ELSEVIER

Polymer 42 (2001) 8833–8839

polymer

www.elsevier.com/locate/polymer

Thermomechanical properties and morphology of blends of a hydroxy-functionalized hyperbranched polymer and epoxy resin

D. Ratna[a,*], G.P. Simon[b]

[a]Naval Materials Research Laboratory, Shil-Badlapur Road, Chickloli, Anandanagar P.O., Addl Ambernath (E), Thane 421 506, Maharashtra, India
[b]Department of Materials Engineering, Monash University, Clayton, Vic. 3800, Australia

Received 4 September 2000; received in revised form 2 February 2001; accepted 8 May 2001

Abstract

Curing as well as the phase separation behavior of blends of a hydroxy-functionalized hyperbranched polymer (HBP) and epoxy resin have been studied by several techniques. The HBP strongly enhance the curing rate due to the catalytic effect of hydroxy groups. The phase separation has been investigated for various HBP contents and as a function of cure conditions used as well. The thermal and dynamic viscoelastic behavior of the blends have been examined and compared to the unmodified epoxy matrix. Finally, impact properties have been discussed in terms of the morphological behavior for an epoxy matrix modified with various amounts of HBP. © 2001 Published by Elsevier Science Ltd.

Keywords: Hyperbranched polymer; Epoxy; Toughness

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 more 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 to distinguish them from their more perfect counterpart. These are being produced in sufficient quantities to allow investigation of their utility in conventional engineering applications. Due to compact three-dimensional structure of dendritic polymers, these molecules mimic the hydrodynamic volume of spheres in solution or melt 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 has been shown to exhibit melt and solution viscosities that are an order of magnitude lower than linear analogs 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 resin [12,13]. The present paper discusses the studies on curing of a hydroxy-functionalized HBP and epoxy blends and characterization of the modified cured networks with respect to their thermomechanical properties and morphology.

2. Experimental

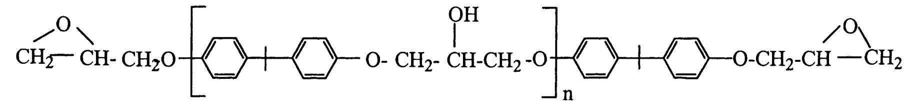
2.1. Materials

The epoxy resin used was a liquid diglycidyl ether of bisphenol A (DGEBA) (DER 331 Dow epoxy resin)

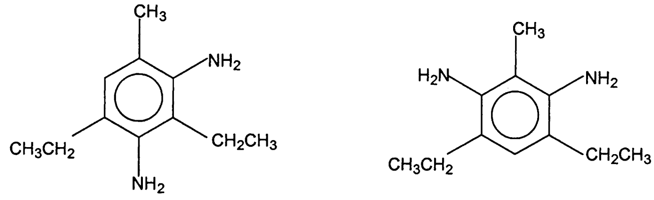
---

* Corresponding author. Tel.: +91-251-681950.
E-mail address: ratna@ncml.ernet.in (D. Ratna).

PII: S0032-3861(01)00341-X

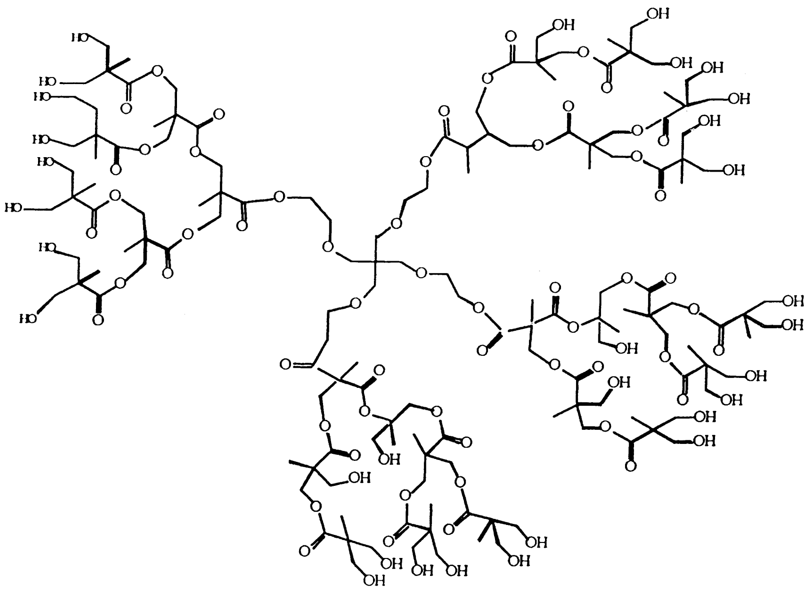


Diglycidyl ether of bisphenol-A



3,5-Diethyltoluene-2,4-diamine

3,5-Diethyltoluene-2,6-diamine



HBP

Fig. 1. Chemical structures of epoxy resin, curing agent and HBP.

containing 5.27 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, hardener are shown in Fig. 1.

The dendritic polymer used was a fifth-generation (G-5) Perstorp hyperbranched polyols. These are developmental materials based on polyester chemistry and have on average 128 –OH end groups per molecule and theoretical molecular weight and polydispersity index of 14,000 g mol^{-1} and 2.0, respectively. The HBP molecules are synthesized from a pentaerythritol ($C_5H_{12}O_4$) core and multiple 2,2-diethylol propionic acid ($C_5H_{10}O_4$) chain extenders or repeat units. The developmental resins are available in moderate quantities under the trade name of Boltorn. A schematic illustration of three generation HBP is shown in Fig. 1.

2.2. Preparation of DGEBA/HBP blends and curing

The HBP was dissolved in acetone and the solution was added to DGEBA. The mixture was stirred and heated until a homogeneous solution was observed. The acetone was then removed under reduced pressure. The temperature was raised to 100°C and stoichiometric amount of DETDA (23 g per 100 g of DGEBA) was added under stirring condition. Once a homogeneous solution was obtained, the solution was degassed for 10 min and poured into a preheated mold and cured for 4 h at 100°C. The blends containing 0–20% (by weight) of HBP were made. In order to study the effect of cure temperature on the properties modified networks, the 10% HBP containing mixture was cured at different temperatures (120, 140, 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.

Differential scanning calorimeter (DSC) dynamic mode measurements were carried out with a Perkin–Elmer DSC-7 (in a dry nitrogen atmosphere and calibrated with an Indium standard) working with 8–10 mg samples (uncured) in aluminum pans. Runnings at constant heating rate of 10°C $\min^{-1}$ were performed in a temperature range 50–300°C for every mixture. The heat evolved during the reaction of the mixture has been directly determined by integration of the exothermic peaks. The glass transition temperature, T_g was taken in a second scan as the beginning point of the endothermic shift in the DSC scan. The T_gs of DGEBA/HBP blends polymerized using the cure schedule were also determined from the same instrument.

The viscosity was measured using a Haake Rotoviscometer (Haake RV III) at a shear rate range of 0–100 s^{-1} using an MV III head having a clearance of 0.96 mm between the concentric cylinders of the viscometer.

2.3. Characterization of cured networks

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 of the cured blends were measured using a Micromeritics pycnometer. Approximately, 4 g of resin known to four decimal places 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 strength 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 determinations on four samples.

A low voltage scanning electron microscope (SEM), (JEOL, 840 JSM) 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 photomicrographs were obtained under conventional secondary electron imaging conditions with an accelerating voltage of 20 kV.

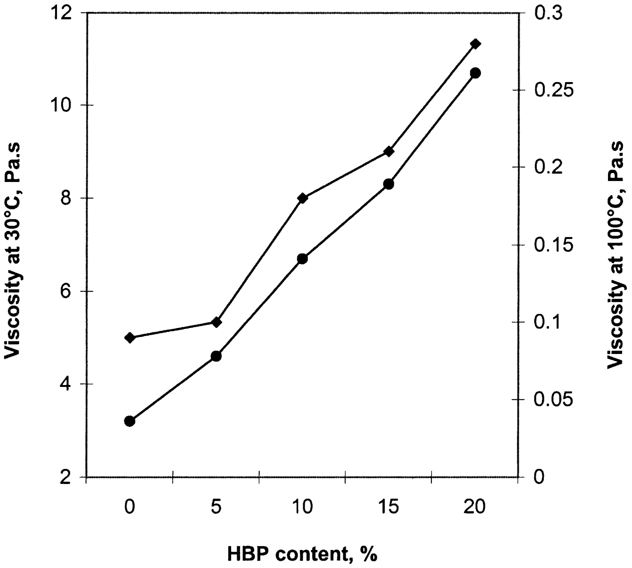


Fig. 2. Effect of HBP loading on viscosity of blends at 30°C (–◆–) and at 100°C (–●–).

3. Results and discussions

The viscosities of DGEBA/HBP blends (without DETDA) at 30 and 100°C are shown in Fig. 2. It is clear from the figure that viscosity increases with increase in HBP. However, the increase in viscosity is much lower than that reported in case blends of DGEBA and linear thermoplastic or rubber [14–16].

All the DGEBA/HBP blends were subjected to DSC scan up to 300°C and these are shown in Fig. 3. From the DSC plots, the enthalpy of reaction (ΔH_p) and the temperature corresponds to the peak exotherm were determined and presented in Fig. 4. The heat evolved during the curing reaction is often used to estimate the reaction rate and conversion [17,18]. Although the residual heat of reaction

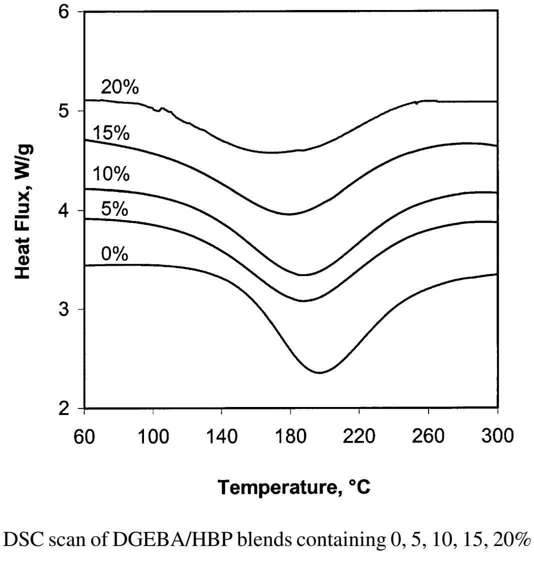


Fig. 3. DSC scan of DGEBA/HBP blends containing 0, 5, 10, 15, 20% HBP.

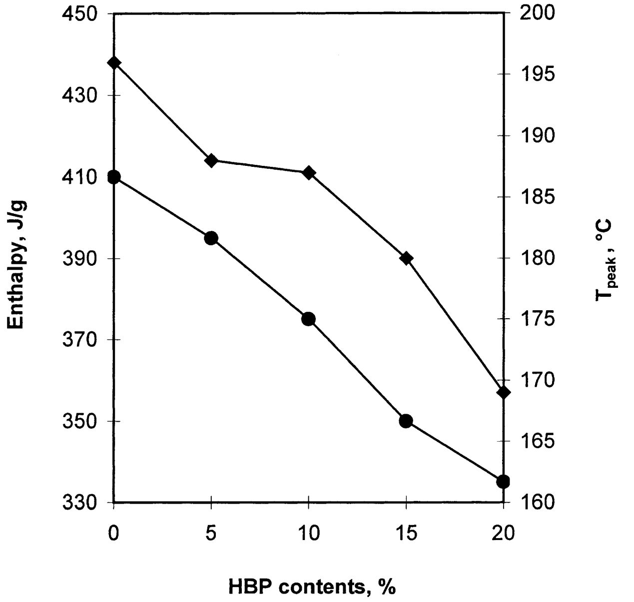


Fig. 4. Effect HBP loading on enthalpy (–◆–) and T_{peak} (–●–).

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 characteristics [18]. It is clear from the figure that the peak exotherm is shifted to lower temperatures with increasing concentration of HPB due to enhanced reaction rate. This can be interpreted in terms of intermolecular transition state — according to this mechanism [19] strong hydrogen-bonding species, such as acid and alcohols, stabilize the transition state encourages the nucleophilic attack of amine. This behavior is different from that observed in case of other linear liquid rubbers or thermoplastics and DGEBA blends where significant increase in T_{peak} was observed [20,21]. In that case, the delay has been attributed to the viscosity effect, which retards the movement of reactive molecules. Nevertheless, the HBP apparently did not modify the mechanism of epoxy matrix polymerization as the total enthalpy as shown in Fig. 4, decreased proportionately to the rubber amount in the mixture. The ΔH_p of unfilled epoxy/DETDA was found to be 101 kJ mol^{-1} (expressed in terms of mass of epoxide/amine mixture), which compares with 91.4 kJ mol^{-1} found by Barton [18] for DGEBA/diaminodipheny methane (DDM) system and values ranging from 100 to 118 kJ mol^{-1} for phenyl glycidyl ether type epoxy–amine reactions tabulated in a review by Rozenberg [22].

Though not shown, it was clear from DSC analysis that the HBP does not react with DGEBA up to 250°C. Hence, there is no possibility of formation of chemical bonding between HBP and DGEBA matrix cured at 200°C. However, because of the presence of large number of surface hydroxy groups, the HBP is expected to from strong hydrogen bond with DGEBA matrix, which is necessary for effective toughening [23,24].

After curing in DSC cell up to 300°C, each sample was allowed to cool down to room temperature and subjected to 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 in the experimental, were also analyzed by DSC. The results were reported in Table 1. It is well established that shifts in glass transition temperatures (T_g) of component polymers can be used to evaluate miscibility and immiscibility in polymer blends [25,26]. The thermal properties of the DGEBA/HBP blends showed behavior typical of an immiscible, uncompatibilized blend, in which no significant deviation from the pure component values for either T_g exhibited by the blends. The T_gs of DGEBA and HBP are 200 and 45°C, respectively. The blends containing up to 10% of HBP show T_gs similar to the neat DGEBA and a slight reduction in T_g was observed in case of higher concentration, i.e. 15 and 20%. This is the strong point of these blends compared to the DGEBA/liquid rubber blends where a significant depression in epoxy T_g was observed [27–29]. The expected HBP T_g, in the blends, could not be discernible by DSC. However, it was clearly identified by DMTA analysis, which will be discussed shortly.

The clearly lower T_gs observed for dynamically scanned DGEBA/HBP blends with respect to those polymerized with the cure schedule outlines the importance of control of cure temperature. Thus, the difference shown in T_g values quoted in Table 1 for the blends cured by the above referred ways would be connected to distinct levels of segregation through phase separation during the dynamic curing, and during polymerization with the cure schedule. In the case of dynamic scan, the HBP does not get sufficient time to undergo phase separation completely. However, difference in T_g observed in this case is much lower than reported earlier [30] using acrylate based liquid rubber. This is expected as the T_g of the acrylate based rubber (−50°C) was much lower than that of the HBP (45°C).

The loss tangent vs. temperature plots are shown in Figs. 5 and 6. As 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 molecular slips resulting in viscous flow is low. Also, above

Table 1
Thermal properties of DGEBA/HBP blends

	DGEBA/HBP					
	100/0	95/5	90/10	85/15	100/20	0/100
T_g (°C)[a]	200	198	198	193	188	45
T_g (°C)[b]	200	191	183	177	170	–

[a] Values determined from DSC analysis of the cured networks, polymerized using cure schedule.

[b] Values correspond to second run after a dynamic scan up to 300°C.

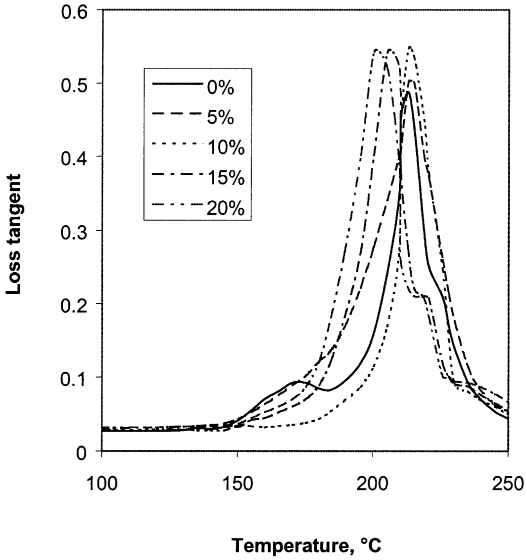


Fig. 5. Loss tangent vs. temperature plots of DGEBA/HBP blends 0, 5, 10, 15, 20% HBP.

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.

All the blends show two relaxation peaks; one at high temperature (at ca. 215°C) due to glass transition of DGEBA and other at ca. 60°C, which is attributed to the HBP. This indicates that there is phase separation between HBP and DGEBA. The height of the low temperature relaxation peak gradually increases with increasing concentration of HBP. Similar observation was reported by Lee et al. [31] for carboxyl-terminated copolymer of butadiene and acrylonitrile (CTBN)/DGEBA systems. The decrease in tan δ peak temperature (T_g) at higher concentration of HBP is attributed to the dissolution of some HBP into the DGEBA matrix.

The effect of cure temperature on the T_g of the DGEBA/HBP blend containing 10% of HBP is shown in Fig. 7. The T_g of the modified networks slowly decreases with increase in cure temperature. This indicates that as the cure temperature increases, the amount of HBP, which remains dissolved in the epoxy matrix increases. The reduction in T_g with cure temperature is lower compared to that observed in DGEBA/rubber blends [30] due to higher T_g of HBP.

The density of the blends were also determined and reported in Fig. 8. It is found that the densities of the blends are higher than that of the DGEBA. This is in contrary to the observation in case of linear polymer and epoxy blend where the density was reported [32,33] to be reduced. The density of HBP (1.28 g cm^{-3}) is higher than that of DGEBA (1.17 g cm^{-3}). This is attributed to the compact structure of the HBP.

The effect of HBP modification on the impact strength of modified networks is reported in Fig. 9. The HBP addition only led to a small improvement in impact strength up to 10% of HBP concentration and significant improvement in impact strength was found at higher concentration. The blend containing 20% HBP shows impact strength (1.5 kJ m^{-1}), which is approximately twice the value for neat DGEBA (0.7 kJ m^{-1}). The impact behavior of these blends is different from that reported in DGEBA/rubber blend, which shows a maxima at about 10–15% of HBP concentration [27–30].

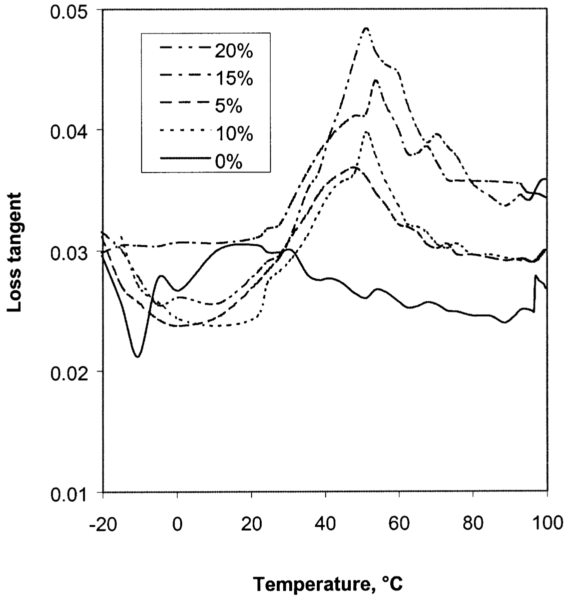


Fig. 6. Loss tangent vs. temperature plots showing the HBP relaxation.

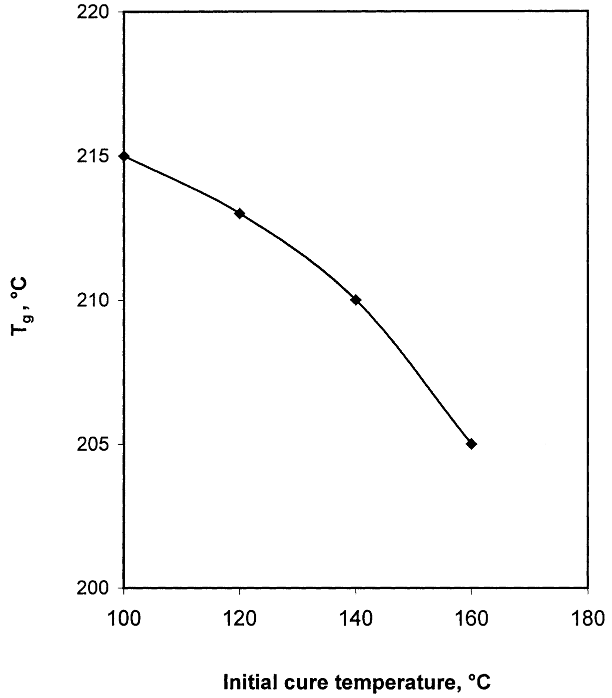


Fig. 7. Effect of cure temperature on T_g of cured blends.

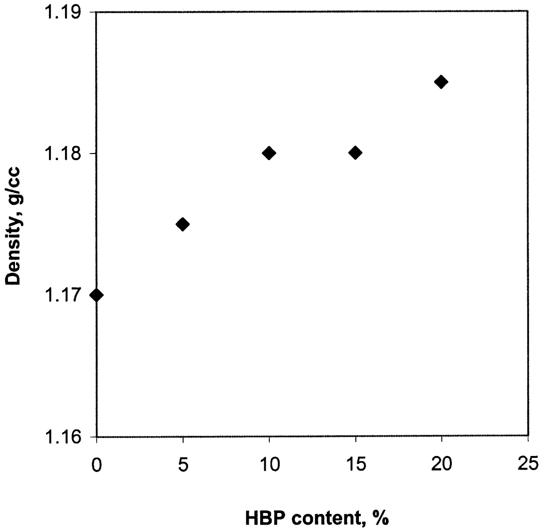


Fig. 8. Plot of density vs. HBP content of DGEBA/HBP blends.

The impact behavior of the modified epoxy networks can be explained in terms of morphology observed by SEM. The SEM microphotographs for unmodified DGEBA cured with DETDA at 100°C and the blends containing 10 and 20% HBP are shown in Fig. 10. From the photograph (Fig. 10a), one can see the smooth glassy fractured surface with crack in different planes in case of unmodified DGEBA. This indicates brittle fracture of the unmodified epoxy network, 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 epoxy matrix. Up to 10% HBP, the morphology was discrete without any connectivity between the particles. As the HBP concentration increases, the connectivity between the dispersed HBP particles increases and the morphology transformed to near cocontinuous at higher concentrations (Fig. 10c). Similar observation was reported by others using linear thermoplastic [20,34].

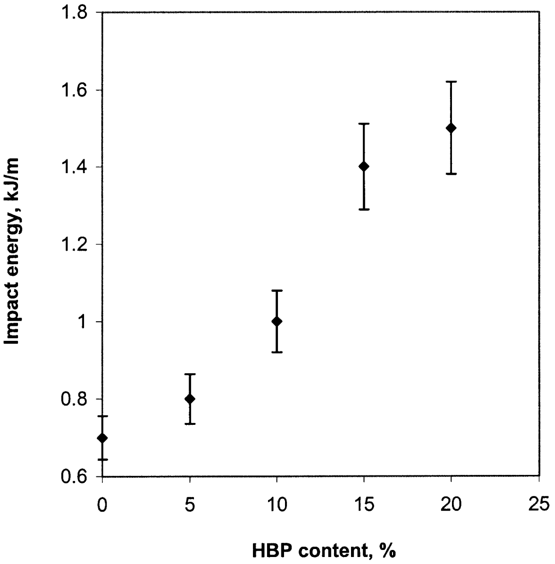


Fig. 9. Effect of HBP loading on the impact strength of DGEBA/HBP blends.

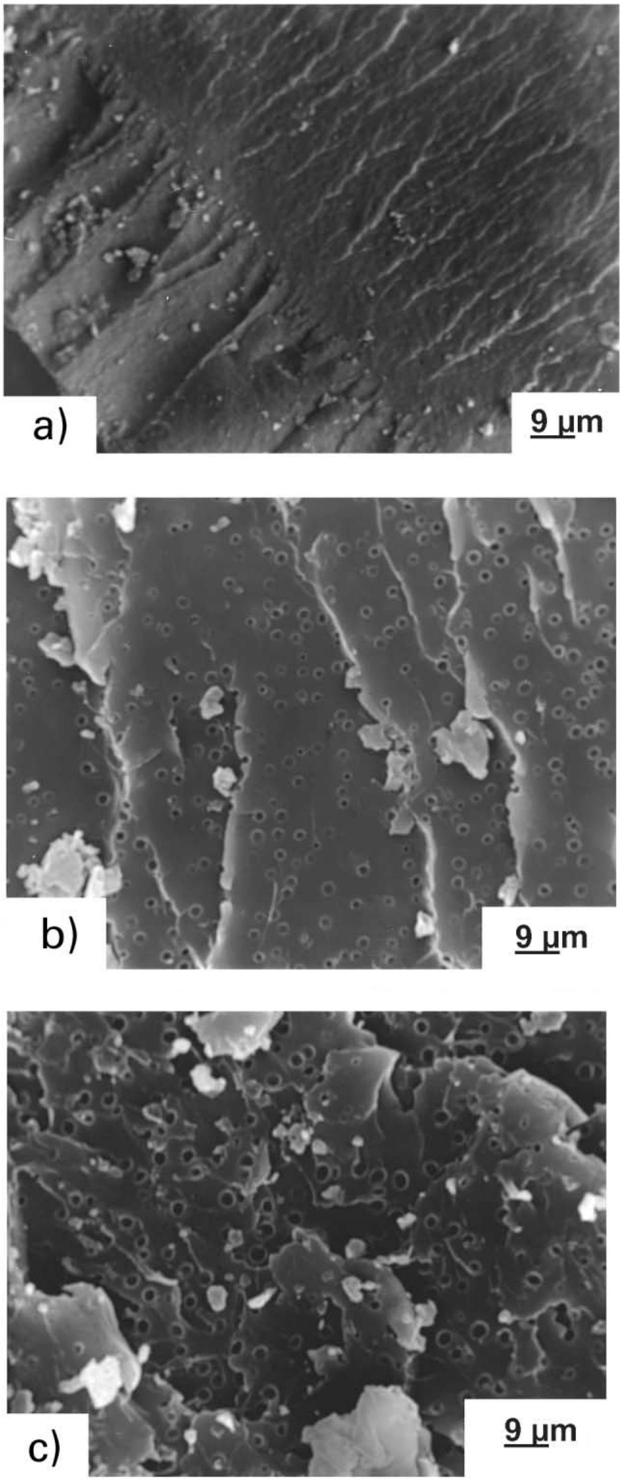


Fig. 10. SEM photographs for fracture surfaces of: (a) neat DGEBA cured with DETDA at 100°C; (b) 10% HBP containing blend; (c) 20% HBP containing blend.

The morphology of the 10% HBP containing blends cured at 140 and 160°C is shown in Fig. 11. The small

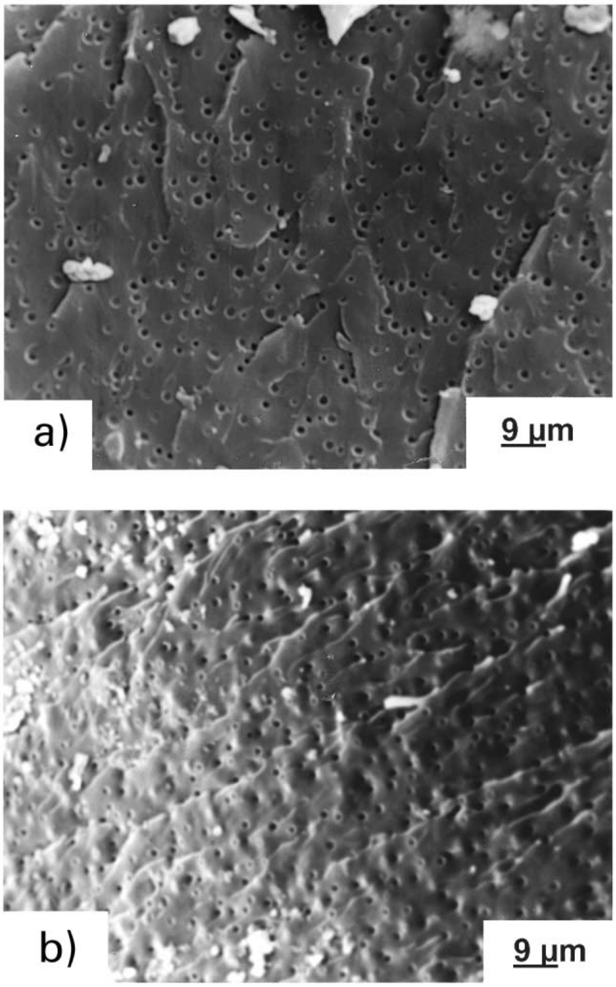


Fig. 11. SEM photographs for the fracture surfaces of 10% HBP containing blend (a) cured at 140°C and (b) cured at 160°C.

size of the discrete particles with unimodal distribution increased with increase in the curing temperature. This seems to indicate that phase separation started in the gelation region, so the particle growth was not possible because of the diffusional restriction exiting after gelation of the epoxy matrix. Similar observation was reported by Kim et al. [35] in case of CTBN modified epoxy and Moller and co-workers [36] in case of thermoplastic toughened epoxy.

4. Conclusion

HBP accelerates the DGEBA–amine curing reaction due to catalytic effect of hydroxy group. The blends exhibit behavior like a typical incompatible blend when cured at 100°C. The compatibility increases with increase in cure temperature. The improvement in impact strength was more observed at higher concentration (>10%). SEM analysis indicates transformation of morphology from discrete to bicontinuous as concentration of HBP increases.

Acknowledgements

Dr D. Ratna is grateful to Department of Science and Technology for a BOYSCAST fellowship.

References

[1] Desimone JM. Science 1995;269:1060.
[2] Morikawa A, Kakimoto M, Imai Y. Macromolecules 1991;24:3469.
[3] Jansen JF. US Patent 5 788 989; 1997.
[4] Milco LA. US Patent 5 731 095; 1998.
[5] Breton MP. US Patent 5 266 106; 1998.
[6] Winnik FM. US Patent 5 098 475; 1998.
[7] Billmeyer FW. Textbook of polymer science. New York: Wiley, 1984.
[8] Uppuluri S, Kenneth SE, Tamalia DA, Dvornic P. Macromolecules 1998;31:4498.
[9] Massa D, Shriner KA. Macromolecules 1995;28:3241.
[10] Carr PL, Davies GR, Feast WJ, Stainton NM, Ward IM. Polymer 1996;37:2395.
[11] Khadir A, Gauthier M. ANTEC'97 Proceedings, 1997. p. 3732.
[12] Boogh L, Bo P, Manson EJ-A. Polymer 1999;40:2249.
[13] Wu H, Xu J, Liu Y, Heiden PA. J Appl Polym Sci 1999;72:151.
[14] Hourston DJ, Lane JM. Polymer 1992;33:1379.
[15] Ratna D, Banthia AK. Polym Int 2000;49:281.
[16] Ratna D, Banthia AK, Deb PC. J Appl Polym Sci 2000;78:716.
[17] Horie K, Hiura H, Sawada M, Mita I, Kambe H. J Polym Sci A-1 1970;8:1357.
[18] Barton JM. J Macromol Sci, Chem A 1974;8:25.
[19] Smith IT. Polymer 1961;2:95.
[20] Martinez I, Martin MD, Eceiza A, Oyanguren P, Mondragon I. Polymer 2000;41:1027.
[21] Verchere D, Sautereau H, Pascault JP, Moschair SM, Riccardi CC, Williams RJJ. J Appl Polym Sci 1991;42:467.
[22] Rozenberg BA. Adv Polym Sci 1985;75:113.
[23] Manternal S, Pascault JP, Sautereau H. In: Riew CK, editor. Rubber toughened plastics, Advances in chemistry series 222. Washington, DC: American Chemical Society, 1989. p. 193.
[24] Ratna D, Banthia AK. J Adhes Sci Technol 2000;14:15.
[25] Paul DR. Polymer blends. New York: Academic Press, 1978.
[26] Paul DR. Encyclopedia of polymer science and engineering, vol. 12. New York: Wiley, 1986. p. 399.
[27] Chen D, Pascault JP, Sautereau H. Poym Int 1993;32:361.
[28] Achary PS, Gouri C, Ramamurty R. J Appl Polym Sci 1991;42:743.
[29] Achary PS, Latha PB, Ramaswamy R. J Appl Polym Sci 1990;41:151.
[30] Ratna D, Simon GP. Polymer 2001;42:4209.
[31] Lee WH, Hodd KA, Wright WW. In: Riew CK, editor. Rubber toughened plastics, Advances in chemistry series 222. Washington, DC: American Chemical Society, 1989. p. 263.
[32] Verley RJ, Hawthorne DG, Hodgkin, Simon GP. J Polym Sci, Part B: Polym Phys 1997;35:153.
[33] Chang TD, Brittain JO. Polym Engng Sci 1992;22:1228.
[34] Mimura K, Ito H, Fujioka H. Polymer 2000;41:4451.
[35] Kim DS, Kim SC. Polym Engng Sci 1994;34:1598.
[36] De Graaf LA, Hempenious MA, Moller M. Polym Prepr 1995;36:787.