

Effects of Liquid Natural Rubber (LNR) on the Mechanical Properties of LNR Toughened Epoxy Composite

(Kesan Getah Asli Cecair (LNR) Terhadap Sifat-sifat Mekanik Komposit Epoksi Diperkuat LNR)

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ABSTRACT

The effects of liquid natural rubber (LNR) on the morphology and mechanical properties of rubber modified epoxy were investigated. Epoxy composites were prepared in four different compositions of LNR (3, 5, 7 and 9phr) by using twin screw extruder. The samples for tensile, fracture toughness and impact tests were prepared according to ASTM D 638, D 5045 and D 256. The elastomeric nature of rubber can act as energy dissipating centre to cause the ductile fracture for the rubber modified epoxy. They was an obvious increment of fracture toughness where maximum value was observed with 3 phr LNR. A clear increment of impact strength at 3 phr LNR was observed, followed by a small increment at 5 phr and no further increment at 7 and 9 phr LNR. The tensile strength showed a similar trend with impact strength and Young's modulus. SEM micrographs showed an increment of rubber particle size when the amount of LNR was increased and caused the mechanical properties to drop.

Keywords: Epoxy resin; liquid natural rubber; mechanical properties; toughness

ABSTRAK

Kesan getah asli cecair (LNR) terhadap morfologi dan sifat-sifat mekanik bagi komposit epoksi telah dikaji. Komposit epoksi disediakan di dalam empat komposisi LNR (3, 5, 7 & 9 phr) dengan menggunakan mesin penyemperitan skru-berkembar. Sampel bagi ujian tegangan, ketahanan patahan dan hentaman disediakan mengikut ASTM D 638, D 5045 and D 256. Elastomer getah dapat bertindak sebagai pusat penyesapan tenaga dan menyebabkan kepatahan mulur berlaku bagi epoksi termodifikasi getah. Peningkatan ketahanan patahan yang jelas didapati dengan nilai maksimum adalah pada 3 phr LNR. Kenaikan yang jelas didapati bagi kekuatan hentaman pada 3 phr LNR dan diikuti dengan kenaikan kecil di 5 phr dan tiada kenaikan lebih lanjut pada 7 dan 9 phr LNR. Kekuatan tegangan telah menunjukkan satu kecenderungan yang sama dengan kekuatan hentaman dan modulus Young. Mikrograf SEM jelas menunjukkan kenaikan saiz partikel getah apabila jumlah LNR meningkat dan menyebabkan penurunan sifat-sifat mekanik.

Kata kunci: Ketahanan; getah asli cecair; resin epoksi; sifat mekanik

INTRODUCTION

The versatility of the highly cross-linked epoxy resins made it one of the most useful and popular thermoset polymers and possesses many good properties including high strength, excellent creep resistance, high thermal, chemical and environmental stability. These resins are widely applied as coatings, castings, structural adhesives and matrix resins in advanced composite materials. As a result of their high cross-link densities, structural epoxy materials are inherently brittle with poor resistance to crack initiation and growth. It can fail prematurely when exposed to mechanical stresses (Kinloch 1989; Mulhaupt & Buchholz 1996).

Toughness may be defined as resistance to impact i.e., low-impact polymers have Izod impact strengths greater than 105 J/m (Seymour 1989). Toughness also implies energy absorption and it can be achieved through various deformation mechanisms during crack propagation

and before a failure occurs (Pearson & Yee 1993). The brittleness of cured thermosets causes it to have fracture energies two orders of magnitude less than engineering thermoplastic and three orders of magnitude less than metals (Bascom & Hunston 1989). Unmodified thermosets are usually single-phase whereas incorporation of a second phase of dispersed rubbery particles into thermosetting polymers can induced phase separation to occur and leads to form a two-phase morphology system. When rubbery particles or domains are correctly dispersed in discrete form throughout the thermoset matrix and it can be greatly increase the fracture energy or toughness without significantly impairing the other desirable engineering properties (Huang et al. 1993; Kinloch 1989; Kinloch et al. 1983).

Synthetic liquid rubber commonly used to modify epoxy resin by addition of certain amount into thermoset resin. It contributes a significant improvement to

the mechanical properties of modified epoxy resin (Balakrishnan et al. 2005; Pearson & Yee 1993; Ratna & Simon 2001; Saadati et al. 2005). Liquid natural rubber (LNR) has the active group such as $-OH$, $-OOH$ and $-C=O$ in the isoprene chain (Ibrahim & Zuriati 1989; Ibrahim & Sahrim 1992). Therefore, LNR can act as a good toughening agent and disperse into epoxy matrix to improve the toughness of cured epoxy.

The objectives of this study were to investigate the mechanical properties of epoxy resin toughened with liquid natural rubber (LNR) and their morphology and toughening mechanisms.

MATERIALS AND METHODS

DGEBA epoxy resin (Epikote 1004) and the curing agent - Dicyandiamide (DICY or Epikure P104) were supplied by ASA CHEM. Natural rubber was purchased from Rubber Research Institute of Malaysia (RRIM).

Photodegraded natural rubber (1 kg) was cut approximately into $1\text{ cm} \times 1\text{ cm} \times 1\text{ cm}$ cube. After that, it was mixed in toluene solvent with 0.2 g methylene blue, 0.26 g rose bengkal and 10 mL methanol. Liquid natural rubber was formed when exposed under UV in a photoreactor after 12 days.

The DGEBA epoxy resin and DICY were pre-mixed in high speed mixer machine at 1000 rpm for 30 min with 100:3 ratio. After that, the mixture was fed into a twin screw extruder machine by a feeder with the machine speed 80 rpm. The temperature range set was 105, 108, 112 and 115°C. At the same time, 3 phr (parts per hundred of rubber) LNR was fed into twin screw extruder machine by liquid pump. The mixture was cool down at the room temperature followed by crashing the mixture into powder form after it came out from machine. The powder mixture was shaped into mold at 140°C, pre-heated for 3 min and full-pressed for 10 min by a hot press machine. Finally, the composite was left in the oven for 2 h at 160°C for the post cure process. The whole process was repeated with LNR concentration of 5, 7 and 9 phr.

Tensile tests were performed on a dumb-bell shaped type I sample according to ASTM D 638. The dimensions of the tensile specimens were 50 mm \times 3 mm in the working section. The 5 mm/min crosshead speed and 115 mm gauge length were used. The tensile strength (MPa) and failure strain (%) were measured under a 10 kN load cell using Instron machine. The values were taken from an average of tests.

The three point test was performed by using Testometric M350-10CT Universal Testing Machine, UTS, to determine the mode I fracture toughness, K_{IC} , with single edge notch bend (SENB) specimens. The tests were carried under a crosshead speed of 10 mm/min as recommended by ASTM standard D 5045. Specimens with $44 \times 10 \times 5\text{ mm}^3$ dimension were prepared and a sharp-notch was cut by the rotary saw machine. Subsequently, a drop weight tapping machine was used to generate a natural crack by inserting a fresh razor blade and tapping with a drop weight.

K_{IC} were determined from the load-displacement curve in the unit of $\text{MPa m}^{1/2}$ when specimens fail. The values were taken from an average of 5 specimens.

The Izod impact strength of the notched specimens was carried out according ASTM D256 by Ray Ran Universal Pendulum Impact Machine. Specimens with dimension of $63 \times 12.7 \times 3\text{ mm}^3$ were prepared and an angle of 60° with 2.54 mm depth was cut by rotating saw using Ray Ran motorized notching cutter machine. The impact tests were carried out at room temperature and impact energy was reported in KJ/m. The values were taken from an average of 8 specimens.

Scanning electron micrograph (SEM) was recorded using a Philip SL30 model with an electron voltage of 20kV to examine the fracture surfaces of toughened epoxy specimens. A thin section of the fractured surface was cut and sputter coated with a thin layer of gold prior to analysis.

RESULTS AND DISCUSSION

TENSILE PROPERTY

The tensile property of the rubber toughened epoxy is shown in Table 1. The result showed that tensile strength of LNR toughened epoxy was lower than the neat epoxy except for the 3 phr LNR toughened epoxy which showed a higher value. It was also observed that the failure strain increased with the increasing of LNR composition and dropped at 9 phr. Meanwhile, Young's modulus was found to have slight increment at 3 and 5 phr and subsequently decreased at 7 and 9 phr. The slight increment in tensile strength and Young's modulus may be caused by entanglement between the epoxy and LNR (Ozturk et al. 2001). The result confirmed that by addition of LNR into epoxy matrix, tensile strength of the composites dropped while Young's modulus was slightly increased. This may be due to large rubber particles size formed and act as crack initiator as shown in their morphology micrograph in the following section. The obvious increment for the failure strain may due to some amount of LNR diffused go into epoxy (Ratna 2001; Thomas et al. 2008).

FRACTURE TOUGHNESS PROPERTY

The neat epoxy resin and the fracture toughness of rubber toughened epoxy with different composition of LNR is shown in Figure 1. The addition of LNR enhanced the K_{IC} : 160, 87, 82 and 65% for the 3, 5, 7 and 9 phr, respectively. In fact, the results showed that the 3 phr LNR-toughened epoxy resin gave the maximum value of the K_{IC} . No further increase was recorded on further loading of rubber due to the bigger size of rubber particles were observed at higher LNR concentrations. Rubber particles can act as plasticizer when some amount of rubber goes into the epoxy matrix or act as flexibilizer when rubbers incorporated into epoxy matrix. Both of these effects can increase toughness of the matrix during the deformation under shear occur (Kinloch

TABLE 1. Tensile properties with different loading of LNR

LNR (phr)	Tensile strength (MPa)	Failure strain (%)	Young's modulus (MPa)
0	48.9	2.7	2414
3	53.87	4.9	2463
5	48.54	6.2	2433
7	42.07	9.1	2370
9	29.69	7.1	2279

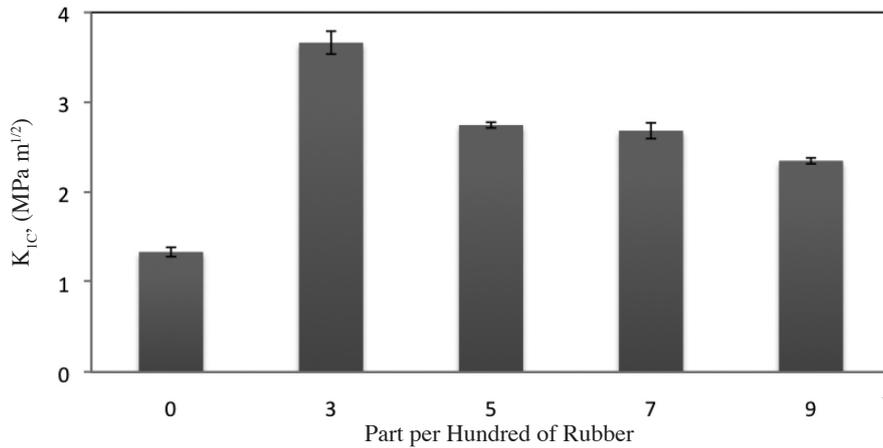


FIGURE 1. Fracture toughness of LNR-toughened epoxy with different loading of LNR

& Hunston 1987; Pearson and Yee 1993). Since, the active groups of LNR may react with epoxy ring and caused better interphase adhesion and consequently an obvious increment was obtained.

IMPACT PROPERTY

Figure 2 shows the impart strength of rubber toughened epoxy containing different amount of LNR. From the result, it was found a clear increment of impact strength at 3 phr LNR was observed and followed with slight increment at 5 phr and no further increment at 7 and 9

phr LNR compared with neat epoxy. A similar trend was observed in fracture toughness result and maximum strength was obtained with 3 phr LNR. Saadati et al. (2005) also had reported similar results where the fracture and impact results were not complementary. It may due to the fact that these two tests were done under different speed condition. The fracture toughness was performed in relatively low speed and more rubber particles have time to respond and tolerate. The impact test was performed at a high speed and the rubber particles would not have time to respond.

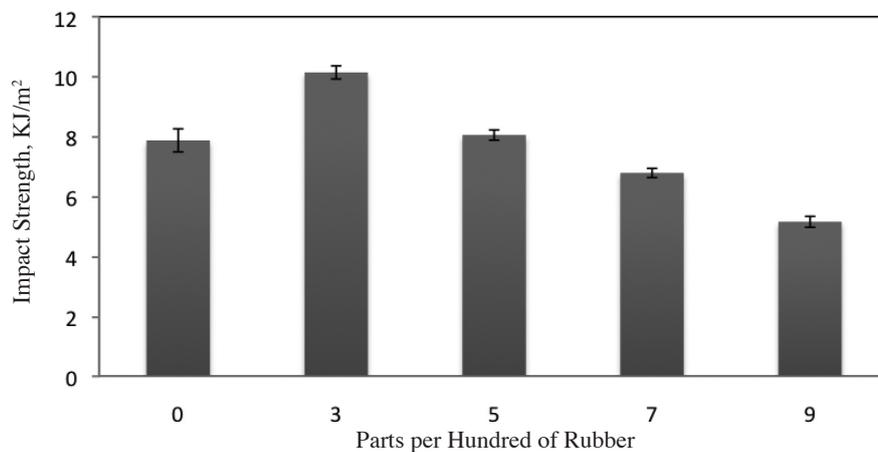


FIGURE 2. Impact strength of LNR-toughened epoxy with different loading of LNR

MORPHOLOGY

In order to correlate the mechanical properties of the toughened epoxy resins with the morphology, the SEM micrographs of fracture surfaces for the neat epoxy and LNR-toughened epoxy with different composition at same magnification (1000x) were recorded (Figure 3). The morphology of neat epoxy fracture surface (Figure 3a) shows smooth, glassy, rivery fractured surface with ripples and no shear deformation line was found. It indicates that no significant plastic deformation had occurred and no energy dissipating mechanism was operated here.

Inversely, the fractured surface of LNR-toughened epoxy clearly showed two distinct phases – a continuous epoxy matrix and dispersed rubber phase. Rubber particles present will act as energy dissipating center in the epoxy

matrix. As a result, rubber particles would respond to the triaxial stresses near the crack tip and make the localized shear yielding occurs. This was followed by the rubber bridging mechanism in the crack tip zone in the epoxy matrix and plastic void growth initiated by cavitation or debonding of the rubbery particles from the surface (Huang et al. 1993). From the micrographs, deformation lines were observed to propagate through rubber particles and it proved the ductile fracture did occurred. Increments of rubber particles were observed when rubber composition was increasing. Similar observations were found by Lee et al. (1989). According to Thomas et al. (2008) the effectiveness for rubber particles to act as stress concentrators and dissipate energy can be influenced with increment of rubber particles size. In

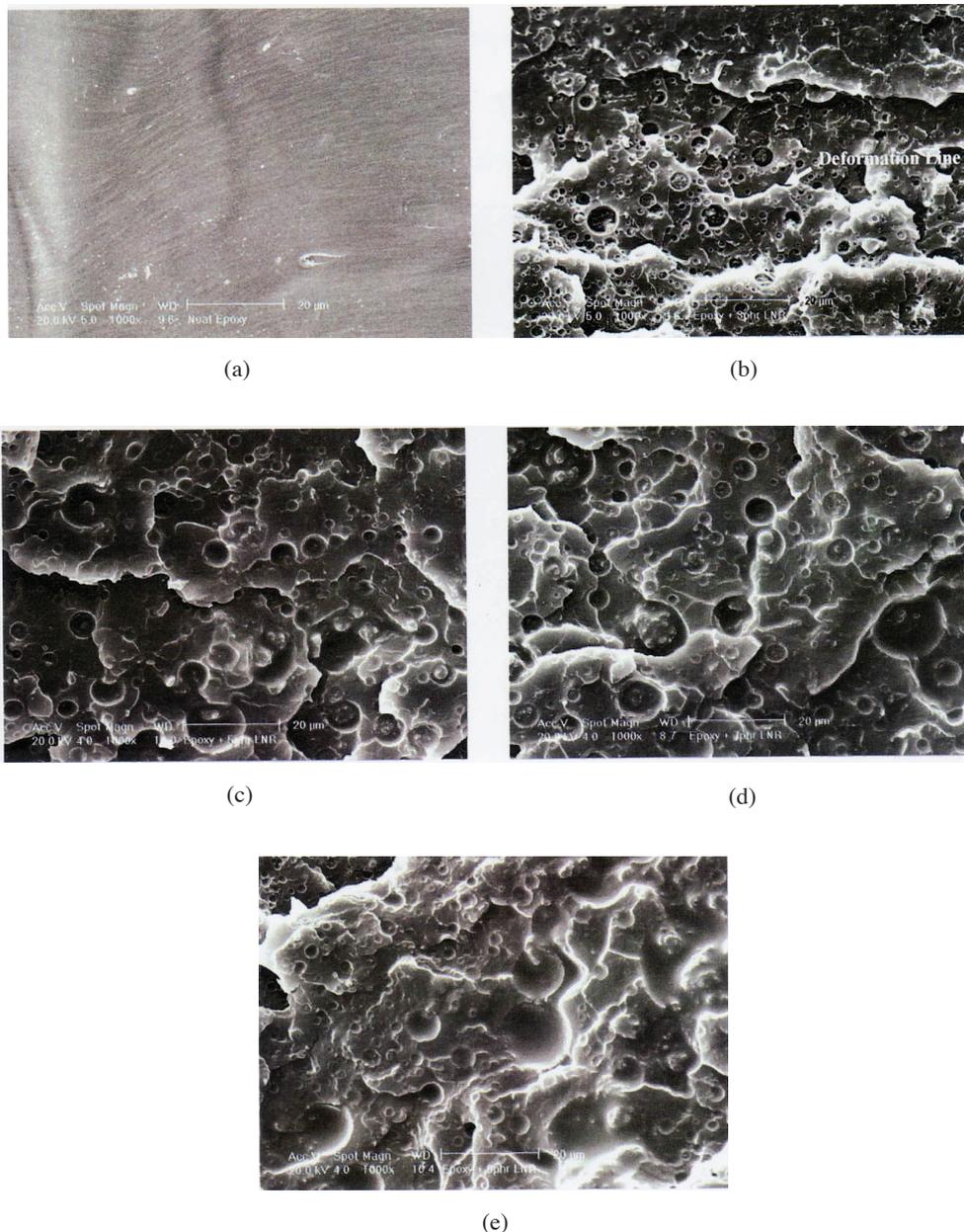


FIGURE 3. SEM micrographs of (a) neat epoxy, (b) 3 phr blend, (c) 5 phr blend, (d) 7 phr blend and (e) 9 phr blend

small rubber particles size, crack energy propagates through the particle and can be dissipated. Meanwhile, rubber particles will have less interfacial adhesion when the size of particles became larger at higher composition. It may cause rubber particles to be pulled out due to the crack propagating through the interface between rubbers particles and matrix. Not much crack energy was dissipated because the crack was not propagated through the rubber particles. Chikhi et al. (2002) pointed that the excessive liquid rubber composition led to agglomeration because they have not reacted with epoxy resin hence resulting poor interface with matrix.

CONCLUSION

The mechanical performance of epoxy was influenced by the inclusion of various phr of LNR. The addition of LNR into epoxy matrix led to the evolution in the morphology. LNR toughened (3 phr) epoxy gave the best mechanical properties i.e. the optimum value of tensile strength, fracture toughness and impact strength. Rubber particles size increased with the increase of LNR loading and was the main reason for the decrease of the mechanical properties.

REFERENCES

- Balakrishnan, S., Start, P.R., Raghavan, D. & Hudson, S.D. 2005. The influence of clay and elastomer concentration on the morphology and fracture energy of performed acrylic rubber dispersed clay filled epoxy nanocomposites. *Polymer* 46: 11255-11262.
- Bascom, W.D. & Hunston, D.L. 1989. Fracture of elastomer-modified epoxy polymer: a review. In: Riew, C.K. (ed.). *Rubber-Toughened Plastics*, pp. 135-172. Washington: American Chemical Society.
- Chikhi, N., Fellahi, S., Bakar, M. 2002. Modification of epoxy resin using of reactive liquid (ATBN) rubber. *European Polymer Journal* 38: 251-264.
- Huang, Y., Hunston, D.L., Kinloch, A.J. & Riew, C.K. 1993. Mechanisms of toughening thermoset resins. In: Riew, C.K. & Kinloch, A.J. (ed.). *Toughened Plastics I*, pp. 1-38. Washington: American Chemical Society.
- Ibrahim, A. & Sahrim, A. 1992. Liquid natural rubber as a compatibiliser in the blending of natural rubber with polypropylene. *Materials Forum* 16: 353-357.
- Ibrahim, A. & Zuriati, Z. 1989. Pendepolimeran fotokimia getah asli. *Sains Malaysiana* (18)2: 99-109.
- Kinloch, A.J. 1989. Relationship between the microstructure and fracture behavior of rubber-toughened thermosetting polymer. In: Riew, C.K. (ed.). *Rubber-Toughened Plastics*, pp. 67-92. Washington: American Chemical Society.
- Kinloch, A.J. & Hunston, D.L. 1987. Effect of volume fraction of dispersed rubbery phase on the toughness of rubber-toughened epoxy polymers. *Journal of Materials Science Letters* 6: 131-139.
- Kinloch, A.J., Shaw, S.J., Tod, D.A. & Hunston, D.L. 1983. Deformation and fracture behaviour of a rubber-toughened epoxy: 1. Microstructure and fracture studies. *Polymer* 24: 1341-1354.
- Lee, W.H., Hodde, K.A. & Wright, W.W. 1989. Phase-separation and transition phenomena in toughened epoxies. In: Riew, C.K. (ed.). *Rubber-Toughened Plastics*, pp. 263-287. Washington: American Chemical Society.
- Mulhaupt, R. & Buchholz, U. 1996. Compatibilized, segmented liquid rubbers as epoxy-toughening agents. In: Riew, C.K. & Kinloch, A.J. (ed.) *Toughened Plastics II*, pp. 75-94. Washington: American Chemical Society.
- Ozturk, A., Kaynak, C. & Tincer, T. 2001. Effects of liquid rubber modification on the behaviour of epoxy resin. *European Polymer Journal*. 37: 2353-2363.
- Pearson, R.A. & Yee, A.F. 1993. Toughening mechanisms in thermoplastic-modified epoxies: 1. Modification using poly(phenylene oxide). *Polymer* 34(17): 3658-3670.
- Ratna, D. 2001. Phase separation in liquid rubber modified epoxy mixture. Relationship between curing conditions, morphology and ultimate behavior. *Polymer* 42: 4209-4218.
- Ratna, D. & Simon, G.P. 2001. Mechanical characterization and morphology of carboxyl randomized poly(2-ethyl hexyl acrylate) liquid rubber toughened epoxy resins. *Polymer* 42: 7739-7747.
- Saadati, P., Baharvand, H., Rahimi, A. & Morshedean, J. 2005. Effect of modified liquid rubber on increasing toughness of epoxy resins. *Iranian Polymer Journal* 14(7): 637-646.
- Seymour, R.B. 1989. Origin and early development of rubber-toughened plastics. In: Riew, C.K. (ed.). *Rubber-Toughened Plastics*, pp. 3-13. Washington: American Chemical Society.
- Thomas, R., Ding, Y., He, Y., Yang, L., Moldenaers, P., Yang, W., Czigany, T. & Thomas, S. 2008. Miscibility, morphology, thermal, and mechanical properties of a DGEBA based epoxy resin toughened with a liquid rubber. *Polymer* 49: 278-294.

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