

Toughening of Trifunctional Epoxy Using an Epoxy-Functionalized Hyperbranched Polymer

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ABSTRACT: Chemorheology of curing as well as the phase separation behavior of an epoxy-functionalized hyperbranched polymer (HBP)-modified triglycidyl p-amino phenol (TGAP) epoxy mixtures has been studied by several techniques. There was little change in gel time as a result of addition of HBP up to 10% of HBP, even though the HBP reacts at a slower rate with amine hardeners compared to the TGAP alone. The thermal and dynamic viscoelastic be-

havior of the modified matrices have been examined and compared with the unmodified TGAP matrix. Finally, impact properties have been discussed in terms of the morphological behavior for a TGAP matrix modified with various amounts of HBP. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 89: 2339–2345, 2003

Key words: thermosets; toughening; morphology

INTRODUCTION

Epoxy resins are a class of versatile thermosetting polymers which are widely used in structural adhesives, composites, surface coatings, and electrical laminates.¹ This is because of their high strength, low creep, very low cure shrinkage, excellent resistance to corrosion, good adhesion to many substrates, and appropriate electrical properties.^{1,2} A major drawback, which inhibits further proliferation of epoxy resins into various industrial applications, is that in the cured state they are brittle materials having fracture energy of about two orders of magnitude lower than engineering thermoplastics and three orders lower than metals.³ Hence, modification of epoxy resin to impart fracture toughness has been the subject of intense investigation throughout the world.

Toughness implies energy absorption and is achieved through various deformation mechanisms before failure occurs and during crack propagation.⁴ Toughening can be achieved by reduction of crosslink density or use of plasticizers, which leads to increased plastic deformation. However, this approach may seriously affect modulus and thermal properties of the material for only a modest increase in toughness. The most effective approach is the introduction of a second component capable of phase separation, such as reac-

tive liquid rubber,^{5,6} engineering thermoplastic,^{7,8} or core-shell particles.^{9,10} An attraction of liquid rubber such as carboxyl-terminated copolymer of butadiene and acrylonitrile (CTBN) as a modifier is their solubility in base epoxy with the formation of initially a homogeneous solution. As the curing reaction proceeds, the molecular weight increases and the phase separation occurs at some stage, leading to the formation of a two-phase morphology.^{11,12} Such a two-phase system having a small amount of rubber (5–10 wt %) often shows outstanding fracture properties as the rubber particles dispersed and bonded to the epoxy matrix act as centers for dissipation of mechanical energy by cavitation and shear yielding.^{6,12} The improvement in fracture toughness is generally achieved without a significant reduction of thermal and mechanical properties of the crosslinked epoxy resin.

However, the main deficiency of CTBN is the high level of unsaturation in their structure, which provides sites for degradation reaction in oxidative and high-temperature environment.¹³ The presence of double bonds in the chain can cause oxidation reaction and/or further crosslinking with the loss of elastomeric properties and ductility of the precipitated particles.¹⁴ Secondly, there remains a possibility that traces of free acrylonitrile, which is carcinogenic, might exist and limit the use of these materials.¹⁵ The saturated liquid rubbers such as siloxane,¹⁶ polyurethane,¹⁷ and acrylates^{18–20} have been reported as an alternative to CTBN.

The modification of epoxy with linear liquid rubber results in significant increase in prepolymer viscosity and can cause processing problem. Very recently, a new class of reactive liquid rubber, which are den-

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dratic hyperbranched polymers (HBPs), has been investigated as a modifier for epoxy resin.^{21–23} The advantages of HBPs over conventional toughening agents are that HBPs offer much lower prepolymer viscosity because of their spherical structure and lack of chain entanglement and stronger adhesion with the matrix due to the presence of high density of surface functional groups. However, the studies on epoxy–HBP blends are limited to difunctional epoxies. To our knowledge, no studies have been reported on the blends of HBP and trifunctional epoxy.

We have examined in this work the suitability of HBP materials for toughening a trifunctional epoxy. The present article discusses the studies on the curing of an epoxy-functionalized HBP and a trifunctional epoxy blends and characterizes the cured networks with respect to their thermomechanical properties and morphology.

EXPERIMENTAL

Materials

The epoxy resin used was a triglycidyl p-amino phenol (TGAP), Araldite MY 0510 of Ciba Speciality Chemicals, with a molecular weight of 277 mol g⁻¹ and 9.41 mmol epoxide per gram of resin. The curing agent, Ethacure 100, of Albemarle, 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 Figure 1.

The epoxy functional dendritic hyperbranched polymer (Boltorn E1) with an epoxy equivalent weight of ~ 875 g eq⁻¹ and a molecular weight of ~ 10,500 g mol⁻¹ was supplied by Perstorp Speciality Chemicals (Sweden). Boltorn E1 consists of a highly branched aliphatic polyester backbone with in average 11 reactive epoxy groups per molecule. A schematic representation of HBP is shown in Figure 1.

Preparation of TGAP–HBP blends and curing

The HBP-filled samples were prepared by dissolving the HBP in the TGAP at 100°C with thorough stirring. The modified resin was mixed with a stoichiometric amount (41:100 w/w) of DETDA by continuously stirring the mixture for 5 min at 100°C. The mixtures were cured in an aluminum mold at 120°C for 3 h after having been degassed under vacuum for 10 min. Blends containing 0–20% (by weight) HBP were made. Afterward, the samples were postcured at 200°C for 2 h, allowing them to cool gradually to room temperature. Thus, in this work, TGAP–HBP blend means the blend includes stoichiometric amount of DETDA.

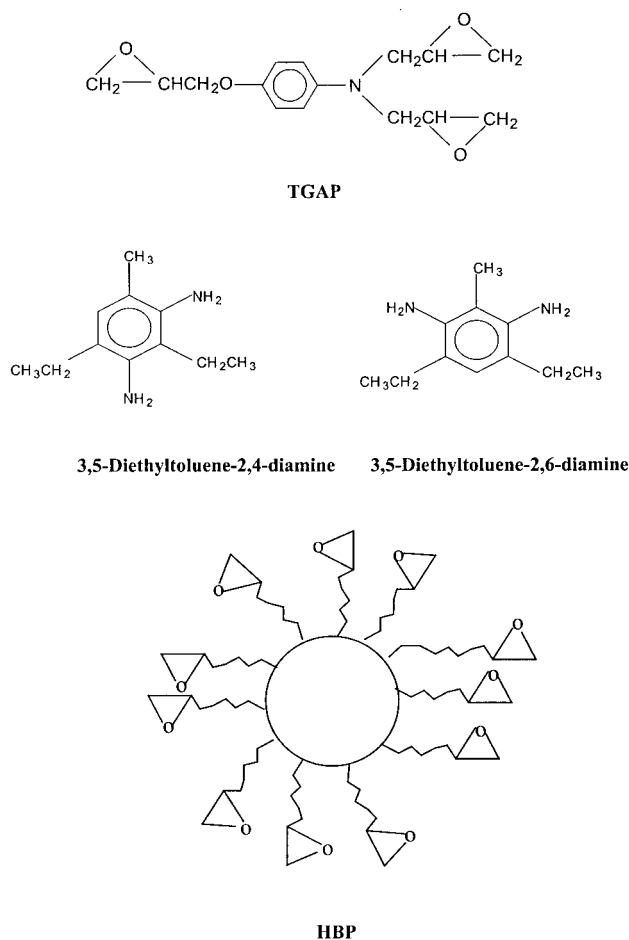


Figure 1 Chemical structures of TGAP, DETDA, and HBP.

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 of 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. The T_g s of cured networks were determined from the same instrument.

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.

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⁻¹ heating rate using liquid nitrogen for subambient region. Dynamic moduli and loss factors were obtained

by dual-cantilever mode for the sample of size 45 mm × 10 mm × 2 mm.

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 17.5 psi.

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 4 cm in diameter. The sample size used for the test was 80 mm × 80 mm × 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⁻¹. 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.

RESULTS AND DISCUSSION

The rheological measurements carried out as detailed above permitted the characterization of gelation and vitrification process during cure. The change in tanδ of TGAP-HBP blend containing 10% HBP at various frequency during curing at 140°C is shown in Figure 2.

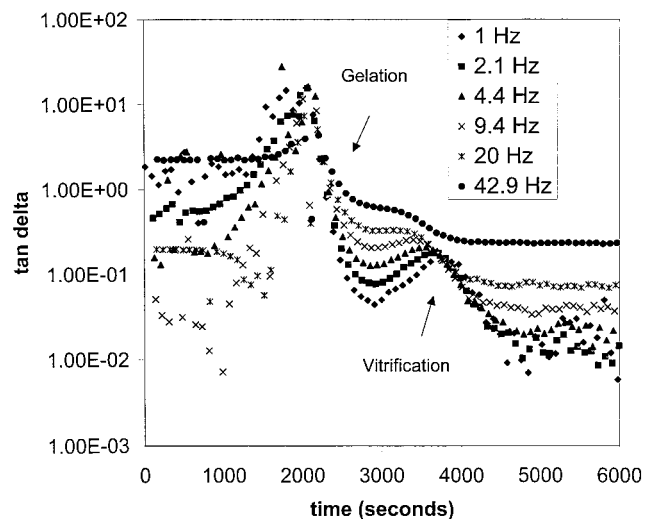


Figure 2 Loss tangent vs. time plots for 10% HBP-containing TGAP-HBP blend at 140°C using various frequencies (1–43 Hz).

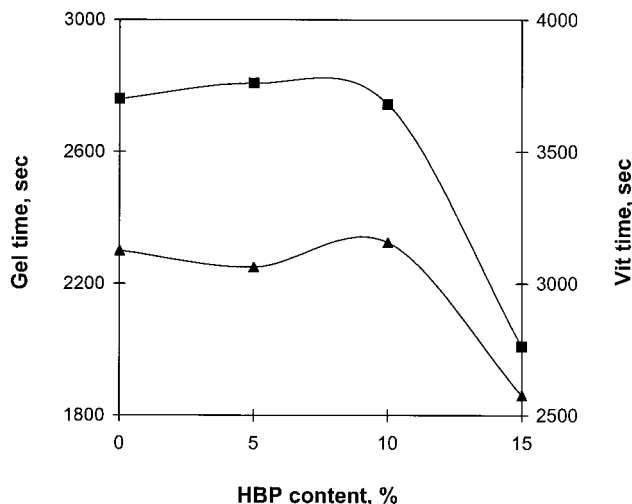


Figure 3 Effect of HBP modification on the gel time and vitrification time of TGAP-HBP lends.

Gelation, which is defined as the point where loss tangent becomes independent of frequency,²⁴ can be seen to occur at the point where the curves first intersect after the initial peak. Another peak has appeared soon after the first intersection. This can be attributed to vitrification. This observation is different from that reported earlier using diglycidyl ether of bisphenol A (DGEBA)-DETDA system,²³ where only single peak was identified. Varley et al.²⁵ have reported similar observation during flexural braint analysis of thermoplastic modified epoxy system.

The effects of HBP modification on gel time and vitrification time are shown in Figure 3. It is clear that up to 10% of HBP, there is no effect on gelation and vitrification. This indicates that the phase separation process does not affect the thermoset cure. The gel time decreases at higher concentration of HBP due to dilution effect caused by the dissolved HBP.

TGAP and TGAP-HBP blends having different concentration of HBP were mixed with a stoichiometric amount of DETDA and subjected to DSC scans up to 300°C. DSC traces for the unmodified TGAP, HBP, and the blends are shown in Figure 4. The heat evolved during the curing reaction is often used to estimate the reaction rate and conversion.^{26,27} 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.²⁸ It is clear from the figure that HBP shows peak exotherm at a higher temperature (257°C) compared to TGAP (196°C), which indicates that epoxy groups of HBP are less reactive than that of TGAP. However, the blends show peak exotherm at the same temperature (196°C) as neat TGAP. This behavior is different from that observed in case of other liquid rubbers such as carboxyl-terminated poly (2-ethyl

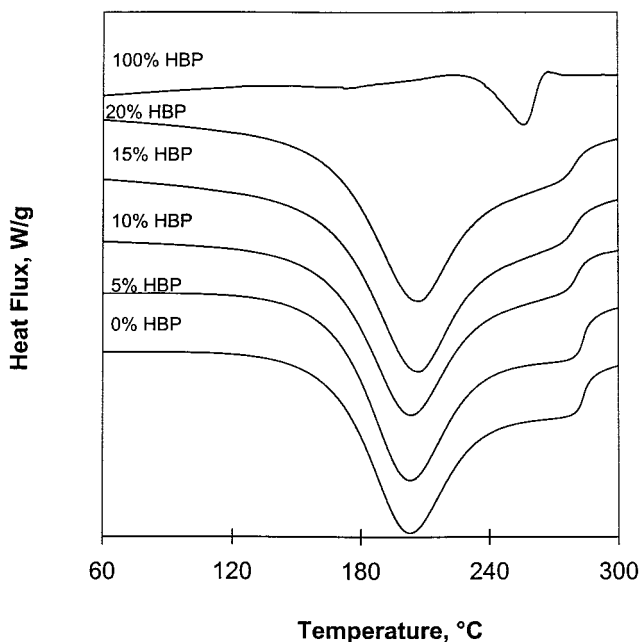


Figure 4 DSC scans of TGAP-HBP blends containing 0%, 5%, 10%, 15%, and 20% HBP.

hexyl acrylate) (CTPEHA), where significant increase in T_{peak} was observed.^{20,29} In those cases, 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. The viscosity of HBP at 25°C (15 Pa s) is about three times lower compared to the CTPEHA (42 Pa s) reported earlier.^{20,29}

The enthalpy of reaction (ΔH_p) determined from the DSC curves and the theoretical values calculated from rule of mixture for various blends are presented in Figure 5. The close agreement of experimental results with the theoretical values indicated that HBP did not modify apparently the mechanism of epoxy matrix polymerization. The ΔH_p of pure TGAP-DETDA was found to be 620 J g⁻¹, which corresponds to 111.6 kJ mol⁻¹ (expressed in terms of mass of epoxide/amine mixture), which compares reasonably well with the literature reports that have found the values to lie between 103 and 110 kJ mol⁻¹.³⁰

After curing in DSC cell up to 300°C, each sample was allowed to cool down to room temperature and subjected to a second run. From the DSC trace, obtained in the second run, the T_g was determined. The modified networks cured using the cure schedule mentioned above were also analyzed by DSC for determination of T_g . The results were reported in Figure 6. It is clear from the figure that up to 10% of HBP, there is no change in T_g of the cured TGAP and a slight reduction in T_g was observed at higher concentrations. This indirectly implies that there is phase separation.

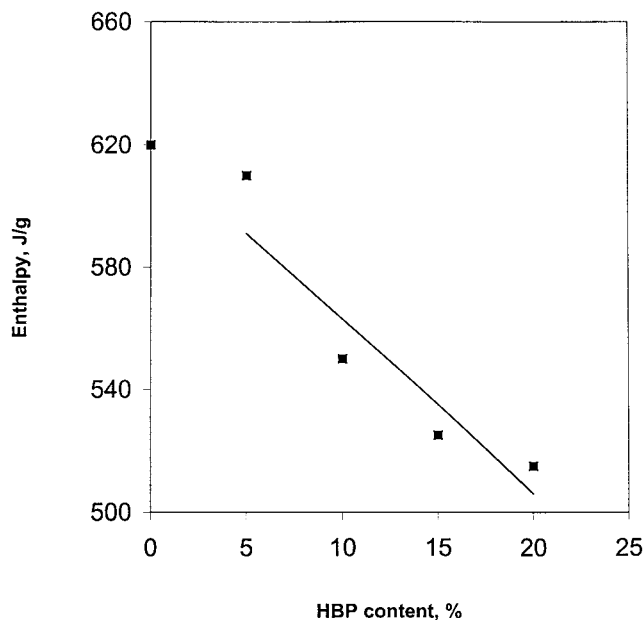


Figure 5 Plot of enthalpy of curing vs. HBP content: experimental value (box) and (line). Theoretical value calculated from rule of mixture.

The slight reduction in T_g in the cases of the modified networks having higher concentrations of HBP (15%, 20%) can be attributed to the dissolution of certain amount of HBP in the epoxy matrix. The amount of dissolved HBP increases with increase in the concentration of the added HBP causing more and more reduction of TGAP T_g . A modest reduction of epoxy T_g is reported by others using CTBN³¹ and acrylate-based liquid rubber³² as toughening agents.

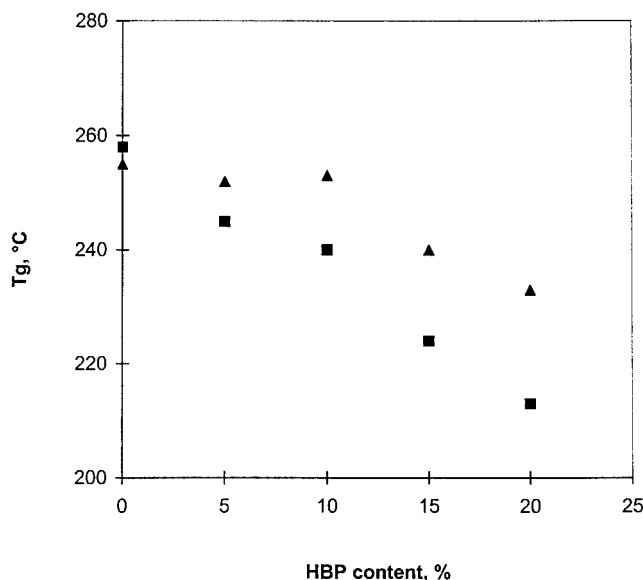


Figure 6 T_g s of TGAP-HBP blends: (triangle) values for cured networks, polymerized using cure schedule; (square) values correspond to second run after a dynamic scan up to 300°C.

The clearly lower T_g s observed for dynamically scanned HBP-modified mixtures with respect to those polymerized with the cure schedule outline the importance of the control of cure temperature. Thus, the difference shown in T_g values for the mixtures cured by the above-referred ways (Fig. 6) would be connected to distinct levels of segregation of HBP through phase separation during the dynamic curing and during polymerization with the cure schedule. In the case of dynamic scan, the rubber does not get sufficient time to undergo phase separation completely.

The rubber T_g is not discernible in DSC. However, it is detected clearly by DMA, which is related to mechanical relaxation. The advantage of DMA over many other methods in the determination of T_g is that it is sensitive enough to detect even weak transitions. In fact, all the properties measured by this technique generate strong well-defined signals that are not clouded by background noise or other interferences.

Loss tangent vs. temperature plot of cured TGAP, HBP, and TGAP-HBP blend containing 10% HBP are shown in Figure 7. The TGAP-HBP blend sample shows two peaks: one at high temperature (ca. 284°C) for TGAP, and another at low temperature (ca. -35°C) for HBP. There is no change in TGAP T_g as a result of modification. This is the unique property of the HBP-modified epoxy compared to the other liquid rubber such as CTBN and epoxy blends, where significant depression in epoxy T_g was observed due to incom-

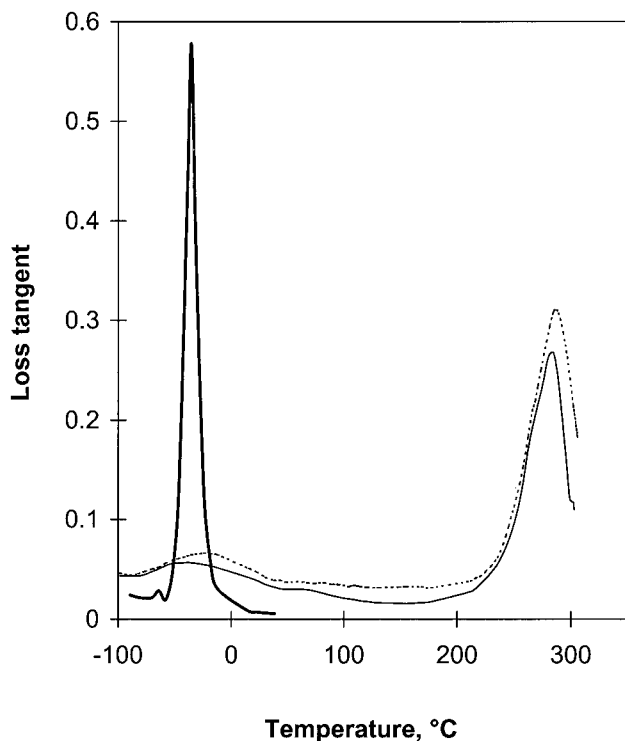


Figure 7 Loss tangent vs. temperature plots of TGAP (thin line), HBP (thick line), and 10% HBP containing blend (dashed line).

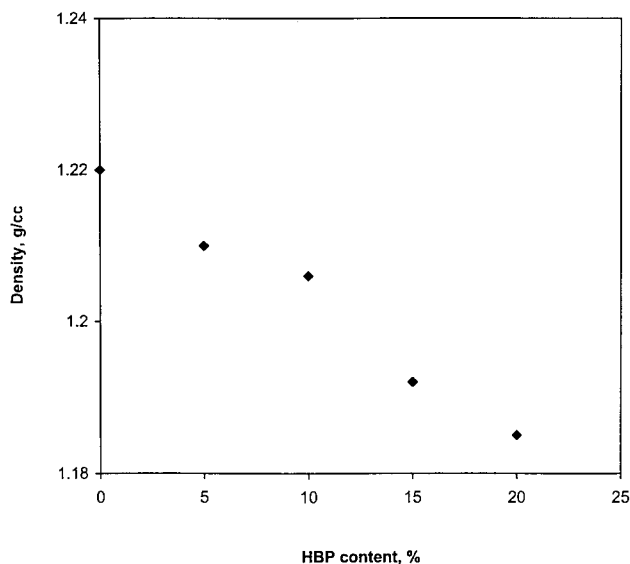


Figure 8 Effect of HBP modification on density of the blends.

plete phase separation.¹³⁻¹⁵ Recently, there have been reports^{33,34} that considerable improvement in toughness could 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.²⁹

The density of the cured blends were determined and reported in Figure 8. It was found that the densities of the blends are lower than that of the TGAP. This is expected as the density of the cured HBP (1.06 g cc^{-1}) is lower than the density of the cured TGAP (1.22 g cc^{-1}).

The effect of HBP modification on impact strength of the blends is shown in Figure 9. It can be seen that TGAP-HBP blends show higher impact strength. The impact strength rapidly increases up to 10% HBP concentration and remains almost unchanged up to 20%. The impact strength of the blend containing 10% HBP is 1.3 kJ m^{-1} , which is about 100% higher compared to that observed in the case of unmodified TGAP network (0.7 kJ m^{-1}). This behavior is different from that reported earlier using acrylate-based liquid rubber where the impact energy passes through a maximum at about 10% of modifier concentration.^{20,32,33} The impact behavior can be explained in terms of the results of SEM analysis of the fracture surfaces, which will be discussed shortly.

The SEM photographs for the fracture surfaces of cured TGAP and 10% and 20% HBP-containing blends are shown in Figure 10. From Figure 10(a), one can see the smooth glassy fractured surface with crack in different planes in case of unmodified TGAP. This indicates brittle fracture of the unmodified TGAP, 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 TGAP matrix. In the case of 10% HBP-modified sample, the HBP particles are uniformly distributed throughout the matrix. The particles have dimension in the range of 3–4 μm and their distribution is bimodal in nature. Figure 10(b) shows the broken HBP particles and a stress-whitened zone. Stress whitening is due to the scattering of visible light from the layer of the scattering centers, which in this case are voids.^{34,35} The generation of the voids is due to the cavitation of rubbery HBP particles, which is the most important energy-dissipating mechanism in the case of rubber-toughened epoxies.^{36,37} Uniform distribution of the rubber particles throughout the matrix is very important for toughening, as it allows the yielding process to operate throughout the matrix.^{35–38} This explains why the HBP-modified TGAP exhibits higher impact strength in comparison to the unmodified TGAP. In case of the mixture having 20% HBP, the particles are found to be bigger compared to that observed in 10% HBP-containing blend. However, the uniform particle distribution is retained without any agglomeration, unlike in the linear liquid rubber-modified epoxy network, where agglomeration was observed beyond 10% rubber concentration.^{20,27,31} That is why no reduction in impact strength was observed up to 20% of HBP concentration.

CONCLUSIONS

Epoxy-functionalized HBP cures at a slower rate compared to TGAP. Addition of HBP into TGAP has little

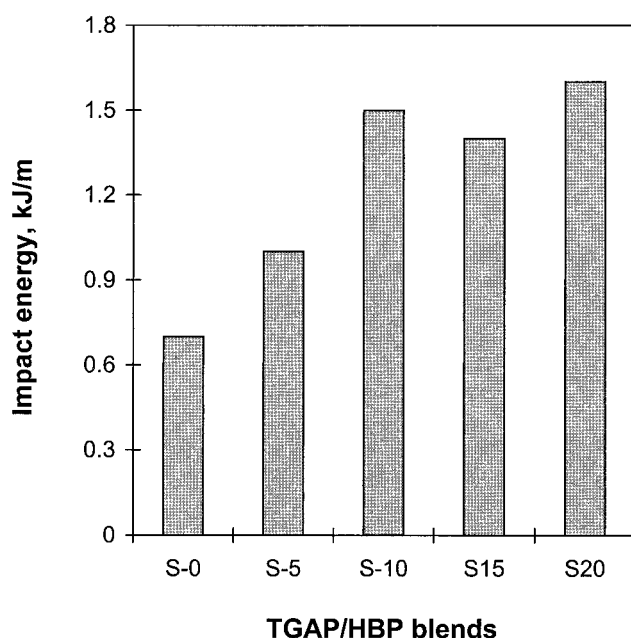


Figure 9 Effect of HBP loading on the impact strength of DGEBA–HBP blends.

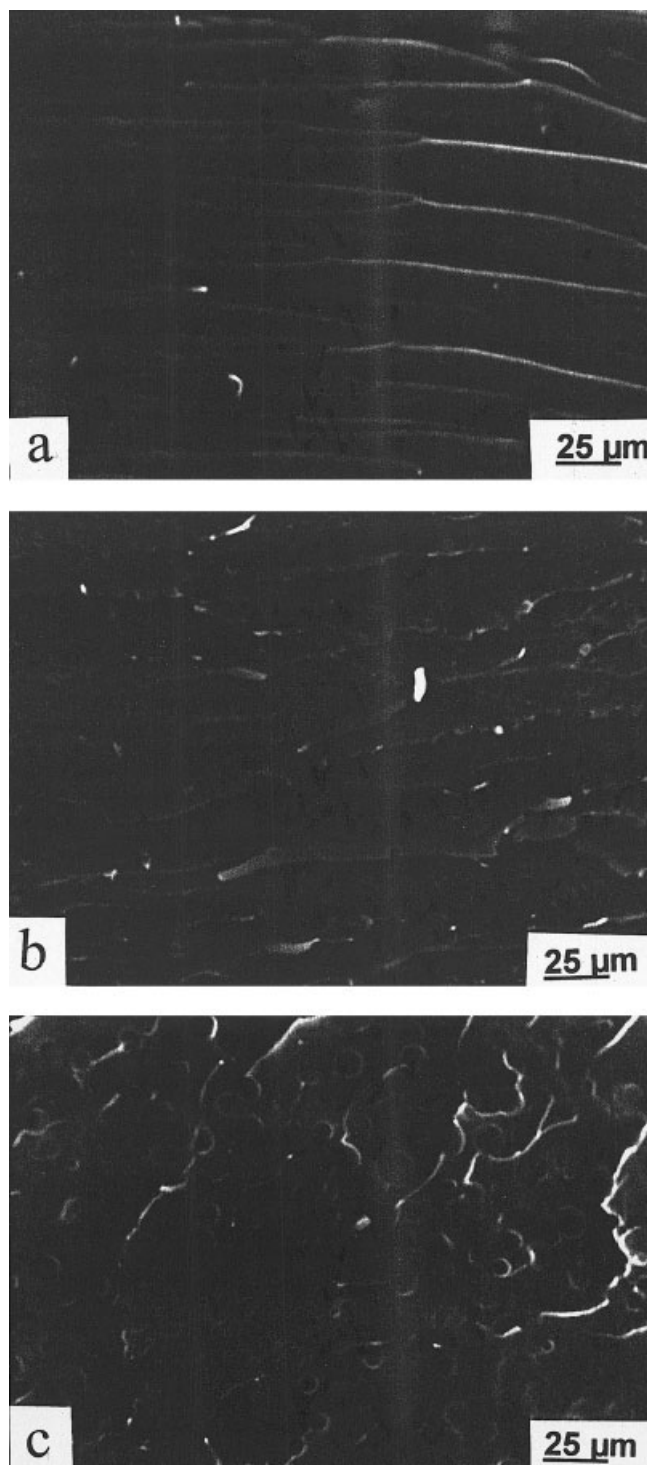


Figure 10 SEM photographs for fracture surfaces: (a) neat TGAP, (b) 10% HBP-containing blend, (c) 20% HBP-containing blend.

effect on gel time and vitrification time up to 10% of HBP and slight reduction was observed at higher concentration. The HBP is miscible with TGAP at 120°C and results in almost complete phase separation after curing up to 10% of HBP concentration. The amount of dissolved HBP increases with further increase in HBP

content. Impact strength of the modified networks increases strongly up to 10% of HBP concentration and increases only marginally thereafter up to 20% HBP.

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