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Studies on blends of epoxy-functionalized hyperbranched polymer and epoxy resin

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An epoxy-functionalized hyperbranched polymer (HBP) was used to toughen a conventional epoxy resin, diglycidyl ether of bisphenol A (DGEBA) cured with diethyltoluene-2,6-diamine (DETDA). There was little change in gel time as a result of addition of HBP, even though the HBP reacts at a slower rate with amine hardeners compared to DGEBA alone. Phase separation was investigated for various HBP contents and as a function of cure conditions as well. The thermal and dynamic viscoelastic behavior of the modified matrices have been examined and compared to the DGEBA epoxy matrix. It appears that the HBP which phase separates does not react as fully as when it is reacted with the amine alone. Nonetheless, good improvement in impact strength as a result of incorporation of HBP were observed and explained in terms of morphological behavior for a DGEBA matrix modified with various amounts of HBP. © *2003 Kluwer Academic Publishers*

1. Introduction

Dendritic polymers are a new class of three dimensional, man made molecules produced by multiplicative growth from small molecules that incorporates repetitive branching sequences to create a novel molecular architecture. Over the last few years, synthesis of a large number of dendritic polymers have been reported in the open literature [1, 2] and in patents [3, 4]. They have potential applications in a variety of fields such as biomedical applications, catalysis and commercial coatings [5, 6]. However, actual exploitation of dendritic polymer technology, particularly in engineering applications, is limited due to difficulties in synthesizing them in large quantities.

Recently, dendritic-type polymers have been produced by a new, lower cost hybrid synthetic process that generates ultrabranched, polydisperse molecules. These materials are called hyperbranched polymers so as to distinguish them from their more perfect counterpart. These are now being produced in sufficient quantities to allow investigation of their utility in conventional engineering applications. Due to the compact, three-dimensional structure of dendritic polymers, these molecules mimic the hydrodynamic volume of spheres in solution or melts and flow easily past each other under applied stress. This results in a low melt viscosity, even at high molecular weights, due to a lack of restrictive interchain entanglements [7]. Indeed, dendritic polymer have been shown to exhibit melt and solution viscosities that are an order of magnitude lower than linear analogues of similar molecular weight [8, 9]. The high density of functional terminal groups on dendritic polymer also offers the potential for tailoring their compatibility either through conversion of dendritic polymer end groups to chemically suitable moieties or through in situ reaction to form covalently bound networks. These two properties low viscosity and tailorable compatibility, make them excellent candidates as flow additives that could act simultaneously as toughening agents. Some initial studies have been done on thermoplastics and HBP blends [10, 11], with less literature available on the properties of blends of HBP and thermoset like epoxy resins [12].

Epoxy resins are successfully toughened by blending them with carboxyl-terminated copolymer of butadiene and acrylonitrile (CTBN) [13–15]. However, the main deficiency of CTBN is the high level of unsaturation in their structure, which provides sites for degradation reactions in oxidative and high temperature environments [16]. The presence of double bonds in the chain can cause oxidation reaction and/or further cross-linking with the loss of elastomeric properties and ductility of the precipitated particles [17]. Secondly, there remains a possibility that traces of free acrylonitrile, which is

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carcinogenic, might exist and limit the use of these materials [18]. Saturated liquid rubbers such as siloxane [19], polyurethane [20], acrylates [21, 22] and so on, have been reported as an alternative to CTBN. However, rubber modification results in considerable increase in prepolymer viscosity which can cause difficulties in processing. The use of HBP offers the possibility of good internal bonding rubber phase and low initial viscosity.

The aim of the present work is to investigate a new modifier, which could toughen epoxy resins without compromising the ease of processability. Boogh *et al.* [12] investigated the impact behavior and morphology of blends of HBP, having various epoxy contents, and a low T_g epoxy. The present paper discusses the detailed curing behavior, thermomechanical properties and morphology of the blends of a commercially available HBP, and high T_g epoxy as a function of HBP composition and cure temperature.

2. Experimental

2.1. Materials

The epoxy resin used was a liquid diglycidyl ether of bisphenol A (DGEBA) (DER 331 Dow epoxy resin) containing 5.27 mmol epoxide per gram of resin. The curing agent, Ethacure 100, of Albemarle Corp., USA, is a mixture of the two diethyltoluene diamine (DETDA) isomers (74–80% 2,4 isomer and 18–24% 2,6 isomer). The chemical structures of the epoxy resin and hardener are shown in Fig. 1.

The epoxy functional dendritic hyperbranched polymer (Boltorn E1) with an epoxy equivalent weight of ~875 g/eq and a molecular weight of ~10500 g/mol, was supplied by Perstorp Speciality Chemicals, Sweden [12]. Boltorn E1 consists of a highly branched aliphatic polyester backbone with in average 11 reactive epoxy groups per molecule. The epoxy groups on the Boltorn E1 are secondary, in the middle of an aliphatic chain attached to the hydroxy-terminated hyperbranched precursor.

2.2. Preparation of DGEBA/HBP blends and curing

The HBP-filled samples were prepared by dissolving the HBP in the DGEBA at 100°C with thorough stirring. The modified resin was mixed with a stoichiometric amount (23 : 100 w/w) of DETDA by continuously stirring the mixture for 5 min at 100°C. The mixtures were cured in an aluminum mold at 100°C for 3 h after having been degassed under vacuum for 10 min. Blends containing 0–20% (by weight) HBP were made. In order to study the effect of cure temperature on the properties modified networks, the 15% HBP containing mixture was cured at different temperatures (120°C, 140°C, 160°C). Thus in this work, DGEBA/HBP blend means the blend including stoichiometric amount of DETDA and curing temperature means 100°C, unless otherwise specified. Afterwards, the samples were post cured at 200°C for 2 h, allowing them to cool gradually to room temperature.

2.3. Characterization of blends

Differential scanning calorimeter (DSC) dynamic mode measurements were carried out on reactive resins with a Perkin Elmer DSC-7 (in a dry nitrogen atmosphere and calibrated with an Indium standard) using 8–10 mg samples in aluminum pans. Thermal scans at constant heating rate of 10°C min^{-1} were performed in a temperature range 50–300°C for all the mixtures. The heat evolved during the reaction of the mixture has been directly determined by integration of the exothermic peaks.

A Bohlin CS 10 controlled stress rheometer was used to study the variation in rheological properties during cure. A parallel plate assembly (40 mm diameter) was used in the oscillatory mode over a range of frequencies from 1 to 43 Hz. Gelation was defined as the point where the loss factor (tan δ) becomes independent of frequency [23]. The point where the loss tangent vs. time plots at various frequencies (1 Hz, 2.1 Hz, 4.4 Hz, 9.4 Hz, 20 Hz and 42.9 Hz), intersect each other is thus

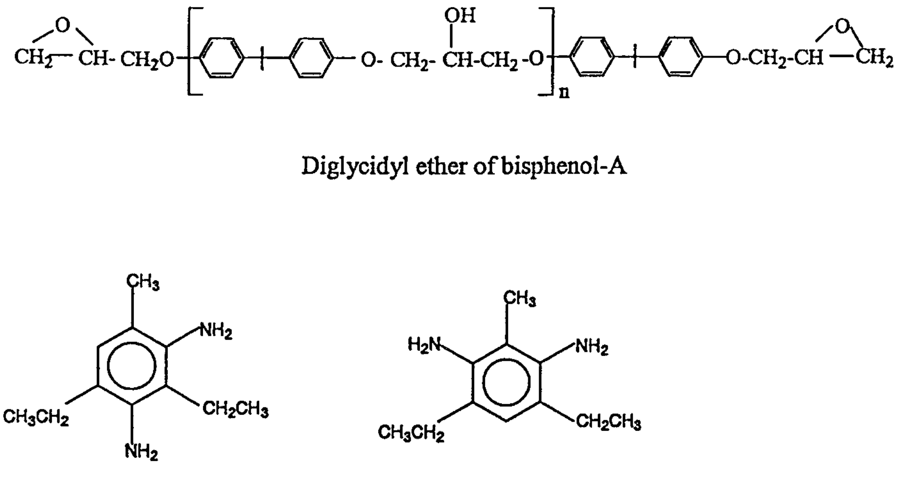

Figure 1 Chemical structures of DGEBA and curing agent.

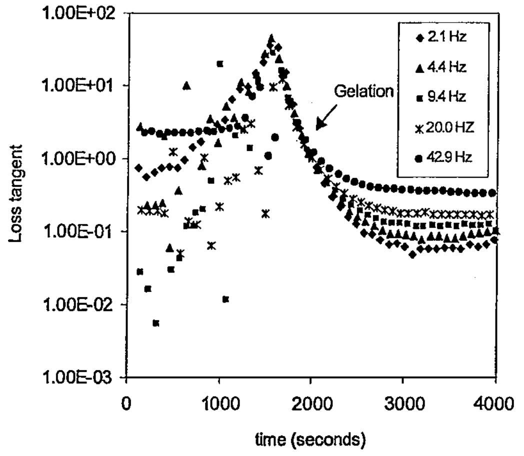

Figure 2 Loss tangent vs. time plots for 10% HBP containing blend at 140°C using various Frequency (1–43 Hz).

taken as gel point. A representative curve showing loss tangent vs. time plots for 10% HBP containing blend at 140°C for various frequencies is shown in Fig. 2.

Dynamic mechanical analysis (DMA) was carried out for cured epoxy samples by a Dynamic Mechanical Thermal Analyzer (DMTA MK IV, Rheometric Scientific) at a fixed frequency of 1 Hz with 3°C/min heating rate using liquid nitrogen for subambient region. Dynamic modulii and loss factors were obtained by dual cantilever mode for the sample of size 45 mm x 10 mm x 2 mm.

The dynamic mechanical properties of the unreacted HBP/amine liquid were also required, and to carry this out a Perkin Elmer DMA7 was also used in the penetration probe configuration. This DMTA has the advantage of applying a cyclical oscillation to a downward-thrusting probe. If a liquid sample is contained in a small vessel, such as a DSC pan, then the sample can be cooled and the glass transition readily obtained by thermal scanning and observing the loss tangent. A heat rate of 3°C/minute and a frequency of 1 Hz was also used.

Density was measured using a Micromeritics pycnometer. Approximately, 4 g of resin was sealed in a pressure chamber prior to measurement. The instrument performed 10 density measurements and produced the average along with the standard deviation. The pressure that the chamber reached during the fill and purge cycle was approximately 120 kPa.

Impact strengths of the modified epoxy samples were determined by an instrumented falling dart impact tester (Radmana, ITR 2000). The annular hole on the specimen fixture was 40 mm in diameter. The sample size used for the test was 80 mm x 80 mm x 5 mm. The impact test was carried out at room temperature (25°C) and impact energy (calculated from the area of the load vs. deformation curve) was reported in J/m. the quoted result is the average of the determination on four samples.

A low voltage scanning electron microscope (SEM) (JEOL, JSM 840) was used to examine the fracture surfaces of the toughened epoxy samples. A thin section of the fracture surface was cut and mounted on an aluminum stub using a conductive (silver) paint and was sputter coated with gold prior to fractographic examination. SEM photo micrographs were obtained under conventional secondary electron imaging conditions with an accelerating voltage of 20 kV.

TABLE I Thermal properties of DGEBA/HBP blends

HBP (%)	T_{peak} (°C)	$(\Delta H_{\text{p}})_{\text{exp}}$ (J/g)	$(\Delta H_{\text{p}})^{\text{a}}_{\text{theo}}$ (J/g)
0	196	410	410
5	196	400	392
10	196	380	374
15	198	350	348
20	200	330	338
100	257	50	50

[a] Calculated from rule-of-mixtures of the component values.

3. Results and discussion

In order to study the cure characteristics of the blends, all the epoxy formulations having different concentrations of HBP were subjected to DSC scans up to 300°C. DSC traces for the unmodified DGEBA, HBP and the blends with stoichiometric amounts DETDA are shown in Fig. 3. The heat evolved during the curing reaction is often used to estimate the reaction rate and conversion [24, 25]. Although the residual heat of reaction near the completion of curing cannot be measured by DSC, the amount of heat evolved as measured by DSC is still a valuable reference in determination of curing characteristic [26]. From the DSC plots, the enthalpy of reaction (ΔH_{p}) and the temperature corresponds to the peak exotherm were determined and presented in Table I. It is clear that HBP shows peak exotherm at higher temperature (257°C) compared to DGEBA (196°C) which indicates that epoxy groups of HBP are less reactive than that of DGEBA. This has been discussed in some detail elsewhere [27] and is related to the fact that the reactivity of the amine-epoxy units where the epoxies are attached to a hyperbranched polymer is less because of topological constraints of the hyperbranched structure and, importantly, the hydroxyl groups formed in the HBP shell molecules do not possess sufficient mobility required for catalyzing the reaction.

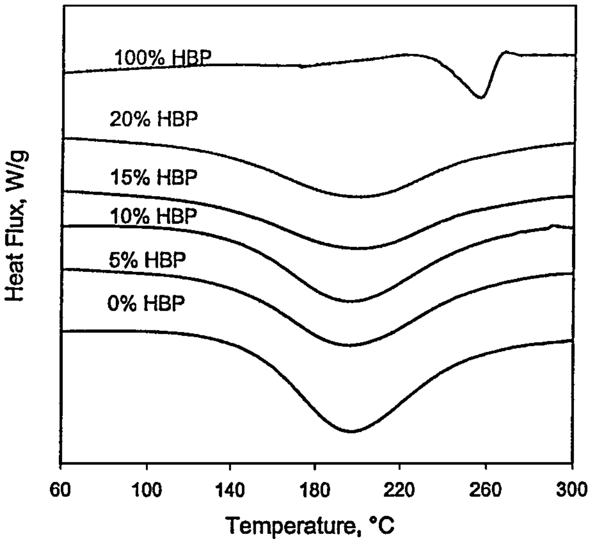

Figure 3 DSC scans of DGEBA/HBP blends containing 0%, 5%, 10%, 15%, 20% HBP.

TABLE II Effect of concentration of HBP and cure temperature on gel time

HBP content (%)	Temperature (°C)	Gel point (min)
0	160	17.4
5	160	18.4
10	160	18.8
10	140	32.1
10	120	67.2
15	160	16.5
20	160	16.8

However, the modified epoxy resin containing 5 and 10% of HPB show peak exotherm at the same temperature (196°C) as neat DGEBA. Slight shifts in peak exotherm were observed in case of higher HBP concentration. This can be attributed to lower reactivity of the epoxide groups of HBP as reflected by peak exotherm at higher temperature (257°C). By comparison, this behavior is different from that observed in case of other liquid rubbers like carboxyl-terminated poly (2-ethyl hexyl acrylate) (CTPEHA) reported earlier [28] where significant increase in T_{peak} was observed. In that case the delay has been attributed to the viscosity effect, which retards the movement of reactive molecules. Blending of HBP with epoxy, however, does not lead to any significant increase in viscosity and hence the reaction rate remains unaffected. Nevertheless, the HBP apparently did not modify the mechanism of epoxy matrix polymerization as the total enthalpy, as shown in Table I, is close to the value expected from the rule-of-mixtures. The ΔH_{p} of unfilled epoxy/DETDA was found to be 101 kJ/mol (expressed in terms of mass of epoxide/ amine mixture) which compares well with 91.4 kJ/mol found by Barton [25] for the DGEBA/DDM system and values ranging from 100–118 kJ/mol for the phenyl glycidyl ether type epoxy-amine reactions tabulated in a review by Rozenberg [29].

The rheological measurements carried out as detailed in the experimental section permitted the characterization of gelation and vitrification process during cure. The effects of HBP concentration and temperature on gel time are shown in Table II. It is clear that gel time decreases with increase in cure temperature due to increase in reaction rate. There was no systematic change in gel point observed as a function of HBP concentration. This is expected as it was observed in the DSC experiments (Fig. 3) that incorporation of HBP has little effect on curing rate.

HBP is compatible with DGEBA at the cure temperature used (100°C). When the homogeneous mixture of DGEBA and HBP is cured, the epoxy groups of DGEBA react rapidly. Curing results the formation hydroxyl groups which decreases the compatibility of DGEBA and HBP leading to the formation of two-phase microstructure. The hardener molecules at the interface are expected to react with both the epoxy groups of DGEBA and unreacted epoxy group of HBP to form chemical bonds with the rigid matrix and HBP particles which is necessary for effective toughening [30, 31].

In order to study the phase morphology all samples were examined by DMTA analysis, this being a powerful way to study the relaxation and miscibility behaviour of polymers and blends. In general, in a viscoelastic loss spectrum as the temperature is increased, it is observed that the damping goes through a maximum in the transition region and then decreases in the rubbery region. The damping is low below T_g as the chain segment in that region is frozen. Below T_g, the deformations are thus primarily elastic and the amount of molecular slipping resulting in viscous flow, is low. Also above T_g, in the rubbery region, the damping is low because the molecular segments are free to move, and consequently there is little resistance to flow. In the transition region, on the other hand the damping is high because of the initiation of micro-Brownian motion of the molecular chain segments and their stress relaxation. It is well established that the shifts in loss tangent peak temperature i.e., glass transition temperature can be used to evaluate miscibility and immiscibility of polymer blends [32, 33].

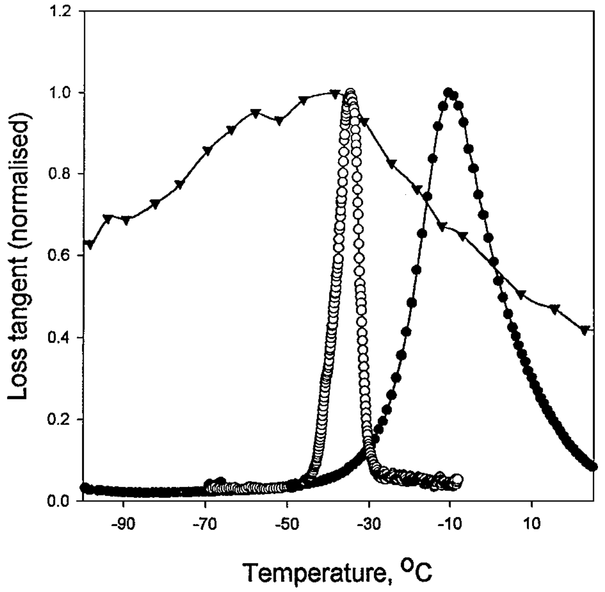

Figure 4 Loss tangent vs. temperature of HBP in three states: uncured monomer mixed with amine (○), cured with amine (●), and as a 20% HBP component in DGEBA (▼). (Note: for comparison all data has been scaled to a peak maxima of 1).

Before presenting the results of the blends, it is necessary to show results of the HBP component alone, both cured and uncured. This is because we found that the T_g of the HBP peak varies, depending on whether it is the uncured HBP, fully cured HBP or the HBP component of a phase-separated DGEBA/HBP blend and these results are shown in Fig. 4. It can be seen that, despite the exotherm of the neat HBP and amine shown in scanning DSC really occurring after about 220°C (Fig. 2), significant cure occurs for these samples that have been postcured to 200°C—increasing the T_g from −39°C (uncured HBP and amine) to −11°C (cured HBP). Also shown is the HBP relaxation peak which is the peak from the phase-separated HBP component in a mixture with DGEBA (which has 20% HBP). The T_g of this component is broad, the maxima ranging from −35 to −45°C, approximately the same, or slightly higher than the loss maxima of the HBP alone (recall that the glass transition of the HBP and amine uncured is measured by a different dynamic mechanical device than the solid samples). It thus appears that the HBP that phase

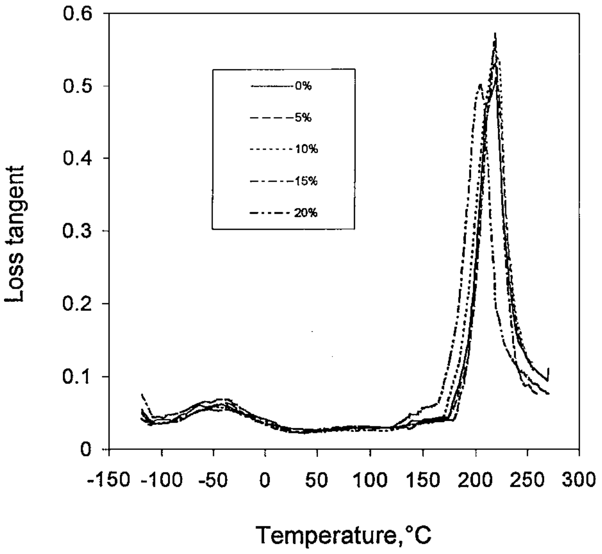

Figure 5 Loss tangent vs. temperature plots of DGEBA/HBP blends containing 0%, 5%, 10%, 15% and 20% HBP.

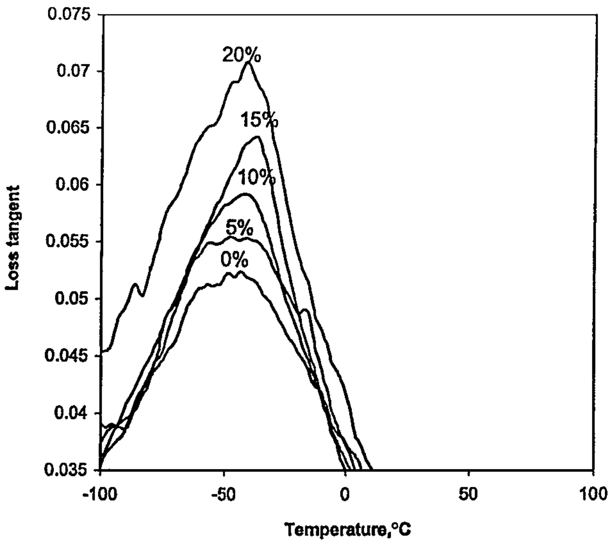

Figure 6 Loss tangent vs. temperature plots showing the HBP relaxation.

separates in the 20% mixture is not as fully cured as it is when mixed solely with the amine. It may be that the amine does not partition equally into the HBP phase, but remains a little more preferentially in the DGEBA phase, or in some other way the cure of the HBP phase is inhibited.

Fig. 5 shows the full loss tangent results as a function of temperature for DGEBA and the DGEBA/HBP blends The DMTA results for DGEBA/HBP blends (containing less than 15% HBP) showed behavior typical of an immiscible blend, all the modified networks show two relaxation peaks. One at high temperature (ca. 217°C) is due to the glass transition of epoxy and the other at low temperature (at ca. −39 to −35°C) due to the HBP phase. The T_g of the rigid DGEBA phase changes little with addition of HBP. Up to 10% of HBP concentration there is no change in T_g of the DGEBA-rich phase as a result of modification. Only a slight decrease in DGEBA T_g was observed in the case of higher concentration (15%, 20%) of HBP. This implies that there is little phase mixing between the HBP and the DGEBA matrix. This is the unique property of the HBP modified epoxy compared to the other liquid rubber like CTBN and epoxy blends where significant depression in epoxy T_g was observed due to incomplete phase separation [13–15]. Recently Ratna *et al.* [33, 34] reported that considerable improvement in toughness can be achieved without any sacrifice in T_g, by blending an acrylate based liquid rubber with an ambient temperature curing epoxy. However, using the high temperature curing epoxy system, a modest sacrifice in T_g was observed [28].

As stated before, the HBP glass transition appears to be lower than that of cured HBP alone, however its location is fairly invariant with HBP content. The height of the low temperature relaxation peak can be seen to increase gradually with increasing concentration of HBP (Fig. 6) as would be expected in a phase separated system and increasingly higher concentrations. A similar observation has been reported by Lee *et al.* [36] for DGEBA/CTBN blend system. However, this is in disagreement with Boogh *et al.'s* [12] observation that has reported absence of a HBP relaxation peak using a different DGEBA resin/isophorondiamine system. The unmodified DGEBA shows a broad peak at lower temperature (at ca. −60°C) as well. This broad peak can be identified as the β-relaxation of the epoxy resin, which is often attributed to the glyceryl-like groups in DGEBA [37].

The tan δ vs. temperature plots for the DGEBA-phase portion of the DMTA spectra of 15% HBP modified DGEBA samples cured at different initial cure temperatures (but all post cured) are shown in Fig. 7. The T_g of the modified epoxy networks decreases with increasing initial cure temperature. This indicates that as the cure temperature increases the amount of HBP which remains dissolved in the epoxy matrix increases. This can be explained by considering the fact that phase separation proceeds until gelation, when diffusion of modifier molecules within the continuous matrix phase is inhibited [12, 38]. From the onset of phase separation, the structure is evolving up to gelation at which article dimension and interparticle distances are fixed. As the curing temperature is increased, the times available for particle nucleation and growth becomes considerably shorter partly because the compatibility is increased and phase separation is initiated at higher conversion [12, 38, 39].

The densities of the cured blends were determined and are reported in Fig. 8. It was found that the densities of the blends are lower than that of the DGEBA. This is expected as the density of the cured HBP/amine mixture (1060 $\text{kg} \cdot \text{m}^{-3}$) is lower than the density of cured DGEBA (1160 $\text{kg} \cdot \text{m}^{-3}$). In fact, as stated before, the HBP phase in the blend is probably less cured than the HBP cured with amine alone, and thus is likely less than the value of 1060 $\text{kg} \cdot \text{m}^{-3}$, although this cannot be directly determined.

The effect of HBP modification on the impact strength of modified networks is reported in Fig. 9. It is clear from the figure that impact strength increases with an increase in HBP concentration, attains a maximum and then decreases. The maximum impact strength was achieved at 15% HBP concentration. The optimum

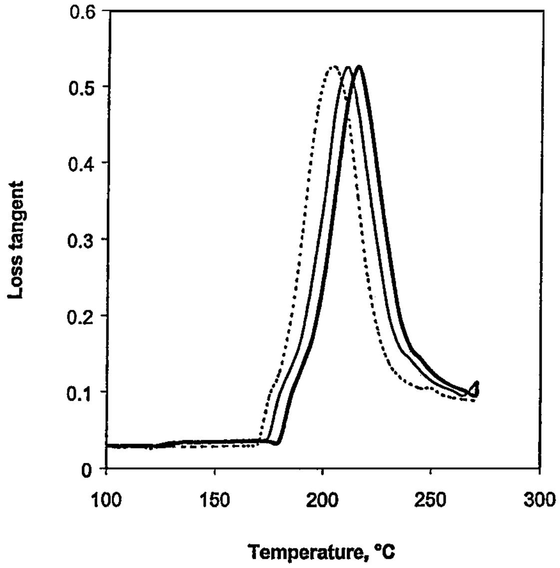

Figure 7 Loss tangent vs. temperature plots of 15% HBP containing blend cured at 120°C (——), at 140°C (——) and at 160°C (- - -).

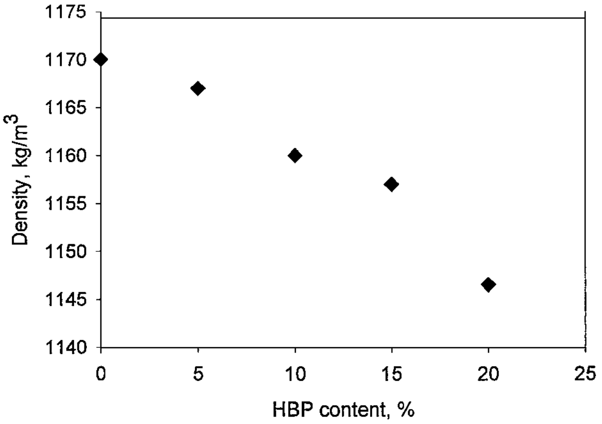

Figure 8 Effect of HBP modification on density of the blends.

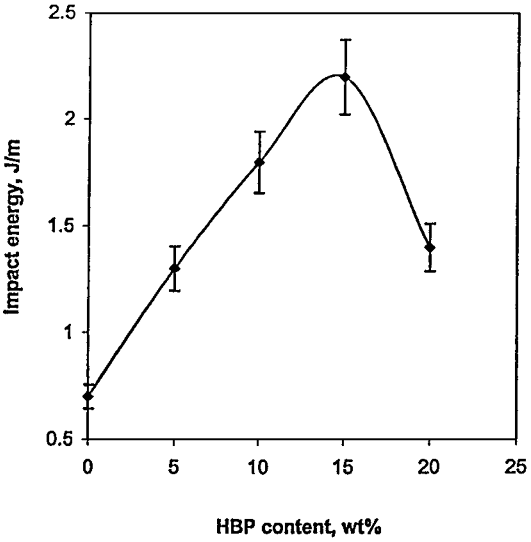

Figure 9 Effect of HBP loading on the impact strength of DGEBA/HBP blends.

impact strength is about three times higher than the value observed for unmodified DGEBA. The improvement in impact strength was found to be higher than the conventional toughening agent CTBN, and acrylate based liquid rubber reported earlier [28, 30].

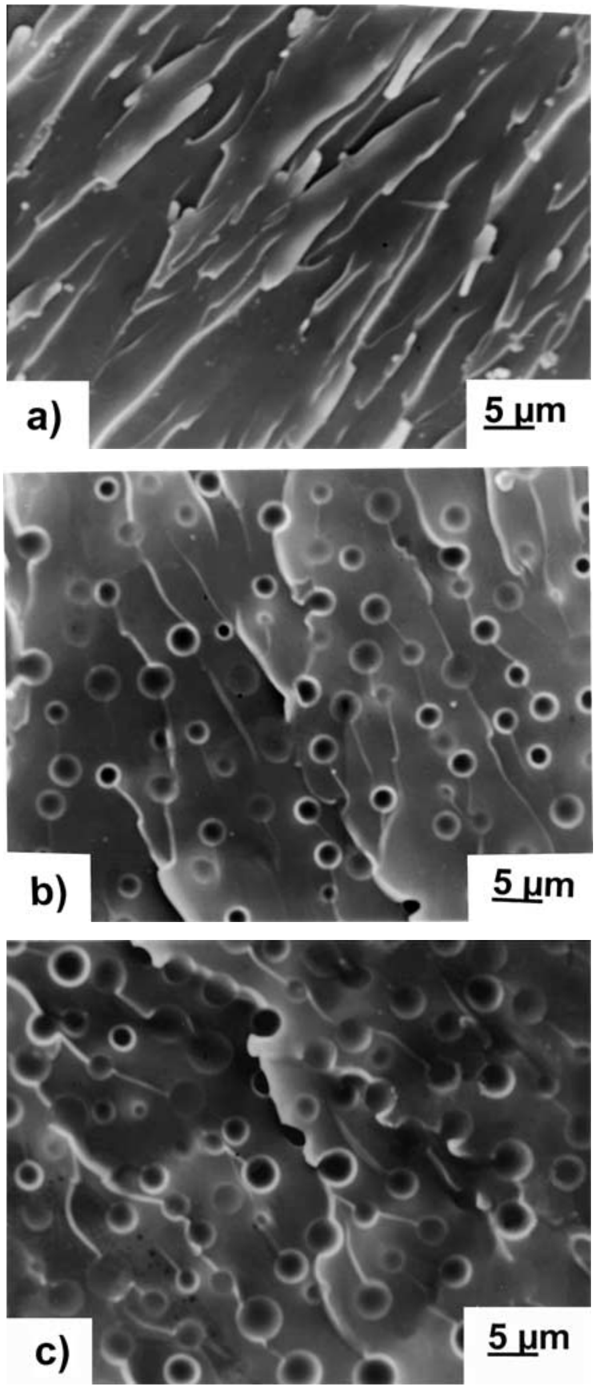

Figure 10 SEM photographs for fracture surfaces of (a) neat DGEBA (b) 15% HBP containing blend (c) 20% HBP containing blend.

The impact behavior of the DGEBA/HBP blends can be explained in terms of morphology observed by SEM. The SEM microphotographs for unmodified epoxy and 10, 15 and 20% HBP containing blends are shown in Fig. 9. From the micrographs (Fig. 10a) one can see the smooth glassy fractured surface with cracking in different planes in the case of unmodified DGEBA. This indicates brittle fracture of the unmodified DGEBA, which accounts for its poor impact strength. The fracture surfaces of the modified networks consist of two distinct phases; globular HBP particles dispersed in continuous DGEBA matrix. In the case of 15% HBP modified samples the HBP particles are uniformly distributed throughout the matrix. The particles have dimensions in the range of 2–3 μm and their distribution is bimodal. The micrograph (Fig. 10b) shows the broken HBP particles and a stress-whitened zone. Stress whitening is due to the scattering of visible light from

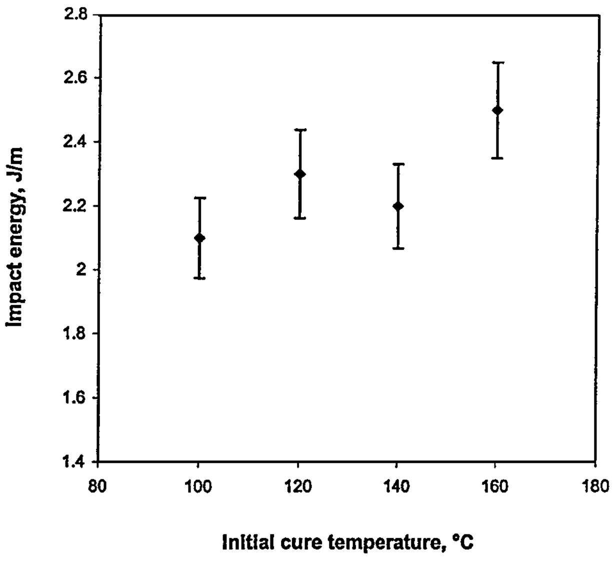

Figure 11 Effect of initial cure temperature on impact strength of DGEBA/HBP blends.

the layer of the scattering centers, which in this case are voids [39, 40]. The generation of the voids is due to the cavitation of rubbery HBP particles and is an important aspect of the dissipation of energy in rubber toughened epoxies [41, 42], both because cavitation absorbs energy, and importantly because it encourages the yielding of the polymer matrix, a process favoured by uniform distribution of the rubber particles throughout the matrix [39, 41–43]. This explains why the HBP modified DGEBA exhibits higher impact strength in comparison to the unmodified DGEBA. In the case of the mixtures having 20% HBP the particles are very close together and some have merged, indicating that the system was on the verge of becoming co-continuous. The toughening mechanism operating may have been undergoing a change due to change of morphology. The existence of an optimum concentration is reported in various rubber toughened epoxy systems due to destruction of uniform morphology as a result of agglomeration [23, 34, 41, 42].

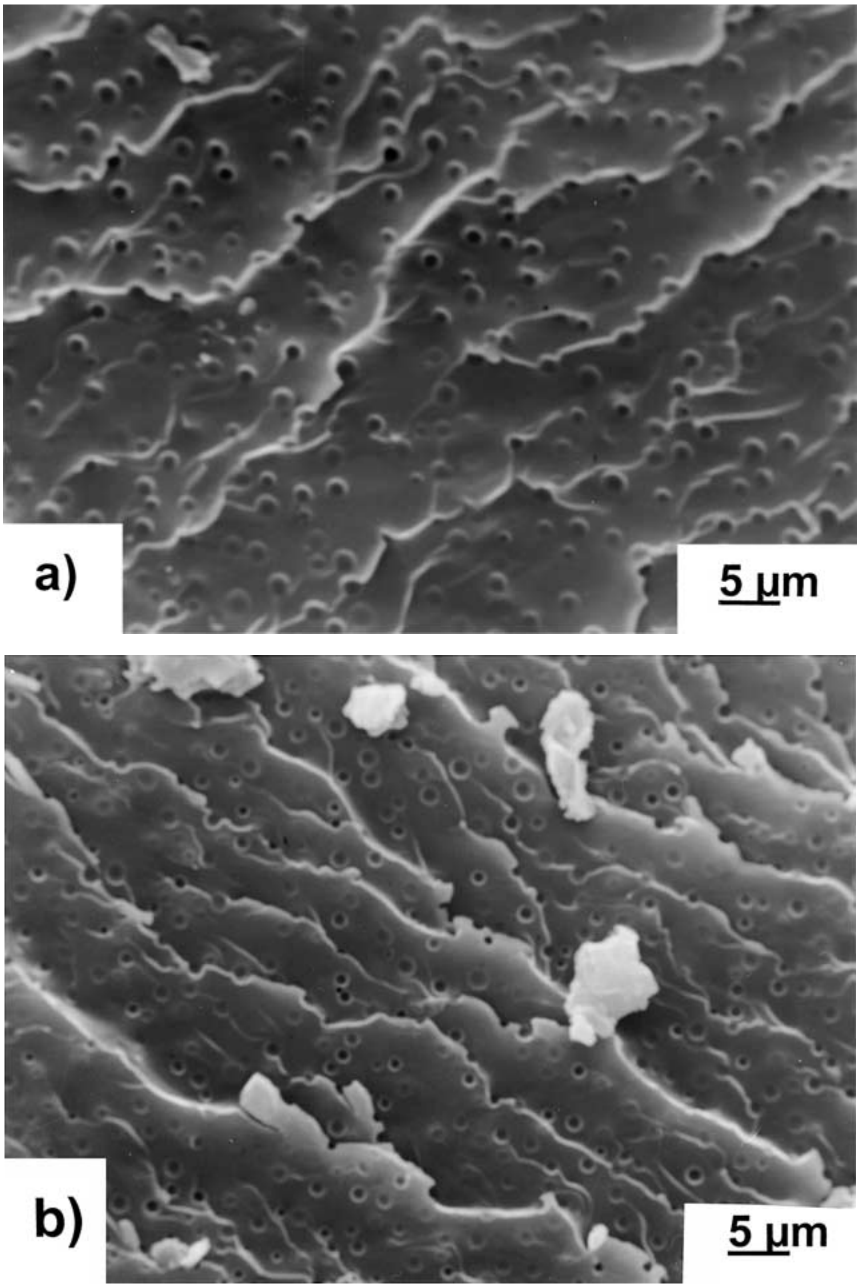

Figure 12 SEM photographs for the fracture surfaces of 15% HBP containing blend: (a) cured at 140°C and (b) cured at 160°C.

The effect of initial cure temperature on the impact strength of the modified networks containing 15% HBP was also investigated. It was found that a marginal increase in impact strength was observed as a result of increase in cure temperature (Fig. 11). The morphology of the modified networks cured at 140°C and 160°C are shown in Fig. 12. The morphology remains similar, irrespective of cure temperature. This behavior is different from that observed in the case of linear liquid rubber and DGEBA blends where the particle size distribution transformed from bimodal to unimodal as the cure temperature increased [44]. In this work, the particle size decreased with increase in cure temperature. Particle size decreases from 2–3 μm to 1–2 μm due to increase in cure temperature from 100°C to 160°C. However, the rubber particles of the observed size are reported to perform equally [45]. Hence the slight increase is impact strength can be attributed to the decrease in T_g of the networks due to dissolution of some HBP in the DGEBA matrix. This makes the matrix more ductile and it is well known that rubbery particles perform better in a more ductile matrix [46, 47].

4. Conclusion

Epoxy-functionalized HBP cures at a slower rate compared to DGEBA. Addition of HBP into DGEBA has little effect on the rate of the curing of blends. The HBP is miscible with DGEBA at 100°C and results in almost complete phase separation after curing, with the HBP phase being less cured than the neat HBP and amine, under the same conditions. The amount of dissolved HBP increases with increase in the cure temperature. Incorporation of HBP into DGEBA leads to a significant increase in toughness. The optimum toughness was obtained at 15% of HBP concentration and the improvement in toughness is higher compared to the conventional toughening agents.

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