J Mater Sci (2010) 45:1769–1781
DOI 10.1007/s10853-009-4154-8

Epoxy resin/liquid natural rubber system: secondary phase separation and its impact on mechanical properties

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Received: 18 August 2009 / Accepted: 18 December 2009 / Published online: 20 January 2010
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Abstract An investigation was carried out to explore the morphology and mechanical properties of diglycidyl ether of bisphenol A epoxy resin (DGEBA) with liquid natural rubber possessing hydroxyl functionality (HLNR). Though modification of epoxies by synthetic rubber has been extensively studied not much attention has been paid to liquid natural rubber. Photo depolymerisation of natural rubber enables us to synthesise low molecular weight oligomers by varying the experimental parameters. Epoxy resin was cured using nadic methyl anhydride as hardener in presence of *N*,*N*-dimethyl benzyl amine accelerator. Hydroxylated natural rubber of different concentrations is used as modifier for epoxy resin. The addition of such chemically modified liquid rubber to an anhydride hardener–epoxy resin mixture has given rise to the formation of a two-phase microstructure in the cured systems, consisting of spherical particles of liquid natural rubber strongly bonded to the surrounding matrix, there by providing the required mechanism for toughness enhancement. Subinclusions of epoxy resin were present in the elastomer domains as secondary particles (particle in particle morphology) as evidenced from the SEM (scanning electron micrograph) photomicrographs. The origin of the so-called secondary phase separation is due to the combined effect of hydrodynamics, viscoelastic effects of rubber phase, diffusion, surface tension, polymerisation reaction and phase separation. In a dynamic asymmetric system, the diffusion of the fast dynamic phase is prevented by the slow dynamic phase, and hence the growth of fast dynamic phase gets retarded due to the slow dynamic phase. In the case of low viscosity blends the growth of fast dynamic phase turns fast and hence diffusion of fast dynamic phase cannot follow geometrical growth and cannot establish local concentration equilibrium and hence double phase separation takes place. The double phase separation is responsible for the enhanced impact and toughness behaviour of the blends. The mechanical behaviour of the liquid rubber-modified epoxy resin was evaluated in terms of tensile and flexural properties.

Introduction

Epoxy resins are considered as one of the high performance thermosetting polymers which find extensive industrial applications in electrical and electronics devices, in surface coatings, high performance adhesives and sealing compounds, in aerospace and other engineering fields [1]. But cured epoxy systems are characterised by a relatively low toughness, that means poor resistance to crack propagation. To overcome this problem, several approaches have been employed to improve epoxy resin toughness which include the addition of nano fillers [2, 3], rubbers [4–6], thermoplastics, polyethersulfones, polyetherimides, polyetheresters, etc. [7–11].

Toughening can be attributed to the incorporation of a small amount of elastomers as a discrete phase of microscopic particles embedded in the continuous rigid

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resin matrix. The use of rubber particles as a second phase to the epoxy resin to increase the toughness of the brittle matrix has been considered extensively. The pivotal work of Mc Garry and Willner [8] using epoxy resins modified with various functionalised butadiene-acrylonitrile rubbers have found significant improvement in toughening [8, 9]. The final properties of the multiphase polymer blends depend on the morphology of the system. The spherical liquid rubber domains can cause sufficient stress transfer and thereby prevent the material from catastrophic failure. Bucknall and Patridge [12] observed that the miscibility of CTBN rubber depends on the type of the epoxy resin used while Verchere et al. [13] found a similar increase in miscibility with the increasing acrylo-nitrile content of CTBN. Ratna et al. [14] reported a slight decrease in Young's modulus and yield strength due to the increase in the dissolved rubber in the epoxy–amine matrix.

Bascom et al. [15] and Manzione et al. [16] observed an optimum for the mechanical properties at 15 wt% of CTBN. The toughening observed in the system was attributed to the presence of small rubber particles with a narrow size distribution. Ramaswamy and coworkers [17] reported the toughening effect of epoxidised hydroxyl terminated polybutadiene (EHTPB) on epoxy resins cured with an amine. Lap shear strength and T-peel strength were found to increase with the increase in EHTPB content up to 10 phr. This was attributed to the higher toughness produced by the dispersed rubber particles. At higher EHTPB content, the rubber phase became continuous and flexibilisation effect predominated over toughening effect of EHTPB. Cure behaviour, fracture toughness, dilatometric studies and cryogenic applications are discussed in recent works [18–23].

It is well known that based on the composition, chemical reaction, thermodynamics and kinetics of phase separation in the binary mixture, different phase morphologies can be obtained. This is controlled by the curing condition, composition and molecular weight of the toughner. As the average molecular weight of resin is reached, binary epoxy systems become heterogeneous as proposed in the mean field theory of Flory–Huggins [24]. In recent years secondary phase separation in epoxy-based blends has received a lot of attention. The secondary phase separation is caused by asymmetric molecular dynamics as suggested by Tanaka [25–27]. The origin of dynamic asymmetry might be due to the difference in the molecular weight and the T_g between the components in polymer blends. Secondary phase separation was known since the beginning of 1980s. It is well known that the domain size increases due to the hydrodynamic flow and diffusion. In a dynamic asymmetric system, the diffusion of the fast dynamic phase is prevented by the slow dynamic phase, and hence the growth of fast dynamic phase gets retarded due to slow dynamic phase. In the case of low viscosity blends the growth of fast dynamic phase turns fast and hence diffusion of fast dynamic phase cannot establish local concentration equilibrium and hence double phase separation takes place [28].

The main aim of the present article is to analyse the secondary phase morphologies of hydroxylated liquid natural rubber (HLNR) modified epoxy-anhydride system by SEM and to evaluate the effect of secondary phase morphologies on the mechanical properties. Although several papers are available on liquid rubber/epoxy system, no report has been made on secondary phase separation in these systems. It is also important to add that though the modification of epoxies by synthetic rubber has been extensively reported, so far no serious attempts have been done using liquid natural rubber. Though photo depolymerisation of natural rubber is a time-consuming process, there is scope for getting different molecular weights by varying the experimental conditions. The easy availability of the natural rubber and its comparatively low cost favour the preparation of the epoxy–liquid natural rubber blends. In view of this, a detailed investigation has been carried out on the morphology and mechanical properties of epoxy resin/liquid natural rubber.

Materials

Natural rubber

Natural crumb rubber, Indian Standard Natural Rubber (ISNR-5L), having number average molecular weight ($\overline{M_n}$) 820,000, and intrinsic viscosity in benzene at 30 °C 445 dL/g, was supplied by Rubber Research Institute of India, Kottayam. The characterisation of ISNR-5L is given in Table 1.

Epoxy resin

Unmodified Bisphenol A based epoxy resin (LAPOX B-11) supplied by Atul Polymers India Limited was used. It is a medium viscosity resin used mainly for solvent-free coatings and building applications. LAPOX B-11 has epoxide index 5.2–5.5 eq/kg and epoxide equivalent 182–192 g/eq, and viscosity 9000–12000 mPa s at 25 °C.

Table 1 Characteristics of ISNR-5

Specification	ISNR-5	Sample used
Dirt content (%max)	0.10	0.08
Volatile matter (%)	0.8	0.6
Ash content (%)	0.75	0.62
Wallace plasticity (P_0, min)	30	43
PRI (min)	60	68
Mooney viscosity (ML_{1+4} at 120 °C)	–	65–70

Other additives

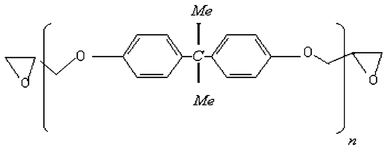
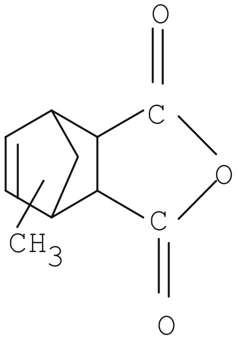
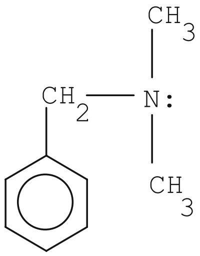
Nadic methyl anhydride (K 68) supplied by Atul (India) Ltd. was used as the curing agent *N*,*N*-dimethyl benzyl amine also supplied by Atul (India) Ltd was used as the accelerator. H_2O_2 (30 wt%) supplied by E. Merck (India) was used for the photodegradation of natural rubber. Toluene was supplied by E. Merck (India). Table 2 provides the chemical structure of the above compounds.

Experimental methods

Preparation of HTNR

The photochemical degradation of natural rubber as adopted by Ravindran et al. [29] was carried out in sunlight with constant stirring for about 50 h. The photo depolymerisation was carried out in a 5 wt% solution of NR in toluene mixed with 30 wt% H_2O_2 and methanol in volume ratio 20:1:3, respectively, in a flat bottomed 1 L flask. Irradiation was carried out in sunlight with constant stirring for about 50 h. The use of masticated rubber increases concentration of rubber solution which in turn increases production rate and extent of depolymerisation. HLNR of any desired molecular weight could be prepared by suitable choice of the reaction mixture and exposure time. The viscosity of the liquid decreased considerably. The organic layer was separated and toluene was removed by distillation to recover the depolymerised rubber. It was purified by precipitating with methanol. The product obtained was degassed in vacuum oven and analysed. The extent of depolymerisation was found to increase with decreasing concentration of NR,

Table 2 Chemical structure and source of materials used

Material	Chemical structure	Source
Lapox B-11		Atul Polymers India Limited
Nadic methyl anhydride (K-68)		Atul Polymers India Limited
N,*N*-dimethyl benzyl amine (DY 062)		Atul Polymers India Limited
Hydrogen peroxide	H_2O_2	E. Merck (India) Ltd. Bombay
Toluene	C_6H_5–CH_3	E. Merck (India) Ltd. Bombay
Methanol	CH_3–OH	E. Merck (India) Ltd. Bombay

increasing amount of H_2O_2 and also by longer exposure time.

GPC analysis

Gel permeation chromatography (GPC) provides a quick and efficient method for polymer fractionation and computation of molecular weight distribution curve. A Waters 410 Differential Refractometer in association with Waters 510 pump was used to determine the molecular weight. Ultra Styragel columns having pore size of 50, 100 and 1000 nm operated with THF at 1 mL/min was used. The data acquisition was done by a UV absorbance detector set at 254 nm and differential refractive index detector. Typical sample concentration was 0.2 wt% and the instrument was calibrated with polystyrene standards with $M_{\mathrm{p}} \sim 32500$.

IR analysis

The IR spectra of HLNR and LAPOX B-11 were taken in Nicolet Magna-560 FTIR spectrometer using chloroform as solvent. A calibration curve was prepared using 1,4-butanediol of different concentrations.

Proton NMR analysis

The ^{1}H NMR spectrum of HTNR sample was recorded in $CDCl_3$ using an NMR Bruker DPX 300 FTNMR Spectrometer operating at 300 MHz.

Modification and curing of epoxy resin

LAPOX B-11 was modified with HLNR. 100 g epoxy resin was mixed with stoichiometric amounts of nadic methyl anhydride and *N*,*N*-dimethyl benzyl amine, which acted as catalyst. HLNR of various concentrations, 5, 10, 15 and 20 wt%, were used to modify the epoxy resin. Mixing was done by heating in oil bath at a temperature of 60 °C using a magnetic stirrer. Curing was done at different temperatures 140, 160, 180 °C, and finally at 200 °C for 2 h each. Fourier Transform Infra red (FTIR) spectroscopy was used for the characterisation purposes of the prepared formulation.

Measurement of mechanical properties

The tensile properties were measured with the Universal Testing Machine—FIE Tensile Testing Machine (Model TNE 5000)—at a cross-head speed of 10 mm/min and a gauge length of 50 mm, in accordance with ASTM D 638. The sample size was $100 \times 10 \times 2$ mm^3. The tensile strength and Young's moduli of elasticity of epoxy modified with hydroxylated natural rubber were determined. The stress–strain behaviour and elongation at break of various samples were determined. Tensile modulus was taken as the slope of the initial linear portion of the stress–strain curve.

The flexural properties are due to bending of a material and its capacity to bear the load with minimum resulting deflection. Flexural properties were determined in three-point bend mode according to ASTM D790 using rectangular specimens of size $120 \times 10 \times 3$ mm at a cross-head speed of 10 mm/min. Flexural stress–strain curve was plotted and the slope of the initial linear portion of the stress–strain curve was taken as the flexural modulus. Toughness was measured as the area under the stress–strain curve.

Fracture surface analysis

Morphological examinations of the cured systems were made using a scanning electron microscope. The fracture surface was coated with a thin layer of gold using a high vacuum gold sputter in a low voltage SEM JEOL, JSM 5600 LV. The SEM micrographs were obtained under conventional secondary electron imaging conditions with an accelerating voltage of 20 kV. SEM photomicrographs of both the cryofractured surfaces as well as toluene extracted cryofractured surfaces were taken. From the SEM photomicrographs, using the following equations the number average diameter, weight average domain diameter, area average domain diameter and volume average domain diameter have been estimated using the following equations. Image analysis technique was used to compute the size of the dispersed rubber phase.

The number average domain diameter is calculated from

$$D_{\mathrm{n}}^{-} = \sum n_{\mathrm{i}} D_{\mathrm{i}} \Big/ \sum n_i \tag{1}$$

The weight average domain diameter is calculated from

$$D_{\mathrm{w}}^{-} = \sum n_{\mathrm{i}} D_{\mathrm{i}}^2 \Big/ \sum n_{\mathrm{i}} D_{\mathrm{i}} \tag{2}$$

Surface area average domain diameter is calculated using

$$D_{\mathrm{a}}^{-} = \sqrt{\sum n_{\mathrm{i}} D_{\mathrm{i}}^2 \Big/ \sum n_{\mathrm{i}}} \tag{3}$$

Volume average domain diameter is obtained by using the equation

$$D_{\mathrm{v}}^{-} = \sum n_{\mathrm{i}} D_{\mathrm{i}}^4 \Big/ \sum n_{\mathrm{i}}^3 \tag{4}$$

where n_{i} is the number of particles in the diameter range D_{i}.

The polydispersity index was calculated using the following equations:

$$\text{Poly dispersity index, PDI} = D_{\mathrm{w}}^{-} \big/ D_{\mathrm{n}}^{-} \tag{5}$$

where, n_{i} is the number of domains having diameter D_{i}.

Results and discussion

Characterisation of epoxy resin

Epoxy resins are basically polyethers. LAPOX B-11 is diglycidyl ether of bisphenol A. IR spectrum of LAPOX B-11 is shown in Fig. 1a. The presence of an absorption peak at ~3500 cm^{-1} is due to the –OH stretching vibrations. The symmetrical stretching frequency of the epoxy ring occurs near 1250 cm^{-1}. Another band appearing at 950–810 cm^{-1} is attributed to asymmetrical ring stretching in which the C–C bond is stretching during contraction of the C–O bond. A third band known as the "12 micron band" appears in the 840–750 cm^{-1} region. The C–H stretching vibrations of epoxy rings occur in the 3050–2990 cm^{-1} region of the spectrum [30, 31].

Characterisation of HTNR

Hydroxylated natural rubber is obtained by the photochemical depolymerisation of natural rubber. Chemical and spectroscopic analyses showed that HLNR contains epoxy groups along with the hydroxyl groups.

Infra red analysis

The IR spectrum of HLNR is given in Fig. 1b. The peaks in the spectrum are assigned the values as given in Table 3. A broad band at 3600–3400 cm^{-1} showed the presence of primary hydroxyl groups in HLNR. Other bands at 1310 and 1035 cm^{-1} also indicate the presence of hydroxyl groups [29].The absorption at 870 cm^{-1} shows the presence of epoxy group. Other bands are characteristic of natural rubber (*cis*-1,4-polyisoprene). The presence of epoxy group was reported by earlier studies [32]. The band at 1250 cm^{-1} corresponds to symmetrical stretching (ring breathing frequency) of epoxy group [33, 34] in which all ring bonds stretch and contract in phase. Another band appears at 840 cm^{-1} which is attributed to asymmetrical ring C–H stretching involving the C–C bond but a band corresponding to the isoprene unit also falls in this region. A third band assigned for epoxy ring is in the 840–750 cm^{-1} region but this region is masked in the spectrum by the chloroform band. The stretching frequency of C–H bonds present on the epoxy ring occurs at 3050–2999 cm^{-1} region.

NMR analysis

The proton NMR spectrum of HLNR is given in Fig. 1e. The NMR spectrum comprises the signals for the protons present in the structure. The signal at 1.2 ppm is mainly due to the secondary hydroxyl group. Proton NMR of HLNR is very similar to that of natural rubber which confirms that the *cis*-1,4-poly isoprene structure is retained in HLNR [33]. The resonances at 2.03 ppm (H_1 and H_4), 1.67 ppm (H_3) and 5.12 ppm (H_2) are characteristic of isoprene units. H_1 and H_4 indicate the presence of methylene protons. The methyl protons in the isoprene units (H_3) are confirmed by the peak at 1.67 ppm. H_2 shows the presence of olefinic hydrogen. Other peaks at 1.25 and 1.10 ppm show the presence of products due to side reactions.

GPC analysis

Gel permeation chromatographic analysis gave the number average molecular weight. The chromatogram obtained from Waters 410 Differential Refractometer is given in Fig. 1d. The peak corresponds to a molecular weight M_n^- as 8398.

Characterisation of modified resin

IR spectrum of cured resin

Before the onset of curing, FTIR spectra shows characteristic peaks at 860 and 915 cm^{-1} due to oxirane group of epoxy and at 1310, 1420, 1700–1730 and 1825 cm^{-1} for carboxyl group, 1650 cm^{-1} for carbonyl stretching and 1620 cm^{-1} as for N–H bending. IR spectra of cured resin (Fig. 1e) showed characteristic absorption bands at 3433 cm^{-1} (OH stretching) 1729 cm^{-1} (C–O str) and 1249 cm^{-1} (of epoxy group). On curing, formation of a stretched peak in the region 850–950 cm^{-1} was observed. Disappearance of peaks confirms the reaction of the group with the progress of reaction (for e.g. disappearance of the band at 910 cm^{-1} due to the epoxy and disappearance of 1700–1730 cm^{-1} due to COOH group). The –OH stretching bands of cured and uncured resins showed that this band has sharpened to some extent due to cross linking reaction [33].The –OH stretching is shifted from 3410–3433 to 3430 cm^{-1}. The group of bands around 2930–2800 cm^{-1} indicates the C–H stretching vibrations due to aliphatic moieties. A sharp and well-resolved medium band around 1280 cm^{-1} may be assigned to an $-Ar-O-CH_2-$ linkage. The bands at 3030 and 1500 cm^{-1} are attributed to aromatic breathing frequency due to the bisphenol A moiety. The strong and sharp band around 1100 cm^{-1} may be assigned to the secondary –OH group. The sharp bands observed at 840 and 720 cm^{-1} may be assigned to the substituted aromatic system (850, 1150 and 1250 of epoxy moiety). The band around 3420 cm^{-1} is attributed to the N–H stretching vibration due to the secondary –NH– group. The sharp band observed at 1730 cm^{-1} may be assigned to the C–O stretching vibration due to the aromatic ester group [35].

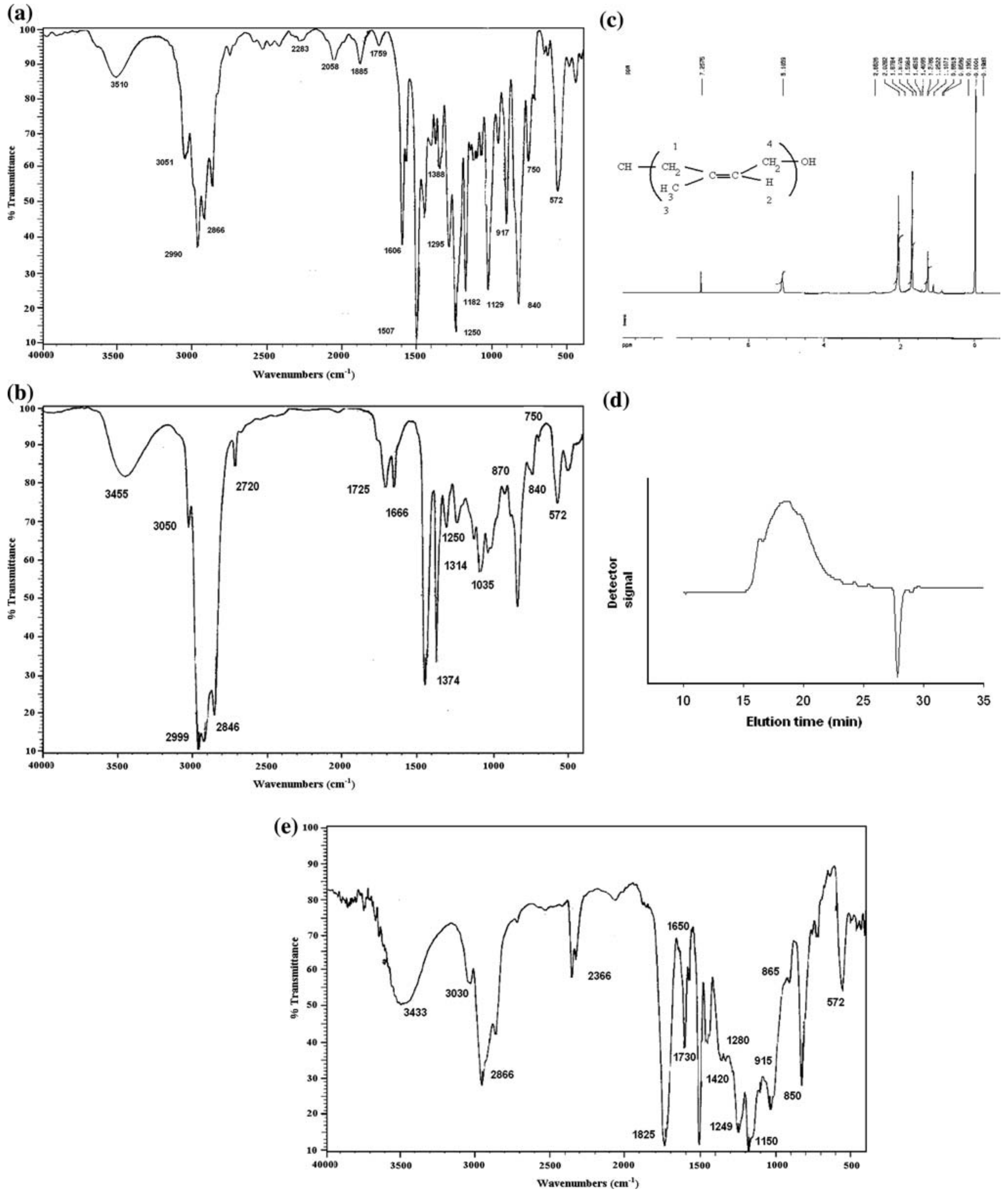


Fig. 1 IR spectrum of **a** epoxy resin, **b** HLNR. **c** NMR spectrum of HLNR. **d** Sketch of GPC of HLNR. **e** IR spectrum of modified epoxy resin cured at 180 °C

Table 3 IR frequencies of HLNR

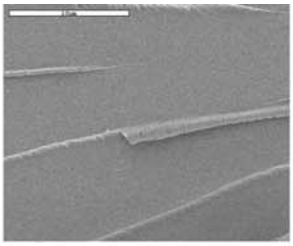
Peak position (cm^{-1})	Characteristic groups
3600–3400	O–H Str. (broad)
3040	m, C–H Str.
2920	s, C–H asym Str., $–CH_2–$
2860	s, C–H sym. Str., $–CH_3$
1660	m, C=C, *cis*-vinylene
1450	s, C–H asym., def, $–CH_3$
1375	s, C –H sym., def, $–CH_3$
1310	m, O–H def, in plane, prim. and sec. alcohol
1035	m, C–O Str. aliph. prim. alcohol
885	m, $–CH_3$ def
870	Epoxide
830	s, C–H out of plane, def, in $–CHR=CCR^1$

Morphology of the blends

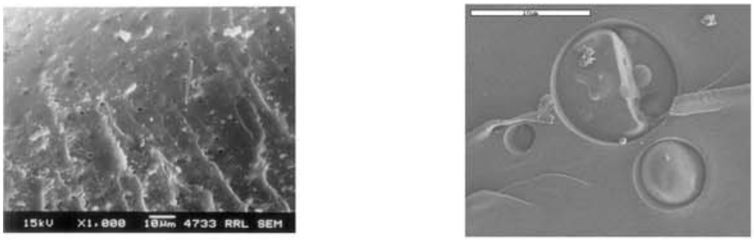
Morphology characterisation by scanning electron microscopy plays a critical role in the establishment of the morphology–property relationship. Scanning electron micrographs show broken rubber particles and stress-whitened zone. The dissolved rubber in the epoxy matrix makes the matrix more ductile and increases its toughness [36, 37]. In order to have a clear understanding of the microstructure, both unextracted and extracted (toluene) surfaces were examined by SEM. The SEM micrograph of cryogenically fractured surface of the unmodified epoxy in Fig. 2a shows a smooth glassy fracture surface with cracks in different planes indicating brittle fracture. It possesses distinctive fast-fracture features; that is, the surface is relatively smooth and very limited plastic deformation can be observed. Unlike the neat epoxy, fracture surface of the rubber-modified ones are rough indicating massive shear deformation. Energy is absorbed during plastic deformation in the case of the modified epoxy network giving rise to a higher toughness and impact strength [23]. Figure 2b represents the modified epoxy sample with 5 wt% HLNR–epoxy. Here rubber domains appear as small spheres of size 1 μm in the epoxy matrix. Toluene was used for etching the samples in order to remove the rubber phase. The etched surfaces of the cryogenically fractured rubber-modified networks consist of two distinct phases—globular rubber particles uniformly distributed through out the continuous epoxy matrix. Domain size increases to 2.77 μm as the concentration of the liquid rubber is enhanced. The samples were etched using toluene for 24 h duration. It is evident from Fig. 2d that the etched surfaces show holes dispersed in the epoxy matrix, the rubber domains being etched out in toluene. The morphology of the unextracted samples, on the other hand, shows clear double phase separation. They contain cross-linked epoxy subinclusions in the rubber domains (particle in particle morphology). The etched surface for 10 wt% HLNR–epoxy as represented by Fig. 2d shows holes uniformly distributed in the epoxy matrix and the unetched tensile fracture surface given by Fig. 2e shows secondary phase separation of cross-linked epoxy in the dispersed rubber phase. The size of the domains reach a critical value of 6 μm in the case of 15 wt% rubber-modified epoxy. The relative dark region is the continuous epoxy matrix in which HLNR domains are dispersed. In fact, this region shows the brittle fracture characteristic of the epoxy matrix. The comparatively brighter region, exhibits ductile shear yielding and is the HLNR phase and the spherical particles inside the HLNR phase, are cross-linked phase separated epoxy particles. A careful examination of the SEM micrograph of unextracted HLNR-modified epoxy sample revealed good adhesion between epoxy phase and HLNR phase. From the SEM micrographs of the unextracted samples of HLNR–epoxy system (Fig. 2c, e, g, i) one can understand that the rubber-modified epoxy shows clear evidence of secondary phase separation. In the case of 20 wt% HLNR/epoxy, domain size increases to 9 μm and the uniform morphology is disturbed due to agglomeration, as evident from the micrograph (Fig. 2i). The presence of agglomerates act as defects and initiates catastrophic failure. At 20 wt% HLNR–epoxy, the rubber particles are found debonded from the matrix generating large voids, which are less effective in toughening the epoxy matrix. Stress whitening is observed in rubber-modified epoxy blends—10 wt% HLNR–epoxy and above. It is due to the scattering of visible light from the layer of the scattering centre, i.e. the voids. The generation of the voids is due to the cavitations of rubber particles, which is the most important energy-dissipating mechanism in the case of rubber-toughened epoxy [38].

A schematic representation of the secondary phase separation of epoxy in the HLNR phase is shown in Fig. 3a. Upon mixing epoxy resin with liquid natural rubber and cross-linker at 100 °C a homogeneous mixture is obtained. This upon curing at 180 °C, reaction-induced phase separation takes place leading to the formation of complex phase morphologies as shown in Fig. 3a. It is important to add that the extent of secondary phase separation increases with increase of the rubber content. This is manifested by the increase of cross-linked epoxy particles in the dispersed rubber phase. At 20 wt% of the rubber phase, the cross-linked epoxy particles in the rubber phase have undergone agglomeration as evident from the SEM photo micrographs shown in Fig. 2i. It is very clear that the submicron particles of cross-linked epoxy phase touch each other giving rise to grape like bundles. This is further schematically shown in Fig. 3b. This structure formation has a strong influence on the toughness of the sample as discussed in the following section.

Fig. 2 a–i SEM of HLNR modified epoxy resin at the cure (extracted and unextracted)

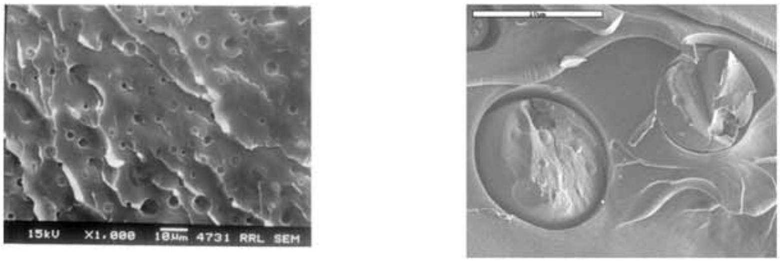


(a) Neat resin



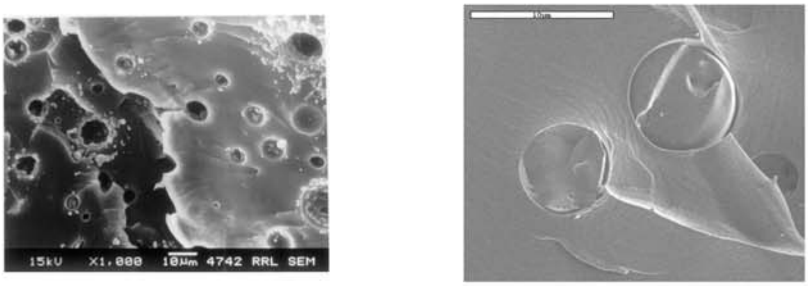
(b) 5 wt% rub (extracted)

(c) 5 wt% (unextracted)



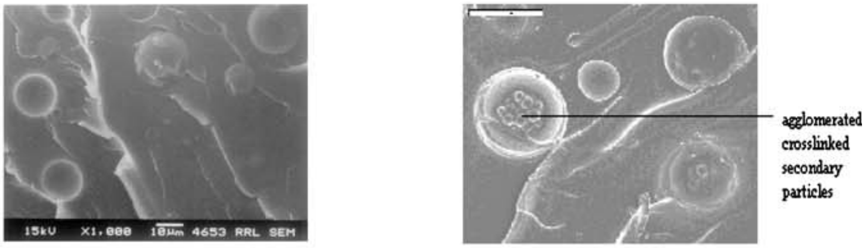
(d) 10 wt% rub(extracted)

(e) 10 wt% rub (unextracted)



(f) 15 wt% rub(extracted)

(g) 15 wt% rub (unextracted)



(h) 20 wt% rub (extracted)

(i) 20 wt% rub (unextracted)

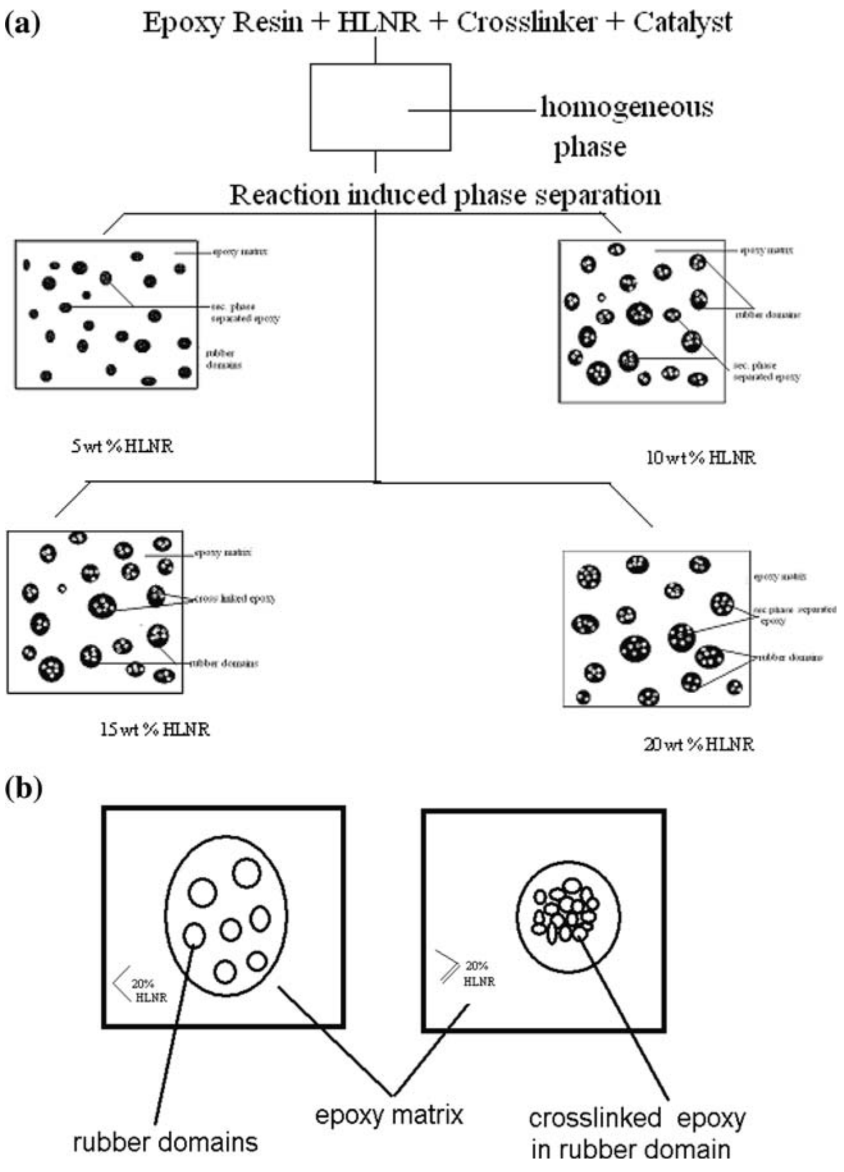


Fig. 3 Schematic representation of **a** secondary phase separation in rubber-modified epoxy resin, **b** <20 and ≥20 wt% rubber-modified epoxy resin

For the 5 wt% HLNR-modified epoxy, the HLNR particles are dispersed in a continuous epoxy matrix as shown in Fig. 3a. The rubber domains are comparatively small but contain small particles of secondary phase separated cross-linked epoxy in them. The 10 wt% HLNR-modified epoxy blends with significant larger HLNR domains shows enhanced secondary phase separation. The 15 wt% rubber and the 20 wt% HLNR-modified epoxy system represent a similar behaviour, but with considerable increase in the size of the secondary phase separated particles.

The major reasons for secondary phase separations, in a dynamic asymmetric system, can be the combined effects of diffusion, hydrodynamics and viscoelasticity of the thermosetting phase. It should be noted that in the case of epoxy/rubber blends phase separation phenomena is very complicated since phase separation in thermoset/rubber blends is coupled with polymerisation, gelation and vitrification and hence a realistic description of phase separation is not possible. Double phase separation is a usual observation in modified thermosetting polymers. With increasing rubber concentration, as a result of coalescence, the droplets merge together. Consequently, the interfacial area reduces rapidly which leads to a destabilisation between the two phases, and finally to a double phase separation process.

The variation of the domain sizes at the cure temperature 180 °C is plotted in Fig. 4. It is found that the size increases steadily (i.e. number average diameter varying from 1 to 9 μm) with increase in composition from 5 to 20 wt% rubber. There is tremendous increase in the size of the particles as the concentration is increased. The rubber domains dispersed in the matrix enhances the toughness of

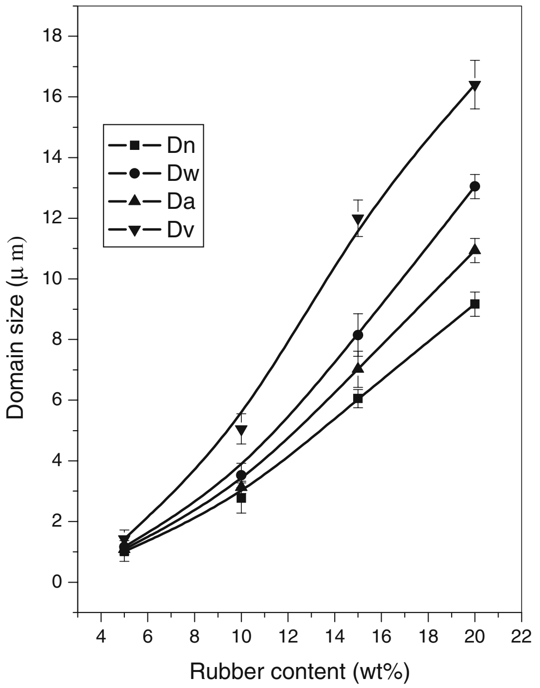


Fig. 4 Variation of domain size with rubber content at 180 °C

the samples. Since curing is complete at this temperature, the morphology of the particulate phase is also steady. The particles are enormously big as evident from the scanning micrographs for 20 wt% blends. It is known that rubber particles of 4–8 µm are responsible for toughening. Smaller particles of 1–3 µm toughen the system through shear banding while larger particles toughen through cavitation and shear yielding [39].

Mechanical properties

Tensile test

The results of mechanical testing at the cure temperature 180 °C are summarised in Table 4. The stress–strain curves of the modified and unmodified epoxy resin are given in Fig. 5. The stress–strain behaviour of the modified epoxy at the cure temperature shows a Hookean behaviour at first followed by plastic deformation. The neat epoxy specimens broke in a brittle manner with no apparent yielding. It shows the typical behaviour of thermosetting resins. Similar curves for epoxy resin modified with 5, 10, 15 and 20 wt% HLNR lie beneath that of the neat resin. The stress at break decreased with increase in HLNR concentrations as the rubber particles act as stress concentrators causing a decrease in the mechanical properties like tensile strength, Young's modulus, elongation at break, flexural strength, flexural strain and modulus but with enhancement in toughness. In samples with higher content of rubber there is secondary phase separation of cross-linked epoxy inside the rubber domains dispersed in the continuous epoxy matrix, as evident from the SEM micrographs (Fig. 2c, e, g, i). With increase in concentration of the liquid rubber tensile strength and modulus are found to decrease. The variation of tensile strength is

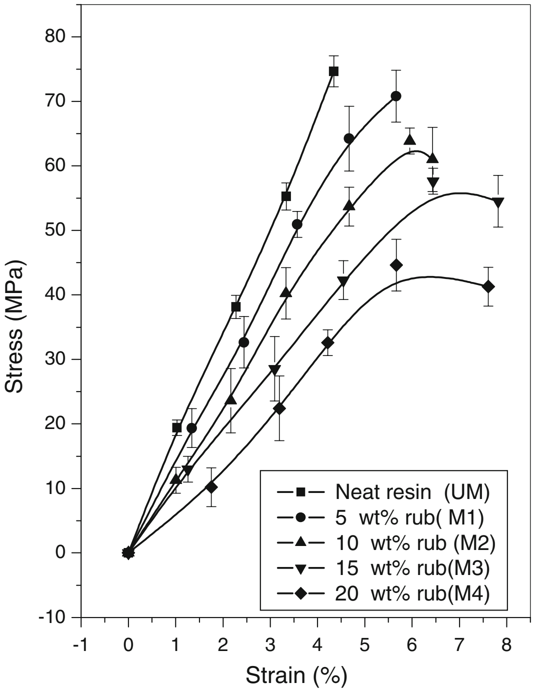


Fig. 5 Stress–strain behaviour of sample cured at 180 °C

Table 4 Tensile and flexural properties of modified and unmodified epoxy at the cure temperature 180 °C

Properties	Neat epoxy	Epoxy + (5 wt% rub)	Epoxy + (10 wt% rub)	Epoxy + (15 wt% rub)	Epoxy + (20 wt% rub)
Tensile strength (MPa)	74.7	70.8	61.2	57.6	44.6
Young's modulus (MPa)	1682	1307	974	767	625
Elongation at break (%)	4.3	5.7	6.4	7.8	7.6
Flexural strength (MPa)	89.2	80.2	69.1	53.3	47
Flexural strain (%)	3.6	3.7	3.8	3.9	3.9
Flexural modulus (MPa)	2496	2246	1900	1823	1742
Toughness (J)	160.7	216.9	238.2	269.5	244.8

shown in Fig. 6a. It is well known that modifiers affect tensile properties according to their size distribution and interfacial bonding. The variations of elongation at break with rubber content are depicted in Fig. 6b. The elongation at break increased with HLNR content from 5 to 15 wt% liquid rubber. Young's modulus or tensile modulus is defined as the ratio of the uniaxial stress over the uniaxial strain in the range of stress in which Hooke's law holds. It is a measure of the stiffness of an isotropic elastic material. This can be experimentally determined from the slope of the initial linear portion of the stress–strain curve created during tensile tests conducted on a sample of the material. It describes tensile elasticity or the tendency of an object to deform along an axis when opposing forces are applied along that axis. For unmodified sample the apparent modulus is high and the incorporation of low modulus rubber particles in the matrix decreases the modulus of the cured resin. Toughness values as indicated by the area under the stress–strain curve are plotted as a function of cure temperature, domain size and as a function of rubber concentration in Fig. 6c–e, respectively. It is found that these values increase with increase in temperature and HLNR concentrations. Maximum toughness is acquired by the 15 wt% rubber composition at the cure temperature 180 °C. This is due to the secondary phase separated epoxy dispersed in the rubber phase. For 20 wt% sample, toughness

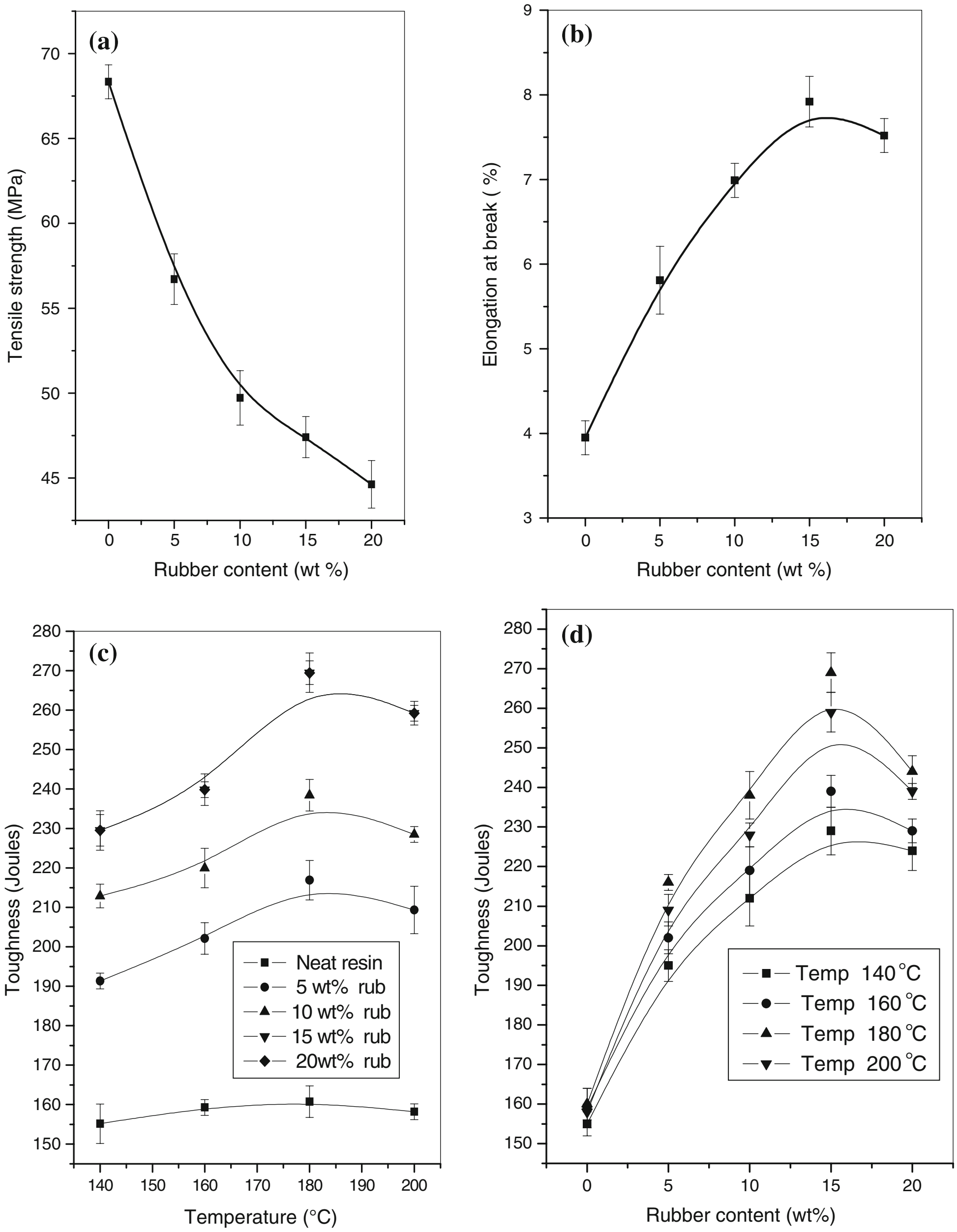
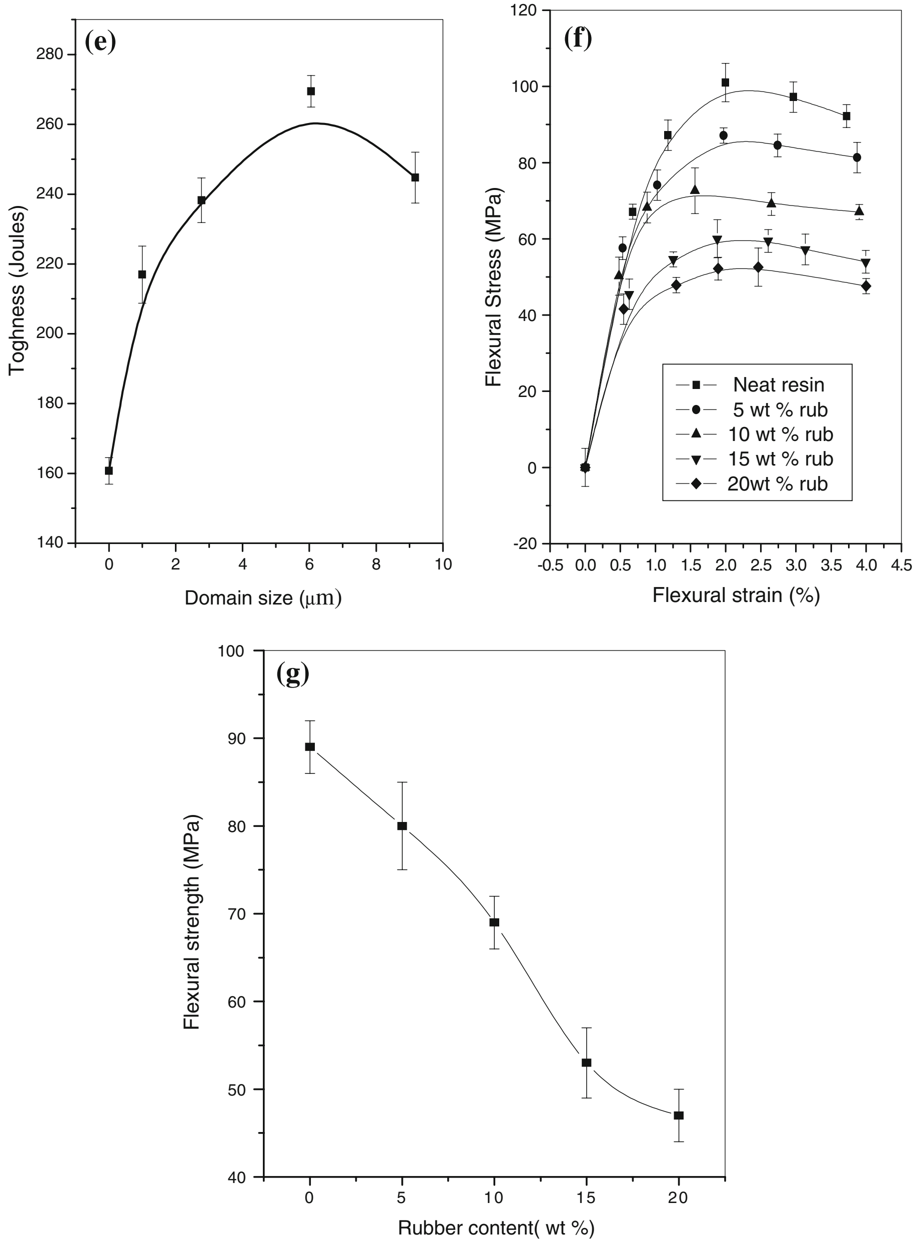


Fig. 6 Variation of **a** tensile strength with rubber content, **b** elongation at break with rubber content, **c** toughness with temperature, **d** toughness with rubber content, **e** toughness with domain size. **f** Flexural stress–strain behaviour at the cure temperature 180 °C. **g** Variation of flexural strength with rubber content

Fig. 6 continued



is marginally decreased and the decrement in the toughness is attributed to the bigger particle size of the rubber domains (Table 5) and also due to the agglomerated cross-linked secondary epoxy phase in the rubber phase as shown in Fig. 2i. It is observed that up to a critical particle size of 6 μm the toughness values go on increasing due to the phase separated cross-linked epoxy dispersed in the rubber phase and then decreases. From SEM analysis it is observed that in the case of 20 wt% rubber there are bigger rubber domains due to the coalescence of smaller ones which debond due to weaker forces of attraction between the matrix and the modifier and hence the decrease in mechanical properties. The 15 wt% rubber composition gives maximum toughness.

The flexural stress–strain behaviour of the modified epoxy at the cure temperature 180 °C is depicted in Fig. 6f and is similar to the tensile stress–strain variation. Flexural strength as a function of rubber content as seen from Fig. 6g decreases due to the presence of soft rubber phase, which remains in the epoxy matrix. Similar observation was reported by many authors [14, 32, 34].

Conclusions

A low molecular weight liquid rubber, HLNR, was developed by the photo depolymerisation of natural rubber. It was characterised by chemical and spectroscopic

Table 5 Domain sizes of rubber particles in the blends

Sample code	$\bar{D}_n$ (μm)	$\bar{D}_w$ (μm)	$\bar{D}_a$ (μm)	$\bar{D}_v$ (μm)	PDI
Ep + 5 wt% rub	1.00	1.17	1.08	1.42	1.15
Ep + 10 wt% rub	2.77	3.52	3.12	5.05	1.27
Ep + 15 wt% rub	6.05	8.14	7.02	12.00	1.34
Ep + 20 wt% rub	9.17	13.04	10.93	16.40	1.42

methods. It can be used as a toughening agent for epoxy. Toughness reaches its maximum for 15 wt% HLNR though a marginal decrease is observed in Young's modulus, tensile strength and flexural properties. SEM analysis reveals that the prevailing toughening mechanism for the epoxy resin under consideration is through localised plastic shear yielding and cavitation induced by the presence of HLNR. As the HLNR content increased, the morphology exhibited secondary phase separation where the rubber domains in the epoxy matrix contained cross-linked epoxy particles. As the amount of liquid rubber in the epoxy resin increased, the extent of secondary phase separation become more prominent as evidenced by the large number of cross-linked epoxy particles in the dispersed rubber phase, up to 15 wt% rubber. Each domain of HLNR in epoxy matrix acts as stress concentrators which increase the toughness through cavitation. However, at 20 wt% of rubber, the secondary phase separated epoxy particles agglomerate to form a network-like structure. This leads to a decrease in the impact strength. The improvement in toughness is attributed to the secondary phase separated epoxy particles in the rubber domains. These enhance shear localisation by acting as stress concentrators. Thus, HLNR can be employed as an effective toughner for epoxy resin.

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