

PROPERTY AND MORPHOLOGY STUDY OF AN EPOXY RESIN MODIFIED WITH ETBN

Yuefang Li, Zhibin Zeng, Kang Peng and Huanliang Du

Institute of Electronic Engineering, Chinese Academy of Engineering Physics, Mianyang 621999,
China

Email: yuefangli_caep@163.com

Keywords: Epoxy modification, ETBN, Fracture toughness

ABSTRACT

Epoxy terminated butadiene acrylonitrile (ETBN) liquid rubber was physically blended with epoxy resin, which formed a two-phase morphology upon curing with diethanolamine. Volume fraction of rubber particles dispersed in epoxy matrix increased with ETBN loadings. The thermal and mechanical properties of the cured resin were investigated, which had correlations with micron-scale morphologies. Glass transition temperature of the cured epoxy decreased with the addition of ETBN up to 5 phr and remained unchanged at higher ETBN loading. It was estimated that up to around 3% ETBN was dissolved into the epoxy matrix. Both tensile strength and Young's modulus decreased abruptly when the content of ETBN increased to above 10 phr, due to the formation of occluded rubber agglomerations as large as 200 μm . Appreciable improvements in cohesive fracture toughness were observed in all the ETBN-modified epoxy, which could be ascribed to cavitation of rubber particles and shear banding. Epoxy/kovar adhesive toughness was studied using wide-tapered double cantilever beam specimens, and a maximum 36% improvement was observed for epoxies containing 20 phr ETBN.

1 INTRODUCTION

Epoxy resins are widely used as structural adhesives, encapsulating and potting materials, and matrix materials for reinforced composites, by virtue of their high cohesive and adhesive strength, excellent electrical insulation and versatility in formulating. The intrinsic brittleness of the epoxy networks, however, renders them poor resistance to crack growth and restricts their practical applications. A convenient method to toughen epoxy is through the incorporation of a compliant rubber phase, which is known to improve the fracture toughness of the epoxy network remarkably with a relatively small sacrifice of the thermal and mechanical properties [1].

Butadiene acrylonitrile copolymers are most commonly-used liquid rubber modifiers to toughen epoxy, typically with the functional terminals of carboxyls (CTBN) [2-5], amines (ATBN) [6, 7] and epoxides (ETBN) [8]. Liquid rubbers are initially dissolved in epoxy precursors and precipitates out to form a second phase during the curing process. Cohesive fracture toughness of the rubber-modified epoxies is highly dependent on their phase morphologies [9-12], which are influenced by the compatibility of the two phases and the gelation kinetics that vary from different compositions and cure schedules [13, 14]. Among the massive investigations on the toughening effects of CTBN and its derivatives on epoxy resin, multi-functional amines and anhydrides are generally employed as epoxy hardeners [6, 12, 15-18].

Strong adhesive toughness of epoxy is desirable to avoid crack or delamination at the interface of multi-materials. However, large bulk toughness does not necessarily guarantee good adhesive toughness, which is also affected by other factors, such as type of the substrate [19], thickness of the adhesive [20], and modulus mismatch between the adhesive and the substrate [21]. The toughening effect of liquid rubber on the adhesive toughness of epoxy resin between metal substrates is less well-studied.

In the present study, we explored the modification effects of epoxy-terminated butadiene acrylonitrile rubber (ETBN) on an epoxy resin cured by diethanolamine (DEA). DEA is a unique hardener that cures epoxy by tertiary-amine catalyzed etherification mechanism with rather slow

reaction rate and low heat release [22], which is extensively used for applications requiring low curing stress and heat. ETBN contents were adjusted in the range of 0 to 20 phr. The effects of ETBN content on thermal properties, tensile behaviors, fracture toughness of bulk epoxy and epoxy-kovar adhesive joint, and phase morphologies were studied in details, and attempts have been made to correlate them.

2 MATERIALS AND METHODS

The epoxy precursor (WSR 618, a diglycidyl ether bisphenol-A with an epoxide equivalent of 185 ~ 208) (DGEBA) was purchased from Nantong Xingchen Synthetic Material. The curing agent diethanolamine (DEA) was purchased from Aladdin. ETBN rubber (CHX100, acrylonitrile = 25% with the epoxide value of 0.0625) was produced by Beijing Devote Chemical and used as the toughening agents.

Compositions of the toughened epoxy networks were listed in Table 1. The DGEBA precursor and ETBN were mixed at moderate temperature with stirring for 5 h, to which DEA was added and mixed for another 30 min to allow a thorough blending. The mixture was then degassed under vacuum to remove air bubbles. Afterwards, the mixture was casted into preheated aluminium moulds and cured at 70 °C for 10 h and 90 °C for 16 h.

To measure the glass transition temperature (T_g) of epoxy, differential scanning calorimetry (DSC) was conducted in the temperature range from 0 °C to 120 °C with a heating rate of 10 °C/min using DSC 1 (Mettler Toledo).

Tensile tests were performed using dumbbell-shaped samples according to ASTM D638 on a MTS 800 instrument equipped with a 10 kN load cell. A crosshead speed of 5 mm/min was used for all measurements. At least five specimens were tested for each composition.

Compact tension (CT) specimens were employed to evaluate cohesive fracture toughness of the ETBN modified epoxy, which were fabricated according to ASTM5045 with a width of 36 mm and a thickness of 8 mm. A precrack was introduced to each CT specimen by tapping a fresh razor blade into the machined notch. At least five specimens were tested for each rubber content. The tests were performed on the MTS 800 instrument with a crosshead rate of 1 mm/min.

Wide-tapered double cantilever beam (WTDCB) specimens with kovar as the substrate and epoxy as the adhesive were fabricated and tested according to the method described by Kessler et al [23]. Prior to use, all the kovar substrates were polished, cleaned with acetone and water, and dried. Polytetrafluoroethylene film was used as the constant thickness spacer and the preinserted notch. Adhesive fracture toughness was evaluated via mode I fracture test of WTDCB specimens at a crosshead rate of 1 mm/min.

Fracture surfaces of the CT specimens were examined using a scanning electronic microscope (ProX, Phenom). The apparent diameters of the rubber particles were measured from the SEM micrographs using image processing software. The number-average diameter (D_n), the weight-average diameter (D_w) and the polydispersity index (PI) of the rubber domains were calculated from the following equations:

$$D_n = \sum n_i D_i / \sum n_i \quad (1)$$

$$D_w = \sum n_i D_i^2 / \sum n_i D_i \quad (2)$$

$$PI = D_w / D_n \quad (3)$$

where n_i is the number of particles within the diameter range i .

The volume fraction of the rubber particle (V_p) was estimated assuming the volume fraction is isotropic using the following equation [12]:

$$V_p = (\pi/4) \sum n_i D_i / A_T \quad (4)$$

where A_T is the area of the micrograph used for analysis.

The surface-to-surface inter-particle distance (d_p) was also estimated. The total number of rubber particles (n_T) in the micrograph was counted. Assuming the same number of identical squares fill up the area A_T , the lateral length (a) of the square is:

$$a = \sqrt{A_T/n_T} \quad (5)$$

d_p is the difference between the lateral length of the square and the diameter of the particle:

$$d_p = a - D_n = \sqrt{\frac{A_T}{n_T}} - D_n \quad (6)$$

| Sample | DGEBA(phr) | DEA (phr) | ETBN (phr) |
|--------|------------|-----------|------------|
| E0 | 100 | 14 | 0 |
| E2 | 100 | 14 | 2 |
| E5 | 100 | 14 | 5 |
| E10 | 100 | 14 | 10 |
| E15 | 100 | 14 | 15 |
| E20 | 100 | 14 | 20 |

Table 1.Epoxy compositions.

3 RESULTS AND DISCUSSIONS

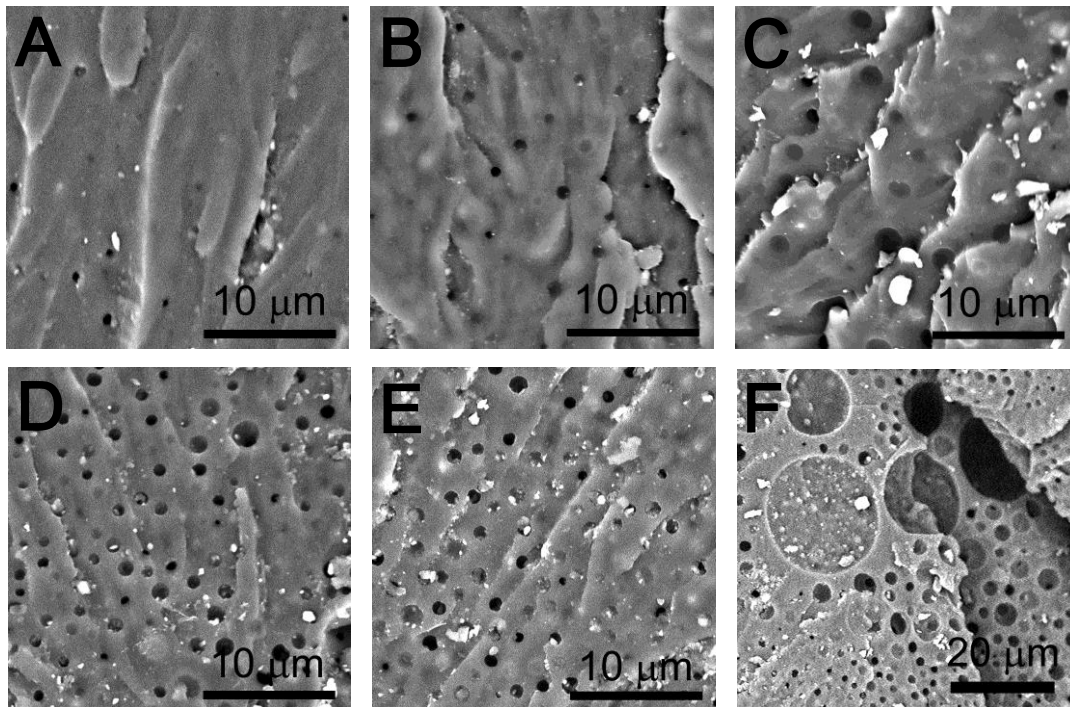


Figure 1. SEM micrographs of the phase morphologies of E2(A), E5 (B), E10 (C), E15 (D) and E20 (E&F).

| sample | D_n (μm) | D_w (μm) | PI | V_p (%) | d_p (μm) |
|--------|------------|------------|------|-----------|------------|
| E2 | 0.62 | 0.64 | 1.04 | 0.4 | 8.6 |
| E5 | 0.93 | 0.97 | 1.05 | 1.9 | 4.7 |
| E10 | 1.20 | 1.28 | 1.07 | 7.1 | 2.9 |
| E15 | 1.04 | 1.11 | 1.06 | 9.8 | 2.1 |
| E20 | 1.17 | 1.51 | 1.29 | 14.5 | 1.9 |

Table 2.Morphological parameters of the rubber particles obtained from SEM.

Previously we studied the effect of stoichiometry on the thermal and mechanical properties of DGEBA/DEA epoxies, and found that the maximal T_g and ductility of epoxy resins occurred when 14 phr DEA reacted with DGEBA [24]. Slightly excess amount of DGEBA did not significantly reduce the ductility of the cured epoxy while excess DEA led to extremely brittle epoxy networks [24]. Therefore the weight ratio of DGEBA and DEA was kept constant at 100:14 while varying the content of ETBN.

ETBN is one type of reactive liquid rubbers that is known to precipitate upon curing of epoxy, causing microphase separations. As the properties of ETBN-modified epoxy is closely related to the micron scale phase structure, a thorough analysis of the phase morphology was carried out.

As shown in Figure 1, all the modified specimens, including E2, exhibited a two-phase morphology with isolated rubber domains dispersed in continuous epoxy matrix. The rubber domain has the feature of spherical particles with diameters depending on ETBN contents. It is known that the size of the rubber particles is controlled by two major factors: the compatibility between liquid rubber and epoxy matrix [14], and the curing kinetics of epoxy [13]. Specifically, the higher the content of the polar acrylonitrile groups in ETBN, the more compatible ETBN is with epoxy. As the acrylonitrile content of ETBN used in the current study is 25 wt%, a smaller rubber particle size is expected, which is consistent with our observation from the SEM images. Several parameters regarding the particle size and distribution were analyzed from Figure 1 and listed in Table 2.

There was a scarce distribution of rubber particles in E2, which occupied merely 0.4% by volume, suggesting the majority amount of liquid rubbers was dissolved into the epoxy matrix. In E5 and epoxy specimens with higher ETBN loading, the averaged diameter of the rubber particles increased slightly, ranging mostly from 0.5 to 1.5 μm in diameter. However, in E15 and E20, heterogeneous size distribution of the rubber particles developed, which showed extremely large rubber domains with diameter up to 200 μm . As shown in Figure 1(E), the large rubber domains had occluded features that contained smaller particles. Similar observations have been reported by Thomas et al when toughening epoxy with polybutadiene rubber, which were explained by delay of gelation due to the high viscosity and smaller reactivity with higher loading of liquid rubbers [25]. Though systematic kinetic study was not herein conducted, we indeed observed that the E15 and E20 resins required longer gelation time during the sample preparation.

It should be noted that all the estimated results in Table 2 did not consider the contributions from the large domains, which should lead to smaller average diameter and volume fraction for E15 and E20. Nevertheless, the volume fraction of the rubber particles increased linearly while the distance between particles decreased with the increment of ETBN content. Ignoring the subtle density difference between ETBN and epoxy, there was a discrepancy between the feeding content of liquid rubber and the estimated volume fraction of the precipitated rubber particles, from which the amount of dissolved ETBN in epoxy matrix upon saturation was deduced to be around 3% by volume.

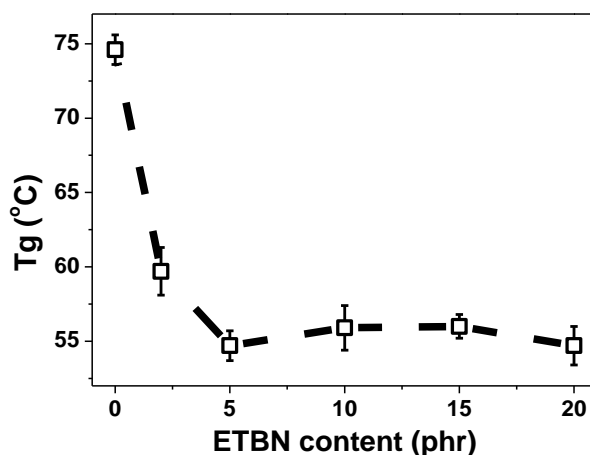


Figure 2. T_g of epoxy as a function of ETBN content.

The relationship between T_g of the epoxy samples and ETBN contents is shown in Figure 2. It can be seen that the addition of merely 2 phr ETBN had induced a sharp decrease of T_g from 74 °C to 59 °C, indicating that a distinct amount of ETBN dissolved in epoxy matrix and plasticized the glass transition [13, 18], which is consistent with SEM observation. As the acrylonitrile content in ETBN was relatively high, the reduction of T_g was quite significant [26]. T_g decreased further when the content of ETBN increased to 5 phr, and remained almost unchanged when the contents of ETBN varied from 10 phr to 20 phr. This phenomenon again demonstrated that the dissolved ETBN in epoxy matrix reached a saturation state when ETBN content was above 5 phr.

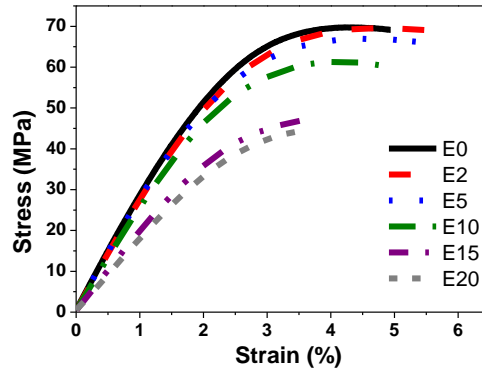


Figure 3. Stress-strain curves of ETBN-modified epoxies.

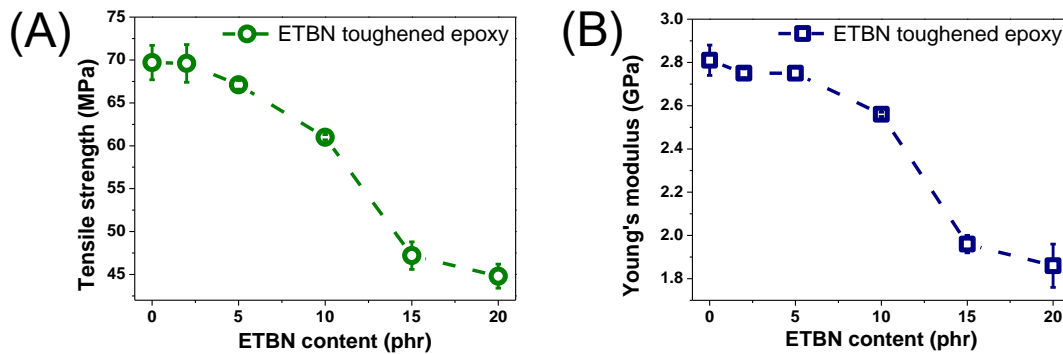


Figure 4. Tensile strength (A) and Young's modulus (B) of epoxy as a function of ETBN content.

Figure 3 shows the stress-strain curves of the ETBN modified epoxy, and the dependences of tensile strength and Young's modulus upon ETBN content were depicted in Figure 4. The elongations at break for E2, E5 and E10 were slightly higher than that of the neat epoxy, while E15 and E20 showed typical brittle fracture and thus lower elongation at break. This result contradicted with most literature reports that the ductility of epoxy could be greatly enhanced with the modification of liquid rubbers [7, 16, 27]. At high ETBN loadings, tensile strength of the ETBN-modified epoxy also decreased significantly. Since measured at large strain, both tensile strength and elongation at break are sensitive to the flaws and micron scale structures in the material. For E15 and E20, the presence of large rubber domains could have acted as defects that initiate catastrophic fracture at lower strain, resulting in lower tensile strength and elongation at break.

With the increasing ETBN content, the Young's modulus of the modified epoxy decreased and was always lower than that of the neat epoxy. Thomas et al reported the reduction of modulus with an increase of free volume due to the plasticizing effect of the dissolved liquid rubber in epoxy matrix [25]. Such effect was not obvious in DGEGA/DEA epoxy, as indicated by the slightly reduced modulus in E2 and E5. Much lower Young's modulus occurred in E15 and E20, which could be

attributed to the large volume fraction of dispersed rubber domains that had negligible modulus compared to that of neat epoxy [27].

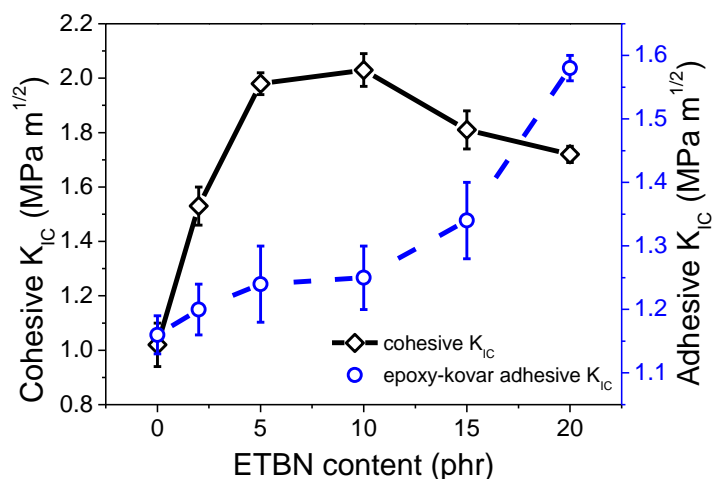


Figure 5. Cohesive and adhesive K_{Ic} of epoxy as a function of ETBN content.

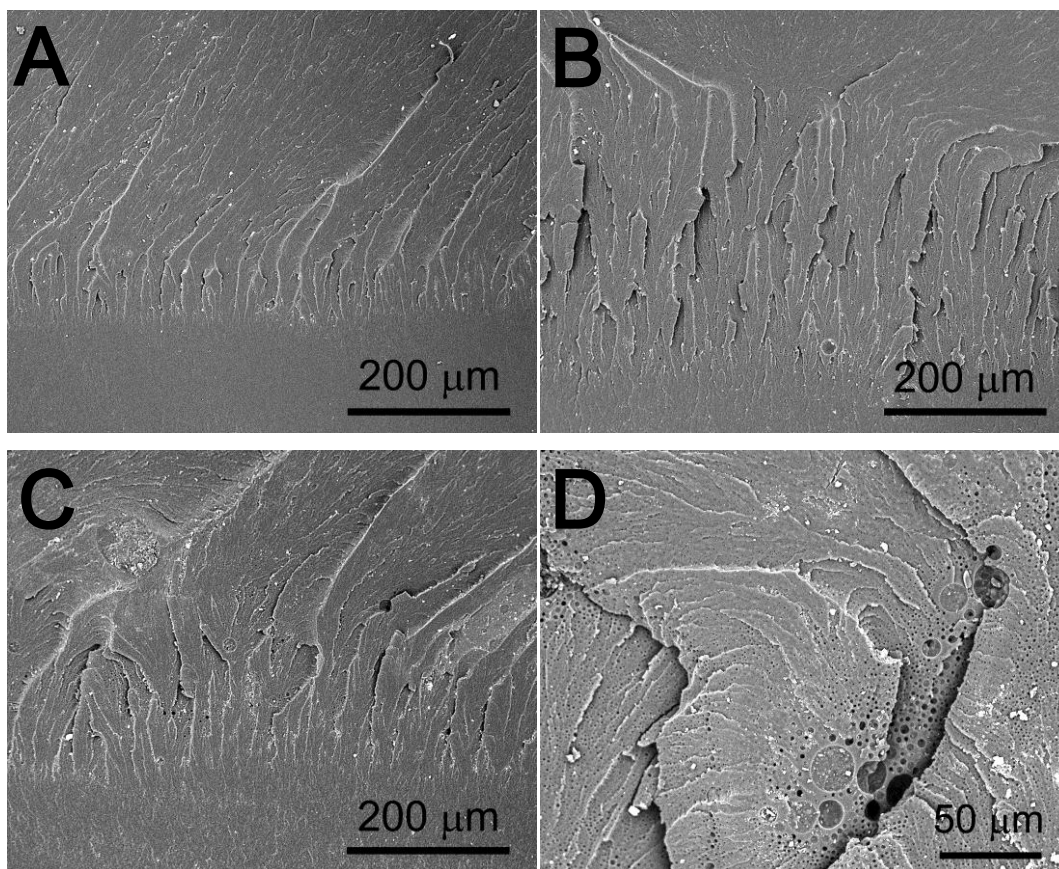


Figure 6. SEM photographs of the cohesive fracture surface of E2(A), E10 (B), E15 (C) and E20 (D) in front of the crack tip.

Cohesive fracture toughness (K_{Ic}) and epoxy-kovar adhesive K_{Ic} of the ETBN-toughened epoxies were studied using CT specimens and WTDCB specimens respectively. As shown in Figure 5, all the toughened epoxy networks exhibited higher cohesive K_{Ic} than neat epoxy. Specifically, the cohesive K_{Ic} of epoxy increased rapidly as ETBN content increased from 0 to 5 phr, reached a maximum value

at 10 phr, and then decreased slowly at higher ETBN contents. The E10 specimen had a K_{Ic} of 2.05 MPa m^{1/2}, which is around twice of the K_{Ic} of the neat epoxy. The epoxy-kovar adhesive K_{Ic} was dependent on the mode of fracture. Though the addition of ETBN at high loading improved the adhesive between epoxy and the kovar substrate, both fracture behaviors at the epoxy-kovar interface and inside the bulk epoxy were observed. The latter fracture mode led to unstable crack propagation and a higher K_{Ic} , which increased with the increment of ETBN content.

Figure 6 shows the SEM images of fracture morphologies of the ETBN-toughen epoxy. It should be noted that the fracture surface of neat epoxy was smooth and had few ripples, exhibiting typical brittle fracture feature that accounted for the lower cohesive K_{Ic} of the material. The fracture surface of E2, though seemed identical to E0 by visual inspection, exhibited narrow plastic deformation bands with the width of around 55 μ m close to the crack tip. The width of the bands varied with the ETBN content, which increased to 250 μ m in E10 and decreased to 100 μ m in E15. The appearance of the plastic deformation bands was accompanied with cavitation of rubber particles. Therefore it was deduced that formation of rubber cavities and induced matrix shear yielding were the main toughening mechanism for these materials. In E20, however, a region of cavitated rubber particles was found near the crack tip without any evidence of shear deformation in the matrix. The large rubber cavities, as shown in Figure 6(D), seemed to bridge the crack propagations, which according to Pearson et al had smaller contributions to fracture toughness compared with plastic void growth and shear banding [11].

9 CONCLUSIONS

ETBN liquid rubber was employed to toughen DGEBA/DEA epoxy. Influence of ETBN loading on the micron scale morphology of the epoxy network as well as thermal and mechanical properties was thoroughly investigated. The following conclusions were drawn from our results: 1) ETBN behaved more like a covalently-bonded plasticizer at lower concentrations, which mainly affected T_g rather than mechanical properties of Epoxy; 2) Efficient ETBN toughening occurred for DEA-cured epoxy containing 10 phr ETBN, which presented optimal cohesive K_{Ic} and slightly higher adhesive K_{Ic} ; 3) Higher ETBN contents could cause undesired ETBN agglomerations and bring in adverse effects on the mechanical properties of epoxy.

ACKNOWLEDGEMENTS

This work was sponsored by the innovation foundation of the Institute of Electronic Engineering, Chinese Academy of Engineering Physics. The authors would like to thank Prof. Longcheng Tang in Hangzhou Normal University for his kind instructions in the measurement of cohesive fracture toughness.

REFERENCES

- [1] R. Bagheri, B.T. Marouf, R.A. Pearson, Rubber-Toughened Epoxies: A Critical Review, *Polymer Reviews*, **49**, 2009, pp. 201-225 (doi: 10.1080/15583720903048227).
- [2] L.-Z. Guan, L.-X. Gong, L.-C. Tang, L.-B. Wu, J.-X. Jiang, G.-Q. Lai, Mechanical Properties and Fracture Behaviors of Epoxy Composites With Phase-Separation Formed Liquid Rubber and Preformed Powdered Rubber Nanoparticles: A Comparative Study, *Polymer Composites*, **36**, 2015, pp. 785-799 (doi: 10.1002/pc.22995).
- [3] H. Zhou, S. Xu, A new method to prepare rubber toughened epoxy with high modulus and high impact strength, *Materials Letters*, **121**, 2014, pp. 238-240 (doi: 10.1016/j.matlet.2014.01.160).
- [4] M.R. Dadfar, F. Ghadami, Effect of rubber modification on fracture toughness properties of glass reinforced hot cured epoxy composites, *Materials & Design*, **47**, 2013, pp. 16-20 (doi: 10.1016/j.matdes.2012.12.035).
- [5] R. Thomas, J. Abraham, S. Thomas, S. Thomas, Influence of carboxyl-terminated (butadiene-co-acrylonitrile) loading on the mechanical and thermal properties of cured epoxy

- blends, *Journal of Polymer Science Part B-Polymer Physics*, **42**, 2004, pp. 2531-2544 (doi: 10.1002/polb.20115).
- [6] H. Dou, B. Tian, Y. Huang, Y. Quan, Q. Chen, G. Yin, Improved mechanical properties of ATBN-toughened epoxy networks by controlling the phase separation scale, *Journal of Adhesion Science and Technology*, **30**, 2016, pp. 642-652 (doi: 10.1080/01694243.2015.1117268).
- [7] N. Chikhi, S. Fellahi, M. Bakar, Modification of epoxy resin using reactive liquid (ATBN) rubber, *European Polymer Journal*, **38**, 2002, pp. 251-264 (doi: 10.1016/s0014-3057(01)00194-x).
- [8] K. Zhao, X.-X. Song, C.-S. Liang, J. Wang, S.-A. Xu, Morphology and properties of nanostructured epoxy blends toughened with epoxidized carboxyl-terminated liquid rubber, *Iranian Polymer Journal*, **24**, 2015, pp. 425-435 (doi: 10.1007/s13726-015-0334-3).
- [9] R. Bagheri, R.A. Pearson, Role of particle cavitation in rubber-toughened epoxies: II. Inter-particle distance, *Polymer*, **41**, 2000, pp. 269-276 (doi: 10.1016/s0032-3861(99)00126-3).
- [10] D.S. Kim, K. Cho, J.K. Kim, C.E. Park, Effects of particle size and rubber content on fracture toughness in rubber-modified epoxies, *Polymer Engineering and Science*, **36**, 1996, pp. 755-768 (doi: 10.1002/pen.10463).
- [11] R.A. Pearson, A.F. Yee, Influence of particle size and particle size distribution on toughening mechanisms in rubber-modified epoxies, *Journal of Materials Science*, **26**, 1991, pp. 3828-3844 (doi: 10.1007/bf01184979).
- [12] D. Verchere, J.P. Pascault, H. Sautereau, S.M. Moschiar, C.C. Richardi, R.J.J. Williams, Rubber-modified epoxies. IV. Influence of morphology on mechanical properties, *Journal of Applied Polymer Science*, **43**, 1991, pp. 293-304 (doi: 10.1002/app.1991.070430208).
- [13] R. Thomas, S. Durix, C. Sinturel, T. Omonov, S. Goossens, G. Groeninckx, P. Moldenaers, S. Thomas, Cure kinetics, morphology and miscibility of modified DGEBA-based epoxy resin - Effects of a liquid rubber inclusion, *Polymer*, **48**, 2007, pp. 1695-1710 (doi: 10.1016/j.polymer.2007.01.018).
- [14] B. Russell, R. Chartoff, The influence of cure conditions on the morphology and phase distribution in a rubber-modified epoxy resin using scanning electron microscopy and atomic force microscopy, *Polymer*, **46**, 2005, pp. 785-798 (doi: 10.1016/j.polymer.2004.11.090).
- [15] X. Song, S. Xu, Curing kinetics of pre-crosslinked carboxyl-terminated butadiene acrylonitrile (CTBN) modified epoxy blends, *Journal of Thermal Analysis and Calorimetry*, **123**, 2016, pp. 319-327 (doi: 10.1007/s10973-015-4989-y).
- [16] G. Tripathi, D. Srivastava, Effect of carboxyl-terminated poly (butadiene-co-acrylonitrile) (CTBN) concentration on thermal and mechanical properties of binary blends of diglycidyl ether of bisphenol-A (DGEBA) epoxy resin, *Materials Science and Engineering a-Structural Materials Properties Microstructure and Processing*, **443**, 2007, pp. 262-269 (doi: 10.1016/j.msea.2006.09.031).
- [17] M.L. Arias, P.M. Frontini, R.J.J. Williams, Analysis of the damage zone around the crack tip for two rubber-modified epoxy matrices exhibiting different toughenability, *Polymer*, **44**, 2003, pp. 1537-1546 (doi: 10.1016/s0032-3861(02)00829-7).
- [18] C.W. Wise, W.D. Cook, A.A. Goodwin, CTBN rubber phase precipitation in model epoxy resins, *Polymer*, **41**, 2000, pp. 4625-4633 (doi: 10.1016/S0032-3861(99)00686-2).
- [19] A.J. Bell, A.J. Kinloch, The effect of the substrate material on the value of the adhesive fracture energy, $G(c)$, *Journal of Materials Science Letters*, **16**, 1997, pp. 1450-1453 (doi: 10.1023/a:1018538116968).

- [20] D.L. Hunston, A.J. Kinloch, S.S. Wang, MICROMECHANICS OF FRACTURE IN STRUCTURAL ADHESIVE BONDS, *Journal of Adhesion*, **28**, 1989, pp. 103-& (doi: 10.1080/00218468908030877).
- [21] V. Tvergaard, J.W. Hutchinson, On the toughness of ductile adhesive joints, *Journal of the Mechanics and Physics of Solids*, **44**, 1996, pp. 789-800 (doi: 10.1016/0022-5096(96)00011-7).
- [22] D. Adolf, R. Chambers, Verification of the capability for quantitative stress prediction during epoxy cure, *Polymer*, **38**, 1997, pp. 5481-5490 (doi: 10.1016/S0032-3861(97)00077-3).
- [23] M.R. Kessler, N.R. Sottos, S.R. White, Self-healing structural composite materials, *Composites Part a-Applied Science and Manufacturing*, **34**, 2003, pp. 743-753 (doi: 10.1016/s1359-835x(03)00138-6).
- [24] Y.F. Li, M.Z. Xiao, Z. Wu, K. Peng, C.M. Han, W. Xiang, J.Y. Dai, Effects of epoxy/hardener stoichiometry on structures and properties of a diethanolaminecured epoxy encapsulant, *IOP Conference Series: Materials Science and Engineering*, **137**, 2016, pp. 1-8 (doi: 10.1088/1757-899X/137/1/012012).
- [25] R. Thomas, D. Yumei, H. Yuelong, Y. Le, P. Moldenaers, Y. Weimin, T. Czigany, S. Thomas, Miscibility, morphology, thermal, and mechanical properties of a DGEBA based epoxy resin toughened with a liquid rubber, *Polymer*, **49**, 2008, pp. 278-294 (doi: 10.1016/j.polymer.2007.11.030).
- [26] N.T. Kamar, L.T. Drzal, Micron and nanostructured rubber toughened epoxy: A direct comparison of mechanical, thermomechanical and fracture properties, *Polymer*, **92**, 2016, pp. 114-124 (doi: 10.1016/j.polymer.2016.03.084).
- [27] K. Xiao, L. Ye, Effects of rubber-rich domains and the rubber-plasticized matrix on the fracture behavior of liquid rubber- modified Araldite-F epoxies, *Polymer Engineering and Science*, **40**, 2000, pp. 2288-2298 (doi: 10.1002/pen.11361).