

## Synthesis and application of hyperbranched poly(urethane-urea) finishing agent with amino groups

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**ABSTRACT:** The isocyanate-terminated linear polyurethane prepolymer (LPPU) was successfully synthesized via step-by-step polymerization, with isophorone diisocyanate (IPDI) and polytetramethylene ether glycol (PTMG,  $M_n = 2000$  g/mol) used as raw materials, dibutyltin dilaurate (DBTDL) as the catalyst, 1,4-butanediol (BDO) as the chain extender and anhydrous ethanol (EtOH) as the blocking agent. Then the hyperbranched poly(urethane-urea) (HBPU) containing amino groups was synthesized by grafting LPPU on amino-terminated hyperbranched polymers ( $\text{NH}_2$ -HBP). The molecular structure of LPPU and HBPU were characterized by means of FT-IR and  $^1\text{H-NMR}$ . It was founded that LPPU and HBPU were successfully synthesized as anticipated. The thermal stability and crystalline morphology of LPPU and HBPU were characterized and analyzed by TG and XRD. Additionally, it was also found that, after addition of 10% HBPU, the water absorption rate, water vapor transmission rate, and water vapor permeability increased markedly by 162.02%, 400.00%, 260.00%, respectively. The tensile strength of membrane decreased by 24.57% and the elongation at break increased by 26.92%. Compared with the leather finished by commercial PU finishing agent, the leather finished by HBPU presented better properties. The water vapor permeability of the leather finished by increased by 13.0%, and the dry- and wet-rub resistances and the physical and mechanical performances were excellent. © 2016 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2016**, *133*, 44139.

**KEYWORDS:** applications; dendrimers; hyperbranched polymers and macrocycles; membranes; polyurethanes; synthesis and processing

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### INTRODUCTION

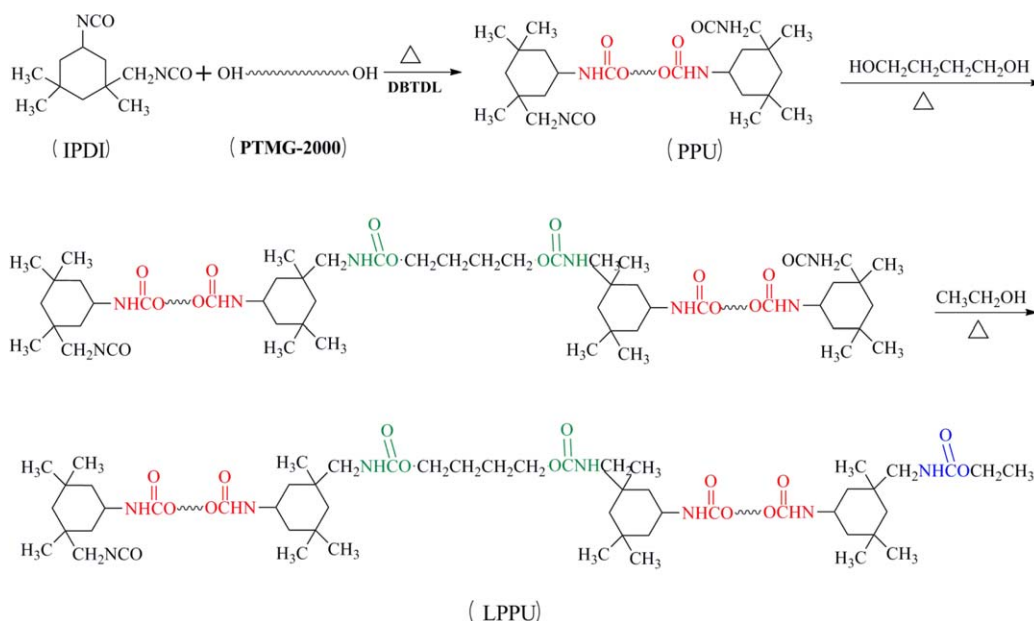
Hyperbranched polymer is a kind of highly branched macromolecules with a large number of end-groups. Owing to its special molecular structure, hyperbranched polymer has excellent properties, such as good solubility, high reactivity, and low viscosity, etc.<sup>1–4</sup> Thus, hyperbranched polymers have been widely used in biomedical materials, nonlinear optical materials, tanning, surface modification, supramolecular chemistry, and nano materials.<sup>5–10</sup>

With abrasion resistance, high strength, and chemical resistance, polyurethane (PU) has been widely used in synthetic leather and leather finishing agent.<sup>11,12</sup> However, PU film has poor moisture adsorption and vapor permeability, which directly influence the wearing comfort of product significantly. Recently, a lot of studies on the application of hyperbranched polymer in PU field have been reported. A series of hyperbranched polyurethane (HBPU) has been prepared.<sup>13–16</sup> Ren *et al.*<sup>14</sup> studied that the blend films of PU and amino-terminal hyperbranched polymers (HBP- $\text{NH}_2$ ). They found that the moisture absorption and mechanical properties of the blend films increased with the addition of 3% HBP- $\text{NH}_2$ . Kantheti *et al.*<sup>15</sup> studied that different generations of 1,2,3-triazole-rich hyperbranched polyether

polyols and application for the development of moisture-cured polyurethaneurea coatings. They found that the coatings showed considerable enhancement in thermal stability, glass transition temperature, and corrosion resistance properties with an increase in generation number. Anila *et al.*<sup>17</sup> studied that hyperbranched polyurethane with low viscosity. They found that the face of the finished leather was smooth and bright, the adhesion of leather and coating was strong. In addition, the existence of many reactive end groups gave rise to better the absorption properties of the coating.

However, hyperbranched polyurethane also has a few inefficiencies, such as poor mechanical properties including tensile modulus and low electrical conductivity that limit to address many avant-garde applications.<sup>18,19</sup> Although hyperbranched polyurethanes makes some properties worse, they have other excellent functions. In this study, hyperbranched polymer is used to increase the hydrophilic groups in PU, so as to improve the sanitary properties of leather.

In this article, LPPU was prepared in which the IPDI, PTMG-2000, BDO, EtOH were used as raw materials. Then LPPU was grafted on  $\text{NH}_2$ -HBP. Finally, a new kind of hyperbranched poly



**Scheme 1.** Synthesis equation of LPPU. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

(urethane-urea) was synthesized. It can be used to improve the sanitary properties of leather.

## EXPERIMENTAL

### Materials

NH<sub>2</sub>-HBP (CYD-WU438,  $M_n = 2454$  g/mol) was produced by Shanghai Weihai CY dendrimer Technology Co., Ltd.; IPDI was analytical pure grade and obtained from Shanghai D&B chemical Technology Co., Ltd. PTMG-2000 was provided by Tianjin Kemiou Chemical Reagent Co. in China and was dried in vacuum at  $100 \pm 5^\circ\text{C}$  for 2 h to remove H<sub>2</sub>O before used. 1,4-Butanediol, anhydrous ethanol, dibutyltin dilaurate, acetone, *N,N*-dimethyl-formamide (DMF), pyridine and di-*n*-butylamine were purchased from Tianjin Fuchen Chemical Reagent Factory. The above chemical were analytical grades and used without further purification. The solvent polyurethane finishing agent (6303B) was provided by Yantai Huada Chemical Industry Co., Ltd.

### Synthesis of LPPU

The synthesis equation of the part isocyanate-terminated linear polyurethane prepolymer (LPPU) is shown in Scheme 1.

Firstly, PTMG-2000 (20.00 g) was charged into a 250 mL four-necked round-bottom flask equipped with a thermometer, mechanical stirrer, reflux condenser, and constant voltage dropping funnel. Then the flask was fastened into an oil bath at about  $60^\circ\text{C}$  to melt PTMG-2000. The temperature was then raised to  $80^\circ\text{C}$ , and 5.55 g IPDI was added dropwise into the flask and stirring was kept at 200 rpm. Then DBTDL (0.07 wt %, based on the total mass of raw materials) was added. The temperature was raised to  $85^\circ\text{C}$ , stirring at 200 rpm for about 1.5 h until the NCO content reached the theoretical value. After the temperature was reduced to  $60^\circ\text{C}$ , certain amount of BDO was added dropwise, and the reaction was carried out at  $85^\circ\text{C}$  for about 2.5 h. Finally, the temperature was reduced to  $60^\circ\text{C}$ , and quantitative EtOH was added to continue reacting at  $80^\circ\text{C}$

for about 2 h, and then the NCO content was determined by the standard dibutylamine back-titration method. During the reaction, DMF was used as solvent. The calculation equation of theoretical NCO value was as follows.

$$W_{\text{NCO}} = \frac{(n_{\text{NCO}} - n_{\text{OH}}) \times 42.02}{m_{\text{IPDI}} + m_{\text{OH}}} \times 100\%$$

$W_{\text{NCO}}$  was the NCO content.  $m_{\text{IPDI}}$  and  $m_{\text{OH}}$  were the weight of IPDI and polyol.  $n_{\text{NCO}}$  and  $n_{\text{OH}}$  were the mol mass of NCO and OH.

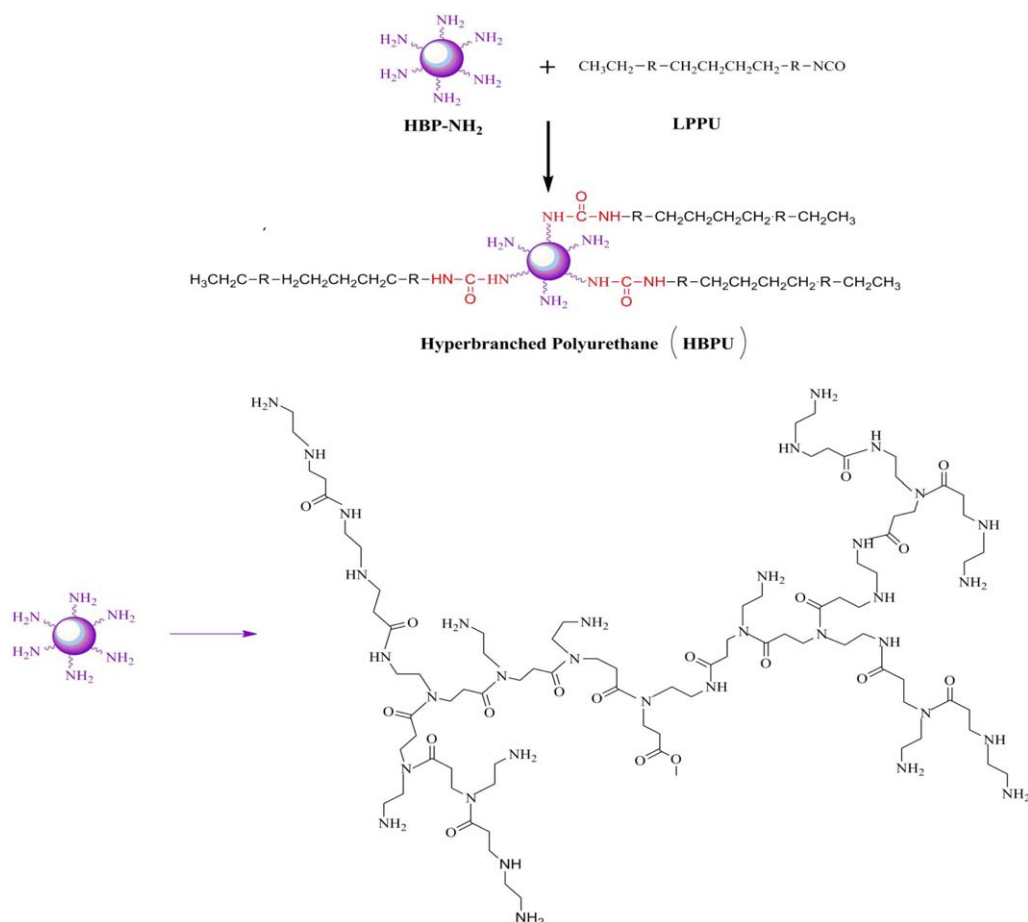
### Synthesis of HBPU

Synthesis equation of the hyperbranched polyurethane (HBPU) is shown in Scheme 2.

Firstly, the primary amino content of NH<sub>2</sub>-HBP was determined by the salicylaldehyde method, and then NH<sub>2</sub>-HBP was dissolved in DMF to prepare a mixture with 50% concentration. LPPU was added into a 250 mL flask equipped with a thermometer, mechanical stirrer, and constant voltage dropping funnel, and then NH<sub>2</sub>-HBP solution was added according to the  $n(-\text{NCO}:-\text{NH}_2)$  was 1:1. The reaction was carried out in ice water bath for about 1 h. Finally, the resultant polymers were purified by dissolving in acetone to remove remaining NH<sub>2</sub>-HBP, as a result, yellow viscous HBPU was obtained. According to the GB/T 2793-1995 and literature,<sup>20</sup> the solid content and amino value were determined. The specific measurements as shown in Table I.

### Preparation of HBPU Film

The HBPU mixture (solid content: 30 wt %) was poured into a polytetrafluoroethylene glass mold (15 cm × 15 cm × 2 mm). Then it was dried in vacuum drying oven at  $65^\circ\text{C}$  for 6 h until the solvent completely evaporated. Finally, the specimen was taken out from the vacuum drying oven and put into the desiccator for tests. LPPU and PU films were obtained by the same method.



**Scheme 2.** Synthesis equation of HBPU. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

### Preparation of Blend Films

The PU solution (solid content: 30%) and 10% HBPU (based on the weight of dry PU) were mixed together, and then they were dissolved in DMF to achieve a final total solid concentration of 20% (w/w). After centrifugal degassing, they were allowed to stand for 12 h. The mixtures were cast into a polytetrafluoroethylene glass mold (15 cm × 15 cm × 2 mm) and dried in vacuum drying oven at 80 °C for 2 h. Finally, the specimen was taken out from the vacuum drying oven and put into the desiccator for tests.

### Leather Finishing

The finishing formula was indicated in Table II.

First, the finishing agent was prepared in accordance with Table II. Second, surface liquid (mNH<sub>3</sub>·H<sub>2</sub>O: m EtOH: mH<sub>2</sub>O = 5:10:8:5) was prepared, clean dishcloth which was dipped the liquid was used to gently wipe the leather surface to remove dust and dirt and make the leather surface clean. When the surface of leather

was dry, it was sprayed with the finishing agent twice. Finally, the samples were dried in vacuum drying oven at 60 °C.

### Characterization and Measurement

**Characterization of HBPU.** Fourier transform-infrared (FT-IR) spectrometer (VECTOR-22, BRUKER Company, Germany) was used to identify the structure of HBPU. The LPPU and HBPU were dried at 80 °C for 6 h to remove unreacted monomer and solvent, and then they were determined using thin film method.

The <sup>1</sup>H-NMR spectra were measured using a spectrometer (ADVANCEIII 400 MHz BRUKER Company, Germany) at 25 °C, D<sub>2</sub>O, DMSO-d<sub>6</sub>, and TMS were used as solvent and internal standard substance.

Gel permeation chromatography (GPC) was measured using a spectrometer (DIONEX BJ/U 3000, DIONEX Company) at 40 °C. The standard sample was sodium nitride. As the mobile phase was water, the flow speed was 1 mL/min.

**Table I.** Properties of HBPU

	Appearance	Solid content (%)	Viscosity (cps, 30 °C)	Amino value (mmol/g)
HBPU	Light-yellow	27.8	4580	0.04555

**Table II.** The Finishing Formula

Formulation	PU	HBPU	Butyl acetate
1	10	0	100
2	0	10	100

Thermogravimetric (TG) was performed from room temperature to 600 °C at a heating rate of 10 °C/min using a thermogravimetric analyzer (TGA-Q500, TA Company) in nitrogen atmosphere.

X-ray diffraction (XRD) was obtained using diffract meter (D/Max-3c, HITACHI Company, Japan). The analysis was conducted at 40 kV and 40 mA with Bragg's angle  $2\theta$  from about 5° to 60° at the rate of 5° min<sup>-1</sup>.

**Physical and Mechanical Properties of HBPU.** The water absorption rate (WAR) of the blend film was measured at room temperature. It was calculated according to dry weight ( $W_1$ ) and wet weight ( $W_2$ ) of film. The formula is as follows:

$$\text{WAR} = \frac{W_2 - W_1}{W_1} \times 100\%$$

where  $W_1$  was the weight of the blend film dried in an oven at 50 °C for 24 h and  $W_2$  was the weight of film soaked in deionized water for 24 h.

The water vapor transmission rate (WAT) of the blend film was measured according to the static method. First, 30 mL deionized water was added into a cup, and the film was fixed on the top of the cup, the cup was then weighted quickly ( $m_1$ ). Next, the weighted cup was placed in a dryer with full of some concentrated sulfuric acid. Third, the dryer was placed in the constant temperature and humidity chamber (temperature: 25 °C; humidity: 90% RH) for 24 h. The cup was taken out and weighted as  $m_2$ . The WAT of the blend film, expressing in units of mg 10 m<sup>-2</sup> 24 h<sup>-1</sup>, was calculated by the following equation:

$$\text{WAT} = m_1 - m_2$$

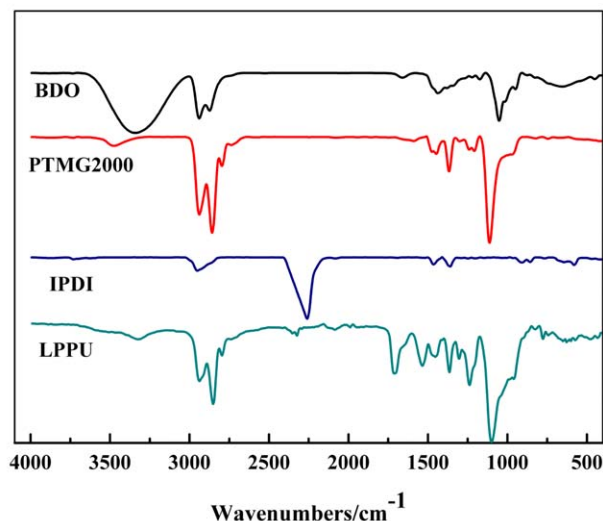
The water vapor permeability (WVP) was measured according to GB/T-12704-1991. First, 12 mL deionized water was added into a cup, and the blend film was fixed on the top of the cup. Next, the cup was subsequently placed in the constant temperature and humidity chamber (temperature: 38 °C; humidity: 50% RH) for 1 h. Third, the cup was taken out and weighted as  $m_1$ . Finally, after 24 h  $m_2$  was weighed accurately. The WVP of the blend film, expressing in units of g m<sup>-2</sup> d<sup>-1</sup>, was calculated as shown:

$$\text{WVP} = \frac{24 \times (m_1 - m_2)}{S \cdot t}$$

where  $S$  is the test area of the sample,  $t$  is the test time of the sample.

The tensile strength and elongation at break of the blend film were tested using a tensile tester (TS-2000-S, Taiwan High Speed Rail Co., Ltd., China). The test was conducted with extending speed of 100 mm min<sup>-1</sup> and the dumb-bell shaped specimens were prepared according to GB1040-79. The average value was calculated after each specimen was tested for three times.

The dry-rubbing and wet-rubbing fastness of the blend film were tested using a dyeing friction fastness instrument (Y571L A, Laizhou Electron Instrument Co., LTD, China) according to GB/3920-1997.



**Figure 1.** FT-IR spectra of BDO, PTMG2000, IPDI, and LPPU. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

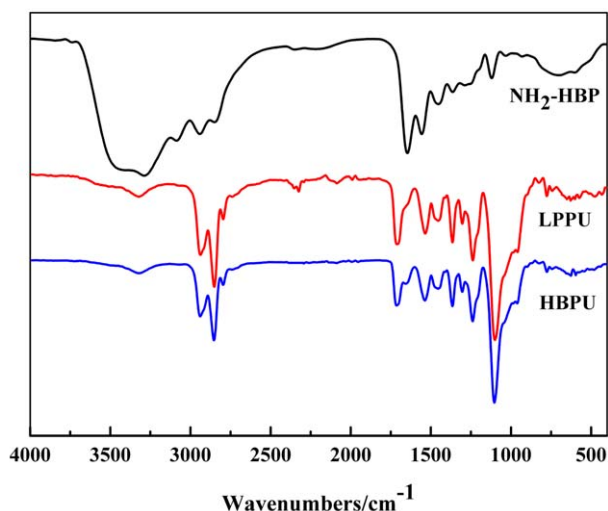
## RESULTS AND DISCUSSION

### Characterization

**FT-IR Analysis.** Figure 1 shows the FT-IR spectra of BDO, PTMG-2000, IPDI, and LPPU. According to the characteristic bands of the HBPU-urea samples in literature,<sup>21,22</sup> the signals were assigned as follows. There were three stretching vibration absorption peaks assigned to the characteristic functional groups of —NHCOO—, i.e., N—H at 3328 cm<sup>-1</sup>, C=O at 1711 cm<sup>-1</sup> and C—N at 1535 cm<sup>-1</sup> in LPPU spectrum. The appearance of these peaks indicated the formation of —NHCOO— through the reaction of —NCO and —OH. In the absorption peaks of PTMG-2000 and LPPU, 1100 cm<sup>-1</sup> belongs to the functional group of —C—O—C—. Moreover, the absorption peak of NCO at 2300 cm<sup>-1</sup> in the LPPU spectrum indicates that the reaction was carried out in accordance with the expected route, and only part NCO was reacted.

Figure 2 shows the FT-IR spectra of NH<sub>2</sub>-HBP, LPPU, and HBPU. In NH<sub>2</sub>-HBP spectrum, the absorption peaks of N—H appeared at 3400 cm<sup>-1</sup> and 700 cm<sup>-1</sup>. There are two stretching vibration absorption peaks assigned to the functional groups of —NHCOO—, i.e., N—H at 3300 cm<sup>-1</sup> and C=O at 1645 cm<sup>-1</sup> in HBPU spectrum. The absorption peak of NCO at 2300 cm<sup>-1</sup> existed before NH<sub>2</sub>-HBP was added into LPPU. When the reaction between NH<sub>2</sub>-HBP and LPPU was completed, the peak of NCO disappeared. Indicating that the reaction was conducted as anticipated.

**<sup>1</sup>H-NMR Analysis.** The representative NMR spectra of NH<sub>2</sub>-HBP, LPPU, HBPU is shown in Figure 3(a–c). The resonance area or chemical shift and position of proton in NH<sub>2</sub>-HBP, LPPU, and HBPU are displayed in Table III. The major difference in HBPU and LPPU spectrum is identified with arrow in the Figure 3(b,c). According to the characteristic bands of the HBPU-urea samples in literature,<sup>19</sup> the appearance of new peaks at 7.70 ppm, that the —NH<sub>2</sub> group hyperbranched polymer reaction with —NCO group to formed the urethane bond. So



**Figure 2.** FT-IR spectra of NH<sub>2</sub>-HBP, LPPU, and HBPU. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

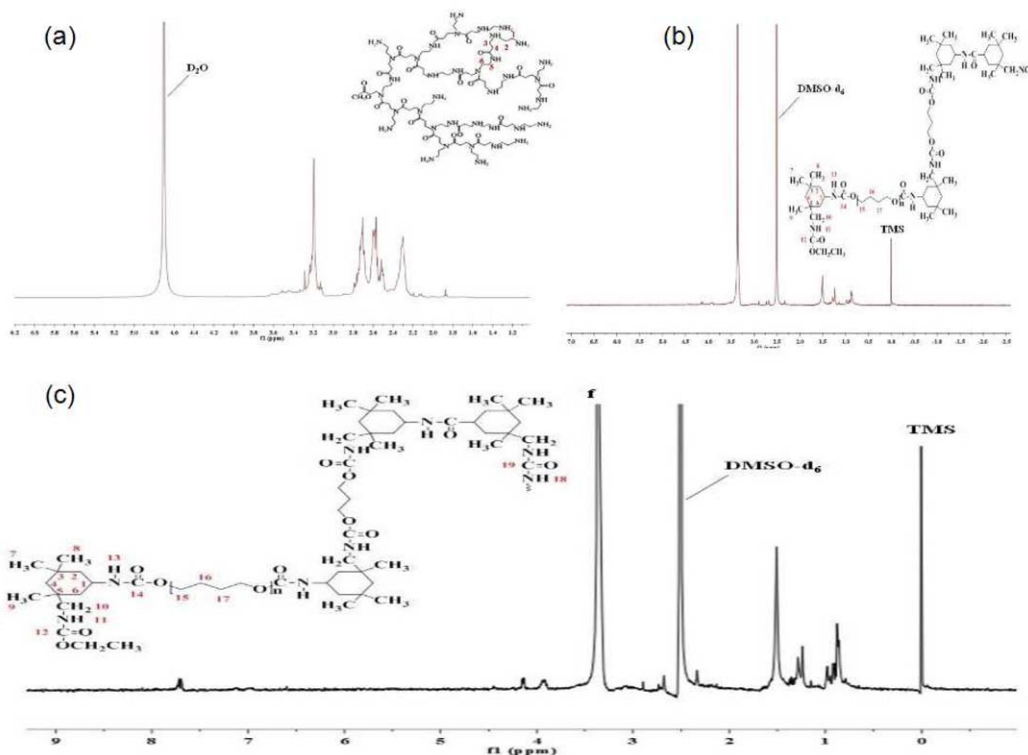
we have concluded from NMR analysis that the disappearance of —OH and —NCO groups and the formation of urethane polymer chains. So the chemical shift of proton in —NHCOO—, which indicated that the reaction was performed as anticipated.

**GPC Analysis.** The GPC of LPPU (a) and HBPU (b) were shown in Figure 4. The specific data as shown in Table IV. As can be seen from the Table IV,  $M_n$  (HBPU)/ $M_n$  (LPPU) was 1.852,  $M_w$  (HBPU)/ $M_w$  (LPPU) was 2.242, in which the relative molecular mass distribution of LPPU and HBPU was 2.01 and 2.41,

respectively. The relative molecular mass distribution index of HBPU was larger, because the grafting reaction is random. From the GPC analysis, we can see that the number average relative molecular weight of LPPU and HBPU was 13,098, 24,253, respectively.

**TG Analysis.** Figure 5 shows the TG curve of LPPU (a) and HBPU (b). As shown in Figure 5(a), the loss of weight before 240.5 °C was hardly noticeable, and the weight loss rate was only about 1.05%, mainly due to the volatilization of a small amount of solvent in the sample. When temperature was raised to 348.6 °C, the weight loss rate increased rapidly. The most decomposition rate was at 413.6 °C. As can be seen from Figure 5(b), the initial thermal decomposition temperature of HBPU was 269.5 °C, higher than that of LPPU. Then the temperature continued to rise, the decomposition rate of the product gradually increased. When the temperature reached 470.5 °C, the decomposition was almost complete and the residual amount was about 4.38%, suggesting that HBPU has better thermal stability.

**XRD Analysis.** Figure 6 shows the XRD spectra of LPPU and HBPU. All diffraction peaks of LPPU and HBPU are found at around  $2\theta = 20^\circ$ , showing HBPU has certain crystallinity. The degree of crystallinity was accordingly calculated with the aid of Jade 5.0 software (Materials Data). The data of LPPU and HBPU were 4.05% and 2.65%, respectively, which was attributed to the introduction of NH<sub>2</sub>-HBP. As NH<sub>2</sub>-HBP itself has no highly geometric symmetry and contains a lot of branched chains, and the volume of side groups is bigger, hyperbranched structures was formed in HBPU, resulting in the decrease of the crystallinity.



**Figure 3.** <sup>1</sup>H-NMR spectrum of (a) NH<sub>2</sub>-HBP, (b) LPPU, (c) HBPU. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

**Table III.**  $^1\text{H-NMR}$  Chemical Shifts of  $\text{NH}_2\text{-HBPU}$ , LPPU, HBPU Measured at Room Temperature

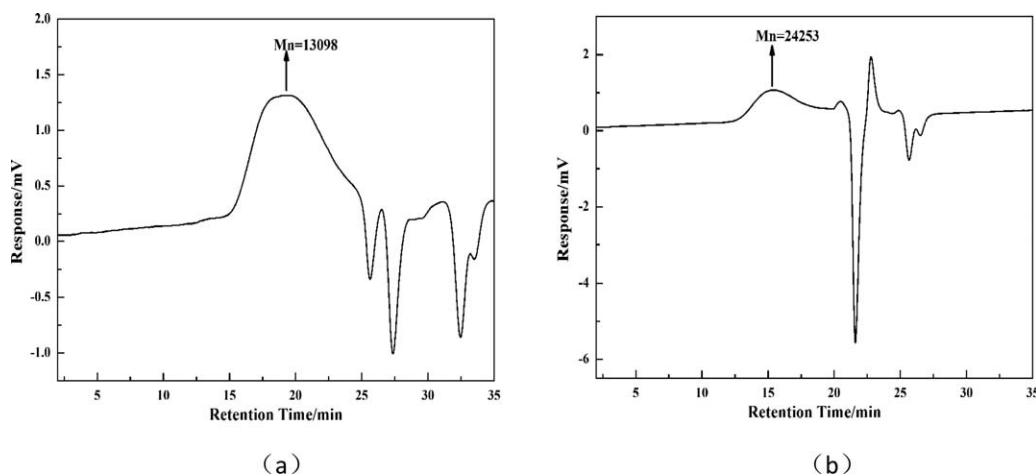
Structure	Position	$^1\text{H NMR}$ chemical shift (ppm)
Figure 3(a)	H-1	2.57-2.67
	H-2	2.43-2.64
	H-3	2.73-2.75
	H-4	2.29-2.49
	H-5	3.17-3.42
	H-6	2.73-2.75
Figure 3(b)	H-1	3.36
	H-2	1.85
	H-3	—
	H-4	1.72
	H-5	—
	H-6	1.63
	H-7	1.15
	H-8	0.92
	H-9	1.03
	H-10	2.68-2.90
	H-11	6.99
	H-12	—
	H-13	7.14
Figure 3(c)	H-18	7.70
	H-19	—

### The Application Performance of HBPU

**Test Result of Sanitary and Mechanical Performances of PU Film and HBPU/PU Blend Film.** As shown in Table V, the moisture absorption rate, moisture transmission, the WVP of

HBPU/PU blend film were significantly greater than those of PU film. The reason was that large number of active amino groups in HBPU led to the hydrophilic group content increasing on the film surface and the microporous was formed, which was helpful for the transport of water molecules. The tensile strength of leather finished by HBPU was more than that of the leather finished by PU. On the one hand, the special hyperbranched structure influenced the tightness between molecular chains. On the other hand, because of the existence of hydrogen bonds, the relative slip between molecular chains became difficult. However, the tearing strength and elongation at break became weaker. This is because the hyperbranched structure of HBPU finishing agent increased the stress concentration of finishing agent. Little change was found in elongation at break because the soft segment of HBPU was hydroxyl-terminated polyether, and the rotation of molecular chains was easy, but the molecular inter-atomic forces increased with the excessive crosslinking between the molecular chains. As a result, the movement of molecular chains was hindered (Table V).

**The Application Performance in Leather.** The application experiment shows that the WVP value of the finished leather reduced compared to that of crust. As the film formed by finishing agent was tight and blocked the transport channels of water vapor molecules, the WVP decreased. Comparatively, the WVP of the leather finished by HBPU was superior to that of the leather finished by PU. This was because HBPU contained a large number of hydrophilic groups, which helps the transport of water molecules. The dry and wet rub fastness of leather finished by HBPU was nearly the same with that of leather finished by PU. The tensile strength of leather finished by HBPU finishing agent was more than that of the leather finished by commercial PU finishing agent. However, the tensile strength and elongation at break decreased because the hyperbranched

**Figure 4.** GPC spectrum of (a) LPPU and (b) HBPU.**Table IV.** GPC Characteristics of LPPU and HBPU

	$M_n$	$M_w$	$M_p$	$M_z$	$M_z + 1$	Polydispersity
LPPU	13,098	26,352	21,318	42,658	56,695	2.01
HBPU	24,253	59,081	45,544	130,244	227,169	2.43

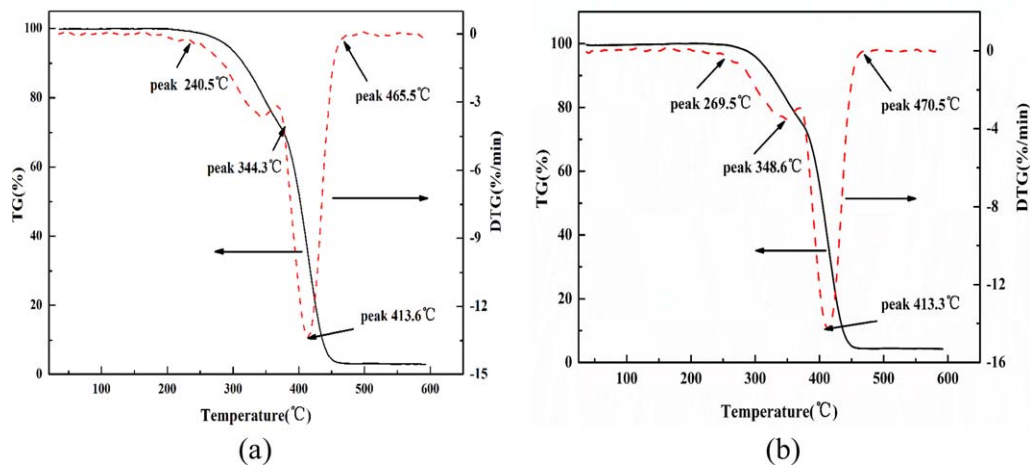


Figure 5. The thermogravimetric analysis of (a) LPPU and (b) HBPU. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

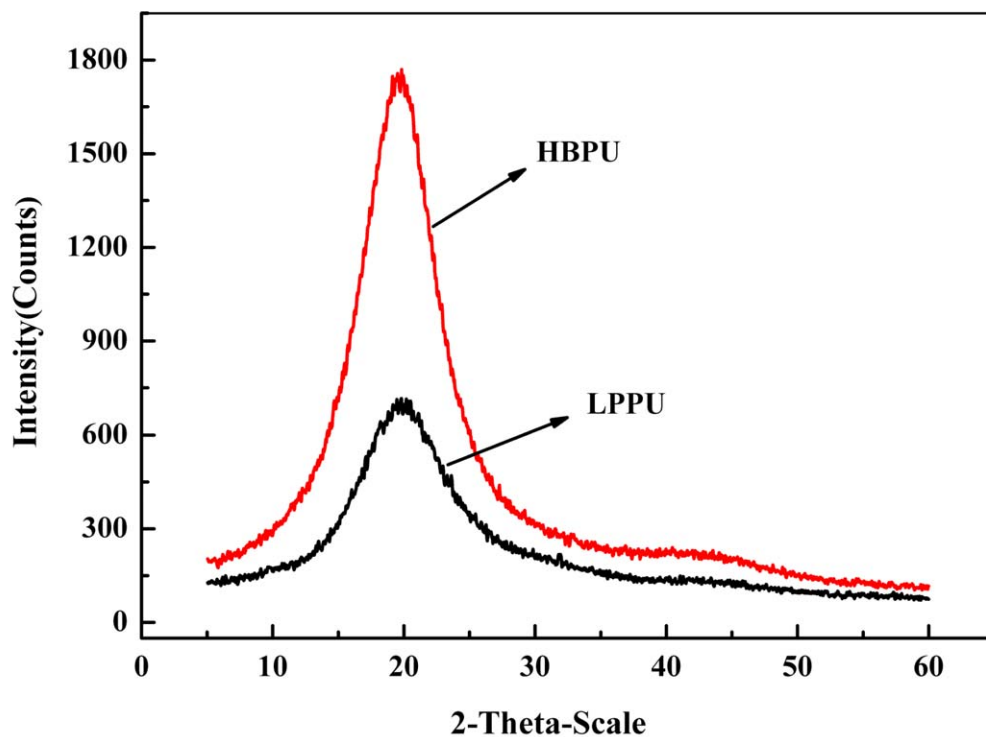


Figure 6. XRD spectrum of LPPU and HBPU. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table V. Properties of PU Film and HBPU/PU Blend Film

Sample	WAR/%	Water vapor transmission rate/g/(m <sup>2</sup> d)	WAP/mg·10 cm <sup>-2</sup> 24 h <sup>-1</sup>	Tear strength/MPa	elongation at break/%
PU film	0.79	94.31	51.3	20.84	348.51
PU/HBPU film	2.07	471.57	184.7	15.72	442.34
Percent change	162.02↑	400.00↑	260.0↑	24.57%↓	26.92%↑

Table VI. Physical and Mechanical Properties of Finished Leather

	Crust leather	Leather finished by HBPU	Leather finished by commercial PU
Dry-rub fastness (grade)	4	5	5
Wet-rub fastness (grade)	3-4	4-5	4-5
WVP (mg·10 cm <sup>-2</sup> ·24 h <sup>-1</sup> )	1206.95	1019.8	902.2
Tensile strength (MPa)	10.43	23.59	21.09
Tear strength (N/mm)	55.77	68.41	75.86
Elongation at break (%)	82.80	91.58	99.19

structure of HBPU finishing agent facilitated the increase of the stress concentration of finishing agent (Table VI).

## CONCLUSIONS

A hyperbranched polyurethane finishing agent with amino groups was synthesized and characterized. The results of FT-IR and <sup>1</sup>H-NMR indicated that the HBPU was synthesized as the anticipated route. The thermal decomposition temperature and crystalline of HBPU were 269.5 °C and 2.65% respectively, showing that HBPU has good thermal stability and certain crystallinity.

The application results of HBPU in synthetic leather showed that when the dosage of HBPU was 10%, the water absorption, moisture transmission, WVP, and the elongation at break increased, respectively. However, the tensile strength decreased. The dry and wet rub resistance of leather finished by HBPU were excellent, while the WVP value was 1019.8 mg 10 cm<sup>-2</sup> 24 h<sup>-1</sup>, increased by 13.0%.

## ACKNOWLEDGMENTS

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