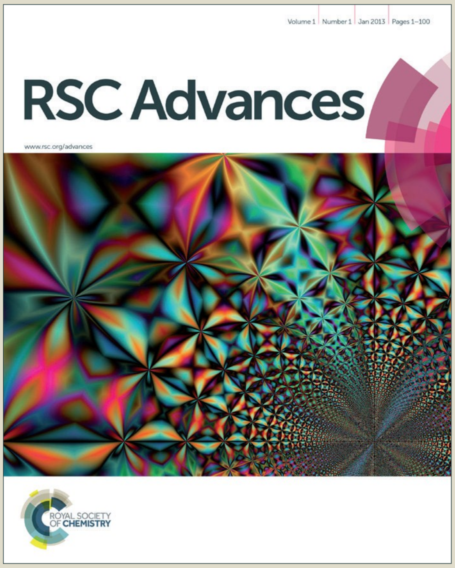
RSC Advances



ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/advances

Hyperbranched Polyurethane as a Highly Efficient Toughener in Epoxy Thermosets with Reaction-Induced Microphase Separation

Zai-Ping Zou, Xiao-Bing Liu, Ye-Ping Wu, Bing Tang, Mao Chen and Xiu-Li Zhao*
Institute of Chemical Materials, China Academy of Engineering Physics,
Mianyang 621900, Sichuan, China
Correspondence to: XL Zhao (E-mail: zhxl75@163.com)

Abstract: Hyperbranched polyurethane (HBPU), with poly (tetrahydrofuran) flexible segments between the branching points, was designed and prepared by a simple one-pot method. The HBPU and the linear analog polyurethane (LPU) were used as tougheners in the diglycidyl ether of bisphenol A (DGEBA)/amine system, respectively. The HBPU was miscible with DGEBA resin without affecting the favorable processability of the epoxy blends. It was proved that a good phase separation structure with strong interface interaction was formed in the DGEBA/HBPU thermosets and the HBPU was more effective than LPU in toughening epoxy resin. After adding 10 wt% HBPU, the impact strength of samples was 3 times as large as the neat epoxy. Meanwhile, the flexural strength and glass storage modulus of the thermosets were hardly affected with the addition of HBPU while obvious decreases were observed in the DGEBA/LPU thermosets. Especially, unlike most of the hyperbranched polymer tougheners, the introduction of HBPU also simultaneously improved the rubbery plateau modulus, glass-transition temperature and thermal stability of the epoxy thermosets.

1. Introduction

As one of the most important thermosetting materials, epoxy resins have been widely used in various technological applications, such as surface coatings, electrical laminates, adhesives and molding compounds, due to the excellent thermomechanical properties and superior processability [1-3]. However, the usage of epoxy resin is restricted due to poor impact resistance which is related to the high cross-linking density and chain stiffness of the cured network. To eliminate this drawback, different tougheners [4-7], such as rubbers, glass particles and engineering thermoplastics, are added into the epoxy. But they usually limited the processability and led the decrease of glass-transition temperature (T_g) and modulus of epoxy thermosets.

These problems could be overcome by introducing hyperbranched polymers (HBPs) [8-18]. Due to their special chemical and physical properties, such as globular structure, large amount of terminal groups and highly branched structure, HBPs have higher reactivity, lower viscosity and higher solubility than their linear analog polymers with similar molecular weight [19]. Thus, the HBPs are considered as a new kind of ideal modifier in epoxy which may improve the toughness and other properties simultaneously. There are some typical progresses in the homogeneous modified epoxy system. Zhang and his coworkers [20] reported that the toughness and strengths of the epoxy thermosets modified by epoxide-terminated HBPs could be simultaneously improved without forming phase separation, but reductions in T_g and heat-resistant properties were observed. Meng et al. [16, 21, 22] used epoxide-terminated hyperbranched polyether as a modifier for the epoxy resin, non-phase-separated thermosets with improvements in the toughness, strengths and T_g could be obtained. However, the increase of toughness was limited in most of the homogeneous modified epoxy systems.

It is well-known that HBPs could toughen epoxy resins, especially in the phase-separated modified epoxy systems [8-10, 23-25]. The phase separate structures could deflect the cracks and absorbs impact energy to improve the toughness of epoxy thermosets. And the effect of toughening depended on the particle size, distribution and matrix/particle interaction [8, 26]. Hydroxyl-terminated HBPs were typical examples for toughening epoxy thermosets. It could effectively improve the toughness of DGEBA thermosets, but other mechanical properties and the T_g of thermosets would often decrease to some degree [9, 10, 26, 27]. By partially modifying or completely redesigning the HBPs' structures, it is possible to strengthen the interfacial interaction with the epoxy matrix and adjust the particle size and distribution in the thermosets, which could ameliorate the problems mentioned above[28-30]. But it is still a big challenge to achieve balanced enhancement in mechanical properties without sacrificing the thermomechanical properties in the phase-separated modified epoxy systems.

Kinds of HBPs have been used to modify the epoxy during the two decades. But there are few examples about the hyperbranched polyurethanes (HBPUs). Polyurethane has a lot of excellent properties, depending on the structural composition of soft and hard segments, which make it become one of the most fascinating polymers [31]. And there have been many researches about linear polyurethane toughening epoxy by interpenetrating polymer network (IPN) method [32-34]. In our previous work, the in-situ toughening of epoxy thermosets with HBPU-PEG have been explored. Though the impact strength of the modified thermosets increased 128.7% compared to the neat epoxy, the T_g, modulus and thermal stability decreased slightly [35].

These precedents mentioned above inspired us to further investigate the use of HBPU with the aim that not only to increase T_g, modulus and thermal stability, but also to improve the toughness to a larger extent by introducing phase separate structure. In this work, a hydroxyl-terminated HBPU, with poly (tetrahydrofuran) space segments between the branching points, was synthesized by the one-pot method. The introducing of poly (tetrahydrofuran)-1000 into the HBPU could improve the compatibility with epoxy resin before curing and lead to a desired particle size in the phase-separated thermosets which would facilitate the toughness characteristics. After adding HBPU, a phase separation structure with strong interface interaction was formed in the DGEBA/amine system. The T_g and decomposition temperature of DGEBA/HBPU thermosets increased to some extent. Compared with earlier investigations, the introduction of HBPU here efficiently improved the toughness and thermal properties of epoxy thermosets without compromising other mechanical properties.

2. Experimental

2.1. Materials

Isophorone diisocyanate (IPDI, 99.0%) was obtained from Tokyo Chemical Industry Co., Ltd. Diethanol amine (DEA, 99%) and dibutyltin dilaurate (DBTL, 95%) were purchased from Aladdin Reagent Co., Ltd. 1, 4-Butanediol (BD, analytical reagent grade) was obtained from Guangdong Guanghua Chemical Factory Co., Ltd. And DGEBA was purchased from Nantong Xingchen Synthetic Material Co., Ltd. (epoxy equivalent weight=182–192 g/equivalent). Curing agent 593 (Addition compound of diethylenetriamine and butylglycidyl ether) was obtained from Zhonghao Chenguang Research Institute of Chemical Industry. Poly (tetrahydrofuran) or polytetramethylene ether glycol (PTMG, molecular weight=1000 g/mol) was purchased from Sigma-Aldrich and dried in a round flask under high vacuum at 110 °C–120 °C for 4 h. N,N-dimethylformamide (DMF, analytical reagent grade) was obtained from Guangdong Guanghua Chemical Factory Co., Ltd and dried using 4 Å molecular sieves for 24 h.

2.2. Synthesis of HBPU

IPDI (44.46 g, 200 mmol) and PTMG (100 g, 100 mmol) were dissolved in 150 mL DMF in a three-neck flask equipped with a nitrogen inlet, dropping funnel and a magnetic stirrer. Then 0.05 wt% DBTL (69.5μL) was added and the mixture was stirred at 55 °C. After 1.5 h, a viscous pre-polymer A_2 was obtained. The change in -NCO value was determined using a standard dibutylamine back-titration method. Another 100 mL DMF was added into the three-neck flask and the resulting solution was cooled to 0~5 °C. Then the monomer B*B_2 (DEA, 10.50 g, 100 mmol) was dissolved in 50 mL DMF and dropwise added into the flask at this low temperature. The reaction setup was maintained at this temperature for 1 h. The ice bath was removed and 0.1 wt% DBTL was added to the mixture. Then the mixture was stirred at 60 °C for about 4 h and kept at 70 °C for another 5 h. Finally, the reaction was stopped by the addition of DEA. The polymer solution was precipitated in deionized water several times and dried under vacuum at 70 °C for 24 h. A transparent viscous polymer was obtained (Mw = 18692 g/mol, Mn = 6730 g/mol, PDI = 2.77, T_g = 3 °C).

^{13}C-NMR (THF-d_8): δ (ppm) = 21.30, 21.51 [CH_3, ring], 24.70-40.22 [CH_2, soft segment; C, CH_2, CH_3, ring], 42.62 [CHN, urea and urethane], 44.53-45.95 [N-CH_2-CH_2-OC(O); CH_2-NH, *trans*; CH_2, ring], 49.66-50.36 [N-CH_2-CH_2-OH], 53.37, 53.12 [CH_2-NH, *cis*], 60.12 [CH_2-OH, t], 60.45 [CH_2-OH, l], 61.95-62.22 [CH_2-O-CH_2, soft segment; CH_2-OC(O), l and d], 154.09-160.01 [C=O, urea and urethane].

2.3. Synthesis of LPU

The synthesis of pre-polymer was the same as the method stated above. The mole ratio of IPDI: PTMG: BD is 2: 1: 1. The pre-polymer A_2 was obtained. An appropriate amount of BD was dissolved in DMF and added to the flask all at once. Then, the temperature was raised to 60 °C and 0.1w% DBTL was added into the solvent. The reaction time was determined by the gel permeation chromatography. When the molecular weight of LPU is similar to the HBPU, the reaction was stopped by the addition of DEA. The polymer solution was precipitated in deionized water several times and dried under vacuum at 70 °C for 24 h. A transparent solid was obtained (Mw = 25490 g/mol, Mn = 9766 g/mol, PDI = 2.61, T_g = -11 °C).

2.4. Samples preparation

An appropriate amount of HBPU or LPU was added to DGEBA resin under stirring at 80 °C until a transparent and homogenous solution was obtained. When the mixture was cooled to room temperature, stoichiometric amount of curing agent-593 was added into the solutions under stirring (26.50g curing agent for per 100g epoxy resin). Then the solution was degassed for 15 min and poured into a preheated mold. The blends were cured at 80 °C for 4 h and then cooled to room temperature. After trimming and sanding, all the samples were heat treated at 80 °C for another 2 h. The thermosets containing 0, 5, 10 and 15 wt % HBPU or LPU were prepared for the tests.

2.5. Characterization techniques

A Nicolet Avatar 320 Fourier transform infrared (FTIR) spectrometer was used to determine the infrared spectra of the samples in the form of KBr pallets. Nuclear magnetic resonance (^{13}C-NMR) spectra of the HBPUs were recorded by a 600-MHz Bruker Fourier transform AVANCE 600 spectrometer using tetrahydrofuran (THF)-d_8 as the solvent. The molecular weight and their distribution of the HBPU and LPU were obtained by a gel permeation chromatography 515 [hyphen] 2410 system with THF as the eluent at ambient temperature. Calibration was performed with linear polystyrene standards. The T_g of the HBPU and LPU were determined by Perkin-Elmer DSC-7 differential scanning calorimeter from -40 °C to 80 °C at a scanning rate of 10 °C /min under nitrogen atmosphere.

Rheometric measurement of uncured epoxy blends was executed in the parallel plated (geometry of 20 mm) mode with a RS-600 rotational rheometer. Complex viscosity (η*) of the blends were recorded as a function of angular frequency (ω=0.1–100 rad/s, T=25 °C) and temperature (40-160 °C, frequency=1Hz), respectively. The inner temperature of curing epoxy is detected by inserting a thermometer into a 60 g DGEBA/amine/HBPU (10 wt%) blends in a 80 °C oven.

The dynamic mechanical thermal analysis (DMTA) of the thermosets at 1.0 Hz were carried out on a Rheometrics RSAIII with a double cantilever bending configuration from -110 °C to 110 °C. The heating rate was 3 °C /min and the size of the samples was 45 × 12 × 2 mm^3. Thermal stability was characterized using a Perkin Elmer Pyris 1 thermogravimetric analyzer (TGA) from 25 °C to 650 °C (10 °C /min) under nitrogen.

The impact strength of the cured samples was characterized by a Suns PTM1100-B1 impact tester according to ISO 179: 1993. And the flexural strength tests were performed on a Suns test machine according to ISO 178: 1993. The samples were adjusted in the test environment for 24 h. The sample size for both of the tests was 80 × 10 × 4 mm^3 and an average value of five samples was taken for each test. The fracture surface morphology of the impact test samples, which was coated with a thin gold layer, was observed using an APOLLO 300 scanning electron microscope (SEM) at voltage of 10 KV.

3. Results and discussion

3.1. Synthesis and characterization of the hyperbranched polyurethanes

HBPU in this work was prepared by the one-pot procedure (“A_2+B*B_2” technique) [35-38]. The pre-polymer A_2 was first synthesized by the reaction of PTMG with excess IPDI. Since the reactivity of -NCO with -NH- is much higher than that of -NCO with -OH [37], the A_2 was allowed to react with the DEA under a low temperature to obtain an AB_2 monomer containing one -NCO and two -OH groups. Finally, the HBPU was polymerized from the AB_2 monomers by raising the temperature. The synthesis route is depicted in Scheme 1.

Scheme 1. The synthesis routes of HBPU and LPU.

Fig. 1 shows the FTIR spectrum of HBPU, IPDI and DEA. The bands at 1705 cm^{-1} (-NHCOO-) and 1632 cm^{-1} (-NHCON-) in the HBPU curve correspond to the C=O stretching vibrations. The band at 1536 cm^{-1} (-NHCO-) can be assigned to the bending vibrations of hydrogen-bonded -NH- [39]. These results indicate the formation of urethane and urea linkages. The characteristic peak of C-O-C at 1125 cm^{-1} confirms the introduction of PTMG into the HBPU. In addition, the strong absorption band attributed to -NCO groups at 2270 cm^{-1} disappears in the HBPU, indicating the completion of the reaction [38].

Fig. 1. FTIR spectra of DEA, IPDI and HBPU.

The degree of branching (DB) is generally determined from NMR spectroscopy by a comparison of the peaks integration of the respective units in the HBP. DB can be calculated using equation (1) by Frechet [40] method as follow:

$$DB_{Frechet} = \frac{D + T}{D + L + T} \qquad (1)$$

where D, L and T refer to the number of dendritic, linear and terminal units in the structure of the polymer （Scheme 1）. For a hyperbranched polymer made from AB_2 type monomer, D=T - 1. Therefore, DB can be calculated by equation (2) [38]:

$$DB_{Yan} = \frac{2D}{2D + L} \qquad (2)$$

In this work, for the HBPU made from A_2 and B*B_2 monomers, linear unit had one -OH group and terminal unit had two. Due to the interaction between the two -OH groups of terminal units, the peak of terminal and linear units can be separated in the ^{13}C-NMR spectrum [38] (Seeing the T (a) and L(b) in the Fig. 2). So DB can be calculated with equation (2). The ^{13}C-NMR spectrum of HBPU is shown in Fig. 2. As can be seen, the DB for this HBPU is about 0.67. The value of DB indicates that the HBPU exhibit a dendritic-like structure rather than a linear structure. Thus, the analysis of FTIR and ^{13}C-NMR spectra confirms that the HBPU was successfully synthesized.

Fig. 2. The ^{13}C-NMR spectrum of HBPU.

3.2 Rheological properties of epoxy blends

In most of the researches about HBPs toughening DGEBA, solvents were used to facilitate the compatibility and processability of the HBPs and epoxy resin [9-13, 24-26]. But in this study, the introduction of PTMG-1000 soft segments could improve the flexibility of HBPU and benefit to the compatibility with the DGEBA resin, even at room temperature, to form a homogeneous mixture without requiring the use of solvents.

Hyperbranched polymers also have a low viscosity. In order to explore the rheological properties of HBPU and epoxy blends, the rheometric measurement was carried out. The complex viscosity (η^*) of HBPU and LPU was determined by varying the angular frequency as shown in Fig. 3. The viscosity of HBPU is much lower than that of the LPU and the shear-thinning behavior is more obvious for the LPU sample. Because HBPU's dendritic-like structures lead to less intermolecular entanglement compared with their linear analogue polymers with similar molecular weight [19].

Fig. 3. Complex viscosity of HBPU and LPU as a function of angular frequency at 25 °C.

Fig. 4 shows the evolution of the complex viscosity as a function of angular frequency at 25 °C of the epoxy blends without hardener. The viscosity values of DGEBA/HBPU blends hardly changed as the angular frequency gradually increased. But for the DGEBA/LPU blends, the viscosity decreased with increasing the angular frequency, especially at higher frequency (10-100 rad/s) or higher LPU content (15 wt% LPU). These results indicate that DGEBA/LPU blends show a non-Newtonian behavior and that the intermolecular entanglement of LPU is much higher than that of HBPU. In addition, all the blends had higher viscosity than the neat epoxy resin and the viscosity values of blends increased with raising the modifier content. By adding 5 wt% HBPU, the viscosity of mixture was close to that of neat epoxy resin. Though the viscosity of DGEBA/HBPU blends was increased by adding more HBPU, the viscosity value still maintained at a low level. However, the DGEBA/LPU blends had much higher viscosity compared with the DGEBA/HBPU blends. Even though adding 5 wt% LPU, the viscosity value of blend was still larger than that of 10 wt% HBPU/epoxy blends. When the LPU content was 15 wt%, the viscosity of DGEBA/LPU blends was almost ten times larger than that of the neat epoxy resin. The specific phenomenon mentioned above reveals that the usage of HBPU in the epoxy resin hardly affects the processability compared with the analogues LPU.

Fig. 4. Complex viscosity of neat epoxy and modified epoxy blends as a function of angular frequency at 25 °C. (H5, H10 and H15: The epoxy thermoset contains 5 wt%, 10 wt% and 15 wt% HBPU, respectively. L5, L10 and L15: The epoxy thermoset contains 5wt%, 10wt% and 15 wt% LPU, respectively.)

3.3 Curing mechanism of the DGEBA/HBPU thermosets

Since there are few researches about the HBPU toughening epoxy resin, the curing mechanism of the DGEBA/HBPU thermosets is investigated here. Fig. 5 shows the phase separation process of the DGEBA/HBPU (10%) blend at 80 °C. As mentioned above, the blend was transparent and homogeneous at the beginning of the curing. The phase separation occurred at 220 s and gradually became translucent or opaque within 20 s. The DGEBA/LPU blend had a phenomenon similar to the DGEBA/HBPU blend but the phase separation started at 240 s. The turbid liquid was generated by the reaction-induced phase separation. And the driving force of phase separation was the unfavorable entropy resulting from the exploding in the molecular weight of epoxy network during curing, which led to a higher mixing free energy [8, 30].

Fig. 5. The phase separation process of DGEBA/HBPU (10%) blends.

The curing mechanism of the epoxy/HBPU/amine system is complex, but it can be summarized in Scheme 2. The reaction of epoxy ring and the primary amine to form a secondary amine and the further epoxy ring opening reaction with the secondary amine to form a tertiary amine are the main reactions during the curing process (Scheme 2a). And there may be etherification reactions between -OH and epoxide through proton donor-acceptor complex [41, 42] (Scheme 2b and 2c).

Scheme 2. The possible curing mechanism of the HBPU modified epoxy thermosets.

Researches about the hydroxyl-ended HBPU modified by epoxy resin, which cured with poly (amido amine) hardener, demonstrated that the -OH of HBPU could react with epoxy resins [43, 44]. In this work, there was also chemical reaction between HBPU and epoxy resin beyond 120 °C, even without curing agent. Just as shown in the Fig. 6, the viscosity of neat and modified epoxy rapidly decreased with increasing the temperature before 120 °C. But DGEBA/HBPU blend's viscosity rapidly increased at about 120 °C and a rubber-like solid was obtained. The same phenomenon was observed in our previous work[35] and it indicated that there was a reaction between the HBPU and epoxy resin beyond 120 °C. HBPU could act as a crosslinking center during the curing, which could improve the cross-linking density of the modified epoxy.

Fig. 6. Complex viscosity of neat and modified epoxy without hardener as a function of temperature.

For the DGEBA/amine/HBPU system cured at 80 °C in this paper, the inner temperature of epoxy blends could easily reach 125 °C or higher temperature through our detection, so some of HBPU could also be partially or totally incorporated into the epoxy network, leading to a higher cross-linking density of the epoxy matrix. Moreover, the large amount of polar groups in the HBPU introduced more hydrogen bonds and covalent bonds at the interface, leading to a stronger interfacial interaction compared to that of DGEBA/LPU thermosets.

3.4 Mechanical properties of the epoxy thermosets

It is well-known that HBPs could toughen epoxy resins effectively, especially in the phase-separated modified epoxy systems. The impact strengths of modified thermosets containing various contents of HBPU or LPU were investigated by means of impact testing. And the results are shown in the Fig. 7 (a). It can be found that both of the HBPU and LPU were efficient in improving the impact strength.

Fig. 7. Effect of modifier content on the (a) impact strength and (b) flexural strength.

For the DGEBA/LPU thermosets, the separate microphase structure was also formed. The impact strength increased up to the maximum by adding 5 wt% LPU and the maximum impact strength reached 25.01 kJ/m^2 which was a 160% increase compared with 9.87 kJ/m^2 of neat epoxy sample. The enhancement in toughness is related to the formation of separate microphase structures which prevent the crack to freely develop and absorb the impact energy. However, the impact strength of the DGEBA/LPU thermosets decreased apparently with the increase of LPU content. Because the particle dispersion in the thermosets would become worse and more defects could generate in the epoxy thermosets with increasing the content of LPU.

There were many investigations about the traditional hydroxyl-terminated HBPs toughening epoxy thermosets, few of them have reported an increase of impact strength higher than 2-fold to our knowledge. But for the DGEBA/HBPU thermosets, the impact strength reached 29.78 kJ/m^2 when the HBPU content was 10 wt%, which was three times of that of the neat epoxy thermosets. At 15% HBPU/epoxy thermoset, the impact strength slightly decreased which was still at a high level. The highly improvement of toughness in the

DGEBA/HBPU thermosets can be attributed to a good phase separation of HBPU, acting as soft particles like LPU but having a better interfacial interaction with the epoxy matrix. Upon loading, the strong interface interaction facilitated the stress transfer between the HBPU particles and epoxy matrix. In addition, the HBPU incorporated in the epoxy could improve the flexibility of the epoxy network. The two factors mentioned above also lead to a higher toughness in the DGEBA/HBPU thermosets than that of the DGEBA/LPU thermosets.

The flexural strengths of the epoxy thermosets are presented on the Fig. 7 (b). It is noticed that the flexural strengths of DGEBA/HBPU thermosets decreased slightly as the modifier content increased compared with the neat epoxy thermoset. The reduction of flexural strength might be related to the introduction of separate phase structures as a result of a dilution effect of material. But the flexural strengths of DGEBA/HBPU thermosets were more acceptable than the DGEBA/LPU thermosets and significant reduction in flexural strength was observed in other phase-separated epoxy systems modified with HBPs. This could be also contributed to the higher cross-linking density and stronger interfacial interactions in the DGEBA/HBPU thermoset.

3.5 Thermomechanical properties of the epoxy thermosets

All the epoxy thermosets were investigated by the DMTA and the results are shown in the Table I. The test temperature was in the range of -110 °C to 110 °C, which was below the β-relaxation temperature and then gradually entranced to the rubbery region of epoxy thermosets.

Table I. DMTA results of epoxy thermosets.

Sample	Er (MPa)	Eg (GPa)	V_e (mol/cm^3)	Tg (°C)
Neat DGEBA	6.62	2.85	-/-	65.3
H5	9.64	2.74	1.02×10^{-3}	70.3
H10	8.83	2.53	9.33×10^{-4}	72.1
H15	8.35	2.32	8.80×10^{-4}	73.9
L5	7.15	2.21	7.53×10^{-4}	67.8
L10	6.27	1.88	6.57×10^{-4}	66.1
L15	5.68	1.65	5.94×10^{-4}	64.3

The storage modulus varied linearly with temperature at the rubbery region between 90-110 °C, where segments in the polymer structures moved in a cooperative way, but cross-linking networks prevented any liquid flow [45]. The rubbery plateau modulus (E_r) can be observed in the elastomeric modulus at 105 °C and the values are list in Table I. All of the DGEBA/HBPU samples had higher E_r compared with DGEBA/LPU samples. It is well known that the E_r would increase as cross-linking density increases in the similar epoxy systems[46]. For all the modified thermosets, it is possible to calculate the average cross-linking density from E_r [46, 47]:

$$E_r = 3\varphi v_e RT \qquad (3)$$

where *φ* refers to a constant which could be obtained from the behavior of ideal rubbers networks, R is the gas constant and T is the absolute temperature. The v_e refers to the concentration of the elastic chains between cross-links which can be used to evaluate the average cross-linking density and the calculating results are shown in the Table I. As can be seen from v_e, the average cross-linking density of DGEBA/HBPU thermosets was higher than that of the DGEBA/LPU samples. It confirms that some HBPU was incorporated into the epoxy network and the introducing of HBPU would improve the cross-linking density of the epoxy matrix. Nevertheless, the low functionality and big steric hindrance of long chain LPU restricted the intermolecular polar interaction [48], so the reaction of LPU with epoxy was limited and didn't contribute to the cross-linking density. Since more second-phase particles were generated at higher modifier content, the average cross-linking density of modified thermoset became smaller as the modifier content increased.

It seems contradictory that the DGEBA/HBPU thermosets have higher average cross-linking density while they possessed better toughness than LPU modified epoxies. But it is should be noted that the toughness of epoxy resin is related to the cross-linking density and chain stiffness of the cured network. Though the crosslink density is increased by adding HBPU, the HBPU incorporated in the epoxy also improved the flexibility of the network. Besides, as mentioned above, the stronger interface interaction in the DGEBA/HBPU thermosets facilitated the stress transfer upon loading. These positive factors dominated the higher toughness of HBPU modified epoxies than DGEBA/LPU thermosets.

The glass storage modulus (E_g) at 25 °C was also evaluated and the results are shown in Table I. As can be seen, there is a reduction of E_g with the addition of modifier, which is related to the defects in the phase separated thermosets. Further addition of HBPU decreased this parameter, but it is still at a desirable value and higher than that of the DGEBA/LPU thermosets. This can be contributed to the higher cross-linking density and stronger interfacial interaction in the DGEBA/HBPU thermosets.

The tan δ as a function of temperature of DGEBA/HBPU and DGEBA/LPU thermosets is depicted in Fig. 8. The peak temperature of the tan δ can be regarded as the T_g of the thermoset and the results are presented in the Table I.

Fig. 8. Tan δ of (a) DGEBA/HBPU thermosets and (b) DGEBA/LPU thermosets as a function of temperature.

As mentioned above, the increases in the toughness of epoxy thermosets were often accompanied by apparently decrease in T_g. But in this work, when adding 5, 10 and 15 wt% HBPU, the T_g of modified thermoset increased by 5.0, 6.8 and 8.6 °C, respectively, compared to that of the neat epoxy thermoset [Fig. 8 (a)]. The improvement in T_g could be attributed to the higher cross-linking density of the continuous epoxy phase and strong interfacial interaction between particles and surrounding epoxy, which would restrict the mobility of epoxy network. It is also noted that the T_g of DGEBA/HBPU thermosets increased as the HBPU content increased, indicating the higher cross-linking density of the epoxy phase at the higher HBPU content. In the case of the DGEBA/LPU thermosets [Fig. 8 (b)], the addition of LPU had limited contribution to the cross-linking density, so it is easy to understand that the change of T_g was slight. For the 15 wt% LPU/epoxy thermoset, the T_g even decreased due to more dissolution of the flexible LPU in the epoxy matrix.

It is well known that the β-relaxation in the epoxy arises from the motion of the hydroxyl ether structural units [-CH_2-CH(OH)-CH_2-O-] and other parts in the molecular chains [49]. After adding HBPU or LPU, the β-transition peak of modified thermosets between -20 ~ -90 °C became higher and stronger compared with the neat epoxy thermoset. [See insets in Fig. 8 (a) and (b)]. It indicates that the motion of polymer chain was highly improved due to the phase separation. And the PU molecules partially or totally trapped into the epoxy network could also improve the capacity to deform plastically, which could also facilitate the toughness of thermosets.

3.6 Thermal stability of the epoxy thermosets

The thermal stability of thermosets was measured by thermogravimetric analysis (TGA). Fig. 9 shows the TGA and the differential thermal gravimetric (DTG) curves of all the epoxy thermosets. And the results are summarized in Table II.

As we can see from Fig. 9 (a), the initial decomposition temperatures ($T_{5\%}$) of all the modified thermosets, which correspond to the temperature when 5% of the initial weight is lost, increased by 19.4-26.8 °C compared with the neat epoxy. Similar tendency was observed in the temperatures at 10 wt% decomposition ($T_{10\%}$), but the degree of increase was smaller than $T_{5\%}$, which is related to the rapidly decomposition of the urethane linkages (NH-CO) of the PU molecular. Such an improvement in the $T_{5\%}$ and $T_{10\%}$ may be attributed to two factors: (a) the HBPU or LPU particles are surrounded by the epoxy matrix in the phase separation structures, which restricts the elimination of volatile segments and delays the thermal decomposition behavior[30], (b) higher cross-linking density of the epoxy phase in the modifier thermosets and the strong interaction among the PU molecular and epoxy network limit the thermal motion of epoxy networks.

Table II. TGA results of epoxy thermosets.

Sample	$T_{5\%}$ (°C)[a]	$T_{10\%}$ (°C)[b]	T_{max} (°C)[c]	Char yield at 600 °C (wt%)
Neat DGEBA	276.7	323.8	361.7	9.85
H5	297.9	330.8	360.2	9.74
H10	301.0	326.5	358.5	8.37
H15	296.6	327.1	361.4	8.78
L5	296.1	328.3	361.5	9.51
L10	301.8	326.4	358.8	9.05
L15	303.5	329.1	358.5	8.42

[a] The temperature at 5 wt% decomposition.
[b] The temperature at 10 wt% decomposition.
[c] The temperature of the maximum decomposition rate.

Fig. 9. (a) TGA and (b) DTG curves of HBPU, LPU and the epoxy thermosets with different modifier contents.

The DTG curves [Fig. 9 (b)] of all the thermosets are unimodal. The peak of the DTG curves corresponds to the degradation of the cross-linking network and the maximum degradation rate temperatures (T_{max}) remain similar for all the thermosets. It is also noted that there are some small fluctuations around 400 °C for the DTG curves of modified materials, which is related to the decomposition of the soft segments (C-C or C-O) in the PU molecular chain.

In typical phase-separated modified epoxy materials, improvement in toughness is often accompanied by the decreases in other thermomechanical properties. However, as previously shown, different phenomenon was observed in our epoxy thermosets. In order to explain the influence of HBPU on the properties of epoxy thermosets, schematic illustration of separate particles in the cured network of the DGEBA/HBPU thermosets is shown in Fig. 10. When adding HBPUs into the epoxy/amine system, most of them would separate out from the epoxy blends, which would facilitate the toughness characteristics. And plenty of hydrogen bonds and covalent bonds could strengthen the interfacial interaction, which benefited to the load transfer capacity with the surrounding networks. In addition, the cross-linking density of the epoxy phase can also be improved due to the covalent linkage between the HBPU and epoxy. Therefore, it is easy to understand that the toughness, E_r, T_g and thermal stability were simultaneously improved without coming at the cost of other mechanical properties in the DGEBA/HBPU thermosets.

Fig. 10. Schematic illustration of separate particles in the cured network of the DGEBA/HBPU thermosets.

3.7 Morphology analysis of the epoxy thermosets

The fracture surfaces of the thermosets, which were investigated by scanning electron microscopy, are presented in Fig. 11. It can be observed that the fracture surface of neat epoxy specimen [Fig. 11 (a)] shows homogeneous and smooth morphology without any sign of deformation, which confirms its poor impact strength. However, globular morphologies were observed on the fracture surface of modified thermosets. The second-phase particles were separated from the fracture surfaces after impact test, which left a lot of globular domains. It indicated the formation of separate phase structures in the modified thermosets. The cavitation of the particles affected the development of cracks and the plastic deformation of the matrix absorbed the impact energy, leading to a higher impact resistance of the modified samples.

Fig. 11. SEM images of impact-fractured surfaces of epoxy thermosets with different HBPU or LPU contents. (a: neat epoxy; b: the optical photograph of thermosets; c1, c2 and c3 for H5, H10 and H15, respectively; d1, d2 and d3 for L5, L10 and L15, respectively.)

The size of second particles is also important and it is well-known that the most effective particle diameters for secondary component used as toughener ranges from 100 nm to 10 μm [50-52]. Fig. 11 (c1-c3) show that the average diameter of micro-particles increased from 200nm to 500nm as the HBPU content increased, which confirms the rationality of introducing PTMG-1000 into the HBPU structure. It is also noted that the particle diameters of the DGEBA/LPU thermosets [Fig. 11 (d1-d3)] were bigger than that of the DGEBA/HBPU thermosets due to the aggregation of linear polyurethane molecular. And the samples containing HBPU showed better particle distribution due to the globular structure and lower viscosity, resulting in a higher fracture resistance than that of DGEBA/LPU thermosets. Furthermore, it can be observed from the optical photograph shown in Fig. 11 (b) that the epoxy thermosets became less transparent with increasing the HBPU content. This is because the higher HBPU content and bigger particles scattered the light to a larger extent [53]. So we can judge the extent of phase separation by observing the appearance of the epoxy samples.

4. Conclusion

In this paper, a hydroxyl-terminated HBPU and the analog LPU has been synthesized and used as modifiers for the epoxy thermosets. Rheometric measurement shows that the usage of HBPU wouldn't affect the processability of epoxy blends. The HBPU was more effective than LPU in toughening epoxy thermosets. And it is possible to improve three-fold impact resistance of the epoxy matrix by adding 10% HBPU. Moreover, the flexural strengths and glass storage modulus of DGEBA/HBPU thermosets were hardly influenced and higher than that of the DGEBA/LPU thermosets. In particular, the E_r and T_g of DGEBA/HBPU thermoset increased to some degree due to the improvement of cross-linking density. And the thermal stability of all the modified thermosets was also obviously improved.

The introduction of PTMG into the HBPU is of great benefit to the compatibility with epoxy resin before curing and lead to an appropriate particle size in the phase-separated thermosets. And a good phase separation structure with strong interface interaction was formed in the DGEBA/HBPU thermosets. Compared with the LPU and most of the hyperbranched polymers, this kind of HBPU significantly enhanced the impact strength and thermal properties of epoxy matrix without affecting processability and other mechanical properties to a large extent. Therefore, hydroxyl-terminated HBPU could be considered as a promising modifier in improving the toughness of epoxy thermosets.

Acknowledgments

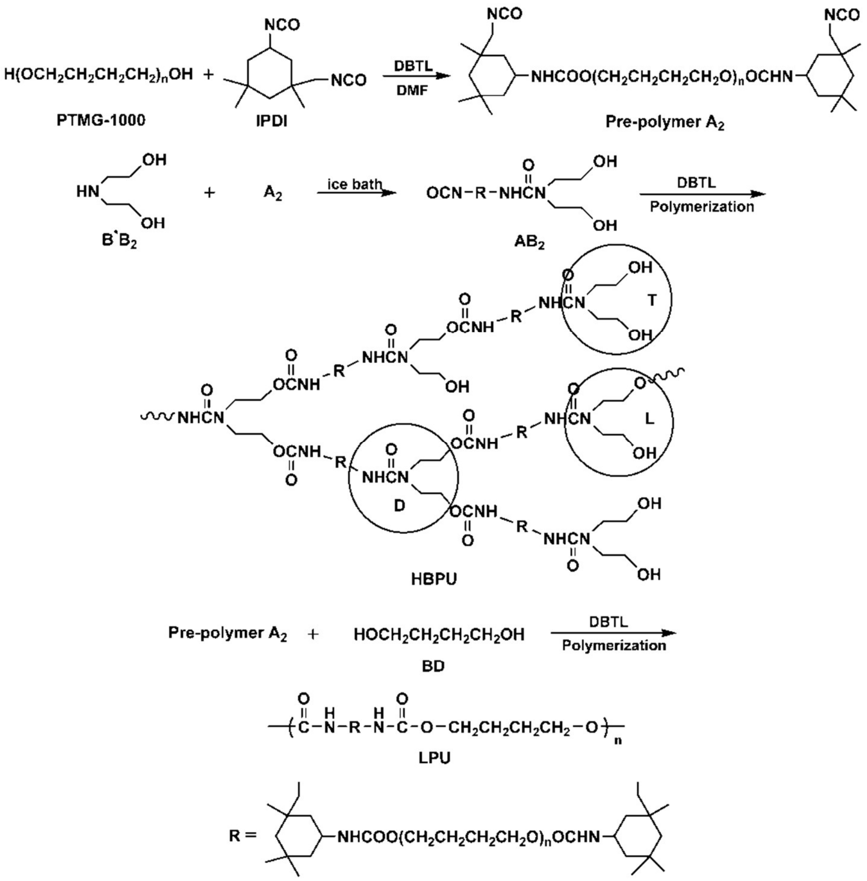
The authors express their gratitude to the financial support of the National Natural Scientific Foundation of China Projects (no. 21304081, 21404094 and 51273183). The authors also would like to thank Analytical & Testing Center of Sichuan University, P.R. China and Professor Zhang Junhua for the help of NMR and GPC characterization.

References

1. H. Lee and K. Neville, *Handbook of epoxy resins*, McGraw-Hill, New York, 2nd edn., 1982.
2. L. Gu, T. Wang, W. Zhang, G. Liang, A. Gu and L. Yuan, *RSC Adv.*, 2013, **3**, 7071-7082.
3. J. Xin, P. Zhang, K. Huang and J. Zhang, *RSC Adv.*, 2014, **4**, 8525-8532.
4. B. B. Johnsen, A. J. Kinloch, R. D. Mohammed, A. C. Taylor and S. Sprenger, *Polymer*, 2007, **48**, 530–541.
5. Y. Liang and R. Pearson, *Polymer*, 2010, **51**, 4880-4890.

6. X. L. Jiang and Y. Fan, *J. Appl. Polym. Sci.*, 2012, **124**, 2423-2429.
7. T. H. Hsieh, A. J. Kinloch, K. Masania, J. S. Lee, A. C. Taylor and S. Sprenger, *J. Mater. Sci.*, 2010, **45**, 1193-1210.
8. L. Boogh, B. Pettersson and J.A. E. Månson, *Polymer*, 1999, **40**, 2249-2261.
9. D. Ratna and G. Simon, *Polymer*, 2001, **42**, 8833-8839.
10. D. M. Dhevi, S. Jaisankar and M. Pathak, *Eur. Polym. J.*, 2013, **49**, 3561-3572.
11. G. G. Buonocore, L. Schiavo, I. Attianese and A. Borriello, *Composites Part B*, 2013, **53**, 187-192.
12. J.P. Yang, Z.K. Chen, G. Yang, S.Y. Fu and L. Ye, *Polymer*, 2008, **49**, 3168-3175.
13. L. Pan, S. Lu, X. Xiao, Z. He, C. Zeng, J. Gao and J. Yu, *RSC Adv.*, 2015, **5**, 3177-3186.
14. C. Acebo, X. Fernández-Francos, F. Ferrando, À. Serra and X. Ramis, *Eur. Polym. J.*, 2013, **49**, 2316-2326.
15. C. Acebo, X. Fernández-Francos, M. Messori, X. Ramis and À. Serra, *Polymer*, 2014, **55**, 5028-5035.
16. X. Miao, Y. Meng and X. Li, *Polymer*, 2015, **60**, 88–95.
17. X. Xiao, S. Lu, B. Qi, C. Zeng, Z. Yuan and J. Yu, *RSC Adv.*, 2014, **4**, 14928-14935.
18. T. Liu, Y. Nie, L. Zhang, R. Chen, Y. Meng and X. Li, *RSC Adv.*, 2014, **5**, 3408-3416.
19. C. Gao and D. Yan, *Prog. Polym. Sci.*, 2004, **29**, 183-275.
20. D. Zhang, Y. Chen and D. Jia, *Polym. Compos.*, 2008, **30**, 918–925.
21. L. Luo, Y. Meng, T. Qiu and X. Li, *J. Appl. Polym. Sci.*, 2013, **130**, 1064-1073.
22. T. Liu, Y. Nie, R. Chen, L. Zhang, Y. Meng and X. Li, *J. Mater. Chem. A*, 2015, **3**, 1188-1198.
23. P. G. Parzuchowski, M. Kiźlińska and G. Rokicki, *Polymer*, 2007, **48**, 1857-1865.
24. D. Ratna and G. P. Simon, *J. Appl. Polym. Sci.*, 2010, **117**, 557-564.
25. R. Mezzenga, C. Plummer, L. Boogh and J.-A. Månson, *Polymer*, 2001, **42**, 305-317.
26. J. P. Yang, Q. P. Feng, Z. K. Chen and S. Y. Fu, *J. Appl. Polym. Sci.*, 2011, **119**, 863-870.
27. H. Wu, J. Xu, Y. Liu and P. Heiden, *J. Appl. Polym. Sci.*, 1999, **72**, 151-163.
28. R. Mezzenga, L. Boogh and J.A. E. Månson, *Composites Science & Technology*, 2001, **61**, 787–795.
29. M. Flores, X. Fernández-Francos, E. Jiménez-Piqué, D. Foix, À. Serra and X. Ramis, *Polym. Eng. Sci.*, 2012, **52**, 2597-2610.
30. M. Flores, X. Fernández-Francos, F. Ferrando, X. Ramis and À. Serra, *Polymer*, 2012, **53**, 5232-5241.
31. S.L. Huang and J.Y. Lai, *Eur. Polym. J.*, 1997, **33**, 1563-1567.
32. K. H. Hsieh, J. L. Han, C. T. Yu and S. C. Fu, *Polymer*, 2001, **42**, 2491–2500.
33. D. Li, Y. Wang, Y. Liu, Z. Xie, L. Wang and H. Tan, *J. Appl. Polym. Sci.*, 2015, **132**.
34. S. Xia, Y. Liu, F. Pei, L. Zhang, Q. Gao, W. Zou, J. Peng and S. Cao, *Polymer*, 2015, **64**, 62-68.
35. B. Tang, X. Liu, X. Zhao and J. Zhang, *J. Appl. Polym. Sci.*, 2014, **131**.
36. A. R. Fornof, T. E. Glass and T. E. Long, *Macromol. Chem. Phys.*, 2006, **207**, 1197-1206.
37. M. Abdelrehim, H. Komber, J. Langenwalter, B. Voit and B. Bruchmann, *J. Polym. Sci., Part A: Polym. Chem.*, 2004, **42**, 3062-3081.
38. C. Gao and D. Yan, *Macromolecules*, 2003, **36**, 613-620.
39. H. Kalita and N. Karak, *Polym. Eng. Sci.*, 2012, **52**, 2454-2461.
40. C. Hawker, R. Lee and J. Fréchet, *J. Am. Chem. Soc.*, 1991, **113**, 4583-4588.
41. C. C. Riccardi and R. J. Williams, *J. Appl. Polym. Sci.*, 1986, **32**, 3445-3456.
42. L. Shechter, J. Wynstra and R. P. Kurkjy, *Ind. Eng. Chem.*, 1956, **48**, 94-97.
43. S. Gogoi, S. Barua and N. Karak, *Chem. Eng. Sci.*, 2015, **127**, 230-238.
44. H. Deka and N. Karak, *J. Appl. Polym. Sci.*, 2010, **116**, 106-115.
45. K. Ngai and C. Roland, *Macromolecules*, 1993, **26**, 2688-2690.
46. V. Pistor, F. G. Ornaghi, H. L. Ornaghi and A. J. Zattera, *Mater. Sci. Eng., A*, 2012, **532**, 339-345.
47. S. Pellice, D. Fasce and R. Williams, *J. Polym. Sci., Part B: Polym. Phys.*, 2003, **41**, 1451-1461.
48. J. H. Oh, J. Jang and S.H. Lee, *Polymer*, 2001, **42**, 8339-8347.

49. G. Pogany, *Br. Polym. J.*, 1969, **1**, 177-179.
50. R. A. Pearson and A. F. Yee, *J. Mater. Sci.*, 1991, **26**, 3828-3844.
51. A. Lazzeri and C. Bucknall, *J. Mater. Sci.*, 1993, **28**, 6799-6808.
52. S. Wu, Q. Guo, M. Kraska, B. Stühn and Y.W. Mai, *Macromolecules*, 2013, **46**, 8190-8202.
53. Y.Q. Li, S.Y. Fu, Y. Yang and Y.W. Mai, *Chem. Mater.*, 2008, **20**, 2637-2643.



Scheme 1.

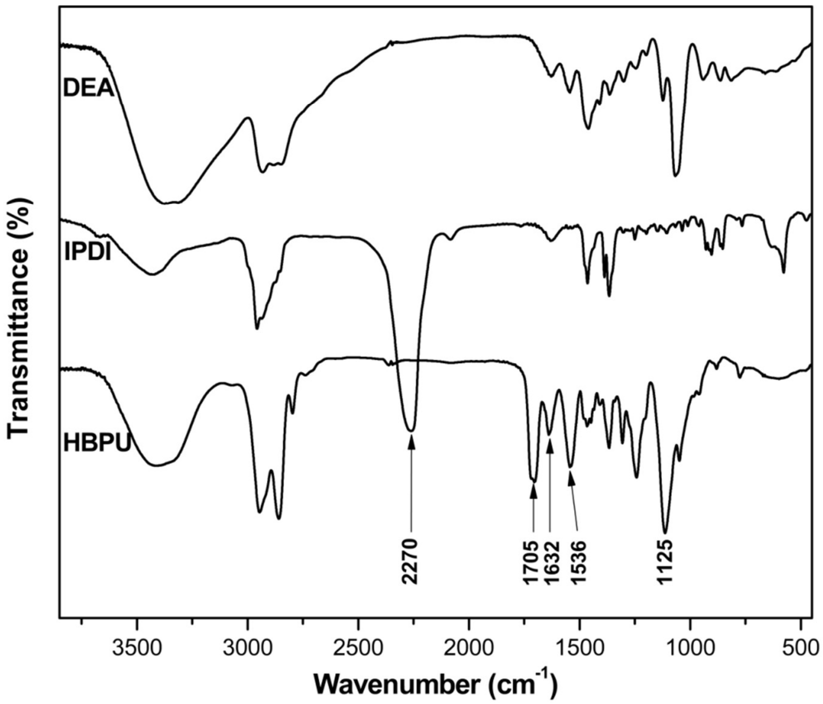
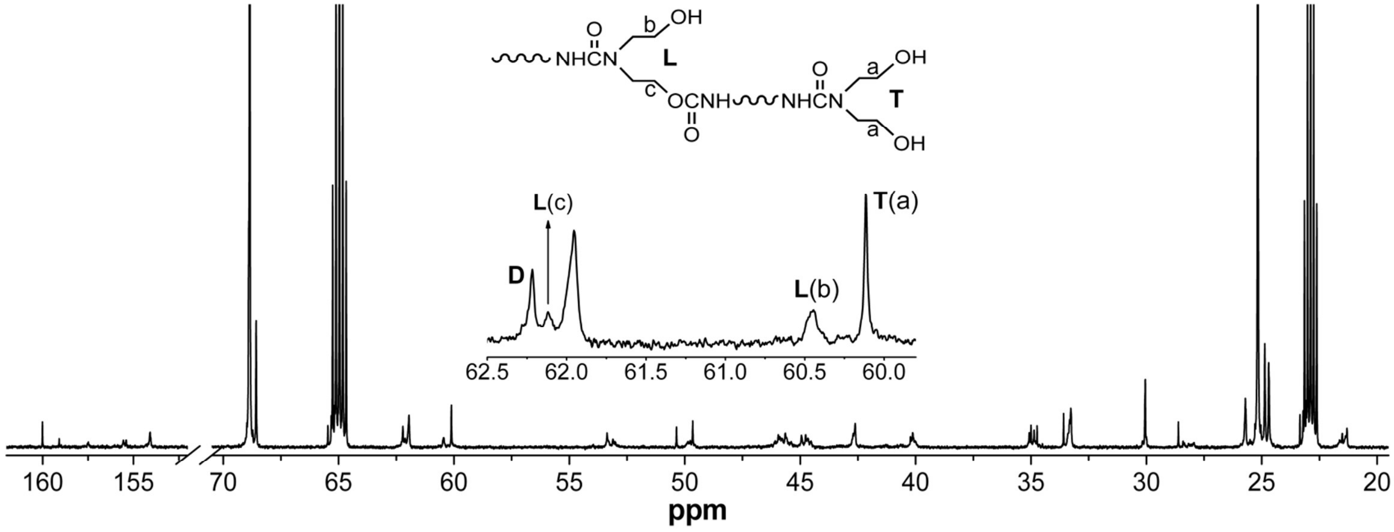
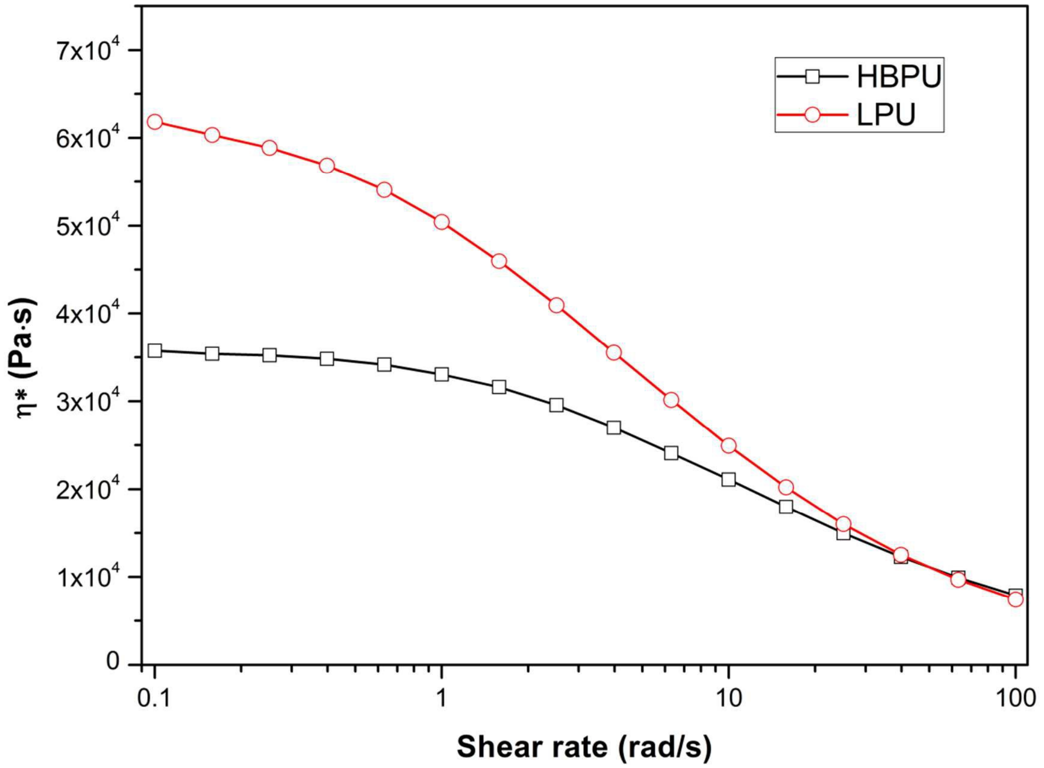


Fig. 1.



NHCN
O
b
OH
L
c
OCNH
O
NHCN
O
a
OH
T
a
OH
L(c)
T(a)
D
L(b)
62.5
62.0
61.5
61.0
60.5
60.0
160
155
70
65
60
55
50
45
40
35
30
25
20
ppm

Fig. 2.



HBPU
LPU
η* (Pa·s)
7x10^4
6x10^4
5x10^4
4x10^4
3x10^4
2x10^4
1x10^4
0
0.1
1
10
100
Shear rate (rad/s)

Fig. 3.

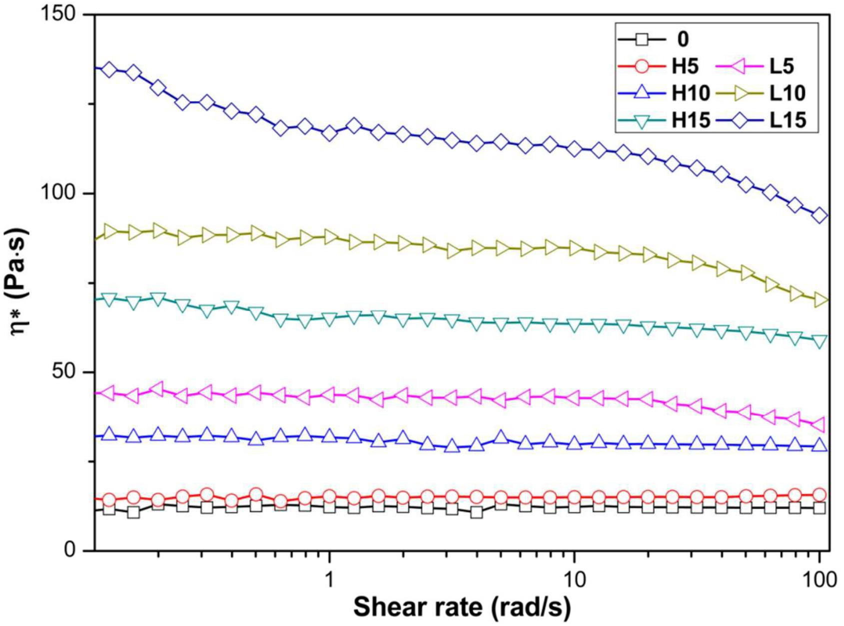


Fig. 4.

Fig. 5.

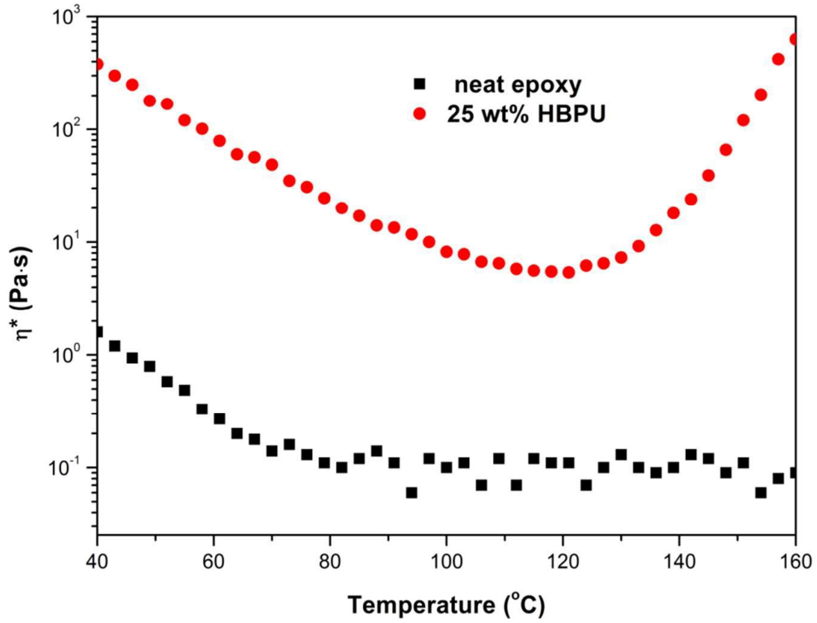
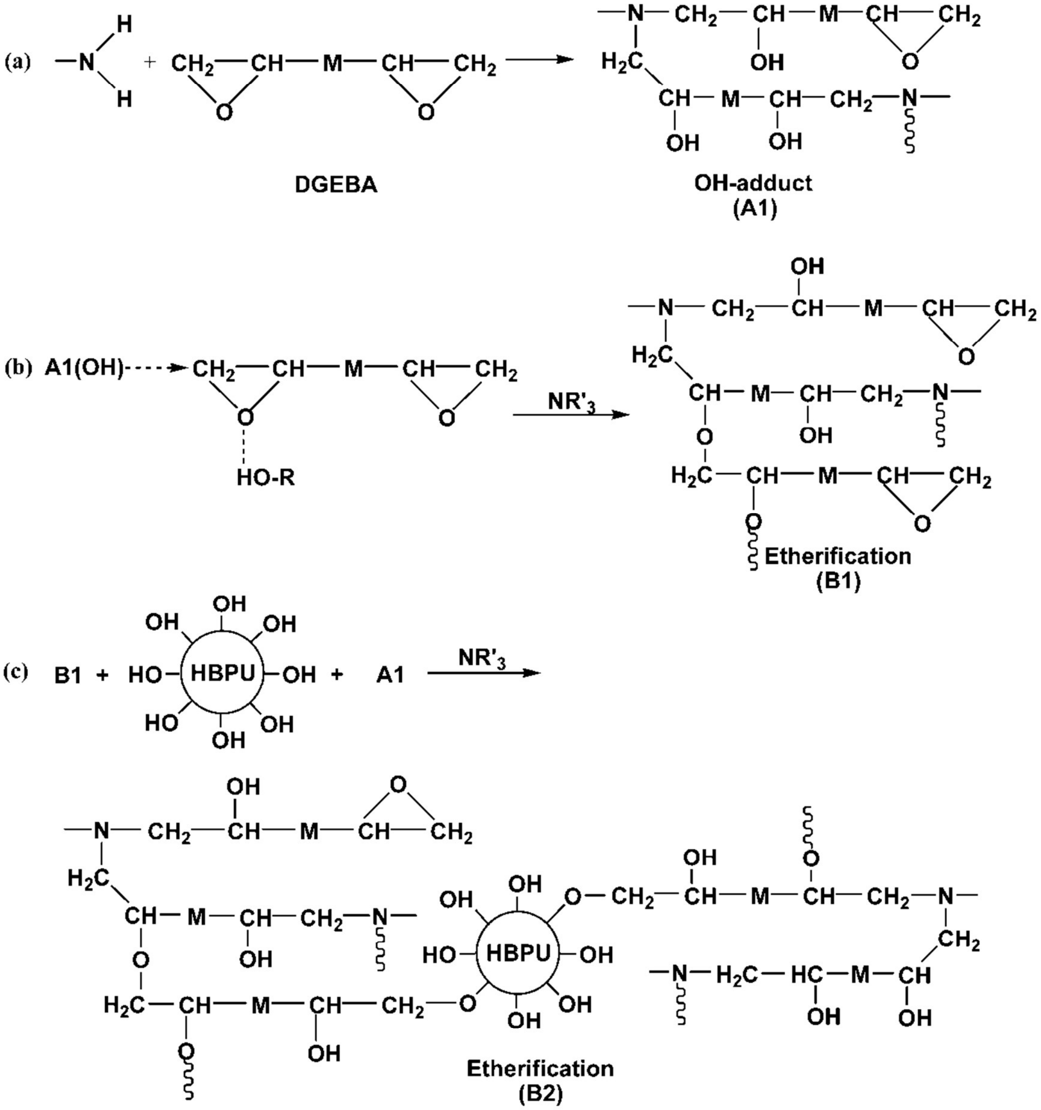


Fig. 6.


(a)
DGEBA
OH-adduct
(A1)
(b) A1(OH)
HO-R
NR'3
Etherification
(B1)
(c) B1 + HBPU + A1
NR'3
HBPU
Etherification
(B2)

Scheme 2.

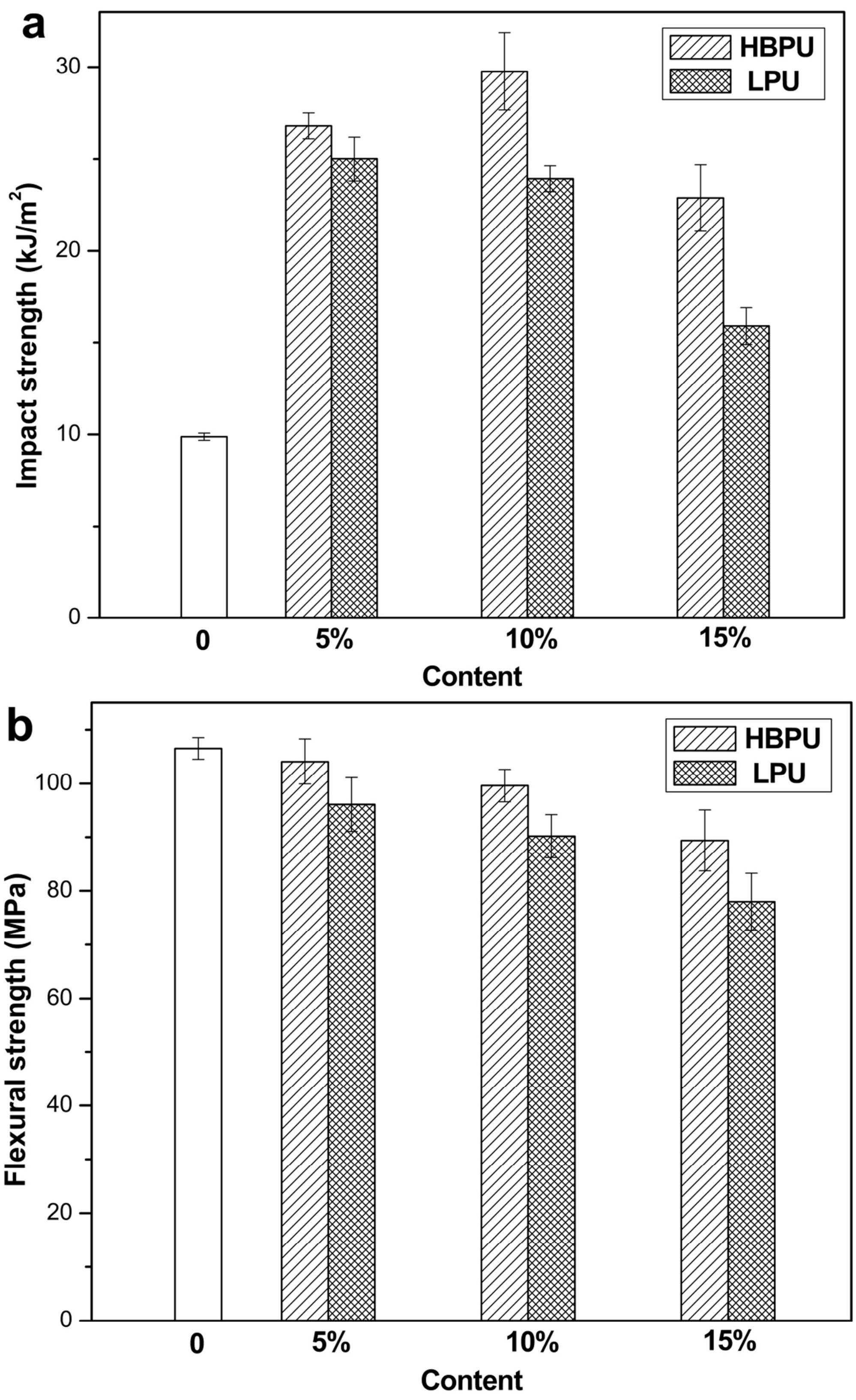

a
HBPU
LPU
Impact strength (kJ/m²)
0
10
20
30
0
5%
10%
15%
Content
b
HBPU
LPU
Flexural strength (MPa)
0
20
40
60
80
100
0
5%
10%
15%
Content

Fig. 7.

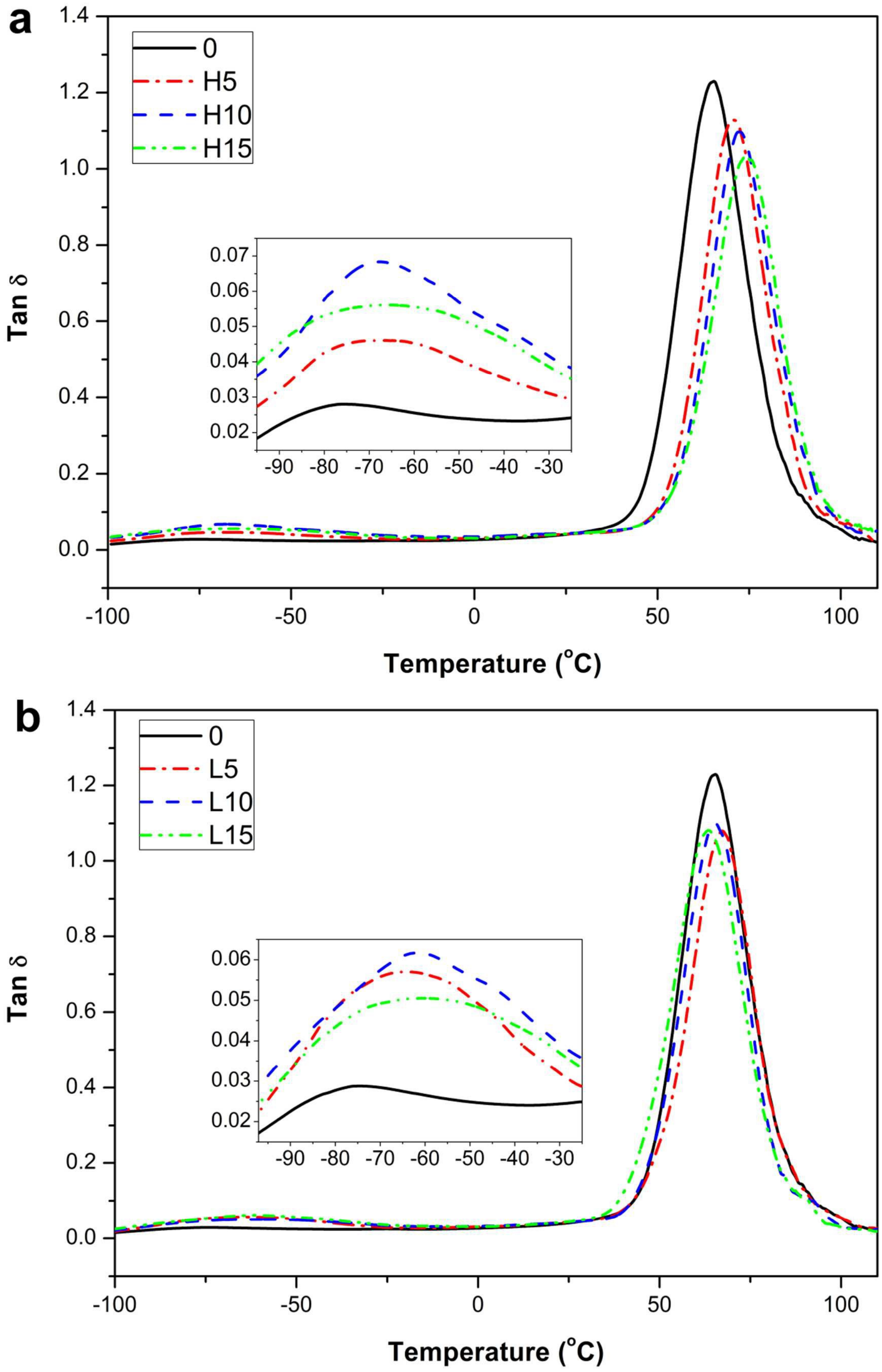

a
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
Tan δ
0
H5
H10
H15
0.07
0.06
0.05
0.04
0.03
0.02
-90 -80 -70 -60 -50 -40 -30
-100 -50 0 50 100
Temperature (°C)
b
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
Tan δ
0
L5
L10
L15
0.06
0.05
0.04
0.03
0.02
-90 -80 -70 -60 -50 -40 -30
-100 -50 0 50 100
Temperature (°C)

Fig. 8.

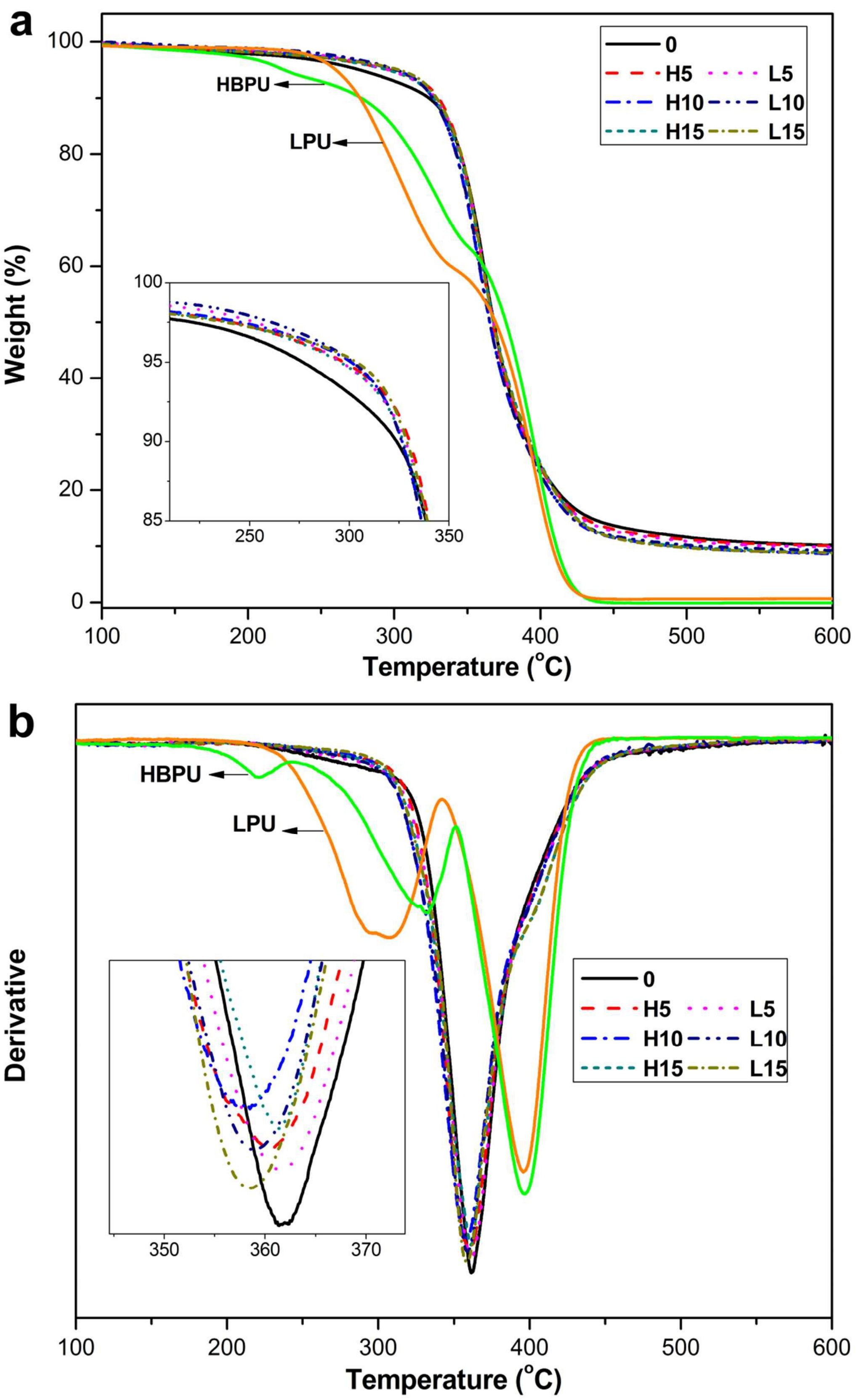

a
Weight (%)
100
80
60
40
20
0
100
200
300
400
500
600
Temperature (°C)
HBPU
LPU
0
H5
L5
H10
L10
H15
L15
100
95
90
85
250
300
350
b
Derivative
HBPU
LPU
350
360
370
Temperature (°C)

Fig. 9.

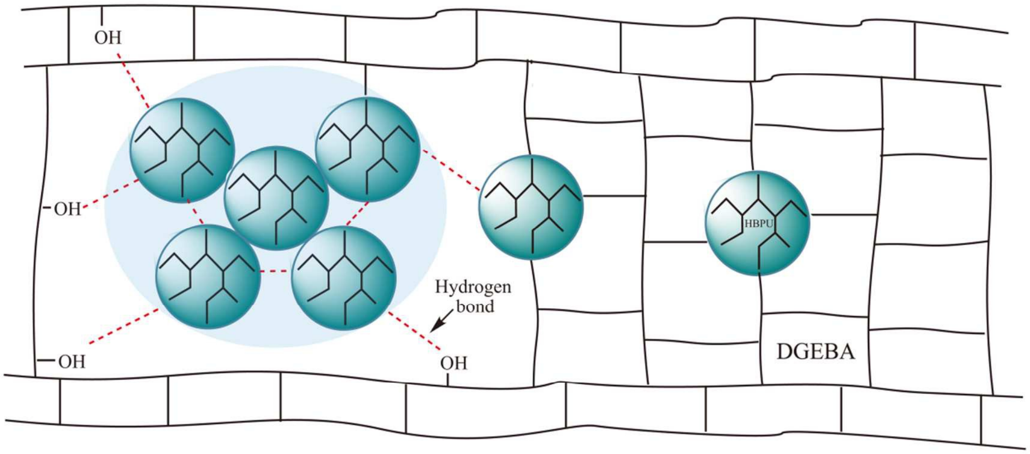

OH
OH
Hydrogen bond
HBPU
OH
OH
DGEBA

Fig. 10.

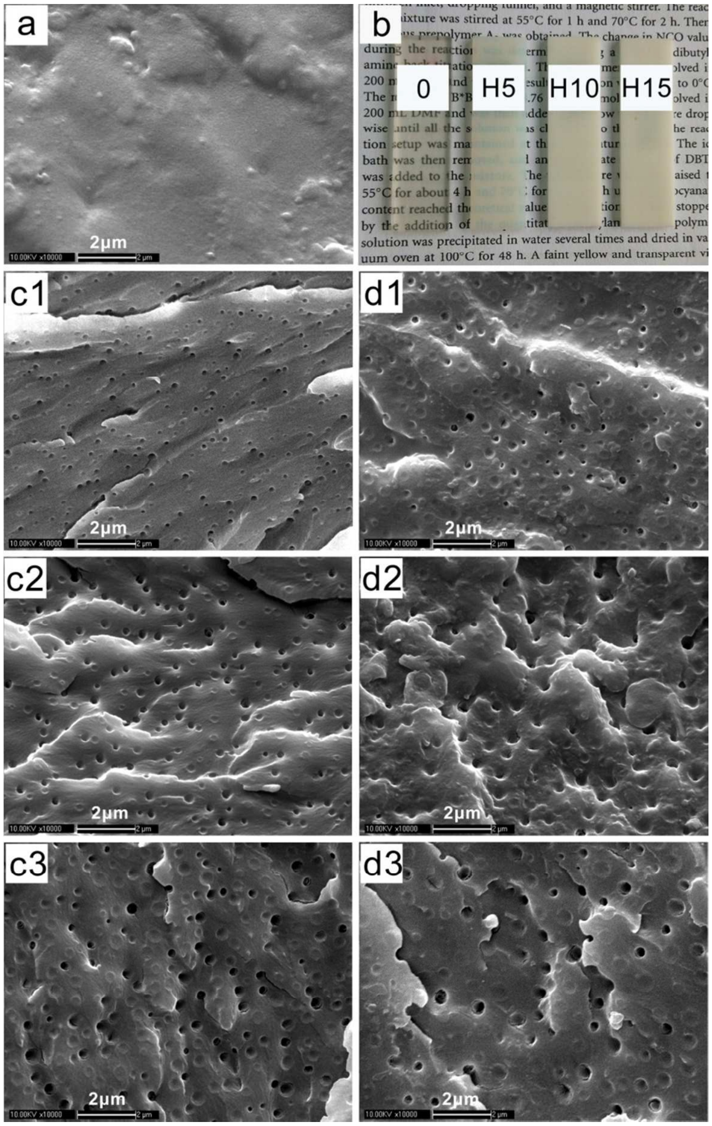
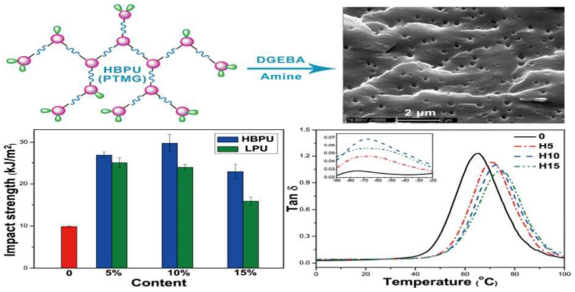

a
b
0
H5
H10
H15
c1
d1
c2
d2
c3
d3
2μm

Fig. 11.



Improvements in the toughness and thermal properties without affecting other mechanical properties in the hyperbranched polyurethane modified epoxy were demonstrated.