Toughening of Epoxy Resin with Functionalized Core-Sheath Structured PAN/SBS Electrospun Fibers

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ABSTRACT: Core-sheath structured electrospun fibers with styrene-butadiene-styrene (SBS) block copolymer as a rubbery core and polyacrylonitrile (PAN) as a hard sheath were prepared by coaxial electrospinning, and used to improve the toughness of epoxy resin. The surface of the fibers was aminated by reacting PAN with diethylenetriamine to improve the interfacial interaction between the fibers and epoxy. Scanning and transmission electron microscopies confirm the core-sheath structure of the PAN/SBS fibers. The Charpy impact energy is increased by the addition of electrospun fibers. When the content of aminated core-sheath fibers is 4 wt %, the Charpy impact energy is increased by 150%. Dynamic mechanical analysis shows that the glass transition temperature of epoxy is not decreased by the addition of core-sheath fibers. The high impact resistance is attributed to the rubbery core of the fibers that can absorb and dissipate impact energy, and the chemical bonding between the fibers and epoxy. © 2014 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2014**, *131*, 41119.

INTRODUCTION

Epoxy resin is one of the most widely used thermosetting polymers that has been applied in coatings, adhesives, and advanced composites. However, epoxy is relatively brittle and the low impact strength results from the highly cross-linked and stiff macromolecular networks that show poor resistance to crack propagation. Up to date, many methods have been developed to improve the mechanical properties of epoxy resin. These successful methods involve the addition of some high performance thermoplastics,[1–5] rubbery particles,[6,7] and liquid reactive rubbers such as carboxyl-terminated butadiene-acrylonitrile copolymers (CTBN) and amine-terminated butadiene-acrylonitrile copolymers (ATBN).[8] Both CTBN and ATBN take part in the curing reaction of epoxy and form elastic microdomains in the resultant resin. The rubber phase has good adhesion to epoxy and high toughness epoxy resin can be achieved when the content of reactive rubber is above certain value. It has been found that the rubber particles inside epoxy resin can increase the toughness through the cavitation of rubber particles or rubber chain extension under the triaxial stress state at the crack tips.[9,10] However, the disadvantage of rubber toughening is that the glass transition temperature and heat resistance of epoxy is decreased, and the mechanical properties, such as tensile strength, can also be decreased by the addition of rubber.[9]

On the other hand, the influence of fibrous nanomaterials, such as carbon nanotubes[11–19] and electrospun polymeric fibers[20,21] on the properties of polymers has been extensively investigated in recent years. It has been shown that carbon nanotubes not only improve the modulus, strength and stiffness but also the impact resistance of epoxy resin.[17–19] The nanotube pullout and breakage are responsible for the toughness improvement. However, the increase of impact resistance is rather limited, for example, the increase of critical stress intensity factor (K_{IC} value) is below 60%.[8] Electrospun fibers are characterized with a diameter of several tens of nanometers and extremely high aspect ratio, which has attracted great research interests in recent years. Some electrospun fibers have been incorporated into polymer matrixes to improve the mechanical properties.[22–26] For example, Liu et al.[22] reported the composite films of electrospun cellulose fibers and poly(vinyl alcohol) with increased the mechanical properties and good transparency. Fong et al.[23] reported that addition of 5% (mass fraction) of nylon-6 electrospun fibers increased the flexural strength of a dental restorative composite resin by 36%. Nylon-4,6,[24] and crosslinked polystryrene-*co*-glycidyl methacrylate copolymer[25] electrospun fibers remarkably increased the strength and modulus of epoxy resin. Kim et al.[26] reported that poly(benzimidazol) (PBI) electrospun fibers increased the toughness and modulus of epoxy more significantly than PBI whisker-like fibrids. The high surface area,
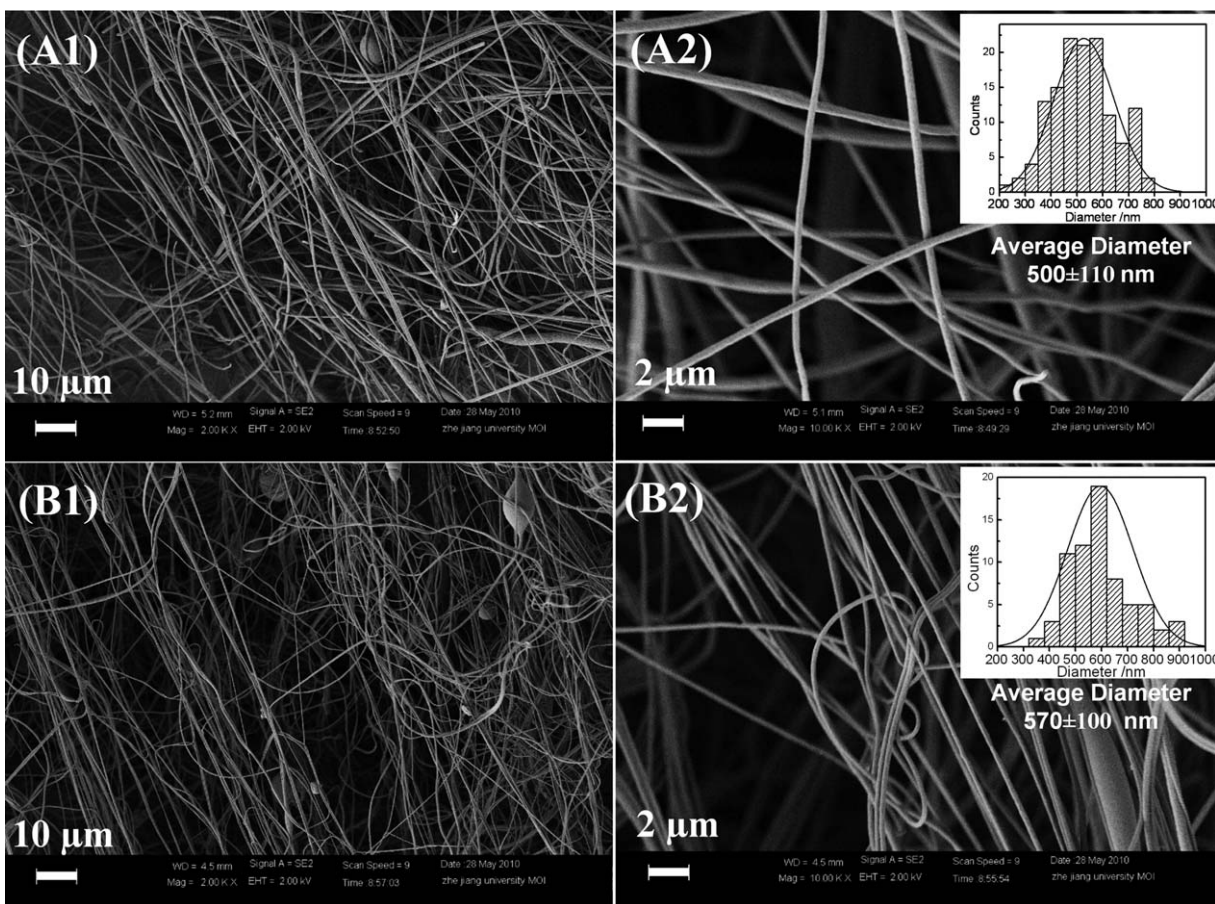
Figure 1. SEM images of (A1, A2) PAN and (B1, B2) PAN/SBS electrospun fibers at low (×2k) and high (×10k) magnifications (concentration of PAN in DMF = 15 wt %, concentration of SBS in THF/DMF = 14 wt %, flow rate of PAN/DMF solution = 1.2 mL/h, flow rate of SBS/THF/DMF solution = 0.3 mL/h, needle to collector distance = 12 cm, voltage = 40 kV). The insets present the size distribution of electrospun fibers.

large aspect ratio, highly stretched macromolecules and reactive surface of the electrospun fibers are responsible for the improved mechanical properties. It is also reasonable to expect that rubbery fibers can be very effective to improve the toughness of polymer matrix. However, to the best of our knowledge, the effect of rubbery fibers on the toughness of polymers has not been investigated up to date.

Coaxial electrospinning provides an effective way of fabricating core-sheath structured fibers with different core and sheath polymers.[27,28] In this work, we investigated the influence of core-sheath structured electrospun fibers, with styrene-butadiene-styrene (SBS) block copolymer as a rubbery core and polyacrylonitrile (PAN) as a hard sheath, on the properties of a diglycidyl ether of bisphenol A type epoxy, with 2-methylimidazole as curing agent. The surface of PAN sheath was aminated to improve the interaction between the electrospun fibers and the matrix. The morphology of the core-sheath fibers, the microstructure and morphology of the core-sheath fiber/epoxy composites were observed by scanning electron microscope (SEM) and transmission electron microscope (TEM). The chemical structure of the aminated core-sheath fibers were confirmed by attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectroscopy. The mechanical

behavior of the modified epoxy resin was evaluated in terms of the Charpy impact strength and dynamic mechanical analysis.

EXPERIMENTAL

Materials

Epoxy resin used in this study with an epoxide equivalent weight of 210–240 and a viscosity of 80 Pa·s at 25°C was purchased from Xuelian Resin Factory (Wujiang, China). 2-Methylimidazole was purchased from Fluka and used as the curing agent. PAN was supplied by Anqing Petrochemical Corporation, and SBS with a commercial brand of YH-805 (the styrene to butadiene ratio of S/B = 40/60) was purchased from Baling Branch Corporation of China Petroleum & Chemical Corporation. Diethylenetriamine N,N-dimethylformamide (DMF) and tetrahydrofuran (THF) were purchased from China Medicine (Group) Shanghai Chemical Reagent Corporation and used without further purification.

Preparation of Coaxial Electrospun Fibers and Surface Amination

To prepare PAN/SBS coaxial fibers, PAN and SBS were dissolved in DMF and a THF/DMF mixture (the THF to DMF volume ratio = 3:1), respectively. The content of PAN/DMF and SBS/THF/DMF solutions was 15 and 14 wt %, respectively.
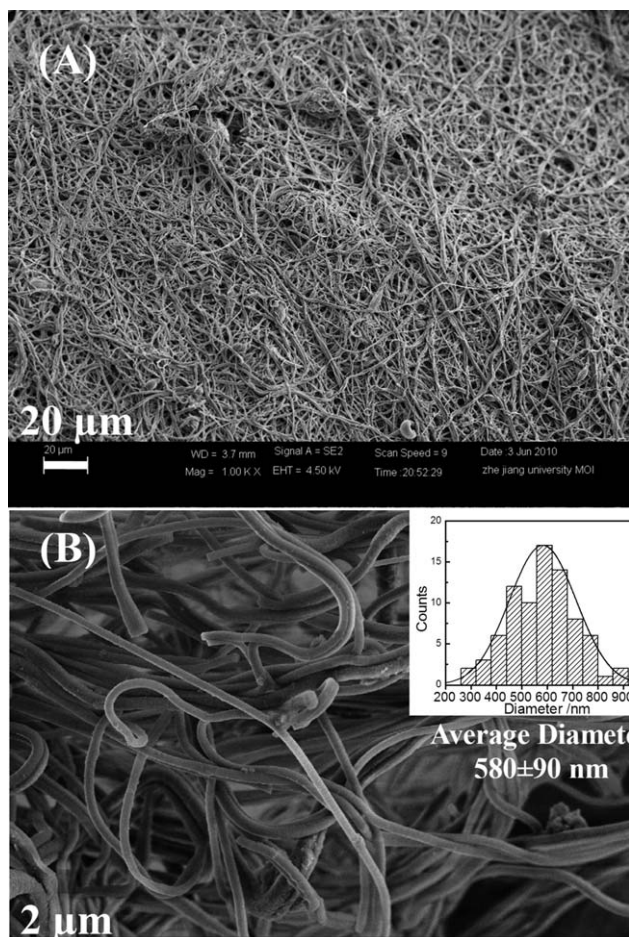
Figure 2. SEM image of aminated PAN/SBS fibers at magnification of (A) ×1k and (B) ×10k. The inset presents the size distribution of aminated PAN/SBS fibers.

The suspensions were magnetically stirred overnight until the polymers were completely dissolved to form uniform and clear solutions. The polymer solutions were then poured into two 50 mL syringes, which were attached to a double syringe pump (WZ-50F6; Medical Instruments Corp. of Zhejiang University, Hangzhou, China). Coaxial electrospinning was then conducted with the PAN/DMF solution as the shell and the SBS/THF/DMF solution as the core on a home-made apparatus built according to the literature[29] with some alterations. The potential voltage was applied to the needle tip with high-voltage power supply equipment (Qiaofeng Electrostatic Equipment Factory, Hangzhou, China). Electrospinning of PAN/SBS fibers was carried out at a voltage of 40 kV and an extrusion rate of 1.2 mL/h for the shell solution and 0.3 mL/h for the core solution under ambient conditions.
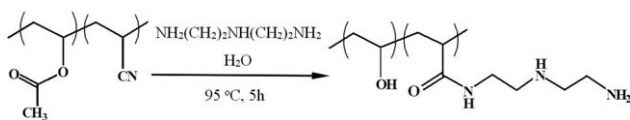
Scheme 1. Proposed surface modification mechanism for the amination of PAN fibers.
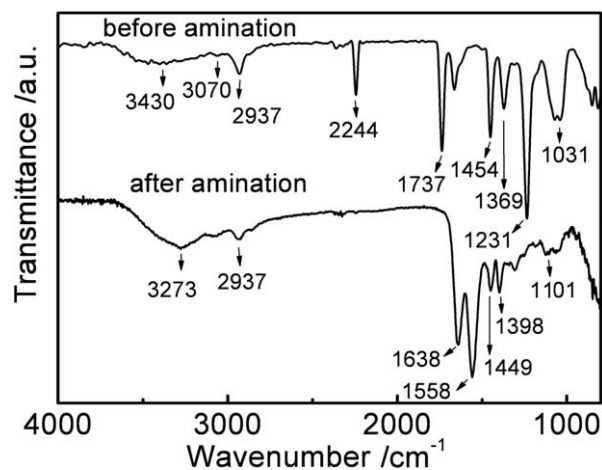

Figure 3. ATR-FTIR spectra of PAN/SBS fibers before and after amination reaction.

Original PAN fibers do not react with epoxy resin. In order to improve the interfacial adhesion between the electrospun fibers and epoxy resin, the surfaces of PAN and PAN/SBS fibers were aminated by reacting PAN with diethylenetriamine. The aminated fibers were prepared in a 100 mL reaction vessel by adding 10 g of the electrospun PAN or PAN/SBS fibers to 500 mL of 10% (v/v) diethylenetriamine solution followed by heating the mixture at 95°C for 5 h. Then, the fibers were sufficiently rinsed with deionized water. The aminated fibers were simply dispersed in 200 mL of deionized water and fragmented in a kitchen blender (JYL-C10; Joyoung, China) into short fibers. The product was filtrated and dried in an oven at 60°C until a constant weight was obtained.

Preparation of Epoxy/Electrospun Fiber Composites

The aminated PAN or PAN/SBS fibers were dispersed in epoxy resin by mechanical stirring and sonication. The mixture was further dried in a vacuum oven at 70°C for 0.5 h to remove residual water. The curing agent, 2-methylimidazole, was then added to the mixture at a curing agent to epoxy weight ratio of 3:100. After degassing under vacuum, the mixtures were pored into rectangular cavities and then heated to 70°C for 12 h to complete the curing reaction.

Characterization

Morphology and size of the electrospun PAN, PAN/SBS fibers before and after surface amination were observed by a scanning electron microscope (FE-SEM) (Utral 55, Carl Zeiss AG, Germany) under an accelerating voltage of 5 kV. The core-sheath structure of PAN/SBS fibers was observed by SEM and transmission electron microscopy (TEM, JEM-1230, JEOL, Japan, operated at an accelerating voltage of 120 kV) before and after removing the SBS core by THF extraction. The fracture surface of the epoxy/fiber composites after the Charpy impact tests was observed by SEM after being spatter coated with a thin layer of gold. The chemical structure of the aminated core-sheath fibers was characterized by ATR-FTIR spectroscopy. The dispersion of the electrospun fibers in epoxy resin was observed by phase
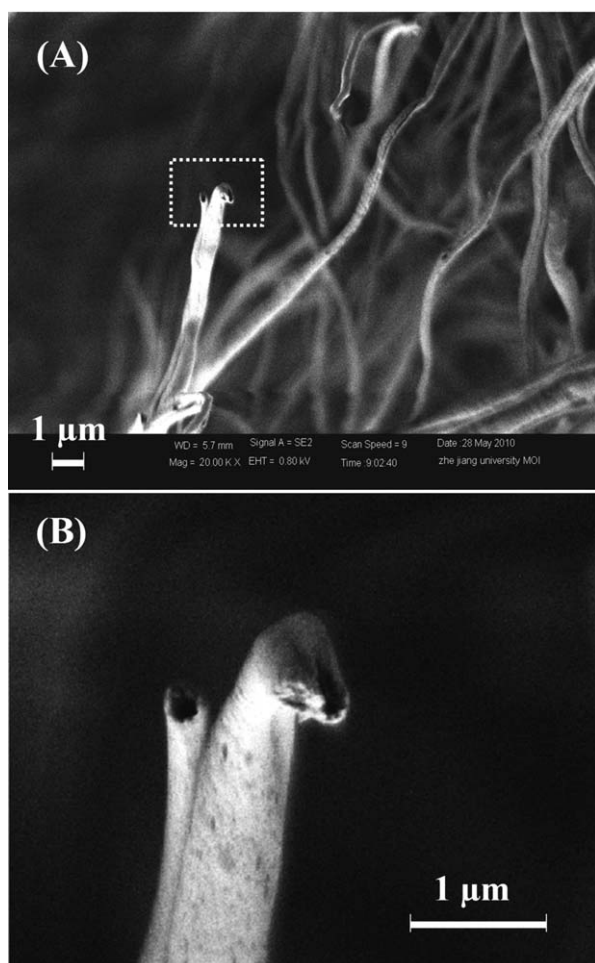
Figure 4. (A) SEM image of electrospun PAN/SBS fibers after the SBS core was removed by THF extraction; (B) provides a zoom-in of the section highlighted by the rectangle in (A).

contrast microscope (BM-8; Shanghai optical instrument factory, China).

Mechanical Properties

Charpy impact strength was measured on a ZBC7000 impact tester (SANS Shenzhen, China) equipped with a hammer. The specimens were unnotched and the size was $50 \times 4 \times 3$ mm^3. The Charpy impact strength was calculated according to eq. (1):

$$IS = \frac{U}{b \cdot d} (kJ/m^2) \qquad (1)$$

where U is the impact energy (KJ), b and d are the specimen width and thickness, respectively. The Charpy impact strength was determined from the average of five specimens and the standard deviation of the values was calculated.

Dynamic mechanical analysis (DMA 242C; Netzsch, Germany) was conducted to determine the dynamic mechanical behavior of epoxy/electrospun fiber composites. DMA measurements were carried out in the single cantilever mode at an oscillatory frequency of 1Hz. The temperature was from 30 to 200°C and the heating rate was 10°C/min. The sample dimensions were $16 \times 5 \times 3$ mm^3.

RESULTS AND DISCUSSION

Morphology of PAN and PAN/SBS Fibers

The morphology of the as prepared electrospun PAN and PAN/SBS fibers are shown in the SEM images of Figure 1. Although some beads can be observed in the SEM images, a large quantity of thin fibers is observed and the amount of beads is very small. Similar to previously reported electrospun fibers,[30] the PAN and PAN/SBS electrospun fibers are straight and the surfaces are smooth and featureless. As shown in the insets of Figure 1, the diameter of PAN fibers ranges from 200 to 800 nm (the average diameter: 520 ± 110 nm). The diameter of the PAN/SBS coaxial electrospun fibers ranges from about 300 to 900 nm (the average diameter: 570 ± 100 nm), which is slightly larger than that of PAN fibers. Nevertheless, this result demonstrates the satisfactory electrospinnability of the PAN/SBS coaxial fibers.

Surface Modification

Figure 2 presents the morphology of aminated PAN/SBS electrospun fibers. It can be found that after reacting with diethylenetriamine, the fibers remain continuous and fibrous, and the
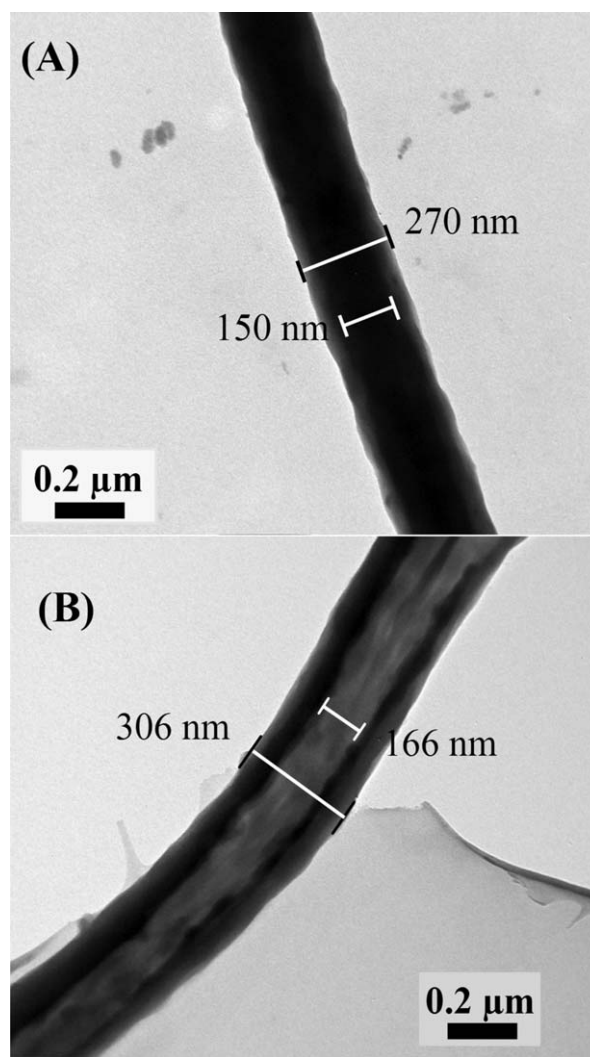

Figure 5. TEM image of electrospun PAN/SBS fibers before (A) and after (B) the SBS core was removed by THF extraction.
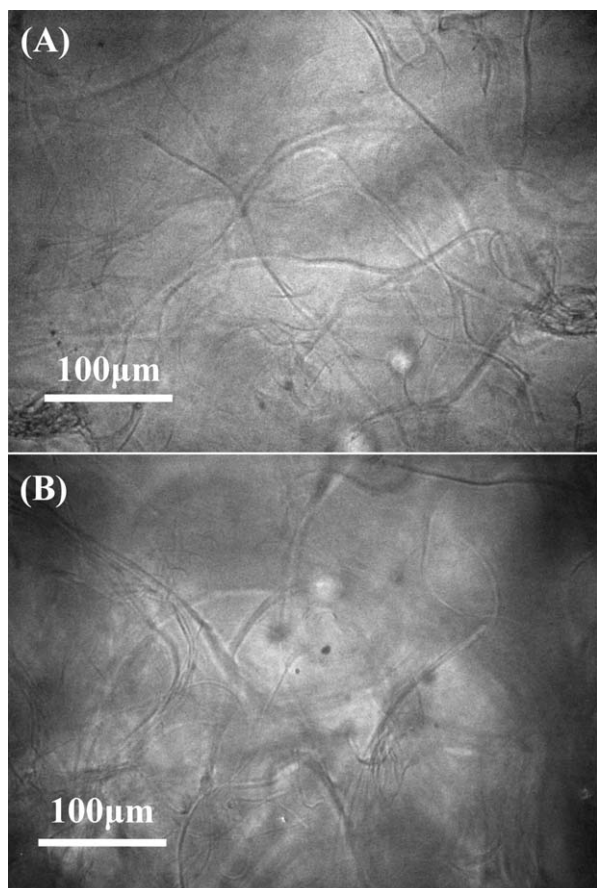
Figure 6. Phase contrast microscopy image of the PAN/SBS electrospun fibers dispersed in epoxy after curing, in which the content of fiber is (A) 2 and (B) 4 wt %, respectively.

diameter of aminated fibers almost remain unchanged, suggesting that the amination reaction occurs on the fiber surface and the fiber structure is not deteriorated by the chemical reaction.

The aim for the amination of electrospun fibers is to introduce amine groups that are reactive with epoxy resin. The mechanism for the amination reaction is presented in Scheme 1. ATR-FTIR spectroscopy was used to characterize the chemical structure of the PAN/SBS electrospun fibers before and after amination. As shown in Figure 3, pure PAN fibers show the characteristic bands at around 3430 cm^{-1} (OH stretching), 3070 cm^{-1} (CH stretching in benzene ring), 2937 cm^{-1} (CH stretching in CH, CH_2, and CH_3 groups), 2244 cm^{-1} (C $\equiv$ N stretching), 1737 cm^{-1} (C=O stretching), 1454 cm^{-1} (CH blending), and 1369 cm^{-1} (symmetric blending of CH_3 in CCH_3). The OH and C=O groups originate from the vinyl acetate co-monomer in commercial PAN. After amination, the C$\equiv$N band at 2244 cm^{-1} decrease greatly and a strong broad band at about 3273 cm^{-1} appears which can be attributed to the stretching vibration bands of amine groups. This suggests that diethylenetriamine has reacted with the surface of the coaxial fibers, converting the C$\equiv$N groups of PAN to amines. In addition, new bands at 1638, 1558, and 1101 cm^{-1} for the aminated PAN fibers can be assigned to the C=O group in amide, the N—H group in amine, and the C—N group in amide

on the fiber surface, respectively. Diethylenetriamine also leads to aminolysis of the acetate ester groups on the surface of the fibers, which can be supported by the disappearance of the bands at 1737 cm^{-1} (C=O stretching), 1454 cm^{-1} (CH blending), 1369 cm^{-1} (symmetric blending of CH_3 in CCH_3). These results confirm that the amide and amine groups, that are reactive with epoxy resin, have been introduced onto the fiber surface.

Structure of PAN/SBS Core-Sheath Fibers

SBS is an elastomer that has been used for the toughening of brittle polymers. For example, Sue et al.[31] reported that clay-modified SBS rubber obviously enhanced the toughness of polypropylene, by forming big shear yielded zones in polypropylene matrix. Elastomeric nanofibers of SBS has been prepared by Fong et al.[32] However, in our study, it was found that during electrospinning, SBS forms large amount of elliptical particles and are seriously adhered with each other, because of its low glass transition temperature. In contrast, we found that core-sheath structured fibers with PAN as the sheath and SBS as the core can be readily prepared by coaxial electrospinning. The PAN sheath not only increases the electrospinnability of SBS but also prevents the adhesion of the fibers because its glass transition temperature is above room temperature. The SBS core inside the fibers will be able to enhance the toughness of epoxy resin.

To illuminate the microstructure of the coaxial PAN/SBS electrospun fibers by SEM, the coaxial fibers were observed by SEM after the SBS core was removed by THF extraction. As shown in Figure 4, the fibers became hollow tubes after extraction, suggesting that SBS was in the center of the fibers. At the same time, the fibers remain continuous, suggesting that the sheath remains intact after THF extraction. TEM images in Figure 5 further present the morphology of PAN/SBS before and after THF extraction. The core-sheath structure is not obvious before SBS is extracted, possibly because the contrast of SBS core and PAN sheath is not high enough in TEM observation. But after THF extraction, the PAN/SBS fibers show a distinct tube-like structure, with an outer diameter of 306 nm and an inner diameter of 166 nm. The inner diameter is also rather uniform,
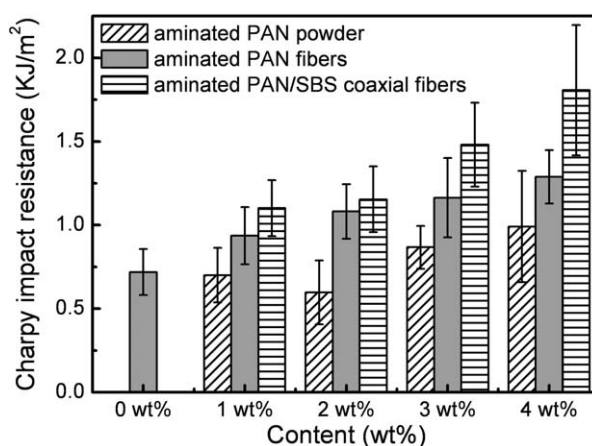

Figure 7. Effect of aminated PAN/SBS fiber, aminated PAN fiber and aminated PAN powder on the Charpy impact strength of epoxy resin.
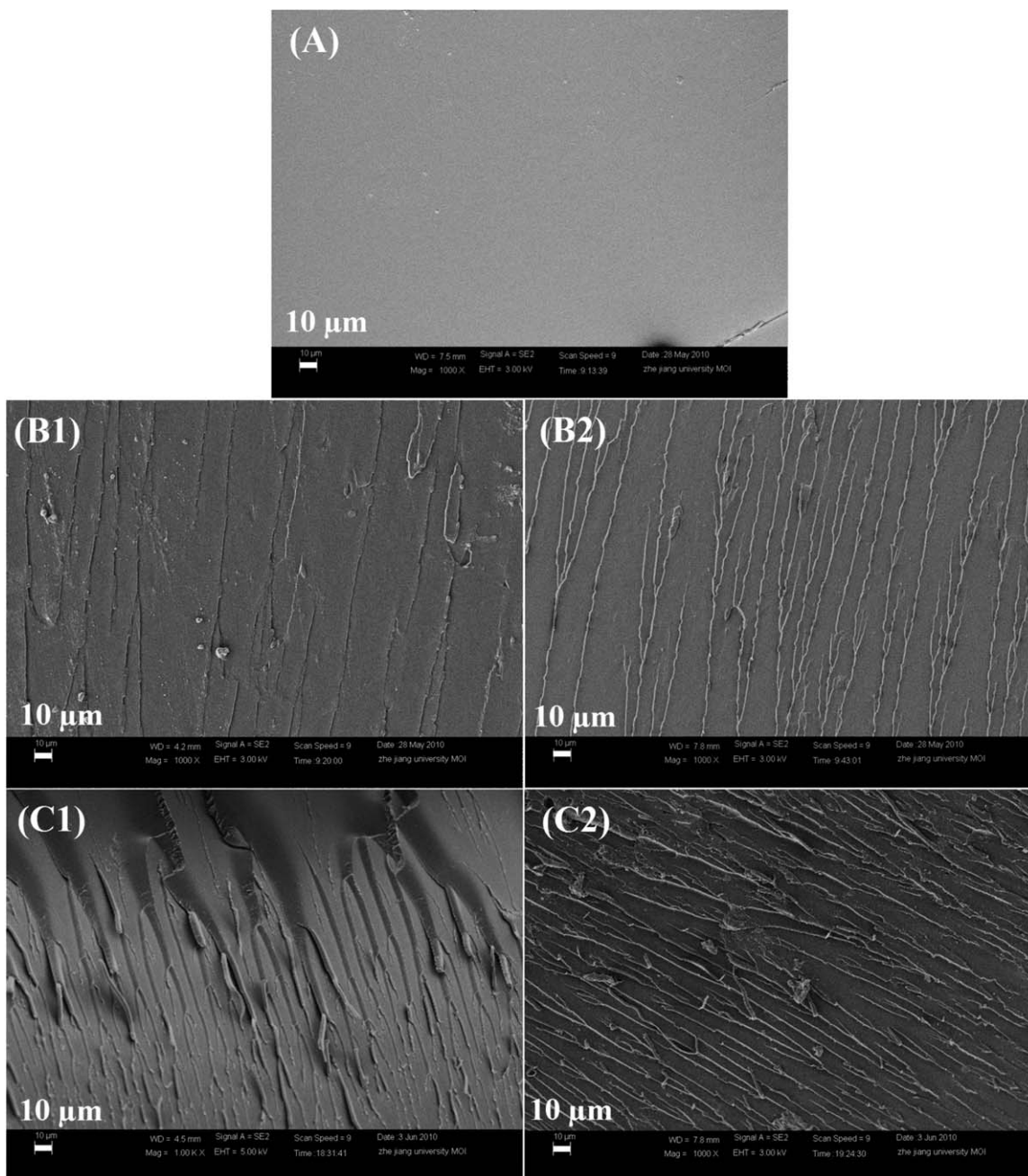
Figure 8. SEM images of the fracture surfaces of neat epoxy resin (A), aminated PAN fiber filled epoxy at a fiber content of (B1) 1 wt % and (B2) 3 wt %, respectively; and aminated PAN/SBS fibers filled epoxy at a fiber content of (C1) 1 wt % and (C2) 3 wt %, respectively.

suggesting that the core-sheath structure is also uniform. The content of SBS in the core-sheath fibers was measured according to the contents of C, H, and N elements by element analysis. Because N element exists only in PAN sheath, the content of PAN can be calculated from the content of N element. Then the content of SBS can be calculated from the C/N ratio. According to the result of elementary analysis, the amount of PAN and SBS is about 57 and 43 wt %, respectively.

Fiber Dispersion in Epoxy

Dzenis et al.[33] reported pioneering works on compounding electrospinning fibers and epoxy by immersing fibers into epoxy composites. The properties of the composites depend on the dispersion of electrospun fibers. In this study, after the aminated PAN fibers were broken into short fibers by kitchen blender in deionized water, slurry fiber suspensions were obtained. After filtration, the short fibers were added to epoxy resin, stirred manually and then sonicated to generate a homogeneous mixture of short electrospun fibers and epoxy. The dispersion of the PAN/SBS fibers in epoxy matrix is observed by optical phase contrast microscopy, as shown in Figure 6. The samples contain 2 and 4 wt % of aminated PAN/SBS fibers, respectively. The electrospun fibers distribute uniformly in the
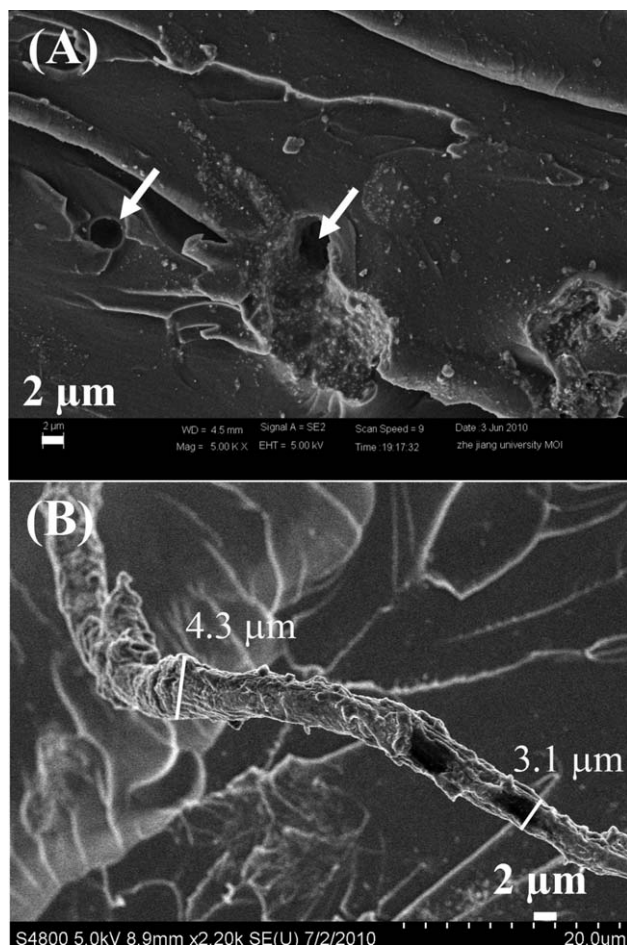
Figure 9. SEM image of impact fractured surfaces of epoxy filled with 4 wt % aminated PAN/SBS fibers at high magnifications, showing (A) holes after fibers are pulled put of the facture surface and (B) fiber stretched out of the facture surface.

composites and randomly oriented, forming networks inside the epoxy matrix. Moreover, the electrospun fibers remain well dispersed after curing reaction and no macroscopic aggregation was observed. The networks of core-sheath fibers with SBS as the rubbery core and PAN as the sheath will definitely contribute to the toughness of epoxy.

Impact Resistance

Figure 7 presents the unnotched Charpy impact strength of epoxy resin filled with aminated PAN powder, PAN electrospun fibers and PAN/SBS coaxial fibers, respectively. The Charpy impact strength increases with the increase of the amount of aminated PAN fibers. When the content of aminated PAN fibers is 4 wt %, the Charpy impact strength is increased to 1.42 KJ/m^2, which is about 89% higher than that for neat epoxy resin (0.75 KJ/m^2). In contrast, the aminated PAN powder does not improve the Charpy impact strength of epoxy resin even when the filler content is 4 wt %. This phenomenon should be related to the properties of PAN and the shape of the PAN powder. PAN cannot adsorb and dissipate impact energy as effective as a rubber, and the powdery PAN does not form continuous phase in epoxy resin. In contrast, the electrospun PAN fibers can form networks

in epoxy resin, which contributes to the increase of toughness of the epoxy resin.

As to epoxy filled with the coaxial PAN/SBS electrospun fibers, the Charpy impact strength obviously increases with the increase of fiber content. For example, the Charpy impact strength was increased to 1.11 KJ/m^2, when the content of PAN/SBS fiber is only 1 wt %, which is higher than that of 2 wt % aminated PAN filled epoxy (1.01 KJ/m^2) and 4 wt % aminated PAN powder filled epoxy (0.99 KJ/m^2). This suggests that the coaxial electrospun fibers with rubbery cores are more effective to increase the toughness of epoxy. When the mass fraction of aminated coaxial fibers is increased to 4 wt %, Charpy impact strength is increased to 1.75 KJ/m^2, which is improved by about 150% for neat epoxy resin. As aforementioned, the amine groups on the surfaces of aminated coaxial fibers can react with the surrounding epoxy resin. This enhances the interfacial interaction between them. Furthermore, the SBS core inside the coaxial fibers is a thermoplastic elastomer, which can effectively absorb impact energy. As pointed out by Kunts et al.,[34] rubber particles play a role in dissipating stored elastic energy during tearing, leading to the increase of impact resistance. On the other hand, rubber is able to store elastic energy during stretching and dissipate irreversibly elastic energy when the rubber failed.[15] The electrospun PAN/SBS coaxial fibers have much thinner fiber diameter and very large length-to-diameter aspect ratio, and thus can form interconnected networks in epoxy resin, therefore, can increase the impact resistance at relatively low filler content. When the content of PAN/SBS fiber was above 4 wt %, the viscosity of epoxy was increased remarkably and it was difficult to remove bubbles inside the resin, which apparently reduced the mechanical properties of epoxy.

On the other hand, previous studies have shown that micrometer sized polymeric fibers, such as ductile poly(ethylene terephthalate) (PET) fibers[35] and aramid fibers,[36] can greatly improve the mechanical properties of epoxy resin. The fibers pullout, fibers breakage, and formation of numerous fracture lines in smaller steps are responsible for the improvement of the toughness,[6] and the properties of the thermoplastic fiber filled composites greatly depend on the fiber strength and the interfacial interaction between the fiber and matrix. To further understand the mechanism for the toughening of epoxy by electrospun fibers, the morphology of the fracture surfaces of electrospun fibers filled epoxy was observed. As shown in Figure 8, similar to what has been observed by Papila[25] and Wei.[37] et al., neat epoxy shows a smooth fracture surface and has large fracture steps, suggesting poor resistance to the applied impact. With the addition of electrospun fibers into composites, the fracture surface becomes rougher, and numerous fracture lines in smaller steps appear on the fracture surface, as shown in Figure 8. The fracture lines are parallel to the direction of crack propagation and are branched. These phenomena suggest that the energy consumption for the PAN and PAN/SBS fiber filled epoxy resin. Furthermore, the fracture lines grow in large quantity with the increase of the addition of aminated PAN and PAN/SBS fibers. Moreover, compared with aminated PAN fibers filled epoxy, aminated PAN/SBS fibers filled epoxy shows a much rougher fracture surface for the same filler content. And large amount of
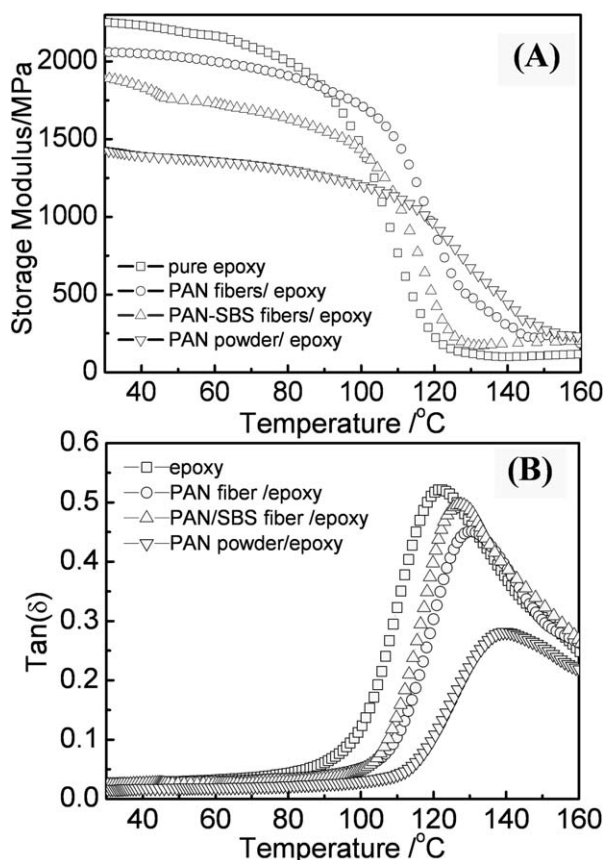
Figure 10. Storage modulus(A), tanδ(B) curves of pristine epoxy resin and epoxy resin filled with aminated PAN/SBS fiber, aminated PAN fiber and aminated PAN powder at a filler content of 4 wt %.

fibers are pulled out of the fracture surface. The fibers are parallel to the direction of fracture lines and the size of the fibers is larger than that of pristine fibers, suggesting that the fibers are encapsulated by a layer of epoxy resin. Similar morphology has not been observed in pure epoxy and PAN fiber reinforced epoxy. The deformation of the rubbery SBS cores and fiber breakage are responsible for the high fracture energy absorption in PAN/SBS fiber reinforced epoxy. When a micro scale crack is initiated under impact load, the coaxial fibers dissipate the impact energy, resist the crack propagation, and results in more fracture steps. The high magnification SEM image in Figure 9(A) shows that there are some holes on the fracture surface, suggesting that some PAN/SBS fibers are pulled out of epoxy matrix. Figure 9(B) also shows that some fibers stretched out of the surface are not smooth as the pristine fibers but are rather rough and the diameter of the fiber is about 3.1–4.3 μm, which is much larger than aminated PAN/SBS fibers, suggesting that the fiber is encapsulated by a layer of epoxy resin. This further demonstrates the strong interaction between aminated PAN fibers and epoxy resin.

DMA

The dynamic mechanical behavior of electrospun fiber filled epoxy was studied by DMA, as shown in Figure 10. The storage modulus is decreased at room temperature after epoxy is filled with 4 wt % aminated PAN powders, PAN fibers and PAN/SBS

fibers, as shown in Figure 10(A). This is because PAN has a relatively low storage modulus as a linear polymer. However, in contrast to PAN powder, the decrease of storage modulus is relatively small for electrospun PAN and PAN/SBS fibers. Furthermore, the decrease of the storage modulus is not as serious as that observed for reactive rubber modified epoxy.[38] The storage modulus at temperatures above the glass transition temperature 150°C was increased to some extent, possibly due to the strong interfacial adhesion between electrospun fibers and epoxy, as well as the interconnected network structure of the fibers. Similar phenomenon was also observed in ethylene diamine modified poly(styrene-*co*-glycerol methacrylate) fiber/epoxy composites.[26] It was also found from Figure 10(B) that the loss tangent (tanδ) peaks decrease to some extend and shift significantly to a higher temperature for epoxy filled with aminated PAN powders, PAN fibers and PAN/SBS fibers, suggesting the increase of T_g of the composites. Even though there is SBS inside the core of PAN fibers, the peak temperature increases to 127°C, which is about 6°C higher than that of neat epoxy resin. This should result from the chemical reaction between aminated PAN and epoxy resin, which increases the cross-linking density in the fiber/matrix interface region and decrease the mobility of the chain segment of the cured epoxy. In contrast, for reactive rubber toughening epoxy, the loss tangent peak temperature is decreased by about 15°C, because part of the rubber can dissolve in epoxy matrix and thus increase the chain mobility of epoxy.[10]

CONCLUSIONS

Core-sheath structured electrospun fibers with PAN as the sheath and SBS as the core were prepared by coaxial electrospinning and used as the toughening agent of epoxy resin after surface amination. Both aminated PAN and PAN/SBS fibers can obviously improve the toughness of the epoxy, whereas the coaxial fibers are much more effective. Although the storage modulus of the fiber filled epoxy is somewhat decreased, the T_g values are increased compared with that of neat epoxy, suggesting that the heat resistance of epoxy is not decreased by the introduction of the PAN/SBS coaxial fibers. The PAN/SBS coaxial fiber filled epoxy can be used as adhesives and the matrix of fiber reinforced composites with improved toughness and heat resistance. Besides epoxy, this study can also provide a novel and effective method for the toughening of other thermosetting polymers.

ACKNOWLEDGMENTS

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