6$
	GF-PANI#4 (90% PANI)	$3.6 \times 10^1$	40%	36% PANI, 4% GF	$1.9 \times 10^6$
	PANI powder (100% PANI)	$3.5 \times 10^1$	60%	60% PANI, 0% GF	$1.2 \times 10^4$

When the four types of GF-PANI materials, as well as neat PANI powder, are used as conductive fillers in the epoxy resin, different maximum filler contents (maximum processible viscosities) are reached, depending on the ratio of PANI to the glass fiber content in the filler, as seen in Table I. Fine glass fibers have a more pronounced effect than that of PANI on the viscosity increase of the composites; therefore, the higher the ratio of PANI to the glass fiber content in the filler, the higher is the maximum filler content which can be reached. The first two compositions of the GF-PANI fillers contain relatively low contents of PANI and high contents of glass fiber; hence, the maximum filler contents of GF-PANI#1 and #2 in epoxy are less than 20%. These two epoxy/GF-PANI composites are insulating because of the too low PANI content. With decrease of the glass fiber content and thus increase of the PANI content (GF-PANI#3 and #4 in Table I), higher maximum filler contents are possible. The electrical conductivity behavior of the epoxy/GF-PANI composites is displayed in Figure 2, for the GF-PANI fillers containing 80% (#3), 90% (#4), and 100% PANI. The percolation threshold of the epoxy/

GF-PANI#3 composite, taken at  $10^8$  ohm cm, is around 20% GF-PANI or approximately 16% PANI (glass fiber-free basis). This value is much lower than is the percolation threshold of epoxy/PANI-powder, which is around 40% PANI. SEM micrographs of the epoxy/30%GF-PANI#3 composite in Figure 3 clearly show that PANI-coated glass fibers interconnect PANI particles in the epoxy resin, acting as conductive bridges, thus giving a higher number of contact points. Therefore, in the presence of glass fiber, a lower PANI content is needed to form conductive networks throughout the matrix polymer. Upon further increase of the PANI content in the GF-PANI composite, the conductivity level of the epoxy/GF-PANI composite becomes similar to that of the epoxy/PANI-powder composite. The percolation threshold of the epoxy/GF-PANI#4 composite is around 35% GF-PANI (32% PANI, glass fiber-free basis).

The role of the PANI-coated glass fibers as conductive bridges depends on two factors, that is, the adhesion of PANI onto the surface of the glass fiber and on the fiber's aspect ratio. Damage of either factor leads to a resistivity increase. This was proved by the fol-

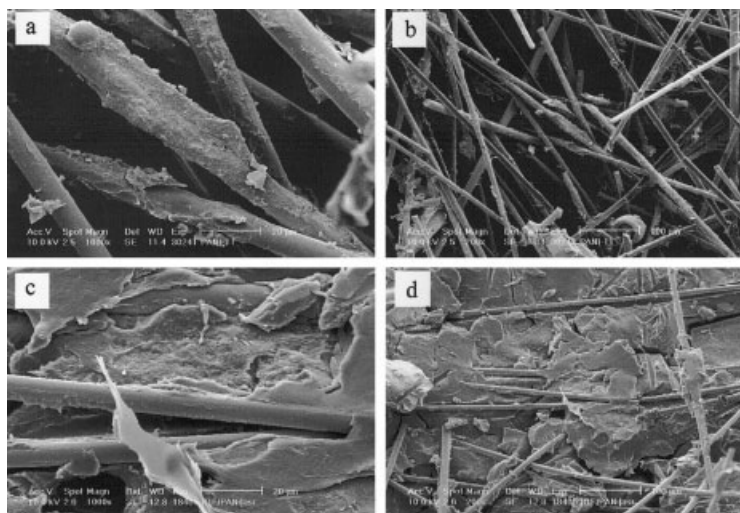
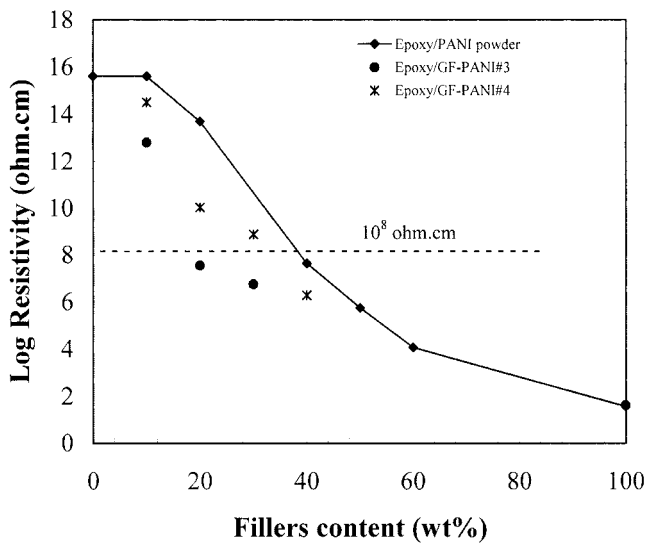
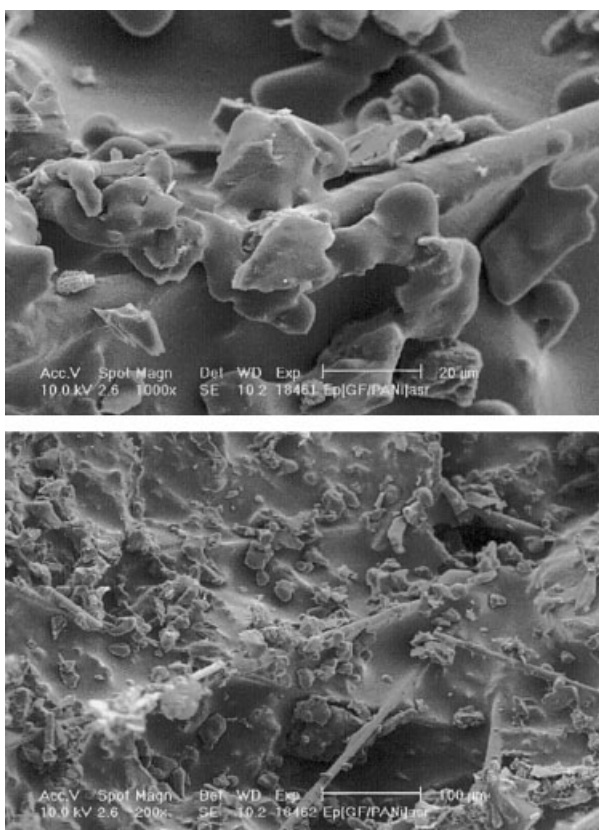


Figure 1 SEM micrographs of (a,b) GF-PANI#1 (20% PANI) and (c,d) GF-PANI#3 (80% PANI), at two magnifications.

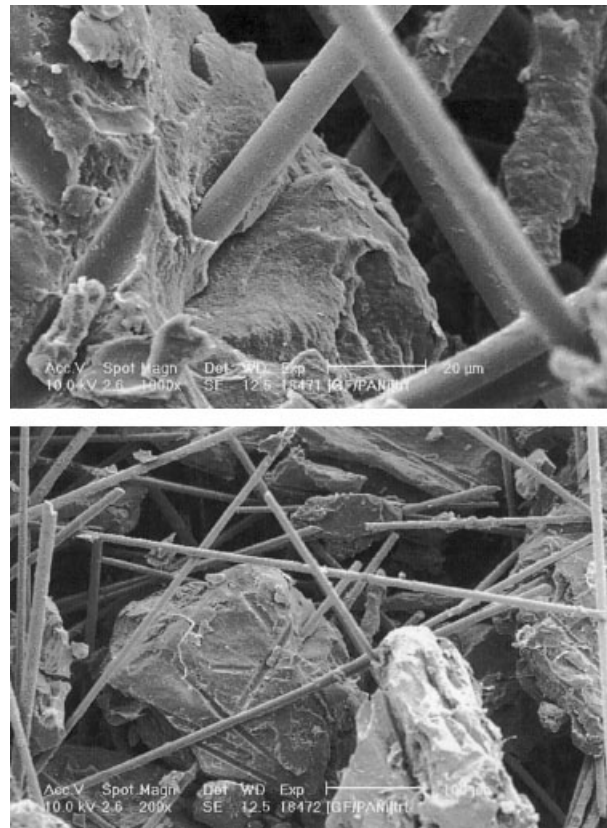


**Figure 2** Electrical resistivity versus filler content of epoxy/PANI-powder composite and two kinds of epoxy/GF-PANI composites.

lowing two experiments: (1) A certain amount of GF-PANI#3 material was placed in a high-speed blender and vigorously stirred for 5 min. Then, the epoxy/hardener system was added and mixed by hand at a



**Figure 3** SEM micrographs of epoxy/30% GF-PANI#3 composite at two magnifications.



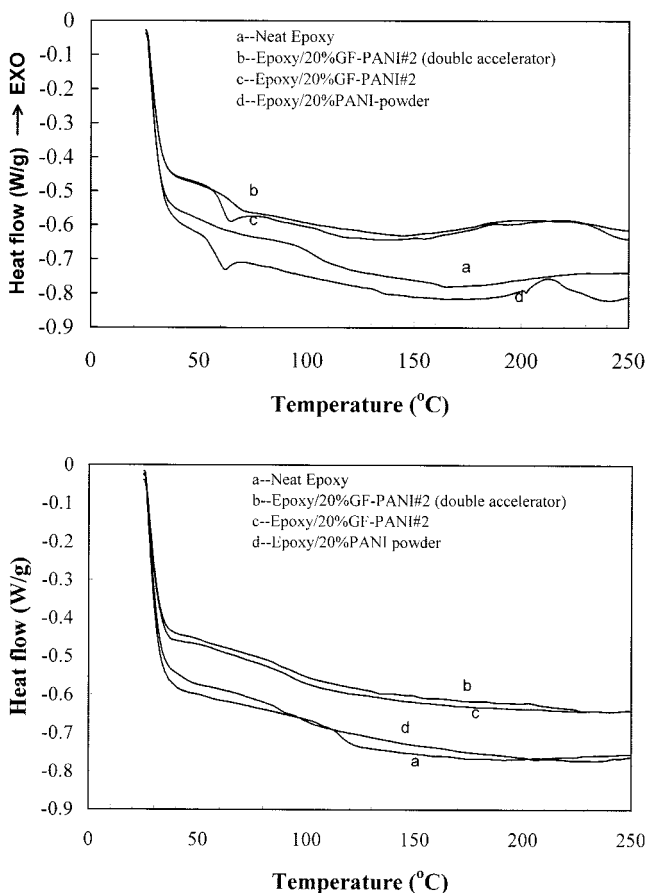
**Figure 4** SEM micrographs of GF-PANI#3 (80% PANI) after 5 min stirring in a blender, at two magnifications.

proportion of 70 epoxy to 30 GF-PANI#3. (2) A epoxy/GF-PANI#3 (70/30) mixture was mixed on a paint-mill instead of by hand. The resistivities of the composites prepared by the above two methods were  $\sim 5 \times 10^{10}$  ohm cm, four orders of magnitude higher than that of the originally studied one. Such a resistivity value lies on the resistivity curve of the epoxy/PANI-powder composite, which implies that the role of PANI-coated glass fibers as conductive bridges has been completely destroyed. Figure 4 shows SEM micrographs of the GF-PANI#3 material after 5-min vigorous stirring. It can be observed that the GF-PANI matlike structure has disappeared, compared with the untreated GF-PANI#3 [Fig. 1(c,d)]. PANI is observed as individually dispersed particles. Each glass fiber passes through several PANI particles, thus resulting in a decreased contact area between fibers and PANI particles. Also, it can be seen that the surfaces of glass fibers are cleaner than are the mechanically untreated ones. This is because vigorous stirring detaches PANI from the surface of the fibers where adhesion is weak. In summary, glass fiber and PANI are less contacted to each other after vigorous stirring, leading to the increased resistivity of the epoxy composite. Paint-mill processing severely breaks the glass fibers, which can be visually observed. The glass fibers have become

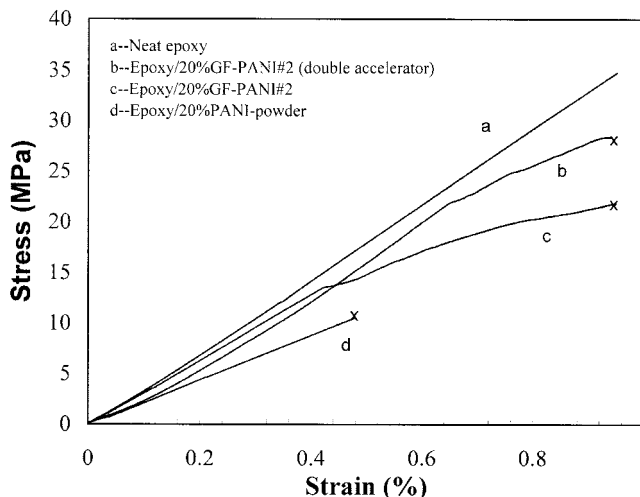
powderlike, thus increasing the resistivity of the composite.

### Thermal analysis and mechanical properties

DSC thermograms of the first and second runs of the cured neat epoxy, the epoxy/20%GF-PANI#2 composite, the epoxy/20%GF-PANI#2 (double amount accelerator) composite, and the epoxy/20%PANI-powder composite are shown in Figure 5(a,b). The  $T_g$  of the neat epoxy is about 110°C [curve (a)], while the  $T_g$  of the epoxy/20%PANI-powder appears at about 60°C [curve (d)]. Since all the composites underwent the same curing procedure, the low  $T_g$  found for the epoxy/20%PANI-powder composite stems from an incomplete cure, as further indicated by the exothermic reaction at 215°C. The epoxy/20%GF-PANI#2 composite containing less PANI shows a slightly higher  $T_g$  at about 65°C [curve (c)]. With the application of a double accelerator concentration, the curing process of the composite accelerates. The more complete cure level leads to a higher  $T_g$  value of the composite, as seen in curve (b). After the first DSC run,



**Figure 5** DSC thermograms, (a) first run and (b) second run, of neat epoxy, epoxy/20%GF-PANI#2 composite, epoxy/20%GF-PANI#2 (double accelerator concentration) composite, and epoxy/PANI-powder composite.



**Figure 6** Stress-strain curves in flexure of neat epoxy, epoxy/20%GF-PANI#2 composite, epoxy/20%GF-PANI#2 (double accelerator concentration) composite, and epoxy/PANI-powder composite.

the curing reactions are completed; therefore, in the second DSC run [Fig. 5(b)], all epoxy/filler composites behave similarly.

Figure 6 illustrates the stress-strain behavior in the flexure of the four studied composites. The epoxy/20%PANI-powder composite exhibits the lowest modulus and the lowest ultimate flexural strength [curve (d)]. This is attributed to the weak interfacial adhesion between PANI particles and the epoxy matrix. An incomplete cure may also affect the mechanical properties. Using PANI-coated glass fibers to replace a part of the PANI powder significantly increases the modulus and strength of the composite, as seen in Figure 6 [curve (c)]. The modulus of the epoxy/20%GF-PANI#2 composite is close to that of neat epoxy. Compared with curve (c), the application of a double accelerator concentration [curve (b)] further increases the strength of the composite, but slightly decreases its modulus. It has thus been shown that the addition of glass fibers to epoxy/PANI systems (containing a regular concentration of an accelerator) may be advantageous to create conductive composites without practically impairing their mechanical properties relative to the neat epoxy matrix.

### CONCLUSIONS

Conductive composites consisting of an epoxy-anhydride matrix with PANI-coated glass fiber (GF-PANI) combined with bulk PANI as conductive fillers were developed and characterized. GF-PANI materials containing different PANI contents reach different possible maximum filler contents (maximum processible viscosities) in the epoxy matrix. The best conductivity result was obtained with the GF-PANI filler

containing 80% PANI. The percolation threshold of the epoxy/GF-PANI (80% PANI) composite is around 20% GF-PANI or 16% PANI (glass fiber-free basis), much lower than that of the epoxy/PANI-powder composite (40% PANI). The PANI-coated glass fibers act as conductive bridges, giving a higher number of contact points than in the case of PANI particles alone. This effect is destroyed by either breakage of the fibers or damage of the adhesion between PANI and the glass fiber surfaces through severe mechanical processing. The presence of PANI-coated glass fibers significantly improves the modulus and strength of the epoxy/PANI composite.

## References

1. Bouguettaya, M.; Védie, N.; Chevrot, C. *Synth Met* 1999, 102, 1428.
2. Peltola, J.; Cao, Y.; Smith, P. *Adhes Age* 1995, 38, 18.
3. Kathirgamanathan, P. *Polymer* 1993, 34, 2907.
4. Jia, W.; Tchoudakov, R.; Segal, E.; Joseph, R.; Narkis, M.; Siegmann, A. *Synth Met*, in press.
5. *Glass Reinforced Plastics*; Morgan, P., Ed.; Iliffe: London, 1961; p 1.
6. Malinauskas, A. *Polymer* 2001, 42, 3957.
7. Segal, E.; Aviel, O.; Narkis, M. *Polym Eng Sci* 2000, 40, 1915.
8. Jia, W.; Segal, E.; Narkis, M.; Siegmann, A. *Polym Adv Technol* 2002, 13,16.
9. *Ullmann's Encycl Indust Chem A* 1988, 11, 9.