

Highly Efficient *In Situ* Toughening of Epoxy Thermosets with Reactive Hyperbranched Polyurethane

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ABSTRACT: Hyperbranched polyurethane (HBPU), with low-molecular-weight polyethylene glycol space segments between the branching points, was synthesized by a pseudo one-pot procedure. HBPU was characterized by Fourier transform infrared spectroscopy, nuclear magnetic resonance spectroscopy, and gel permeation chromatography. The HBPU was used as a modifier of diglycidyl ether of bisphenol A (DGEBA)/anhydride system. The rheological properties of HBPU-G3/DGEBA blends were investigated by rotational rheometer. A slight decrease in viscosity of modified blends was observed by adding low content of HBPU and there was chemical reaction between HBPU and epoxy resin even without a hardener. The mechanical and thermal properties of the HBPU-G3/DGEBA thermosets were characterized and compared with that of the neat epoxy thermosets. Their impact fracture surfaces were investigated by scanning electron microscopy, and the results indicated that no phase separation occurred in the DGEBA/anhydride system after the introduction of HBPU, which was confirmed by dynamic mechanical analysis and thermogravimetric analysis. After addition of 10 wt % HBPU, the toughness of the modified thermosets was found to be significantly improved without sacrificing their processability and thermal and mechanical properties to a large extent. © 2014 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2014**, *131*, 40614.

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INTRODUCTION

Epoxy resins are considered as one of the most important classes of thermosetting polymers. They are widely used as coatings, electronic materials, adhesives, molding compounds, and composites because of their superior thermomechanical properties and excellent processability.¹ However, the major drawback associated with their application is related to their inherent brittleness, which affects the durability of components and place strong constraints on design parameter. Therefore, to overcome these problems, many attempts have been made to improve the toughness of epoxy thermosets by introducing glass particles,^{2–5} rubbers,^{6–11} and engineering thermoplastics^{12–15} in the matrix, but they would affect other properties of the thermoset, for example, rubbers result in a significant decrease in the modulus and in the glass-transition temperature to various degrees; glass particles can be filtered out during impregnation of the composite fiber structure; and engineering thermoplastics lead to increase in epoxy viscosity and cause a processing problem.

In the last years, new kinds of tougheners based on hyperbranched polymers have been reported.^{16–21} They have been

found to effectively toughen the epoxy thermosets as well as solve the problems related to processability of the blends, thermal and mechanical properties of the thermosets, and compatibility of tougheners and epoxy resin.¹⁷ Because of their unique chemical and physical properties, such as highly branched structure, large amount of terminal functional groups, and lack of intermolecular entanglement, hyperbranched polymers have higher solubility and lower solution or melt intrinsic viscosity compared with their linear analog polymers with similar molecular weight.²²

The typical hyperbranched polymers toughening epoxy resin are hyperbranched polyesters (HBP), and a lot of studies have been carried out during the decades. It has been shown that the hydroxyl-terminated HBPs could effectively toughen epoxy resin but significantly decrease both T_g and E' to various degrees^{18,23} because of the incomplete phase separation of thermosets. On the other hand, the epoxy-functionalized HBPs could improve the toughness of epoxy thermosets several times, much higher compared with hydroxyl terminal HBPs, without introducing negative effects on thermal and mechanical properties. This was

because the former induced a phase separation resulting in a finely dispersed particulate structures with good interfacial adhesion between the particles and epoxy matrix.^{16,17} In these toughening systems, it was noticed that the modified epoxy resin blends were initially a homogenous mixture, and phase separation occurred upon curing. In contrast, improvements in toughness of epoxy thermosets with HBPs that did not introduce phase separation were also reported.^{24–27} It could be because of a high physical compatibility between the modifier and the epoxy resin or the modifier is chemically incorporated into the network structure. The toughness improvement can be explained by an *in situ* homogenous reinforcing and toughening mechanism²⁵ or fibril formation which would absorb large energy under the impact.²⁸

Most of the research reported until now was focused on hyperbranched polyester (including aliphatic, aromatic ones, and their derivatives) modified epoxy resin. Examples of hyperbranched polyurethanes (HBPU) are relatively rare. In our previous work, the linear polyurethane (LPU) toughening epoxy resin was investigated. The toughness was effectively improved by the incorporation of LPU particles. However, by the addition of LPU, the T_g and modulus of modified thermosets were decreased to various degrees.²⁹ HBPU-modified epoxy resin was studied in this work. There are some advantages to synthesis of HBPU: (1) HBPU can be synthesized under a mild condition because of the high reactivity of isocyanate groups ($-NCO$); (2) HBPU with various of properties could be easily obtained by tailoring the structure between the branching points, which usually the spacer segments are different molecular weight polyether such as polyethylene glycol (PEG), poly(propylene glycol), and polycaprolactone diol.^{30–32}

In this work, HBPU, with a low-molecular-weight PEG space segment between the branching points, has been synthesized by a pseudo one-pot procedure. The PEG as a soft segment could improve the flexibility of hyperbranched polyurethane molecule as well as the compatibility with epoxy resins. Therefore, the compatibility of HBPU with epoxy resin would also be improved. Finally, it attempts to improve the toughness of diglycidyl ether of bisphenol A (DGEBA) by utilization of HBPU as a toughener. HBPU is expected to efficiently improve the toughness and do not affect other properties of the epoxy thermosets.

EXPERIMENTAL

Materials

Isophorone diisocyanate (IPDI, 99%), diethanol amine (DEA, 99%), catalyst dibutyltin dilaurate (DBTL, 95%), methyl nadic anhydride (MNA, $\geq 95\%$, mixture of isomers), and benzyldimethylamine (99%) were obtained from Aladdin Reagent Co., Ltd. (Shanghai, China). Dibutylamine (chemically pure) was purchased from Chengdu Kelong Chemical Reagents Factory. 1,4-Butanediol (BD, analytical reagent grade), *N,N*-dimethylformamide (DMF, analytical reagent grade), and PEG (molecular weight = 600 g/mol) were purchased from Guangdong Guanghua Chemical Factory Co., Ltd. PEG was dried in a round flask under high vacuum at 90°C–100°C for 2 h. DGEBA was

obtained from Nantong Xingchen Synthetic Material Co., Ltd. (epoxy equivalent weight = 182–192 g/equivalent). The solvent DMF was freed from moisture using 4 Å molecular sieves. All these reagents were used as received without further purification unless stated otherwise.

Synthesis of HBPU

IPDI (37.04 g, 167 mmol) and PEG-600 (50 g, 83.3 mmol) were added into a three-neck, round bottom flask equipped with a nitrogen inlet, dropping funnel, and a magnetic stirrer. The reaction mixture was stirred at 55°C for 1 h and 70°C for 2 h. Then, a viscous prepolymer A_2 was obtained. The change in NCO value during the reaction was determined using a standard dibutylamine back-titration method. The prepolymer was dissolved in 200 mL DMF, and then the resulting solution was cooled to 0°C. The monomer B^*B_2 (DEA, 8.76 g, 83.3 mmol) was dissolved in 200 mL DMF and was then added at this low temperature dropwise until all the solution was charged into the flask. The reaction setup was maintained at this temperature for 1 h. The ice bath was then removed, and an appropriate amount of DBTL was added to the mixture. The temperature was then raised to 55°C for about 4 h and 70°C for about 20 h until the isocyanate content reached theoretical value. The reaction was then stopped by the addition of the quantitative dibutylamine. The polymer solution was precipitated in water several times and dried in vacuum oven at 100°C for 48 h. A faint yellow and transparent viscous polymer was obtained.

Synthesis of LPU

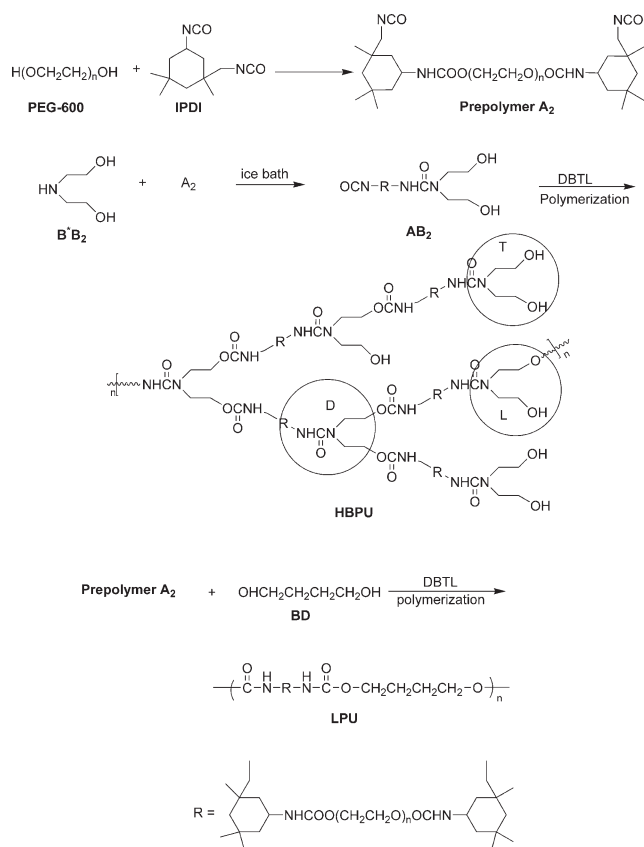
The synthesis of prepolymer is the same with the HBPU which is stated in the former part. The mole ratio of IPDI : PEG-600 : BD is 2 : 1 : 1. A viscous prepolymer A_2 was obtained, and it was dissolved in DMF. An appropriate amount of BD was dissolved in DMF and added to the flask all at once. Then, quantitative DBTL was added into the solvent. The temperature was then raised to 55°C for about 1 h. The reaction time was determined by the gel permeation chromatography. When the molecular weight of LPU is similar to the HBPU-G3's, the reaction was stopped by the addition of quantitative dibutylamine. The polymer solution was precipitated in water several times and dried in vacuum oven at 100°C for 48 h. A transparent solid was obtained.

Preparation and Curing of DGEBA/HBPU Blends

Generation three (G3) of HBPU was used to modify epoxy resin. An appropriate amount of HBPU-G3 was added to DGEBA resin under stirring and heated to 90°C until a homogenous and clear solution was obtained. Stoichiometric amounts of MNA and benzyldimethylamine were added under stirring. Once a homogenous solution was obtained, the solution was degassed for 10 min and poured into molds. Then, the blends were cured in a multistage process at 90°C for 2 h and 120°C for 1 h and postcured at 150°C for 4 h. The thermosets containing 0, 5, 10, and 15 wt % HBPU were made.

Characterization

The infrared spectra of the samples were recorded on a Nicolet Avatar 320 Fourier transform infrared (FTIR) spectrometer using KBr pellets. Nuclear magnetic resonance (¹³C-NMR) spectra of the polymers were recorded by a 400-MHz Bruker Fourier



Scheme 1. Synthesis route of linear polyurethane (LPU) and hyper-branched polyurethane (HBPU).

transform AVANCE 600 spectrometer using dimethylsulfoxide- d_6 as the solvent. The molecular weight and distribution of the polymers were determined by a gel permeation chromatography 515[hyphen]2410 system with tetrahydrofuran as the eluent at ambient temperature. Calibration was performed with linear polystyrene standards. The glass-transition temperature (T_g) of the HBPU was characterized by Perkin-Elmer DSC-7 differential scanning calorimeter from -50°C to 100°C at a scanning rate of $10^\circ\text{C}/\text{min}$ under nitrogen atmosphere. The second heating scans were used for T_g determination; T_g was defined as the halfway point of transition heat flow.

Rheological properties of uncured epoxy blends were carried out in the parallel plated (geometry of 20 mm) with a RS-600 rotational rheometer. Complex viscosity (η^*) of the uncured blends were recorded as a function of angular frequency ($\omega = 0.1\text{--}100$ rad/s, $T = 25^\circ\text{C}$) and temperature ($40^\circ\text{C}\text{--}160^\circ\text{C}$, frequency = 1 Hz), respectively. Thermal stability of the cured samples was characterized using a Perkin Elmer Pyris 1 thermogravimetric analyzer from 25°C to 800°C at a heating rate of $10^\circ\text{C}/\text{min}$ under nitrogen atmosphere. Analysis of the dynamic mechanical properties was carried out for cured samples on a Rheometrics RSA-III in a three-point bending configuration from -40°C to 160°C . The frequency used was 1.0 Hz, and the heating rate was $3^\circ\text{C}/\text{min}$. The size of the samples was $45\text{ mm} \times 12\text{ mm} \times 2\text{ mm}$.

The impact strength of the modified cured samples was determined by a Suns PTM1100-B1 impact tester according to ISO

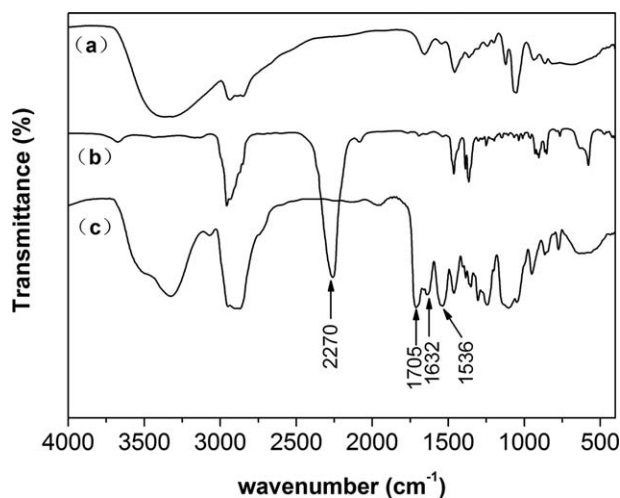


Figure 1. FTIR spectra of (a) DEA, (b) IPDI, and (c) HBPU.

179: 1993. The samples were adjusted in the test environment for 16 h before test. The average value of at least three measurements for each sample was recorded. The impact strength W was calculated by the equation:

$$W = 1000 E / (b \times h)$$

where E , b , and h are impact energy, width, and thickness of the sample, respectively. The flexural strength of the cured samples was measured by a Suns test machine according to ISO 178: 1993. The sample size used for both the tests was $80 \times 10 \times 4\text{ mm}^3$.

The impact fracture surface morphology of the samples, which were coated with a thin layer of gold, was examined by an APOLLO 300 scanning electron microscope at an accelerating voltage of 10 kV.

RESULTS AND DISCUSSION

Characterization of the HBPU

The HBPU used as the modifier of epoxy resin in this work was prepared by a pseudo one-pot procedure, i.e., the so-called “ $A_2 + B^*B_2$ ” technique.^{30,33,34} The prepolymer A_2 was first prepared by the reaction of PEG with excess diisocyanate. It is well known that the reactivity of isocyanate with NH is much higher than isocyanate with OH.³³ So the prepolymer A_2 was allowed to react with the DEA under a low temperature to obtain an AB_2 monomer containing a urea group as well as one isocyanate and two hydroxyl groups as much as possible. Finally, by raising the temperature, the HBPU was polymerized from the AB_2 monomers. The different generations of HBPU were obtained by controlling the reaction time. The synthetic pathway is depicted in Scheme 1.

FTIR spectrum is widely used for monitoring the reaction process of the polymerization. The FTIR spectrum of IPDI, DEA, and HBPU are shown in Figure 1. The band corresponding to the free —NH groups diminished, and the band assigned for the hydrogen-bonded —NH groups appeared. This result indicated that the majority of —NH groups in urethane and urea linkages (—NHCOO— and —NHCON—) participated in hydrogen bonding with urethane and urea carbonyl or with the

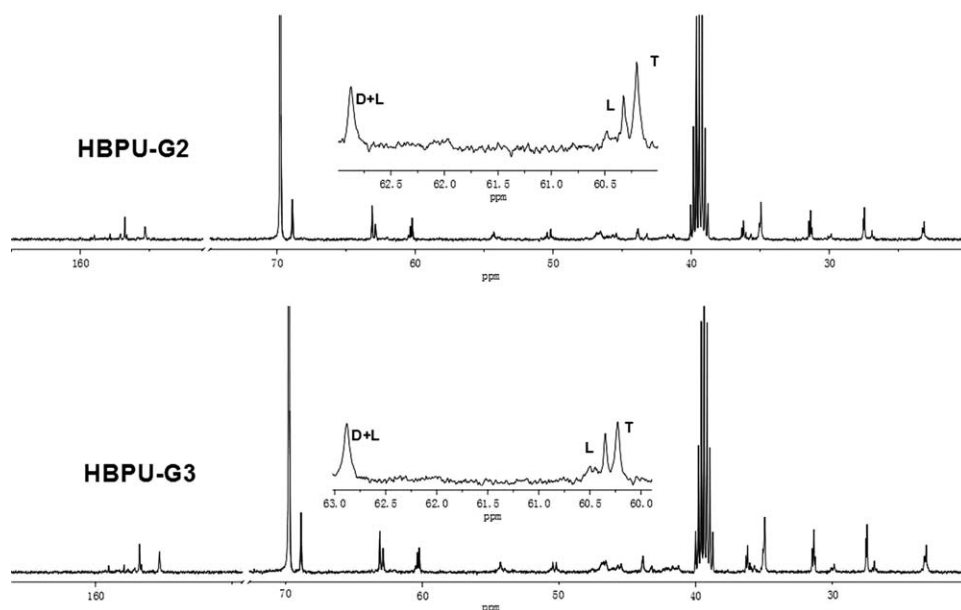


Figure 2. The ^{13}C -NMR spectrum of HBPU-G2 and HBPU-G3.

terminal hydroxyl groups.³⁵ The band at 1705 cm^{-1} ($-\text{NHCOO}-$) and 1632 cm^{-1} ($-\text{NHCON}-$) were attributed to the $\text{C}=\text{O}$ stretching vibrations; the band at 1536 cm^{-1} ($-\text{NHCO}-$) corresponds to the bending vibrations of $\text{N}-\text{H}$. Furthermore, the absorption band due to $-\text{NCO}$ groups disappeared at 2270 cm^{-1} indicating the completion of the reaction.³⁴

The characterization of degree of branching (DB) of HBPU was carried out by NMR spectroscopy. DB can be calculated from Fréchet's equation as follows³⁶:

$$\text{DB} = (D+T)/(D+T+L) \quad (1)$$

where D , T , and L refer to the number of dendritic, terminal, and linear units, respectively, in the structure of the polymer. In eq. (1) $T = D + 1$; therefore,

$$\text{DB} = (D+1+D)/(D+1+D+L) = (2D-1)/(2D+L-1) \approx 2D/(2D+L) \quad (2)$$

When the molecular weight of the hyperbranched polymer is high enough, eq. (1) can be similar to eq. (2).³⁴ DB is generally determined from NMR spectroscopy by a comparison of the integration of the peaks for the respective units in the hyperbranched polymer. In this study, each linear part has one hydroxyl group, and terminal part has two hydroxyl groups; however, the branched parts do not have hydroxyl group. Because of the interaction between the two hydroxyl groups of the terminal parts, the peak of terminal and linear parts can be separated in the ^{13}C -NMR spectrum.³⁴ Furthermore, dendritic, terminal, and linear units could also be determined by comparing with the model compounds.³³ The corresponding ^{13}C -NMR peaks of HBPU are shown in Figure 2. DB of different generation HBPU are listed in Table I. As can be seen, the DB for HBPU-G2 and HBPU-G3 were 52% and 45%, respectively.

These values of DB indicated that the HBPU exhibit a dendritic structure rather than a linear structure. In summary, the FTIR and NMR spectra confirmed that the hyperbranched polymer was successfully synthesized.

Rheological Properties of Epoxy Blends

Hyperbranched polymers are interesting structures because they present less intermolecular entanglements compared with their linear analog polymers with the similar molecular weight, which resulted in a lower solution or melt viscosity.²²

In this study, we synthesized an LPU whose molecular weight is similar to the HBPU-G3's. HBPU-G3 and 3, 5, 7, and 10 wt % of the LPU were added in epoxy resin. Then the rheological properties of the uncured modified epoxy blends were investigated by Rotational Rheometer. The complex viscosity of the epoxy blends without hardener at 25°C was determined by varying the angular frequency as shown in Figure 3.

In Figure 3(a), the HBPU/epoxy blends exhibited that the viscosity values were slightly decreased as the angular frequency gradually increase, which show likely a Newtonian behavior. Moreover, we can observe that the addition of 3, 5, and 7 wt % of the HBPU in the epoxy resin slightly decreased the viscosity values when compared with neat epoxy resin. Lowest viscosity can be obtained for 5 wt % HBPU/epoxy blends. By adding 7 wt % HBPU, the viscosity was increased compared with 5 wt % HBPU/epoxy blends, but it was still maintained on a lower value compared with that of the neat epoxy. This property of decrease in the epoxy resin viscosity with the addition of HBPU was also reported by other authors.³⁷ However, in Figure 3(b), the LPU/epoxy blends exhibited that the viscosity values were decreased apparently as the angular frequency gradually increase, especially at a higher frequency (20–100 rad/s) or higher content of LPU (7 and 10 wt %). This indicated that LPU/epoxy blends exhibited a non-Newtonian behavior, and that the intermolecular entanglement of HBPU is much

Table I. Characteristics of LPU and Different Generation of HBPU

Polymer	DB (%)	M_n (g/mol)	M_w (g/mol)	PDI	T_g ($^{\circ}\text{C}$) ^a
LPU	-	8,540	21,350	2.5	-
HBPU-G2	52	3,342	6,101	1.83	-8
HBPU-G3	45	4,870	12,899	2.65	3.7

^aGlass-transition temperature of HBPU obtained by differential scanning calorimetry.
PDI: Polydispersity Index.

lower than that of LPU because there are much branching structures in the HBPU molecule. Moreover, we could observe that the viscosity of the LPU/epoxy blends was much higher than that of the HBPU/epoxy blends. Even though, by the addition of 3 wt % LPU, the viscosity is still increased more than two times compared with 10 wt % HBPU. The specific phenomenon revealed that the use of HBPU as modifier of epoxy resin did not worsen but improve the processability of the resin at a relatively low content of HBPU.

Figure 4 shows the viscosity of neat epoxy and modified epoxy without hardener as a function of temperature. As we can see, without the hardener, viscosity of all the blends rapidly decreased as the temperature increased. At about 120 $^{\circ}\text{C}$, 25 wt % HBPU/DGEBA blend's viscosity rapidly increased, and a rubber-like transparent solid was obtained. However, the neat epoxy and amine terminated liquid nitrile rubber (ATBN)/epoxy were always liquid even at 160 $^{\circ}\text{C}$. The result indicated that there might be a chemical reaction between the HBPU and epoxy, which resulted in a crosslinking structure in the blends. However, that phenomenon was not observed in HBP/epoxy system.²³ Thus, the process of HBPU blending with epoxy resin should be operated under 120 $^{\circ}\text{C}$. However, HBPU could play a role of crosslinking center during the curing process, which could change the crosslinking density of the epoxy networks.

Mechanical Properties of the Thermosets

All of the blends were clear in appearance except the 15 wt % HBPU/DGEBA blend, which was a little turbid, indicating that the epoxy was almost saturated with dissolved HBPU. However, the turbidity disappeared by the addition of MNA, because of

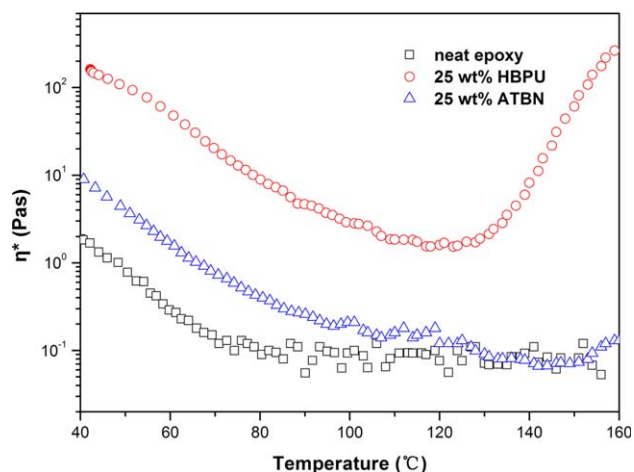


Figure 4. Complex viscosity of neat and modified epoxy without hardener as a function of temperature. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

the dilution effect or the change in polarity of the blends that lead to a more homogenous epoxy mixture. After being cured, all the blends always presented transparent appearance, which indicated that homogenous structures were formed.

To investigate the effect of the contents of HBPU on the properties of thermosets, impact test and three-point bend test were performed. Figure 5(a) shows the impact strength of the epoxies modified with contents of HBPU. Apparently, the impact strength of the modified epoxy matrices increased initially to a maximum and then decreased as the HBPU contents increased further. The maximum impact strength was achieved at 10 wt % HBPU, and the impact strength increased 128.7% compared with that of neat epoxy sample; from 12.9 KJ/m^2 for the neat resin to 29.5 KJ/m^2 for the modified resin. At 15% of HBPU, the impact strength slightly decreased, but it was still 49.5% higher compared with the neat epoxy. It is well known that the segment mobility of crosslinks in a thermoset strongly affects its toughness.³⁸ In this work, the HBPU molecules contained many soft segments, which would improve the flexibility of the network. So, the impact strength was significantly improved.

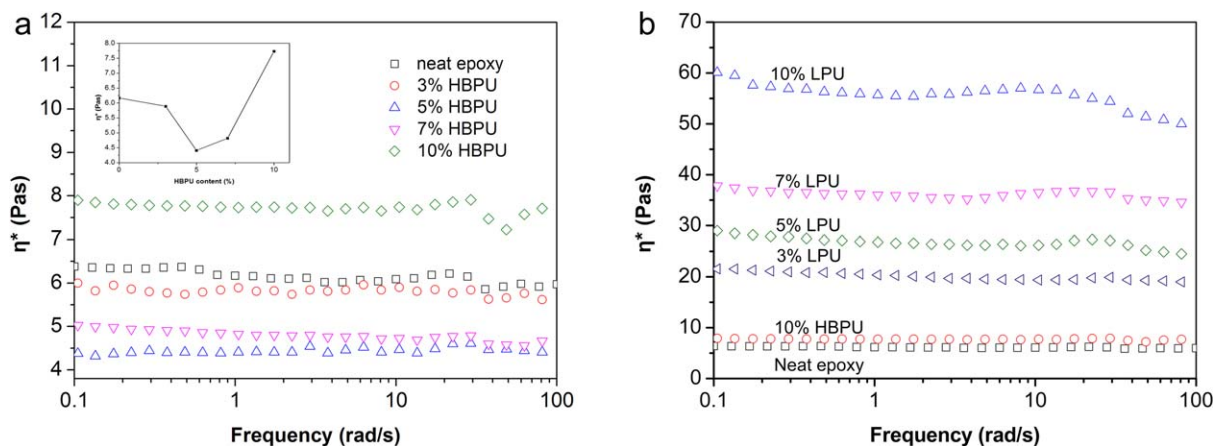


Figure 3. Complex viscosity of neat and modified epoxy blends without hardener as a function of angular frequency at 25 $^{\circ}\text{C}$, and viscosity as a function of HBPU contents at an angular frequency of 1 rad/s. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

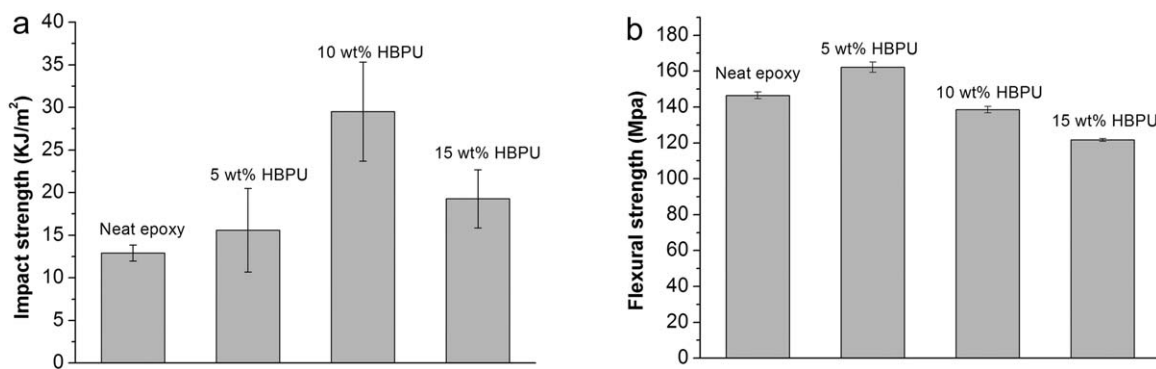


Figure 5. Effect of content of HBPU on the (A) impact strength and (B) flexural strength.

It was noticed that the flexural strength [Figure 5(b)] of the modified thermosets also improved after the introduction of HBPU. At 5 wt % of HBPU, the flexural strength reached 162.2 MPa, which was an 11% increase compared with 146.5 MPa of the neat epoxy thermosets. However, the flexural strength slightly decreased as the HBPU content increased to 10 wt %. The reason might be related to the decrease in crosslinking density as a result of the dilution effect of the uncrosslinked HBPU,³⁹ which is indicative of increasing plasticization of the cured epoxy thermosets.⁴⁰

Thermal and Thermomechanical Properties of the Thermosets

The modified thermosets were investigated by dynamic thermomechanical analysis (DMTA). The $\tan \delta$ and storage modulus (E') as a function of temperature are depicted in Figures 6 and 7, respectively, and the thermomechanical data are presented in Table II.

In Figure 6, it can be seen that the $\tan \delta$ curves of modified thermosets showed a single peak, which is similar to the neat epoxy thermoset, at the temperature range of -40°C to 160°C . Furthermore, in this work, the HBPU-G3 was characterized by differential scanning calorimetry with a glass-transition temperature of 3.7°C (Table I). However, as we said above, no relaxa-

tion is observed at -40°C to 40°C related with a second phase, and the appearance of a narrow $\tan \delta$ peak width conforms the good compatibility between HBPU and DGEBA resins. These facts evidenced that there was not a phase separation and that homogenous thermosets were formed. On the one hand, the HBPU has good compatibility with epoxy; on the other hand, the HBPU molecules can be incorporated into epoxy networks by covalent bond. The peak temperature of the $\tan \delta$ was regarded as the glass-transition temperature (T_g) of the sample, and the values are listed in Table II. By the addition of 5 wt % HBPU, no significant decrease in T_g was observed. A further addition of HBPU slightly decreased the T_g value. At 10 and 15 wt % HBPU, the T_g decreased by 2°C and 7°C , respectively, which were still better than some typical hyperbranched polymer toughening epoxy system.^{24,39–42} These trends could be attributed to two factors: on the one hand, the chemical incorporation of the HBPU into the epoxy networks would result in a higher crosslinking density which would lead to a shift in T_g to higher temperature; on the other hand, the glass-transition temperature of HBPU-G3 is 3.7°C . Therefore, it was easy to understand that T_g would be reduced by the introduction of HBPU with low glass-transition temperature.⁴³ So, these factors should result in appearance of maximum T_g as the content of HBPU increased. In addition, the maximum $\tan \delta$ values of

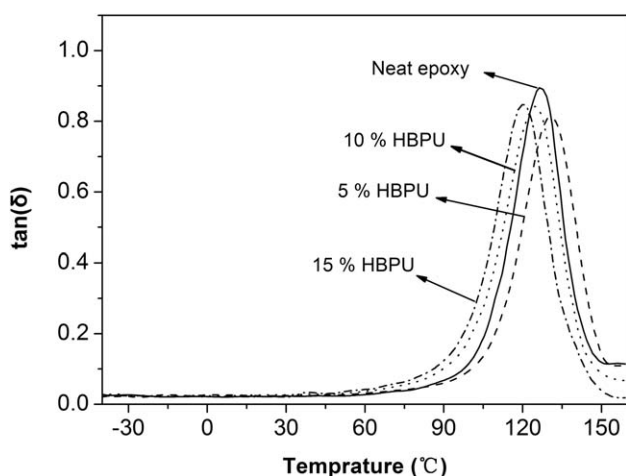


Figure 6. $\tan \delta$ of cured neat and modified epoxies as a function of temperature.

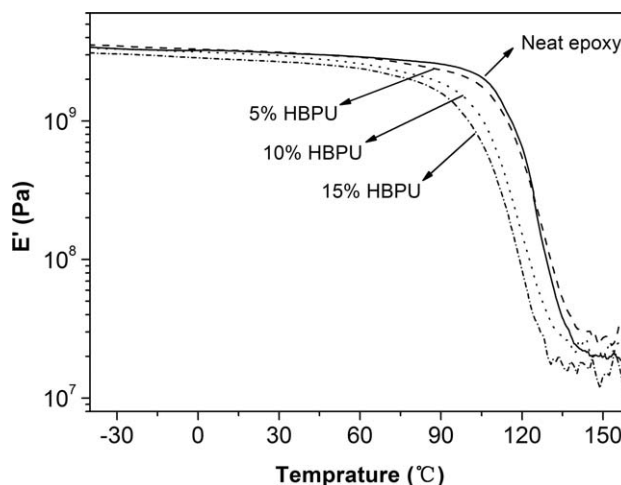


Figure 7. The storage modulus (E') of cured neat and modified epoxies as a function of temperature.

Table II. Effect of the Loading of HBPU on the Mechanical Properties of Modified Epoxy

Samples	T_g (°C) ^a	$\tan \delta$ ^b	(GPa) ^c	(MPa) ^d
Neat epoxy	126.3	0.90	3.07	20.9
5 wt % HBPU	130.6	0.81	3.11	24.1
10 wt % HBPU	124.6	0.84	2.89	22.3
15 wt % HBPU	119.8	0.85	2.63	16.3

^aGlass-transition temperature obtained by dynamic mechanical analysis (DMA).

^bThe peak value of $\tan \delta$ curves.

^cThe storage modulus obtained by DMA at an ambient temperature (35°C).

^dStorage modulus of material at the rubbery region at a temperature of $\tan \delta + 30^\circ\text{C}$.

modified thermosets were lower than that of the neat one. This result would be also related with a higher crosslinking density and lower damping properties of epoxy thermosets with HBPU.²⁴

Figure 7 shows the storage modulus (E') of cured neat and modified epoxies as a function of temperature. As can be seen, the storage modulus (Table II) also reached a maximum value in the rubbery region with the addition of HBPU. Again, further addition of HBPU decreased this parameter, but it was still higher than that of the neat epoxy thermosets until the HBPU content was beyond 15 wt %. The trend was confirmed that the crosslinking density was increased by the addition of HBPU. It is well known that the rubbery plateau modulus increases with increasing crosslinking density.²⁸

The thermal stability of the thermosets was investigated by thermogravimetric analysis (TGA). Figure 8 shows the TGA and the corresponding differential thermogravimetric (DTG) curves of HBPU and the epoxy resins containing different content of HBPU. From the TGA curves, the temperature of initial decomposition temperature (T_i), which corresponds to the temperature when 5% of the initial weight are lost, and maximum degradation rate temperature (T_{max}) are listed in Table III.

The DTG curves for all thermosets investigated were single peak, indicating that a homogenous structure of the matrix was

Table III. Thermal Stability Factors for HBPU/Epoxy Thermosets Calculated from TGA Curves

Samples	T_i (°C) ^a	T_{10} (°C) ^b	T_{max} (°C) ^c	Char yield (wt %) ^d
HBPU	225	258	345	2.8
Neat epoxy	282	323	425	18.2
5 wt % HBPU	275	311	417	16.3
10 wt % HBPU	294	336	424	17.5
15 wt % HBPU	264	299	414	14.3

^aTemperature of 5% weight loss.

^bTemperature of 10% weight loss.

^cTemperature of the maximum degradation rate.

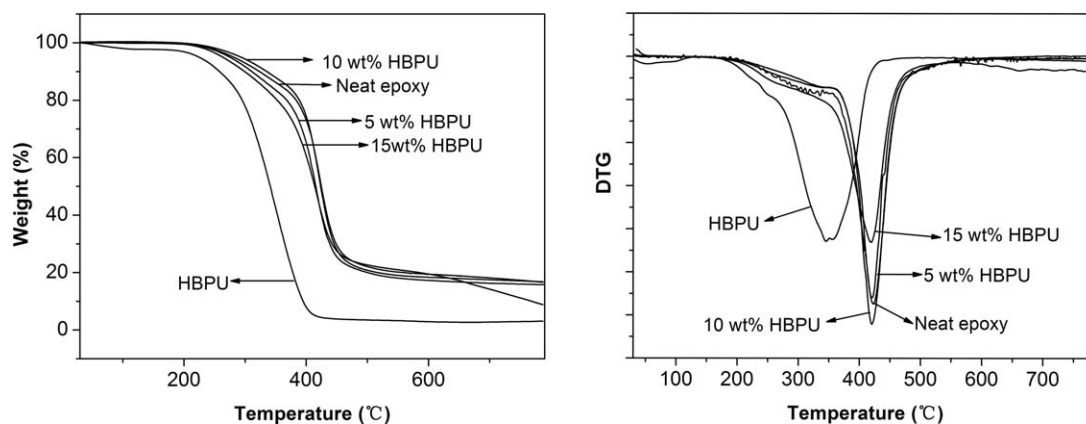
^dResidue at 700°C.

formed without apparent differences in thermal stability. The peak observed in DTG curves correspond to the degradation of the thermosets, and it remains similar for all the samples. The initial decomposition temperature decreased with increasing the content of HBPU. However, the decrease was not significant. Otherwise, as we can see, the thermal stability of HBPU was enhanced by the cooperation with the epoxy network, which may prevent the elimination of volatile fragments.

Morphology Analysis of the Thermosets

The toughness behaviors of the modified thermosets can be explained in terms of morphology observed by scanning electron microscopy. The fracture surfaces of the blends after impact tests were investigated by scanning electron microscopy, and the results are shown in Figure 9.

The typical fracture surface of neat epoxy specimens [Figure 9(a)] clearly appears as a smooth, fracture surface with cracks in different planes and without any sign of deformation, and this accounts for its poor impact strength. However, the fractured surface of HBPU-modified epoxy system exhibited a heterogeneous morphology, and there was not apparent sign of phase separation compared with the typical phase separation system which has some particles with size of a few micrometers.^{10,16,18,23,44} This was a visible evidence that a homogenous thermoset was formed. Moreover, the roughness fracture surface suggested that the modified resin will break more

**Figure 8.** TGA and DTG curves of the neat epoxy, HBPU, and HBPU/epoxy thermosets with different HBPU contents.

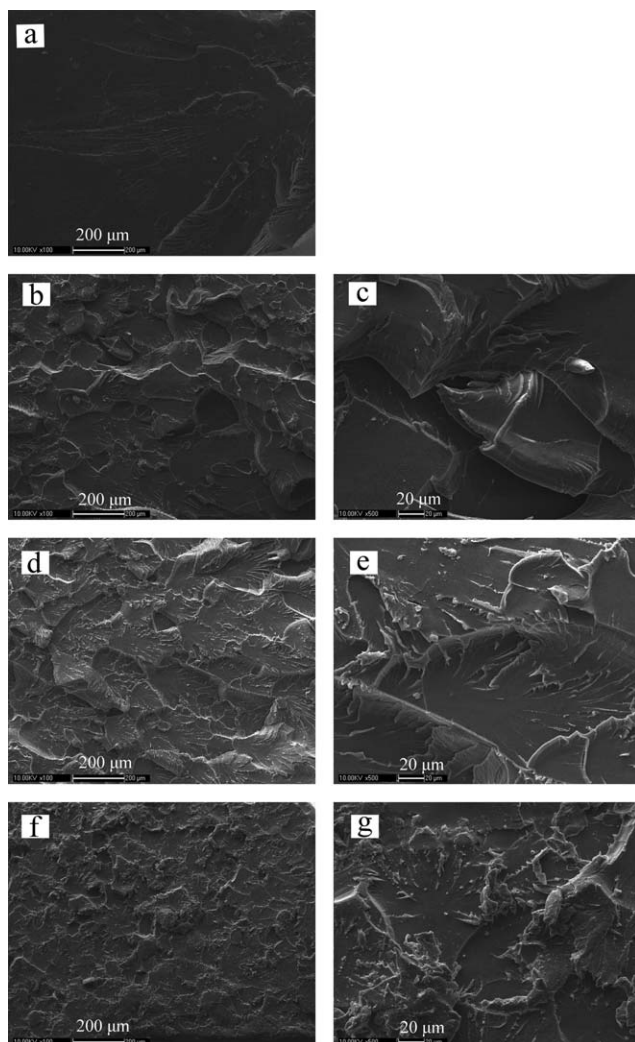


Figure 9. Scanning electron microscopy image of impact-fractured surfaces of modified epoxy resin with different HBPU contents: neat epoxy (a); 5 wt% HBPU (b) $\times 100$, (c) $\times 500$; 10 wt% HBPU (d) $\times 100$, (e) $\times 500$; 15 wt% (f) $\times 100$, (g) $\times 500$.

yieldingly compared with the neat one. The toughness improvement should be based on *in-situ* homogenous reinforcing and toughening mechanism,²⁴ which was confirmed by dynamic mechanical analysis and TGA.

CONCLUSION

HBPU with short soft chain between the branching points has been synthesized, and HBPU-G3 was used as the modifier of DGEBA/anhydride systems. On comparing the rheological properties between HBPU and its linear analog polyurethane it was found that the addition of HBPU would not increase the viscosity of epoxy blends sharply. On the contrary, with the addition of lower content of HBPU, the viscosity of the epoxy blends would slightly decrease. Furthermore, the HBPU could react with epoxy resin at a high temperature even without the addition of hardener. Impact strength of the epoxy thermosets was improved by adding HBPU, and the highest improvement was obtained when 10 wt % of HBPU was added to the epoxy resin.

The impact strength increases 128.7% compared with the neat epoxy sample; from 12.9 KJ/m² for the neat resin to 29.5 KJ/m² for the modified resin. Flexural strength followed the same trend, and the best improvement was obtained when the addition of HBPU was 5 wt %. The addition of the HBPU slightly reduced the value of the glass-transition temperature and improved the damping properties. The thermal stability of the modified thermosets was not significantly changed. By addition of HBPU into the DGEBA/epoxy system, a homogenous fracture surface without phase separation could be observed. Finally, one can conclude that HBPU as a modifier can effectively improve the toughness of epoxy resin without sacrificing processability, stiffness, and thermal stability.

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