

Mechanical and Tribological Properties of Epoxy Modified by Liquid Carboxyl Terminated Poly(butadiene-co-acrylonitrile) Rubber

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ABSTRACT: Diglycidyl ether of bisphenol A (DGEBA)-based epoxy resin was modified using liquid carboxyl-terminated poly(butadiene-co-acrylonitrile) (CTBN) rubber. The liquid CTBN contents used ranged from 2.5 to 20 parts per hundred parts of resin (phr). Mechanical properties of the modified resins were evaluated and the microstructures of the fracture surfaces were examined using SEM technique. The changes in storage modulus and the glass transition temperature were also evaluated using dynamic mechanical analysis (DMA). The tribological tests were performed using a ball-on-disc tribometer. The worn surfaces and the ball counter-mates after tribological tests were investigated using optical microscope technique. The results revealed the influence of liquid CTBN content on mechanical and tribological

properties, and also microstructure of the modified epoxy resins. Impact resistance increased whereas the storage modulus and the hardness decreased when the CTBN rubber was introduced to the epoxy network. The coefficient of friction of the CTBN-modified epoxy was lower than that of the neat epoxy. The CTBN content of lower than 10 phr was recommended for improving the wear resistance of epoxy resin. Changes in tribological properties of the CTBN-modified epoxy correspond well to those in mechanical changes, especially the toughness properties. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 125: 361–369, 2012

Key words: thermosets; toughness; mechanical properties; rubber-modified epoxy resin; tribological properties

INTRODUCTION

Epoxy resin is one of the thermoset polymers that crosslink when mixed with a catalyzing agent or a hardener. Because of the highly crosslink character, the neat epoxy resin generally exhibits many favorable properties including high modulus, relative high-chemical resistance, high-temperature performances, good adhesion, and bonding characteristics.^{1–3} Besides, epoxy performs the ease of manufacturing with additives and has a lower price as compared to other advanced polymers such as poly(ether ether ketone) (PEEK) and polyimide (PI).⁴ These all make it one of the most extensive uses in tribological studies.^{5–14} However, the crosslinking structure of epoxy is known to inhibit the effectively transfer-film formation, which is one of the key for producing materials with low coefficient of friction.¹⁴ Moreover, the neat resin is rela-

tively brittle and has poor resistance to crack initiation and growth, resulting in a poor wear resistance. Therefore, almost all the epoxies used as high-performance resins for many industrial applications are modified by adding other materials to make toughened epoxy resins or to make reinforced epoxy composites.

Several methods^{15–35} have been proposed to increase the toughness of epoxy resins. One of the most successfully methods involves the addition of modified reactive rubbers, e.g., carboxyl-terminated butadiene acrylonitrile copolymer (CTBN)^{15–23} the amine-terminated butadiene acrylonitrile copolymer (ATBN),^{19,24} acrylic rubber,^{25,26} and hydroxyl terminated polybutadiene (HTPB),^{27,28} to the uncured epoxy resin and controlling the reaction to obtain the rubber particles dispersed in the polymer matrix. Kunz and Beaumont¹⁵ found the improvement in toughness and mechanical properties of CTBN rubber-modified epoxy resins in the temperature range -20 to $+110^{\circ}\text{C}$. Kinloch et al.^{16,17} found that the toughness of CTBN-modified epoxy resins increased, but the modulus and yield strength decrease slightly with volume fraction of the dispersed rubbery phase. Bartlet et al.¹⁸ found that the impact strength behavior of epoxy networks enhanced with the reactive rubber (CTBN), but it exhibited the optimum for 15% CTBN.

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The size and the distribution of rubber particles were reported to strongly influence the impact resistance of final products.^{19,29,30} Kunz and Beaumont¹⁹ compared the morphology and toughness of CTBN and ATBN-modified epoxy resins. They found that ATBN-modified epoxies had a diffuse-appearing interface between the dispersed rubber phase and the epoxy matrix, in contrast to the sharp boundaries of CTBN particle interfaces. However, both rubbers produced essentially identical toughness values.

It has been reported in the literatures^{20,22,29,33} that the rubber particles could increase toughness by activating cavitation, inducing crack bridging and promoting shear yielding of the matrix. Pearson and Yee²⁹ explained that the toughening mechanisms of rubber-modified epoxies involved both cavitation, which relieved the triaxial tension at the crack tip, and shear band formation, that created a large plastic zone. Besides, the compatibility between rubber and epoxy phases was reported to strongly affect the toughening behavior of the rubber-modified epoxy resins.^{22,27} Chen and Jan²² found that the fracture energy of the CTBN-modified epoxy resins significantly increased if the rubber/matrix interfacial interaction was enhanced by encapping CTBN with the flexible diglycidyl ether of propylene glycol. They suggested that the interaction between cavitation and localized shear yielding should be accounted for toughening mechanism of rubber-modified epoxy resin. Ozturk et al.²⁷ performed the addition of silane coupling agent (SCA) to enhance the interaction between HTPB and epoxy matrix. They found the improvement in tensile strength and plastic deformation of the epoxy systems by pre-reacting HTPB with SCA and hardener. Thomas et al.²⁸ investigated the miscibility, thermal and mechanical properties of epoxy resins toughened with liquid HTPB. They found that the maximum impact properties were observed as the amount of liquid HTPB was 10 parts per hundred (phr), but the poor flexural and other mechanical properties were found due to the inclusion of rubber. Tripathi and Srivastava³² modified the epoxy resins with CTBN liquid rubber using an aromatic amine hardener. They found that the impact strength increased with higher concentration of CTBN, whereas the mechanical properties like tensile and flexural strength reduced. Tripathi and Vastava³⁴ also investigated the mechanical properties and chemical resistance of the films of coating based on CTBN rubber-modified epoxy resins. They reported that the epoxy modified with 15 wt % CTBN offered better chemical resistance and thermal stability than other modified samples.

Although researchers have found that reactive liquid rubber could improve the toughness or resistance to crack of the thermoset epoxy, the effect of liquid rubber on wear behavior of the thermoset ep-

oxy has been rarely known. One of the interesting work done by Yu et al.¹² was the use of rubber nanoparticles to prepare the epoxy composites. They found that the 5 wt % content of the rubber nanoparticles was the most effective in reducing the wear mass loss and coefficient of friction of the epoxy-piperidine system. The improvement of the wear resistance of epoxy nanocomposites was proposed to be because of the improved toughness by the rubber nanoparticles. Ma et al.³⁵ employed the rubber nanoparticles to improve the mechanical properties and to toughen an epoxy thermoset matrix. They found that the rubber nanoparticles caused much less Young's modulus deterioration but toughened epoxy resins in a similar degree in comparison with liquid rubber that formed microscale particles during curing. Therefore, it is interesting to study the tribological behaviors of the epoxy resin modified with liquid rubber. In this work, the microparticle rubber toughened epoxy resin was prepared. The reactive liquid CTBN rubber was used as a toughening agent. The influence of toughness enhancement on the wear behaviors of epoxy resin was investigated. We attempt to improve wear resistance of diglycidyl ether of bisphenol A (DGEBA) epoxy resin using cycloaliphatic amine as a hardener. The objectives of the present work were to investigate the tribological and mechanical properties of the CTBN-modified epoxy resins and to characterize the wear mechanisms. In addition, the relationship between the mechanical and tribological performance of the CTBN-modified epoxy resins and their relevant microstructure were also established.

MATERIALS AND METHODS

Materials

The epoxy used in this study was diglycidyl ether of bisphenol A, DGEBA (EPON 828) with epoxy equivalent weight of 185–192 g/eq. The hardener used was cycloaliphatic amine (EPIKURE 3383) with equivalent weight of 114 g/eq. Both chemicals were from HexionTM Specialty Chemicals, USA. The reactive liquid rubber was carboxyl-terminated acrylonitrile butadiene copolymer (CTBN) with molecular weight (M_n) of 3800 containing acrylonitrile of 8–12 wt % from Aldrich, Singapore. All chemicals were used as received without further purification.

Preparation of rubber toughened epoxy resins

DGEBA epoxy was mixed with required quantities of liquid CTBN rubber at 80°C for 45 min while mechanical stirring. The mixture was then degassed in vacuum oven and ultrasonicated to remove the entrapped bubbles. Once the mixture had cooled

down at room temperature, the stoichiometric quantity of curing agent was then added prior to hand mixing for 3–5 min. Finally, the mixture was poured into molds and cured at 25°C for 16 h and postcure at 100°C for 2 h as recommended from a manufacturer for the neat epoxy resin. The rubber-modified epoxy resins containing 2.5, 5.0, 10, 15, and 20 phr of CTBN rubber were named here as 2.5-CTBN, 5-CTBN, 10-CTBN, 15-CTBN, and 20-CTBN, respectively.

Impact testing

Izod impact tests were performed at room temperature using pendulum impact tester (Yasuda Seiki Seisakusho 9347, Intro Enterprise) according to ASTM D256-10. At least five specimens were tested and the average results were reported with standard deviation.

Scanning electron microscope (SEM)

The fracture surfaces obtained from the impact tests were examined at magnification of 1500x using the scanning electron microscope (JEOL JSM-5800, Japan) with 10 kV working energy. All samples were gold coated to prevent the charging before the surface observation.

Dynamic mechanical analysis (DMA)

Storage modulus (E') and $\tan \delta$ were determined using dynamic mechanical analyzer (Mettler Toledo, DMA/SDTA 861e, Switzerland). Specimens of rectangular shape ($63 \times 12 \times 3 \text{ mm}^3$) were analyzed in 3-point-bending mode. The measurement was carried out from -20°C to $+130^\circ\text{C}$ with $3^\circ\text{C}/\text{min}$ of heating rate, at 1 Hz of frequency.

Tribological testing

Tribological test was carried out using a ball-on-disc tribometer (CSM Instrument, model 18-272, German) at ambient condition. The sample surface was rubbed against stainless steel ball with sliding velocities of 0.10 m/s for 500 m under applied loads of 3 and 5 N. The sliding ball and sample surface were then cleaned using lens paper towels soaked in isopropanol before testing. The wear track radius (R) and the ball end spherical radius (r) were 6.0 mm and 3.175 mm, respectively. The friction coefficient (μ) was obtained using Amonton's first law of friction as expressed in eq. (1).

$$\mu = F/W, \quad (1)$$

where F is tangential force and W is normal force in the unit of N. To access the wear damage and wear mechanisms, rubbed surfaces and stainless steel

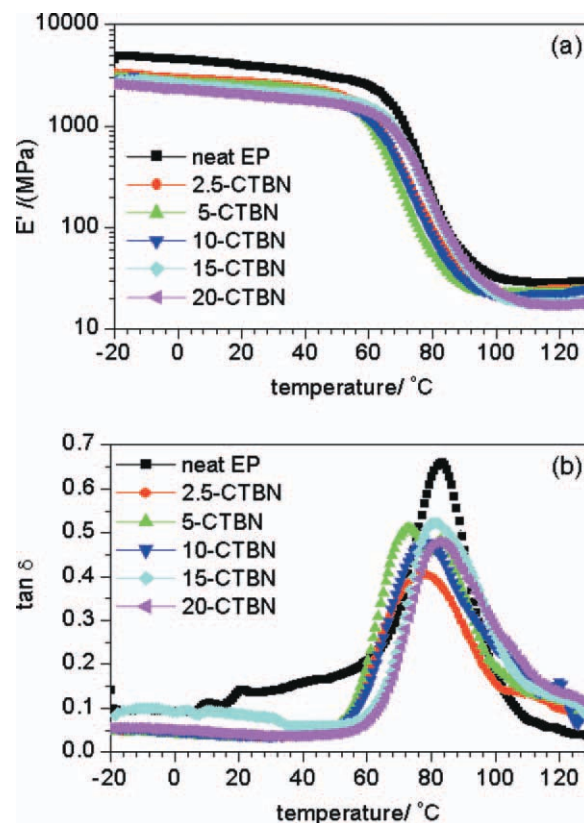


Figure 1 Temperature dependence of (a) storage modulus and (b) $\tan \delta$ of the neat epoxy and the epoxies modified with CTBN 2.5, 5, 10, 15, and 20 phr. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

balls from tribological testing were analyzed using optical microscope (OM). The wear volume loss (V) in the unit of cubic millimeter was calculated from the wear track width (d) in the unit of mm as given in eq. (2).

$$V = 2\pi R(r^2 \sin^{-1}(d/2r) - (d/4)(4r^2 - d^2)^{1/2}). \quad (2)$$

The wear rate (k) in the unit of $\text{mm}^3/(\text{Nm})$ was calculated using eq. (3).

$$k = V/(Ws), \quad (3)$$

where W is the normal force and s is sliding distance in the unit of m.

RESULTS AND DISCUSSION

Mechanical properties

Dynamic mechanical analysis of CTBN-modified epoxy resins was analyzed to investigate the influence of liquid CTBN content on the stiffness and the glass transition temperature. The results are represented in Figure 1.

TABLE I
Storage Modulus and T_g of the CTBN-Modified Epoxy Resins

Sample	Storage modulus at 25°C/MPa	Storage modulus at 120°C/MPa	T_g (°C)
Neat EP	3851	28.7	83.5
2.5-CTBN	2664	24.5	77.8
5-CTBN	2500	22.6	73.3
10-CTBN	2248	22.0	78.3
15-CTBN	2204	18.0	80.9
20-CTBN	1982	17.3	82.1

Figure 1(a) shows the temperature dependence of storage modulus (E'), which measured the stiffness and load bearing capability of the epoxy resin. The storage modulus of all the studied resins decreased as the temperature increased. One sharp drop in storage modulus, indicated the glass transition temperature (T_g), was observed over the temperature range of this study (from -20°C to $+130^\circ\text{C}$). It was found that the storage modulus of an epoxy resin below and above its T_g decreased when the rubber was added. To facilitate the comparison among those rubber-modified epoxy resins, the E' at the below and at the above T_g s are summarized in Table I. The E' at the below T_g zone (at 25°C) is referred as the storage modulus at glassy region, while the modulus at the above T_g zone (at 120°C) is referred as the rubber plateau storage modulus. It was found that the glassy storage moduli of all the modified epoxy resins were lower than that of the neat epoxy resin. The higher amount of the CTBN rubber, the lower the stiffness of the resin would be. The storage modulus was by 48.5% reduction as the 20-phr-CTBN rubber was added. The decreases in the moduli were attributed to the presence of low modulus rubber particles in the epoxy matrix. The similar effect was also found for the storage modulus at 120°C . It decreased with the liquid CTBN loading. The significant reduction of the storage modulus at 120°C with addition of the liquid rubber was observed (i.e., by 14.6%, 21.3%, 23.3%, 37.3%, and 39.2% reduction for the modified resin containing the 2.5, 5, 10, 15, and 20 phr-liquid CTBN, respectively). From the theory of the rubber elasticity,³⁶ the plateau storage modulus (E'_{plat}) at a given temperature above T_g is proportional to the crosslink density. Thus, it could be inferred from the reduction of the E'_{plat} that the presence of the liquid CTBN rubber reduced the crosslink density at the interface of the modified epoxy resins. The explanation, offered by Thomas et al.,²⁸ was that during the curing of epoxy resin the phase separated rubber domains occupied the space in between the reaction sites, thereby impairing the crosslink reaction at a particular site.

Figure 1(b) shows the damping properties of the neat and the rubber-modified epoxy resins. The

glass transition temperatures (T_g) identified from $\tan \delta$ at the peak maxima of the neat and the modified epoxy resins are summarized in Table I. The neat resin illustrated the highest value. Only the minimal changes in the T_g toward the lower temperature range from that of the neat epoxy was observed. T_g dropped with incorporation of 2.5 and 5 phr-CTBN rubbers but then increased slightly with further additions. Similar results were reported by others researchers.^{21,23} At least four possible effects were responsible for this observation. One of the effects was the reduction in crosslink density at interface due to the presence of rubber particles as previously discussed. The second effect was the plasticizing action of small levels of rubber dissolved in the matrix. Additionally, the T_g of the rubbery CTBN phase was also lower than the T_g of the neat CTBN.²³ Verchere et al.²¹ gave the alternative explanation. An increase in free volume caused by the thermal hydrostatic stresses applied to the rubber inclusions was accountable for the T_g lowering.²¹ Lastly, the steric effects arising from the presence of the rubber particles led to the suppressed relaxation mobility in the epoxy segments. For the modified resins with CTBN larger than 5 phr, the steric effects were possibly enhanced and brought on the slight increase of T_g as compared to those at lower rubber loading.

The hardness results are given in Figure 2. It was found that the neat epoxy resin had the highest hardness, and the hardness decreased with the increased CTBN content. The results agree with the moduli obtained from DMA. The reduction in hardness was attributed to the lowered crosslink density of the resin in the presence of rubber particles and/or the plasticization effect of the CTBN rubber partially dissolved in epoxy matrix as already discussed.

Figure 3 shows the impact strength of the liquid CTBN-modified epoxy resins as a function of liquid CTBN content. The improvement in impact strength could be correlated with toughness enhancement. All rubber-modified epoxy resins showed higher

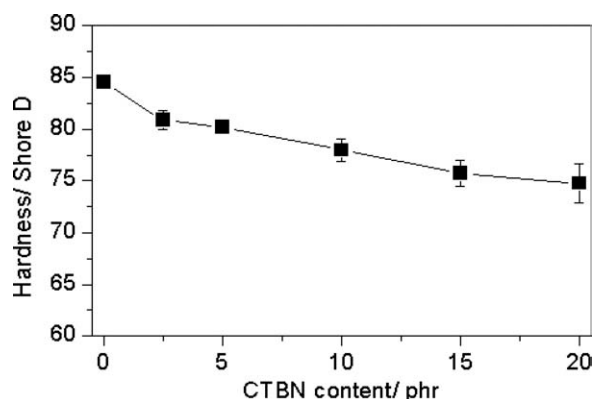


Figure 2 Hardness of the rubber-modified epoxy resins as a function of the CTBN content.

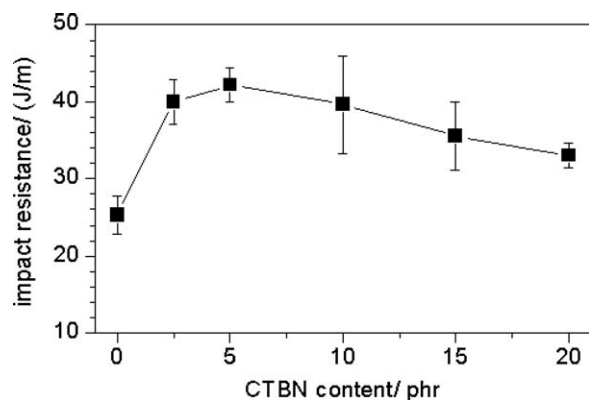


Figure 3 Impact strength of the rubber-modified epoxy resins as a function of the CTBN content.

impact strength than the neat resin. However, the impact strength reached the maximum at 5 phr-CTBN rubber, and above this optimum rubber content a falling tendency was observed. The modified epoxy containing 5-phr CTBN had the impact strength of about 67% higher than the neat resin. For epoxy containing 20-phr CTBN, the impact strength was about 22% lower than the maximum. One of the possible reasons for the increased impact strength of the rubber-modified epoxy resin in comparison to that of neat epoxy was the ductility of the epoxy matrix attained by the incorporation of rubber. The ductility enhancement was due to the reduction in crosslink density and/or the plasticization effect as previously discussed. The effective stress concentration of the phase separated rubber-rich particles has been known to amplify plastic deformation of a highly brittle matrix to a certain extent, leading to the increases in values upon the optimum level of rubber content.³⁷ The other reason was the cavitations or crack bridging induced by the rubber phase. On the other hand, comparatively lower performance of the present rubber at high content was attributed to poor interaction between the epoxy matrix and the rubbers.²⁷ In addition, the agglomeration of rubber particles as the CTBN content increased was also responsible for the decreasing tendency of impact strength after an optimum level of 5-phr rubber inclusion. This will be evidenced by microstructure investigations.

Microstructure of fracture surface

To understand how CTBN rubber particles affect the impact strength and fracture behavior, the fracture surfaces of samples obtained from the impact tests were studied. Figure 4 shows the SEM micrographs of the fracture surfaces for the neat epoxy and the rubber-modified epoxy resins. The neat epoxy exhibited the fracture behavior of brittle material in which was evidenced by very smooth fracture surface [Fig.

4(a)]. The micrographs of the modified epoxy matrix [Fig. 4(b,c)] exhibited two phases. The CTBN rubber phases appeared as spherical particles with average diameters in a range of 0.87–4.70 μm , and they were well-dispersed in the epoxy matrix. The maximum rubber particle size of the modified epoxy resin at low CTBN content (5-phr) was lower than that of the modified resin at high-CTBN content (20-phr). The average diameter of rubber particles increased steadily with the amount of CTBN (see Table II).

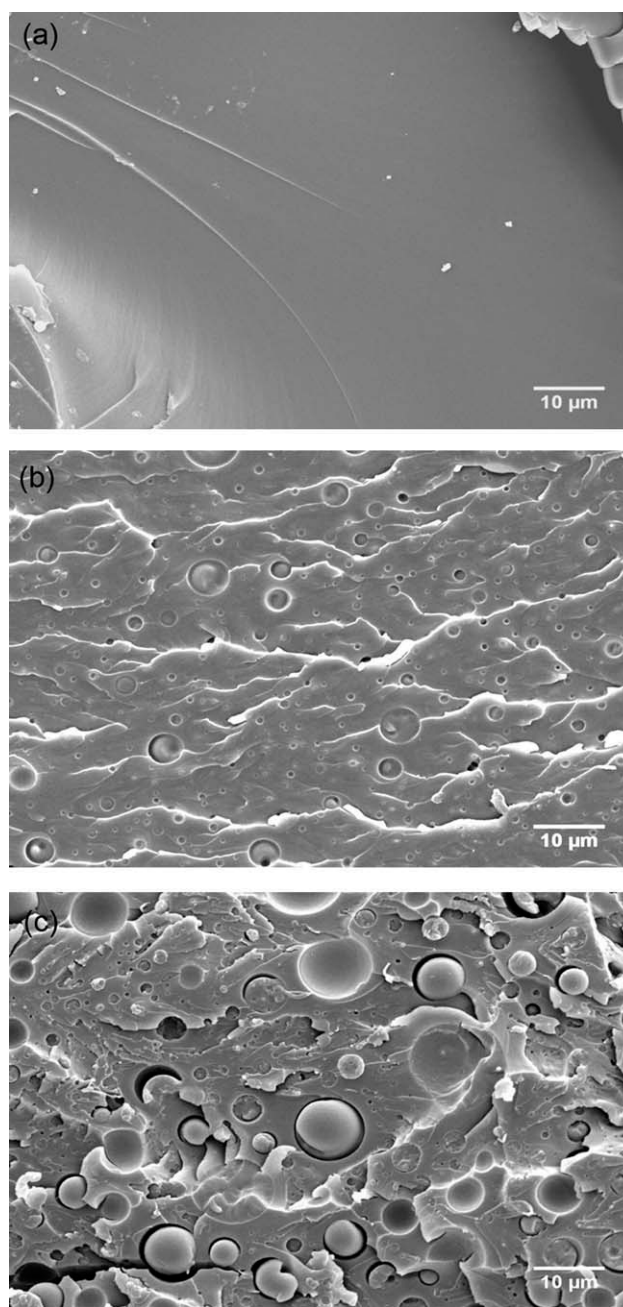


Figure 4 Scanning electron micrographs of the fracture surface of (a) the neat epoxy; (b) the rubber-modified epoxy resin containing 5 phr CTBN (5-CTBN); and (c) the rubber-modified epoxy resin containing 20 phr CTBN (20-CTBN).

TABLE II
Rubber Particle Size in the Matrix of the CTBN-Modified Epoxy Resins

Sample	Maximum diameter (μm)	Minimum diameter (μm)	Average diameter (μm)	Standard deviation
2.5-CTBN	2.97	0.25	0.87	0.638
5-CTBN	5.00	0.45	1.17	0.923
10-CTBN	6.43	0.39	1.73	1.25
15-CTBN	10.31	0.74	2.73	1.81
20-CTBN	11.94	1.52	4.70	2.53

The increase in domain size with the incorporation of rubber was attributed to the agglomeration of the dispersed rubber particles. These data are well correlated with the impact strength results. For the epoxy resin modified with low CTBN content, it was found from Figure 4(b) that a large number of white deformation lines developed through the rubber particles. No rubber particles were pulled out from the epoxy matrix, but only internal cavitation was observed. Also there was no obvious phase separation between the rubber and epoxy. The results indicated the presence of chemical bond formation and strong interaction between the rubber particles and the epoxy matrix.²⁷ By contrast, at the high-CTBN content [Fig. 4(c)] most of the rubber particles were pulled out, the void formation occurred, and the particle

deformation was observed. It was found from Figure 4(b,c) that the interparticle distance between the neighboring particles decreased with inclusion of rubber. When the interparticle distance decreased, the stress concentration effect increased. Consequently, the epoxy matrix supported the average load higher than the applied load and yielded.³⁷ This may be responsible for the debonding around the rubber in the epoxy modified with high-rubber content. The similar observation was also found by Thomas et al.²⁸ The poor interaction between the particles and the epoxy matrix was found in high-modified epoxies as compared to those in low modified epoxies.

Tribological properties

Figure 5 shows the coefficients of friction as a function of sliding distance under the applied loads of 3.0 and 5.0 N. The coefficient of frictions of the neat and the modified epoxy resins rose at the run-in period (approximately before 40 m), and then a steady state was reached. It was found that the coefficients of friction of the neat and the modified epoxy resins under the applied load of 3.0 N were slightly lower than those of 5.0 N. Meanwhile, the coefficients of friction of all CTBN-modified epoxy resins were lower than those of the neat epoxy under both applied loads. To facilitate the comparison among the modified epoxy resins, average values of the steady state coefficients of friction were calculated in a range of 400–500 m. The results are given in Table III. Under the applied load of 3.0 N, the steady state coefficient of friction tended to decrease with increasing CTBN loading. Under the

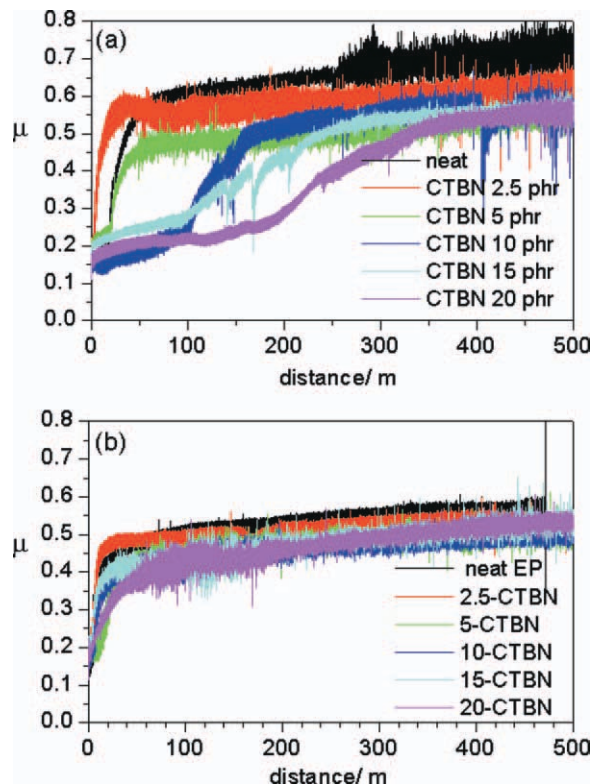


Figure 5 Coefficients of friction of the neat epoxy and the rubber-modified epoxy resins (2.5-CTBN, 5-CTBN, 10-CTBN, 15-CTBN, and 20-CTBN) as a function of sliding distance at the applied loads of (a) 3.0 N; and (b) 5.0 N. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

TABLE III
Coefficient of Friction of the Neat Epoxy and the CTBN-Modified Epoxy Resins at the Testing Loads of 3.0 and 5.0 N

Sample	Steady state coefficient of friction	
	Load 3 N	Load 5 N
Neat EP	0.711 ± 0.020	0.565 ± 0.019
2.5-CTBN	0.610 ± 0.023	0.529 ± 0.011
5-CTBN	0.540 ± 0.013	0.499 ± 0.008
10-CTBN	0.562 ± 0.028	0.489 ± 0.005
15-CTBN	0.560 ± 0.010	0.525 ± 0.008
20-CTBN	0.550 ± 0.013	0.525 ± 0.006

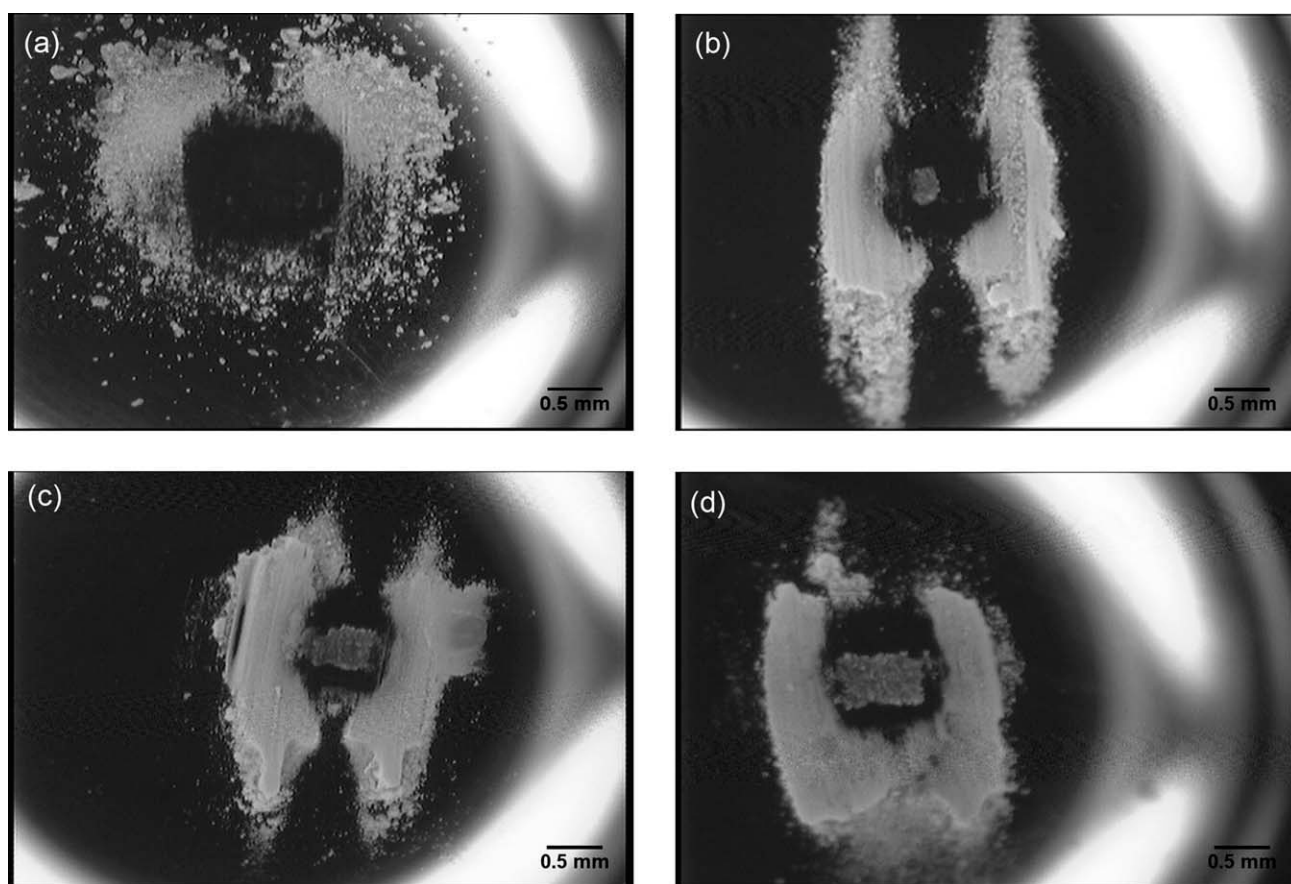


Figure 6 Optical micrographs of the stainless steel balls after sliding against (a) the neat epoxy; (b) the rubber-modified epoxy 2.5-CTBN; (c) the rubber-modified epoxy 5-CTBN; and (d) the rubber-modified epoxy 20-CTBN.

applied load of 5.0 N, the coefficient of friction decreased with the addition of CTBN upon 10 phr but then increased gradually with further additions.

To elucidate the effects of CTBN rubber on the wear behavior, the sliding-ball counter-mates and wear tracks from tribological tests were investigated using optical microscope. The results obtained are shown in Figures 6 and 7. In Figure 6(a), transfer film did not occur on the surface of the sliding ball for the neat epoxy resin, but only loose debris (chips) was formed with no tendency to adhere to the ball counter-mate. Thus, the wear mechanism was mainly the abrasion. Larsen et al.^{4,10} suggested the formation of the transfer film in the modified epoxy. The formation of the transfer films indicated that the dominant wear mechanism changed to the adhesion. It was found from Figure 6(b–d) that the addition of CTBN led to the formation of transfer films on the sliding-ball surface. The thermal softening due to the frictional heat^{4,15} and the decrease in crosslink density which enhanced the deformation were responsible for the transfer-film formation. The presence of the transfer film on the ball counter-mates could be associated with the lower coefficient of friction of CTBN-modified epoxy resins as com-

pared to the neat epoxy. In addition, the formation of transfer film could greatly affect the sliding characteristics of the modified epoxy resins.³⁸ As shown in Figure 6(d), thicker film was formed on the surface of ball sliding on the 20-CTBN modified resin. When the thick and lumpy transfer film was created, an abrupt movement or even a seizure of the sliding contact could occur.³⁸ This resulted in a higher friction as observed when adding CTBN rubber of larger than 10 phr (see Table III).

Figure 7(a) shows the worn surface of the neat epoxy resin after performing the tribological test at the applied load of 5.0 N. Small cracks across the wear track and materials wave which occurred due to the brittle nature of the epoxy³⁹ were observed. Some ploughing grooves due to three body abrasiveness left traces on the worn surface of the neat resin. The results suggested that the wear process was governed by the material deformation and microploughing type of abrasive wear. Figure 7(b–d) shows the worn surface of the CTBN-modified resins. It was found from Figure 7(b) that the worn surface of the 2.5-CTBN modified resin exhibited the scale-like damage pattern. This damage pattern could be found to be generated under a repeating load during

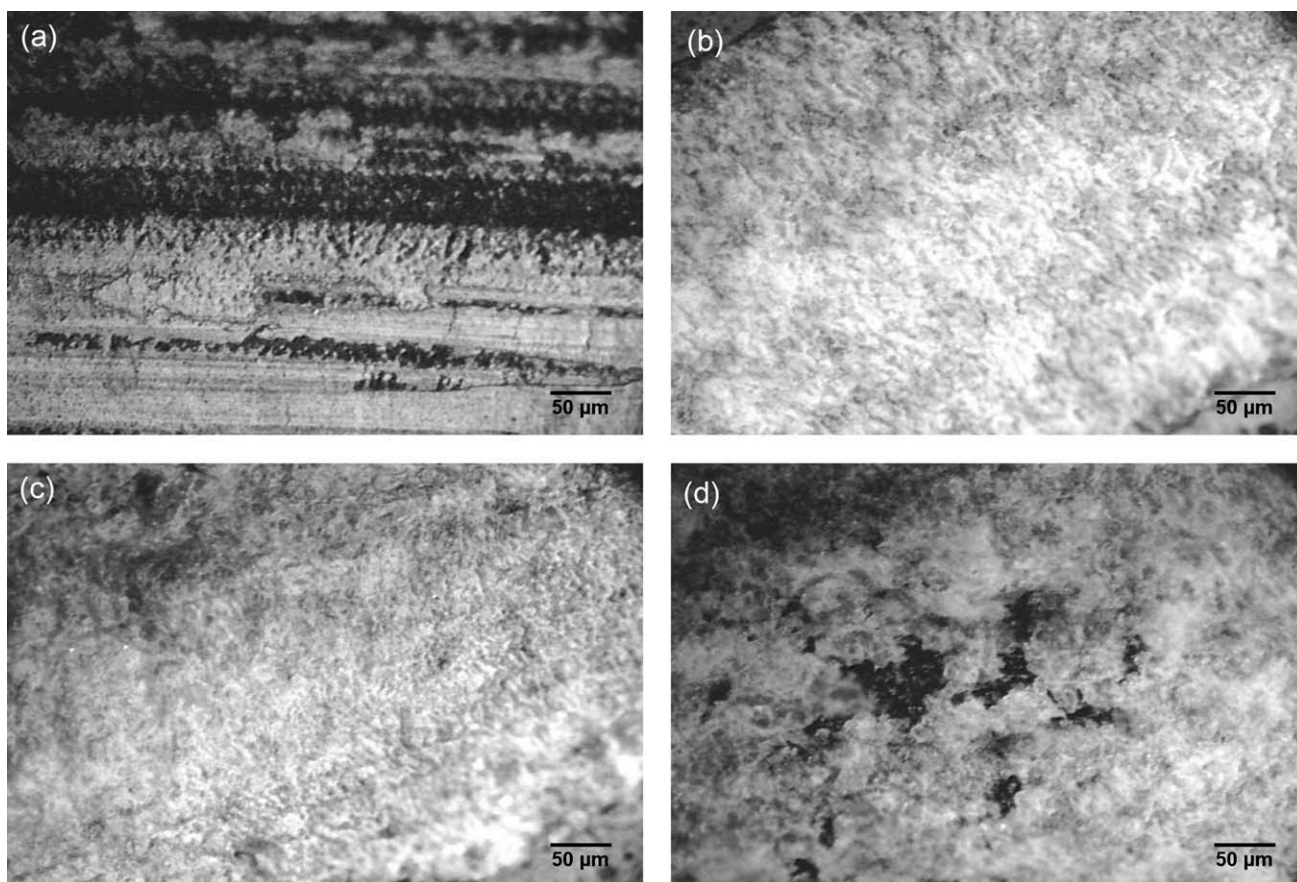


Figure 7 Optical micrographs of worn surfaces of (a) the neat epoxy; (b) the rubber-modified epoxy 2.5-CTBN; (c) the rubber-modified epoxy 5-CTBN; and (d) the rubber-modified epoxy 20-CTBN.

sliding.¹³ For the worn surface of the 5-CTBN modified epoxy resin [see Fig. 7(c)], the ploughing grooves were found besides the scale pattern. The formation of such grooves was frequently observed when adhesive wear occurred. The possible mechanism of these grooves involved ploughing the epoxy surface by the work-hardened transfer particles.³⁸ As the CTBN content increased to 20 phr [see Fig. 7(d)], more severe surface damages caused by the adhesive wear were observed. The surface delamination was found instead of the ploughing grooves. It should be noted that discussion on the tribological reaction mechanism was not given in this work, but will be considered for further investigations. However, it was worth mentioning by selected literatures^{12,40,41} that the tribochemical reaction mechanism can be induced by thermal and mechanical effects. The thermally induced reaction at the surface asperity was due to flash temperature, leading to thermal degradation and/or oxidation,^{12,40} whereas the mechanically induced reaction was associated with the repeated action of the shear stress within the three-body agglomerates which led to the chain scission.⁴¹

Figure 8 shows the wear rates (k) as a function of CTBN content under the applied loads of 3.0 and

5.0 N. It was found that the wear rates of the neat and the modified epoxy resins increased with increasing applied loads. At the applied load of 3.0 N, the wear rate decreased with the addition of liquid CTBN rubber upon 5 phr and then increased with further increasing CTBN content. One possible reason for the improved wear resistance at low CTBN content was toughness enhancement as indicated in Figure 2. Another reason was the formation

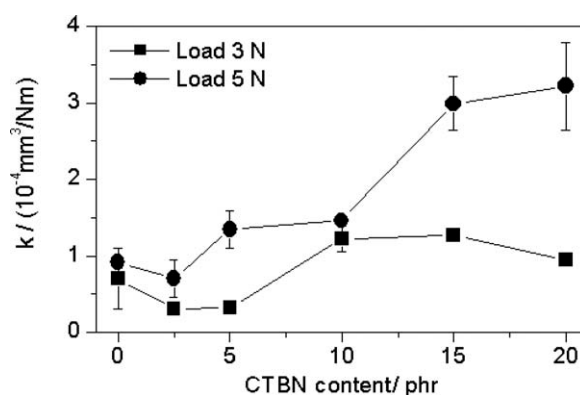


Figure 8 Wear rate of the rubber-modified epoxy resins as a function of the CTBN content.

of transfer film. The transfer film formed on the ball surface probably acted as protective layers which could not allow a direct contact between the hard ball and the epoxy surface, and then softened the wear. At the applied load of 5.0 N, the addition of 2.5-phr CTBN rubber showed the most effective to reduce the wear rate of epoxy, but a higher wear rate than the neat epoxy was found when the CTBN was further added. The result was possibly because the poor adhesion between rubber particles and epoxy matrix, leading to an ease for polymer removal during wear process. In addition, the ductility enhancement which was responsible for the toughening mechanism became a key part when CTBN was more added. The high-rubber-modified epoxy was so soft that it was readily to worn away. This result does not agree with that reported by Yu et al. who investigated the wear behavior of epoxy modified with the rubber nanoparticles.¹² Unlike the rubber nanoparticles, the presence of the large amount of rubber microparticles could not improve the wear resistance of epoxy resin. It could be postulated from the results that the improved material toughness alone was not always the requirement for tribological optimization. The high-wear resistance of the modified epoxy resins would exhibit only if the increasing toughness compensated the decreasing stiffness.

CONCLUSIONS

The effect of CTBN rubber particles on the mechanical and tribological properties was studied. The results suggested that impact resistance of epoxy resin enhanced whereas the storage modulus reduced, when CTBN rubber was incorporated to the epoxy resin. These results were because the presence of the liquid CTBN rubber reduced the cross-link density at the interface of the modified epoxy resins, and hence increased the ductility. The coefficient of friction of the modified epoxy resins was lower than that of the neat epoxy due to the formation of transfer film. However, the addition of CTBN rubber of less than 10 phr was recommended for reducing the wear rate of the epoxy. The combination effects of increasing toughness and formation of transfer film were responsible for the wear behavior of the CTBN-modified epoxy resins.

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