

Synthesis of Hyperbranched Polyester-Amides and Their Application as Crosslinkers for Polyurethane Curing Systems

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ABSTRACT: A series of hyperbranched polyester-amides (S1, S2, S3) with trimethylolpropane as a core molecule were synthesized using core-dilution/slow monomer addition strategy. The products were characterized by FTIR, ¹³C NMR, GPC, TGA, hydroxyl value measurement, and viscosity measurement. The result showed that the hyperbranched polyester-amides synthesized had narrow molecular weight distribution and high degree of branching (DB). The hyperbranched polyester-amides synthesized were used as crosslinkers for polyurethane curing systems and the mechanical properties of

the polyurethane curing systems were investigated. It was found that the best tensile property and tear strength were obtained when the S2 were used as crosslinkers and the molar ratio of —OH and —NCO was 1 : 1. It was also found that the polyurethane curing systems had the highest hardness and *T_g* when the S3 were used as crosslinkers. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 121: 957–963, 2011

Key words: hyperbranched polyester-amide; polyurethane; crosslinker; mechanical property

INTRODUCTION

In recent years, dendrimers and hyperbranched (HB) polymers have attracted considerable attention in the field of polymer materials because of their remarkable properties, such as three-dimensional morphology, a large number of reactive end-groups, very high solubility, low intrinsic, and solution viscosity due to the lack of chain entanglement resulting from their compact molecular structure.^{1–3} Compared to the dendrimers, the HB polymers are less precise in the molecular structure, but can be synthesized in a one-pot process which make them relatively inexpensive, furthermore they possess many of the desirable properties for which the dendrimers are noted. Now HB polymers have been paid more and more attention.⁴ HB polymers can be synthesized by several different methods.^{5–7} The most common pathway is using classical condensation reaction. However, there are disadvantages to this method, as the HB polymers prepared using this method possess low regularity of molecular structure and broad molecular distribution.⁸ However, the properties of HB polymers are essentially determined by the molecular structure of obtained

polymers, therefore the controlled synthesis of the desired HB polymers is important to the systematic investigation of structure–property relationship of HB polymers.⁹ Some studies have demonstrated that the presence of core molecules in the preparation of HB polymers, could provide the products with narrow molecular weight distribution.^{9–11} Cheng¹² utilized kinetic models to investigate the influence of multifunctional core molecules on the preparation of HB polymers and found that it was dependent on discrepant polymerization mechanism.

Polyurethane materials have been widely applied in many areas, including coating, adhesives, foam, rubber, etc. Generally, the polyurethane are prepared using polyurethane prepolymers combined with chain extenders (short chain dibasic alcohol) and/or crosslinkers having a functionality of three or more. Similarly to the other polymer materials, the mechanical properties of polyurethane materials are largely dependent on the chemical crosslinking and the presence of secondary intermolecular force. The former depends on the crosslinker nature and the latter is created by the H-bonds, which link the carbonyl and amine group of adjacent chains.^{13–15} Thus, the type of crosslinkers used for preparing polyurethane strongly effects the mechanical properties of polyurethane materials. HB polymers that have a large number of active end-groups, high solubility, and low viscosity, are a very promising crosslinkers for using in polyurethane materials.

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Recently some papers dealing with the use of HB polymers in crosslinked materials have been published. Benthem¹⁶ used the hyperbranched polyester-amide as a crosslinker of carboxyl-containing polyester powder coating. It was found, surprisingly, that this powder coating gave smooth films of high quality with a high blister formation threshold. Nasar et al.¹⁷ synthesized an amine-terminated hyperbranched polyamide and using such polymer as a crosslinker in making polyurethane elastomers, the result showed that the mechanical properties of the elastomers were enhanced slightly (tensile strength increased from 7.8 to 10.9 MPa). Xia et al.¹⁸ studied the curing reaction and the mechanical performance of hyperbranched polyester/epoxy/anhydride curing systems and found that the mechanical properties of the curing systems were improved effectively. Cao and Liu¹⁹ prepared a series of novel hyperbranched polyurethane copolymers using hyperbranched polyester as a crosslinker and investigated the phase transition behavior and the morphology of the products. It was shown that these hyperbranched polyurethane copolymers were good polymeric solid–solid phase change heat storage materials.

Hyperbranched polyester-amides was introduced by DSM recently and have had some successful examples of applications.^{16,20} However, the hydroxyl-terminated hyperbranched polyester-amide hasn't been used in synthesizing polyurethane materials until now. This HB polymer has a large number of terminal hydroxyls, which can react with isocyanate groups of the polyurethane prepolymer and generate crosslinking network. In addition, it contains plenty of amide and ester groups which can create H-bonds via linking the carbonyl and amine groups of adjacent chains in the polyurethane network. Furthermore, it is envisioned that such crosslinked polymers may show novel properties as the crosslinker used possesses a three-dimensional morphology. In this article, the synthesis of the hydroxyl-terminated hyperbranched polyester-amides with narrow molecular weight distribution using core-dilution/slow monomer addition strategy was presented, and the mechanical properties of the polyurethane curing systems using the synthesized polymers as crosslinkers were also investigated.

EXPERIMENTAL

Materials

Succinic anhydride, trimethylolpropane (TMP), and diisopropanolamine(DIPA) were purchased from Chinese Medical Group (Shanghai, China). Dibutyltin dilaurate was purchased from Shanghai Chemical (Shanghai, China). Polyurethane prepolymer based on 4,4'-methylenebis phenylisocyanate (MDI) having

–NCO content of 4.9% was obtained from Shandong Mingfeng Coating (Jinan, China). All other chemicals were analytical-grade or high-reagent-grade.

Synthesis of hyperbranched polyester-amides (HBP)

The HBP were synthesized by polycondensation of AB₂-type monomer. In a single-necked flask, 13.32 g (0.1 mol) DIPA, 10.01 g (0.1 mol) succinic anhydride and 50 mL solvent *N,N*-dimethylacetamide (DMAc) were introduced. The mixture reacted under magnetic stirring for 3 h at room temperature, then removed the solvent via vacuum distillation and the AB₂-type monomer with one carboxyl group and two hydroxyl groups was obtained.

The 23.33 g (0.1 mol) AB₂-type monomer synthesized was dissolved using xylene and then was added dropwise to a four-necked flask which involved 60 mL xylene and 1.49 g (0.011 mol) TMP (core molecule) under vigorous stirring. The reaction mixture was heated and allowed to reflux for 8 h under nitrogen and the water generated was removed through a water separator in the reaction process. Then the solvent was removed via vacuum distillation and the Simple 1 (S1) was prepared. With the same synthesis method, changing the molar ratio of core molecule (C) and AB₂-type monomer (M) as 1 : 21, Sample 2 (S2) was prepared and changing the molar ratio of C and M as 1 : 45, Sample 3 (S3) was obtained. The synthetic route of HBP was shown in Figure 1.

Preparation of polyurethane curing systems

The mass of HBP with 1 g polyurethane prepolymer consumed was calculate according to the following equation²¹:

$$X = \frac{-\text{NCO}\% \times 56100 \times (-\text{OH} : -\text{NCO})}{42 \times [\text{OH}]} \quad (1)$$

In the eq. (1), *X* was the mass of HBP with 1 g polyurethane prepolymer consumed; –NCO% was the content of the isocyanate groups in the polyurethane prepolymer; –OH : –NCO was the molar ratio of the hydroxyl groups in the HBP and the isocyanate groups in the polyurethane prepolymer; [OH] was the hydroxyl value of HBP.

The calculated amount of polyurethane prepolymer, HBP/N, *N*-dimethylform amide (DMF) solution (HBP/DMF = 1/1, w/w), and dibutyltin dilaurate (5% weight of the prepolymer) were introduced into a single-necked flask equipped with a mechanical stirrer. After rapidly stirring in a thermostatic oil-bath at 60°C, the mixture was cast into the different molds for mechanical property measurements. Subsequently, all the molds were placed in a

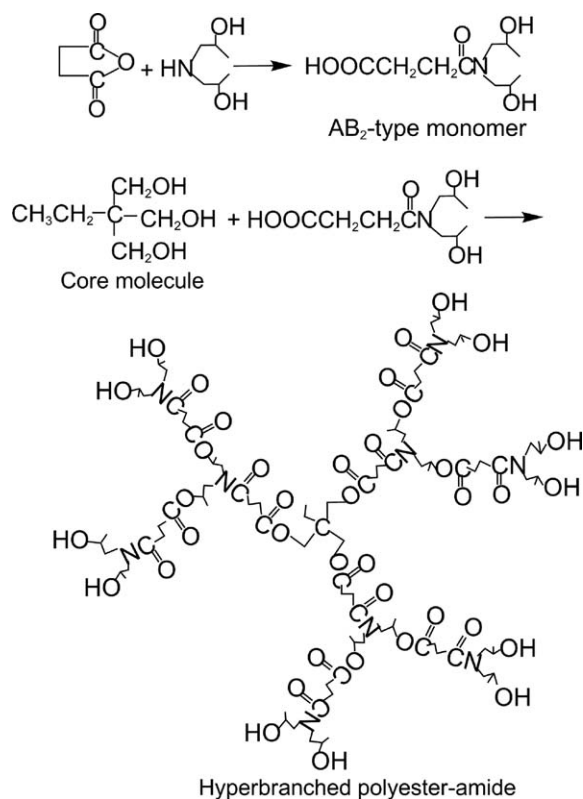


Figure 1 Synthetic process of hyperbranched polyester-amides.

vacuum oven and were cured at 70°C for 2 h, followed by postcure at 100°C for 9 h for the full conversion. Then the polyurethane curing systems using HBP as crosslinkers were prepared. The preparation route of the polyurethane curing system was shown in Figure 2. The test specimens were

placed in a dryer for 7 days at room temperature before mechanical property measurements. For simplicity, the polyurethane curing systems with different HBP were noted PU-S1, PU-S2, and PU-S3, respectively.

Measurements

Fourier transform infrared (FTIR) spectra in the range of $400\text{--}4000\text{ cm}^{-1}$ was recorded on a Firtensor 27 spectra. Samples were pressed into potassium bromide (KBr) pellets. ^{13}C NMR spectra were collected on a Bruker AV400 spectrometer using CD_3OD as solvent. Molecular weight and molecular weight distribution were measured by gel permeation chromatography (GPC, Waters-244 system). Polystyrene was used as stationary phase column. THF was used as the eluent and the flow rate was 1.0 mL min^{-1} . Viscosity was measured using a rotational viscosimeter (Shanghai Tianping Instrument Corp. 3[#] rotor, 60 r min^{-1}). Hydroxyl value was measured using the acetic anhydride/pyridine refluxing method.²² TGA (Perkin-Elmer Pyris Diamond) was used to analyze the thermodynamic property of HBP.

Tensile property measurement of the polyurethane specimens was carried out in accordance with GB 528-1998 (at a rate of 50 mm min^{-1}). Tear strength was measured in accordance with GB 529-1999 (at a rate of 50 mm min^{-1}). Measurements of tensile property and tear strength were carried out using an Instron Universal Testing Machine. Shore A hardness was measured according to GB 531-1992 using a LX-A rubber hardness tester (Yingkou Experimental material). Glass transition temperature (T_g) was determined using differential scanning calorimetry

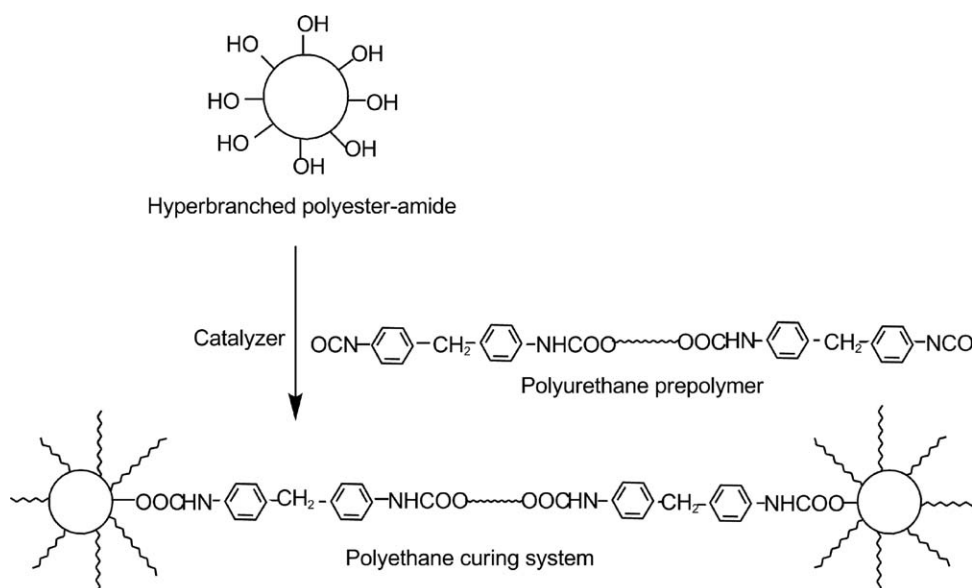


Figure 2 Preparation process of polyurethane curing systems.

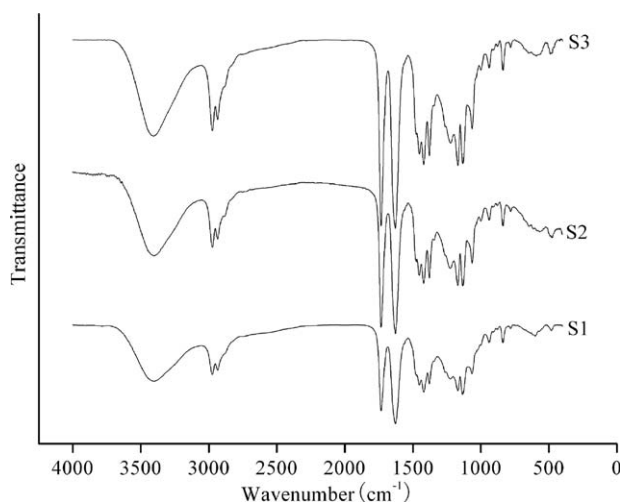


Figure 3 FTIR spectra of hyperbranched polyester-amides.

(DSC, Perkin-Elmer Diamond) at a heating rate of $10^{\circ}\text{C min}^{-1}$. The sample was heated from -120 to 200°C . For each type of mechanical property measurement, five specimens were made and the average value was calculated.

RESULTS AND DISCUSSION

IR spectroscopy analysis of HBP

Figure 3 represents the FTIR spectra of S1, S2, and S3. A strong absorption band is observed at 3300 –

3500 cm^{-1} , indicating the presence of numerous hydroxyl groups. The characteristic peaks at 2850 – 2970 cm^{-1} are assigned to the methyl and methylene groups. The ester group stretch occurs at 1740 cm^{-1} and the absorption at 1650 cm^{-1} is the vibration of the amide groups. The other FTIR absorption bands are due to C–H bending vibration 1350 – 1470 cm^{-1} , C–N stretching vibration (1138 cm^{-1}), and C–O stretching vibration (1050 cm^{-1}). The FTIR spectra of S1, S2, and S3 are quite similar because their chemical structures resemble each other.

^{13}C NMR spectroscopy analysis of HBP

The ^{13}C NMR spectra of S1 is shown in Figure 4. δ : 16.81, 20.16, methyl carbons; δ : 34.22, 37.04, methylene carbons; δ : 54.02, 56.37 C–N; δ : 63.86, 64.75, C–O; δ : 169.47, 171.72, 173.66, carbonyl carbons in amide groups; δ : 176.32, 178.44, carbonyl carbons in ester groups. The signals at 169.47, 171.72, and 173.66 should be attributed to the carbonyl carbons of dendritic (D), linear (L), and terminal (T) fraction, respectively (Fig. 4). The DB of hyperbranched polyester-amides can be calculated from the integration ratio of D, L, T using Fréchet's definition.²³ The DB of S1, S2, S3 are 0.68, 0.59, 0.46, respectively (Table I).

Molecular weight and molecular weight distribution of HBP

The data of GPC is summarized in Table I. It is shown that the molecular weights of the HBP

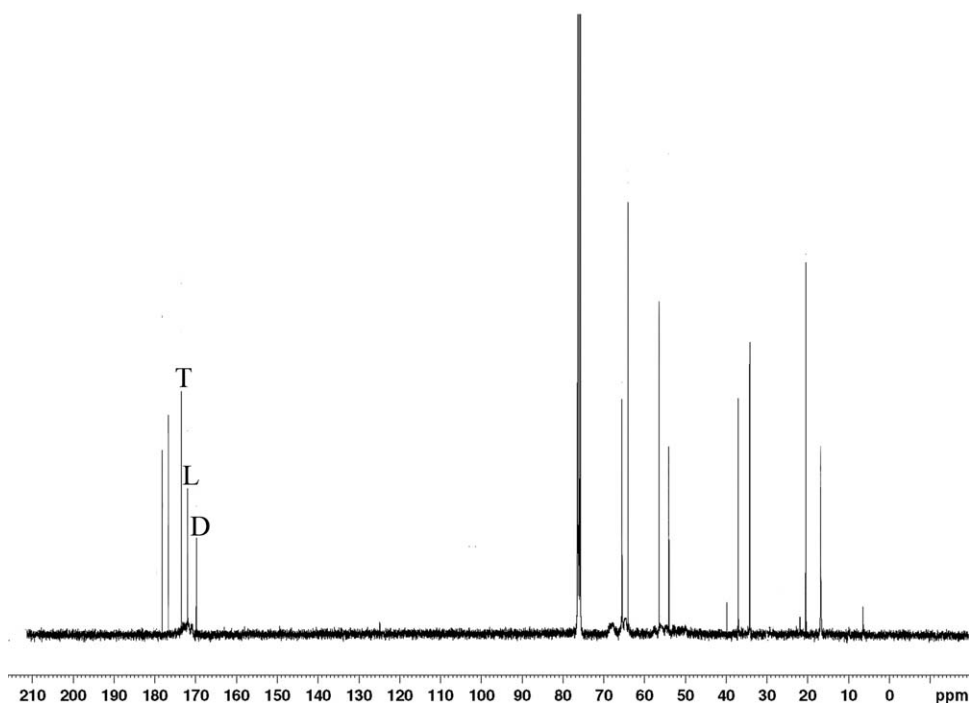


Figure 4 ^{13}C NMR spectra of the S2.

TABLE I
Measurements of Hyperbranched Polyester-Amides

Sample	Yield (%)	DB	M_n (g mol ⁻¹)	M_w (g mol ⁻¹)	PD	[OH] _t (mgKOH g ⁻¹)	[OH] _m (mgKOH g ⁻¹)	Viscosity (Pa S ⁻¹)
S1	90	0.68	1098	1307	1.19	325.47	329.12	0.71
S2	91	0.59	2021	2668	1.26	289.61	294.26	0.73
S3	93	0.46	3167	4434	1.35	274.55	279.31	0.77

PD: polydispersity(M_w/M_n); [OH]_t: theoretical hydroxyl value; [OH]_m: measured hydroxyl value; DB: degree of branching.

increase with reducing the molar ratio of core molecule and AB₂-type monomer. Generally, the measured molecular weight of the HB polymer using GPC is lower than its factual value. This is because the measurement method is based on linear polystyrene with the known molecular weight as a standard sample. However, the relationship between the molecular weight of the HB polymer and its hydrodynamic radius (R_h) is different from the relationship between the linear polymer molecular weight and its R_h . The R_h of the HB polymer is much smaller than the linear polymer with the same molecular weight. Therefore the linear polystyrene as a standard sample for GPC results in lower measured molecular weights of the HBP than their factual value. The corresponding polydispersities of S1, S2, and S3 are 1.19, 1.26, and 1.35, respectively. In an ideal case, the effect of core molecular functionality on the molecular weight distribution can be described by the following equation⁹:

$$PD = 1 + \frac{1}{f} \quad (2)$$

In the eq. (2), PD is the polydispersity; f is the core molecular functionality. In this study, the functionality of the core molecule is 3 and the ideal polydispersity according to eq. (2) is 1.33. The polydispersity measured for S1 and S2 are lower than the ideal value calculated while the value of S3 is a little higher than the ideal value. This reveals that the products synthesized possess low molecular weight distribution and relatively regular molecule structure due to the core dilute/slow monomer addition strategy. The results of theoretical analysis¹⁰ and computer simulation⁹ have demonstrated that using slow addition of AB_{*m*}-type monomers to B_{*f*} core molecules strategy to prepare hyperbranched polymers could provide products with controlled molecular weights, lower polydispersity and enhanced degree of branching. We also find that the polydispersity increases as the molecular weights increase, this maybe because the more by-products of low molecular weights were generated when synthesized the HBP of higher molecular weights.

Hydroxyl value and viscosity analysis of HBP

The hydroxyl value and the viscosity of the HBP are summarized in Table I. It is found that both the theoretical and experimental hydroxyl value decrease when the molecular weights of the HBP increase. The reason is that, with the increase of molecular weights, the number of terminal hydroxyl groups increase simultaneously, but the increase extent of the former is larger than the latter, therefore the hydroxyl value decreases. It is also observed that the experimental value is slightly larger than the theoretical value. The major cause may be that the products synthesized are not ideal spherical structure, and there are flaws and irregular structures in the molecules, hence the actual molecular weights are lower than the theoretical value and the experimental hydroxyl value is slightly larger than the theoretical hydroxyl value. But the difference is little, hence the structure of HB polymers synthesized are in accordance with theoretical structure.

The measured viscosity of S1, S2, and S3 is 0.71, 0.73, and 0.77 Pa S⁻¹, respectively. The viscosities of these products are much lower than the corresponding linear polymers with the same molecular weights due to the lack of chain entanglement resulting from their compact molecular structure. In addition, the viscosity of linear polymers increases rapidly with increasing molecular weights, but the viscosity of the HBP synthesized only increases slightly. The HBP synthesized possess an approximately spherical morphology, increasing the molecular weights, doesn't change the hydrodynamic volume much, so the viscosity is little changed.

Thermodynamic property of HBP

Figure 5 shows the TGA curves of S1, S2, and S3. The three curves are similar. The weight loss phenomenon before 76°C is mainly due to some residual solvent and small molecule by-products. The largest weight loss concentrates in about 300°C, which is the amide bond and ester bond rupture. The TGA result reveals that the HBP possess a good thermal stability.

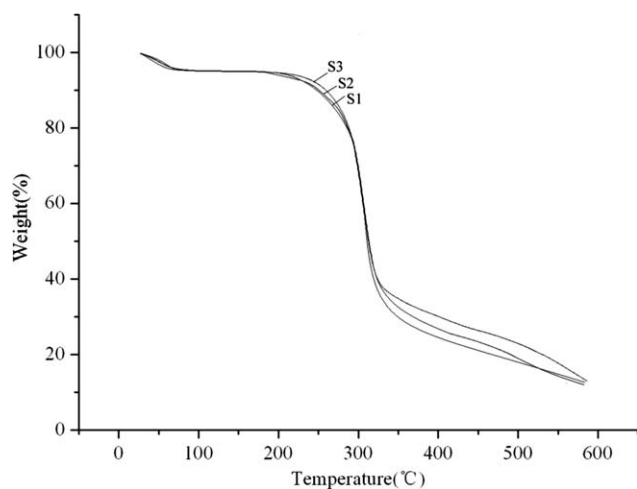


Figure 5 TGA curves of hyperbranched polyester-amides.

Tensile property of polyurethane curing systems

The tensile property of polyurethane curing systems with different HBP content and HBP of different molecular weights was measured and the results are

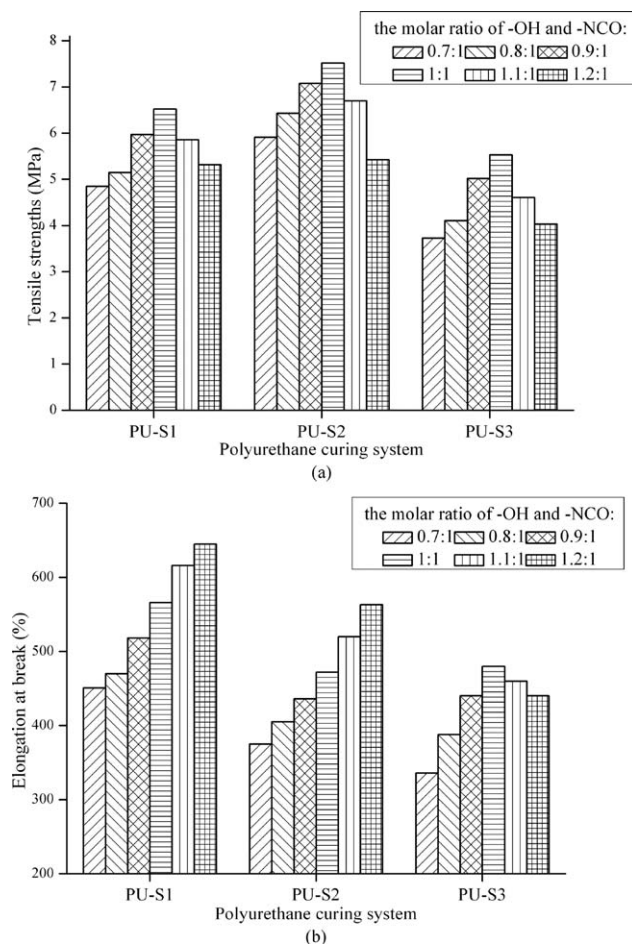


Figure 6 Tensile strength (a) and elongation at break (b) of polyurethane curing systems with different HBP content and HBP of different molecular weights.

TABLE II

Mechanical Property of Polyurethane Curing Systems

Test specimen	Tear strength (N mm^{-1})	Shore A hardness	T_g ($^{\circ}\text{C}$)
PU-S1	25.74	80	-55
PU-S2	31.53	82	-46
PU-S3	22.86	86	-38

The measurement was carried out using the formulation which the molar ratio of $-\text{OH}$ in HBP and $-\text{NCO}$ in polyurethane prepolymers was 1 : 1.

shown in Figure 6. Generally the tensile property is very sensitive to the amount of crosslinkers presented in the polymer. It is found that the tensile strength of polyurethane specimens [Fig. 6(a)] increases with the increase of the HBP content, reaching the maximum when the molar ratio of $-\text{OH}$ and $-\text{NCO}$ is 1 : 1, and then decreases as the HBP content further increases. The reason for this phenomenon is that the crosslinking density of the polyurethane network increases with the increase of HBP content. In addition, there are a lot of amide and ester groups in HBP which can create hydrogen bonds between the adjacent molecular chains and the number of hydrogen bonds also increases as the HBP content increases. These two factors contribute to the improvement of the tensile strength. However, higher concentration of the HBP results in reducing the tensile strength. This maybe due to presence of excessive HBP, which don't participate in crosslinking reaction and cause plasticization. We also find that the tensile strength of PU-S2 is greater than PU-S1 and PU-S3. With increasing molecular weights, the number of terminal hydroxyl groups exponentially increases, which enhances crosslinking in three-dimensional direction. But for higher molecular weights (G4), on account of having more terminal hydroxyl groups, may generate local gelation with the polyurethane prepolymer around a HBP molecule, which leads to a low diffusion coefficient in the polyurethane networks, hence the tensile strength decreases. The elongation at break [Fig. 6(b)] increases with the increase of HBP content. The HBP molecular chain is flexible, the number of flexible chain segments in the polyurethane network increase as the HBP content increases, so the elongation at break increases. It is also found that the elongation at break of PU-S1 is highest. The number of hydroxyl groups in S1 molecule is lowest, which leads to consumption of S1 as highest for polyurethane curing systems with the same molar ratio of $-\text{OH}$ and $-\text{NCO}$, therefore presence of more flexible chain segments in PU-S1 than the other two curing systems and resulting in the highest elongation at break of PU-S1.

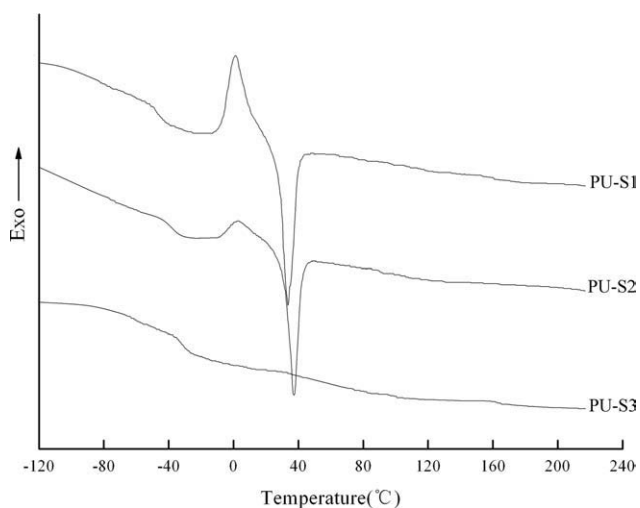


Figure 7 The DSC second run spectra of polyurethane curing systems.

Other mechanical property of polyurethane curing systems

Tear strength, hardness, and DSC analysis of the polyurethane curing systems with the HBP of different molecular weights were evaluated using the formulation which the molar ratio of $-OH$ and $-NCO$ was 1 : 1, since this formulation exhibited the best tensile property.

The value of tear strength, hardness, and T_g are summarized in Table II. It is found that the PU-S2 exhibits the highest tear strength. The incorporation of the 3D HBP imparts a 3D crosslinked network architecture. With the increase in molecular weights, the crosslinking density of the polyurethane curing systems in three-dimensional direction increases, hence the tear strength increases. The tear strength of PU-S3 decreases also due to gelation.

The PU-S3 exhibits the highest hardness. The reason is that the PU-S3 involves more hard chain segments than the other two curing systems, which is due to the lowest consumption of the crosslinker (S3); in addition, the crosslinking density of PU-S3 is higher than the other two curing systems.

The DSC second run spectra recorded for the polyurethane curing systems is shown in Figure 7. The T_g of PU-S1, PU-S2, PU-S3 is -55 , -46 , -38°C , respectively. For the curing system with the HBP of higher molecular weights, the T_g is shifted to higher temperature. It indicates that the curing systems will become more brittle (higher T_g). For PU-S1 and PU-S2, the endothermic melting peak and the exothermic crystallization peak of soft-segments are also visible.

CONCLUSIONS

Three type of hydroxyl-terminated hyperbranched polyester-amides (S1, S2, S3) with trimethylolpropane as a core molecule were synthesized. These polymer products possess low molecular weight distribution. Using the HBP as crosslinkers, the polyurethane curing systems were prepared and their mechanical properties were measured. The results show that the best tensile property and tear strength of the polyurethane curing systems were obtained when the S2 were used as crosslinkers and the molar ratio of $-OH$ and $-NCO$ was 1 : 1. It is also found that the polyurethane curing systems with S3 as crosslinkers exhibit the highest hardness and T_g . This study demonstrated the excellent potential of these hydroxyl-terminated hyperbranched polyester-amides as crosslinkers for polyurethane curing systems.

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