Polym. Bull. (2010) 64:877–890
DOI 10.1007/s00289-009-0178-0

ORIGINAL PAPER

Synthesis and properties of highly branched poly(urethane–imide) via $A_2 + B_3$ approach

Dan Liu · Shaomin Zeng · Qian Hu · Changfeng Yi · Zushun Xu

Received: 7 June 2009 / Revised: 4 August 2009 / Accepted: 27 September 2009 /

Abstract A series of highly branched poly(urethane–imide) (HBPUI) were synthesized via $A_2 + B_3$ approach using isophorone diisocyante (IPDI), polycarbonatediol (PCDL), 3,3′,4,4′-Benzophen-onetetracarboxylic dianhydride (BTDA), and poly(oxyalkylene) triamine (ATA) as materials. The structure of the products was characterized by FT-IR and ^{13}C-NMR. The molecular weights were characterized by gel permeation chromatograph (GPC). The solution viscosity, thermal, and mechanical properties were measured by rotational rheometer, differential scanning calorimetry (DSC), thermal gravimetric analysis (TGA), tensile tests, and dynamic mechanical analysis (DMA), respectively. The HBPUI showed lower viscosity than that of linear poly(urethane–imide) (LPUI), nevertheless T_g of HBPUI was higher than that of LPUI. TGA indicated that the thermal degradation of poly(urethane–imide) occurred above 300 °C, which was higher than conventional polyurethane. The tensile strength of HBPUI was obviously improved by increasing the content of BTDA and the molar ratio of $[A_2]/[B_3]$. The effects of the content of BTDA and the molar ratio of $[A_2]/[B_3]$ on the storage modulus of the polymers were also studied.

Keywords Highly branched · Poly(urethane–imide) · Synthesis · Properties

---

D. Liu · S. Zeng · Q. Hu · C. Yi · Z. Xu
College of Materials Science and Engineering, Hubei University, Wuhan 430062,
People's Republic of China

Z. Xu (✉)
Ministry-of-Education Key Laboratory for the Green Preparation and Application of Functional Materials, Hubei University, Wuhan 430062, People's Republic of China
e-mail: zushunxu@hubu.edu.cn

Introduction

Polyurethane was one of the most important industrial materials due to its excellent abrasion resistance and mechanical properties. It was widely utilized in the field of coatings, adhesives, thermoplastic elastomers, and so forth [1, 2]. Unfortunately, the conventional polyurethane was known to exhibit weak mechanical properties and poor heat resistance. In general, its acceptable mechanical properties rapidly vanished at 80–90 °C, and thermal degradation took place at about 200 °C [3], its application had largely been limited [4]. How to improve the thermal stability and mechanical properties was a challenge in the field of polyurethane. As we all know, the thermal stability and mechanical properties of polyurethane were governed mainly by the chemical structure of its backbone that consist of various hard segments and soft segments. Therefore, extensive research efforts had been devoted to modify its structure in the past few decades. An effective way was to copolymerize with high performance polymers [5]. Until now, a series of copolymers had been prepared, such as poly(urethane–urea), poly(urethane–epoxy), poly(urethane–imide), and poly(urethane–diacetylene). Polyimide, which composed of imide structure in the backbone and possessed remarkable thermal stability, high mechanical strength, and good dielectric properties [6–8], would be the best candidate both for copolymerization and polymer alloying. Various attempts had been made to incorporate imide component as hard segment into polyurethane. Reaction of Isocyanate-terminated polyurethane prepolymers with acid anhydrides was the most commonly utilized method to gain poly(urethane–imide) [9, 10]. There were some reports on the reaction of isocyanate-terminated polyurethane prepolymer with diols, diacids [11–13], or diamines [14] containing in-built imide groups. Because of the great reactivity of isocyanates, imidization took place in a single step at a lower temperature, making the imide function introduced into the polyurethane backbone conveniently [9]. Reaction of an amine-terminated polyurethane prepolymers with acid anhydride was another modification method utilized by researchers [15, 16]. Some other modified methods to gain poly(urethane–imide) were also reported including the reaction of epoxy resins containing imide structure with blocked polyurethane prepolymers [17] and the utilization of intermolecular Diels–Alder reaction between 4-methyl-1,3-phenylenebis(2-furanylcarbamate) and various bismaleimides [18, 19].

Poly(urethane–imide) obtained by the above methods, which were mostly linear, exhibited better mechanical properties and improved thermal stability compared to typical linear polyurethane. However, the properties could be further improved through other ways. Chemical crosslinking was an effective way to modify polyurethane, which produced a three-dimensional network structure and reduced macromolecular degradation to a negligible amount. Comparing with conventional linear analogs, a small amount of hyperbranched architecture was sufficient for manifold increase in chemical resistance, durability, and tensile strength [20]. Polymer systems with highly branched network had attracted a great deal of attention in scientific and industrial areas due to their unique features and properties such as three-dimensional architecture, unentangled structure, low melting viscosity, good solubility, and large amounts of terminal functional groups [21]. Early efforts toward the preparation of irregularly branched and highly branched polymers focused on the polymerization of AB_x-type ($x \geq 2$) monomers [22, 23]. In order to generate such highly branched structure, extensive synthetic strategies including high selective reactivity [24] and nonisocyanate ways [25] had been described subsequently. However, alternatives should be found to replace the classical synthesis of hyperbranched polymers using more commercially available monomers. Similar hyperbranched structure could be obtained by the A_2 plus B_3 approach. This methodology offered a facile route for gaining polymers with enhanced mechanical and thermal properties because the length of the segments of the hyperbranched polymers between the branching points were sufficient for entanglements. In addition, the $A_2 + B_3$ approach might be more important in industrial applications due to the commercial availability and symmetrical functionality [26, 27]. Recently, a novel alternative approach to functionally nonsymmetrical AB_x-type ($x \geq 2$) monomers which was called Couple-monomer methodology (CMM) or $A_2 + bB_2$ approach, had been reported by Yan [28, 29] and Bruchmann [30].

Although many kinds of linear poly(urethane–imide) had been prepared, the preparation of highly branched poly(urethane–imide) had not yet been reported. Therefore, our study was attempted to prepare highly branched poly(urethane–imide) via $A_2 + B_3$ approach using an isocyanate-terminated prepolymer that incorporated with imide component as an A_2 oligomeric monomer and triamine as a B_3 monomer. The obtained highly branched poly(urethane–imide) films displayed superior tensile properties and improved thermal properties in comparison with linear poly(urethane–imide). The structure of the products was characterized by FT-IR and ^{13}C-NMR. The molecular weights were characterized by gel permeation chromatograph (GPC). The solution viscosity of highly branched poly(urethane–imide) was evaluated with rotational rheometer. The thermal properties, mechanical properties, and the storage modulus were studied with differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), tensile tests, and dynamic mechanical analysis (DMA), respectively.

Experiment

Materials

All the chemical reagents were analytical grade. Polycarbonatediols (PCDL, Mn = 1,000, Asahikasei Chemicals Co., Japan) was degassed and dried under high vacuum (20 Pa) at 100 °C for 2 h before used. Isophorone diisocyante (IPDI) was obtained from Fluka, Germany. 3,3′,4,4′-Benzophenonetetracarboxylic dianhydride was purchased from Alfa Aesar, USA. Trimethyllolprorane tris[poly(propylene glycol) amine terminated] ether (ATA) was obtained from Aldrich, USA. The catalyst dibutyltin dilaurate (DBTL, Tianjin Chemical Co., China) were used as received. N,N′-dimethyl-formamide (DMF) was vacuum distilled and stored over 4 Å molecular sieves.

Synthesis of highly branched poly(urethane–imide)

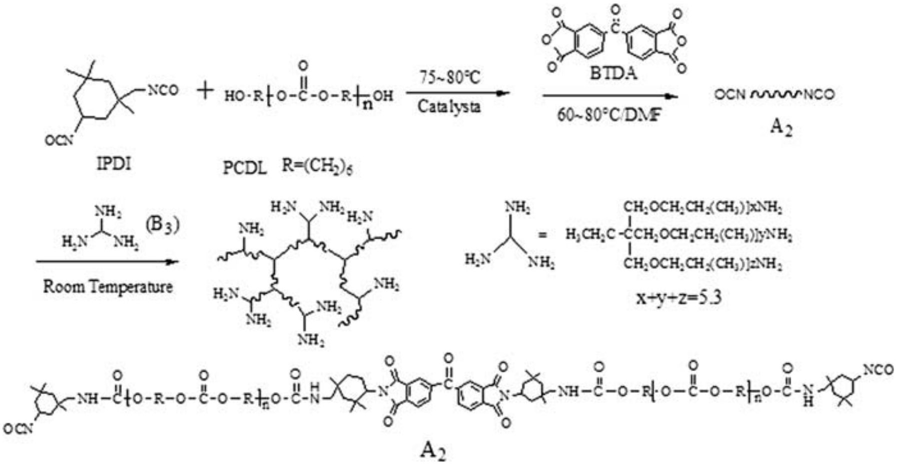
All reactions were carried out in a four-necked, round-bottom flask equipped with a magnetic stirrer, thermometer, condenser, addition funnel, and nitrogen inlet system. The isocyanate end-capped polyurethane prepolymer was formed through the reaction of PCDL (0.005 mol, 5 g), IPDI (0.008 mol, 1.7783 g) at 80 °C for 2–3 h with 50 ppm DBTL catalyst. The reaction was allowed to proceed till the NCO content reached the theoretical value as determined by di-n-butylamine back-titration (DBBT) method. Then, appropriate amount of BTDA/DMF solution was added into the solution, the reaction temperature was maintained at 60 °C for 3 h, and at 80 °C for 1 h. The total solid content of reaction mixture was fixed at 20 wt%. The obtained NCO-terminated poly(urethane–imide) A_2 was cooled to room temperature, and added dropwise into the B_3/DMF solutions (20 wt%) with an addition funnel. During the reactions, the [B] was always excess, and gelation was not observed. The HBPUI films were obtained by casting the solutions on a polytetrafluoroethylene (PTFE) plates and allowing them to dry at 50 °C for 2 days. After demolding, the films were submitted to vacuum drying for 24 h.

A schematic representation of the synthesis route for HBPUI was shown in Scheme 1. Different formulations and molecular weights of HBPUI were listed in Table 1.

Measurements

FT-IR analysis

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



Scheme 1 Synthesis route for the highly branched poly(urethane–imide)

Table 1 Synthesis parameters and molecular weights of HBPUI

Sample	nIPDI/(nPCDL + nBTDA)	The content of BTDA (wt%)[a]	$[A_2]/[B_3]$	Mn	M_w	PDI
HBPUI-1	1.33	6	0.6	1,189	4,226	3.55
HBPUI-2	1.33	6	0.7	1,550	6,767	2.70
HBPUI-3	1.33	6	0.8	1,793	6,924	1.54
HBPUI-4	1.33	6	0.9	2,131	7,970	3.74
HBPUI-5	1.5	6	0.9	2,665	10,681	4.00
HBPUI-6	1.1	6	0.9	2,827	10,871	3.85

[a] The content of BTDA (wt%) = mBTDA/(mIPDI + mPCDL + mBTDA + mATA)

Gel permeation chromatography (GPC)

Gel permeation chromatography 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.

NMR analysis

The ^{13}C-NMR analysis was conducted on a Varian INOVA-600 spectrometer at 600 MHz. DMSO-d6 was used as solvent and tetramethylsilane as internal reference.

Viscosity measurements

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

DSC

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 20 °C/min.

Thermogravimetric analysis (TGA)

TGA of the precipitated highly branched poly(urethane–imide) 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.

Tensile tests

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

Dynamic mechanical analysis (DMA)

The modulus of HBPUI samples were measured using DMA Q800-0637 instrument (TA instruments Inc., USA) in tensile mode at a frequency of 1 Hz and with a heating rate 3 °C/min by scanning the films from −80 to 100 °C. Storage modulus (E′) as a function of temperature was obtained.

Results and discussion

FT-IR spectra analysis

Figure 1 showed the FT-IR spectroscopic analysis of the polyurethane prepolymer (a), NCO-terminated poly(urethane–imide) A_2 (b), and highly branched poly(urethane–imide) (c). From the Fig. 1a, we could see that the band at 3,435 cm^{-1} was fairly broad, which was attributed to the stretching vibration of free and hydrogen-bonded N–H groups. The absorption band appearing at approximately 1,700 cm^{-1} belonged to the functional groups of C=O from urethane stretching vibrations. In the curve b, the band appeared at 1,782 cm^{-1} was assigned to the asymmetric stretching vibration of C=O of the imide groups, characteristic spectral absorbance at 1,385 and 1,244 cm^{-1} were related to C–N stretching vibration, confirming that the heterocyclic imide rings were successfully incorporated into the polyurethane backbone. In the curve c, the absorption peak of NCO at 2,274 cm^{-1} disappeared, indicating that the reaction between A_2 and B_3 was complete. The absorption peak at 1,782 cm^{-1} became weak in the curve c, but the peaks of 1,743 and 1,667 cm^{-1} elongated and intensified. There were large amounts of hydrogen bonding interactions among molecules, and so carbonyl bond length elongated and resulted in a decrease in the bonding force constant as well as the bond order of C=O bond. As a consequence, the peak at 1,782 cm^{-1} shifted to low stretching vibration frequency [8].

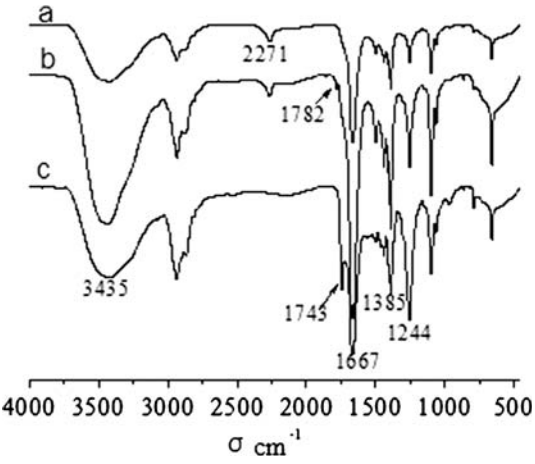


Fig. 1 FT-IR spectra of **a** PU prepolymer; **b** NCO-terminated A_2; **c** highly branched poly(urethane–imide)

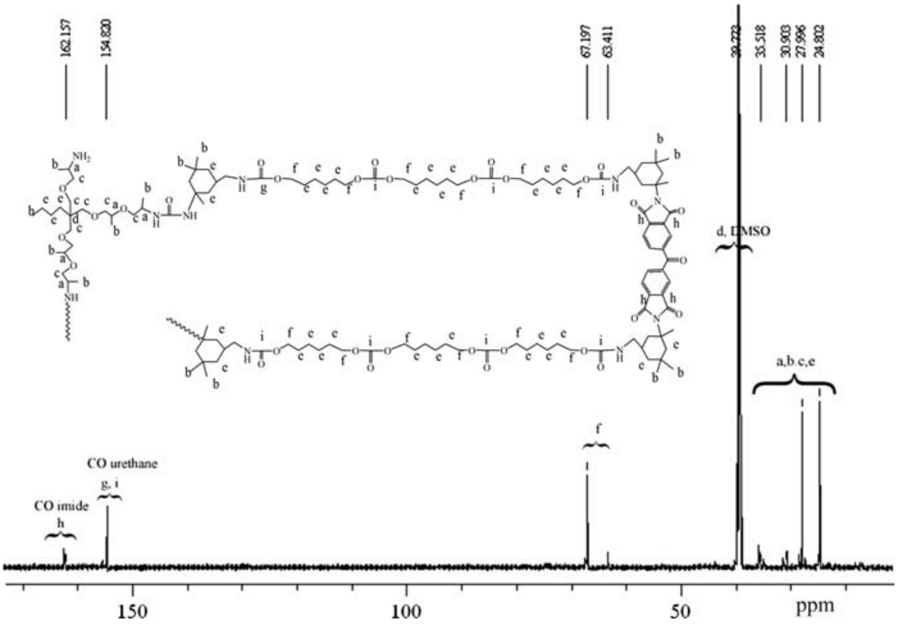


Fig. 2 ^{13}C-NMR spectrum of highly branched poly(urethane–imide)

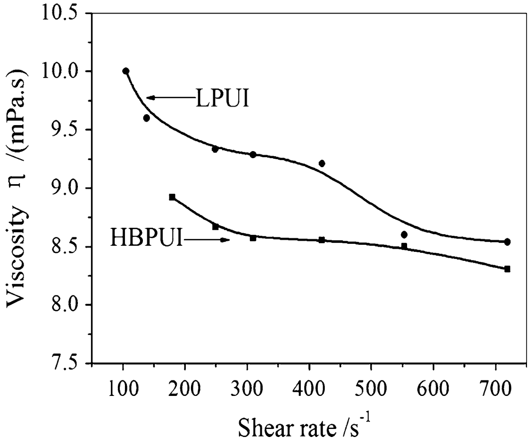
^{13}C-NMR analysis

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 ^{13}C-NMR spectrum of the poly(urethane–imide). The appearance of two peaks at δ162.157 and δ154.820 ppm were assigned to the carbonyl groups. The peak at δ162.157 ppm was attributed to the functional groups of C=O from the imide groups, signifying that the BTDA was successfully incorporated into the polyurethane backbone, which was consistent with the FT-IR spectroscopic analysis formerly described for the poly(urethane–imide). The other peak observed at a lower chemical shift was attributed to the urethane carbonyl groups, indicating the formation of polyurethane in the main chain.

Solution viscosity characteristics

The solution viscosities of the HBPUI and LPUI were measured in DMF solvent at 25 °C, and the results were presented in Fig. 3. It was a clear tendency that the viscosities of the HBPUI and LPUI decreased as increasing the shear rate. When the shear rate increased, the long polymer chains could array along with the shear orientation more effectively, so an increasing shear rate could result in low viscosity. It also could be observed that the HBPUI had lower viscosity compared with linear poly(urethane–imide), which greatly confirmed the fact that three-dimensional structure existed in the HBPUI could lead to the reduced viscosity.

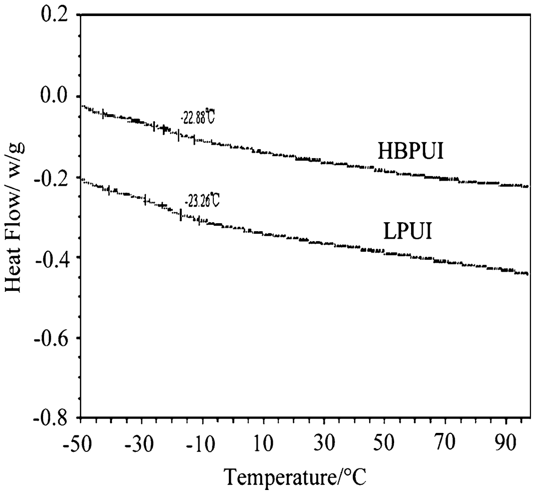
Fig. 3 Solution viscosities of the HBPUI and LPUI variation as a function of the shear rate (nIPDI/(nPCDL + nBTDA) = 1.7, BTDA = 6wt%, solid content 10 wt%)



DSC analysis

It was well known that the glass-translation temperature (T_g) of the polymers was affected by a number of factors such as chain links, mobility, chain–chain interaction, molecular structure, and nature of end groups. Figure 4 showed the DSC curves of HBPUI and LPUI. The glass-translation temperature of HBPUI was slightly higher than that of LPUI. This was due to the highly branched structure and large amounts of urethane and urea linkage and NH_2 end groups existed in the HBPUI, leading to the number of the hydrogen bonds was much higher than that of LPUI. Therefore, the T_g increased. However, the T_g did not change obviously. The reason was that the T_g of soft segment depended on the degree of phase mixing of soft and hard segment. The HBPUI had long chain between the branching points, and the chemical composites of the long chain were similar to the soft segment of the LPUI.

Fig. 4 The DSC curves of LPUI and HBPUI (nIPDI/(nPCDL + nBTDA) = 1.33, BTDA% = 6 wt%, $[A_2]/[NH_2] = 0.3$)



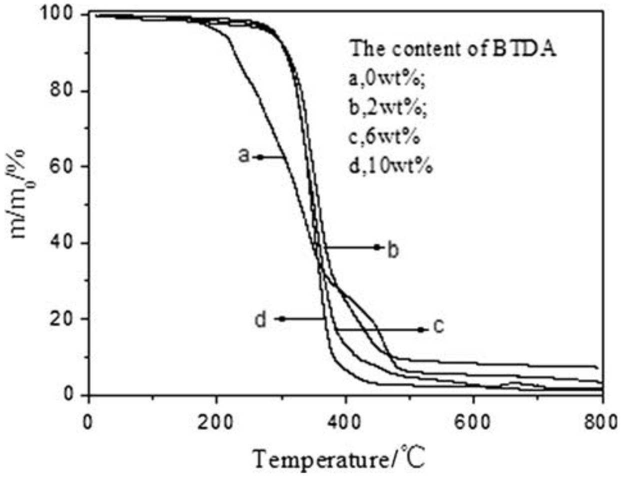


Fig. 5 TG curves of HBPUI with variation in the content of BTDA (nIPDI/(nPCDL + nBTDA) = 1.33, $[A_2]/[B_3] = 0.9$)

Thermogravimetric analysis

The thermal behavior of the resulting polymers was evaluated by TGA under nitrogen atmosphere. Thermal properties data were summarized in Table 2 and the TG curves were shown in Fig. 5. The degradation temperature was comparatively low in HBPUI having less imide content. Therefore, an increase of imide content could increase thermal stability of HBPUI. As shown in Table 2, the thermal decomposition temperature of HBPUI increased with the increase of the BTDA content. It was clearly observed that the 10 wt% weight loss decomposition temperature of HBPUI films were above 300 °C. In contrast, conventional, highly branched polyurethane decomposed at a temperature of 228 °C, which was much lower than that of HBPUI. The desirable thermal stability of HBPUI was ascribed to the incorporation of imide rings in the polymer backbones, revealing that this approach was very efficient to improve the thermal stability of polyurethane. However, the main compositions of the HBPUI backbones were still urethane and urea, which caused the main weight loss. Therefore, with the increase of the content of BTDA, the thermal stability was improved slowly. In our experiments, the content of the BTDA was not higher than 10 wt% because

Table 2 Temperature at 10 and 50% weight loss of HBPUI samples

Sample	The content of BTDA (wt%)	Temperature at 10% weight loss (°C)	Temperature at 50% weight loss (°C)
HBPUI-a	0	228	330
HBPUI-b	2	306	347
HBPUI-c	6	308	351
HBPUI-d	10	310	359

polyurethane was a two-phase polymer. If more BTDA were incorporated, it would result in phase separation. The mechanical properties of the HBPUI would decrease.

Tensile properties

Tensile measurements were performed and the results were shown in Fig. 6 in the form of stress–strain curves. In general, tensile strength increased and elongation at break decreased with an increase in hard segment content of the polymer. Additionally, it had been suggested that the segment of heterocyclic imide groups also had great influence on the tensile strength and elongation at break in our experiments. As seen from Fig. 6, all the HBPUI films with different content of BTDA as hard segment showed high tensile strength and low elongation at break. The tensile strength increased from 7.41 to 51.71 MPa but the elongation at break decreased from 1,345 to 600% with the content of BTDA varied from 2 to 10 wt%. This behavior might be due to the strong enhancement of intermolecular interactions including the intermolecular force and hydrogen bonding with increasing hard segment in the molecular chains. On the other hand, the segment of heterocyclic imide groups in the polymer chains was extremely rigid, thus leading to large improvement of the tensile strength. The flexibility and elasticity were provided by the soft segment, when the soft segment in the molecular chains decreased, thereby the elongation at break decreased.

Stress–strain curves for linear poly(urethane–imide) (LPUI) and highly branched poly(urethane–imide) (HBPUI) were shown in Fig. 7. The tensile strength of LPUI was 7.12 MPa, the elongation at break was 1,011%. In comparison with LPUI, all the HBPUI showed stronger tensile strength but weaker elongation at break because of the highly branched structure. With the increase of the molar ratio of $[A_2]/[B_3]$, the degree of branching (DB) and molecular weights of HBPUI increased [31]. As shown in Table 1, the molecular weights (M_w) of HBPUI increased from 4,226 to 7,970. The intermolecular interactions including the intermolecular force and hydrogen bonding were enhanced because of the high molecular weight and large

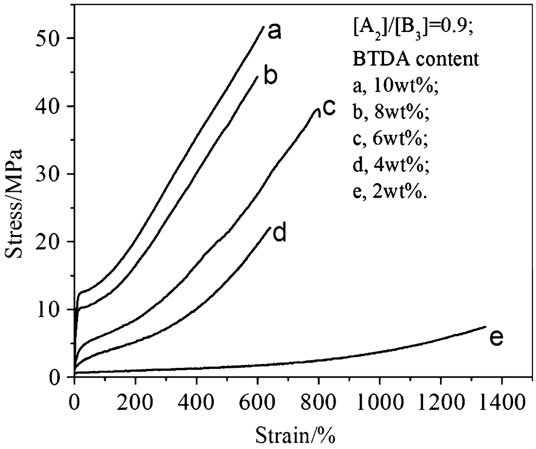


Fig. 6 Stress–strain curves of HBPUI films with different BTDA content

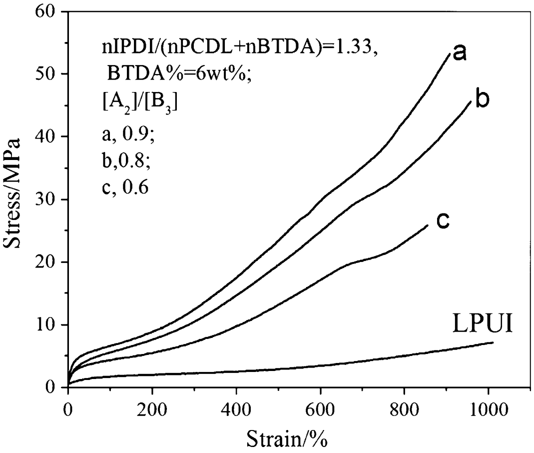


Fig. 7 Stress–strain curves of HBPUI films with different $[A_2]/[B_3]$ ratios

amounts of NH_2 end groups per macromolecule. Thus, tensile strength increased and the elongation at break decreased. As could be seen from Fig. 7, when the molar ratio of $[A_2]/[B_3]$ increased from 0.8 to 0.9, the tensile strength of the HBPUI films were in range of 45.7–53.3 MPa, but the elongation at break decreased from 959 to 909%.

DMA analysis

The mechanical properties of the traditional hyperbranched polymers were poor because these polymers were lack of chain entanglement. The macrostructure of hyperbranched polymers synthesized via $A_2 + B_3$ approach was similar to traditional hyperbranched polymers, but there were long chain between the branching points which were long enough for entanglement in unit structure in these polymers. Therefore, the resulting polymers showed superior mechanical properties. The dynamic mechanical properties of HBPUI films as a function of temperature were shown in Figs. 8 and 9. Figure 8 showed the storage modulus for different $[A_2]/[B_3]$ ratio of HBPUI. It was clear that, as expected, the storage modulus of HBPUI samples were much higher than that of LPUI samples because of the highly branched structure. The modulus of HBPUI increased with increasing the ratio of $[A_2]/[B_3]$. This behavior might be associated with the hydrogen bond concentration and DB value in the polymers. It was suggested that the DB increased with increasing the $[A_2]/[B_3]$ [31], and large amounts of NH_2 end groups formed per macromolecule.

The influence of different BTDA content on the storage modulus of HBPUI films was illustrated in Fig. 9. It could be found that only a small amount of BTDA could improve the storage modulus. The results should be interpreted through the presence of imide groups in the polymer chains. The rigidity of hard segment of material could be largely improved resulting from the incorporation of BTDA that containing extremely rigid heterocyclic units. We could see that the more BTDA content in the HBPUI was, the higher storage modulus was. Therefore, increasing the amount of BTDA in the HBPUI could lead to an enhancement of the storage modulus.

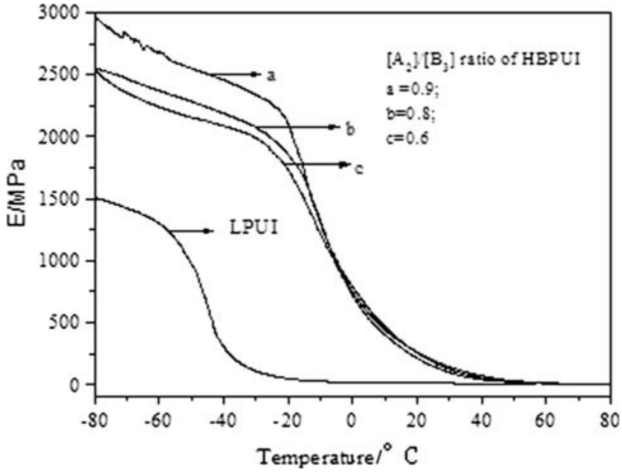


Fig. 8 Dynamic mechanical analysis plots of HBPUI with different [A_2]/[B_3] ratio and LPUI

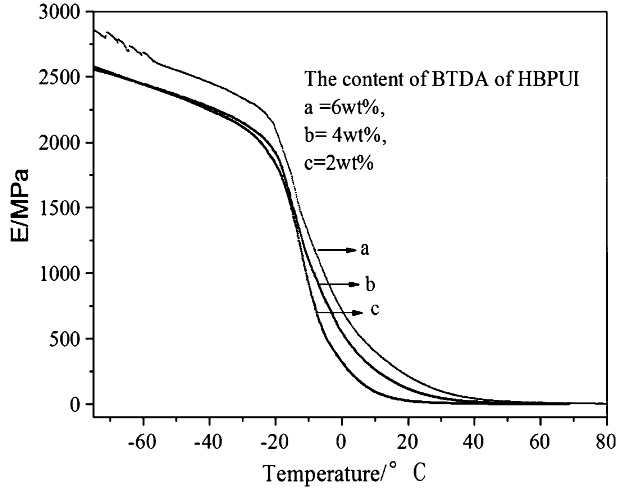


Fig. 9 Dynamic mechanical analysis plots of HBPUI with different BTDA content

Conclusion

A series of highly branched poly(urethane–imide) (HBPUI) were successfully synthesized via the reaction of isocyanate terminated polyurethane prepolymer containing imide groups as an A_2 oligomeric monomer and triamine as a B_3 monomer. As a result of introduction of imide component and highly branched structure, the thermal properties and mechanical properties of HBPUI were improved remarkably. The HBPUI showed lower viscosity than that of linear poly(urethane–imide) (LPUI), nevertheless T_g of HBPUI was higher than that of LPUI. Introducing imide component into polyurethane was an effective way to improve the thermal degradation temperature of polyurethane, which was 80 °C higher than the conventional, highly branched polyurethane. The tensile strength of HBPUI was greatly affected by increasing the content of BTDA and the molar ratio of $[A_2]/[B_3]$, the maximum tensile strength was up to 53.3 MPa when the content of BTDA was 6 wt% and the molar ratio of $[A_2]/[B_3]$ was 0.9. However, the results of elongation at break were opposite. Simultaneously, the storage modulus was enhanced considerably by increasing the content of BTDA and the molar ratio of $[A_2]/[B_3]$.

Acknowledgments The research was supported by Innovation Group Foundation and Elitist Foundation of the Provincial Science & Technology Department, Hubei, China.

References

1. Park SH, Chung ID, Hartwig A, Kim BK (2007) Hydrolytic stability and physical properties of waterborne polyurethane based on hydrolytically stable polyol. Colloids Surf A Physicochem Eng Aspects 305:126–131. doi:10.1016/j.colsurfa.2007.04.051
2. Takeichi T, Ujiie K, Inoue K (2005) High performance poly(urethane–imide) prepared by introducing imide blocks into the polyurethane backbone. Polymer 46:11225–11231. doi:10.1016/j.polymer.2005.09.075
3. Fabris HJ (1976) Advance in urethane science and technology. Technomic, Westport, CT
4. Zuo M, Takeichi T (1999) Preparation and characterization of poly(urethane–imide) films prepared from reactive polyimide and polyurethane prepolymer. Polymer 40:5153–5160. doi:10.1016/S0032-3861(98)00726-5
5. Liu J, Ma DZ, Li Z (2002) FTIR studies on the compatibility of hard-soft segments for polyurethane–imide copolymers with different soft segments. Eur Polym J 38:661–665. doi:10.1016/S0014-3057(01)00247-6
6. Ghosh MK, Mittal KL (1996) Polyimide: fundamentals and applications. Marcel Dekker, New York
7. Wilson D, Stenzenberger HD, Hergenrother PM (1990) Polyimides. Blackie, Glasgow
8. Mishra AK, Chattopadhyay DK, Sreedhar B, Raju KVSN (2006) FT-IR and XPS studies of polyurethane-urea-imide coatings. Prog Org Coat 55:231–243. doi:10.1016/j.porgcoat.2005.11.007
9. Liao DC, Heich KH (1994) Synthesis and characterization of bismaleimides derived from polyurethanes. J Polym Sci Part A Polym Chem 32:1665–1672. doi:10.1002/pola.1994.080320908
10. Sendijavic A, Sendijavic V, Frisch KC (1990) Synthesis and properties of urethane-modified polyimides. J Polym Sci Part A Polym Chem 28:3603–3615. doi:10.1002/app.1983.070s281126
11. Wang TL, Huang FJ (1998) Synthesis and properties of poly(amide–imide–urethane) thermoplastic elastomers. Polym Int 46:280–284. doi:10.1002/(SICI)1097-0126(199808)46:4<280:AID-PI992>3.0.CO;2-#
12. Yeganeh H, Barikani M, Khodabadi NF (2000) Synthesis and properties of novel thermoplastic poly(urethane–imide)s. Eur Polym J 36:2207–2211. doi:10.1016/S0014-3057(99)00284-0
13. Lee TJ, Lee DJ, Kim HD (2000) Synthesis and properties of liquid crystalline polyurethane elastomers. J Appl Polym Sci 77:577–585. doi:10.1002/(SICI)1097-4628(20000718)77:3<577:AID-APP13>3.0.CO;2-X
14. Radlmann E, Koehler A, Nischk G (1971) Polyurethane elastomers with polyimide or ployamic structure for highly elastic filaments/films. DE2017511
15. Jeon JY, Tak Tae M (1996) Synthesis and characterization of block copoly(urethane–imide). J Appl Polym Sci 62:763–769. doi:10.1002/(SICI)1097-4628(19961031)62:5<763:AID-APP7>3.0.CO;2-U
16. Salah HAA (1991) Synthesis and properties of poly(urethane–urea–imide) block copolymers. Polym J 23:815–821. doi:10.1295/polymj.23.815
17. Nair RP, Nair CPR, Francis DJ (1999) Effect of imide-oxazolidinone modification on the thermal and mechanical properties of HTPB-polyurethanes. J Appl Polym Sci 71:1731–1738. doi:10.1002/(SICI)1097-4628(19990314)71:11<1731:AID-APP2>3.0.CO;2-M

18. Patel HS, Vyas HS (1991) Poly(urethane–imide)s. Eur Polym J 27:93–96. doi:10.1016/0014-3057(91)90132-8
19. Patel HS, Vyas HS (1992) Kinetic studies on epoxy resins cured with a novel polyamine. High Perform Polym 4:41–48. doi:10.1088/0954-0083/4/1/005
20. Jena KK, Chattopadhyay DK, Raju KVSN (2007) Synthesis and characterization of hyperbranched polyurethane–urea coatings. Eur Polym J 43:1825–1837. doi:10.1016/j.eurpolymj.2007.02.042
21. Cheng KC, Chuang TH, Chang JS, Guo WJ, Su WF (2005) Effect of feed rate on structure of hyperbranched polymers formed by self-condensing vinyl polymerization in semibatch reactor. Macromolecules 38:8252–8257. doi:10.1021/ma050640s
22. Chen A, Yao C, Zeng S, Yi C, Xu Z (2008) Preparation and properties of hyperbranched polyurethanes via oligomeric A2 + bB2 approach. Polym Bull 61:363–371. doi:10.1007/s00289-008-0959-x
23. Spindler R, Fréchet JMJ (1993) Synthesis and characterization of hyperbranched polyurethane prepared from blocked isocyanate monomers by step-growth polymerization. Macromolecules 26:4809–4813. doi:10.1021/ma00070a013
24. Feast WJ, Rannard SP, Stoddart A (2003) Selective convergent synthesis of aliphatic polyurethane dendrimers. Macromolecules 36:9704–9706. doi:10.1021/ma035511v
25. Clark AJ, Echenique J, Haddleton DM, Straw TA, Taylor PC (2001) A noniscocyanate route to monodisperse branched polyurethanes. J Org Chem 66:8687–8689. doi:10.1021/jo016075i
26. Kricheldorf HR, Schwarz G (2003) Cyclic polymers by kinetically controlled step-growth polymerization. Macromol Rapid Commun 24:359–381. doi:10.1002/marc.200390063
27. McKee MG, Unal S, Wilkes GL, Long TE (2005) Branched polyesters recent advances in synthesis and performance. Pro Polym Sci 30:507–539. doi:10.1016/j.progpolymsci.2005.01.009
28. Gao C, Yan D (2003) "$A_2 + CB_n$" approach to hyperbranched polymers with alternating ureido and urethane units. Macromolecules 36:613–620. doi:10.1021/ma021411y
29. Gao C, Yan D (2004) Hyperbranched polymers from synthesis to applications. Pro Polym Sci 29:183–275. doi:10.1016/j.progpolymsci.2003.12.002
30. Abdelrehim M, Komber H, Langewalter J, Brigitle V, Bruchmann B (2004) Synthesis and characterization of hyperbranched poly(urea–urethane)s based on $AA^*$and B_2B^* monomers. J Polym Sci Part A Polym Chem 42:3062–3081. doi:10.1002/pola.20154
31. Fornof AR, Glass TE, Long TE (2006) Degree of branching of highly branched polyurethanes synthesized via the oligomeric A_2 plus B_3 methodology. Macromol Chem Phys 207:1197–1206. doi:10.1002/macp.200600096