Preparation and Properties of Highly Branched Waterborne Poly(urethane-urea) via A_2 + B_3 Approach

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ABSTRACT: A series of highly branched waterborne poly(urethane-urea)s (HBWPUs) containing pendant carboxylate anion as the hydrophilic groups were prepared via A_2 + B_3 approach using isocyanate end-capped polycarbonatediols as an A_2 oligomeric monomer and triamine as a B_3 monomer. The structure of the products were characterized by FTIR and ^{13}C-NMR. The particle size, solution viscosity, thermal and mechanical properties were measured by photon correlation spectroscopy (PCS), rotational rheometer, differential scanning calorimetry (DSC), thermal gravimetric analysis (TGA), dynamic mechanical analysis (DMA) and tensile tests, respectively. It was found that the particles size mainly depended on the molar ratio of nNCO/nOH and the content of hydrophilic groups; the HBWPUs showed lower viscosity but higher T_g compared with linear waterborne polyurethane. The tensile testing, DMA measurements and rehological measurements revealed that the molar ratio of $[B_3]/[A_2]$ had significant influence on the viscosity and tensile strength. With increasing the molar ratio of $[B_3]/[A_2]$, both the viscosity and the tensile strength decreased. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 116: 817–824, 2010

Key words: highly branched; waterborne poly(urethane-urea); properties

INTRODUCTION

Highly branched polymers including dendritic, hyperbranched, and mutlibranched polymers have attracted more attention in recent years due to its unique structure and properties such as three-dimensional structure, low intrinsic viscosity, good solubility, and a large number of terminal functional groups.[1,2] Monodisperse, well-defined, and perfectly branched dendrimers are prepared by a stepwise growth procedure, but the stepwise nature of their synthesis makes large-scale production difficult since the growth of a single generation requires several reactions and purification steps.[3,4] However, irregularly branched and polydisperse hyperbranched polymers are synthesized by a one-pot polymerization of AB_x-type (x ≥ 2) monomers, which makes the large-scale synthesis possible at a reasonable cost. Therefore, hyperbranched polymers have being paid more attention in the science and industrial fields in recent years.[5]

Hyperbranched polymers were first introduced by Flory[6] in 1952. Flory presented hyperbranched polymers from a theoretical point of view, describing the intermolecular condensation of AB_x-type monomers.

Since Kim and Webster[7] reported the hyperbranched polyphenylenes in the early 1990s, many hyperbranched polymers had been prepared using condensation,[8] addition,[9] and ring-opening polymerization,[10] and so forth. But it is difficult to prepare the hyperbranched polyurethane in a conventional ways because of the inherent high reactivity of the isocyanate. First reports on the successful preparation of hyperbranched polyurethanes did not appear until 1993. Spindler and Fréchet[11] synthesized hyperbranched polyurethanes from the AB_2-type monomers which contained one hydroxyl group (A) and two blocked isocyanate groups (B). In the same year, Kumar and Ramakrishnan[12] reported the preparation of hyperbranched polyurethanes using an AB_2-type monomer 3,5-dihydroxybenzoyl azide in a Curtius type rearrangement. Azide chemistry was also utilized by others to prepare hyperbranched polyurethanes which were derived from AB_2-type monomers that contained very short ethylene oxide units.[13] Hong et al.[14] used the similar strategy to prepare hyperbranched polyurethane contained very short ethylene oxide units. A number of other synthetic strategies followed for preparing hyperbranched polyurethane, including high selective reactivity[15] and nonisocyanate ways.[16]

With the further studies recently, there had been an increasing interest in A_2 + B_3 systems because of the possibility that commercially available monomers might be important in industrial applications.[17]

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Hyperbranched and dendritic polymers typically had short distance between branching points, which did not enable entanglements.[18] The oligomeric A₂ and B₃ methodology offered a facile approach for obtaining products with improved properties and performance. Because the segments length of the highly branched polymers were sufficient for entanglements leading to enhanced mechanical properties.[19] Long[20,21] utilized isocyanate end-capped polyether as oligomeric A₂ and triamine or trimethylol as B₃ monomers to get different products. The resulting polymers displayed some mechanical properties. They also investigated the structure development in this procedure by experimental studies and kinetic Monte-Carlo simulations.[22] However, this approach had an inherent difficulty in controlling the polymerization reaction with respect to the premature gelation as predicated in Carother's and statistical mechanics equations.[23] This route needed a lot of solvent to avoid premature gelation. Recently, Yan[24,25] and Bruchmann[26,27] independently reported a new method to prepare hyperbranched polymers, which was called Couple-monomer methodology or $A_2 + CB_2$ approach. This strategy was based on the principle of nonequal reactivity of different functional groups. The rapid reaction between A and C led to the formation of AB_2-type monomer. Further polymerization of the compounds formed *in situ* gave a soluble hyperbranched polymer rather than a gel. Hyperbranched polyurethanes were prepared using the selective reaction of hindered isocyanates in a self-cross-linking reaction in an industrial scale.

The solvent-based polyurethane was becoming restricted by many regulations which were implemented to restrict solvent emissions (volatile organic compounds).[28,29] Therefore, the development of waterborne polyurethane had been motivated not only environmental considerations as nonpolluting systems but economical requests as well. Although many kinds of dendritic and hyperbanched polymers had been prepared, there was only a few reports on the highly branched waterborne polyurethane. So the aim of this article was to prepare highly branched waterborne polyurethane (HBWPUs) via $A_2 + B_3$ approach using isocyanate end-capped polycarbonatediols (PCDL) as an A₂ oligomeric monomer and triamine as a B₃ monomer. We controlled the degree of branching by varying the molar ratio of $[B_3]/[A_2]$. Dimethylolpropionic acid (DMPA) was the hydrophilic monomer, and the particle size was measured by photon correlation spectroscopy (PCS). The structure of the highly branched waterborne polyurethane was characterized by FTIR and NMR. The miscibility and properties of the HBWPUs films were evaluated by DSC, DMTA, respectively. Furthermore, the thermal and mechanical properties were measured by TGA and

tensile tests. And we compared the properties of the HBWPUs with that of the linear waterborne polyurethane (LWPUs).

EXPERIMENT

### Materials

All the chemical reagents were analytical grade. Polycarbonatediols (PCDL, $M_n = 1000$) were purchased from Asahi Kasei Chemicals Corporation, Japan. The diols were degassed in a round flask under vacuum at 80–90°C for 2 h before used. Trimethyllolprorane tris[poly(propylene glycol) amine terminated] ether (PTA) was obtained from Aldrich (USA). 2, 4-tolylene diisocyanate (TDI, Tianjin Yuanli Chemical, China), Dimethylolpropionic acid (DMPA, Heshibi Reagent, China), and catalyst dibutyltin dilaurate (DBTL, Tianjin NO.1 Chemical Reagent Factory, China) were used as received. N-methy-l-2-pyrrolidone (NMP, Sinopharm Group Chemical Reagent, China), terahydrofuran (THF, Tianjin Bodi Chemical, China) and isopropyl alcohol (IPA, Tianjin Bodi Chemical, China) were dried by 4 Å molecular sieves for 24 h before used.

Synthesis of highly branched waterborne polyurethane (HBWPU)

All the reactions were conducted in four-necked, round-bottom flasks equipped with an over head stirrer, thermometer, condenser and nitrogen inlet. A schematic representation of the synthesis route for HBWPUs was shown in Scheme 1. The isocyanate end-capped A₂ oligomeric monomer was formed through the reaction of PCDL, TDI and DMPA in bulk at 80°C for 2–3 h with 50ppm DBTL catalyst. Then, the prepolymer was cooled to room temperature and dissolved to form 20 wt % solution in THF/IPA (75/25 vol/vol). The carboxylic groups of the prepolymer were neutralized with triethylamine. The prepolymer solution was added dropwise into the 20 wt % B₃ solutions in THF/IPA (75/25 vol/vol) with an additional funnel. The reaction was conducted at room temperature and completed within 30 min to ensure very small reaction between IPA and isocyanate. During the reactions, the [B] was always excess, and gelation was not observed. The polymers were dispersed with deionized water at room temperature and the solvents were removed to obtain stable highly branched waterborne polyurethanes (solid content, 30 wt %).

The HBWPUs films were obtained by casting the dispersions on a polytetrafluoroethylene (PTFE) plate and allowing them to dry at room temperature for 5 days and the at 50°C for 2 days. After demolding, the films were submitted to vacuum drying for 24 h.
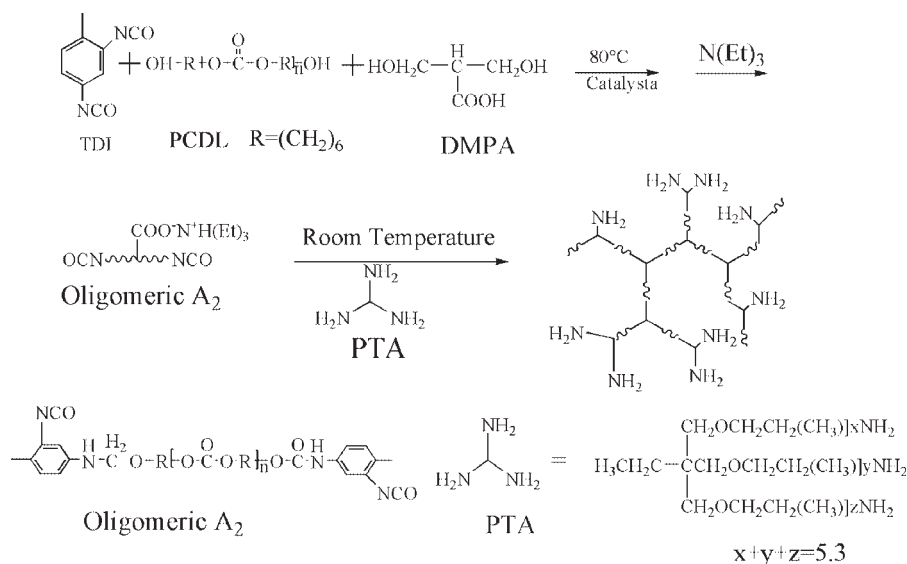
Scheme 1 Synthesis route for the highly branched waterborne polyurethane.

Synthesis of Linear Waterborne Polyurethane (LWPU)

All the reactions were conducted in four-necked, round-bottom flasks equipped with an over head stirrer, thermometer, condenser and nitrogen inlet. The isocyanate end-capped A_2 oligomeric monomer was formed through the reaction of PCDL, TDI and DMPA in bulk at 80°C for 2–3 h with 50ppm DBTL catalyst. Then, the prepolymer was cooled to room temperature and dissolved to form 20 wt % solution in THF/IPA (75/25 vol/vol). The carboxylic groups of the prepolymer were neutralized with triethylamine. The prepolymer solution was added dropwise into the ethanediamine solutions in THF/IPA (75/25 vol/vol) with an additional funnel. The reaction was conducted at room temperature and completed within 30 min to ensure very small reaction between IPA and isocyanate. During the reactions, the ethanediamine was always excess. The polymers were dispersed with deionized water at room temperature and the solvents were removed to obtain stable highly branched waterborne polyurethanes.

The LWPUs films were obtained by casting the dispersions on a polytetrafluoroethylene (PTFE) plate and allowing them to dry at room temperature for 5 days and the at 50°C for 2 days. After demolding, the films were submitted to vacuum drying for 24 h.

Measurements

A Fourier transform infrared spectrometer (Spectrum One, Perkin–Elmer) was used to identify the structure. Solid samples were dissolved in tetrahydrofuran, and were coated on KBr disks.

The ^{13}C-NMR spectra were measured by a VarianINOVA-600 NMR spectrometer at 150 MHz, using DMSO-d6 as solvent andtetramethylsilane as internal reference.

Gel permeation chromatography (GPC) measurements were conducted on an Agilent 1100 liquid chromatography–mass spectrometry at 30°C in THF with a flow rate of 1.0 mL/min using polystyrene standards.

Viscosity measurements and flow curves were obtained at 25°C with a rheometric scientifics rotational rheometer (NXS-11A, Chengou Instrument factory, China).

Particle size was determined by photon correlation spectroscopy (PCS; Autosizer Loc-Fc-963 apparatus, Malvern Instruments). The samples were diluted to an appropriate concentration and taken in a cuvette. The cuvette was placed in a sample holder and the temperature was maintained at 25°C. The samples were measured with 670-nm-wave-length laser light at a 90° scattering angle.

DSC thermograms were obtained on a Perkin–Elmer DSC-7 differential scanning calorimeter. Samples were placed in aluminum pans and measurements were performed under nitrogen atmosphere by raising the temperature from −60 to 150°C at a rate of 10°C/min.

TGA was performed under nitrogen atmosphere from 30 to 600°C at a heating rate of 10°C/min using a Perkin–Elmer TGA-7 thermogravimetric analyzer.

The tensile tests were performed on an electronic universal testing machine (Shenzhen Sans testing machine, China) at 20°C with a crosshead speed of 25 mm/min.

The modulus of HBWPUs samples were measured using DMA Q800-0637 instrument (TA instruments) in tensile mode at a frequency of 1 Hz and with a heating rate 3°C/min by scanning the films from
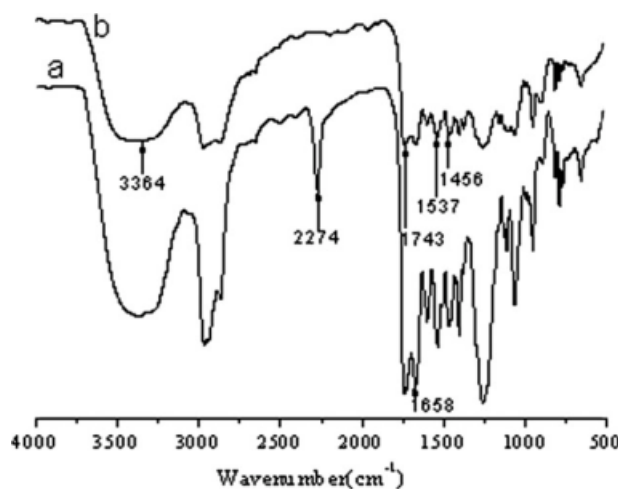
Figure 1 The FTIR spectra of the oligomeric anionomer (A₂) before (a) and after (b) added into the B₃ solutions.

$-60°C$ to $100°C$. Storage modulus (E') and tan δ as a function of temperature at a constant frequency were obtained.

RESULTS AND DISCUSSION

FTIR spectra analysis

It was known that the reactivity of NH groups with isocyanate was much different from OH groups with isocyanate, the amino could react with isocya-nate quickly at a lower temperature but hydroxyl couldn't[30] and all the reactions were completed within 30 min. So there were only a little reaction between IPA and isocyanate. The result could be approved by FTIR analysis. Figure 1 showed the FTIR spectroscopic analyzes of the synthesized waterborne polyurethane. The curve (a) was the FTIR spectrum of the oligomeric monomer (A_2), and curve (b) was the FTIR spectrum of A_2 after adding into the B_3 solutions. From the Figure 1(a), we could see that the absorption peak of NCO at 2274 cm^{-1} was very prominent before the A_2 was added into the B_3 solutions. When the reaction between A_2 and B_3 was completed, the NCO peak disappeared. In curve (b), the absorption peaks of the HBWPUs at $3364, 1743, 1537,$ and 1456 cm^{-1} were correspond to the functional groups of —NH—, —C=O, —COO—, —CNH, respectively. It proved the urethane groups were formed in the HBWPUs. Besides, the typical C=O in urea group appeared at 1658 cm^{-1}, which implied the formation of urea linkages.

¹³C-NMR analysis

NMR spectra were useful in polymer characterization and allowed us to have a deep insight into the structure of the polymer chains. Figure 2 showed the assignment of the ¹³C-NMR spectrum of the HBWPUs.The appearance of two peaks at $\delta = 156.58$ ppm and $\delta = 154.34$ ppm were assigned to the
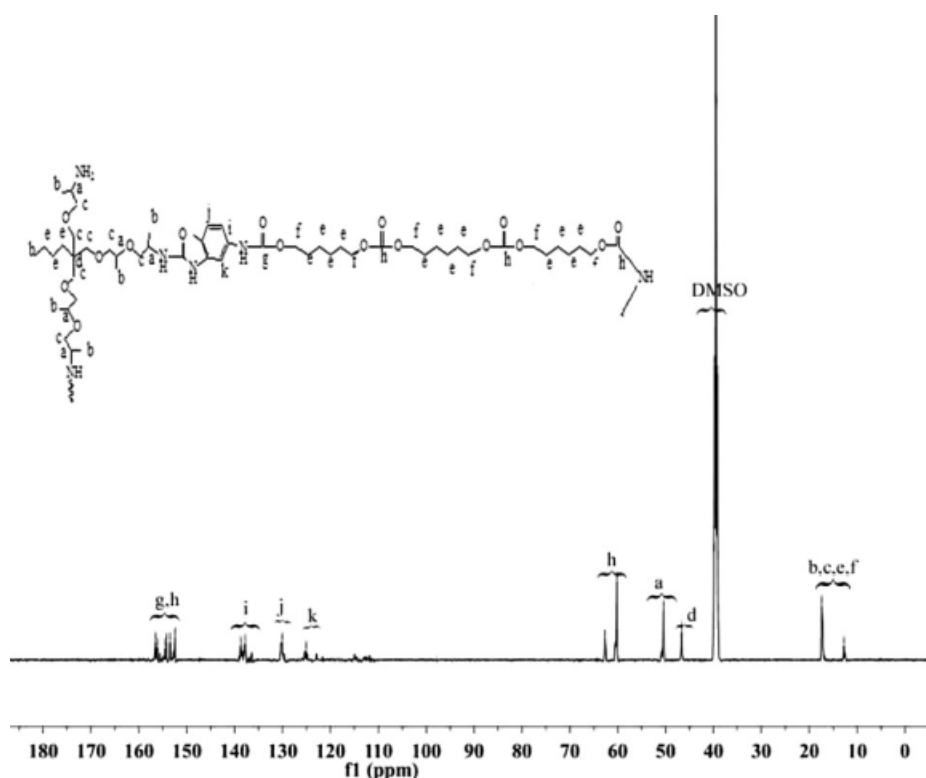
Figure 2 The ¹³C-NMR analysis of HBWPU.

TABLE I
The Molecular Weight of HBWPUs

Sample	nNCO/nOH	Content of DMPA[a]	$[B_3]/[A_2]$	M_w ($\times10^3$)	M_n ($\times10^3$)	PDI
HBWPU1	1.3	7 wt %	1.0	3.54	8.01	2.26
HBWPU2	1.3	7 wt %	0.9	3.87	8.82	2.28
HBWPU3	1.3	7 wt %	0.8	4.21	10.1	2.38
HBWPU4	1.1	7 wt %	1.2	7.6	24.6	3.48

[a] Content of DMPA = mDMPA / (mTDI + mPTA + mDMPA + mPCDL) × 100%.

carbonyl groups. The peak at $\delta = 154.34$ ppm corresponded to the functional groups of C=O from the urethane groups, signifying that the polyurethane was successfully synthesized, which was consistent with the FTIR spectroscopic analysis formerly described for the poly(urethane-urea). The peak at $\delta = 45.8$ ppm was related to the branched unit (quaternary carbon atom). The DB of highly branched polymer was usually calculated from ^{13}C-NMR analysis of model compounds. In our experiment, we chose PTA as branch monomer. As shown in Figure 1, there were more than two repeat units (OCH$_2$CH$_2$CH$_3$) between the end groups (NH$_2$) and branching points (quaternary carbon atom), as a result, the variation of amino-terminal groups had no influence on the chemical shift of quaternary carbon atom, so the change of quaternary carbon atom on the ^{13}C-NMR spectrum could not be observed and the DB could not be calculated. In our experiment, we could not determine the DB value and give direct evidence on the highly branched structure. Nevertheless, compared with LWPUs, the products obtained in our experiment showed lower viscosity, higher T_g value, superior tensile properties and improved thermal stability, which could give sufficient evidence that there were highly branched structure existed in the HBWPUs.

The Table I showed the molecular weights of HBWPUs. For the same content of DMPA and the same nNCO/nOH ratio, the number-average molecular weight (M_n) and the weight-average molecular weight (M_w) increased while the $[B_3]/[A_2]$ ratio falled. For the same content of DMPA, the M_w and the M_n were distinctly increased while the nNCO/nOH ratio decreased.

Particle size

As we knew that the waterborne polyurethane dispersions were two-phase systems. The continuous phase was water and the dispersed phase was solid polymer. The content of the ionic groups and the molar ratio of the nNCO/nOH had great influenced on the particle size of the waterborne ployurethane dispersions. The particle size had a direct effect on the dispersion stability, and the waterborne ployurethane dispersions with small particle size showed better storage stable and possessed high surface energy. The particle size of the HBWPUs were shown in Table II. For the same nNCO/nOH ratio, the particle size of the HBWPUs with higher DMPA content was much smaller. HBWPUs were amphiphilic polymers that ionic centers located on the surface of dispersed particles, whereas hydrophobic chain segments formed the interior of the particles. For the same content of the DMPA, the particle size of the HBWPUs increased and the appearance of the dispersions changed from transparence to milky with the increasing molar ratio of the nNCO/nOH. But the products couldn't be dispersed in water when the nNCO/nOH was 1.7 with the hard segment taking up 65.4 wt %. As seen from the Table

TABLE II
Chemical Composition and Particle Size of Highly Branched Aqueous Polyurethanes[a]

Sample	nNCO/nOH	Content of DMPA (wt%)	Hard segment content (wt %)[b]	Z average size (nm)
HBWPU5	1.1	5	30.3	30.5
HBWPU6	1.1	6	32.5	18.1
HBWPU7	1.1	7	34.8	14.7
HBWPU8	1.3	5	40.1	308
HBWPU9	1.3	6	42.8	127
HBWPU10	1.3	7	45.3	122
HBWPU11	1.5	7	54.6	186
HBWPU12	1.7	7	65.4	–[c]

[a] The molar ratio of $[B_3]/[A_2]$ = 1 : 1.
[b] Hard segment content = (m$_{TDI}$ + m$_{pPTA}$ + m$_{DMPA}$)/(m$_{TDI}$ + m$_{PTA}$ + m$_{DMPA}$ + m$_{PCDL}$) × 100%.
[c] The products couldn't be dispersed in water.
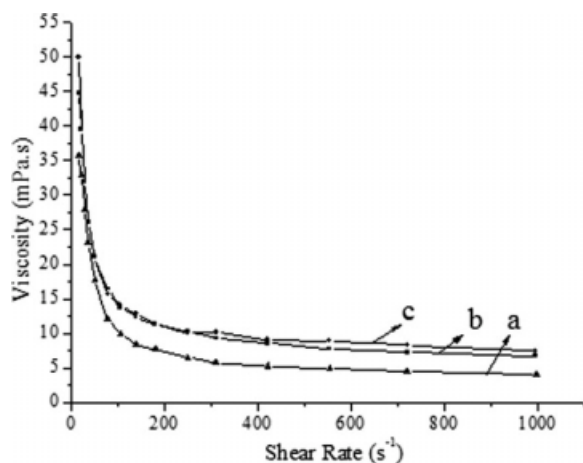
Figure 3 The solution viscosity of the HBWPUs variation as a function of the shear rate with different DMPA content. (a) 6 wt %, (b) 7 wt %, (c) 8 wt %, $[B_3]/[A_2] = 1:1$.

II, the HBWPUs were stable when the nNCO/nOH was 1.3 while the content of DMPA was 6 wt %.

Solution viscosity charateristics of HBWPUs

The effect of the DMPA content on the viscosity of the HBWPUs was shown in Figure 3. All the HBWPUs dispersion possessed a shear thinning behavior at 25°C at 30% solid content. When the ionic group content was 8 wt %, the HBWPUs showed hingher viscosity. It was due to an increase of the hydrophilic structure through the addition of more salt groups and urethane linkages. The viscosity of the HBWPUs was governed by the hydrophilicity in the same external conditions. An increasing amount of ionic groups in a dispersion led to
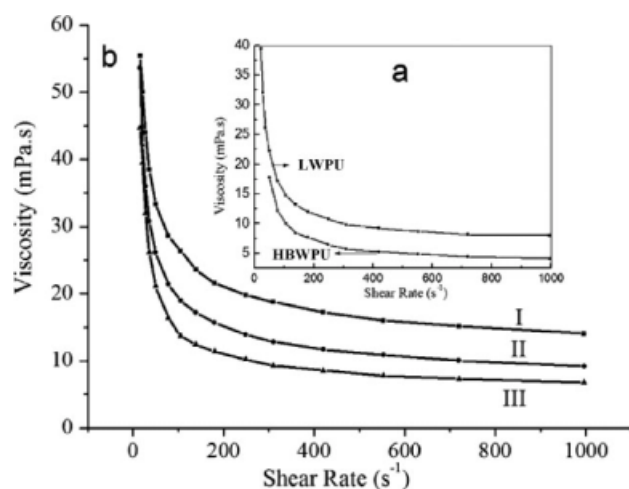

Figure 4 (a), the solution viscosity of the HBWPUs variation as a function of the shear rate with different molar ratio of $[B_3]/[A_2]$ (I, 0.8; II, 0.9; III, 1.0; DMPA, 6 wt %), (b) the flow curves of HBWPU and LAPU with the same chemical composition.

smaller particles and hence more particles. Generally, smaller particles led to larger hydrodynamic volumes and, therefore, induced higher viscosities.

As shown in Figure 4(a), the highly branched waterborne poly(urethane-urea) (HBWPU) showed lower viscosity compared with LWPU because of the three-dimensional structure and little chain entanglement. The molecular weight and the degree of branching (DB) of the HBWPUs increased with the molar ratio of the $[B_3]/[A_2]$ decreasing.[31] The number of the hydrogen bonds between NH_2 and $C=O$ groups increased in HBWPUs due to the increasing the number of NH_2 end groups. So we could observe from Figure 4(b) that the viscosity of the HBWPUs increased with the molar ratio of the $[B_3]/[A_2]$ decreasing.

DSC analysis

It was well known that the glass transition temperature (T_g) of the polymers was affected by a number of factors such as chain links, mobility and chain–chain interaction. These factors included molecular structure, molar mass, and nature of end groups. Figure 5 showed the DSC curves of HBWPUs and LWPUs. All the samples exhibited one glass transition temperature. As we expected, the HBWPUs showed higher T_g compared with linear analog. The chain mobility was restricted because of the highly branched structure of the HBWPUs. There were large amount of urethane and urea linkage and NH_2 end groups in the polymer. The number of the hydrogen bonds in the HBWPUs was higher than that of LWPUs. So the T_g increased. But the T_g didn't change obviously, and the T_g of the HBWPUs and LWPUs were −14.91°C, −16.71°C respectively. Because the polyurethane had hard segment and soft segment, and the T_g of soft segment depended on the degree of phase mixing. The HBWPUs had long chain between the branching points, and the
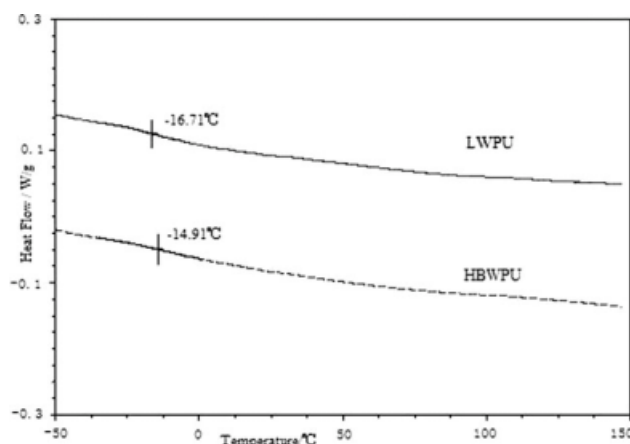
Figure 5 The DSC curves of HBWPU and LWPU.
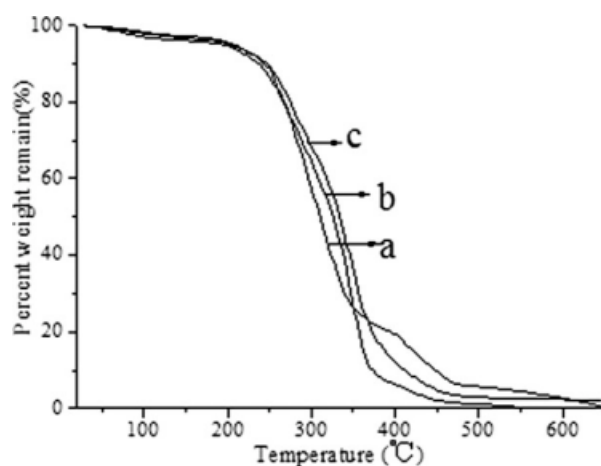
Figure 6 TG curves of HBWPU with variation in nNCO/nOH. (a) nNCO/nOH = 1.5, (b) nNCO/nOH = 1.3, (c) nNCO/nOH = 1.1.
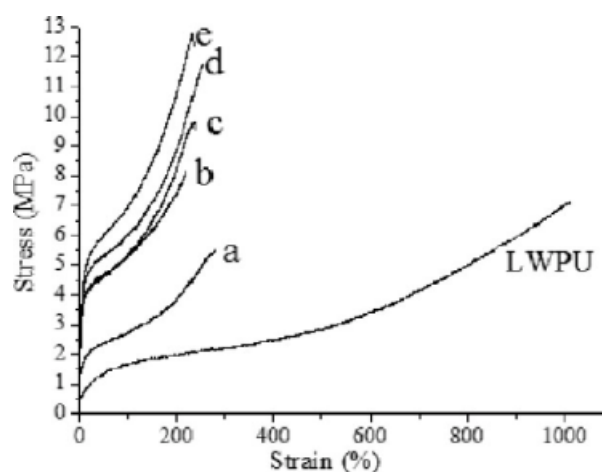
Thermal gravimetric analysis

The decomposition temperature of polyurethane was mostly influenced by the chemical structure of the component having the lowest bond energy. As shown in Figure 6, it was in the hard segment that the initial degradation happened, thus the first observable weight loss occurred through the degradation of the urea groups at 100°C. And the second step was the degradation of urethane at 200°C. It was found that the degradation temperature decreased with the increasing hard segment content. It indicated that the thermal stability of HBWPUs decreased due to the increasing of hard segment content. The temperature at 10 and 40% weight loss of HBWPUs samples were listed in Table III.

Tensile properties

Stress–strain curves for LWPU and highly branched waterborne polyurethanes were shown in Figure 7. The LWPU, which contained 43% hard segment, was an elastomer with tensile strength of 7.12 MPa, and an elongation at break value of 1011%. All the

TABLE III
Temperature at 10 and 40% Weight Loss of HBWPU Samples

Samples	nNCO/nOH	Temperature at 10% weight loss	Temperature at 40% weight loss
HBWPU13	1.1	245°C	318°C
HBWPU14	1.3	232°C	309°C
HBWPU15	1.5	245°C	298°C

Figure 7 Stress–strain curves of LWPU and HBWPU of 7 wt %-dimethylolpropanic acid with different $[B_3]/[A_2]$ ratios. (a) 1.2, (b)1.1, (c) 1.0, (d) 0.9, (e) 0.8.

HBWPUs showed a better tensile strength but weaker elongation at break because of the highly branched structure. With decreasing the molar ratio of $[B_3]/[A_2]$, the tensile strength increased. When more oligomeric A_2 was added, the degree of branching (DB) and molecular weight of HBWPUs increased. The intermolecular interactions including
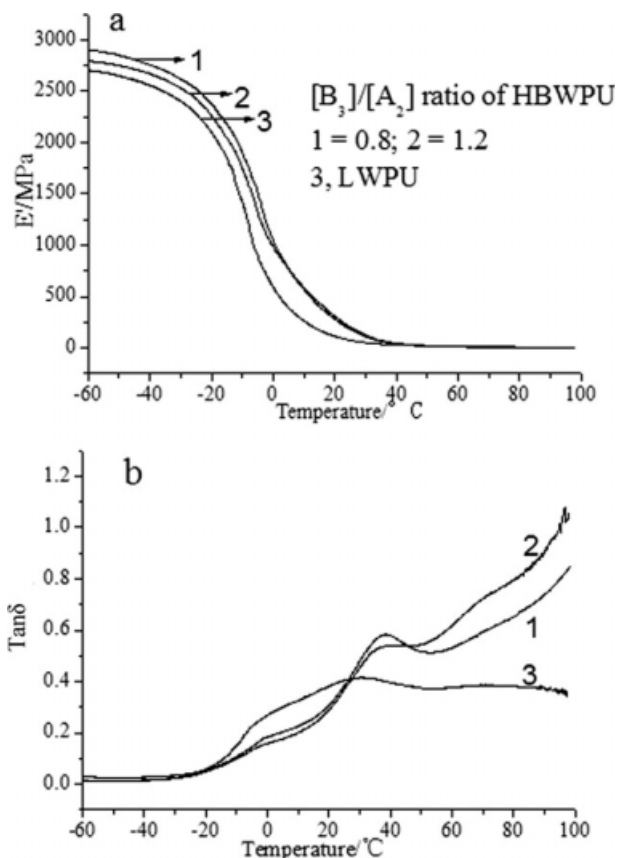
Figure 8 Dynamic mechanical analysis plots of HBWPU with different $[A_2]/[B_3]$ ratio and LWPU.

the intermolecular force and hydrogen bonds were enhanced because of the higher molecular weight and large amounts of NH_2 end groups per macromolecule. The tensile strength and elongation at break were 6.2MPa and 274% while the molar ratio of $[B_3]/[A_2] = 1.2$. And the tensile strength increased to 12.76 MPa while the molar ratio of $[B_3]/[A_2] = 0.8$, but the elongation at break decreased to 235%.

DMA analysis

Figure 8 presented DMA data of HBWPUs and LWPUs samples, where the temperature versus storage modulus (E') curves were shown in (a) and the temperature versus tan δ curves were shown in (b). The LWPUs had the same hard segment. As shown in Figure 8(a), The T_g of the three samples were −16.03°C, −18.69°C, −18.47°C respectively. When the $[B_3]/[A_2] = 1.2$, the T_g was higher than that of LWPUs, which was consistent with the DSC analysis. But the DB was lower when the $[B_3]/[A_2] = 1.2$, so the sample showed similar T_g with LWPUs. As expected, the storage modulus of HBWPUs samples was higher than that of LWPUs samples because of the highly branched structure. With decreasing the molar ratio of $[B_3]/[A_2]$, the modulus of HBWPUs increased. This behavior must be associated with the hydrogen bonds concentration and DB value in the polymers. The DB increased while the $[B_3]/[A_2]$ decreased, and large amounts of NH_2 end groups formed per macromolecule. As was well known, the ─NH groups formed a hydrogen bond with the carbonyl groups (C=O) of the hard and soft segment.

In Figure 8(b), the samples showed two broad damping peaks around −20 and 40°C, which indicated that samples had phase separated morphology, and these temperatures were the glass transition temperatures of soft and hard segment domains, respectively.

CONCLUSION

A series of HBWPUs were successfully prepared via $A_2 + B_3$ approach. DMPA was the hydrophilic monomer, the particle size decreased while the content of DMPA increased and the nNCO/nOH decreased. The particle size of the HBWPUs was about 126.5 nm when the nNCO/nOH was 1.3 and the content of DMPA was 6 wt %. The structure of the products was characterized by FTIR and ^{13}C-NMR respectively. Compared with the LWPUs, the HBWPUs showed lower solution viscosity but higher T_g, tensile strength and storage modulus. The molar ratio of $[B_3]/[A_2]$ had a great influenced on the viscosity, tensile strength and storage modulus. With decreasing the molar ratio of $[B_3]/[A_2]$, the so-lution viscosity increased and the solution viscosity was also affected by the content of DMPA because of the small particle size formed. The tensile strength increased from 6.2 to 12.6 MPa with the $[B_3]/[A_2]$ varied from 1.2 to 0.8. When the $[B_3]/[A_2]$ decreased, the DB increased and large amounts of NH_2 end groups were introduced, so the modulus of the HBWPUs was improved. The TGA showed that the HBWPUs were stable until 100°C when the degradation of the urea groups started.

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