ABSTRACT

A new kind of reactive toughening agent, defined as liquid crystalline polyurethane (LCPB), having both flexible chain and rigid biphenyl mesogenic groups was synthesized by polyaddition of 2,4-toluenediisocyanate (TDI) with diethylene glycol and 4,4'-dihydroxybiphenyl in DMF. The structure and morphology of the LCPB were investigated systematically by Fourier transform infrared spectroscopy (FTIR), differential scanning calorimetry (DSC), wide angle X-ray diffractometry (WAXD) and polarizing optical microscopy (POM), respectively. The POM observation confirmed that the LCPB exhibited nematic texture and good mesophase stability. The LCPB was used to modify the epoxy resin as toughening agents. The mechanical properties, dynamic mechanical behaviour, fracture surface morphology and apparent activation energy \((E_a)\) of the modified systems were systematically investigated. The experimental results revealed that the impact strength of the epoxy resin modified with LCPB reached the highest value of 47.21 kJ/m\(^2\), and it is 1.8 times higher than that of the unmodified system when the content of LCPB loading reached 5 wt%. In addition, the tensile strength and the fracture strength also enhanced with increasing concentration of LCPB. The DMA results showed that the storage modulus in rubbery state and glass transition temperature \((T_g)\) of the modified systems were higher than those of the unmodified system, indicating that the motion of epoxy matrix chains was strongly restricted by the rigidity of mesogenic units, while the \(E_a\) at glassy relaxation process of modified system was about 100-120 kJ/mol higher than that of the unmodified system. The effects of reinforcement on mechanisms of the damaging process of the modified systems were investigated by scanning electron microscopy.

INTRODUCTION

Epoxy resins (EP) are considered as one of the most important classes of thermosetting polymers and are extensively used for their many good properties [1], such as high strength and stiffness, excellent chemical corrosion resistance and electrically insulating properties [2]. Epoxy-based materials are being applied as matrix resins of coatings, adhesives and composites. However, their highly cross-linked structure results in significant brittleness [3-5]. In order to circumvent this toughness problem, impact modifiers are added to epoxy resin in order to produce multiphase blends with improving toughness/stiffness balance [6]. Two types of impact
Modifiers are established: epoxy flexibilizers and epoxy toughening agents. Both are miscible with the uncured epoxy resin and should not deteriorate the low resin viscosity required to afford easy processing. In contrast to flexibilizers, toughening agents improve toughness without sacrificing stiffness and glass transition temperature. The most successful attempt lies in the modification with some reactive liquid rubbers [7-11]. However, the employment of rubbery materials usually leads to significant reductions in the modulus and heat-distortion temperature of epoxy. Recently, high-performance engineering thermoplastics, such as polyethersulfones and polyetherimide [12-15], and liquid crystalline polymers (LCP) as fillers were used to modify epoxy as toughening agents [16]. The experiments indicated that blending LCP with epoxy is an effective toughening method, and besides impact strength, other mechanical properties, like tensile strength and tensile modulus as well as glass transition temperature of epoxy can also be improved [17,18].

Some initial studies have been done on liquid crystalline polymers and epoxy blends, with insufficient literature available on the properties of blends of liquid crystalline polyurethane and epoxy resin [19,20]. In our previous studies [21,22], we described the synthesis of liquid crystalline polyurethanes (LCPU) from 4,4'-dihydroxybiphenyl and 2,4-toluenediisocyanate and used them to modify epoxy resin, mechanical properties, dynamic thermal mechanical properties of LCPU/EP composite. In this work, a new kind of reactive toughening agent containing rigid biphenyl mesogenic groups and flexible chain extender was synthesized to modify the epoxy resin/4,4'-diaminodiphenylsulphone cured system. The rigid mesogenic groups are aimed to keep high modulus and good thermal properties, while the flexible chains are used to improve the toughness [23]. The mechanical properties, morphology of the fractured surface, as well as wide angle X-ray diffraction of the modified systems were investigated. The activation energy (E_a) of a glass transition can also be accomplished by making multiple frequency measurements of the loss modulus peak across the temperature range of the transition.

**EXPERIMENTAL**

**Materials**

4,4'-Dihydroxybiphenyl (>98% purity) and 2,4-toluenediisocyanate (2,4-TDI, >99% purity) were obtained from Shanghai Chemical Reagents Company, China, and used as received without further purification. Diethylene glycol (>98% purity) was purchased from Nanchang Chemical Factory, China. N,N'-Dimethylformamide (DMF) was distilled before use. The epoxy resin used in this study was diglycidyl ether of bisphenol A (DGEBA, E-51, epoxy value: 0.51, supplied by Yueyang Chemical Plant, China, without further purification. 4,4'-Diaminodiphenylsulphone (DDS) purchased from Shanghai Chemical Reagent Company, China, with a molecular mass of 248.31 and purity >96% according to the supplier.

**Synthesis of Liquid Crystalline Polyurethanes Containing Biphenyl Group**

Liquid crystalline polyurethane having biphenyl group (LCPB) was prepared by polyaddition reaction of diethylene glycol with 2,4-TDI and 4,4'-dihydroxybiphenyl. A typical method was as follows: 5.0 g (0.027 mol) 4,4'-dihydroxybiphenyl and 9.4 g (0.054 mmol) TDI dissolved in 20 mL DMF were added dropwise into the reactor. The reaction mixture was stirred for 60°C, and the yellow solution was obtained. Then, 2.85 g (0.027 mmol) diethylene glycol was dropped into the above solution, which was stirred at 85°C for 6 h. The resulting precipitate was washed three times with distilled water and recrystallized from ethanol, and the polymers were dried in vacuo at 60°C. Its molecular structure is shown in Scheme I.

**Curing Procedures**

A mixture of epoxy resin (E-51), DDS and LCPB was degassed in vacuum at 120°C for about 1 h. The resulting mixture was then cast into a preheated mould coated with silicone resin. All samples were cured at 120°C for 2 h, 160°C for 2 h and 180°C for 2 h. The content of LCPB was calculated based on the amount of the epoxy resin.
Measurements
Fourier transform infrared spectroscopy (FTIR) was recorded between 4000 and 400 cm⁻¹ on a Perkin-Elmer 1710 spectrophotometer using KBr pellets at room temperature.

The differential scanning calorimetry (DSC) test was carried out with a Netzsch differential scanning calorimeter (model DSC-204) at heating and cooling rates of 10°C/min under flowing nitrogen, and the temperature rose from 40 to 250°C.

The optical textures were obtained by a Leica DMxRP polarizing microscope (magnification: 200×).

The wide angle X-ray diffraction (WAXD) analysis was performed using a type/Brucker-AXS D8ADVANCE X-ray diffractometer equipped with a computer controller. The measuring conditions were: wavelength, 1.540 Å; start angle, 5°; stop angle, 50°; scanning speed, 4°/min.

The impact strength was measured on a tester, XJJ-5, with no notch in the specimen, according to China National Standard GB1043-79. The specimen was with a thickness of 4 mm and width of 10 mm and length of 80 mm. The tensile strength was examined on an electron omnipotence tester of type RGT-5. The tensile rate was 2 mm.min⁻¹ based on China National Standard GB1040-92. All the final results are average of five specimens.

Thermomechanical properties, modulus and glass transition temperatures were determined using a linear rheometer (Q800 dynamic mechanical analyzer, was made with a TA instruments) in a three point bending, at a frequency of 1.0, 3.0, 5.0 and 10.0 Hz from 30°C to 250°C at a heating rate of 3°C/min, respectively.

The morphology of the fracture surfaces was observed by a scanning electron microscope (SEM: JSM-6380LV, Japan) at an accelerating voltage of 20 kV, and the surface was coated with a thin layer of carbon powder to reduce charge built up on the surface and improve conductivity.

RESULTS AND DISCUSSION

Characterization of the Products
The FTIR analysis is widely utilized to study the hydrogen (H)-bonding of polyurethanes [24,25]. Figure 1 shows the FTIR spectra of LCPB and LCPB-modified epoxy resin recorded at 25°C. LCPB is composed of a mesogenic core of biphenyl ring and a flexible chain and diisocyanate moieties. As it is shown in Figure 1a, LCPB presents the characteristic band of C=O stretching vibration at 1736 and 1674 cm⁻¹, two absorption bands appear at ≈2967 and 2852 cm⁻¹, which are assigned to the asymmetric and symmetric stretching vibrations of CH₂. The peak at 3364 cm⁻¹ may be assigned to free NH groups [26]. Figures 1b-1c are the FTIR spectra of (b) LCPB-modified epoxy and (c) the neat epoxy resin. The wide absorptions due to -OH groups of epoxy resin at 3456 and 3448 cm⁻¹ [27], and the absorptions peak at ~915 cm⁻¹ in (b) were disappeared after the curing.
reaction, the results show that epoxy resin is being cured completely.

DSC is extensively used for investigating the curing reaction of thermoset polymers [28]. Figure 2 shows DSC heating and cooling thermograms for the LCPB sample at a scanning rate of 10°C/min. In both first heating and second cooling processes, two phase transition peaks are evidently observed [29], the crystalline melting temperature (T_m) of the LCPB sample was 173°C and its isotropic temperature (or clearing temperature, T_i) was about 214°C. LCPB exhibits a nematic mesophase between T_m, 173°C, and, T_i, 214°C. The phase behaviour of the LCPB sample is shown in Figure 3. It can be seen that nematic phase was found to appear between the two peaks in each process by an optical polarizing microscope. Therefore, the two endothermic peaks are ascribed to the crystalline-nematic and nematic-isotropic phase transitions in the order of increasing temperature.

Figure 4 represents the wide-angle X-ray scattering patterns of LCPB and LCPB-modified epoxy. From Figure 4a, it can be seen that LCPB possesses high crystallinity, whose diffraction patterns show a series of sharp peaks at 20~30°C [30,31]. The sharp diffraction peaks are indicative of the presence of crystallites in the LCPB. Figure 4b shows the WAXD patterns of the LCPB-modified epoxy. The analysis of the pattern indicates that, it is possible to conclude that the curve of the LCPB-modified epoxy is almost analogous. It has a broad amorphous peak, the contact angles of the peaks are around 2θ ranging between 10° and 30°, which show that LCPB-modified epoxy resin curing networks, is incorporated through the covalent bond and hydrogen bond.

**Mechanical Properties**

The most common approach used to enhance the toughness of epoxy resins is to add a softer second phase or rubber phase into the epoxy resin [32]. The dispersed rubber phase plays an important role in the toughness improvement of the material. Rubber particles, by acting stress concentrators, allow the matrix between the particles to undergo both shear...
and craze deformations. In this study, LCPB contains the chain-extended urea and rigid mesogenic units which act as a softer second phase and stress concentrators. The effect of LCPB modification on the mechanical strength is listed in Table 1. All modified systems achieved even more superior impact strength compared to neat resin system. Especially, by presence of 5 wt% of LCPB contained in the curing system, the impact strength of cured material is 47.21 kJ/m²; that is 1.8 times higher than that of the neat epoxy resin (26.26 kJ/m²). However, when it exceeds 5 wt% to maximum 7 wt%, the impact strength declines a little, yet it is still higher than the unmodified system. The toughening mechanism can be explained in terms of morphological behaviour because the morphological examination can give interesting information on the microstructure of the cured resins. Figure 5 shows the impact fracture surface of the cured system. From Figure 5a, one can see the smooth glassy fractured surface with crack in different planes in case of unmodified system. This is an indication of brittle fracture of the unmodified epoxy network, which accounts for its poor impact strength. As for the modified systems shown in Figures 5b-5d, which indicate tough fracture, the fracture surface in Figure 5b shows branches and appears rougher than the unmodified system; and its impact strength is considerably improved. Fracture surfaces of Figure 5c present large and deep cavities, which are generally the characteristics of rubber-modified epoxy resins. These cavities represent the initial position of the rubber particles, which are pulled out or broken during the fracture process. This ductile fracture was a result of absorption of crack energy in inhomogeneity phase. LCPB was the origin to form anisotropic microfibril during curing, and microfibrils acted as bridge combining both sides of the cracks to induce crazing and transmit load, and led to some plastically deformed materials. The results show that rough appearance on the fracture surface played an important role in improving the impact strength.

Table 1 shows the variation of tensile strength and tensile modulus with liquid crystalline polymer content for the modified systems. The results demonstrate that the tensile strength of the liquid crystalline epoxy resin was higher than that of the unmodified system. This shows that the introduction of a mesogen group into the epoxy resin backbone structure could effectively improve the bonding strength of the epoxy resins. Improvement in tensile properties of the epoxy resin/LCPB blends is due to the fact that the compatibility between the LCPB phase and matrix is enhanced by the addition of soft segments. However, the tensile modulus results showed no significant difference for both materials and were possible due to the introduction of LCPB soft segments into the epoxy matrix. When LCPB was introduced in a ratio larger than 3 wt% into the EP/LCPB copolymer system, the mechanical strength and modulus decreased due to the introduction of more LCPB soft segments.

Dynamic Mechanical Behaviour
The dynamic mechanical properties between 50°C and 250°C for the modified curing systems were investigated by using a Rheovibron dynamic viscoelastomer at a heating rate of 3°C/min and a
frequency of 1.0 Hz.

Figure 6 shows the storage modulus of the curing system modified by LCPB. It can be seen that below 130°C, the storage modulus of the modified curing systems was approximately equal to the unmodified sample. Generally, dynamic modulus would be decreased with the addition of a flexible chain spacer. By increasing temperature, the storage modulus of the modified system appears much higher than that of the unmodified system. This indicates that the motion of epoxy matrix chains is strongly restricted by the rigidity of mesogenic units, which are intended to retain high dynamic modulus and thermal properties of the cured resin. These are rigid units that play a great role in maintaining the high modulus properties of the cured epoxy resin or enhancing the high dynamic modulus of epoxy resin modified by the LCPB toughening agents.

Figure 6. Modulus vs. temperature for EP/DDS/LCPB curing systems: (a) EP/DDS = 100/30, (b) EP/DDS/LCPB = 100/30/2, (c) EP/DDS/LCPB = 100/30/5 and (d) EP/DDS/LCPB = 100/30/7.
Figure 7 shows the tanδ plots of four different LCPB content material specimens as function of temperature. It is observed in Figure 7 that all spectra of cured systems exhibit a transition peak [33]. Compared with the unmodified system, the temperature range of $\alpha$-relaxation for the modified system has gradually shifted to higher temperature increases with respect to increasing frequency. The $\alpha$-relaxation was the contributory factor in the rigidity of mesogenic units in cured epoxy resins network. From the above results, it can be inferred that the LCPB toughening agent has been incorporated into the tight epoxy resin network and has led to the formation of a one-phase microstructure in the modified systems, which contributed to the improvement of impact strength. This could also be confirmed further by impact tests and SEM observation.

**Activation Energy of $T_g$ Relaxation of Curing Process**

A typical Arrhenius plot, log $f$ versus $1/T_g$ absolute temperature yields activation energy ($E_a$) for the $T_g$ relaxation process [34]. Activation energies of four epoxy materials were calculated from the slopes $-E_a/R$ of each plot. Figure 8 is the Arrhenius plot of log $f$ versus $(1/T_g)$ of specimens containing 0, 2, 5 and 7 wt% LCPB, respectively, yielding activation energies ($E_a$) of 363.1, 473.4, 483.9 and 471.4 kJ/mol for the glassy relaxation processes. Coefficients of regression (R) for four specimens are all larger than...
Figure 8. Arrhenius plots of specimens: (a) EP/DDS = 100/30, (b) EP/DDS/LCPB = 100/30/2, (c) EP/DDS/LCPB = 100/30/5 and (d) EP/DDS/LCPB = 100/30/7.

0.98. The \( E_a \) of the modified system was higher than the \( E_a \) of the unmodified system. This is an indication of the interaction between LCPB and epoxy matrix, which greatly impedes the chain mobility in epoxy resin. It is, therefore, noticed that \( E_a \) of the modified system is about 1.3 times that of unmodified system.

CONCLUSION

A new kind of reactive toughening accelerator containing both flexible chain and rigid biphenyl mesogenic groups was synthesized and used to modify epoxy resin E-51/DDS system. The liquid crystalline properties, mechanical properties, dynamic mechanical behaviour and fracture surface morphology of the modified systems were systematically investigated. From experimental results, the following conclusions are obtained:

- The LCPB can act as an effective toughening modifier for the epoxy resin. The impact strength of the cured system modified with LCPB is 1.8 times higher than that of the unmodified system, while the high modulus and good thermal properties are being maintained.

- The linear relationship between \( \log f \) and \( 1/T_g \) was observed and glassy relaxation activation energy of the specimen with different LCPB contents was calculated. The specimen with 5 wt% LCPB has the \( E_a \) value about 1.3 times higher than that of the unmodified system.

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