American Journal of Materials Science 2013, 3(3): 55-61
DOI: 10.5923/j.materials.20130303.02

A Comparison Study of Liquid Natural Rubber (LNR) and Liquid Epoxidized Natural Rubber (LENR) as the Toughening Agent for Epoxy

S. K. Tan[1,*], S. Ahmad[1], C. H. Chia[1], A. Mamun[2], H. P. Heim[2]

[1]School of Applied Physics, Faculty of Science and Technology, Universiti Kebangsaan Malaysia, UKM Bangi, 43600, Malaysia
[2]Institut für Werkstofftechnik, University of Kassel, Mönchebergstrasse-3, Kassel, 34125, Germany

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Abstract Rubber-toughened epoxy resins were prepared using the mechanical stirring method and molded into samples by compression molding. The aim of this study is to modify the brittleness of the epoxy matrix by adding discrete rubbery phases to improve the toughness properties. Liquid natural rubber (LNR) and liquid epoxidized natural rubber (LENR) were used as toughening agents in the epoxy resin to compare the properties of the modified networks. The mechanical and thermal properties have been studied to observe the effect of the modified epoxy network. It was found that by adding the rubbery phase into epoxy resin, the toughness of the epoxy was improved. A composite with 3 wt% of LENR possessed the highest mechanical properties for both flexural and impact properties. The scanning electron micrograph (SEM) demonstrated the discrete rubbery phases between the epoxy and the rubber particles. The glass transition temperature shifted to a lower temperature in the dynamic mechanical analysis (DMA) for the rubber-toughened epoxy.

Keywords Liquid Natural Rubber, Liquid Epoxidized Natural Rubber, Epoxy, Rubber-toughened Epoxy, Toughness, Flexural Test, Impact Test, Scanning Electron Micrograph, Dynamic Mechanical Analysis

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1. Introduction

Epoxy resins are considered one of the most important classes of thermosetting polymers. With their wide-ranging high-performance, epoxy resins are extensively used in many applications including high performance adhesives, aerospace, automobiles and for other engineering purposes [1]. The most widely used epoxy is epichlorohydrin and bisphenol-A derived resins. The outstanding performance characteristics of these resins are conveyed by the bisphenol-A, ether linkages and the hydroxyl and epoxy groups. Bisphenol-A gives the toughness, rigidity and maintains the properties of epoxy in elevated temperatures. The ether linkages provide chemical resistance. The hydroxyl and epoxy groups provide adhesive properties and formulation latitude, or reactivity with a wide variety of chemical curing agents. Once epoxy cured, they are characterized by high chemical and corrosion resistance as well as good mechanical and thermal properties. However, the chief drawbacks of epoxy from industrial use are their brittleness and high cost[2]. Therefore, modifying epoxy resins has attracted intense research interest.

When it comes to modifying the brittle nature of epoxy, an increase in toughness without any reduction in the other important properties is required, such as modulus, thermal properties and environmental corrosion resistance. One of the methods used to improve the toughness of epoxy involves the addition of a rubbery content into the uncured epoxy resins[3]. The rubbery materials that are added to the uncured epoxy are types of copolymers with variable acrylonitrile contents. Studies reported to modify epoxy resin were mostly modified liquid rubber, such as liquid rubber modified by divinylbenzene (DVB), hydroxyl terminated butadiene (HTPB), carboxyl terminated butadiene-acrylonitrile (CTBN), or isocyanate terminated polybutadiene (NCOPBER)[2, 4-6]. The particle size, concentration of liquid rubber, dispersion of liquid rubber in the epoxy matrix, curing and interaction between rubber and epoxy have been taken into consideration and studied to improve the impact strength and the modulus. According to Riew and Smith (1989), the first article concerning rubber as the toughening agent in polymer was published in 1956 by Merz et al., which addressed a rubber-toughening mechanism for a high impact polystyrene (HIPS) system. Since then, many researchers have studied the mechanism of rubber as the toughening agent in plastics[7]. Phinyocheep et al. (2007) discussed poly (ethylene terephthalate) toughened by natural rubber. The impact strength increased by increasing the rubbery phase which is well dispersed in the

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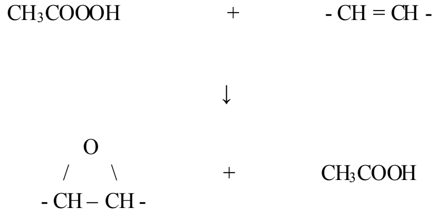
* Corresponding author:
kimmytansk@gmail.com (S. K. Tan)

matrix phase[8]. Therefore, the dispersion of the rubber particles in the matrix is one of the main factors that affect the mechanical properties of the material.

In this report, liquid natural rubber (LNR) and liquid epoxidized natural rubber (LENR) were used as the toughening agent for the epoxy matrix. Based on the theory of rubber as the toughening agent for the matrix, a small amount of rubber particles dispersed in the matrix can have a distinct influence on the final mechanical behavior of the matrix. At first, the natural rubber (NR) used is an elastomer, which is derived from plants and consists mostly of cis–1,4–polyisoprene with a repeating hydrocarbon unit, $(\text{-}CH_2CH_3C{=}CHCH_2\text{-})$[9]. Naturally, NR possesses some abnormal groups, such as epoxide, amine and hydroxyl functions, as reported in the literature. NR shows very interesting physical properties due to its ability to crystallize under stretching. However, it has a low elasticity because the polymer chains are only interlinked at a few points. To increase the elasticity and strength of NR, vulcanization, a curing process involving the addition of sulfur and high heat to create sulfur cross linking, is commonly employed[10, 11].



$$CH_3COOOH \quad + \quad \text{- CH = CH -} \quad \downarrow \quad \overset{O}{\text{- CH – CH -}} \quad + \quad CH_3COOH$$

Figure 1. The epoxidation reaction of natural rubber

The second toughening agent to epoxy that was used in this study was LENR. Epoxidized natural rubber (ENR) is a derivative from the chemical modification of natural rubber (NR), which is derived from the partial epoxidation of the NR molecule, resulting in a new type of elastomer. Figure 1 shows the epoxidation reaction of natural rubber[12]. With a part of C=C double bonds on the NR molecular chains being converted into the polar epoxy groups to obtain ENR, the free volumes of chain phases are decreased and the density and polarity of the derivative is increased. This provides the ENR with excellent air impermeability, oil and organic solvent-proofness, wet road grip performance and so on. During the preparation of ENR, the epoxidation reactions are always accompanied by the further ring-opening reactions of epoxy groups. The nature of the ring-opening products depends on the initial degree of epoxidation. At low modification levels, the majority of epoxy groups are isolated due to the randomness of the epoxidation reaction, and the major ring-opening products are those expected from simple olefin chemistry. ENR can undergo strain crystallization like natural rubber, and hence has superior tensile and fatigue properties[13, 14].

Toughening of epoxy resins with rubber has been studied. Many authors have also made comments on the increasingly wide use of rubber-modified epoxy resins as the structural adhesives and as the matrix for fiber composites. Because of their properties, epoxy resins have many commercial applications. Rubber modified epoxy resin possesses a higher toughness than the unmodified one with only a minimal reduction in the other important properties, such as the modulus. Toughening of epoxy resins is extremely useful because the application of this polymeric material imparts the resistance against mechanical deformation at different loading rates. The rubber toughening of the epoxy system will result in an increase in the hardening modulus. However, there are two factors that must be considered in order to get a toughened epoxy with liquid rubber. First, the liquid rubber should form a rubbery phase, which is dispersed throughout the epoxy resin. Second, the rubbery phase should be well bonded to the matrix through its functional group.

This paper reports the mechanical and thermal properties on LNR and LENR toughened epoxy. Various compositions of liquid rubber were added to the epoxy to study the differences. The effect of two types of liquid rubber in epoxy on the flexural properties and impact properties were studied. The glass transition temperature (T_g) was also observed to understand the effect of liquid rubber on the chain mobility. Morphological analysis was conducted to observe the dispersion of rubber particles in the epoxy matrix.

2. Experimental

2.1. Materials and Sample Preparation

Epoxy resin with the grade of Epikote 828, and Jeffamine polyoxypropylenediamine D230 were purchased from Asachem (M) Sdn. Bhd. Epoxidized natural rubber with grade ENR-50 and natural rubber were obtained from the Rubber Research Institute Malaysia (RRIM).

Liquid natural rubber (LNR) and liquid epoxidized natural rubber (LENR) were prepared by the photosynthesized degradation of the ENR in visible light according to a method described by Abdullah and Ahmad (1992)[15]. A mechanical stirrer was used in this research to mix the materials. First, the LNR or LENR and epoxy were stirred for 1 hour at a speed of 1000 rpm. After 1 hour, the curing agent was added and the mixture was stirred for a further 15 minutes. Finally, the sample was pressed in a mold using compression molding for 15 minutes at 110°C, with 4 minutes preheating. The pressed sample was put into an oven to post cure for 2 hours at 80°C. Samples were prepared with different rubber compositions in the matrix. The neat epoxy was prepared as the control.

2.2. Sample Characterization

Flexural properties were measured under a three-point-bending approach using a Testometric M350-10CT according to ASTM D790. The size of the specimen was 127 by 12.7 by 3.2 m, which was tested flatwise on a support span, resulting in a support span-to-depth ratio of 16. Flexural properties were measured using a 1000 N load cell and a cross head speed of 1.37 mm/min. An impact test was performed using a Ray Ran RR/IMT digital universal impact tester according to ASTM D256. The size of the specimen flatwise before the notch was 63.5 by 12.7 by 3.2 mm. The width of the specimen was the thickness of the sheet. The depth of the plastic material remaining in the specimen under the notch was 10.16 ± 0.05mm. The fractured surfaces of the samples were coated with a gold layer and examined using scanning electron microscopy, SEM (Philips XL-30). Dynamic mechanical analysis (DMA) was evaluated by using a Universal V4.2E TA machine with a single-cantilever mode. Samples were tested at a heating rate of 5°C/min and a frequency of 1 Hz from room temperature to 140°C.

3. Results and Discussion

3.1. Flexural Properties

Figure 2 and Figure 3 show the comparison of the bending properties of rubber-toughened epoxy with neat epoxy.

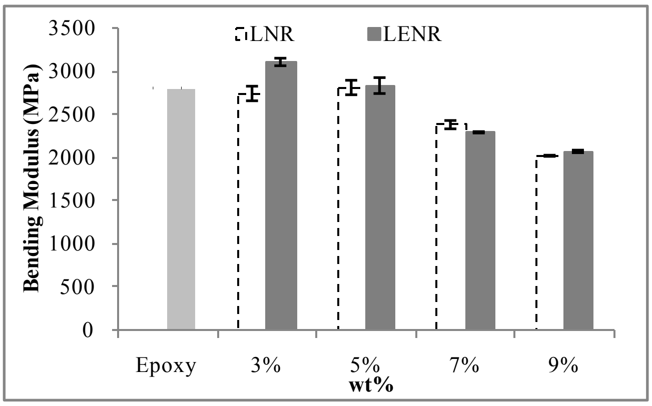


Figure 2. The comparison of bending strength of rubber-toughened epoxy with neat epoxy

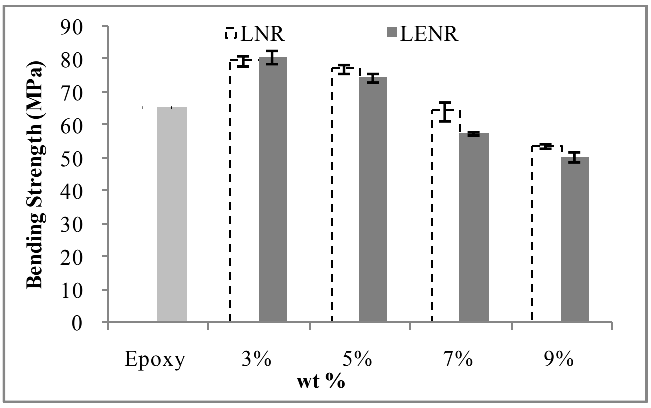
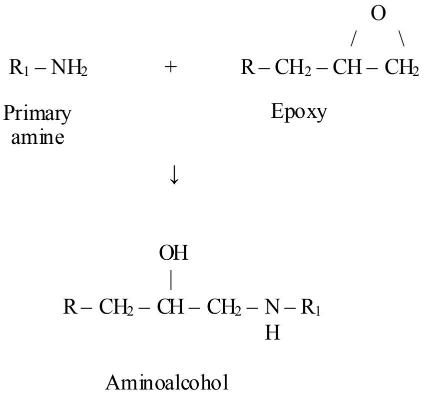


Figure 3. The comparison of bending modulus of rubber-toughened epoxy with neat epoxy

When 3 wt% of LNR was added to the epoxy, the bending strength of the sample increased. When 5 wt% of LNR was added to the epoxy, it showed the optimum result for the bending modulus, which is slightly higher than the neat epoxy. However, the increment was not obvious. The bending modulus and bending strength of 5 wt% LNR toughened epoxy was compared with neat epoxy. The LNR toughened epoxy showed a higher bending strength than the neat epoxy while the bending modulus was maintained. As the content of LNR increased, the bending strength and the bending modulus of the samples decreased gradually. The decrease in the bending modulus showed that the modified system became more ductile.

When LENR was added to the epoxy, both the bending strength and bending modulus were increased. The optimum result for bending properties was achieved with 3 wt% of LENR toughened epoxy. When 3 wt% LENR was added to the epoxy, both the bending modulus and bending strength increased. It is interesting to find that when a small amount of LENR content was added to the epoxy it improved the bending modulus of the epoxy. When stress is applied to the sample, the rubber particles existing in the matrix bear the stress that is applied. The addition of the rubber to the epoxy resin in the system leads to and increases the toughness of the epoxy network. The increase in the main chains mobility caused by the chain extension might be one of the reasons that contributed to the improvement of the mechanical properties. The oxirane groups from LENR participated in the reaction during the curing process[20]. When the curing agent is a "primary" amine, two reactions take place. First (Figure 4), the oxirane ring in the epoxy resin is opened up. The reaction product is an aminoalcohol, and the amine nitrogen still has one hydrogen molecule available for reaction. In a second step (Figure 5), this "secondary" amine can react with yet another epoxy, or oxirane group. Thus, every $-NH_2$, or primary amine group, requires two oxirane groups for a complete reaction. Jeffamine polyoxypropylenediamine used in this study has two primary amine groups in each molecule of diamine[16]. Therefore, with its two primary amine groups, it may react with four oxirane groups from either epoxy resin or LENR. The interaction between curing agent, epoxy resin and LENR is one of the reasons that contributed to the improvement of the mechanical properties. Thus, when it was mixed with the epoxy matrix, the interaction between the LENR and the epoxy contributed to the improvement of the bending properties. However, it was also noted that the bending properties decreased as the content of LENR increased. ENR can undergo strain crystallization because of the elastomeric properties, and hence increase the modulus of the sample[13]. Thus, when LENR was added to the epoxy system, entanglement between the epoxy resin and ENR increased. This contributed to the enhancement of the bending strength of the toughened epoxy system as it could bear the stress that was added to the sample. At the same time, it has the ability to transfer the stress applied very well and improves the bending strength.

Overall, LENR as the toughening agent to the epoxy shows a better result compared to the LNR toughened epoxy. This is due to the oxirane group that is present in the LENR. Both of the figures show that when the content of rubber increases, the bending properties decrease. This is due to the agglomeration of rubber particles with the increase in content of liquid rubber. The agglomeration contributes to the defects and initiates the failure of the samples. According to Bucknall and Smith's theory (1965), the rubber particles initiate the formation of crazes and control their growth. Therefore, the condition of the dispersion of rubber particles inside the epoxy matrix is an important factor affecting the bending properties[17].

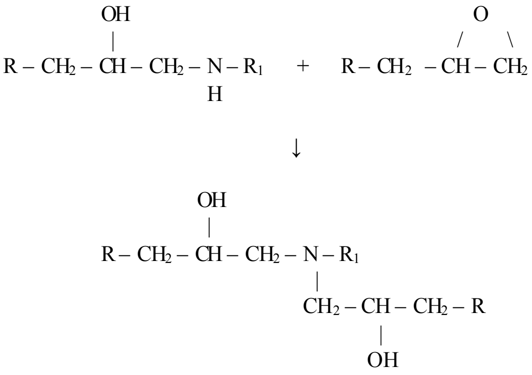


$$\underset{\text{Primary amine}}{R_1-NH_2} + \underset{\text{Epoxy}}{R-CH_2-\overset{\overset{O}{/\ \ \backslash}}{CH-CH_2}}$$

$$\downarrow$$

$$\underset{\text{Aminoalcohol}}{R-CH_2-\overset{OH}{\overset{|}{CH}}-CH_2-\underset{H}{N}-R_1}$$

Figure 4. The reaction of primary amine with epoxy



$$R-CH_2-\overset{OH}{\overset{|}{CH}}-CH_2-\underset{H}{N}-R_1 + R-CH_2-\overset{\overset{O}{/\ \ \backslash}}{CH-CH_2}$$

$$\downarrow$$

$$R-CH_2-\overset{OH}{\overset{|}{CH}}-CH_2-\underset{\underset{CH_2-\underset{\underset{OH}{|}}{CH}-CH_2-R}{|}}{N}-R_1$$

Figure 5. The reaction of "secondary" amine with another epoxy or oxirane group

3.2. Impact Properties

Samples that were used in this testing were all notched samples. The notches in the izod impact specimen serve to concentrate the stress, minimize plastic deformation, and direct the fracture to the part of the specimen behind the notch[4]. In a notched sample, an apparent crack was created; therefore, the amount of energy absorbed depends primarily on the energy to propagate the crack. Figure 6 shows the comparison of impact strength of rubber-toughened epoxy with neat epoxy. When LNR or LENR was added to the epoxy system, the impact strength for both series of samples increased. For the series of LNR toughened epoxy, 5 wt% of LNR toughened epoxy achieved the optimum results. Whilst for the LENR series, when 3 wt% LENR was added to the epoxy resin, it showed the optimum result. However, the impact strength decreased gradually as the LENR content increased. At the same time, 3 wt% of LENR toughened epoxy achieved the highest impact strength in this study. From the impact test, we see that using the rubbery phase as a toughening agent to the epoxy matrix has a beneficial effect. Adding the discrete rubbery phase could improve the impact strength of the epoxy.

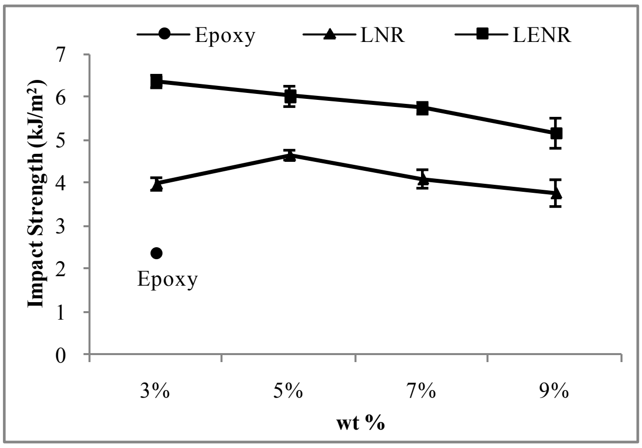


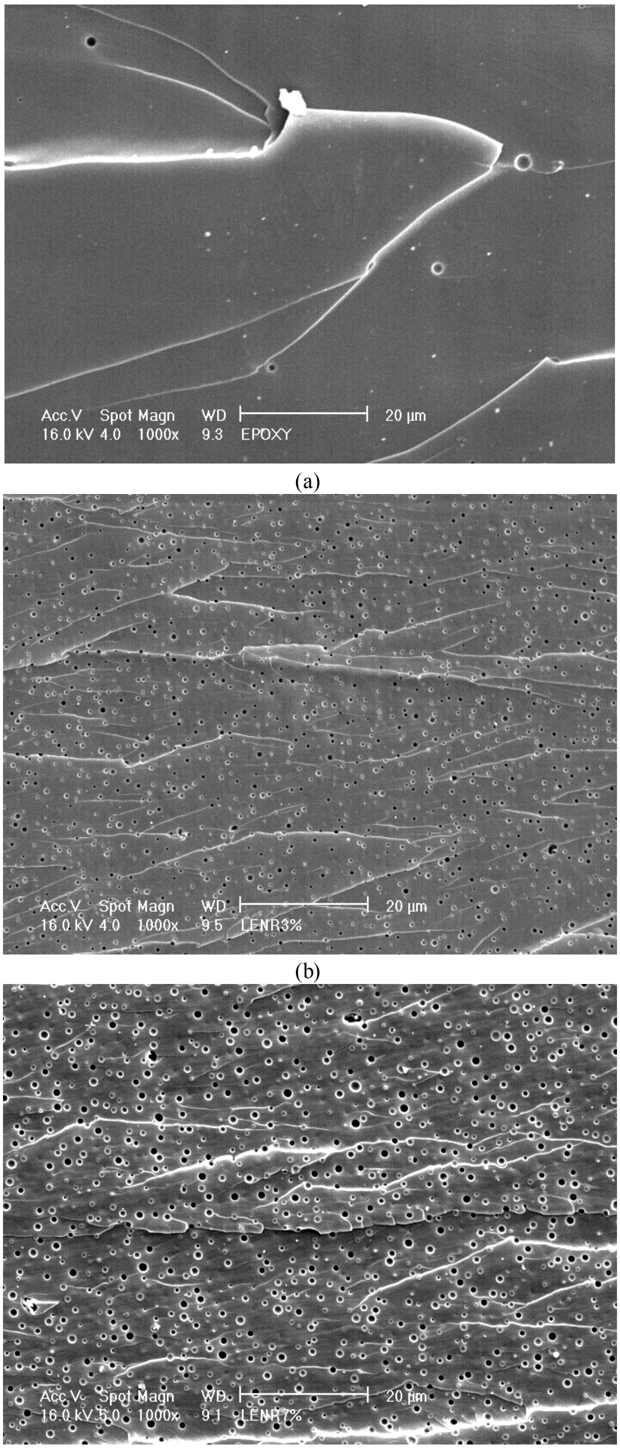
Figure 6. The comparison of impact strength of rubber-toughened epoxy with neat epoxy

The addition of rubber particles to the epoxy might act as an impact modifier to absorb the impact loading and cause the effective stress concentration behavior[8]. Thus, when outer stress was applied, the efficiency of the stress transfer in the rubber-toughened epoxy system increased. The impact property of a material is its ability to absorb and dissipate energy under impact or shock loading. The mechanism of energy dissipation is associated with the damping nature of the toughened epoxy, which is explained by the stress transfer between the rubber rich domains within the epoxy matrix. The comparison between the two types of liquid rubber, as the toughening agent to the epoxy system, shows that the LNR toughened epoxy possessed lower impact performance than LENR toughened epoxy. This is due to the lower compatibility between the rubber particles with the epoxy matrix, which is attributed to the aggregated size of the particles in the LNR toughened epoxy. LENR has better compatibility with the epoxy matrix due to the presence of oxirane groups in LENR, which possessed a good reaction with the epoxy. The improvement of the impact strength can be correlated with the toughness enhancement. Impact strength may not be complementary with the results of the flexural test. This is because the impact strength measurement is very sensitive to the imperfections of the samples, such as voids, bubbles, or any impurities or inclusions that may affect the results of the impact strength[2]. Therefore, normally for the impact test, notches will be made on the sample to serve as the stress concentrator at a specific point, to minimize the plastic deformation when impact stress is applied while the crack propagation will continue behind the notches.

3.3. Morphological Analysis

Rubbers are generally well known for affecting the modulus of a matrix depending on their compatibility with the matrix, the surface area in contact, particle size and the shape of the rubber existing in the matrix, as well as the intrinsic strength of the rubbery phase in the matrix[5]. The impact behavior of the toughened networks can be explained by considering both the toughening and flexibility effects. The flexibility effect is caused by the presence of dissolved rubber inside the epoxy matrix, whereas the toughening process is related to the cavitations in the rubber particles dispersed inside the epoxy matrix[4]. In order to correlate the mechanical properties with the morphological analysis, the particle size and the fracture surfaces of the rubber-toughened epoxy were analyzed by the scanning electron microscope (SEM). Figure 7 shows the morphological analysis of the neat epoxy and rubber toughened epoxy at a magnification of 1000×, showing the differences in the particle size of the samples.

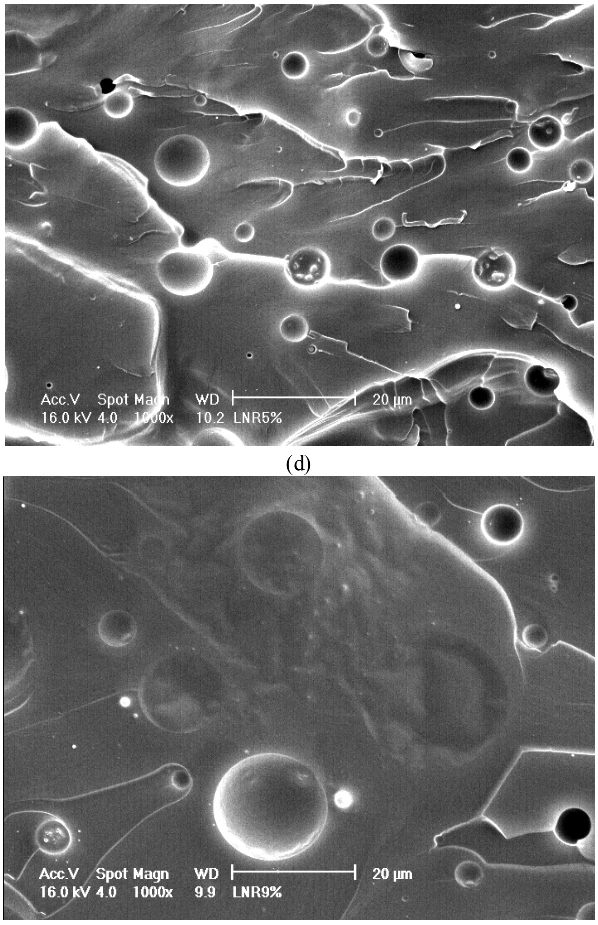
Figure 7 (a) is the fracture surface of the neat epoxy. It can be observed that a few voids exist in the SEM micrograph. The existing voids are an unavoidable issue in the epoxy matrix. These voids could act as the stress concentrators bringing about the brittleness of the cured epoxy. Figures 7 (b) and (c) are SEM micrographs of the fracture surfaces of 3 wt% and 7 wt% of LENR toughened epoxy. Heterogeneous morphology surfaces resulted on the fracture surfaces. The holes observed in the micrograph indicate that the rubber particles dispersed in the epoxy matrix. The cavitations show that the addition of liquid rubber acts as the toughening agent to the epoxy matrix. Figures 7 (b) and (c) also show that there are differences in the particle size of the LENR dispersed in the epoxy matrix. The particle sizes were measured during SEM analysis, and the average results were obtained. The sample with 3 wt% LENR toughened epoxy showed a particle size of about 0.5 to 1.0 µm, whilst the sample with 7 wt% LENR toughened epoxy showed particle size to be about 1.0 to 1.5 µm. This shows that the particle sizes of rubber in the epoxy matrix increased as the LENR content increased. Figures 4 (d) and (e) show the SEM micrograph of 5 wt% and 9 wt% LNR toughened epoxy, respectively. The holes present in the micrograph indicate the LNR rubber particles. In Figure 7 (d), the particle size is about 7.5 to 10 µm, whilst in Figure 7 (e) the particle size is about 5 to 25 µm and is non-uniform. The presence of larger particle sizes is attributed to the agglomeration of the rubber particles with the increase of the rubber content in the epoxy matrix[4, 13]. From the SEM micrographs, the rubber phase appears as a spherical particle in the epoxy matrix. The spherical rubber domain is usually observed in the polymerization induced spinodal decomposition of the rubber modified epoxy systems. The formation of the rubber phase is generally attributed to the spinodal decomposition caused by the increase in the molecular weight of the epoxy matrix when the samples were curing. The phase separation starting from an initial rubber/epoxy co-continuous structure and the influence of surface tension in the separated phase usually results in a spherical rubber particle during cure[18].



(a)

(b)

(c)



(d)

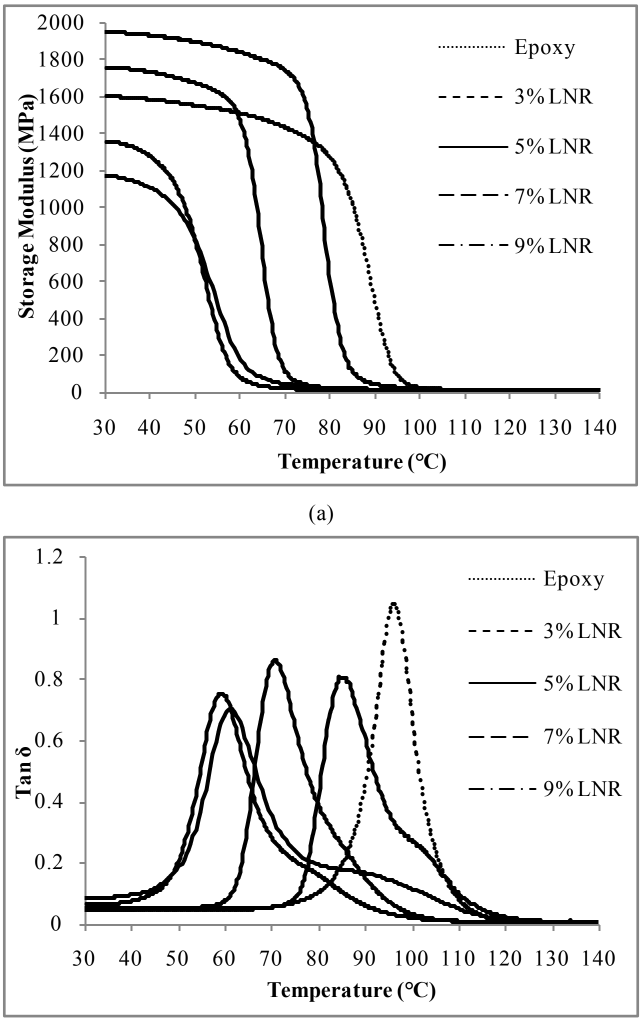
(e)

Figure 7. SEM micrographs of the fracture surface for (a) neat epoxy, (b) 3 wt% LENR, (c) 7 wt% LENR, (d) 5 wt% LNR, and (e) 9 wt% LNR toughened epoxy, at the same magnification of 1000×

When the fracture surfaces of LENR and LNR as a toughening agent to the epoxy matrix were compared, the liquid rubber in LENR toughened epoxy dispersed more evenly and the particle size was smaller compared to the LNR toughened epoxy. The propagation of cracks of LENR toughened epoxy were also found to be finer than the LNR toughened epoxy. This showed that LENR has more potential as a toughening agent for the epoxy matrix. When the propagation cracks between Figures 7 (b) and (c) were compared, it was also found that the 3 wt% LENR toughened epoxy had finer ripples compared with the 7 wt% LENR toughened epoxy. This proves that when the particle size of rubber dispersed in 3 wt% LENR toughened epoxy was smaller and more evenly, it absorbed and transferred the stress that was applied to the system more effectively[8]. Ultimately, this improved the impact and bending properties. The significant dispersion of LNR in the epoxy matrix shows that the LNR was less compatible with the epoxy resin, reducing the interaction between rubber particles and the epoxy matrix. Lower crack growth was observed in Figures 7 (b) and (c) as indicated by the large number of deformation lines. The stress-whitened zones or the amount of deformation lines are proportional to the increase in toughness of the sample[2]. The deformation lines are propagated throughout the rubber domains, which indicate the stress transfer between the rubber particles and epoxy matrix. The energy dissipation mechanism operated in the rubber-modified epoxies was as in the process of stress transfer and associated with the damping nature of rubber-toughened epoxy system. The dissipation energy is represented by the crack propagation lines that gradually reduce as they pass through the rubber particles. The crack propagation lines diffuse and finally become narrow.

3.4. Dynamic Mechanical Analaysis (DMA)

Figure 8 presents the temperature dependence graph of (a) storage modulus, and (b) tan delta of the LNR toughened epoxy. Whilst Figure 9 shows the temperature dependence of (a) storage modulus, and (b) tan delta of the LENR toughened epoxy.



(a)

(b)

Figure 8. Temperature dependence of (a) Storage modulus, and (b) Tan delta of LNR toughened epoxy

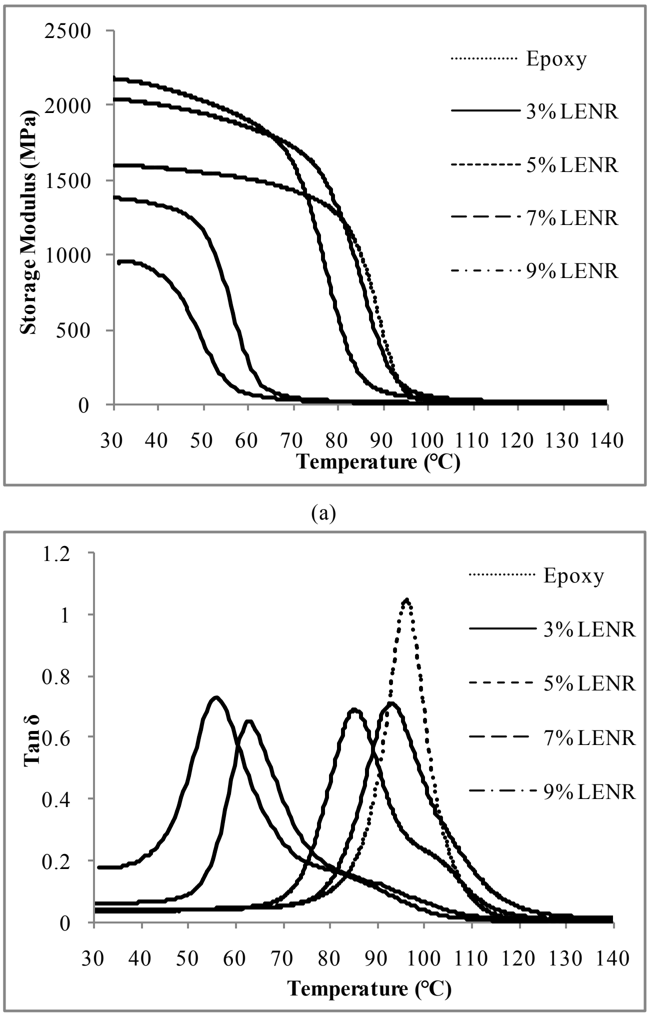
For the storage modulus of LNR toughened epoxy, it shows that 3 wt% and 5 wt% of LNR had a higher storage modulus than the neat epoxy at room temperature. However, 7 wt% and 9 wt% of LNR toughened epoxy had lower storage modulus than the neat epoxy at room temperature.

This shows that the values of the storage modulus at room temperature decreased as the LNR content increased. The same situation also applies to the LENR toughened epoxy, as presented in Figure 9 (a). At a lower concentration of rubber, the phase separated liquid rubber leads to an improvement in the toughness of the epoxy network. At a higher concentration, the liquid rubber flexibilizes the epoxy matrix and reduces the cross-linking density[19]. The decrease in the storage modulus is attributed to the lowering of the cross-linking density and plasticization effect of the liquid rubber into the epoxy matrix. Table 1 shows that the storage modulus of 3 wt% LENR toughened epoxy is higher than the neat epoxy and 5 wt% LNR toughened epoxy. This shows that it had better toughness compared with the LNR toughened epoxy. The impact test already proved that LENR toughened epoxy had higher impact strength. The gradual drops of storage modulus as the temperature increases denote the increase in flexibility of the samples being tested. The drop in storage modulus as the temperature rises indicates that all the modified epoxies pass from hard solid to soft flexible materials.

Table 1. The storage modulus and the glass transition temperature of rubber-toughened epoxy

Sample	Storage Modulus (MPa) (at room temperature)	Glass Transition Temperature, T_g (°C) (derived from Tan δ curves)
Neat epoxy	1598	96.05
3 wt% LENR	1917	75.32
5 wt% LNR	1750	69.91

Tangent delta (δ) curves of samples as a function of temperature were analyzed and presented in Figure 8 (b) and Figure 9 (b). With increasing inclusion of rubber, the peak shifts to a lower temperature. This is attributed to the dissolution of rubber into the epoxy network, forming a homogenous epoxy-rich phase[19]. The neat epoxy shows a peak at around 96°C, which is clearly related to the glass transition temperature (T_g) of the neat epoxy. Therefore, an analysis regarding the T_g derived from Tan δ curves is presented in Figure 10. The addition of liquid rubber lowers the T_g of the cured network. This became more significant when the weight percentage of rubber was higher. This is due to the incorporation of the liquid rubber phase in the epoxy matrix where it acts as a flexibilizer. In addition, it is also related to the lowering of the cross-linking density in the modified epoxies. During the curing of the rubber-toughened epoxy, phase separated rubber domains occupy the space in between the reaction sites of the three dimensional network of epoxy, thereby impairing the cross-linking reaction at that particular site[2]. As a result, it reduces the cross-linking density of cured systems. The overall cross-linking density changes with the incorporation of more rubber. The reduction of the cross-linking density reduces the T_g of rubber-toughened epoxy associated with the increasing mobility chains. When the two types of liquid rubber-toughened epoxy were compared, 3 wt% LENR toughened epoxy had a higher T_g temperature than 5 wt% LNR.



(a)

(b)

Figure 9. Temperature dependence of (a) Storage modulus, and (b) Tan delta of LENR toughened epoxy

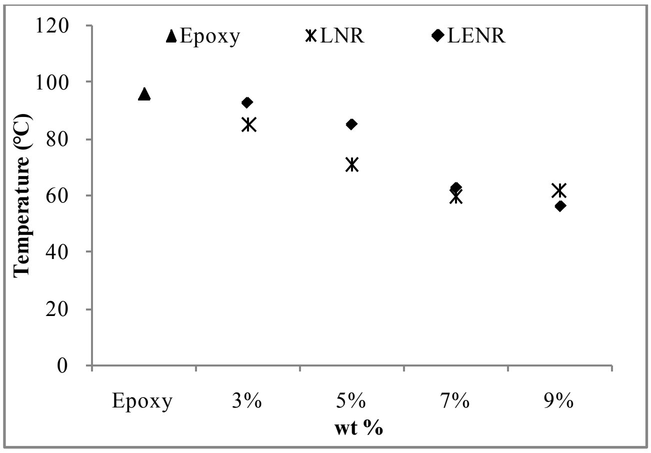


Figure 10. The comparison of glass transition temperature of rubber-toughened epoxy

4. Conclusions

The results show that liquid epoxidized natural rubber is a good potential toughening agent for epoxy resin. With the addition of liquid rubber to the epoxy matrix, a significant increase in the bending properties and impact strength was observed. The sample with 3 wt% of LENR toughened epoxy obtained optimum results for both bending and impact properties. The heterogeneous morphology of the fracture surfaces was obtained by SEM analysis and shows that different particle sizes exist in the rubber-toughened epoxies. From the SEM micrographs, the LENR toughened epoxy had better compatibility with the epoxy resin as the particle size dispersed in the epoxy matrix was smaller and distributed more evenly than LNR. The addition of rubber content to epoxy resin decreased the glass transition temperature. The lower content of rubber in epoxy resin increased the storage modulus, which led to the improvement in the toughness of the epoxy. Overall, LENR as a toughening agent to epoxy resins possessed better mechanical and thermal properties compared to the LNR toughened epoxy. This is because the LENR had better compatibility with the epoxy network.

ACKNOWLEDGEMENTS

The author (S.K. Tan) is thankful to the National Science fellowship of Malaysia for the financial support to the author during her study for this research.

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