Research Article

Synthesis of waterborne polyurethane using snow as dispersant: Structures and properties controlled by polyols utilization

Changqing Fang [a,b,*], Shaofei Pan [a], Zhen Wang [a,b], Xing Zhou [a,b], Wanqing Lei [a,b], Youliang Cheng [a,b]

[a] Faculty of Printing, Packaging Engineering and Digital Media Technology, Xi'an University of Technology, Xi'an, 710048, China
[b] School of Mechanical and Precision Instrument Engineering, Xi'an University of Technology, Xi'an, 710048, China

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ABSTRACT

Waterborne polyurethane (WPU) dispersions have gained attention towards environmentally-friendly synthesis. In this article, a series of waterborne polyurethane emulsions was successfully synthesized and extensively characterized in terms of thermal, mechanical properties, hydrophilic behavior and morphology. Snow was chosen as dispersant instead of commonly used water. Preparation parameters such as intrinsic properties and molecular weight of polyols were discussed systematically. A chain structure was confirmed by Fourier transform infrared (FT-IR) spectroscopy. When comparing the nature of the polyols (PPG, PEG and PNA, 2000 g/mol) of this study, as-synthesized polyether waterborne polyurethane provided higher solid content, viscosity and water-resistance. However, polyester waterborne polyurethane performed differently and it exhibited higher thermal stability and crystallinity. When comparing the samples (WPU-N210, WPU-N220, WPU-N230 and WPU-N240) with different molecular weight of the same polyol (PPG) used as soft segment, the emulsion WPU-N220 with molecular weight of 2000 g/mol PPG provided the highest solid content and lowest viscosity. It was observed that particle size was uniform and highly dispersed for all samples from TEM images. Thermogravimetric, differential scanning calorimetry (DSC) and X-ray diffraction results demonstrated that the emulsion WPU-N230 with molecular weight of 3000 g/mol PPG possessed higher thermal stability and crystallinity than the other samples. The reason was that the T_g and thermal stability were increased with increasing molecular weight. When molecular weight increased, the arrangement of soft segment became more regular and so did the regularity of the molecular chains. This work demonstrated that different polyols as soft segment applied could lead to great differences in the structure and property of the resulting WPU.

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1. Introduction

Innovative technologies have been developed to produce more environmental friendly and less harmful products to meet the growing consumer demands [1,2]. As polyurethane industry develops continuously, waterborne polyurethane (WPU) is playing an important role, due to its environmental-friendly, healthy and safe features [3–5]. Furthermore, WPU has many excellent properties such as high flexibility at low temperature, abrasion resistance, strong adhesion to glass surfaces and film-forming ability at ambient temperature [6–9]. As such, WPU is used in many fields including printing, ink, adhesive, textiles, construction and fiber processing [10–14].

WPU is high molecular compounds which contain polymer groups (−NHCOO−) on macromolecular backbone, and dispersed particles in aqueous solution to form a binary colloidal system [15–17]. Acetone, prepolymer, hot melt and ketamine/ketazime processes are frequently used to prepared WPU in industry [18,19]. Instead, the general method is the mixture of acetone and prepolymer processes. In this method polyol and isocyanate are used to produce polyurethane prepolymer, with terminal isocyanate group (−NCO). Then in the acetone environment, a chain extension reaction occurs on prepolymer with small molecular chain extender and hydrophilic chain extender, which produces polyurethane prepolymer with higher molecular weight. After that, water is used as dispersant to form an emulsion of polyurethane prepolymer.

Finally, residual acetone is removed through vacuum distillation to obtain WPU dispersions.

WPU is block polymer which consists of alternating soft and hard segments [20]. More specifically, the soft segments in WPU are polyols, which contain a lot of types, such as polyesters, polyethers, polycaprolactone, and polycarbonate origin and impact the flexibility of the polyurethane [21,22]. In contrast, hard segments formed by the reaction of isocyanate and chain extender are stiffer and more polarized, and have lower molecular weight. A large number of previous research was focused on how the differences of soft/hard segment influenced WPU properties, such as ionic group content, segmented structure, molecular weight of polyol, type of chain extender, NCO/OH ratio and so on [23–25]. Vanesa García-Pacios et al. [1,25] prepared different types of WPU dispersions by using various diols including polyester, polyether, and different molecular weights of polycarbonate diols. It demonstrated that the properties of the WPU dispersions and films were significantly depended on the nature and molecular weight of polyols.

According to the abovementioned research, WPU is mostly prepared with dispersant of water and few was synthesized with snow. Zhou et al. [26] chose ice, snow and water as dispersant agents to prepare WPU at different temperatures, i.e. 20 °C, 50 °C and 80 °C. The results demonstrated that snow performed better than water as dispersant when comparing the properties of as prepared WPU dispersions and WPU films. In addition, we analyzed the effects of different polyols on WPU properties with snow as dispersant. In the preset work, two series of control experiments were carried out to synthesize different WPUs. One was polyol of similar molecular weight (2000 g/mol) but different substances, namely poly(neopentyl glycol adipate) (PNA), poly(ethylene glycol)(PEG) and poly(propyleneoxide glycol)(PPG); the other one utilized different molecular weight but same polyol, i.e. poly(propyleneoxide glycol)(PPG) with molecular weight from 1000 g/mol to 4000 g/mol. Morphology of the WPU dispersions was determined by transmission electron microscopy (TEM). Structure of the WPU films was measured by Fourier transform infrared spectroscopy (FT-IR). Thermal stability and crystallinity were analyzed by thermogravimetric (TG), differential scanning calorimetry (DSC) and X-ray diffraction (XRD). Solid content, viscosity and water contact angle of the dispersions were also analyzed respectively. The advantages of using snow as dispersant over that of deionized water, is that the rigid hexagonal structure of snowflakes can decrease hard segment and decrease the polar groups in the as-prepared WPU.

2. Experimental

2.1. Materials

Poly(propyleneoxide glycol) (PPG, number-average molecular weight Mw = 1000 g/mol) and poly(ethylene glycol) (PEG, number-average molecular weight Mw = 2000 g/mol) (both supplied by Kemiou Chemical, Tianjin, China), poly(propyleneoxide glycol) (PPG, number-average molecular weight (Mw) from 2000 to 4000 g/mol) (purchased from Siaopharm Chemical, Shanghai, China), and poly (neopentyl glycol adipate) (PNA, molecular weight (Mw) = 2000 g/mol), all of these were used to synthesize polyurethane samples as oligomer glycol and were dried under vacuum at 120 °C for 2 h before use. The diisocyanate used was isophorone diisocyanate (IPDI, 98 wt% purity, supplied by Jingchun Chemical, Shanghai, China), which was liquid at room temperature. Dimethylolpropionic acid (DMPA) and 1,4-butanediol (BDO, 99.5 wt% purity) (both supplied by Fuchen Chemical (Tianjin, China)) were used as hydrophilic chain extender and small molecular chain extender, respectively. 1-Methyl-2-pyrrolidone (NMP,

Table 1
Nomenclature of the WPU dispersions synthesized with different polyols.

Polyols	Molecular weight of the polyols (Mw) (g/mol)	Nomenclature of the WPU
Poly(propyleneoxide glycol)	1000	WPU-N210
Poly(propyleneoxide glycol)	2000	WPU-N220
Poly(propyleneoxide glycol)	3000	WPU-N230
Poly(propyleneoxide glycol)	4000	WPU-N240
Poly(ethylene glycol)	2000	WPU-PEG
Poly(neopentylglycol adipate)	2000	WPU-PNA

99 wt% purity), triethylamine (TEA, 99 wt% purity) and potassium hydroxide (KOH, 85 wt% purity), were supplied by Kemiou Chemical (Tianjin, China). Dibutyltin dilaurate (DBTDL, purchased from Qingxi Chemical Shanghai, China) was employed as catalysator. Small doses of acetone were used in this process, and snow naturally collected in winter in Xi'an China was used as dispersing phase.

2.2. Synthesis of WPU dispersions

Six aqueous polyurethane dispersions were prepared with different polyols of similar molecular weight and same polyol of different molecular weights. Hard/soft segment molar ratio was 4 and NCO/OH ratio was 1.2. DMPA content set as 0.5 wt% (relative to the weight of the prepolymer). The nomenclature of the WPU samples is listed in Table 1, named WPU- N210, WPU-N220, WPU-N230, WPU-N240, with the different molecular weight of PPG, respectively. Others are named WPU-PEG and WPU-PNA.

Polyols, such as PEG, PNA and PPG (molecular weight from 1000 g/mol to 4000 g/mol), were dried before use. One of these polyols and IPDI were mixed in a four-necked flask (250 ml), equipped with a mechanical stirrer, thermometer and spiral condenser in an electric-heated thermostatic water bath. The reaction was carried out at 80 °C for 2.5 h at a stirring rate of 200 rpm, DBTDL was added 2 h later after the first reaction finished, and then DMPA and NMP were added to the mixture at 60 °C. Then the mixture was kept at 80 °C for another 2 h with a stirring rate at 400 rpm. After that the resulting prepolymer was cooled to 40 °C, BDO and a small amount of acetone were added, after 1 h continuous stirring, TEA and snow were added quickly to emulsify and disperse the hydrophilic WPU prepolymer, and the mixture was stirring at 900 rpm. Finally, KOH was used as a neutralizer to adjust the pH to 8.0–9.0. When the reaction completed, the residual acetone was removed by a vacuum drying oven at 50 °C and 0.05 MPa for 1 h.

2.3. Preparation of WPU films

The films were obtained by casting the samples onto Teflon mould and followed by a slow evaporation of the solvent at room temperature for 3 days, then at 50 °C in a vacuum drying oven for 12 h to completely remove the solvent. The vacuum-dried films were stored in a desiccator to avoid moisture.

2.4. Characterization of the WPU

Transmission electron microscopy (TEM) was used to analyze morphology of the WPU dispersions. TEM images were obtained using a JEM-3010 microscope with a field emission gun at 200 kV. The samples were diluted in deionized water before TEM measurement.

Solid content of the WPU was obtained by difference in weight before and after evaporation of water, and their measurements were carried out according to ISO 124:1997 standard. 2 g of WPU was placed in a glass garden at 105 °C in an oven until constant
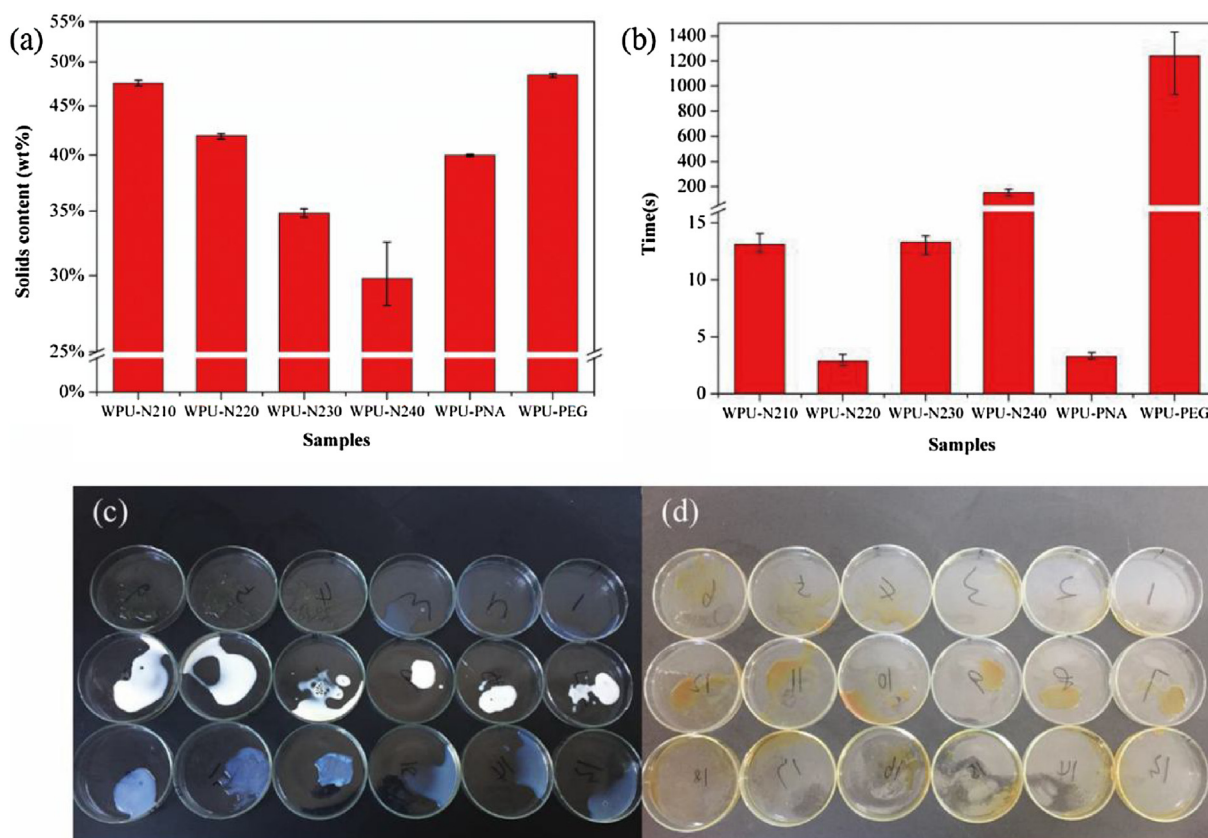
Fig. 1. (a) Solids content of the WPU samples. (b) Vicosity of the WPU samples. (c) and (d) Beginning and end of the solid content test, respectively.

weight was achieved. The solid content of every sample was calculated as the average of three experimental determinations.

Viscosity of the WPU was measured in painted four cup viscometer. The hole at the bottom of the cup was obstructed with a block, and then the sample was poured into the cup, the stopwatch was pressed when the block was removed. The test was finished until nothing flowed out from the hole at the bottom, and the duration time was recorded. The viscosity of each sample was calculated based on the average of twenty measurements.

Fourier transforms infrared spectroscopy (FT-IR) was used to identify the structure of WPU, the infrared spectra was obtained with a Fourier transform infrared spectrophotometer (SHIMADIU FTIR-8400S (CE)), recorded in the transmission mode at room temperature by averaging 128 scans at resolution of $16.0\,cm^{-1}$. The spectra were analyzed in the frequency range of $4000-400\,cm^{-1}$. The sample was obtained by using acetone to dissolve the dried polyurethane films, and dripped it on the potassium bromide flakes uniformly until the acetone evacuation.

Thermogravimetric (TG) experiments were carried out in a MET-TER TOLEDO TGA/DSC 1 analyzer with Gos Controller GC10 STAR^{e} System. Film samples ranging from 5 to 10 mg were placed in an alumina ceramic crucible and heated in nitrogen (flow rate: 100 ml/min) from 50 to 700 °C with a heating rate at15 °C/min.

Differential scanning calorimetry (DSC) analyses were performed in a METLER TOLEDO DSC 823^{e} equipment to acquire thermograms of WPU. Aluminum pans containing 5–10 mg of sample were heated from −100 to 150 °C in nitrogen atmosphere (flow rate: 50 ml/min) at a heating rate of 5 °C/min. The first heating run was executed to remove the thermal history of the samples, the glass transition temperature (T_g) of the polyurethanes samples were obtained from the second heating run.

X-ray diffraction (XRD) was used to analyze the crystallinity of the polyurethane films under an XRD-7000, Shimadzu Limited, Japan with monochromatic Cu Kα radiation. The scanning was measured between 10° and 70° with a scan speed at 8.000 deg/min.

Water contact angle (WCA) measurements were performed with a contact angle meter (Contact Angle System OCA20, Germany). A water drop volume of 2 μl was deposited on the sample surface and the droplet shape was recorded. CCD video and image analysis software were used to determine the water contact angle evolution.

3. Results and discussion

3.1. Characteristics of dispersions

Fig. 1(a) and (b) illustrates the solid content and viscosity, respectively, and Fig. 1(c) and (d) shows the solid content test from the beginning to the end, respectively. The polyurethane emulsions were placed in an oven at 105 °C for several days, the transparent emulsions and the milky white emulsions (Fig. 1(c)) entirely turned into the yellow solid (Fig. 1(d)), which was probably due to the evaporation of water.

Fig. 1(a) shows that the solid content of the polyurethanes decreased with the increase of the molecular weight of polyol. It was obvious in Fig. 1(b) that the vicosity of the samples WPU-N220, WPU-N230 and WPU-N240 augmented with the molecular weight of the polyol increasing. The possible reason was that the soft segment with higher molecular weight might contain the smaller particle size and larger number of particles, which leaded to the stronger affinity between the prepolymer particles and water molecules, consequently the viscosity increased for this reason. However, the smaller and more particles in the WPU needed more water molecules to bind and disperse, which resulted in the decreasing of solid content [25].
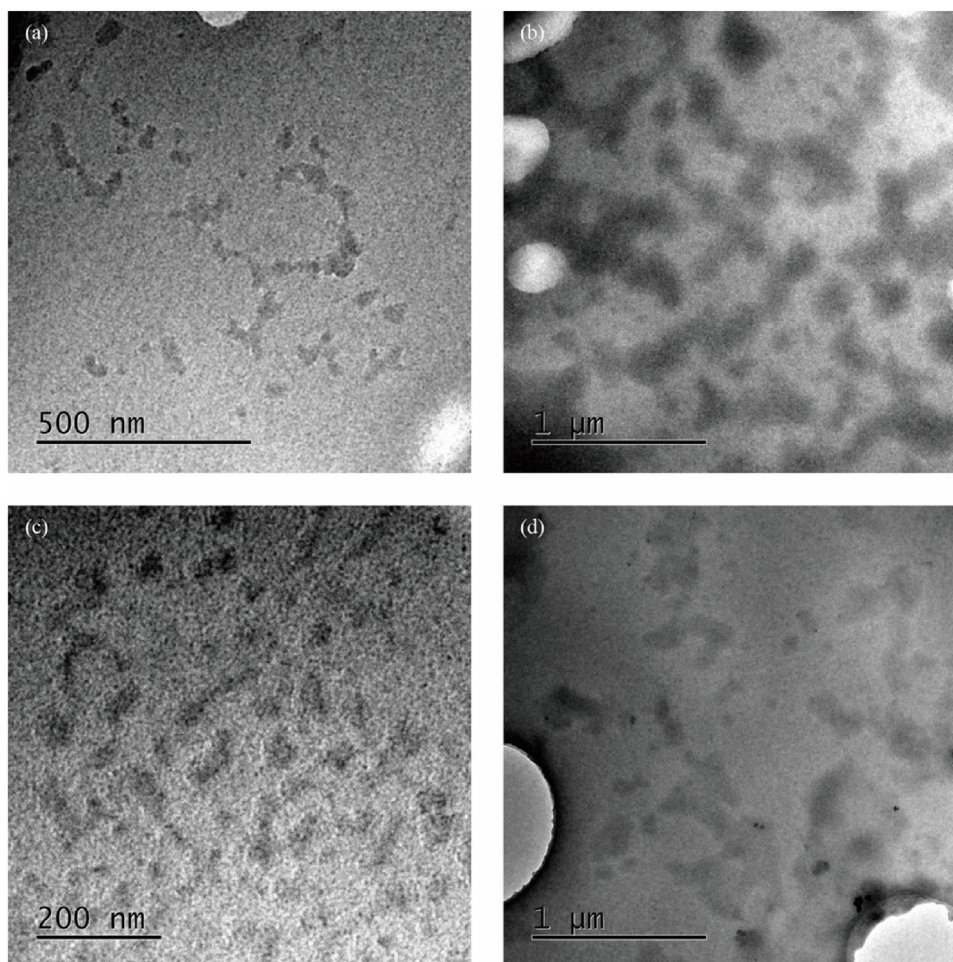
Fig. 2. TEM images of WPU dispersions in synthesis of different polyols. (a) WPU-N210, (b) WPU-N220, (c) WPU-N230, (d) WPU-PNA.

Furthermore, the solid content of polyether waterborne polyurethane was higher than that of polyester, but the viscosity has a contrary tendency. This could be explained that the polyester polyurethane contained ester bond (C=O). When it interacted with water molecules, strong hydrogen bonds were formed which were not conducive to the dispersion of the molecular chain. To some degree, it even made the chain entangled easily. Therefore, for this reason the viscosity of polyester waterborne polyurethane was larger than that of polyether waterborne polyurethane. Since the entangled chains leaded to the poor dispersion, more water were added to improve the dispersion, Therefore the solid content of polyester waterborne polyurethane decreased consequently with the addition of more water [27].

In this study, TEM was used to analyze the morphology of the dispersions of WPU nanoparticles in the process of the initiation of micelles collapse in the WPU. The viscosity of the sample WPU-N240 and WPU-PEG were too high to be emulsified, so it was unable to determine by TEM.

It is shown in Fig. 2 that the dispersions of WPU-N210, WPU-N220 and WPU-N230 composed of spherical particles that formed chains, while the spherical particles of WPU-PNA aggregated together and formed blocks of membrane, and the diameter of these particles was between 32 and 150 nm. The causes of the differences in the size and shape of the particles possibly were the different crimp degree and order degree in the aqueous environment. It is obvious that the sample WPU-N220 had more homogeneous particle size and its nanoparticles had a better dispersibility.

Table 2
Characteristic IR bans of the WPU.

Wavenumber (cm^{-1})	Assignment
3581–3334	st N—H (bonded)
2974–2867	st C—H
2280–2260	st N=C=O
1737–1708	st C=O (urethane)
1666–1649	st C=O (urea)
1560–1554	st C—N + δN—H
1469–1460	δ CH$_2$
1450–1400	st sym (COO⁻)
1249–1236	st asym N—CO—O + (C—O—C)
1236	st (C—O)
1135–1099	st (C—O—C)

3.2. Structures of WPU

The chemical structure of WPU is determined by FT-IR spectroscopy. Fig. 3(a) shows FT-IR spectra of WPU synthesized with a series of PPG with different molecular weight, while Fig. 3(b) shows FT-IR spectra of WPU, which utilized different polyols including PPG, PEG and PNA with the same molecular weight. The assignments of the characteristic IR bands are given in Table 2 [28].

The characteristic IR bands corresponded to N—H stretching at 3581–3334 cm^{-1}, C—N stretching and N—H stretching at 1560–1554 cm^{-1}, C—H stretching at 2974–2867 cm^{-1}, and C=O stretching due to urea (1666–1649 cm^{-1}) and urethane (1737–1708 cm^{-1}) groups. Meanwhile, the FT-IR spectra showed the characteristic C—O—C and N—CO—O stretching
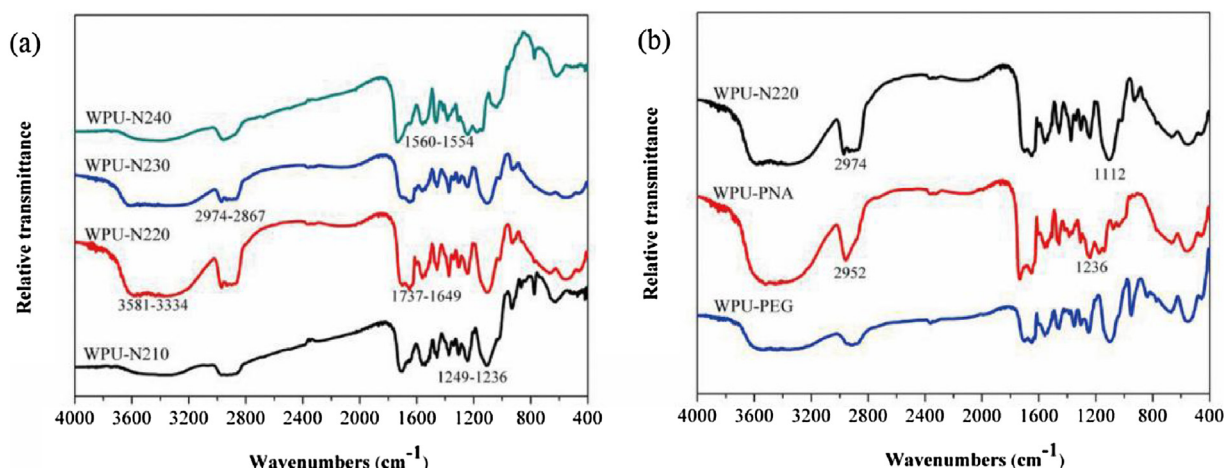
Fig. 3. (a) FT-IR spectra of WPU-N210, WPU-N220, WPU-N230, WPU-N240. (b) FT-IR spectra of WPU-N220, WPU-PNA, WPU-PEG.

Table 3
Main decomposition of the samples.

Samples	Hard segments		Soft segments	
	T (°C)	Weight loss (%)	T (°C)	Weight loss (%)
N210	243.0	33.6	351.8	41.0
N220	255.8	26.6	342.4	57.3
N230	261.3	25.0	331.4	67.9
N240	262.8	17.1	331.4	52.1
PNA	278.2	30.7	351.4	43.0
PEG	263.2	27.6	344.2	62.6

$(1249–1236 \, cm^{-1})$, C—O—C stretching $(1135–1099 \, cm^{-1})$ bands and C—O stretching $(1236 \, cm^{-1})$ bands of the polyol. The isocyanate (—N=C=O) absorption peak at $2280–2260 \, cm^{-1}$ disappeared, indicating that the —N=C=O groups of IPDI at each terminus of the PU prepolymer reacted completely. In conclusion, because of the whole functional groups existed, the polyurethane was prepared, successfully [3].

As seen in Fig. 3(b), a sharp peak $(2950 \, cm^{-1})$ was produced by stretching vibrations of saturated aliphatic alkanes of the sample WPU-PNA. This is an effective way to identify polyether or polyester waterborne polyurethane. Furthermore, the C—O—C stretching band at $1115–1080 \, cm^{-1}$ in the spectra of WPU-PNA was different from the others because of the molecular chain of polyether waterborne polyurethane [1,25,29–31].

3.3. Thermal and crystallinity analyses

TG analysis gave information about the thermal stability and the structure of the polyurethane [1,25,32]. Therefore, TG and derivative thermogravimetric (DTG) were used to analyze the decomposition behavior of degraded WPU films. Differentiated degradation steps of hard and soft segment could be collected, which are listed in Table 3.

As seen in Fig. 4, the curves of the films prepared with different WPU dispersions had a same trend during the decomposition in a nitrogen atmosphere. At the beginning, an obvious weight loss was not observed until the temperature reached the point at which the hard and soft segments began to decompose sequentially. During the first stage of the spectra (from 220 to 340 °C) the hard segments decomposed, namely urea and urethane. The soft segments mainly composed of polyol decomposed in the second stage (from 340 to 460 °C). Obviously, the decomposition of the soft segment occurred rather late than that of hard segment. This was because the hard segment contained a large number of NHCOO groups, while the

soft segment mostly contained the C—C chains. The heat resistance of —NHCOO was not as good as the C—C chain [31]. Finally, the curves turned flat after 460 °C indicated that the films of WPU were decomposed completely.

According to Fig. 4(a) and Table 3, the decomposition temperature of the hard segment increased as increasing the molecular weight of the polyols. The increasing molecular weight of soft segment had an effect of cladding on the hard segment in polyurethane main chain and could isolate the heat to some degree. The decomposition temperature of the hard segment increased. However, the decomposition temperature of the soft segments showed a decreasing trend. As the molecular weight of the soft segment increased, the cladding ability increased for hard segment, however the decomposition of hard segment at low temperature had an effect on the soft segment and therefore the heat resistance of the soft one was worse.

As seen in Fig. 4(b) and Table 3, there is an obvious growing curve of the sample WPU-PNA, and the decomposition temperature of the WPU-PNA sample was higher than WPU-PEG and WPU-PPG samples. There were two main reasons: the higher binding energy of ester bond resulted in the higher temperature of the decomposition; on the other hand, the better crystallinity of the soft segment of the polyester waterborne polyurethane led to the better thermal stability [33].

Further information about phase structure and thermal property of the obtained WPU dispersions can be concluded from DSC determination. DSC thermograms of polymer samples in Fig. 5 show a single glass transition temperature (T_g) in the range from −52.9 to −25.9 °C, indicating this T_g was in the soft segment. It can be observed that the T_g values of WPU-N210, WPU-N220 and WPU-N230 are −43.4, −46.6 and −52.9 °C, respectively (Fig. 5). The increase in the molecular weight of the polyols obviously resulted in the decline in the glass transition temperature of soft segments, which caused that the flexibility of molecular chains and the activity of the segments chain increased with the incline of relative molecular weight. The T_g for WPU-N220, WPU-PEG and WPU-PNA were −46.6, −32.8 and −25.9 °C, respectively. The T_g of WPU-N220 was the lowest and WPU-PNA was the highest, indicating that the T_g of the soft segment of the polyester waterborne polyurethanes was higher than polyether. So the low temperature resistance of polyether waterborne polyurethanes was better. When the polyester applied as soft segment, the capable of forming hydrogen bonds between hard and soft segment was stronger than polyether. Thus the hard phase could be distributed in the soft phase more evenly, which could generate the role of elastic cross-linking, but also increase the intermolecular force and
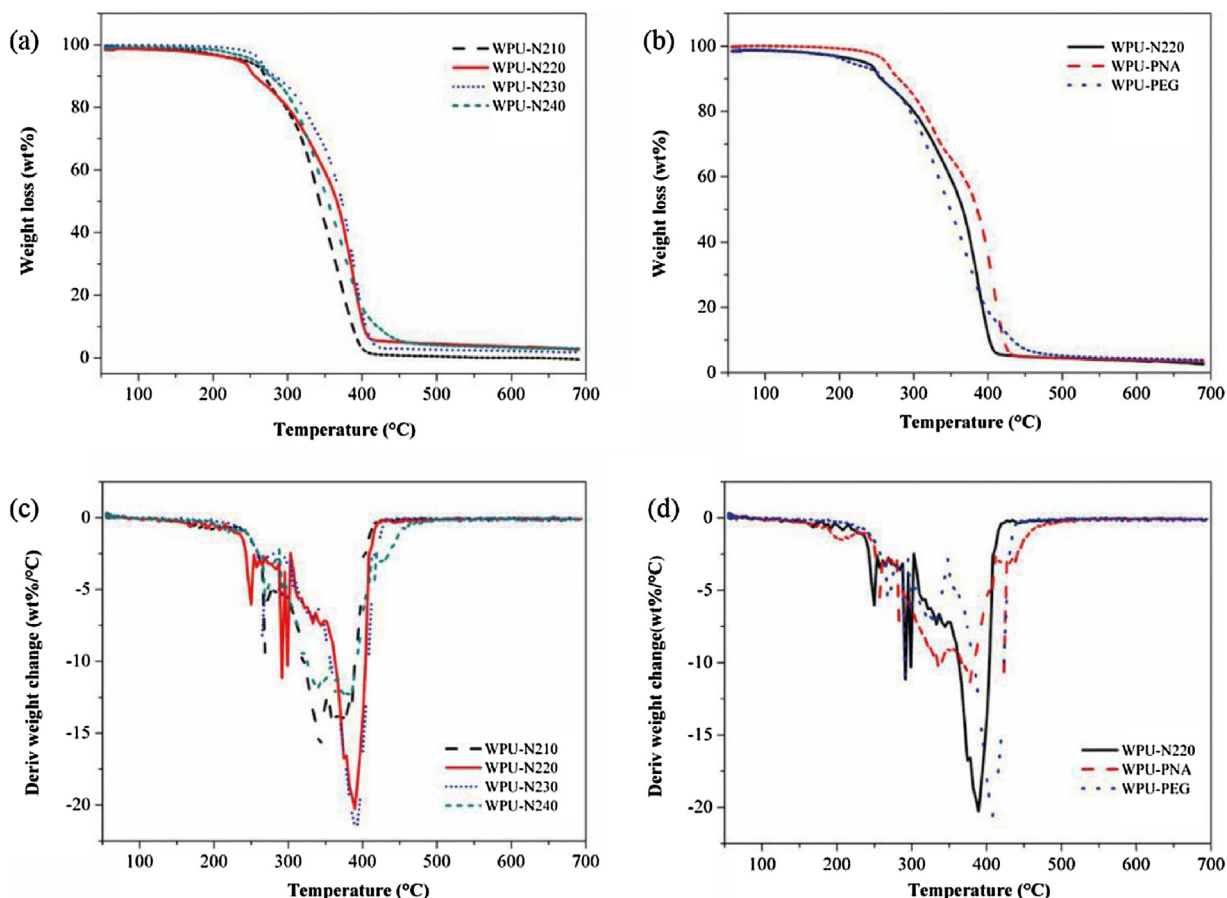
Fig. 4. TG and DTG curves of WPU films. (a) and (c) WPU synthesized with different molecular weights of PPG. (b) and (d) WPU synthesized with PPG, PEG and PNA.
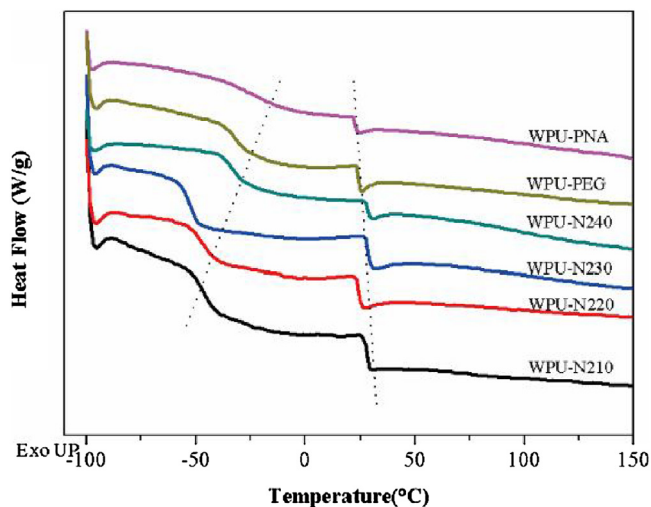

Fig. 5. DSC thermograms of WPU in synthesis of different polyols.
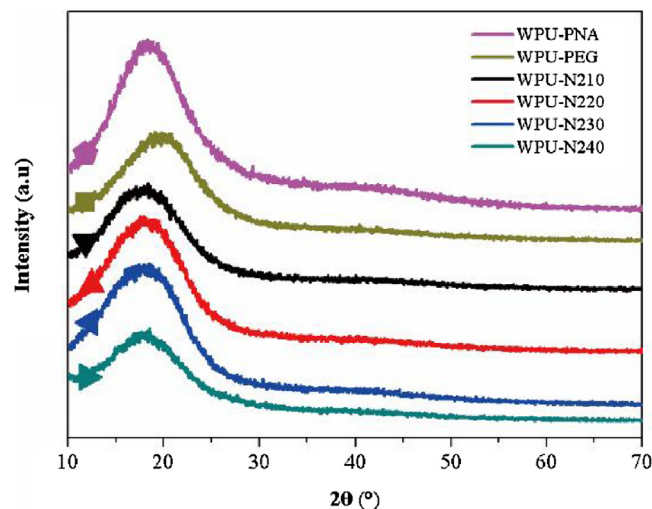

Fig. 6. X-ray diffractograms of the WPU films.

glass transition temperature. As it can be seen in Fig. 5, there is an endothermic peak of all samples at about 30 °C, which arises from a regular arrangement of soft segment and good regularity of the molecular chains that could be further verified by XRD [34].

The crystallinity of the samples was demonstrated by X-ray diffraction. As shown in Fig. 6, there is no sharp crystallinity peak observed. All of the diffraction peaks of the samples are wide and with low intensity, which are typical diffraction peaks of polyurethane. The reason might be that the reaction between the

polyol and IPDI was insufficient to form continuous crystalliza-tion. The two diffraction peaks could be observed at 2θ from $18°$ to $20°$ (main diffraction peak) and $43°$ for each sample, which were the characteristic peaks of the soft segment in segmented polyurethanes.

According to the height of XRD diffraction peak, the higher peak meant the more regular arrangement of soft segments and the bet-ter regularity of the molecular chains [35]. The FWHM of diffraction peaks ($2\theta \approx 18°–20°$) for WPU-N210, WPU-N220 and WPU-N230
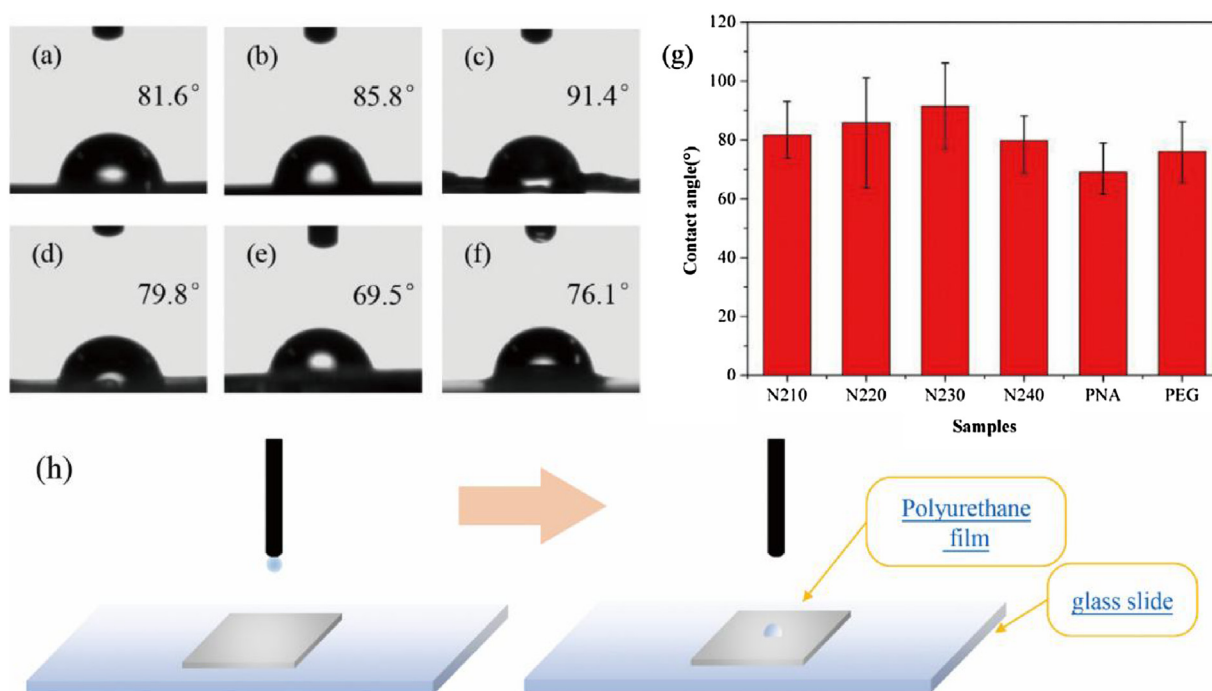
Fig. 7. (a–f) Water contact angles of all the samples. (g) Tendency for all the samples. (h) Cartoon of the water contact angles test.

indicated that the crystallinity of the samples increased with the molecular weight increasing. It can be referred that the activity of the molecular chain was stronger, the structures of the molecular chain was more regular and the soft segment was easier to arrange and crystallize.

We could perceive from Fig. 6 that, the FWHM of diffraction peaks of WPU-PNA was higher than the sample WPU-N220 and WPU-PEG, because polarity and intermolecular forces of ester were stronger than ether, then the polyester waterborne polyurethane had a better regularity of the molecular chains than the polyether polyurethane [33].

3.4. Water contact angle analysis

As seen in Fig.7(a–f), the water contact angles of all samples were around 80°, and the largest and smallest angle were 91.4° and 69.5°, respectively, which meant all the WPU films were hydrophilic. It was obvious that there was an increased trend of the water contact angles of the samples WPU-N210, WPU-N220 and WPU-N230, suggesting that the surface hydrophobicity increased with increasing the molecule weight. The reason was that the water resistance of the ether bond was considerable [36,37]. Since the higher molecule weight of the PPG contained the more ether bonds of polyurethane, which led to the better water-resisting property but poor hydrophilia. However, the sample WPU-N240 broke the trend and we have repeated many times to rule out the accidentally case. The results were reproducible. We conjectured there were many factors could affect the wetting angle including the morphology and structure of WPU particles, surface roughness and polar groups, etc. Notably, WPU-PNA had the smallest contact angle among all samples. One possibility was the water resistance of ester bond was worse than ether bond in the waterborne polyurethane chain [27]. The other reason was that there was double bond in ester bond and the molecular chain was more difficult to rotate, so the plasticity of the molecular chain was worse which resulted

in the decrease of the water resistance of polyester waterborne polyurethane.

4. Conclusions

A series of waterborne polyurethane emulsion was successfully synthesized and snow was chosen as dispersant instead of water. It can be concluded that as-synthesized polyether waterborne polyurethane could provide obviously higher solid content, higher viscosity and higher water-resistance property while polyester waterborne polyurethane could provide higher thermal stability and crystallinity property than XXXX.

In addition, the emulsion of WPU-N220 with molecular weight of 2000 g/mol PPG could provide obviously highest solid content and lowest viscosity properties. Moreover, it was observed that for all samples the particle size was uniform and highly dispersed. TG, DSC and XRD data demonstrated that the emulsion of WPU-N230 with molecular weight of 3000 g/mol PPG could provide higher thermal stability and crystallinity than the other samples. This work demonstrated that different polyols as soft segment lead to great differences in structure and property of WPU.

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