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Synthesis And Characterization Of Liquid Natural Rubber As Impact Modifier For Epoxy Resin

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Abstract

Liquid natural rubber (LNR) with a molecular weight $\overline{M}n = 16 \times 10^3$ was prepared by the depolymerization of deproteinized natural rubber latex (DPNR). The liquid natural rubber (LNR) was characterized by FTIR and H'NMR spectroscopic analysis. LNR was premixed with the epoxy resin (EP) and cured with a diamine curing agent for 1 h at 100 °C and post cured at 110 °C, for 2 h in air oven. The modified EP containing different contents of LNR (5, 10, 15 and 20 phr) were evaluated. Thermal, mechanical and morphology properties were determined. The fracture toughness (K_{IC}) of both unmodified and modified EPs were determined on static loaded single edge notched (SEN-B) specimens at room temperature. The glass transition temperatures (T_g) of the modified EPs were decreased with increasing LNR content. The strengths and modulus of EPs were slightly reduced with the incorporation of LNR. The effect was also reflected in the significant increase in the tensile strain of modified EP. Fracture toughness of the EP was observed to increase with the presence of LNR. The toughening effect became more apparent as the testing speeds were increased from 1 to 500 mm/min. Fracture surface analysis by scanning electron microscopy (SEM) revealed the presence of a two-phase morphology.

Key words: Epoxy resins, Liquid natural rubber (LNR), Modified Epoxy Resin, Toughening, Impact Modifiers

1. Introduction

Epoxy resins (EPs) are considered as 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, tensile strength, low creep, high glass transition temperature, high thermal stability, and 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

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other high performance materials [2]. In order to remain competitive as 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 to toughen EPs is the incorporation of rubber phase into the brittle epoxy matrix, which may be achieved by the use of reactive liquid rubber or preformed rubber particles [3]. Carboxyl, epoxy and amine terminated butadiene-acrylonitrile copolymers (CTBN, ETBN and ATBN) are widely used as toughening agents. These rubbers are initially miscible with the epoxy but during the polymerization the rubber phase separates due to slight immiscibility with the matrix. At proper concentration of rubber, the dispersed rubber phase can improve the toughness without a significant decrease in the other properties of epoxies [4]. The improvement the toughness of rubber-toughened epoxies has been associated with three main toughening mechanisms; crazing, shear banding and elastic deformation of rubber particles. These mechanisms can either act alone, or together, to produce the toughening effect [5]. Many efforts have been made to understand the behavior of the dispersed rubber phase, which separates from the resin before gelation. Sultan and McGarry found that the toughening mechanisms are affected by the rubber particle size [6]. Chen and Jan extensively studied the effect of matrix ductility on the fracture behavior of rubber toughened EPs [7]. Verchere *et.al.*, showed shear deformation of the matrix as the major toughening mechanism [8]. Bagheri and Pearson studied the role of blend morphology in rubber-toughened polymers [9].

Evaluation of effective crosslink density of matrix resin, measurement of glass transition temperature T_g, cure characterization through differential scanning calorimetry (DSC) and dynamic mechanical analysis (DMA) of diglycidyl ether of bisphenol -A (DGEBA) modified with CTBN liquid rubber have also been reported [10]. Recently, some of saturated liquid rubber such as polysulphide [11], acrylate [12], silicone [13] and polyurethane [14] have been reported in the literature as replacement for CTBN. An attempt to toughen the EP using a polyurethane (PU) prepolymer as a modifier via interpenetrating network (IPN) grafting has also been reported [15]. For this purpose, a PU prepolymer has been synthesized based on hydroxyl-terminated polyester resins and used as a modifier for EP at different concentration. Ratna and Banthia [16,17] showed that carboxyl terminated poly(2-ethylhexylacrylate) (CTPEHA) liquid rubber can be used as an impact modifier for EP cured with ambient temperature hardener. However, carboxyl terminated oligomers can only be synthesized by bulk polymerization, which is difficult to control. Qian *et.al.,* [18] studied the synthesis and application of core-shell rubber particles as toughening agents for epoxies. The effect of epoxidized natural rubber (ENR 50 mol %) on the curing behaviors and adhesive strengths of an epoxy (DGEB-A) and dicyandiamide/2-methyl imidazole system was studied by Hong and Chan [19]. Many works in toughening of EP have been reported [10- 20].

This paper reports on our attempt to synthesis reactive liquid natural rubber (LNR) and to investigate its effect as impact modifier for EP. The present work attempts to discuss thermal, mechanical and morphology properties of fracture surface of the above mentioned LNR modified EP.

2. Materials

Deproteinized natural rubber latex (DPNR) having 22 % dry rubber content was supplied by Rubber Research Institute Malaysia (RRIM). Formic acid 98 %, hydrogen peroxide 30 %, methanol was obtained from Fisher Scientific UK. Clear EP 331 with epoxide equivalent weight 182-192 was a liquid diglycidyl ether of bisphenol A, and curing agent was clear epoxy hardener 8161 (isophorone diamine) with amine value 260-284 (mg KOH/gm). Both EP and curing agent were obtained from Euro chemo-pharma, Sdn. Bhd.

3. Experimental

3.1. Preparation of liquid natural rubber (LNR)

The 500 g of deproteinized natural rubber latex (DPNR) was stabilized by adding appropriated amount of nonionic surfactant and sodium chlorite, with stirring at 50 ºC for 2 h. 100 ml of hydrogen peroxide was then added to the mixture. After few minutes the pH was reduced to a value of 5 by adding small amount of diluted formic acid (20 %). The depolymerization reaction took place at 50 ºC with stirring for 14 days. The appropriate amount of methanol was added to the mixture to precipitate LNR.

The yield was then washed by methanol and distilled water, and then dried under the vacuum at room temperature.

3.2.Curing process and sample preparation

EP (100 phr) with varying contents of LNR (5-20 phr) were first mixed together and heated for 20 min, at 60 °C in a water bath with stirring. When the mixture had cool down to 40°C, the 60 phr curing agent (isophorone diamine) was added and the mixing was continued for an 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 1 h at 100°C. The sample was then postcured at 110°C for 2 h in an air oven. At this stage the cured specimen was allowed to cool slowly at room temperature in the mould.

4. Characterization

4.1. Fourier transform infrared spectroscopy

Fourier transform infrared (FTIR) spectra of liquid natural rubber (LNR) was obtained using a Perkin Elmer system 4000 spectrophotometer. The LNR was coated onto zinc selenide (ZnSe) plate then the spectrum was recorded.

4. 2. Nuclear magnetic resonance spectroscopy

Nuclear magnetic resonance (^{1}H'NMR) spectrum was obtained using a Bruker Avance 400 spectrometer with deuterated chloroform as a solvent. Chemical shifts were reported in ppm relative to tetramethylsilan. ^{1}H'NMR analysis was done to determine the chemical structures of LNR and to confirm the extent of epoxy groups in the structure of LNR. ^{1}H'NMR analysis was also used to determine the percentages of epoxy groups in the LNR chain [21, 22].

4.3. Differential scanning calorimetry (DSC)

DSC instrument (Perkin Elmer DSC-6 differential scanning calorimeter) was employed to determine the glass transition temperature (T_g) of both unmodified and liquid natural rubber modified EP. Samples of about 8-10 mg were heated at a rate 10 °C/ min in a nitrogen atmosphere was maintained for all the experiments in the temperature range 30-100 °C.

4.4. Mechanical tests

4.4.1. Tensile properties

Tensile tests were performed on rectangular shaped type V samples according to ASTM D-638. The rectangular shaped samples were cut from the moulded sheets. The ultimate tensile strength, Young's modulus, tensile strain and energy at break were measured using a Instron machine, Model 3366 at room temperature 26 °C. The crosshead speed was set at 2 mm/min. The quoted data is the average of the results from five specimens

4.4.2. Flexural properties

The three points flexural testing was conducted on Instron machine, Model 3366 at room temperature 26 °C. Rectangular shaped specimens were obtained, with dimensions as specified in ASTM D790-02. The crosshead speed was employed of 5 mm/min. Flexural strength, and flexural modulus were calculated. The quoted data is the average of the results from five specimens.

4.4.3. *Fracture* toughness measurement

The fracture toughness (K_{IC}) was measured in terms of critical stress intensity, K_{IC}. Fracture values have been determined using pre-cracked (3.5-4 mm), single edge notched specimens in three points bending (SEN-B) with span of 64mm dimension. These tests were performed using a Instron machine, Model 3366 at crosshead speeds of 1, 100 and 500 mm/min at room temperature (26°C). K_{IC} was determined according to ASTM E399-78 using the following relationship (1) [23]:

$$K_{IC} = \frac{3PSa^{1/2}Y}{2tw^2} \tag{1}$$

Where P is the critical load for crack propagation (N), S, the length of the span (mm), a, the per-crack length (mm), t, the specimen thickness (mm), w, the specimen width (mm) and Y the geometrical factor, given by:

$$Y = 1.93 - 3.07(a/w) + 14.53(a/w)^2 - 25.11(a/w)^3 + 25.8(a/w)^4 \tag{2}$$

4.5. Scanning electron microscopy

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

5. Result and discussion

5.1. LNR characterization

The FTIR spectrum of LNR is given in Figure 1. The depolymerized rubber shows three new major absorption bands, i.e. a broad hydroxyl absorption in the region between 3600-3200 cm^{-1}, and carbonyl absorption band at 1720 cm[1] and the third absorption band appeared at 875 cm^{-1} that indicates the presence of epoxy groups.
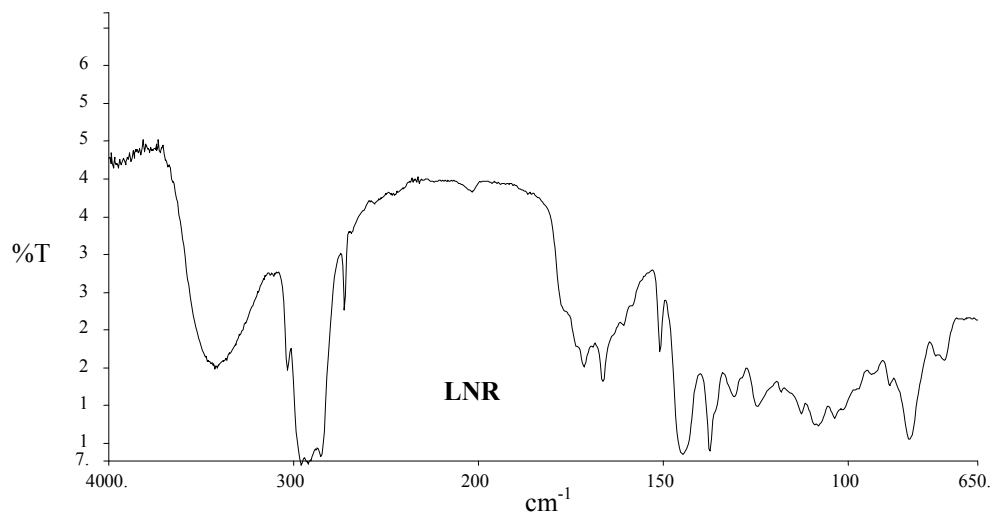

Figure 1: The FTIR spectrum of LNR .

Figure 2 shows the 'H' NMR spectrum for LNR. The major peaks at 1-2.5 pmm (-CH$_2$, -CH$_3$) and 7.3 pmm (CDCl$_3$) were observed in the LNR spectrum. The peaks were observed at 5.1 and 2.7 pmm are attributed to vinylic proton of the isoprene unit and tertiary proton of the epoxy ring respectively. As the C=C double bond was converted to the cyclic epoxide unit. The tertiary proton shifts to 2.7 ppm. These two hydrogen peaks have been widely employed to determine the degree of epoxidation [21,22]. The epoxy contents were determined from the ratio of the area of the peaks at 2.7 ppm divided by the sum of the area of the peaks at 2.7 ppm and 5.1 pmm [24]. From the data presented in Figure 2, the epoxy content can be calculated as:
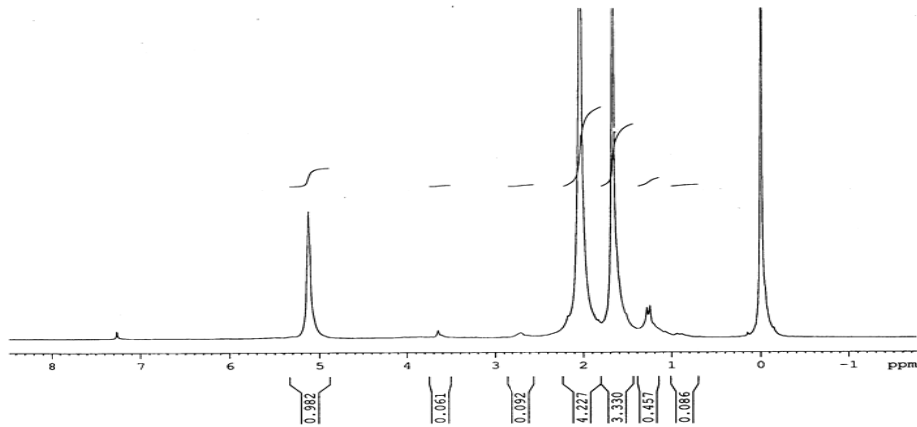
Figure 2: ^{1}H'NMR spectrum of liquid natural rubber (LNR).

Hence the FTIR and ^{1}H'NMR spectra of LNR confirmed the presence of reactive functional groups (hydroxyl, carbonyl and epoxy groups) in the structure of LNR. These groups are expected to enhance the compatibility of rubber with EP.

5.2. Characterization of LNR modified EP

2.2.1. Thermal analysis
The effect of LNR content on the glass transition temperatures (T_g) as obtained from DSC thermograms is shown in Figure 3. The T_g values for all the rubber modified epoxy samples are lower than that of the unmodified epoxy. The decrease in T_g values with increase LNR content can be related to the chemical interaction between the LNR and epoxy matrix, which induces compatibility of LNR/EP. Similar results have been reported elsewhere [25].
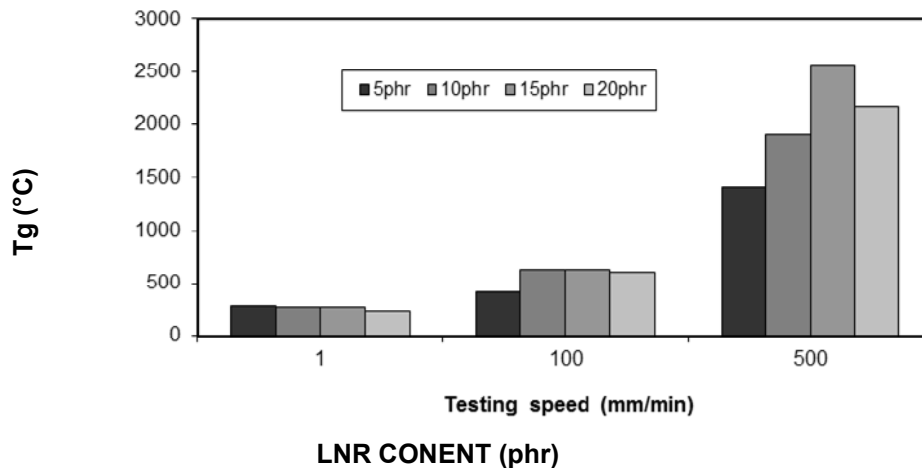

Figure 3: Effect of LNR content on the glass transition temperature (Tg) of EP.

5.2.2. Tensile and flexural properties
Figure 4 shows the stress-strain curves of unmodified EP and 5-20 phr LNR modified EP. As seen in this figure, the modified specimens exhibit a decrease in modulus and in yield stresses. A similar behavior is noticed for the remaining concentrations as shown in Table 1.
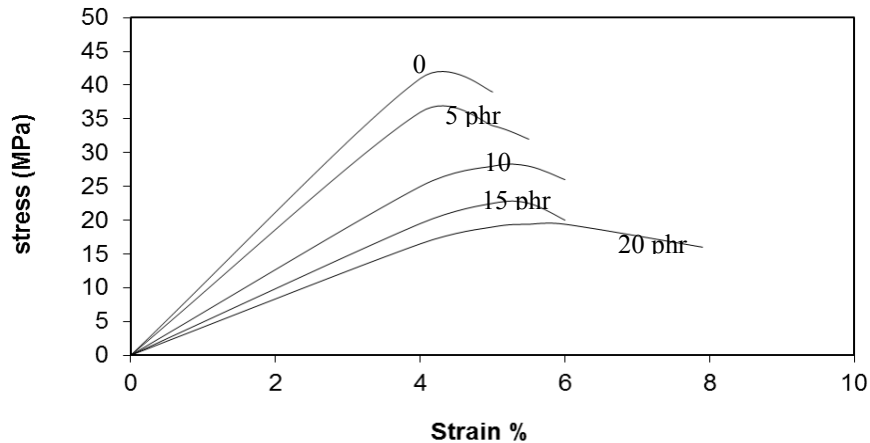
Figure 4: Stress-strain curves of 0-20 phr LNR modified EP.

Table 1 shows the effect of LNR content on the tensile and flexural properties of the EP. As expected, the tensile and flexural strengths and E- modulus of modified EPs are lower than that of the unmodified EP. The decrease of E-modulus can be attributed to the presence of low modulus rubber particles in the epoxy matrix. The reduction in strengths is due to the presence of rubber some of which is which chemically bonded to the epoxy network as evident from the decrease in T_g values. Similar observations have been reported by many researchers using different types of liquid rubbers [25-27]. A more significant reduction in the properties was observed at 15 and 20 phr LNR. This indicates the plasticizing effect of the dissolved rubber [27]. The decrease in Tg with increase in LNR content is another indication of the plasticizing effect of LNR. This concept is also reflected in the increase in tensile strain with incorporation of LNR.

Table 1: Effect of LNR content on the tensile and flexural properties of EP

LNR (phr)	Tensile strength MPa	Strain at break %	Energy at break (N.m)	Young modulus GPa	Flexural strength MPa	Flexural modulus GPa
0	41.00 ± 1.7	5.1 ± 0.9	2.4 ± 1.0	1.56 ± 0.13	93.13 ± 4.5	3.05 ± 0.25
5	35.6 ± 0.7	5.8 ± 0.8	3.7 ± 0.7	1.46 ± 0.03	67.50 ± 5.0	2.21 ± 0.22
10	28.2 ± 1.2	6.0 ± 0.4	3.8 ± 0.7	1.20 ± 0.05	65.50 ± 4.5	2.20 ± 0.23
15	22.4 ± 0.9	6.0 ± 0.8	3.4 ± 0.7	1.08 ± 0.08	47.37 ± 4.3	1.47 ± 0.20
20	19.4 ± 0.8	7.9 ± 0.8	4.0 ± 0.7	0.88 ± 0.12	55.48 ± 6.4	1.86 ± 0.33

5.2.3. Fracture toughness

Figure 5 shows the relationship between the LNR content and fracture toughness (K_{IC}) and the effect of different testing speed on the K_{IC} of EPs. The K_{IC} of the LNR modified EP samples is higher than that of the unmodified epoxy. The improvement in the fracture toughness can be attributed to incorporation of LNR that can increase the fracture resistance of matrix either by enabling plastic deformation to occur in the matrix. In all cases the K_{IC} values increased with increasing LNR content. Hence, the increase in toughness due to the increase in LNR content can be explained in terms of dissolved rubber. This effect makes the matrix more ductile and increases its toughness [28,29]. At low testing speed i.e. 1 mm/min the maximum value of K_{IC} is observed at 5phr LNR content. In this case the rubber particles would have had more time to relax, consequently a small amount of LNR (5 phr) would be enough to make important improvement in the fracture toughness. However the fracture toughness attained maximum value at 15

phr of LNR content at a testing speed of 500 mm/min. In all cases the K_{IC} values decreased with increasing testing speed, the effect of using different testing speed on the K_{IC} of EPs was reported [30].
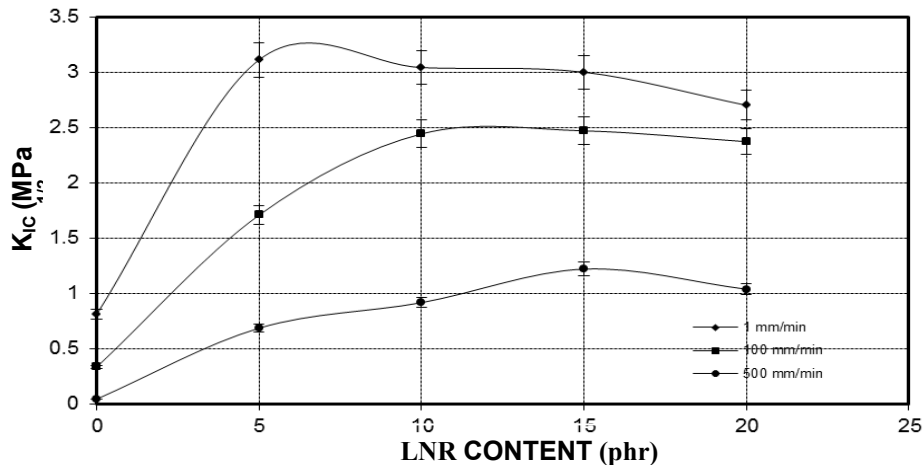

Figure 5: Effect of LNR content and testing speed on the fracture toughness of the EP

5.2.4. Fractography

The phase separation behavior of the LNR modified epoxy system can be obtained by analyzing the SEM images of fracture surface of SEN-B tests. The representative SEM image of LNR/epoxy system is shown in Figure 6. The rubber phase appears as spherical particles. 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 of the molecular weight of the epoxy matrix [31].

In SEM micrograph 6 (a), small crack initiation regions are observed with shiny and very smooth surface, indicating brittle behavior. Similar results have been reported elsewhere [32]. Micrographs (b to e) show the fracture surfaces of modified epoxy (5-20 phr LNR) respectively. A two-phase network is observed with the epoxy as the continuous matrix and the LNR as dispersion phase comprising of spherical particles. The dispersed particles act as stress concentration during fracture, which induce delocalized plastic deformation of the matrix around the particles. Micrographs (b to e), also show the fracture surface of epoxy/LNR/IPD resin system the good bonding at the matrix-particle interphases and matrix plastic dilation can be seen clearly which suggests that matrix was the dominant toughening mechanism in this system, this shear yielding mechanism can be considered to be similar to that of rubber toughening [32-34]. From Figure 6 (b) it can be seen that stress whitening zones developed on the fracture surface of modified epoxy.

This stress whitening effect is related to the local plastic deformation at the crack tip. These perhaps explain the observed increase in fracture toughness of modified EPs compared to the unmodified EP.

Figure 6 (c) and (d) depicts to the fracture surface appearance of modified EP filled with 10 phr and 15 phr LNR. The rubber particles were suspected to cause some localized plastic shear yielding resulting in the observed increase in toughness. It is interesting to note that in case of 15 phr modified epoxy the rubber particles appear to be more uniformly distributed throughout the epoxy. Furthermore, it reveals quantitative evidence for an improvement in the interaction between the two phases. This eventually leads to the enhancement of fracture toughness Figure 6 (d). This is the onset of phase separation as reported elsewhere [35], similar morphology was obtained in the case of 20 phr LNR content with agglomeration of rubber particles apparent as seen in Figure 6 (e). The excess LNR may lead to some agglomeration. This explains the slight reduction in the fracture toughness at 20 phr LNR content.
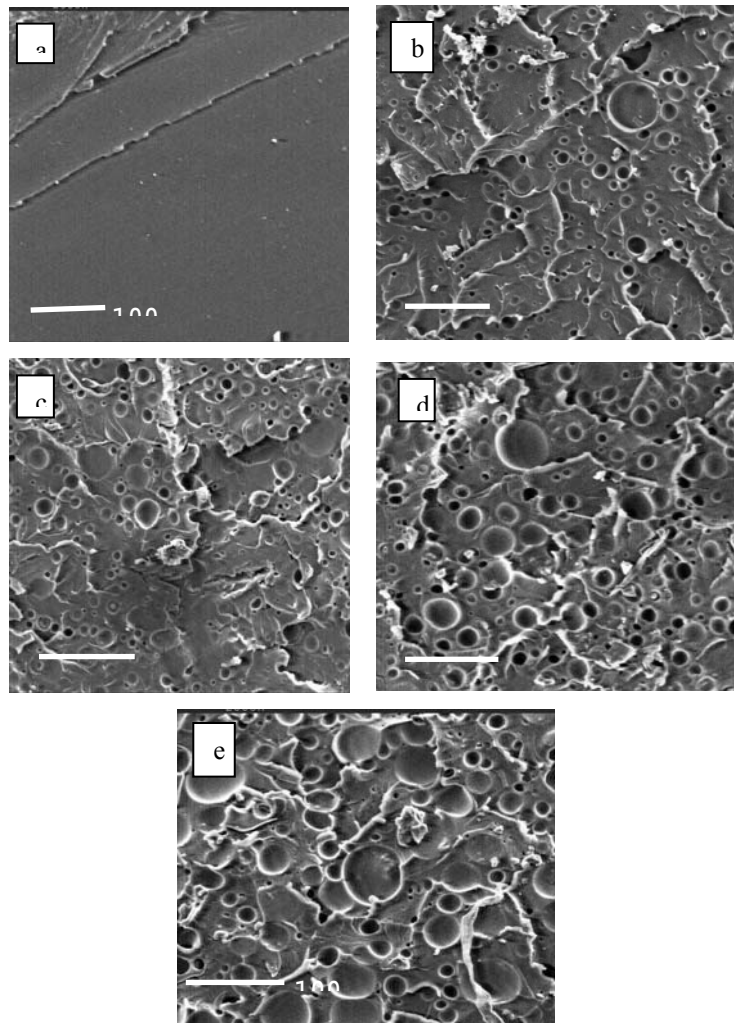
Figure 6: Micrographs of SEN-B fracture surface of (a) unmodified EP and 5-20 phr LNR modified EP (b-e)

6. Conclusions

The FTIR and HNMR analysis evidenced the presence of hydroxyl, carbonyl and epoxy functional groups in the chain of LNR. It can be concluded that the reduction in T_g of EP with increasing rubber content is an indication of the plasticization effect of LNR. Slight decreases in the tensile and flexural strengths were also observed. The incorporation of LNR led to a significant improvement of the fracture toughness of the EP. The toughening effect becomes more apparent at high testing speed.

SEM analysis indicated that the dispersed rubber particles act as stress concentrators during fracture, which induces delocalized plastic deformation of the matrix around the particles. On adding LNR some of the rubber particles accompanied by stress whitening zones developed on the fracture surface of modified EP this stress whitening effect is related to the local plastic deformation at the crack tip. This might explain the observed increase in fracture toughness compared with unmodified EP.

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