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Mechanical Properties of Epoxy Matrix Composites Toughened by Liquid Epoxidized Natural Rubber (LENR)

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Abstract: Epoxy matrix widely used in polymer composites as a reinforcement material due to its outstanding performance. Epoxy matrix exhibit good mechanical and thermal properties such as good stiffness, dimensional stability and high heat distortion temperature. However, it is known that epoxy had brittleness and exhibit low toughness. This study investigates the mechanical properties of brittle epoxy resin when modified by liquid epoxidized natural rubber for toughening purposes. Liquid epoxidized natural rubber (LENR) was introduced to the epoxy with five different loadings of 1%, 3%, 5%, 7% and 9% by weight. The mechanical strength (flexural strength, flexural modulus, tensile strength, tensile modulus and impact strength) of the rubber toughened epoxy composites were investigated. The results showed that the addition of liquid epoxidized natural rubber (LENR) had improved the flexural modulus, flexural strength and impact strength by 47%, 40%, and 22% respectively at 3% loading.

Keywords: epoxy, liquid epoxidized natural rubber, mechanical properties, toughened

1. Introduction

Epoxies are defined as well-established thermoset cross-linked polymers in which the cross-linking is derived from reactions of the epoxy group. Commercial epoxy resin contains aliphatic, cycloaliphatic, or aromatic back bones. The most widely used is epichlorohydrin and bisphenol-A derived resin. Epoxies were developed, principally by Ciba AG (Switzerland) and the Dovoe and Raynolds Co. (USA) [1-3]. Epoxy resins consist of three-dimensional networks or agglomerates of moderate molecular weight. As the molecular polymerize through crosslinking, their rotational and rotational freedom is reduced, which reduces the chances of the primary bonds to be set up with adjacent molecules. The tensile and comprehensive strength of epoxy resins are increased if the distance between crosslinks is shortened. Shorter crosslink distances imply high volume concentration of epoxy group and hence a higher probability of reaction of all the epoxy groups. Epoxy resin also have good properties with good stiffness, specific strength, dimensional stability, high heat distortion temperature and chemical resistance [1, 4-5, 21]. For these reasons, it is also the most common polymer used in fibre and filler reinforced polymers for structural applications. However, epoxy is known to be brittle with poor mechanical properties, in terms of strength and toughness, thus preventing the use of this polymer in applications that require stability and high mechanical performance.

Many researchers reported that to toughen epoxy resin, a common method is introducing particles in the resin, including liquid rubbers, thermoplastics, copolymers, silica nanoparticles, silicate layers, core shell particles, and combinations of these [6-10]. Synthetics rubbers containing methyl, hydroxyl, carboxyl, anhydride or thiol groups potentially react with the epoxy resins. Barcia et al. [11] used hydroxyl terminated polybutadiene (HTPB) as surface modifier in carbon fiber reinforced, epoxy matrix composites. Rubbers with carboxyl groups in the chain however may be cured with the epoxy resin to increase elongation and to decrease the tensile strength and hardness. Bussi and Ishida [12] studied the mechanical properties of the blends of diglycidyl ether of bisphenol-A (DGEBA) based epoxy resin and hydroxyl terminated, internally epoxidized polybutadiene rubber. In order to improve mechanical properties, the epoxidized rubber was pre-reacted with an excess diepoxide to achieve better bonding between the rubber particles and the epoxy continuous phase. Nigam et al. [13] studied the changes in mechanical properties of epoxy cresol novolac (ECN) resin by liquid carboxy terminated copolymer of butadiene acrylonitrile (CTBN) modification.

Extensive study had been carried out to increase the toughness, and these include using glass beads, alumina

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trihydrate and silica. The most successful work involved the addition of a suitable rubber, such as liquid amine-terminated (ATBN) [14], carboxyl-terminated (CTBN) [15-18] hydroxyl-terminated (HTBN) [3-4, 19], epoxy-terminated (ETBN) copolymers of butadiene and acrylonitrile [16], and hydroxyl-terminated and epoxy-terminated polybutadiene to interpenetrating the polymer networks (IPN) structures [14].

In this study, a modification made by adding rubber particles in the form of liquid epoxidized natural rubber (LENR) into epoxy matrix is intended to improve the modulus, strength, toughness and heat deflection temperature. Epoxidized natural rubber (ENR) is a modified natural rubber (NR). A typical formulation of ENR from NR, cis-1, 4- isoprene, employing peracetic acid. The isoprene and epoxidized isoprene act as monomer units that are randomly distributed along the polymer chain. Various degree of epoxidation of NR is commercially available [1-2]. Apart from that a global single step mechanism for ethanol oxidation is also available [7].

2. Materials and Methods

The commercial resin type Epikote 828 of Bisphenol-A-(DGEBA) epoxy cross-lined with an aliphatic curing agent polyoxypropylene diamine Jeffamine D230 were purchased from Asa Chem Sdn. Bhd. Epoxidized natural rubber (ENR) was obtained from Research Institute Malaysia (RRIM). The following reagents and solvents were used without further purification: Ethanol (Systerms), Methanol (Systerms), Methylene blue (Sigma Aldrich), Rosebengal (Sigma Aldrich), and Toluene (J.T.Baker Company) respectively. Liquid epoxidized natural rubber (LENR) was prepared using photochemical degradation technique by dissolved ENR in toluene with rubber to solvent ration of 1:3, weight/volume. 0.2 g methylene blue, 0.26 g rosebengal and 10 ml of methanol were added into the mixture. The mixture was continuously stirred until the rubber was completely dissolved using mechanical stirrer and was exposed to the fluorescent light at the same time. Resultant solution is known as LENR and was yellow pale in color [20]. The formulations recipes were summarized in the Table 1 for all Epoxy/LENR blend.

A direct method like curing agent dispersion was employed to disperse the particles in the epoxy matrix to form the composite. It starts with epoxy matrix was heat at 80 C for 2 hours. Then, the LENR was added into epoxy resin, and stir for 45 minutes followed by the addition of the hardener and subsequent mixing for 30 minutes. The resulting mixed material was degassed under deep vacuum (85°C for 30 minutes) until no bubbles were observed and then cured in a mold at 120ºC for 30 minutes. Several curing cycles with varying temperature and time were also considered and it was found that extending the curing cycle for more than 1 h at 120°C would not improve the mechanical properties substantially. Different amounts of LENR were added to the epoxy: 1, 3, 5, 7 and 9% by weight.

The mechanical tests were carried out as follows the sample conditioned at 20°C and 65% RH. A three-point flexural test and tensile test was performed on a Testometric machine model M350-10CT according to ASTM D790-96 and ASTM D 638 M-9 1a, respectively. Five specimens of dimensions 127 mm × 12.7 mm × 3.2 mm were prepared. Sample were used to obtain the average value for flexural strength and modulus with loading head speed of 1.35 mm/min and span length was fixed at 50 mm. All tests were performed at room temperature. To determine the mechanical performance of impact strength, Izod test was carried out using Digital Impact Testing RR/MT according to standard test method of ASTM D256-9 1a. Six samples of rectangular with dimensions of 60.3mm × 12.7 mm × 3.2 mm, with a notch at the center were used for this testing.

Table 1 Compounding formulation used in Epoxy/LENR blend preparation

Epoxy	LENR	Hardener
70 phr	1.00 - 9.00 phr	30 phr

3. Results and Discussion

3.1 Flexural Properties of the Composite

The results of flexural strength and flexural modulus for the composites, with and without addition of LENR are shown in Fig. 1 and 2, respectively. Since LENR used in this study contained a rubber reactive group, it was added to the neat epoxy to observe its effects on flexural properties. In general, the flexural strength for epoxy composites seems to be improved with the addition of LENR. As shown in Fig. 1, the flexural strength of the composites at 3% was 139.62 MPa as compared to 83.77 MPa for neat epoxy. The improvement was about 40%. The interfacial strength of the composites and the flexural strength of the matrix are the important factors that determine the flexural strength of a composite [3-4]. In this case, the addition of LENR was contributed to a strong interface and hence improved the flexural strength of the composite.

Figure 2 showed, the optimum flexural modulus of the composites at 3% of LENR addition was about 11.71 GPa compared to 6.21 GPa for neat epoxy composite. The improvement was about 47%, and this was mainly due to toughening caused by the LENR modification of the epoxy matrix, which gave rise to good energy absorbing capacity. Rubber domains also were formed after the addition of LENR to improve flexibility and toughness of the composite. When LENR reacted with epoxy during mixing process, the path of the reaction could change. The reactions of LENR used to modify the epoxy matrix, the ring opening reaction between the LENR hydroxyl end group, and hardener. This result may also be correlate with the chain extension leading to flexibility and toughness [3-4]. Furthermore, cross linking during the reaction produces higher chain extensions, and therefore the LENR epoxy composite, should show better mechanical performances at the same extent of cross linking.

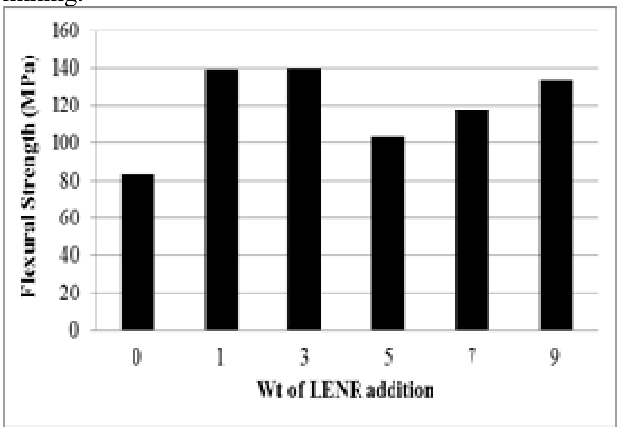

Fig. 1 Flexural strength of epoxy rubber toughened composites.

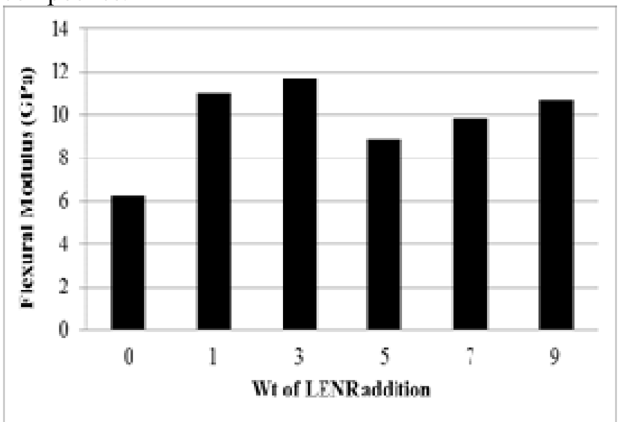

Fig. 2 Flexural modulus of epoxy rubber toughened composites.

3.2 Tensile Strength of the Composites

The tensile strength and tensile modulus of the composite are shown in Figure 3 &4. At 1% addition of LENR, the tensile strength seems to be improved about 20%. Compared with neat epoxy, the addition of 1% LENR will absorb more energy, it may explain the improved in tensile properties and the toughening and strengthening mechanism of the polymer matrix [3-4, 16]. However, the tensile strength start to decrease at higher addition of LENR. This was due to higher amount of rubber content will decrease the stiffness of the composite. The same trend also observed with tensile modulus. Tensile modulus is a measure of the stiffness of an elastic isotropic material and is a quantity used to characterize materials. Due to elastomeric behavior of LENR, the decreases in modulus was expected when it is added to the thermoset resin [2]. This reduction in tensile strength is due to the incompatibility and poor interfacial adhesion between the epoxy and the LENR in the blend system. It also may due to faster reaction between hardener and epoxy than any possible reaction between LENR and epoxy/hardener mixture [3-4].

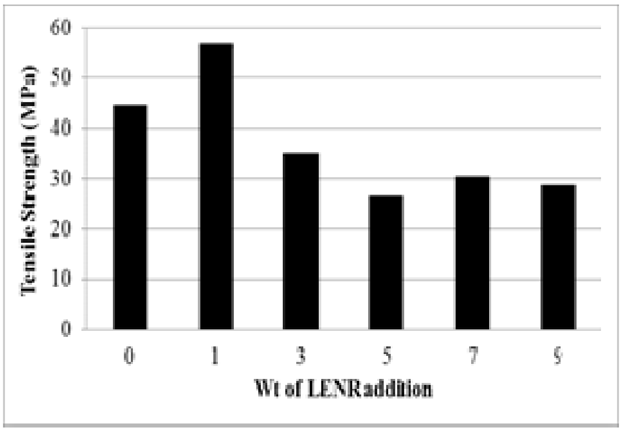

Fig. 3 Tensile strength of epoxy rubber toughened composites.

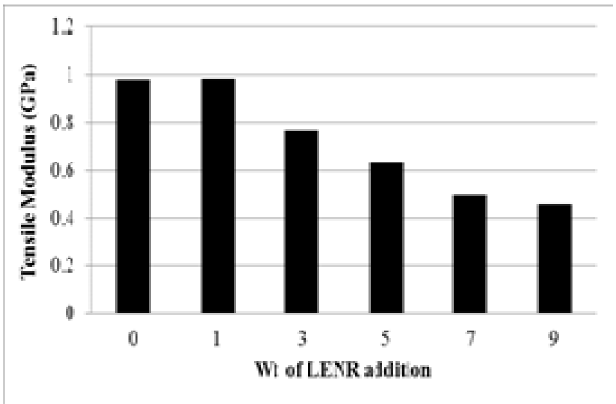

Fig. 4 Tensile modulus of epoxy rubber toughened composites.

3.3 Impact Strength of the Composites

The impact properties of the composites were also given in Figure 5. Since epoxy is a brittle polymer, rubber modification increases its impact strength. When LENR was added to the neat epoxy, the impact strength of the neat epoxy was increased from 5.49 to 6.38 KJ/m2. Moreover, with the addition of 3% LENR, the maximum of impact strength value was obtained (7.07 KJ/m2.). It was about 22% improvement. This increase impact strength may also be correlated with the toughness improvement [3]. LENR addition can be attributed to the increases in entanglement between epoxy resin, and the increase in main chain mobility. Under low loading rates, the entanglement increases the toughness of the specimens with the flexibility effect of LENR molecules [3-4].

4. Summary

In this study, the effects of LENR in epoxy were investigated on mechanical properties. Composites with different LENR ratio were prepared by controlling the micro bubbles formation before curing process. Mechanical tests show epoxy-LENR composites exhibit better modulus of elasticity (MOE), modulus of rupture (MOR) and impact strength than neat epoxy composites. The results have shown that the mechanical behavior of neat epoxy was improved with LENR addition. The results have shown that the addition of liquid epoxidized natural rubber (LENR) improved the flexural modulus and flexural strength by 47% and 40%, respectively, at 3% of LENR addition. When LENR reacted with epoxy during mixing process, the path of the reaction could change. This reaction could cause the flexibility and toughness to increase. Furthermore, the formations of rubber domains in the epoxy matrix led to flexibility and improved toughness. The distorted shape of rubber domains in the epoxy resin matrices was attributed to the higher amount of plastic deformation. These deformation lines are propagated through rubber domains, promoting stress transfer between the particles and epoxy matrix, and this consequently increases its toughness. It was observed that the optimum percentage of LENR addition was at 3% addition of LENR.

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