Epoxy and Hyperbranched Polymer Blends: Morphology and Free Volume

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ABSTRACT: In this work, the phase separation of an epoxy-functionalized hyperbranched polymer (HBP) in a blend with a conventional epoxy resin is examined. Morphology development with the advancement of curing reaction was investigated by hot-stage polarized optical microscope, where it was found that HBP is miscible in epoxy resin solvent at 120°C and undergoes phase separation during the curing reaction, leading to a two-phase microstructure which maintains a dispersed morphology up to 20 wt % HBP. The degree of phase separation and morphology were also investigated using differential scanning calorimetry, and the resultant microstructure was confirmed by atomic force microscopy. The epoxy/HBP blends were characterized by positron annihilation lifetime spectroscopy for their free volume characteristics where behavior typical of miscible blends was seen, likely due to chemical bonding between the two phases. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 117: 557–564, 2010

Key words: epoxy; free volume; morphology; blend

INTRODUCTION

Dendritic polymers are a new class of three-dimensional, synthetic molecule produced by multiplicative growth from small molecules that incorporates repetitive branching sequences to create an unusual architecture. Over the last few years, synthesis of a large number of dendritic polymers has been reported in open literature[1,2] and in patents.[3,4] They have potential applications in a variety of fields such as biomedical, catalysis, commercial coatings, electrical materials, and so on. However, actual exploitation of dendritic polymer technology is still in its infancy, especially in applications where large amounts are required. Synthetic difficulties such as retaining solubility of the growing polymer and maintaining regularity and order in the structure makes the technology extremely costly.

Recently, dendritic polymers have been produced by a new, lower cost hybrid synthetic process that generates very highly branched, polydisperse molecules. These materials are called dendritic hyperbranched polymers to distinguish them from more perfect monodisperse materials.[5,6] They are being produced in sufficient quantities to allow investigation of their utility in conventional engineering applications. Because of the comparatively compact, three-dimensional structure of such dendritic polymers, these molecules mimic the hydrodynamic volume of spheres in solution or in melt and flow easily past each other under applied stress. This results in a low melt viscosity, even at high molecular weights, due to the lack of restrictive interchain entanglements.[7] Dendritic polymers have 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 surface functional 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 additives that could act simultaneously as toughening agents.[10,11] The epoxy/hyperbranched polymer (HBP) blends have been investigated by Boogh and coworkers[12–14] and by us[15–17] and show considerable promise for high performance, structural applications.

Positron annihilation lifetime spectroscopy (PALS) is an important tool for determination of structural parameters of polymeric systems.[18,19] The technique allows the determination of parameters such as ortho-positronium life time and formation probability, which are associated with free volume dimension and concentration, respectively. Patricio et al.[20] investigated free volume properties of polyurethane (PU)/poly (methyl methacrylate) (PMMA)

interpenetrating networks and reported a decrease in free volume when PMMA concentration increases. Wang et al.[21] used PALS technique to study free volume hole properties of three different PUs and disclosed that fractional free volume (f_v) decreases with increasing hard segment content in the PU system. The decrease in free volume is associated with intermolecular interaction and enhanced molecular packing even in the phase separated blends.[22,23] Similar observations have been reported for copolymers and nanocomposites.

We have already reported the thermomechanical properties of epoxy/HBP blends as functions of HBP concentration and cure temperature.[16,17] In this article, studies on reaction-induced phase separation of epoxy/HBP system using polarized optical microscope, phase morphology and resultant free volume properties of the blends will be presented. We believe this is the first report of free volume results using positron annihilation studies for epoxy/HBP blend systems, indeed there has been little positron studies of dendritic polymer systems.

EXPERIMENTAL METHODS

Materials

The difunctional 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 multifunctional epoxy used was tetraglycidyl diaminodiphenyl methane (TGDDM) (Araldite MY-720 of Ciba Speciality Chemicals). The curing agent, Ethacure 100, of Albemarle Corp. is a mixture of the two diethyltoluene diamine (DETDA) isomers (74–80% 2,4 isomer and 18–24% 2,6 isomer). The chemical structure of DGEBA, TGDDM, and DETDA are shown in Figure 1.

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

Preparation of epoxy/HBP blends and curing

The DGEBA/HBP and TGDDM/HBP blends were prepared by dissolving HBP in the epoxy at 100°C, while thoroughly stirring. The modified resin was mixed with a stoichiometric amount 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, and blends containing 0–20% (by weight) HBP were made. The epoxy/HBP mixtures were then cured at 140°C for 2 h, 160°C for 3 h, and finally postcured at 200°C for 2 h. After this, the samples were cooled to room temperature, and the final materials were used for atomic force microscopy (AFM) and free volume studies.

Characterization

The phase separation process of epoxy/HBP blend was investigated by a hot-stage optical microscope (Leika, Germany). The epoxy/HBP blend (100/15) was mixed with a stoichiometric amount of hardener and a drop of resin mixture placed between two transparent films heated to 120°C. The photographs of the resin film were taken at different time intervals, all photographs taken at 500 times magnification.

Atomic force microscopy images were taken using a digital AFM instrument Nanoscope IIIA operated in tapping mode, which gives both height and phase images. A standard AFM probe was used for the measurement. The cantilever shape was rectangular with a length of 10–15 μm and a silicon pyramidal tip with a spring constant of $\sim$0.05 Nm^{-1}. The samples were fractured and the fractured surfaces were analyzed without any surface treatment.

Differential scanning calorimeter (DSC) measurements were carried out on the cured resins with a Perkin Elmer DSC-7, USA (in a dry nitrogen atmosphere and calibrated with an Indium standard) using 8–10 mg sample 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.

PALS was applied to determine free volume properties of the cured blends. A detailed background on the theory and technique of PALS can be found elsewhere.[24,25] PALS is a family of three experimental techniques, namely, positron annihilation lifetime (PAL), Doppler broadening spectroscopy (DBS), and angular correlation of annihilation radiation (ACAR). The DBS gives only qualitative information about the momentum density, which can be probed quantitatively by ACAR. Briefly the antiparticle of an electron, the positron, is used to investigate the free volume between polymer chains. The birth of the positron can be detected by the release of a gamma ray of characteristic energy, which occurs $\sim$ 3 ps after positron emission when the ^{22}Na decays to ^{22}Ne. Once inside the polymer material, the positron forms one of the two possible types of positroniums, an ortho-positronium or a para-positronium, obtained by pairing with an electron abstracted from the polymer environment. The decay spectra are obtained by the "death" event of the positron, para-positronium, or orthopositronium species. By appropriate curve fitting, the lifetimes of the various
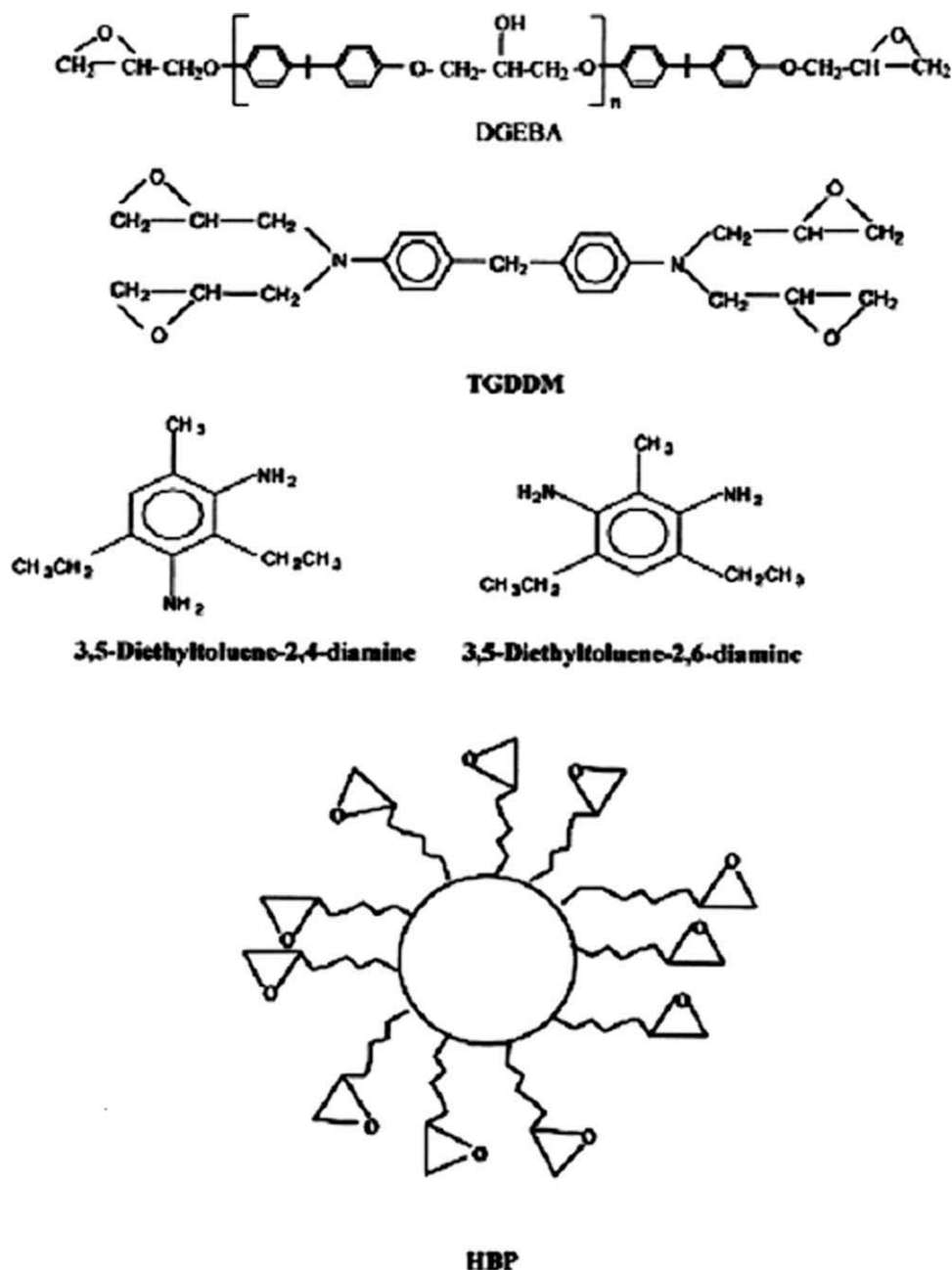
Figure 1 Chemical structures of epoxy resin, hardener, and HBP.

species and their intensity can be determined. The lifetime of orthopositronium (τ_3) and intensity (I_3) have been found to be indicative of the free volume in polymer system, since this is where the relevant species become localized. τ_3 is related to the size of the free volume sites and I_3 to their number concentration.

The PALS unit used was an automated EG & G Ortec fast-fast coincidence system with a [22]Na radioactive source and a resolution of 270 ps measured on [60]Co. A spot source (1 mm diameter) of [22]Na was obtained from dropping a [22]NaCl solution onto very thin titanium foils, with a resultant activity of 40 μCi.

The positron source is sandwiched between two pieces of samples. The thickness of the sample is kept at 1–2 mm, which is adequate to absorb more than 90% of positrons emitted. The experiments were run in a thermally stable environment at 22° C. No source correction was required, confirmed by testing of highly annealed and polished aluminum, which results in the well known, single decay process. Two scintillators detect γ-rays at energy of 0.511 Mev (stop) and 1.28 Mev (start) for timing lifetimes. The spectra were stored and analyzed using computers. Each spectrum consists of 30,000 peak counts and the data were fitted using PFPOSFIT program.[26]

(a) **at room temperature**

(b) **Heating**

(c) **at 120° C- 0 time**

(d) **at 120° C- 20 min**
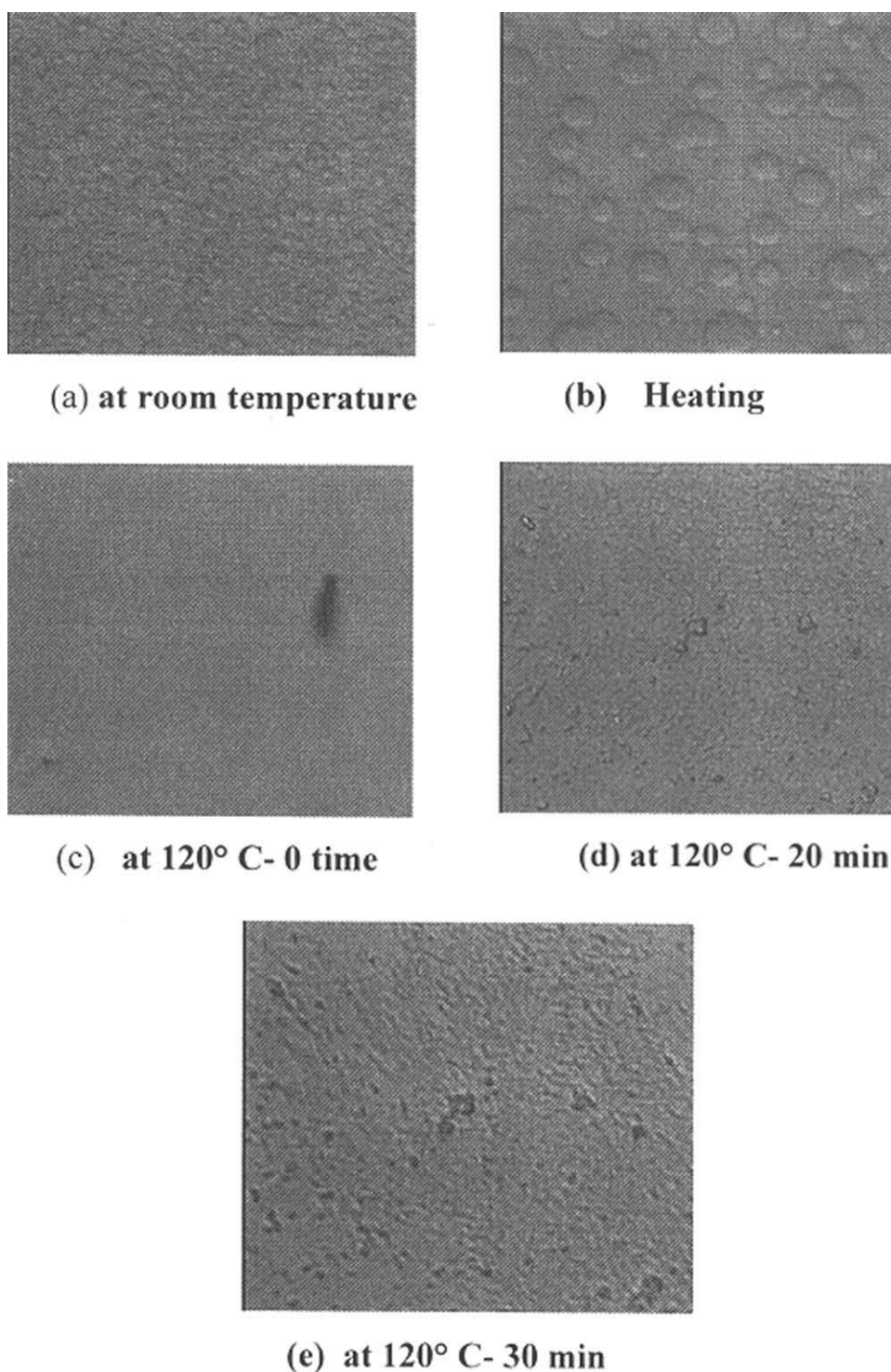
(e) **at 120° C- 30 min**

Figure 2 Optical micrographs of epoxy/HBP/DETDA mixture: (a) at room temperature, (b) heating, (c) at 120°C in zero time, (d) at 120°C after 20 min, (e) at 120°C after 30 min.

RESULTS AND DISCUSSION

Reaction-induced phase separation

The epoxy/HBP blend containing 15 wt % HBP with a stoichiometric amount of DETDA was subjected to hot-stage optical microscopic analysis. The polarized optical microscope photographs for the blend at room temperature (RT), at 120°C in various time are shown in Figure 2. It is clear that at RT, HBP is not miscible with epoxy as can be seen in Figure 2(a) where HBP droplets can be observed in the liquid epoxy medium. When the temperature was increased to 120°C, the system became homogeneous [Fig. 2(c)], indicating miscibility of HBP with epoxy
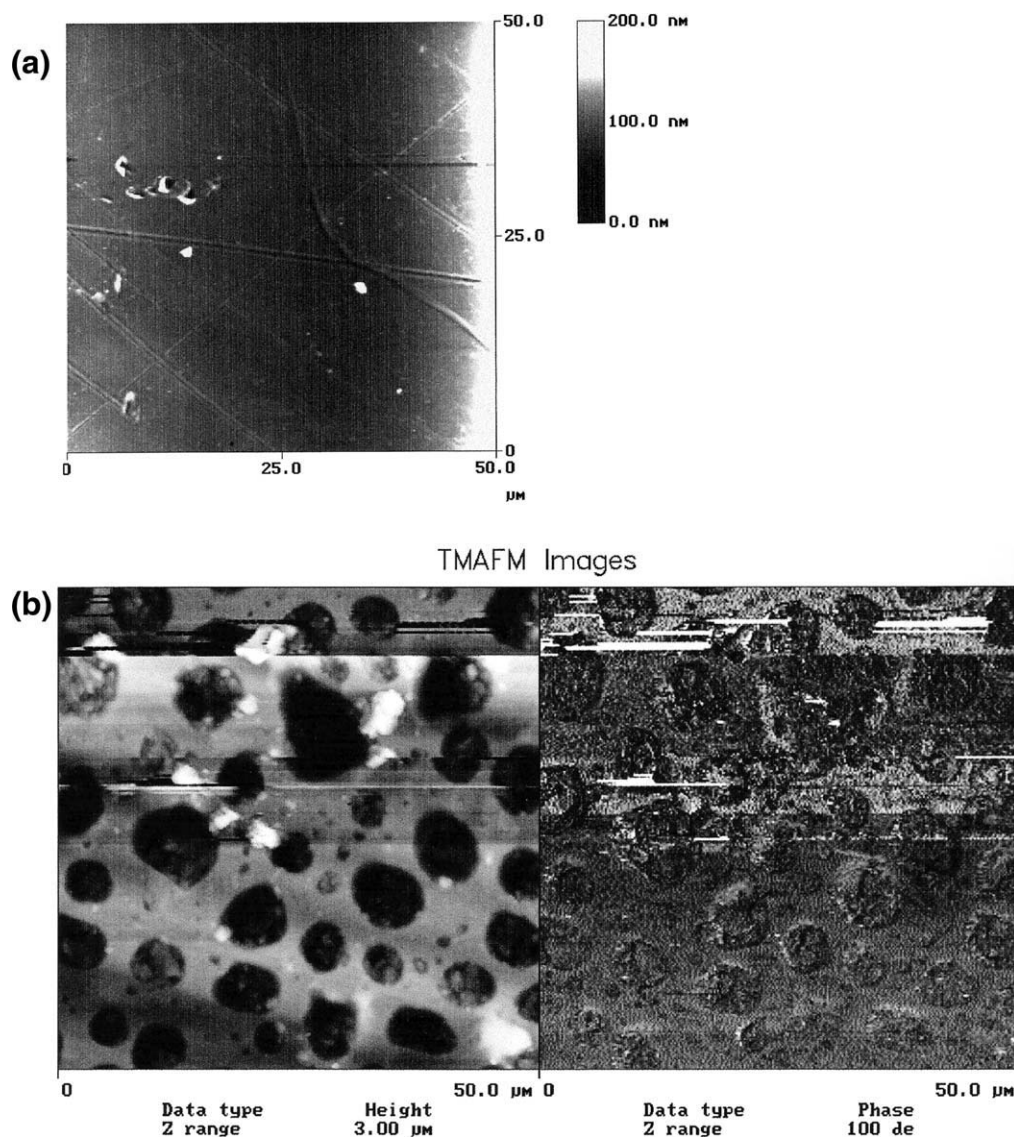
Figure 3 Atomic force micrographs of (a) cured epoxy network (b) epoxy/HBP blend.

at this point. However, when the sample is kept at 120°C, the resin begins to react and crosslink and phase separation slowly occurs [Fig. 2(d,e)]. This can be explained in terms of combinatorial entropy, as follows.

Combining the Flory-Huggins equation and the Hildebrand equation,[27] the free energy of mixing can be expressed as:

$$\Delta G_m / V = \phi_e \; \phi_r (\delta_e - \delta_r)^2 \\ + RT(\phi_e/V_e. \ln \phi_e + \phi_r/V_r. \ln \phi_r) \quad (1)$$

where ϕ_e, ϕ_r are the volume fractions and δ_e, δ_r are the solubility parameters, and V_e and V_r are the molar volume of epoxy and rubber, respectively. Since ϕ_e, ϕ_r are fractions (<1), the second term (change in entropy) is always negative. Thus, the increase in temperature favors the mixing, by

increasing the second term, resulting in HBP solubility with epoxy above 100°C. As the epoxy resin cures, the value of V_e and V_r increases, resulting in a decrease in the second term. At a critical conversion, ΔG_m becomes positive and phase separation occurs. However, if $(\delta_e - \delta_r)$ (the difference between the solubility parameters of the epoxy and the liquid rubber) is very small, then the change in entropy due to the curing reaction will not result in a positive free energy change of mixing (ΔG_m) before gelation.[28] Thus, a moderately slow curing rate is necessary to ensure complete phase separation.

Morphology

SEM studies of epoxy/HBP blends indicated a two-phase microstructure with globular morphology, as reported earlier.[17,29] It was found that the
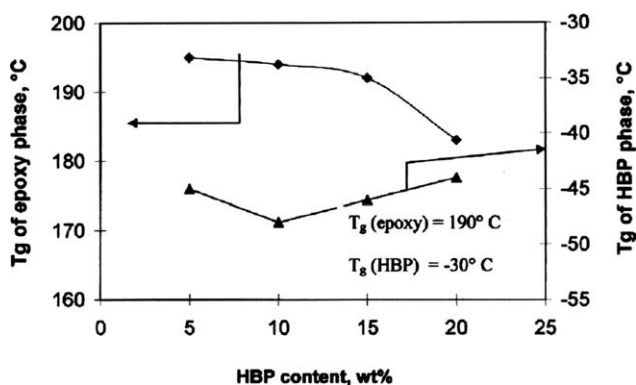
Figure 4 T_g data of both the epoxy phase and the HBP phase for DGEBA/HBP blends as a function of HBP concentration.

morphology is maintained with particle size increasing with an increase in HBP concentration, up to 20 wt %, unlike linear liquid rubber where agglomeration starts above 15 wt % concentration of rubber. It has been observed from previous studies that optimum mechanical properties were obtained at 15 wt % of HBP concentration without a significant sacrifice in T_g. Beyond 15 wt % of HBP concentration, the modulus decreases significantly. That is why we have selected this particular blend to study the microstructure using AFM. The AFM micrographs (both in height mode and phase mode) of epoxy and epoxy/HBP blend (100/15) are shown in Figure 3. They clearly indicate a two-phase morphology, where the micron-size, spherical HBP particles are dispersed in continuous epoxy matrix and the particle distribution was found to be bimodal in nature. DSC analysis shows two T_gs; one for epoxy network and other is due to phase separated HBP. The T_g values for both the components of DGEBA/HBP blends as a function of HBP concentration are shown in Figure 4.

As HBP cures along with the epoxy in the presence of amine hardener through the surface functional groups, it is expected that the T_g of phase-separated HBP will be higher than the T_g of separately cured HBP. However, it was observed that the T_g of phase-separated HBP (–45°C) is lower than the HBP (separately cured) (–30°C). This can be explained by considering thermal shrinkage stress.[30] Triaxial thermal shrinkage stress develops in the dispersed domain phase on cooling through epoxy T_g because the coefficient of thermal expansion of rubbery state is larger than that of the glassy state. The triaxial stress increases the free volume of the rubbery HBP particles and depresses the T_g of the precipitated HBP. It was also observed that there is no change in epoxy T_g due to the addition of HBP up to a concentration of 10 wt % and the epoxy T_g decreases with further increase in HBP concentration. The depression of epoxy T_g in such rubber-toughened epoxy system arises due to incomplete phase separation and dissolution of some amount of rubber in epoxy matrix.[31,32] This indicates that HBP phase separated completely when added in low concentration (up to 10 wt % concentration) and for the formulation with higher concentration of HBP, some amount of HBP remains dissolved in the epoxy matrix leading to the depression of epoxy T_g.

Free volume properties

The basic PALS data acquired in these systems, i.e., orthopositronium (o-Ps) life time (τ_3), gives an indication of the average free volume size and the intensity (I_3), number concentration of free volume sites of DGEBA and TGDDM epoxy networks and their blends with HBP, and is shown in Table I. All the samples were cured at the same temperature as free volume properties are known to be sensitive to curing temperature.[33,34] The τ_3 value of DGEBA is found to be greater than that of TGDDM. However, the number concentration of free volume is higher for TGDDM compared to DGEBA. This indicates that DGEBA has larger free volume sites due to its lower crosslink density but TGDDM has a greater

TABLE I
Basic PALS Data for DGEB/HBP and TGDDM/HBP Blends

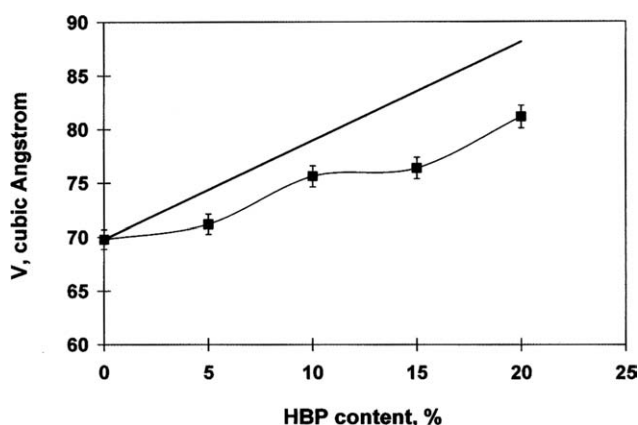| Resin	HBP content (%)	τ_3 (ns)	I_3 (%)	R (Å)
DGEBA	0	1.76 ± 0.01	25.63 ± 0.03	2.62 ± 0.01
TGDDM	0	1.69 ± 0.01	27.24 ± 0.22	2.55 ± 0.02
HBP	0	2.63 ± 0.02	27.84 ± 0.24	3.37 ± 0.02
DGEBA	5	1.79 ± 0.03	25.47 ± 0.22	2.65 ± 0.03
DGEBA	10	1.82 ± 0.02	24.55 ± 0.32	2.68 ± 0.02
DGEBA	15	1.85 ± 0.03	24.55 ± 0.25	2.71 ± 0.02
DGEBA	20	1.89 ± 0.03	24.53 ± 0.27	2.75 ± 0.03
TGDDM	5	1.71 ± 0.02	26.76 ± 0.30	2.57 ± 0.01
TGDDM	10	1.76 ± 0.02	26.14 ± 0.35	2.62 ± 0.02
TGDDM	15	1.77 ± 0.02	26.43 ± 0.22	2.63 ± 0.02
TGDDM	20	1.82 ± 0.02	25.62 ± 0.18	2.68 ± 0.02
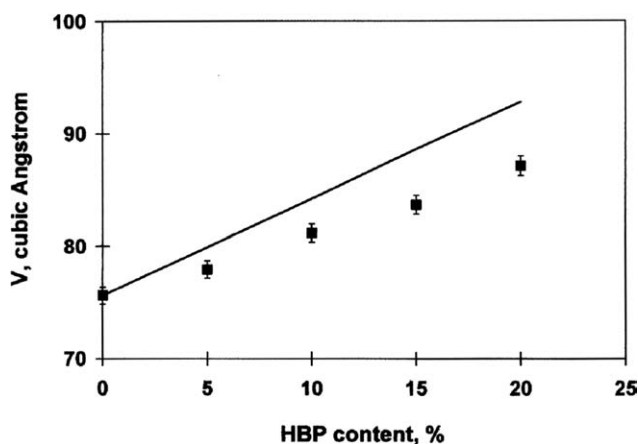
Figure 5 Hole volume, *V,* vs. HBP content plot of DGEBA/HBP blends: solid line indicates values according to the rule-of-mixtures.

number of free volume sites of smaller size. This variation is likely due to the fact that TGDDM being tetrafunctional results in a much tighter network compared to DGEBA, which is bifunctional. The HBP homopolymer was found to contain free volume sites much greater in terms of both size and number compared to the glassy epoxies, due to it being in the rubbery state.[35]
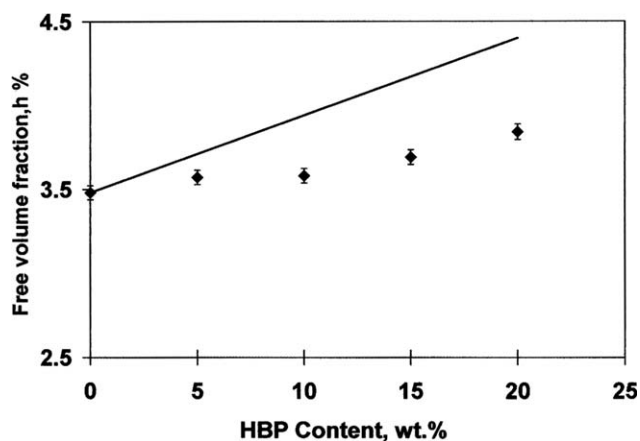
Assuming that free volume sites are of spherical shape, it is possible to estimate the magnitude of free volume radius from the semi-empirical equation[36]

$$\tau_3 = \left[1 - \frac{R}{R_0} + \frac{1}{2\pi}\sin\left(\frac{2\pi R}{R_0}\right)\right]^{-1} \quad (2)$$

with τ_3 being the orthopositronium life time (ns), R the radius (Å), and $R_0 = R + \Delta R$ where ΔR is the fitted empirical electron layer and equals 1.66 Å. The average free volume of a hole, *V,* can be calculated as:

Figure 7 Free volume fraction, *h,* vs. HBP content plot of DGEBA/HBP blends: solid line according to the rule-of-mixtures.

$$V = \frac{4}{3}\pi R^3 \quad (3)$$

and the total fractional free volume h, expressed as a percentage can be determined from[37]

$$h = CV I_3 \quad (4)$$

where V is in Å, calculated from eq. (2), I_3 is in %, and C is a constant empirically determined from comparison with pressure-volume-temperature data and is often found to be equal to 1.8×10^{-3} in polymers.[36,37]

V values as a function of HBP concentration for DGEBA/HBP and TGDDM/HBP blends are shown in Figures 5 and 6, respectively. The corresponding h values as a function of HBP concentration for DGEBA/HBP and TGDDM/HBP blends are presented in Figures 7 and 8, respectively. The neat HBP has higher values of V and h compared to the resin system and thus according to the rule of

Figure 6 Hole volume, *V,* vs. HBP content plot of TGDDM/HBP blends: solid line according to the rule-of-mixtures.
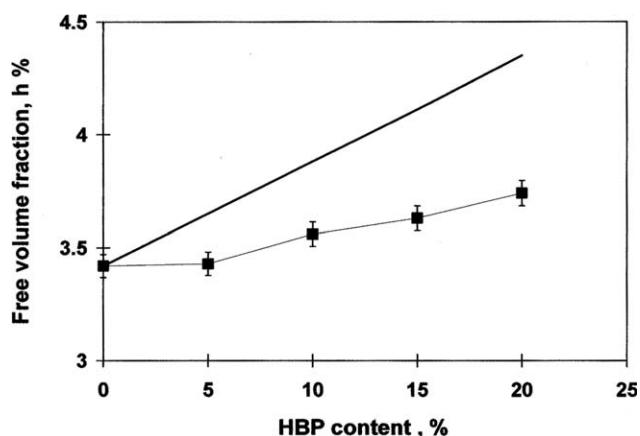
Figure 8 Free volume fraction, *h,* vs. HBP content plot of TGDDM/HBP blends: solid line according to the rule-of-mixtures.

mixture all the blends could be expected to show larger free volume sizes than the corresponding resin systems which is found to be the case. The free volume increases gradually with increase in HBP concentration up to 20 wt % and shows a negative deviation from the rule of mixtures. MacKinnon et al.[38] have shown the change in free volume as the morphology changes from particulate to cocontinuous to phase inverted microstructure. Epoxy/HBP blends are much simpler in the concentration range shown here, showing a consistent globular particulate morphology up to 20 wt % of HBP concentration. We have observed in the data in our work, a negative deviation of V and h from linearity for both the systems. It is also found that deviation increases with increase in HBP concentration. Generally, miscible blends[18,39,40] show a negative deviation in τ_3 (or V) as a function of concentration due to the closer packing of the miscible chains. Likewise, immiscible blends have been reported to demonstrate a positive deviation due to excess free volume at the interface.[19,41] It should be noted that most of the work reported to date has been with miscible and immiscible blends involving thermoplastics. The systems in this study involve a thermoset and a phase-separating rubbery phase, which can also react internally and with the surrounding matrix through epoxy functionalities. Thus, it is less likely that there will be excess free volume at the phase boundaries and a subsequent positive deviation for this reason. In addition, phase separation is not complete, particularly in blends of higher concentration and some HBP remains in matrix in the miscible fashion, also possibly contributing to negative deviation. The amount of dissolved HBP increases with increase in concentration of HBP, as is evident from DSC study, which clearly explains the increase in negative deviation with increase in HBP concentration.

CONCLUSIONS

HBP is miscible with DGEBA and TGDDM at above 100°C and undergoes a reaction-induced phase separation during curing leading to the formation of a two-phase microstructure. The free volume fraction increases with incorporation of HBP with a strong negative deviation. This is related to good (reacted) interfaces and some miscibility of a proportion of the HBP in the epoxy matrix.

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