

Miscibility, Intramolecular Specific Interactions and Mechanical Properties of a DGEBA Based Epoxy Resin Toughened with a Sliding Graft Copolymer*

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Abstract The “sliding graft copolymer” (SGC), in which many linear poly- ϵ -caprolactone (PCL) side chains are bound to cyclodextrin rings of a polyrotaxane (PR), was prepared and employed to toughen diglycidyl ether of bisphenol A (DGEBA) based epoxy resin. The aim of the work is to understand the effect of SGC on the miscibility, morphology, thermal behavior, curing reaction and mechanical performance of the cured systems. From differential scanning calorimetry (DSC) analysis and dynamic mechanical thermal analysis (DMTA) of DGEBA/SGC thermosetting blends, it is found that DGEBA and SGC are miscible in the amorphous state. Fourier transform infrared spectroscopy (FTIR) suggested that the miscibility between SGC and DGEBA is due to the existence of intermolecular specific interactions (*viz.* hydrogen bonding). The impact strength is improved by 4 times for DGEBA/SGC (80/20) blends compared with that of the unmodified system. The increase in toughness of SGC-modified thermosets can be explained by the effect of intermolecular specific interactions of SGC with DGEBA, which is beneficial to induce the plastic deformation of matrix. This is the first report on utilizing this novel supramolecular polymer to toughen rigid epoxy matrix.

Keywords: Epoxy; Sliding graft copolymer; Toughen; Miscibility; Hydrogen bonding.

INTRODUCTION

Epoxy resins are widely used as coatings, electronic materials, adhesives and matrix resins for composites because of their attractive properties such as high strength and adhesion, good thermal property and environmental stabilities^[1–2]. After curing reaction these resins are highly crosslinked and become three-dimensional systems which are found to be insoluble in usual solvents^[3]. There are a wide variety of crosslinking agents or hardeners can be used to cure epoxy resin such as acids^[4], anhydrides^[5] and diamines^[6]. However, the high crosslinked structure of cured epoxy resin causes its poor impact resistance, which limits their potential applications. An efficient way to solve the problem is to reduce the crosslink density of epoxy network to toughen the thermosets by adding a secondary component, such as low molecular weight rubbers^[7–8], thermoplastics^[9], rigid phase^[10–11] and interpenetrating polymer networks^[12–14]. Intrinsically, the toughness of a

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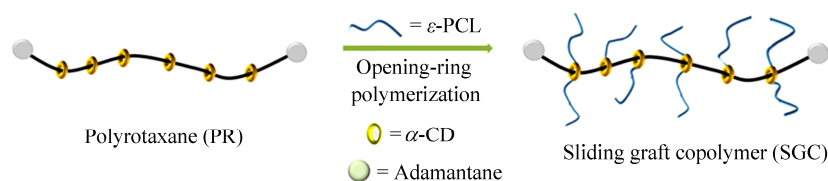
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material is the energy absorption through various deformation mechanisms. There are abundant literatures about toughening diglycidyl ether of bisphenol A (DGEBA) based epoxy thermosets^[15–18]. For example, one successful toughening method is to incorporate a secondary rubbery phase, so that the rubber particles can prevent the crack from free developing after impact and absorb the impact energy. There are many factors contributing to the toughening effect, such as the morphology, particle size and distribution, interparticle distance and matrix-particle adhesion, *etc*^[19]. Especially, if the second phase can bond with the matrix through functioned groups of the modified polymer, the mechanical properties of DGEBA would be improved more markedly. However, in most cases, the secondary component and epoxy matrix are immiscible, limiting the improvement of properties. An effect approach is to exploit favorable intermolecular interactions between them such as hydrogen bonding. The intermolecular specific interactions have been taken as the driving force for miscibility in some thermosetting polymer blends. For example, end carboxyl functional groups of the copolymer of acrylonitrile and butadiene (CTBN) can react with the epoxide groups, leading to strong interfacial adhesion and high toughening effect^[16, 20–21]. In recent years, the hyperbranched polymers (HBPs) with lower viscosity and novel molecular structure have been extensively used to toughen thermosetting resins^[22–23]. But above all, HBPs possess reactive end groups, so they can react or readily be compatible with the surrounding matrix material^[24–26]. The interactions between HBP and DGEBA matrix ensured a good load transfer from the epoxy matrix to the modifier. Thus the miscibility induced by intermolecular specific interactions could give important influence on the morphology and the properties of the modified thermosetting blends^[17]. Clark *et al.* have investigated the effect of miscibility in both anhydride- and amine-crosslinked epoxy/PCL blends on the difference of the resulted mechanical properties due to different miscibility^[27]. The miscibility of amine-crosslinked blends is ascribed to the formation of the intermolecular hydrogen bonding interactions between amine-cured epoxy and PCL. Zheng *et al.* investigated the effect of curing agent on the formation of nanostructures in PEO-*b*-PCL modified epoxy resin thermosetting blends. They found that morphological structures depend on the strength of hydrogen bonding interactions between epoxy matrix and PEO-*b*-PCL^[28].

Recently, we prepared a novel type of polyrotaxane (PR) having polymeric side chains attached to the cyclic molecules, and designated it as “sliding graft copolymer” (SGC)^[29]. The SGC, in which many linear poly- ϵ -caprolactone (PCL) side chains are bound to the cyclodextrin (α -CD) rings of a PR, were synthesized by ring-opening polymerization of ϵ -caprolactone initiated by the hydroxyl groups of PR, as shown in Scheme 1. The bulky adamantane groups at both ends of the linear chains are introduced to prevent the dissociation of the cyclic molecules. The key feature of SGC is that the cyclic molecules (α -CD) and grafted side chains can freely slide and/or rotate along the backbone (PEG) within the restrictions of the main chain length.



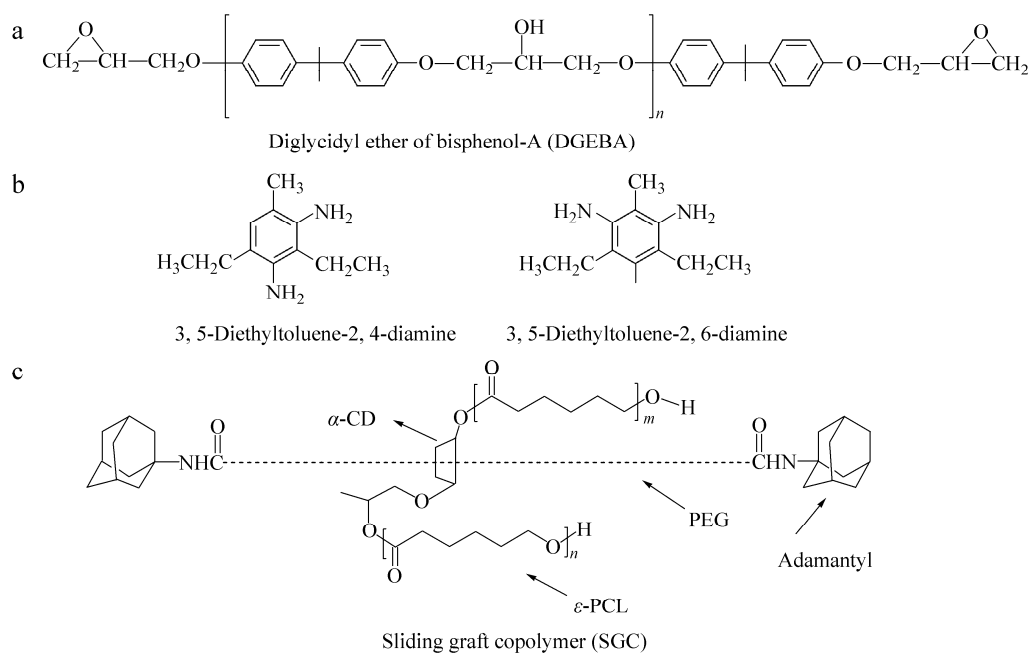
Scheme 1 Schematic illustration of the preparation of a sliding graft copolymer (SGC)

The SGC has very promising processability because of the low entanglement, so that it could lead to low viscosities. Also, there are numerous PCL side chains in SGC, so there is possible to exist favorable interchain specific interactions between SGC and epoxy matrix. Based on above-mentioned analysis we proposed using the previously reported sliding graft copolymer to toughen DGEBA with the curing agent diethyl methyl benzene diamine by one-step melt blending method without solvents. With the aim to improve the toughness of the obtained composites materials, the miscibility, intermolecular specific interactions, morphology, thermal behaviors and mechanical properties of the thermosets are systematically investigated.

EXPERIMENTAL

Materials

The epoxy precursor, diglycidyl ether of bisphenol A (DGEBA, E51) was supplied by Shanghai Resin Co., China. The curing agent, diethyl methyl benzene diamine (E100), of Albemarle is a mixture of two isomers (74%–80% 2,4 isomer and 18%–24% 2,6 isomer). The chemical structures of the epoxy resin and curing agent are shown in Scheme 2(a) and 2(b), respectively.



Scheme 2 Chemical structure of (a) diglycidyl ether of bisphenol-A (DGEBA), (b) curing agent diethyl methyl benzene diamine (E100) and (c) sliding graft copolymer (SGC)

Synthesis of Sliding Graft Copolymer

The chemical structure of SGC is shown in Scheme 2(c). The SGC was prepared by the so-called “bulk polymerization” of ϵ -CL monomers, which was initiated by the hydroxyl groups of the hydroxypropylated CDs and catalyzed by tin 2-ethylhexanoate (stannous octoate, $\text{Sn}(\text{Oct})_2$). In this method, ϵ -CL (10 mL) and hydroxypropylated polyrotaxane (1 g) were added into a 50 mL three-neck flask. The mixture was purged with nitrogen for 30 min under gentle magnetic stirring until the mixture was uniform. In the second phase, after adding $\text{Sn}(\text{Oct})_2$ as the catalyst, the mixture was heated to 100 °C under an argon atmosphere for 3–4 h until the liquid became viscous. Then the liquid was dissolved in toluene (40 mL) and poured into hexane (450 mL) to precipitate the SGC. The resulting SGC was obtained after removing the remaining liquids in vacuo. The SGC ($M_w \sim 852000$ g/mol, as obtained from GPC) contained PEG ($M_w \sim 35000$), α -CD ($M_w \sim 1000$). With about 103 α -CDs per molecule, the SGC has an inclusion ratio of 26%. The synthesis technology of this kind of SGC with the CAS Number of 928045-45-8 JPN has been commercialized, and the SGC can be purchased from Tianjing MicroRheo Supermolecular Materials LLC. More detailed information about SGC can be found in our previous work^[29]. Hydroxypropylated polyrotaxane was supplied by Advanced Softmaterials, Inc. (Tokyo, Japan). Based on information provided by the supplier, polyrotaxane was prepared by the hydroxypropylation of PEG/CD polyrotaxane consisting of PEG 35000, 90–100 hydroxypropylated α -CDs and terminal adamantane moieties.

Preparation of DGEBA/SGC Blends

The ratio of DGEBA/SGC is in proportion, ranging from 100:0, 90:10, 85:15, 80:20, 70:30 by weight. The SGC was first dissolved in the DGEBA and the mixtures were vigorously stirred at 100 °C until the mixtures became

homogeneous. Then equimolar curing agent E100 with respect to the epoxide equivalence of DGEBA (the weight ratio of E100 to DGEBA being 0.23:1) was added to the mixtures under continuous stirring at 80 °C until homogeneous mixtures were obtained again. The ternary mixture was poured into an aluminum mold after being degassed under vacuum for 30 min and cured at 60 °C for 4 h plus 120 °C for 8 h to access a complete curing reaction.

Characterization

Scanning electron microscopy (SEM) (S4700, Hitachi Co., Japan) was used to determine the morphologies of the blends at 1 kV. The samples were fractured under cryogenic conditions for 10 min and the surfaces were coated with a thin gold layer.

Fourier transform infrared (FTIR) spectra were recorded on a Tensor 27 spectrometer. Typically, 32 scans at a resolution of 4 cm⁻¹ were accumulated to obtain one spectrum.

Differential scanning calorimetry (DSC) data were obtained from a Mettler-Toledo DSC instrument under nitrogen, using samples of approximately 6–8 mg. All samples were heated to 200 °C at 50 K/min and kept for 5 min to remove any previous thermal history. Then the samples were cooled to –100 °C at 10 K/min, and reheated up to 200 °C at 10 K/min to determine the glass transition temperature (T_g), cold crystallization temperature (T_c) and melting temperature (T_m).

Dynamic mechanical thermal analysis (DMTA) was carried out with a Dynamic Mechanical Thermal Analyzer (Rheometric Scientific Co.) with a tension mode at 1 Hz and 3 K/min from –100 °C to 200 °C.

Type-V dumbbell-shaped specimens were molded and tested at room temperature according to ASTM D638 by using a CMT 4104 Electrical Tensile Instrument (Shenzhen SANS Test Machine Co., Ltd. China) at 5 mm/min. The impact test specimens were molded with dimensions of approximately 80 mm × 10 mm × 4 mm ($L \times W \times T$), and measured by using a Ceast Resil Impactor according to ISO180-2000.

During the curing processing, we dissolved 0.2–0.3 g sample (W_0) in dimethyl formamide (DMF) solution every 1.5 h. The samples were kept in DMF solution for three days. Then the insoluble matter was precipitated out and subsequently put it into a vacuum oven until a constant weight (W_p). The curing degree (α) can be calculated by the following formula:

$$\alpha(\%) = \frac{W_0 - W_p}{W_0} \times 100\%$$

RESULTS AND DISCUSSION

Evaluation of Curing Degree

In the curing process, epoxy resin undergoes polycondensation to form three-dimensional network. Figure 1 shows the curing degree (α) versus time for neat DGEBA and DGEBA/SGC thermosetting blends containing

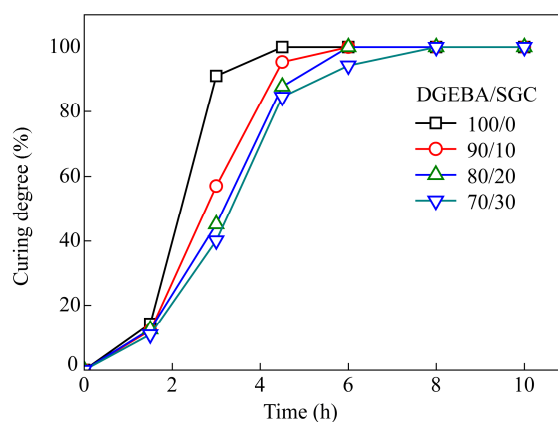
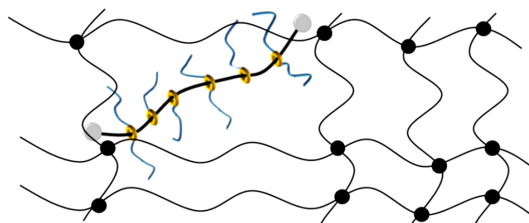


Fig. 1 Curves of curing degree (α) versus time

10 wt%, 20 wt% and 30 wt% SGC at a cure temperature (T_{cure}) of 120 °C. Complete cure ($\alpha = 1$) of the neat DGEBA occurs at a time around 4 h. The complete curing time for the DGEBA/SGC blends increases with the increase of SGC content. Also, it is clear that the curing degree of DGEBA/SGC thermosetting blends is lower than that of neat DGEBA at the same reaction time, particularly in the early stage of the curing process. The reduction of curing degree is attributed to the dilution effect of SGC^[30–32]. During the curing reaction of DGEBA, the SGC can occupy positions between the reaction centers thereby decreasing the density of the reactive groups^[32], as shown in Scheme 3. The delay of reaction rate of EGEBA with the addition of SGC can indirectly demonstrate that the epoxy and SGC is miscible at the molecular scale.



Scheme 3 Schematic model of SGC dispersed in an epoxy resin matrix

Miscibility

Before the curing reaction, all the ternary mixtures composed of DGEBA, curing agent E100 and SGC were homogeneous and transparent at 80 °C, suggesting the components are compatible in the melting state. And after the curing reaction, all the SGC-contained thermosets were still transparent, indicating that the macroscopic phase separation did not take place at least on the scale exceeding the wavelength of visible light. The miscibility of the binary thermosetting blends can be further confirmed by evaluating the glass transition behavior in DSC curves which are presented in Fig. 2. The T_g of neat epoxy is about 108 °C. The DSC curve of pure SGC shows a glass transition at around –50 °C and a sharp melting peak (T_m) at around 33 °C, demonstrating that SGC is a semi-crystallized plastic resin even though its T_g is much lower than room temperature. In the DSC curves of DGEBA/SGC blends, only the glass transition can be observed, indicating the miscibility of epoxy with the SGC. With increasing SGC concentration, the T_g of the thermosetting blends shifts to lower temperatures. A reasonable explanation is the interpenetration of SGC into the epoxy matrix, leading to the decrease of crosslinking density of the cured epoxynetwork. What is more, the melting peak of SGC disappears thoroughly in thermosetting blends, suggesting that SGC are no more crystalline. The disappearance of melting peak of crystalline polymer is characteristic of miscible blends composing an amorphous and a crystalline polymer. The miscibility of the DGEBA and the SGC could be the intermolecular specific interactions between amine-cured epoxy and SGC. Theoretically, the side chains of SGC contain numerous carbonyl groups which are potential to form interchain hydrogen bonding interactions with the amine-crosslinked epoxy. To confirm this interpretation, Fourier transform infrared spectroscopy (FTIR) was measured, as shown in Fig. 3.

All the epoxy groups were consumed as proved by the disappearance of the absorption peak of epoxy group at 913 cm^{-1} in Fig. 3(a). The FTIR spectra of SGC and DGEBA/SGC thermosetting blends in the range of 1680–1780 cm^{-1} are shown in Fig. 3(b). For the pure SGC, a broad band centered at 1724 cm^{-1} is ascribed to the stretching vibration of carbonyl groups in the crystalline region of the side chains PCL of SGC, and the shoulder band centered at 1734 cm^{-1} is characteristic of amorphous chains of PCL, which illustrates that SGC is a semi-crystallized plastic resin at room temperature^[33]. For the SGC-containing thermosets, the main peak of SGC crystals was absent, implying that SGC exist in the amorphous state in the thermosets. In addition, the stretching vibration bands of the carbonyls in the amorphous region were observed to shift to the higher frequencies with increasing SGC content. Meanwhile, a new shoulder peak emerged at lower frequency of 1718 cm^{-1} for the DGEBA/SGC thermosetting blend. The new shoulder bands have been ascribed to the stretching vibration of the hydrogen-bonded carbonyls, *i.e.*, there is the formation of the intermolecular hydrogen bonding interactions between the hydroxyl groups of epoxy matrix and the carbonyl groups of the side chains PCL in SGC^[34]. Thus, it

can be deduced that the formation of the intermolecular hydrogen bonding interactions leads to the good compatibility between the SGC and the epoxy matrix.

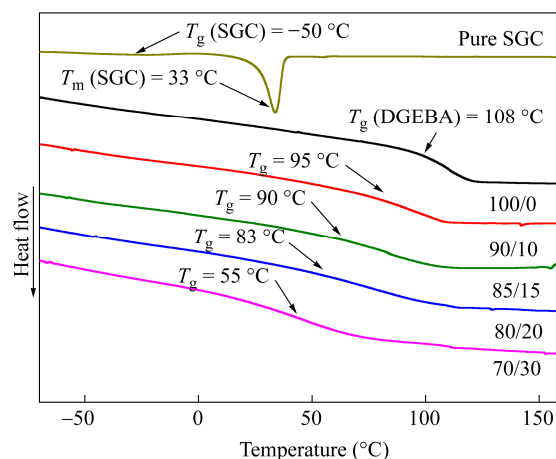


Fig. 2 DSC thermograms (second heating) of pure SGC, neat DGEBA and DGEBA/SGC blends containing 10 wt%, 15 wt%, 20 wt% and 30 wt% SGC

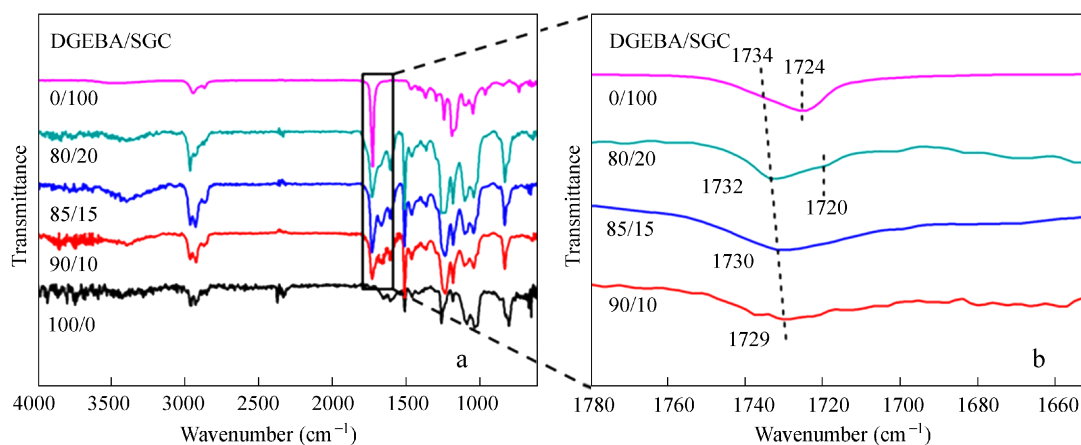


Fig. 3 FTIR spectra in the range of (a) 800–4000 cm^{-1} and (b) 1680–1780 cm^{-1} for DGEBA/SGC blends

Dynamic Mechanical Properties (DMTA)

Dynamic mechanical loss factor ($\tan\delta$) versus temperature of neat DGEBA, and representative modified DGEBA thermosets containing 10 wt%, 20 wt% and 30 wt% of SGC are depicted in the Fig. 4(a). The neat epoxy resin shows a peak at around 120 °C, which is clearly related to the T_g of neat DGEBA. And all the curves of DGEBA/SGC thermosetting blends are unimodal, indicating the homogeneous character of modified materials. Notably, both peak position and peak height significantly changed with increasing the content of SGC. The peak shifts to lower temperatures and this becomes more significant with the increase of SGC content. One reason is that the epoxy is miscible with the SGC in a molecular scale. Another reason could be the decrease in the crosslinking density of the epoxy by the incorporation of SGC, in good agreement with the DSC results.

The storage modulus of the modified epoxies decreased with increasing the content of SGC, as shown in Fig. 4(b). This may be attributed to the decrease of crosslinking density in the modified samples. As to the curing degree that we analysed, during the curing reaction of the epoxy resin, SGC domains could occupy the space between the reaction sites, leading to the impairment of the crosslinking reaction at that particular site. The overall crosslinking density of DGEBA matrix is decreased by the addition of SGC^[32]. Hence the SGC goes into the epoxy matrix and acts as a plasticizer.

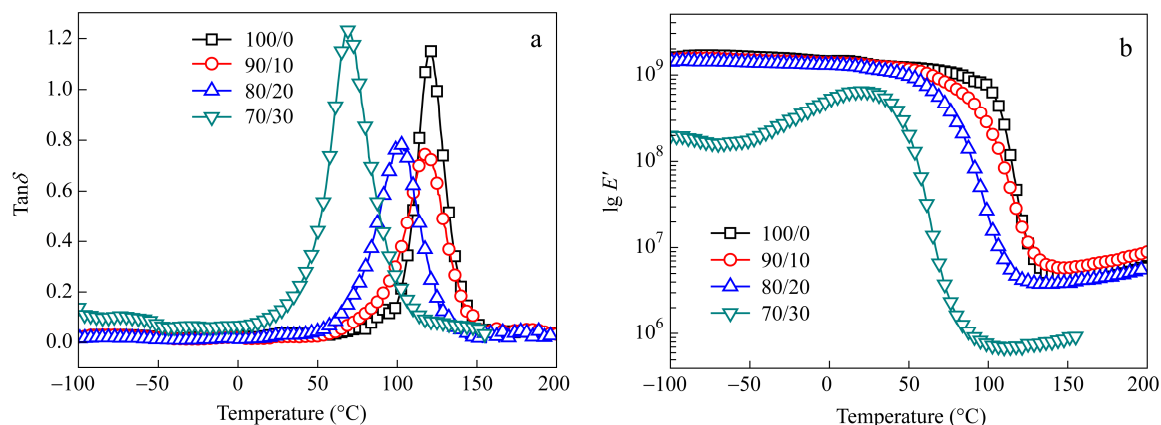


Fig. 4 DMA profiles of neat DGEBA and DGEBA/SGC blends (10 wt%, 20 wt%, and 30 wt%): (a) $\tan\delta$ versus temperature and (b) storage modulus versus temperature

Morphology of Epoxy Thermosets Containing SGC

The SEM of cryo-fractured surfaces of epoxy thermosets containing 0 wt%, 10 wt%, 20 wt% and 30 wt% of SGC are employed to study the phase morphology. As shown in Fig. 5(a), the neat epoxy matrix shows a smooth and glassy fractured surface. It is clear that all the micrographs do not show obvious phase separation appearance due to the strong interfacial adhesion between SGC and DGEBA. For the thermoset containing 10 wt% of SGC, the SGC formed spherical particles with the diameter of ~ 20 – 100 nm embedded in the continuous epoxy matrix. The obtained nanostructured epoxy thermosets could be prepared *via* reaction-induced microphase separation owing to the presence of miscibility in this system^[35]. With increasing the SGC content, the SGC microdomains begin to coagulate and the morphology transformed to near continuous while the concentration of the SGC is 20 wt% (Fig. 5c). With further increasing SGC, the blends displayed remarkably different morphologies. For DGEBA/SGC 70/30 blend, it is seen that SGC domains began to aggregate to bigger size (Fig. 5d), so as to drop the integrated performance of the sample. Thus, when the concentration of the SGC is 20 wt% or less, soft SGC particles can be dissolved in the hard epoxy matrix owing to the presence of miscibility in this system. As the concentration of SGC was higher than 20 wt%, the SGC particles begin to aggregate and a situation was reached where SGC got microphase separated from the epoxy.

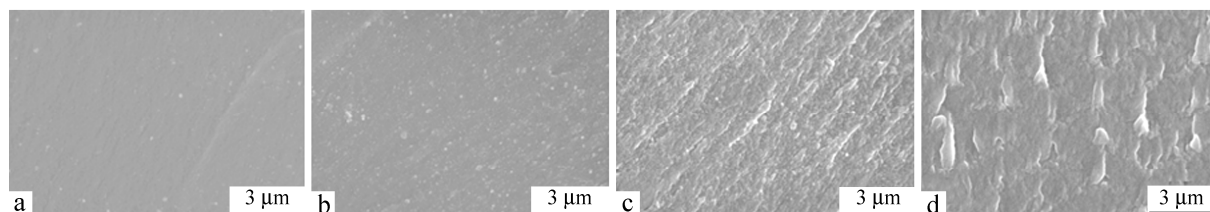


Fig. 5 SEM images of cryo-fractured surface of (a) neat DGEBA, (b) DGEBA/SGC (90/10), (c) DGEBA/SGC (80/20) and (d) DGEBA/SGC (70/30)

Tensile Strength and Related Properties

Stress-strain behaviors of the neat DGEBA and modified epoxies are shown in Fig. 6 and the tensile properties are summarized in Table 1. The neat DGEBA is very rigid and shows a high tensile modulus with a value of 3993 MPa, but its elongation at break of about 18.5% indicates that it undergoes brittle fracture. Whereas, the SGC modified DGEBA samples exhibit a ductile deformation with the appearance of an upper yield stress. As expected, the tensile modulus gradually decreases with increasing the SGC content, which is attributed to the plasticization effect of the SGC in the epoxy matrix. Generally, when a flexible polymer is added to a thermoset resin, its elastomeric character authorizes a decrease in modulus. The decrease in tensile strength and the increase of the elongation at break with SGC content can be related to the stiffness of the modified network. The

decrease of the stiffness in the SGC-modified network epoxy probably may be due to the deduction of the cross-linking density as the modifier SGC occupies the reaction centers during curing reaction.

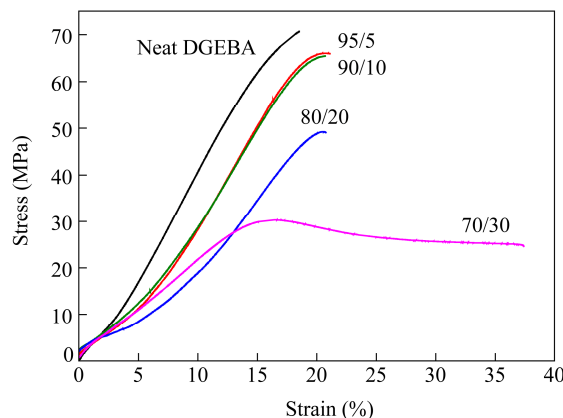


Fig. 6 Stress-strain curves of the neat epoxy and modified epoxies

Table 1. The data of mechanical properties

Sample DGEBA/SGC	Tensile stress (MPa)	Elongation at break (%)	Tensile modulus (MPa)
100/0	70.6	18.5	3993
95/5	66.0	20.5	2145
90/10	64.9	20.7	2283
80/20	48.9	20.9	1154
70/30	26.0	38.5	1832

Figure 7 shows the impact strength of epoxy and the DGEBA/SGC blends. Except the modified DGEBA with 30 wt% SGC, all the DGEBA/SGC blends exhibit higher impact resistance compared to that of neat DGEBA. Among the modified samples, the modified DGEBA with 20 wt% SGC performs the maximum impact strength (280.6 J/m, 4-fold higher than that of the neat epoxy). This phenomenon is caused by the interpenetration of the SGC and flexible side chains in the epoxy matrix, leading to more ductility of the matrix. The decrease in impact strength for the sample containing 30 wt% SGC is due to the aggregation of SGC particles with bigger size as confirmed from the SEM image (Fig. 5d).

Toughening Behavior

The toughness behavior of neat DGEBA and the SGC modified thermosets can be observed by the morphologies by SEM. The fracture surfaces after impact tests were investigated by this technique and the most representative micrographs are shown in Fig. 8 and Fig. 9, respectively. The neat DGEBA thermosets exhibited the smooth glassy fractured surface, as shown in Fig. 8. This indicates brittle fracture of the neat DGEBA, which accounts for its poor impact strength. And all the micrographs of SGC modified DGEBA samples presented a homogeneous appearance without obvious sign of phase separation due to the good compatibility of SGC and DGEBA (Fig. 9). The fracture surface of the modified thermosets with 20 wt% SGC (Fig. 9(b–b2)) is rougher than that of the other modified thermosets, suggesting that the impact specimens break more yieldingly. A higher amount of plastic deformation bands appear in the surfaces of the thermosets when the SGC content is 20 wt%, which helps absorb more fracture energy. Thus, the increase in toughness of DGEBA/SGC thermosetting blends obtained in the present study can be explained by the remarkable plastic deformation of DGEBA. The soft phase SGC interpenetrated in the network of epoxy by acting as stress concentrators under external loading will effectively induce matrix shear yielding under the support of excellent intermolecular specific interactions between SGC and the epoxy network, thus preventing the early destruction of the blends. Because some blends suffer from lower fracture properties due to the serious phase separation and poor interfacial adhesion between

the two components. In the DGEBA/SGC thermosetting blends, there exist the intermolecular specific interactions between SGC and the epoxy matrix, which can enhance the interfacial adhesion. Thus the effect of interfacial adhesion between SGC and DGEBA is supposed to be responsible for remarkable plastic shear yielding of epoxy matrix, ultimately improves the fracture toughness values of the SGC-modified epoxies.

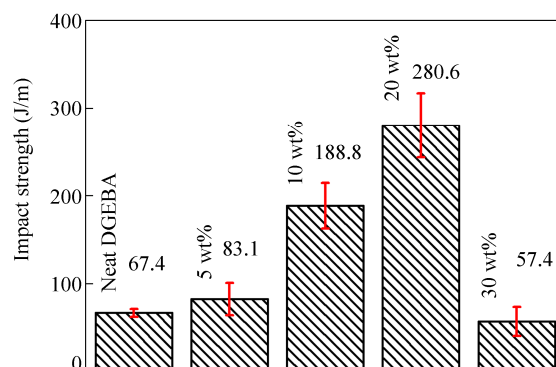


Fig. 7 Impact strength of neat DGEBA and DGEBA/SGC blends with different SGC contents

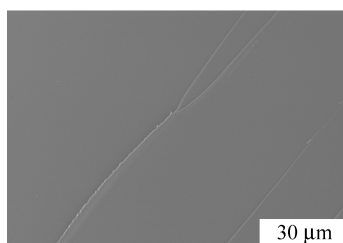


Fig. 8 SEM images of impact-fractured surface of neat DGEBA

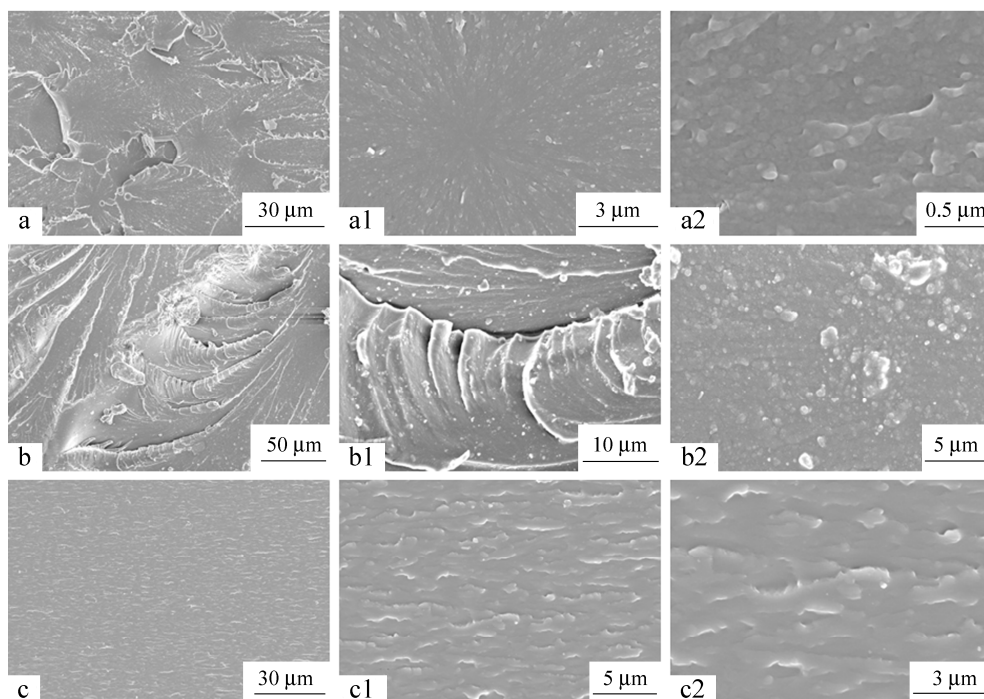


Fig. 9 SEM images of impact-fractured surfaces of DGEBA/SGC thermoset blends: (a–a2): (90/10), (b–b2): (80/20) and (c–c2): (70/30)

CONCLUSIONS

A sliding graft copolymer (SGC) was synthesized to toughen the DGEBA-based epoxy resin using diethyl methyl benzene diamine. The newly synthesized SGC exhibited an attractive molecular structure, in which many linear poly- ϵ -caprolactone (PCL) side chains can slide freely. The thermal behavior, miscibility, curing reaction, morphology and mechanical properties of SGC-modified DGEBA have been systematically studied. The decrease in reaction rate for blending systems is mainly ascribed to the dilution effect by the reduction in the density of the reactive groups. Our results indicate that SGC and DGEBA are miscible due to the intermolecular specific interactions (*viz.* hydrogen bonding) between them, and the semi-crystalline SGC turns to be totally amorphous. The impact strength is improved by 4 times for DGEBA/SGC (80/20) blends compared with that of the unmodified system. The obtained toughening effect of DGEBA by SGC has been attributed principally to the interfacial adhesion between SGC and DGEBA matrix enhanced upon the existence of intermolecular specific interactions, which are supposed to be responsible for remarkable plastic shear yielding of epoxy matrix. In sum, our experimental findings are interesting because it is the first time to employ this novel SGC to toughen epoxy resin. Thus, the data obtained from the present study will be useful for the researchers working in the development of new toughening agents for rigid materials in structural applications.

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