Asian Journal of Chemistry; Vol. 27, No. 10 (2015), 3591-3597

ASIAN JOURNAL OF CHEMISTRY

http://dx.doi.org/10.14233/ajchem.2015.18880

Preparation and Film Properties of Hyperbranched Waterborne Polyurethane

XUECHUAN WANG[1], JING REN[1,*] and TAOTAO QIANG[2]

[1]College of Resource and Environment, Shaanxi University of Science and Technology, Xi'an 710021, Shaanxi Province, P.R. China
[2]Shaanxi Research Institute of Agricultural Products Processing Technology, Xi'an 710021, Shaanxi Province, P.R. China

*Corresponding author: E-mail: 531536261@qq.com

Received: 26 November 2014; *Accepted*: 8 January 2015; *Published online*: 22 June 2015; AJC-17309

Hyperbranched polyurethane has low viscosity, solubility enhancement, film-forming performance is good, good water resistance, thermal stability and physical and mechanical properties, so hyperbranched polyurethane gradually becomes a hotspot in research of leather finishing field in theory and applications. In this paper, hydroxyl-terminated hyperbranched polymer (HPAE) was prepared using nuclear "one-step". Represented by first generation of hydroxyl-terminated hyperbranched polymer, with the polytetramethylene glycol 1000 (PTMG 1000), isophorone diisocyanate (IPDI), 1,4-butanediol (BDO) as the main raw materials, dihydroxy methyl propionic acid (DMPA) as hydrophilic monomer, hyperbranched waterborne polyurethane (HWPU) was synthesized. The structure and properties of hyperbranched waterborne polyurethane were characterized by infrared spectroscopy, scanning electron microscope, atomic force microscope, the X-ray diffraction, the emulsion particle size, thermal gravimetry and other modern instruments and physical and mechanical properties of thin film, film contact angle, heat resistance, water resistance and solvent resistance were studied. The experimental results showed that the heat resistance, solvent resistance and physical and mechanical performance of hyperbranched waterborne polyurethane was significantly enhanced.

Keywords: Hydroxyl-terminated hyperbranched polymer, Hyperbranched waterborne polyurethane, Thin film.

INTRODUCTION

Waterborne polyurethane is polyurethane resin dissolved or dispersed in water to form the binary colloidal system, is the environmental protection high polymer material of meeting the current requirements of sustainable development[1,2], has excellent characteristics of cold resistance, mechanical properties, non-toxic and has a wide range of applications in fabric, leather, footwear and other fields as paint or adhesive and presents the trend of gradually replacing solvent-based polyurethane[3-7]. Traditional polyurethane belongs to the linear structure, has a wide range of applications in leather finishing. Polytetramethylene glycol as soft segment of polyurethane coating has high strength and modulus, hydrolysis resistance, abrasion resistance, resistance to mildew, oil resistance, dynamic performance, the electric insulation performance and low temperature flexibility of performance are also very good[8], it has some characteristics that the usual type of polyester polyurethane elastomers cannot reach[9].

Hyperbranched polymers are a class of highly branched macromolecules with a three-dimensional structure of the ellipsoidal, it has a cavity inside, at the same time, large active functional groups are distributed at its molecular surface and this is different from the nature of the linear polymer having a similar structural unit[10,11]. Because of its highly branched structure, the hyperbranched polymer is difficult to crystallize and no chain winding, greatly improving the solubility. Compared with the same molecular weight of linear molecules, the viscosity is low in the state of molten. The molecular periphery of end groups can be modified to achieve the required performance[12].

Hyperbranched polyurethane has higher degree of crosslinking[13], but also through end of the reaction before the gel point to avoid cross-linking and curing[14,15]. Hyperbranched polyurethane changes the spatial configuration of a conventional network structure of polyurethane to some extent, forming a spheroid polyurethane[16] which has a branched structure, making it have good mechanical properties and thermal stability.

EXPERIMENTAL

Diethanolamine, AR, Chengdu kelon chemical reagent factory; methyl acrylate, AR, Tianjin Kemiou chemical reagent development center; anhydrous methanol, AR, Tianjin chemical reagent factory; trimethylolpropane, AR, Tianjin chemical reagent factory; *p*-toluene sulfonic acid, AR, Tianjin Basf chemical co., Ltd.; polytetramethylene glycol 1000 (PTMG1000), CP, Aladdin reagent (Shanghai) co., Ltd.; isophorone diisocyanate (IPDI), CP, Shanghai dibo chemical technology co., Ltd.; dimethylolpropionic acid (DMPA, 98 %), Aladdin reagent (Shanghai) co., Ltd.; dibutyltin dilaurate (DBTDL), AR, Tianjin fuchen chemical reagent factory; N-methyl pyrrolidone (NMP), AR, Tianjin kemiou chemical reagent development center; tetrahydrofuran (THF), AR, Tianjin fu yu chemical co., Ltd.

Fourier infrared spectrum analyzer, VERTE70, Germany PE company; Vacuum drying oven, DZG-6050SA, Shanghai senxin experimental instrument co., Ltd.; Electronic analytical balance, AL204, Shanghai Renhe scientific instrument co., Ltd.; X-ray diffractometer, D/max2200PC, Rigaku; Synchronous integrated thermal analyzer, STA409PC, German NETZSCH; Field emission scanning electron microscopy, S4800, Beijing pury Seth instrument co., Ltd.; Atomic force microscope, SPI3800N/SPA400, Beijing precision instrument technology co., Ltd.; Laser particle size analyzer, 2000APA, OMEC; Optical contact angle measurement instrument, JGW-360A-L, Chengde Chenghui testing machine co., Ltd.

Synthesis of hydroxyl-terminated hyperbranched polymer: Using nuclear "one-step", reaction once time according to the generation of the hyperbranched polymer to control the molar ratio of monomer and central core. The first generation of hydroxyl-terminated hyperbranched polymer G_1 synthesis reaction principle is as shown in Fig. 1.

Synthesis of hyperbranched waterborne polyurethane: Taking certain amount of polytetramethylene glycol 1000 (PTMG1000) vacuum dehydrated 2 h at 120 °C, making PTMG1000, isophorone diisocyanate (IPDI) and 1,4-butanediol (BDO) in reaction kettle with a agitator and a condenser pipe, adding a small amount of dibutyl tin dilaurate (DBTDL) as catalyst, then the reaction was processed in the oil bath of 88 °C for 1h, then added the first generation of hydroxyl-terminated hyperbranched polymer (HPAE) and the metering dihydroxy methyl propionic acid (DMPA) as hydrophilic chain extender, then continued to react 2.5 h in 85 °C. The acetone was used to adjust viscosity. After cooling to 50 °C, added to the triethylamine in computation to be salt by neutralization degree of 100 %, reacting about 15 min. In terms of solid content of 30 %, the amount of calculation deionized water was weighted up for high speed dispersed, then the hyperbranched waterborne polyurethane emulsion was obtained. The reaction principle was shown in Fig. 2.

Determination of water absorption: The film was weighed accurately as m_1, then immersed in distilled water and removed after 24 h, the quality was weighed as m_2 after wiping the water on the surface with filter paper, the water absorption is calculated as follows:

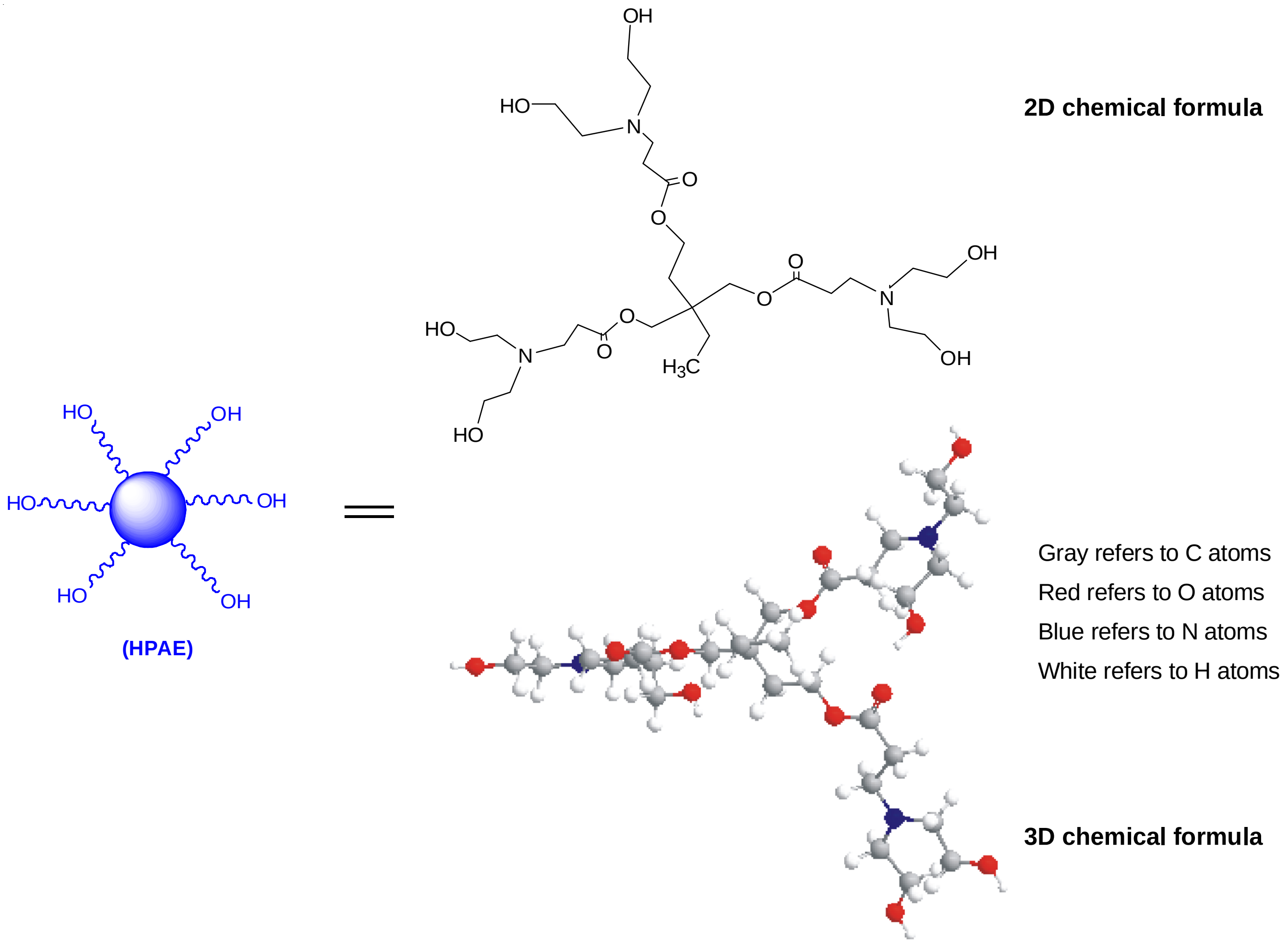


Fig. 1. Structure diagram of first generation of hyperbranched polymer

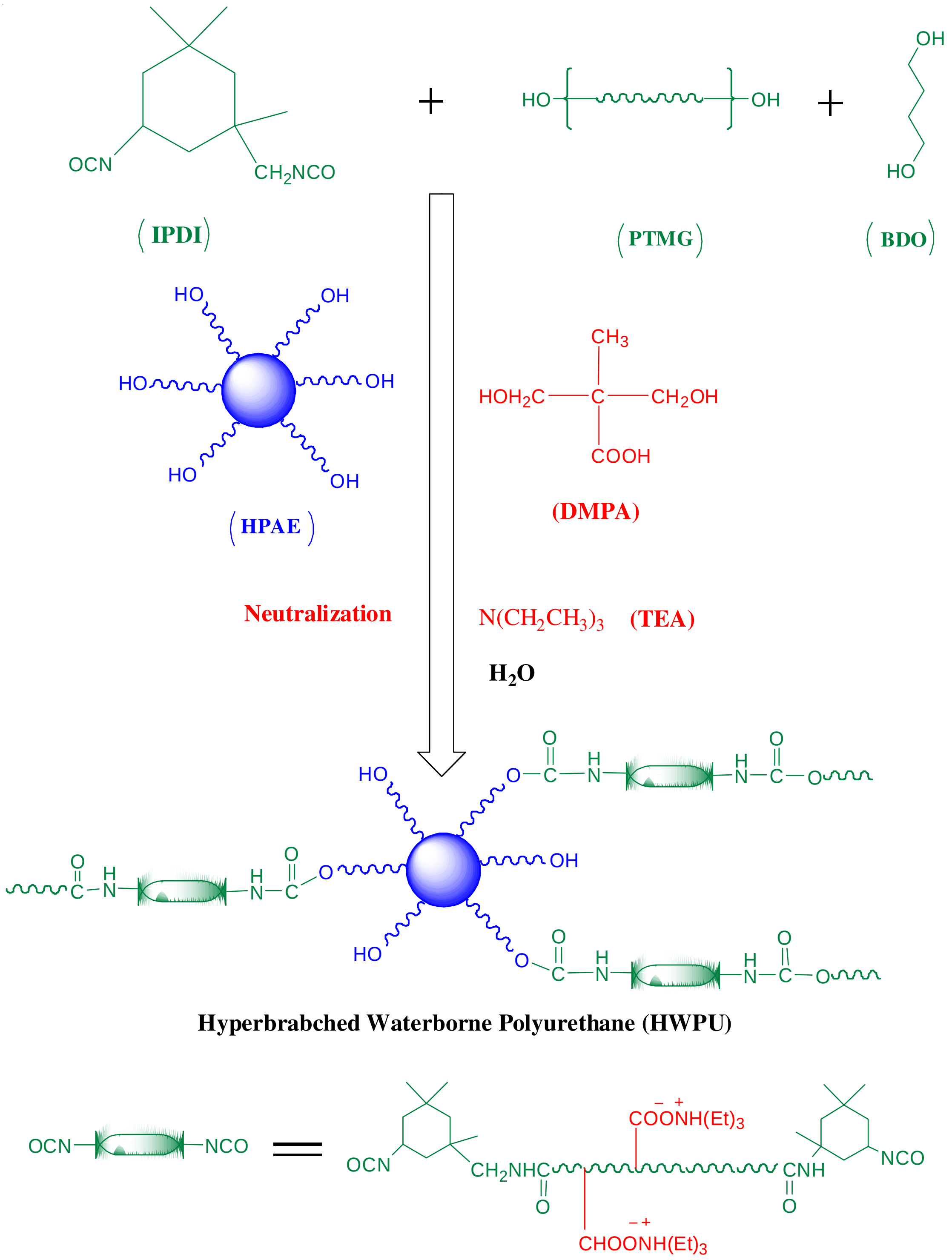


Fig. 2. Synthesis process of hyperbranched waterborne polyurethane

$$\text{Water absorption rate (\%)} = \frac{(m_2 - m_1)}{m_1} \times 100$$

Determination of solvent resistance: Clipping 1 cm closer side of the resin film which is placed in the tetrahydrofuran (THF) after weighing and soaked a period of time (3, 6, 9, 12, 15, 18, 21 and 24 h). Film was taken out, blotted dry with filter paper and dried 6 h in the degree of vacuum 0.1 MPa at 40 °C and finally weighed according to the following formula calculated the dissolution rate of the film in THF.

$$y = \frac{w_0 - w_1}{w_0} \times 100\ \%$$

RESULTS AND DISCUSSION

Fourier transform infrared spectroscopy: Fig. 3 is the infrared absorption spectra of raw materials and synthetic products, it can be seen from the FT-IR spectrograms of hyperbranched waterborne polyurethane, the outside in front of the bending vibration peak of the N-H in carbamate bond is in the

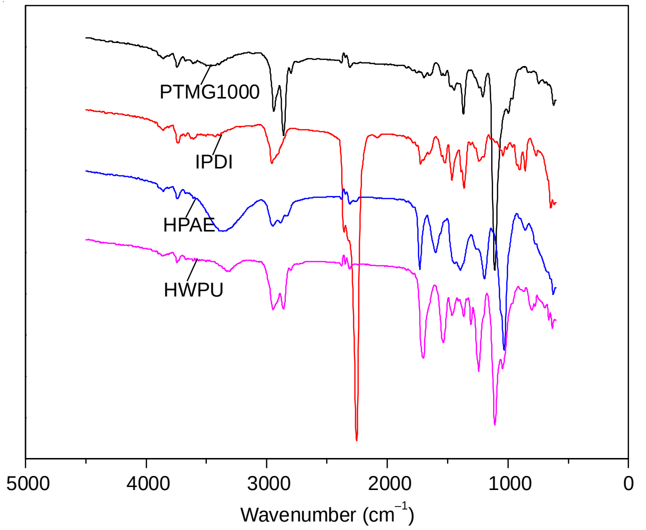


Fig. 3. FT-IR spectrum of raw materials and hyperbranched waterborne polyurethane

661 cm^{-1} nearby, the overlapping absorption peak of N-H and O-H in carbamate bond is in the 3446 cm^{-1}. The -NCO of isophorone diisocyanate absorption peak is in 2262 cm^{-1} nearby, but the -NCO of hyperbranched waterborne polyurethane absorption peak here has disappeared, indicated that the -NCO had completely reacted, the strong O-H stretching absorption peak is in the vicinity of 1720 cm^{-1}, the C-O absorption peak of C=O is near 1250 cm^{-1}, proved that the hyperbranched waterborne polyurethane is containing -COOH. The ether linkage C-O-C stretching vibration peak appears in PTMG1000 around 1110 cm^{-1}. The strong absorption peak near 1679 cm^{-1} is the C=O stretching vibration absorption peak which isophorone diisocyanate and PTMG1000 spectrograms are not exist, so that 1679 cm^{-1} nearby is the C=O of -NHCOO- stretching vibration absorption peak which is generated by reacting the -NCO of isophorone diisocyanate and -OH of PTMG1000.

Scanning electron microscopy (SEM): In order to observe the morphology structure of the film, the film was examined by scanning electron microscope (SEM). After the spraying processing for the film, observing it in the acceleration of 3.0 kv voltage and 10.0k times of magnification. White light districts represent the hard segment of high cohesive energy, forming the dispersed phase. The dark areas represent the soft segment, forming the continuous phase[17,18]. SEM graphs of waterborne polyurethane and hyperbranched waterborne polyurethane are Fig. 4(a), (b), respectively. It can be seen from the diagrams, the hyperbranched waterborne polyurethane is formed network structure and the white light districts of the two waterborne polyurethanes are very few and can hardly see the phase-separated structure of hard and soft segments, indicated the surfaces are all evenly.

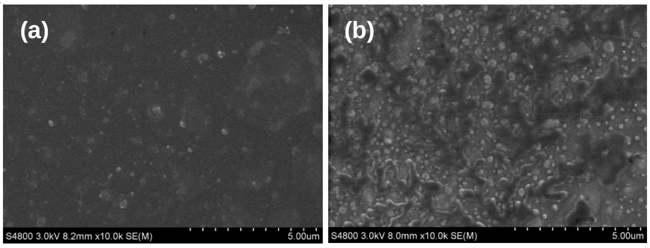


Fig. 4. SEM diagrams of waterborne polyurethane and hyperbranched waterborne polyurethane

Atomic force microscope (AFM): Atomic force microscope graphs of waterborne polyurethane and hyperbranched waterborne polyurethane are Fig. 5(a), (b), respectively. The phase principle of AFM is based on the difference of material hardness and friction, so it can eliminate the impact of surface roughness, have the effect of edge enhancement, while avoiding false impression due to macroscopic surface irregularities plan, showing a real material composition structure. It can be seen from the figure, the bright part represents the hard segment of high cohesive energy, the concave and darker part is soft segment which is a continuous distribution. Data showed that the roughness of hyperbranched waterborne polyurethane is 4.568 nm, waterborne polyurethane is 4.649 nm, so the surface roughness of hyperbranched waterborne polyurethane is better.

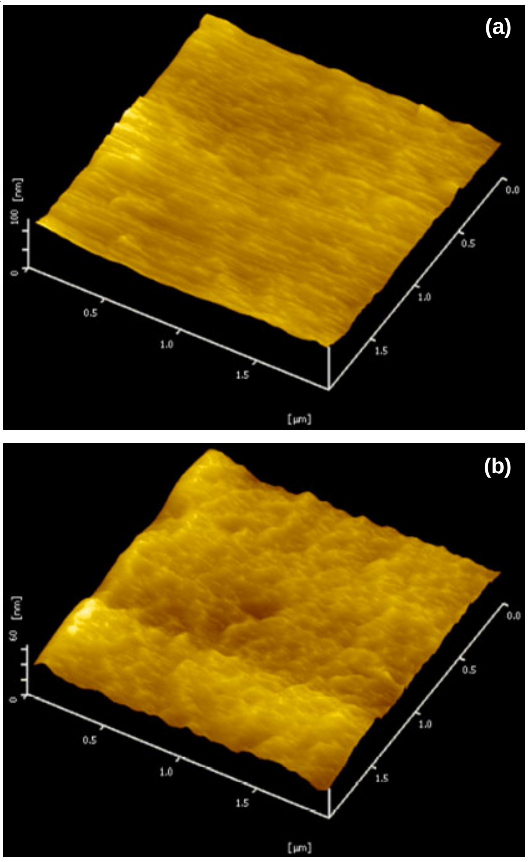


Fig. 5. AFM diagram of waterborne polyurethane and hyperbranched waterborne polyurethane

X-ray diffraction: Fig. 6 is XRD spectrograms of waterborne polyurethane and hyperbranched waterborne polyurethane. As can be seen from the figure, the crystallinities of the two waterborne polyurethanes are non-crystalline system. The crystallinities were measured: hyperbranched waterborne polyurethane: 6.37 %, waterborne polyurethane: 2.07 %. Due to the addition of the hyperbranchd polymer, the polyurethane forms a network structure, reducing the micro-phase mixing degree of hard and soft segment and the movement of soft segment molecular chain would not have been largely restricted, making it easier for the molecular chain movement, which leads to increased crystallinity system.

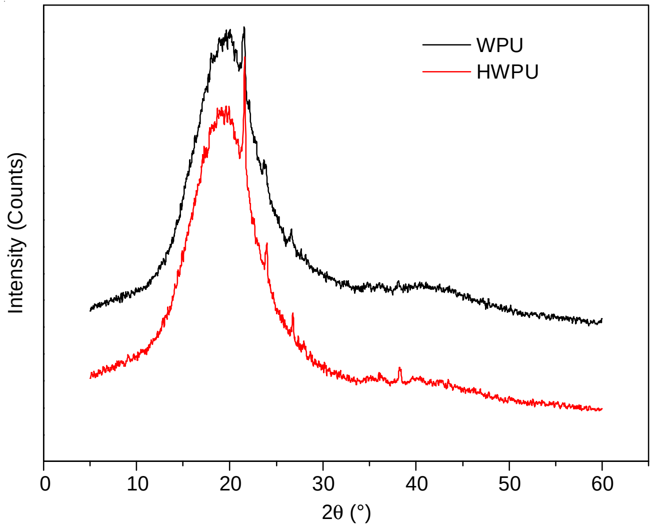


Fig. 6. XRD diagram of waterborne polyurethane (WPU) and hyperbranched waterborne polyurethane (HWPU)

Emulsion particle size: The emulsion particle size distribution for waterborne polyurethane and hyperbranched waterborne polyurethane was shown in Fig. 7. As can be seen from the figure, three types of emulsions are uniformly distributed. From the aspects of data, the surface area average particle size of hyperbranched waterborne polyurethane is 0.114 µm, volume average particle size is 0.169 µm; the surface area average particle size of waterborne polyurethane is 0.203 µm, volume average particle size is 0.199 µm. Two types of polyurethane emulsions are milky and have blue light, no precipitation. The emulsion particle size of hyperbranched waterborne polyurethane is smaller and the smaller emulsion particle size is conducive to the stability of the emulsion.

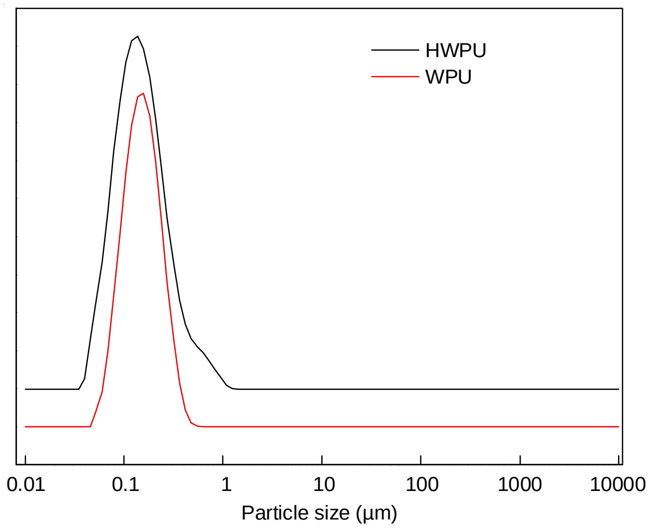


Fig. 7. Emulsion particle size distribution diagram of waterborne polyurethane and hyperbranched waterborne polyurethane

Simultaneous thermal analysis curves: Fig. 8(a) is the simultaneous thermal analysis curves of waterborne polyurethane. As can be seen from the figure, the decomposition temperature of waterborne polyurethane is 240.85 °C; the weight of the sample remains at 93.5 %; the largest decomposition rate appears when the temperature is 294.35 °C and the decomposition rate of waterborne polyurethane is nearly 84 %. The film has been completely decomposed at 437.85 °C, weightlessness is completed, the residual is about 7.87 %. Fig. 8(b) is the simultaneous thermal analysis curves of hyperbranched waterborne polyurethane. It is clear from Fig. 8(b), when the temperature is low, substance of volatilization and decomposition is mainly the trace moisture of resin molecules and other small molecules impurities, the weight loss rate is about 2.39 %, the weight of the sample remains at 95 %. Continue to heat up, the polymer begins to decompose slowly, the decomposition temperature of hyperbranched waterborne polyurethane is 269.01 °C; the largest decomposition rate appears when the temperature is 324.51 °C and the decomposition rate of is nearly 80 %; film weight at 50 % when the temperature is 376.51 °C; at 464.01 °C, the film has been completely decomposed, weightlessness is completed, the residual is about 3.81 %. Due to the addition of the hyperbranchd polymer, the polyurethane forms a network structure, enhances the cohesion of molecules, improves the thermal stability of the thin film at low temperature area, at high temperature the structure will be destroyed. In general, hyperbranched waterborne polyurethane in thermal performance is better than waterborne polyurethane.

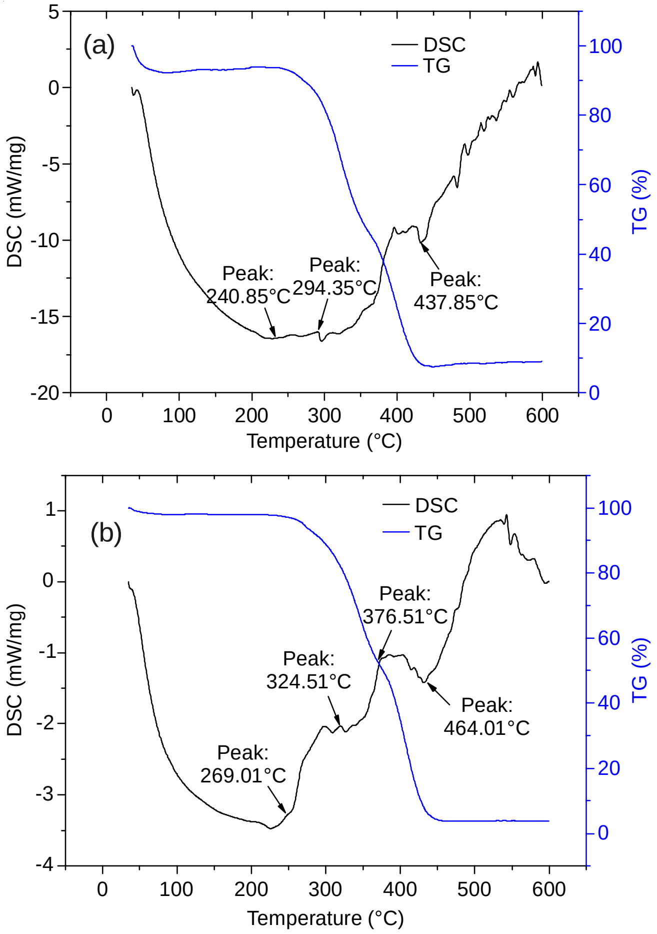


Fig. 8. Simultaneous thermal analysis of waterborne polyurethane and hyperbranched waterborne polyurethane

Physical and mechanical properties: The physical and mechanical properties of two types of the waterborne polyurethanes are shown in Table-1. As can be seen from the table, elongation at break, load elongation and tensile strength of hyperbranched waterborne polyurethane has a greater degree of improvement compared to the waterborne polyurethane, indicating hyperbranched waterborne polyurethane has good physical and mechanical properties. This is due to add the hydroxyl-terminated hyperbranched polymer makes the waterborne polyurethane formed a reticular structure, compared with the general linear structure, network structure has more advantages in terms of mechanical properties.

TABLE-1
PHYSICAL AND MECHANICAL PROPERTIES

	Elongation at break (%)	Load elongation (%)	Tensile strength (MPa)
WPU	133.55	5.85	123.87
HWPU	264.79	29.39	164.90

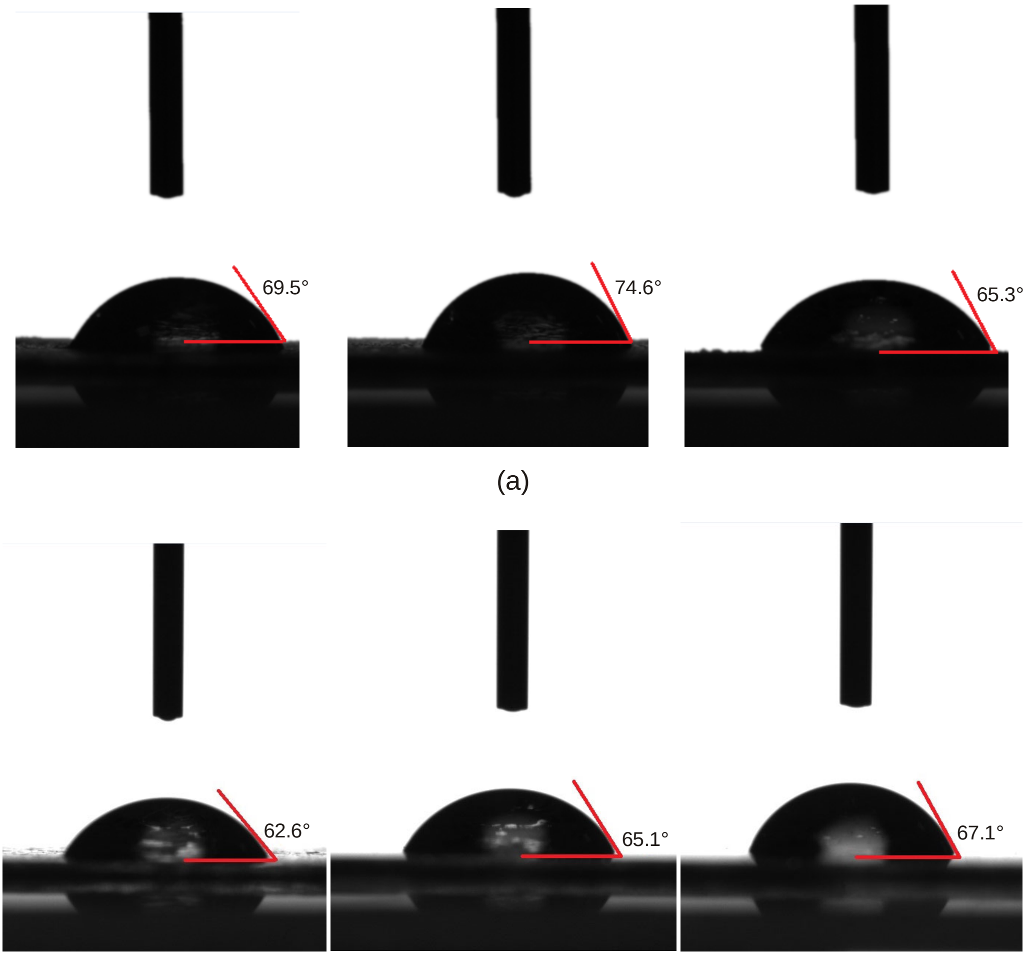
Contact angle: The contact angle graphs of the three different parts of waterborne polyurethane and hyperbranched waterborne polyurethane are Fig. 9(a), (b). In Fig. 9(a), the contact angles of waterborne polyurethane are 69.5°, 74.6°, 65.3°, respectively, the average value is 69.8°; in Fig. 9(b), the contact angles of hyperbranched waterborne polyurethane are 62.6°, 65.1°, 67.1°, respectively, the average value is 64.93°. Therefore, hyperbranched waterborne polyurethane in the hydrophilic is better.

Determination of water absorption rate: Weigh film mass m_1, soaked in distilled water for 24 h, wipe the surface of the water with a filter paper and then said mass m_2, therefore, the water absorptions are:

$$\text{Water absorption rate of waterborne polyurethane (\%)} = \frac{(0.0233-0.0203)}{0.0203} \times 100 = 14.78$$

$$\text{Water absorption rate of hyperbranched waterborne polyurethane (\%)} = \frac{(0.0180-0.0165)}{0.0165} \times 100 = 9.09$$

The water absorption rate of hyperbranched waterborne polyurethane is about 9 % that is significantly lower compared to waterborne polyurethane. The polymer has some crosslinking because of the multifunctional structure of hydroxyl-terminated hyperbranched polymer. Increase hydroxyl-terminated hyperbranched polymer will improve the degree of crosslinking of polymer, the force of molecular chain increases and the movement of molecular chain is blocked, water molecules are difficult into the molecular chain to swell the polymer, therefore the water absorption rate of hyperbranched waterborne polyurethane of film is falling.



(a)

(b)

Fig. 9. Contact angle diagrams of waterborne polyurethane and hyper-branched waterborne polyurethane

Determination of solvent resistance: Fig. 10 shows the dissolution rates in tetrahydrofuran of waterborne polyurethane and hyperbranched waterborne polyurethane. As can be seen from the figure, the 24 h dissolution rate in THF of hyperbranched waterborne polyurethane is 81.84 %, the 24 h dissolution rate in THF of waterborne polyurethane is 96.12 %. Thus, the solvent resistance of hyperbranched waterborne polyurethane is better.

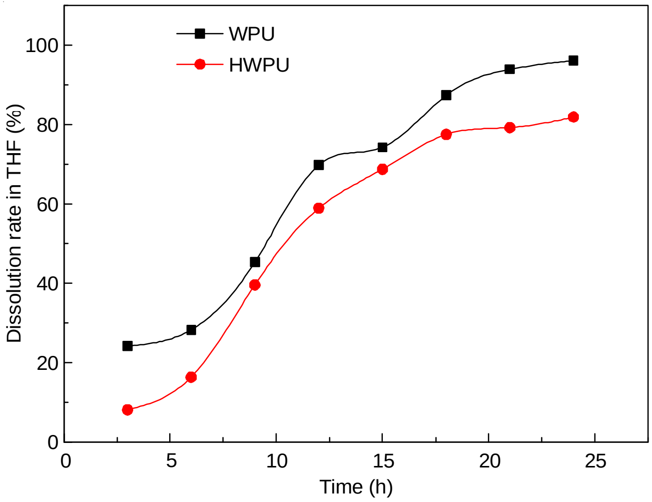


Fig. 10. Dissolution rate of waterborne polyurethane and hyperbranched waterborne polyurethane in the THF

Conclusions

- Hydroxyl-terminated hyperbranched polymer (HPAE) was prepared using nuclear "one-step". Represented by the first generation of hydroxyl-terminated hyperbranched polymer, with the polytetramethylene glycol 1000 (PTMG 1000), isophorone diisocyanate (IPDI), 1,4-butanediol (BDO) as the main raw materials, dihydroxy methyl propionic acid (DMPA) as hydrophilic monomer, hyperbranched waterborne polyurethane (HWPU) was synthesized.
- Hyperbranched waterborne polyurethane is a kind of non-crystalline material. SEM graphs indicated hyperbranched waterborne polyurethane has the structure of network and can hardly see the phase-separated structure of hard and soft segments. The roughness of hyperbranched waterborne polyurethane is 4.568 nm, the surface is more evenly compared to waterborne polyurethane whose roughness is 4.649 nm. The surface area average particle size of hyperbranched waterborne polyurethane is 0.114 μm, volume average particle size is 0.169 μm; the surface area average particle size of waterborne polyurethane is 0.203 μm, volume average particle size is 0.199 μm. Two types of polyurethane emulsions are milky and have blue light, no precipitation. The emulsion particle size of hyperbranched waterborne polyurethane is smaller and the smaller emulsion particle size is conducive to the stability of the emulsion. The physical and mechanical properties of hyperbranched waterborne polyurethane have a greater degree of improvement compared to the waterborne polyurethane. The average value of contact angle of waterborne polyurethane is 69.8°, the average value of contact angle of hyperbranched waterborne polyurethane is 64.93°. Therefore, hyperbranched waterborne polyurethane in the hydrophilic is better. The water absorption rate of hyperbranched waterborne polyurethane is about 9 % and the solvent resistance of hyperbranched waterborne polyurethane is better compared to waterborne polyurethane. As can be seen from the simultaneous thermal analysis curves, the decomposition temperature of waterborne polyurethane is 240.85 °C, the decomposition temperature of hyperbranched waterborne polyurethane is 269.01 °C. Hyperbranched waterborne polyurethane in thermal performance is better than waterborne polyurethane.

ACKNOWLEDGEMENTS

National Natural Science Foundation of China (21276151), Shaanxi Provincial Science and Technology Department of Science and Technology Program (2011SZS007), Shaanxi Province Key Technology Innovation Team (2013KCT-08), Shaanxi University of Science and Technology Innovation Team (TD12-04), Graduate Innovation Fund of Shaanxi University of Science and Technology.

REFERENCES

1. D.H. Jung, E.Y. Kim, Y.S. Kang and B.K. Kim, *Colloids Surf. A*, **370**, 58 (2010).
2. S. Wensheng, X. Tracy, Z. Lin, *et al*., Preparation and Properties of Sulfonic Acid Type Waterborne Polyurethane dispersion, China Polyurethane Industry Association, Fifteenth Annual Meeting Proceedings, pp. 338-343 (2010).
3. D.K. Lee, H.B. Tsai, H.H. Wang, and R.S. Tsai, *J. Appl. Polym. Sci*., **94**, 1723 (2004).
4. V. Garcia-Pacios, Y. Iwata, M. Colera and J.M. Martin-Martinez, *Int. J. Adhes. Adhes*., **31**, 787 (2011).
5. M.A. Pérez-Limiñana, F. Arán-Aís, A.M. Torró-Palau, A.C. Orgilés-Barceló and J.M. Martín-Martínez, *Int. J. Adhes. Adhes*., **25**, 507 (2005).
6. H.X. Li and L.M. Zhu, Polyurethane, Jiangsu Science and Technology Press, pp. 552 (1992).
7. H. Sheikhy, M. Shahidzadeh and B. Ramezanzadeh, *Polym. Bull*., **72**, 755 (2015).
8. S.H.X. Li and Y.J. Liu, Polyurethane Resin and Its Application, Chemical Industry Press, Beijing, pp. 161-122 (2002).
9. X.C.H. Wang, Y.Q. Fu and L.F. Ren, *Functional Materials*, **44**, 289 (2013).
10. P.J. Flory, *J. Am. Chem. Soc*., **74**, 2718 (1952).
11. X.C. Wang, T.T. Qiang and L.F. Ren, *Chinese Leather*, **34**, 14 (2005).
12. T.T. Qiang, X.C. Wang and L.F. Ren, *Leather Chemicals*, **24**, 17 (2007).
13. A. Asif, W.F. Shi, X.F. Shen and K. Nie, *Polymer*, **46**, 11066 (2005).
14. J.Y. Choi, L.S. Tan and J.B. Baek, *Macromolecules*, **39**, 9057 (2006).
15. S. Unal, C. Oguz, E. Yilgor, M. Gallivan, T.E. Long and I. Yilgor, *Polymer*, **46**, 4533 (2005).
16. X.C. Wang, X.Z. Yuan, T.T. Qiang and X. Chen, *Fine Chemicals*, **26**, 68 (2009).
17. Q. Cao, The Study on the Storage and Shape Memory of Hyperbranched Polyurethane, Xiangtan University, Changsha, China (2006).
18. S. Kumari, A.K. Mishra, A.V.R. Krishna and K.V.S.N. Raju, *Prog. Org. Coat*., **60**, 54 (2007).