Preparation and Characterization of Epoxidate Poly(1,2-butadiene)–Toughened Diglycidyl Ether Bisphenol-A Epoxy Composites

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ABSTRACT: By the oxidation of liquid poly(1,2-butadiene) (LPB) with H_2O_2/HCOOH, epoxidate poly(1,2-butadiene) (ELPB) was obtained as a toughening agent to prepare diglycidyl ether bisphenol-A (DGEBA) epoxy composites by using V115 polyamide(PA) as a cross-linking agent. DGEBA, ELPB, and the composites were effectively cured by PA at 100°C for 2 h followed by postcuring at 170°C for 1 h. Thermal gravimetric analysis results in air and nitrogen atmosphere showed that the thermal stability of composites could be improved by the addition of ELPB. Compared with DGEBA/PA, the composites exhibited a decrease in strength at yield but an increase in strain at break with the increase in ELPB amount. The composite with 10% ELPB exhibited both thermal stability and tenacity superior to those of DGEBA/PA and composites with 5 and 20% ELPB, respectively. The improvements in thermal and me-

chanical properties of composites depended on the formation of Inter Penetrating Networks (IPN) among DGEBA/PA/ELPB and their distributions in the matrix. At an appropriate ELPB amount, the IPN, mostly made of DGEBA/PA/ELPB, may be distributed more evenly in the matrix; less ELPB resulted in the formation of IPN mainly made of DGEBA/PA; excessive addition of ELPB resulted in the local aggregation of ELPB/PA and phase separations. The toughening mechanism was changed from chemically forming IPN made of DGEBA/PA/ELPB to physically reinforcing DGEBA/PA by ELPB/PA with the increase in ELPB addition. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 113: 3165–3170, 2009

Key words: epoxy composites; epoxidate polybutadiene; toughness; thermal properties

INTRODUCTION

Epoxy resins have been widely used as coatings, adhesives, and electrical or electronic materials in various industrial fields because of their superior mechanical, thermal, and electrical properties. However, their expansion in industry was restricted by their inherent brittleness. Hence, various attempts were used to improve their toughness by adding some engineering materials, such as carbon nanofiber, nano-clay, polystyrene, and so on.[1–6]

Among these methods, the addition of rubber particles was proved to be one of the most effective ways in enhancing the toughness of epoxy resins.[7–9] The composites of epoxy cresol novalac (ECN) resin modified by liquid carboxyl terminated butadiene acrylonitrile (CTBN) exhibited improvement in tensile, flexural, and impact strength up to 10% of CTBN.[7] By using hydroxyl terminated polybutadiene (HTPB) as a surface modifier in carbon fiber to reinforce the epoxy matrix composites, the HTPB formed

a flexible interface between CF and epoxy matrix so that the mechanical behavior of the system could be improved.[8] The tensile strength and impact toughness values could be improved in the DGEBA matrix with HTPB (1%) as a toughening agent.[10] Besides the toughening agents, the most frequently used curing agents like amines also played an important role in determining the toughness of epoxy.[11–14] Some low molecular weight polyether diamines were used to increase the toughness of epoxy resins; the epoxy cured by these diamines still exhibited obvious ductility even at a cryogenic temperature.[11] Polyamide such as PA66 was considered another kind of curing agents in preparing epoxy composites, but its toughening effect was strongly dependent on the curing temperature, curing time, and fillers used.[14]

However, with the improvement in toughness of epoxy composites by adding rubbers or amines, their thermal properties both in stability and glass transition temperature (T_g) were found decrease significantly. Therefore, some engineering plastics, such as poly(ether imide), poly(ether ketone), poly(ether sulfone), etc., were often used in toughening the epoxy resins.[15–17] DGEBA epoxy resins modified with different contents of SPES exhibited increase in the glass T_g
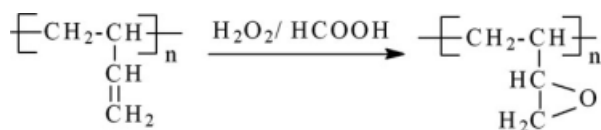
Figure 1 Synthetic schematic plot of epoxide liquid poly(1,2-butadiene) (ELPB).

and fracture toughness with the in increase in SPES content due to the improved intermolecular interactions.[2] Hybrid polymer networks (HPNs) based on unsaturated polyester resin (UPR) and epoxidized phenolic novolac (EPN) resins also showed considerable enhancement in tensile strength, toughness, and thermal stability.[18]

Polybutadiene (PB) was used directly or modified with functional end groups as a toughening agent to make epoxy composites; however, since the existence of fewer functional groups in PB, the toughening mechanism was considered as physical reinforcements, and the phase separation always existed in the composites.[7–9] In this paper, liquid poly(1,2-butadiene) was oxidized to form abundant epoxy groups in its side chains and was used as a toughening agent to make DGEBA epoxy composites. Their structures, thermal stability, tensile properties, and morphology were measured by Fourier transform infrared spectroscopy (FTIR), stress–strain test, thermal gravimetric analysis (TGA), and scanning electron microscopy (SEM).

EXPERIMENTAL

Materials

Materials included diglycidyl ether of bisphenol-A (DGEBA) (D.E.R.332, from Dow Chemical, USA) used as received, polyamide (V115 with amino value of 250 mg KOH/g, from Cognis Chemicals, Germany) used as received, butyl glycidyl ether (BGE) (95%, from Aldrich), liquid poly(1,2-butadiene) (LPB) (terminated by toluene, $M_n = 1020$, from Yanshan Petrochemical, China) used as received, toluene (>99%, from Beijing Chemical Agent, China) distilled before use, anhydrous formic acid (from Beijing Chemical Agent) used as received, and hydrogen peroxide (30% in water, from Beijing Chemical Agent) used as received.

Preparation of epoxidate liquid poly(1,2-butadiene)

One hundred grams of LPB, 350 mL toluene, and 30 mL anhydrous formic acid were put in a 1000-mL, three-necked flask with a mechanic stirrer was then immersed in a water bath, and the mixture was stirred for 15 min. When the temperature reached 50°C, 200 mL hydrogen peroxide was dropped into the flask within 2 h and the mixture was stirred continuously for another 3 h at 50°C. Viscous ELPB with

an equivalent weight of 280 was obtained after the mixture was washed by deionized water for three times followed by vacuum drying at 40°C for 2 h. The synthesis scheme is depicted in Figure 1.

The successful preparation of ELPB from LPB by oxidization can be confirmed by FTIR spectra as shown in Figure 2. The strong peak that appeared at around 910 cm^{-1}, which represented the C—O—C stretching of the epoxide groups, indicates the successful oxidation from LPB to ELPB.[19]

Preparation of the DGEBA/ELPB composites cured by PA

DGEBA was added in a beaker followed by the addition of BGE as diluents so that the reactants could be mixed as homogenously as possible. Under mechanical stirring at 300 rpm, 5%, 10%, and 20% (w/w %) ELPB of DGEBA was separately added into the beakers, and after 15 min stirring, different amounts (calculated based on the epoxide equivalent weight of DGEBA plus ELPB) of polyamide with amine value of 250 were added into the corresponding beakers and stirred continuously for another 5 min. Afterwards, the mixtures in the beakers were transferred into aluminum foil molds to obtain casting samples. The mixtures in the molds were cured at 100°C for 2 h. Finally, the samples were postcured at 170°C for another 1 h to obtain a few samples with approximate size of 20 cm × 2 cm × 0.5 cm (length × width × thickness) for mechanical measurements.

Characterizations

Fourier transform infrared spectroscopy: the liquid sample (LPB and ELPB) was diluted in toluene with analytical grade to make a solution of 1% (by weight) and then the solutions were dropped on KBr pellets. The cured epoxy composites were mixed with KBr directly and then pressed into pellets. The transmittance spectra of the liquid
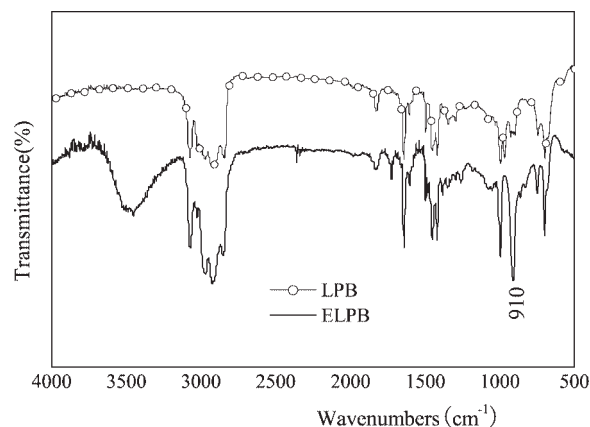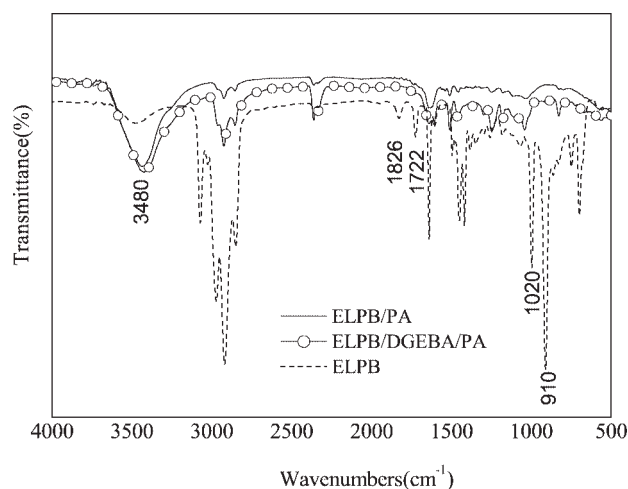

Figure 2 FTIR spectra of LPB and EPLB.

Figure 3 FTIR spectra of ELPB, ELPB cured by PA, and composite with 20% ELPB cured by PA.

Figure 4 TG in air for DGEBA and composites with 5% (5ELPB), 10% (10ELPB), and 20% (20ELPB) ELPB cured by PA.

samples and composites were recorded by using EOUINOX55 spectrophotometer (Bruker) from 500 to 4000 cm^{-1} with a resolution of 1 cm^{-1}.

Thermal gravimetric and DTG analysis: Thermo gravimetric analyses were performed with the thermo gravimetric analyzer WRT-2C (Beijing Optical Instrument, China) from 50 to 800°C in the air and nitrogen atmosphere at a heating rate of 5°C/min, and 10 mg of each sample was loaded into the ceramic crucible.

The tensile (stress–strain) test: the above postcured samples were cut into dumbbell shape and their surfaces were then polished for the stress–strain test. The tensile test was performed by using the computer-controlled Universal electronic material mechanical tester RG-3000A (Shenzhen Mechanical Instrument, China) under a 10 kN load cell with a crosshead speed of 2 mm/min at room temperature.

Scanning electron microscopy: the morphology of the fractured surfaces after tensile test was examined by JSM-6700F scanning electron microscope (JEOL). The fracture surfaces of specimens were coated with gold by using a JFC-1100 ion sputterer at 10 kV and 10 mA for 3 min before examination.

RESULTS AND DISCUSSION

FTIR spectra of ELPB, ELPB/DGEBA cured by PA

Figure 3 shows the FTIR spectra of ELPB, ELPB cured by PA, and composite with 20% ELPB cured by PA, respectively. The peak with greatly enhanced strength at 3480 cm^{-1} was assigned to the hydroxyl group resulted from the ring opening of epoxide group and possibly less of amine end group. After curing, the disappearance of peak at 910 cm^{-1} indicates the sufficient reaction of epoxy with amine end group or amide groups in PA[19,20]; this revealed that both the epoxy groups of ELPB and DGEBA in the composite
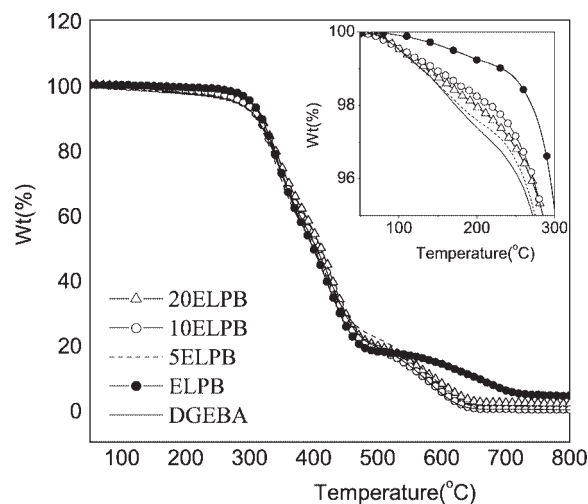
could be effectively cured. In such a case, there are three possible interactions to form Inter Penetrating Networks (IPN) made of ELPB/PA, DGEBA/PA, and DGEBA/PA/ELPB, respectively.[21–25] Therefore, the performances of the composites were determined by these IPN structures in the matrix, depending on the initial proportions of the materials added.

Thermal stability studies

The thermal degradation behaviors of ELPB, DGEBA, and composites in air with ELPB variations cured by PA were studied by TG and DTG analysis, as shown in Figures 4 and 5, respectively. As observed in Figure 4, at weight loss less than 5%, ELPB/PA and all the composites showed higher thermal decomposition temperature than that of DGEBA epoxy; this could be
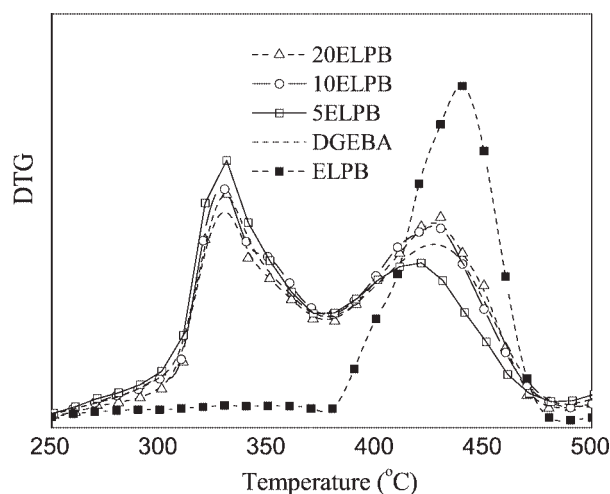

Figure 5 DTG in air for DGEBA and composites with 5% (5ELPB), 10% (10ELPB), and 20% (20ELPB) ELPB cured by PA.
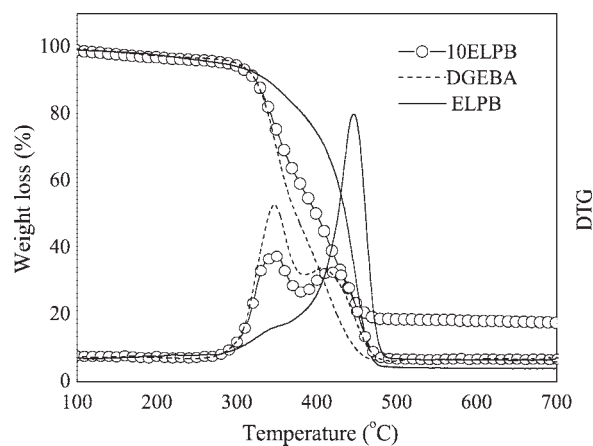
Figure 6 TG and DTG in N_2 for DGEBA, ELPB, and composite with 10% (10ELPB) cured by PA.

attributed to the easier movement of low molecular ELPB during heating and hence providing assistance to the formation of IPN structures made of ELPB/PA and ELPB/PA/DGEBA.[26] The composite with 10% ELPB exhibited higher thermal decomposition temperature than that of the other two composites, indicating that only in a certain range of ELPB amount in the matrix, the IPN structure made of DGEBA/PA/ELPB could be perfectly formed and evenly distributed. In other words, excessive ELPB may result in local aggregation of ELPB/PA, and the IPN structures were most separately formed as DGEBA/PA and ELPB/PA, whereas insufficient ELPB may result in IPN mainly made of DGEBA/PA with only a trivial amount of DGEBA/PA/ELPB. In either case, the thermal stability decreased.

In Figure 5, the initial rapid decomposition temperature for DGEBA/PA and composites appeared at around 330°C, representing the fast decomposition of most side chains in the composites, whereas the second rapid decomposition temperatures appeared at around 400°C, indicating the fast decomposition of main chains in the composites. These two temperatures of composites were always higher than those of DGEBA/PA. However, ELPB cured by PA exhibited slow decomposition speed until a rapid decomposition at about 430°C. These DTG results in air demonstrated that by the addition of ELPB, the decomposing speed of the composites could be slowed down.

To understand the thermal behavior of the composites further, ELPB/PA, DGEBA/PA, and the composite with 10% ELPB were run in N_2 atmosphere. Their TG and DTG curves are shown in Figure 6. At temperatures lower than 300°C, all the samples showed no obvious difference in both weight loss and decomposition speed; however, at temperatures higher than 300°C to around 480°C, DGEBA/PA exhibited higher weight loss and faster decomposing speed than those of ELPB/PA and the composite.

Furthermore, the composite showed much higher residue than those of the other two samples; this may be due to the formation of some stable compounds during the decomposition of IPN made of ELPB/PA/DGEBA.[27] These thermal analyses in N_2 provided further evidence that the thermal stability of the composites could be improved if IPN made of ELPB/PA/DGEBA could be formed in the composite by the proportional addition of ELPB.

Compared with other modified polybutadiene rubbers resulting in a decrease in thermal stability in toughening epoxy,[7–10] epoxidate liquid poly(1,2-butadiene) brought about great enhancement in the thermal stability for these epoxy composites; this could be attributed to its abundant epoxy groups in the ELPB side chains and hence robust IPNs made of DGEBA and ELPB via PAA could be formed in the toughed composites.

Tensile properties

The strength–strain curves of DGEBA/PA, and its composites with 5, 10, and 20% ELPB, respectively, are shown in Figure 7; their strengths at yield and strains at break are listed in Table I. Their strengths at yield exhibited a trend of DGEBA/PA > 10% ELPB composite > 5% ELPB composite > 20% ELPB composite, whereas the tensile strains at break were in the following order: 10% ELPB composite > 20% ELPB composite > 5% ELPB composite > DGEBA/PA. The decrease in tensile strength could be attributed to the less robust structure of linear main chain in ELPB than that of benzene ring in DGEBA, whereas the increase in tensile strain could be due to the easier movement of linear chains in ELPB than that of the benzene ring in DGEBA[28]; however, compared with other polybutadiene toughened
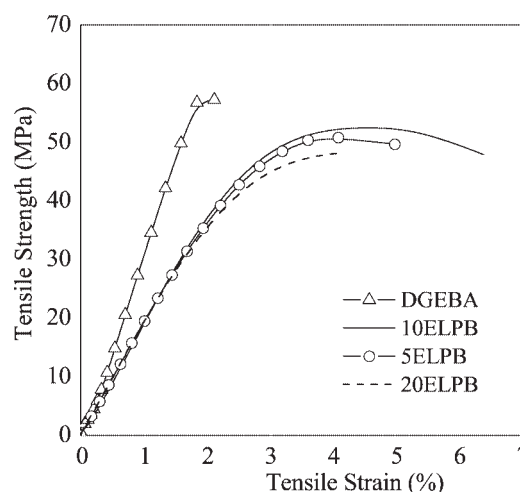

Figure 7 Tensile strength–strain for DGEBA and composites with 5% (5ELPB), 10% (10ELPB), and 20% (20ELPB) ELPB cured by PA.

TABLE I
TABLE I
Tensile Strengths at Yield and Strains at Break for DGEBA and Composites with 5% (5ELPB), 10% (10ELPB), and 20% (20ELPB) ELPB Cured by PA

Samples	Strength at yield (MPa)	Strain at break (%)
DGEBA	58.66	1.85
5ELPB	49.82	5.48
10ELPB	52.65	6.51
20ELPB	47.16	4.23

epoxy composite,[7–9] their lesser extent of decrease in strength suggested the robust IPN formation between DGEBA and ELPB via PA. The composite with 10% ELPB exhibited tensile stress and strain superior to those of the other two composites; this could be attributed to the formation of IPN made of ELPB/PA/DGEBA and its even distribution in the composite. As such, it was possible to achieve a balance so that the enhancement in tensile strain with no decrease in strength could be realized if the amount of ELPB was properly controlled.

Above all, the toughening function of ELPB in DGEBA was considered changing from chemical to physical toughness with the increase in ELPB addition.[6,29] If less ELPB was added, the composite was chemically toughened by the formation of IPN made of ELPB/PA/DGEBA; if an excessive amount of ELPB was added, ELPB/PA could be separated from the curing systems as a second phase; the composite was mainly toughened by physical reinforcement like other rubbers.[7–11]

SEM micrographs

The above conclusions could be confirmed by SEM measurements. The SEM images of the fractured surfaces for the samples of DGEBA/PA and its composites at 5, 10, and 20% ELPB, respectively, are shown in Figure 8. The fracture surface of DGEBA epoxy resin curing by PA [Fig. 8(a)] showed a single phase with typical characteristics of brittle fracture.[2,11] Whereas the fracture surface of the composites had ridges, fiber-like tortuous fracture for 5% ELPB [Fig. 8(b)] and 10% ELPB [Fig. 8(c)] composites were obviously different from that of DGEBA epoxy resins [Fig. 8(a)]; ELPB/PA was evenly dispersed in the matrix resin. Some larger particles that appeared in Figure 8(d) revealed that excessive ELPB aggregated to form particles as a second phase.[11] This demonstrated that the toughening function of ELPB
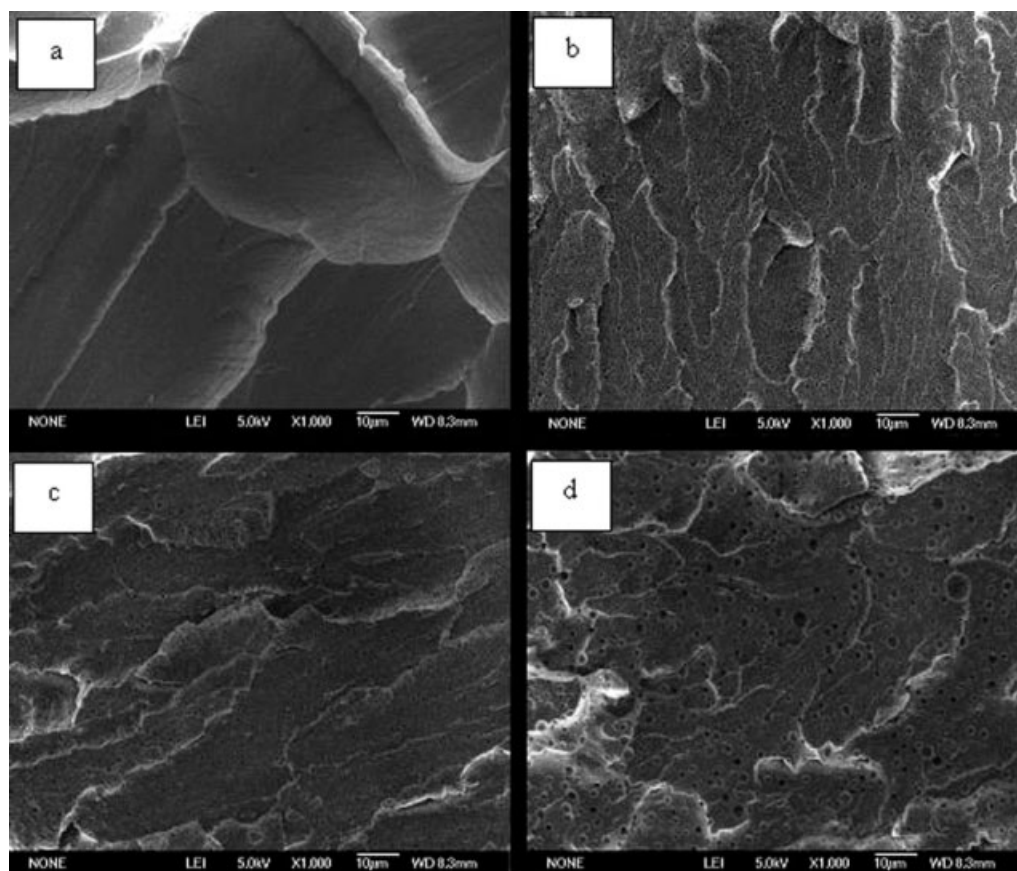

Figure 8 SEM micrographs of the fracture surface for DGEBA (a) and composites with 5% ELPB (b), 10% ELPB (c), and 20% ELPB (d) cured by PA.
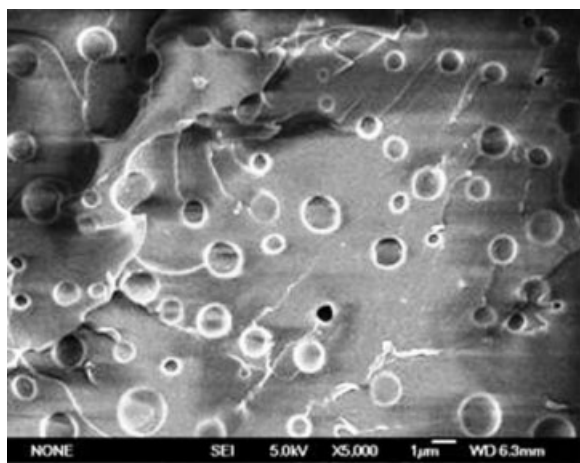
Figure 9 SEM micrograph of the fracture surface with crack formation for composite with 30% ELPB cured by PA.

changed from a chemical network to physical reinforcement, with an increase in ELPB amount.

The typical morphology of the physical reinforcement of rubber to epoxy was observed from the fracture surface of the composite with 30% ELPB, as shown in Figure 9, where the crack was observed around the particles.[2] In this phase, separated morphology, the dispersed ELPB/PA particles acted as stress concentrators to absorb the external energy. When cracks occurred, the progress of the cracks could be prevented by the particles. In this case, the toughness was due to the depression of the crack growth with the formation of the branches.[3,5] However, with the increase in particle size because of the ELPB addition, the crack growth could not be prevented as late as possible; the decrease in strain would be unavoidably aggravated, and this was the case for the composites containing ELPB from 10 to 20%, as observed in Figure 7.

CONCLUSIONS

The DGEBA epoxy composites were successfully prepared by using ELPB as a toughening agent and PA as a cross-linking agent. The disappearance of epoxy group and strength enhancement of hydroxyl group after curing suggested that the curing conditions were appropriate to obtain an effectively cured composite system. The improvements in thermal stability and mechanical strain were attributed to the formation of IPN between DGEBA and ELPB via PA. The composite with 10% ELPB exhibited higher thermal and mechanical properties than those of DGEBA and composites with 5 and 20% ELPB, indicating that the types and amount of IPN formed in the composites were dependent on the amount of ELPB added. The toughening mechanism was a trend from chemical to physical toughness with the increase in ELPB amount, and the ELPB/PA would aggregate to form particles as a second phase if excessive ELPB was added.

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