Compatibility, Mechanical, Thermal, and Morphological Properties of Epoxy Resin Modified with Carbonyl-Terminated Butadiene Acrylonitrile Copolymer Liquid Rubber

A.B. Ben Saleh[1*], Z.A. Mohd Ishak[2], A.S. Hashim[2] and W.A. Kamil[3]

[1] Higher Institute of Qualification of Trainer Preparation, Misurata, P.O. Box 1091 Libya
[2]School of Materials and Mineral Resources Engineering, Engineering Campus,
Universiti Sains Malaysia, 14300 Nibong Tebal, Pulau Pinang, Malaysia
[3] School of Chemical Sciences, Universiti Sains Malaysia, 11800 USM
Pulau Pinang, Malaysia

Corresponding author: abdu702002@yahoo.com

Abstract: *Epoxy resin (EP) was premixed with (0, 5, 10, 15, and 20 phr) carbonyl-terminated butadiene acrylonitrile copolymer (CTBN) liquid rubber and cured with a diamine curing agent (IPD) for one hour at 100°C and post cured at 110°C for two hours in an air oven. The compatibility, reactivity, thermal, mechanical, and morphological properties were determined. The gel time and cure time were increased with an increase of the CTBN content. The gel and cure temperature values for all of the CTBN modified epoxy samples are higher than those of the unmodified EP. The glass transition temperatures (T_g) of the modified EP decreased with increasing CTBN content. The tensile and flexural properties (strength and modulus) of modified EPs were observed to be lower than those of the unmodified EP and decrease with an increase in the CTBN content. Conversely, an increase in the tensile strain with the incorporation of CTBN was observed. The results showed an improvement of the fracture toughness of the EP with the presence of CTBN. The toughening effect became more apparent as the testing speed was increased from 1 to 500 mm min^{-1}. The fracture surface analysis by scanning electron microscopy (SEM) discovered the presence of a two-phase morphology.*

Keywords: epoxy resin, toughening of epoxy resins, liquid rubber, CTBN

1. INTRODUCTION

EPs are considered to be one of the most important classes of thermosetting polymers. They have been used extensively as high performance adhesive composite materials due to their outstanding mechanical and thermal properties such as high modulus and tensile strength, low creep, high glass transition temperature, high thermal stability, and good moisture resistance.[1] In the cured state, EPs are brittle materials that have fracture energies some two orders of magnitude lower than modern thermoplastics and other high performance materials.[2] In order to remain competitive as the materials of choice for many applications such as adhesives and composite matrices, epoxies should be modified to improve their fracture toughness.

One of the successful methods used to toughen EPs is the incorporation of the rubber phase into the brittle epoxy matrix, which may be achieved by the use of reactive liquid rubber or preformed rubber particles.[3] The rubbers are initially miscible with the epoxy, but during the polymerisation the rubber, phase separates due to slight immiscibility with the matrix. At the proper concentration of rubber, the dispersed rubber phase can improve the toughness without a significant decrease in the other properties of the epoxies.[4] The improvement in the toughness of rubber-toughened epoxies has been associated with three main toughening mechanisms: crazing, shear banding, and elastic deformation of the rubber particles. These mechanisms can act either alone or together to produce the toughening effect.[5–7]

An attempt to toughen the EP using a polyurethane (PU) prepolymer as a modifier via an interpenetrating network (IPN) grafting has been reported by Harani et al.[8] For this purpose, a PU prepolymer has been synthesised based on hydroxyl-terminated polyester resins and used as a modifier for the EP at different concentrations. Ratna and Banthia[9] showed that carboxyl terminated poly(2-ethylhexylacrylate) (CTPEHA) liquid rubber can be used as an impact modifier for the EP cured with an ambient temperature hardener. However, carboxyl terminated oligomers can only be synthesised by bulk polymerisation, which is difficult to control. Qian et al.[10] studied the synthesis and application of core-shell rubber particles as toughening agents for epoxies. The effect of the epoxidised natural rubber, ENR (50 mol %) on the curing behaviours and adhesive strengths of an epoxy (DGEB-A) and dicyandiamide/2-methyl imidazole system was studied by Hong and Chan.[11] Many works in toughening of the EP have been reported.[7–11]

The present work attempts to discuss the compatibility between CTBN and the EP, and to investigate the thermal, mechanical, and morphological properties of the modified EP.

2. EXPERIMENTAL

2.1 Materials

The clear epoxy 331, with an epoxide equivalent weight of 182–192, was liquid diglycidyl ether of bisphenol-A (DGEB-A). The curing agent was clear epoxy hardener 8161 [isophorone diamine (IPD)] with an amine value of 260–284 (mg KOH gm^{-1}). Both the EP and curing agent were obtained from Euro Chemo-Pharma Sdn. Bhd. Hycar CTBN 1300 x 8 is a registered trade name of a liquid carboxyl-terminated butadiene acrylonitrile copolymer and was obtained from Noveon.

2.2 Curing Process and Sample Preparation

EP (100 phr) with varying contents of CTBN (5–20 phr) were first mixed together and then heated for 20 min at 60°C in a water bath with stirring. When the mixture had cooled to 40°C, 60 phr of curing agent (IPD) was added and the mixing continued for about 2 min. The mixture was then poured into a mould and left in vacuum for 5–10 min at room temperature (26°C) to remove any air bubbles. The mixture was then cured for one hour at 100°C before being postcured at 110°C for two hours in an air oven. The cured specimen was allowed to cool slowly at room temperature in the mould.

2.3 Reactivity Tests

The curing parameters (gel time, cure time, gel temperature, and cure temperature) of the EP are influenced by the amount of CTBN. A predetermined amount of the EP was cured with a stoichiometric content of the curing agent and various CTBN content (0–20 phr) mixed in a glass beaker. The beaker was immersed in a water bath (60°C) and by using a type 2 thermocouple, the temperature was recorded. The curing conditions were determined from the exothermic curves.

2.4 Differential Scanning Calorimetry (DSC)

The DSC instrument (Perkin Elmer DSC-6 differential scanning calorimeter) was employed to determine the T_g of both unmodified and CTBN-modified EP. Samples of about 8–10 mg were heated at a rate 10°C min^{-1} in a nitrogen atmosphere over the temperature range from 30°C–100°C.

2.5 Mechanical Tests

Tensile and flexural tests were performed according to ASTM D-638 and ASTM D790-02, respectively, using an Instron testing machine Model 3366. The crosshead speed was set at 2 and 5 mm min^{-1} for the tensile and flexural tests, respectively. The ultimate tensile strength, Young's modulus, tensile strain, and energy at the break were measured. The flexural strength and flexural modulus were calculated using the following equations:

$$\text{Flexural modulus} = \frac{L^3 m}{4bd^3} \qquad (1)$$

$$\text{Flexural strength} = \frac{3PL}{2bd^2} \qquad (2)$$

where,

L = span length; P = maximum load; b = specimen width; d = specimen thickness; and m = tangent gradient of the initial straight line of the load versus deflection curve.

The fracture toughness, K_c, was determined according to ISO 13586: 2000 using SEN-B specimens. The application of the Linear Elastic Fracture Mechanics (LEFM) theory facilitates the evaluation of the K_c.[12] The geometry and size of the SEN-B specimens are given in Figure 1. A natural crack was generated by razor blade tapping in the notch. The SEN-B specimens were tested at crosshead speeds of 1, 100, and 500 mm min^{-1}. The values for K_c were calculated using Equation (3):

$$K_C = \frac{P_C \frac{S}{4}}{B \frac{W^2}{6}} \left[1.93 - 3.07\left(\frac{a}{W}\right) + 14.53\left(\frac{a}{W}\right)^2 - 25.1\left(\frac{a}{W}\right)^3 + 25.8\left(\frac{a}{W}\right)^4 \right] \qquad (3)$$

where,

P_c = load at peak (N); B = specimen thickness (m); W = specimen width (m); a = notch length (m); and S = span length (m).

All tests were conducted at ambient temperature and an average value of the five repeated tests was taken for each composition.

2.6 Fractography (SEM Analysis)

The fractured surfaces of the selected SEN-B of unmodified and modified EPs were coated with a thin gold/palladium layer and examined in a SEM (SEM Cambridge Stereoscan 200). SEM inspection was focused in the vicinity of the razor notch, which reflects the failure mode.

3. RESULTS AND DISCUSSION

3.1 Reactivity

Table 1 shows the effect of the CTBN content on the reactivity of the EP. In the CTBN/EP/IPD system, gel time and cure time increased with increasing rubber content. The CTBN molecules may retard the reaction and movement of reactive molecules, which lead to delay in the gel time and cure time.[13] The gel and cure temperature values for all of the rubber-modified epoxy samples are higher than those of the unmodified epoxy are. This observation is in agreement with other linear liquid rubber or thermoplastics and DGEB-A blends, where a significant increase in exothermic peak was observed.[14, 15]

3.2 Thermal Analysis

Figure 1 shows the T_g as obtained from the DSC thermograms of the EP versus CTBN content. The T_g values for all of the CTBN-modified epoxy samples are lower than those of the unmodified epoxy are. This decrease in T_g values can be related to the fact that a chemical interaction occurred between the CTBN rubbery phase and the EP. This is in agreement with the observations that were reported by Ochi and Bell, and Ratna et al.[16,17] It can clearly be seen that the T_g values dropped upon the addition of 10 phr of CTBN, after which a slight increase in T_g was observed. This indicates that a larger amount of CTBN could lead to more interaction with the EP and could form grafting and/or crosslinking.

Table 1: The effect of the CTBN content on the reactivity of the EP.

CTBN content (phr)	Gel time (min)	Gel temp. (°C)	Cure time (min)	Cure temp. (°C)
0	4.0	81	6.0	115
5	4.4	87	7.0	145
10	4.5	92	8.0	142
15	5.1	96	8.0	136
20	6.0	90	9.0	128

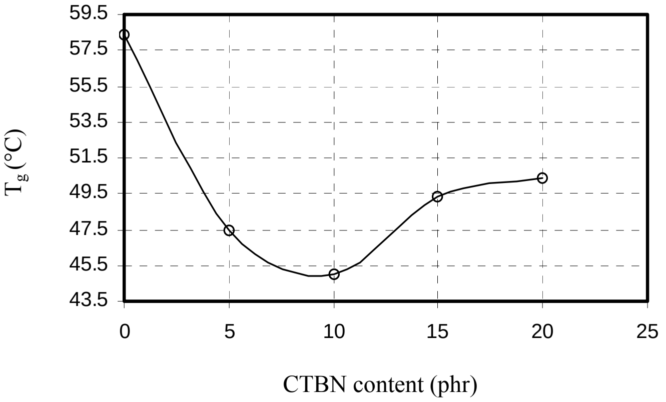


Figure 1: The effect of CTBN content on the glass transition temperatures (T_g) of the EP.

3.3 Tensile Properties

Table 2 shows the effect of CTBN content on the tensile properties of the EP. As expected, the tensile strength and Young's modulus of modified EPs are lower than those of the unmodified EP. The decrease in Young's modulus can be attributed to the presence of low modulus rubber particles in the epoxy matrix. The reduction in strength is also due to the presence of rubber.[18,19] A more important reduction in the properties was observed in the case of the modified epoxy containing a high load of CTBN i.e., 15 and 20 phr CTBN. This indicates a plasticizing effect of the incorporated rubber. The plasticizing effect is also reflected in the increase in tensile strain of CTBN-modified EP.

3.4 Flexural Properties

Figure 2 shows the effect of CTBN content on the flexural strength and modulus of modified EPs. A similar trend was found in the case of the tensile properties; the flexural strength and modulus of modified EPs are lower than those of the unmodified EP. The decrease of the modulus can be attributed to the presence of low modulus rubber particles in the epoxy matrix. The reduction in strength is attributed to the presence of rubber, which is distributed in the epoxy matrix as evident from the decrease in T_g values. Similar findings were reported by other researchers with different types of liquid rubbers.[20, 21]

Table 2: The effect of the CTBN content on the tensile properties of the EP.

CTBN (phr)	Tensile strength (MPa)	Strain at break (%)	Young's modulus (GPa)
0	41.0 ± 1.7	5.1 ± 0.9	1.56 ± 0.13
5	38.3 ± 0.4	6.3 ± 0.7	1.31 ± 0.07
10	25.6 ± 5.0	8.9 ± 1.5	1.06 ± 0.41
15	20.4 ± 3.7	8.8 ± 1.7	0.99 ± 0.31
20	16.6 ± 2.2	7.5 ± 0.9	0.92 ± 0.12

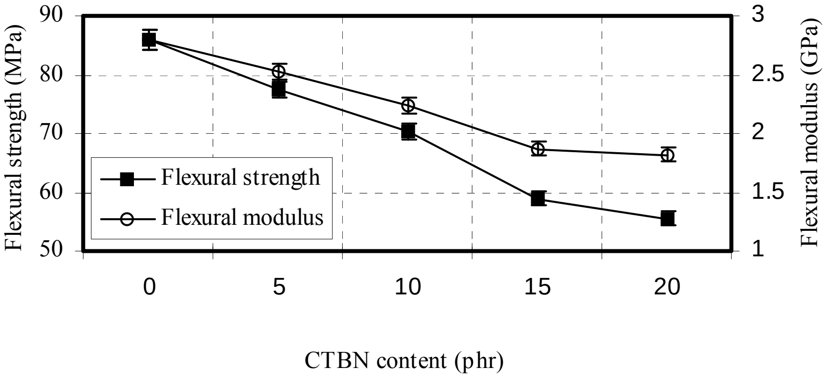


Figure 2: Effect of CTBN content on the flexural strength and modulus of the modified EPs.

3.5 Fracture Toughness and Fractography

The effect of CTBN content and different testing speeds on the K_{IC} of the EPs is shown in Figure 3. The K_{IC} of the CTBN-modified EP samples is higher than those of the unmodified EP. The improvement in the fracture toughness can be attributed to the incorporation of CTBN in the EP that can increase the fracture resistance of the matrix.

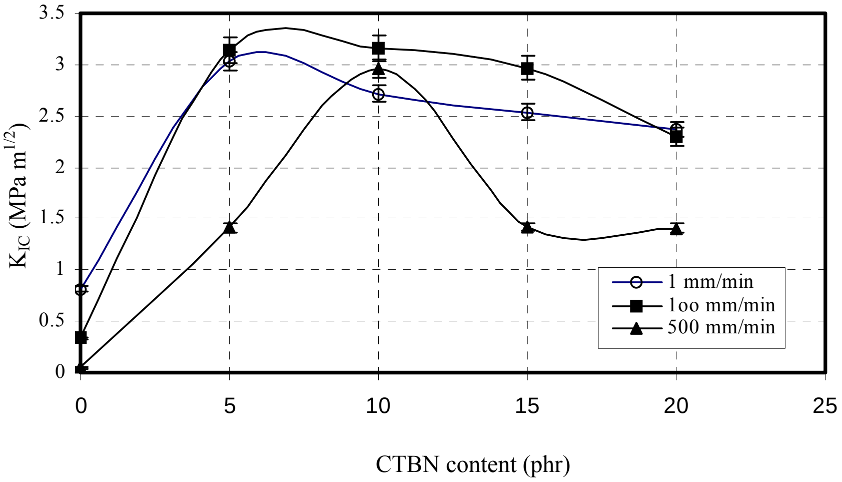
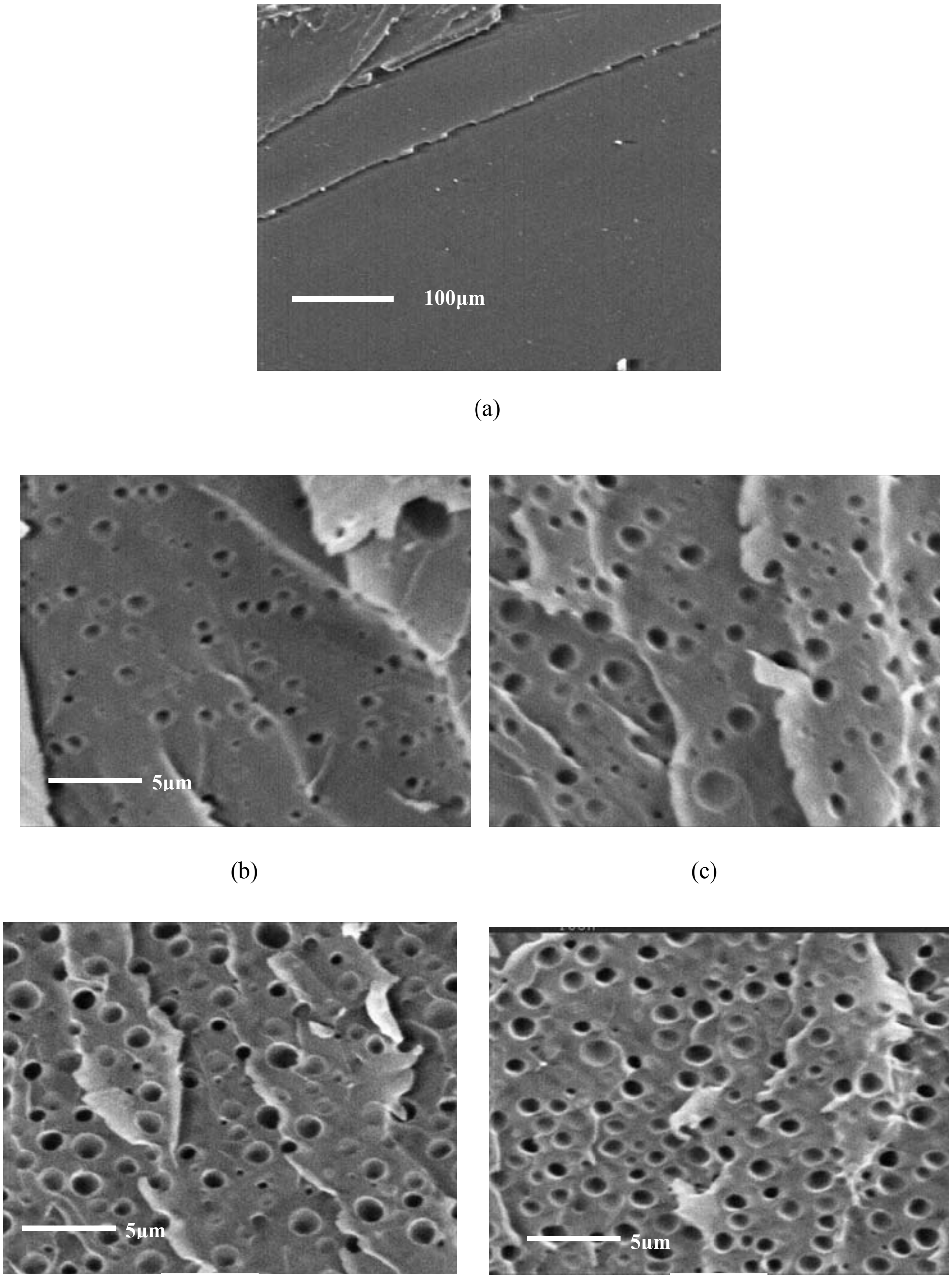


Figure 3: The effect of CTBN content and different testing speeds on the K_{IC} of the EPs.

In order to correlate the mechanical properties of the modified EP with morphology, the fracture surface of the unmodified and CTBN-modified epoxy networks was analyzed by SEM images of the fracture surface of SEN-B tests. The representative SEM images are shown in Figure 4. The shiny and very smooth surface of the unmodified EP [Fig. 4(a)] provides a clear indication for the brittle fracture behaviour. A two-phase network is observed with the epoxy as the continuous matrix and the CTBN as a dispersion phase. The occurrence of cavitation in the presence of shear yielding is observed in all fracture surfaces of the CTBN-toughened EP.[22] The dispersed particles act as stress concentrators during fracture, which has induced localized plastic deformation of the matrix around the particles that induce stress whitening zones developed on the fracture surface of the modified epoxy. This stress whitening effect is related to local plastic deformation at the crack tip. These may explain the observed increase in fracture toughness of CTBN-modified EPs compared with the unmodified EP. Figure 4(b) shows the fracture surface of 5 phr of CTBN filled in the EP system. The cavitated rubber particles dispersed in a continuous epoxy matrix, which has dimensions in the range of 0.64 μm. Figures 4(c) and (d) depict the fracture surface appearance of the modified EP filled with 10 phr and 15 phr of CTBN content, respectively. A slight increase in the rubber particle size can be seen with particle size diameters of 0.85 and 1.04 μm, respectively. It is interesting to note that, in the case of 20 phr of CTBN-modified epoxy [Fig. 4(e)], the excess of CTBN loading led to some agglomeration of cavitated rubber particles throughout the epoxy with an increase of the cavitated rubber particles size (1.40 μm). The increase in the cavitated rubber particles in the epoxy matrix led to the plastisation effect which tends to show the deterioration of important properties as compared to the unmodified resin[23–25], i.e., a steep decrease in the tensile and flexural strengths, and the modulus. To maintain these properties, the recommend amount of CTBN for toughening EP should not be more than 10 phr.

At a low testing speed, i.e., 1 mm min^{-1}, the fracture toughness attained a maximum value at 5 phr of CTBN content, which was 3.03 MPa m$^{1/2}$. Whereas at a high testing speed, i.e., 100 and 500 mm min^{-1}, the fracture toughness reached maximum values at 10 phr of CTBN content, which were 3.60 and 2.96 MPa m$^{1/2}$, respectively. Hence, the optimum amount of CTBN for toughing of the EP ranged between 5 to 10 phr of CTBN content.

CTBN-modified EPs exhibit increased fracture toughness, but also show the deterioration of other important properties as compared to the unmodified resin. For example, a steep decrease in the tensile and flexural strengths, and modulus. Similar findings have been reported by Verchere et al. and Hwang et al.[23–25]



(a)

(b) (c)

(d) (e)

Figure 4: SEM micrographs of the fracture surfaces of 5–20 phr CTBN-modified EP.

4. CONCLUSION

We conclude that CTBN is qualified for the toughening of the EPs because it has good reactivity and acceptable compatibility with the EP matrix, which is supported by the reduction in the glass transition temperatures of the EP with increasing rubber content. The tensile energy and tensile strain at the break was clearly improved with CTBN additives without significant sacrifices in other tensile and flexural properties of the modified EP. SEM analysis indicated that the dispersed rubber particles act as stress concentrators during the fracture and this might explain the observed increase in the fracture toughness of the modified EP compared to the unmodified EP. The toughening effect becomes more apparent at high testing speeds.

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