

Preparation and Properties of Water-Borne Polyurethane with Branched Straight Aliphatic Chains

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ABSTRACT: Water-borne polyurethane with branched straight aliphatic chains (CWPU) was prepared and characterized by FTIR and TEM. The relationship between structure and water-resistance of CWPU was studied. The results showed that the particle size of CWPU emulsion increases and the round particle turns into the spindle-shaped particle with increasing of content of branched straight aliphatic chains. However, the particle size of CWPU emulsion is not sensitive to the increases of length

of branched straight aliphatic chains. The water-resistance and hydrophobic property of CWPU film increase with the increase of content and length of branched straight aliphatic chains. It is attributed to the hydrophobic layer of aliphatic chains enriched on the surface of CWPU film. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 121: 1536–1542, 2011

Key words: polyurethane with branched straight chains; water-borne polyurethane; preparation; characteristic

INTRODUCTION

In the past decades, water-borne polyurethane (WPU) have attracted more and more interest due to their nonpollution, excellent abrasion resistance, chemical resistance, and toughness at low temperature as well as extensive use in coatings and adhesives.¹ The stability of WPU has been studied in many papers and is attributed to the self-emulsified function of pendant hydrophilic groups on polyurethane main chains.^{2,3} The pendant hydrophilic groups on polyurethane main chains included anion, cation, and nonion. WPU with anionic hydrophilic groups is a type of the most important among them. However, the hydrophilic anionic centers easily results in weak water-resistance of WPU, which restricted the application of WPU to a certain extent. In recent years, WPU was usually modified by polyols, crosslinking, hybridization, and nanometer fillers to improve its water-resistance and hydrophobic property.^{4–10} However, the properties of polyurethane were greatly influenced by its backbone structure and its branched structure. Grafting modification is an important method to improve properties of polymer. In our previously works,^{9–12} the authors utilized grafting modification method to pre-

pare new polymeric diols with branched straight chains and used polymeric diols with branched straight chains as raw materials to prepare WPU with branched straight chains and WPU with branched straight chains/montmorillonite nanocomposites. These research results showed that the structure characteristic of branched straight chains obviously influenced mechanical property, adhesive, surface property, and water-resistance of WPU and its nanocomposites. In this study, grafting modification method is used to prepare a series of WPU with branched straight aliphatic chains (CWPU) based on molecular design. The effect of structure and content of branched straight aliphatic chains on the properties of CWPU are also investigated.

EXPERIMENTAL

Materials

Polypropylene glycol (PPG-1000, industrial grade, —OH value 56 mg KOH/g, molar mass 1000 g/mol) was purchased from Jinling Chemical Corp. (China) and dried in vacuum oven at 90°C for 6 h before use. Trimethylol propane (TMP, industrial grade) was purchased from Mitsui Corp. (Japan) and dried in vacuum oven at 40°C for 12 h before use. Isophorone diisocyanate (IPDI, industrial grade) was purchased from BASF Corp. (Germany) and used without purification. Dimethylol propionic acid (DMPA, industrial grade, Perstop Corp. Switzerland) were dried in vacuum oven at 90°C for 12 h before use. *N*-Methyl pyrrolidone (NMP, industrial grade)

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was purchased from Nanjing Ruize Chemical Corp. (China) and dried over 4 Å sieves for 24 h before use. Octadecanol, hexadecanol, dodecanol, and octanol (chemically pure) were purchased from Tianjin Chemical Corp. (China) and dried in vacuum oven at 90°C for 6 h before use. Acetone, triethylamine, and ethylenediamine (chemically pure) were dried over 4 Å sieves for 24 h before use. Dibutyltindilaurate (DBTDL, chemically pure) was purchased from Guangzhou Chemical Corp. (China) and used without purification. Deionized water was prepared in laboratory.

Preparation of water-borne polyurethane with branched straight aliphatic chains

Preparation of water-borne polyurethane without branched straight aliphatic chains (blank CWPU)

WPU without branched straight aliphatic chains was as the blank CWPU. It was prepared at the molar ratio of —NCO group to —OH group 1.6, the DMPA content 6.0 wt % (based on the total weight of reactive mixture) and the degree of neutralization of —COOH group 85%. A 500-mL round-bottomed, three-necked flask with a mechanical stirrer and thermometer was used as the reactor. The reaction was carried out in an oil bath with constant temperature. First, the stoichiometric amounts of PPG-1000, DMPA, NMP, 0.3 wt % DBTDL (based on the total weight of reactive mixture) and IPDI were added successively to the dried reactor. The DBTDL is a catalyst, and the NMP as solvent was used to dissolve DMPA. The mixture was stirred and reacted at 85°C until conversion of —NCO group was close to the theoretical value (based on *n*-dibutylamine titration), then prepolymer with two NCO-terminated groups and pendant carbonyl group was obtained. The prepolymer was then cooled, neutralized by anhydrous triethylamine, and diluted by a small amount of anhydrous acetone to decrease the viscosity. Finally, the acetone solution of neutralized prepolymer was cooled to about 5°C and poured into about 5°C cold deionized water when stirred at high speed and ethylenediamine was added as chain extender to obtain the dispersion. Acetone was removed from the above dispersion under reduced pressure at 40°C, and the blank CWPU emulsion with 40% solid content was obtained.

Preparation of water-borne polyurethane with branched straight aliphatic chains (CWPU)

The scheme of preparing CWPU was shown in Figure 1. The molar ratio of —NCO group to —OH group is 1.6, the DMPA content is 6.0 wt % (based on the total weight of reactive mixture) and the degree of neutralization of —COOH group is 85%. A 500-mL round-bottomed, three-necked flask with a

mechanical stirrer and thermometer was used as the reactor. The reaction was carried out in an oil bath with constant temperature. First, the stoichiometric amounts of PPG-1000, DMPA, NMP, 0.3 wt % DBTDL (based on the total weight of reactive mixture) and IPDI were added successively to the dried reactor. The DBTDL is a catalyst, and the NMP as solvent was used to dissolve DMPA. The mixture was stirred and reacted at 85°C until conversion of —NCO group was close to the theoretical value (based on *n*-dibutylamine titration), then prepolymer A with two NCO-terminated groups and pendant carbonyl group was obtained. Next, the stoichiometric amount of TMP was added into prepolymer A and the mixture was stirred at 85°C until conversion of —NCO group was close to the theoretical value, then prepolymer B with three NCO-terminated groups and pendant carbonyl group was prepared. Third, the stoichiometric amount of primary aliphatic alcohol was added into prepolymer B to react with one —NCO group in prepolymer B at 85°C until conversion of —NCO group was close to the theoretical value, then prepolymer C with two —NCO-terminated groups, pendant carbonyl group and branched straight aliphatic chains was prepared. The prepolymer C was then cooled, neutralized by anhydrous triethylamine, and diluted by a small amount of anhydrous acetone to decrease the viscosity. Finally, the acetone solution of neutralized prepolymer C was cooled to about 5°C and poured into 5°C cold deionized water when stirred at high speed, and ethylenediamine was added as chain extender to obtain the dispersion. Acetone was removed from the above dispersion under reduced pressure at 40°C, and CWPU emulsion with 40% solid content was obtained.

Preparation of CWPU films

Films for the measurements were obtained as follows: CWPU emulsions were poured into polypropylene mold and dried at 50–60°C for 24 h, then dried under vacuum at 40°C for 48 h.

Measurement and characterization

Surface and bulk chemical structure of CWPU film were characterized by attenuated total reflection FTIR (ATR-FTIR) and transmitted FTIR on Vector-33 FTIR spectrometer (German).

Particle size and morphology of CWPU emulsion was observed on Transmission Electron Microscope (TEM, TECNAI G2 12, Netherlands) using an acceleration voltage of 100 kV. The diluted CWPU emulsion was dropped on copper net, dried in oven, and then the dried particles were stained by OsO₄ before observation.

The static contact angles of deionized water on the surface of CWPU film were measured with CA-A

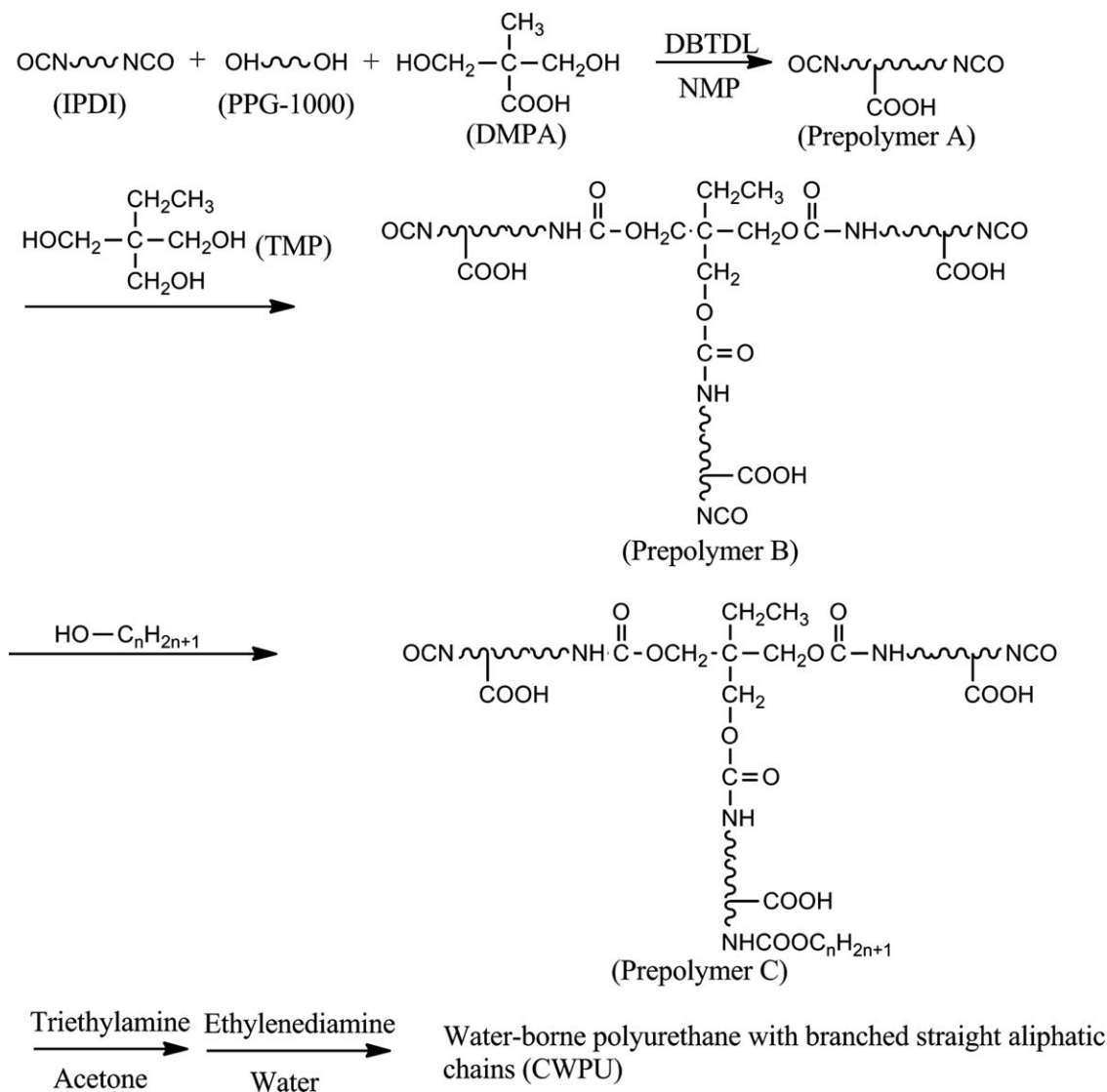


Figure 1 Scheme of preparation of WPU with branched straight aliphatic chains (CWPU).

Contact Angle Instrument (Japan) at room temperature. The arithmetic average of contact angles in five different locations on each film was used as the final result.

Water absorption of CWPU film was measured by weighing film before and after absorption of water. The dimension of films was 30 mm × 30 mm × 1 mm. The water absorption (%) was calculated according to the eq. (1), where w_0 is the film weight before absorption of water and w_1 is the film weight after absorption of water:

$$\text{Water absorption (\%)} = \frac{W_1 - W_0}{W_0} \times 100\% \quad (1)$$

RESULTS AND DISCUSSION

FTIR analysis of CWPU film

Figures 2 and 3 show the ATR-FTIR spectrum and transmitted FTIR spectrum of CWPU film which

contains branched straight hexadecyl chains. The frequency of C—H vibration in the ATR-FTIR spectrum and transmitted FTIR spectrum are similar. The absorption peaks centered at 2953 and 2926 cm^{-1} are attributed to the asymmetrical stretching vibration of —CH₃ bond and —CH₂— bond, respectively. The symmetrical stretching vibration of —CH₃ bond is located at 2855 cm^{-1} and overlapped with that of —CH₂— bond. However, there are obvious difference between the absorption strength of C—H bond in the ATR-FTIR spectrum and transmitted FTIR spectrum, and the difference is magnified in Figure 3. In Figure 3, the absorption peak of —CH₂— bond located at 2926 cm^{-1} in the ATR-FTIR spectrum is sharper and stronger than that in the transmitted FTIR spectrum, which indicates that concentration of —CH₂— group on surface of CWPU film is higher than that in bulk of CWPU film. The branched straight hexadecyl chains are enriched on the surface of CWPU film

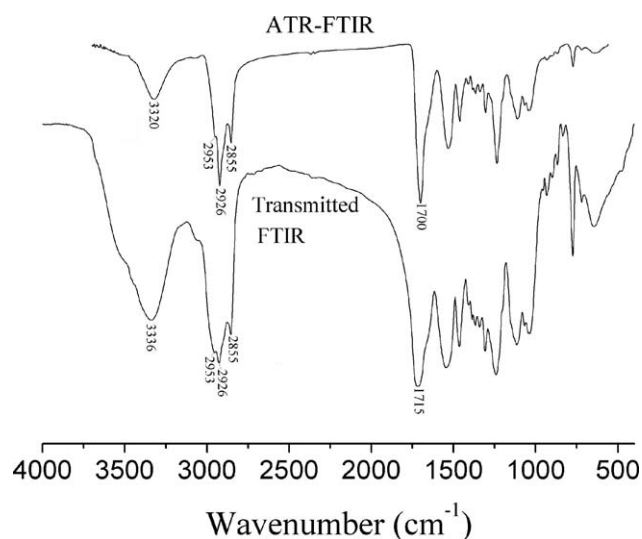


Figure 2 ART FT-IR and transmitted FT-IR spectra of CWPU with branched straight hexadecyl chains.

because the hexadecyl chains with low polarity are arranged on the surface and able to reduce the surface energy spontaneously. The phenomenon was reported in the other emulsion system.^{13–15} Furthermore, the layers of hexadecyl chains reduce the concentration of ether groups on surface and have an

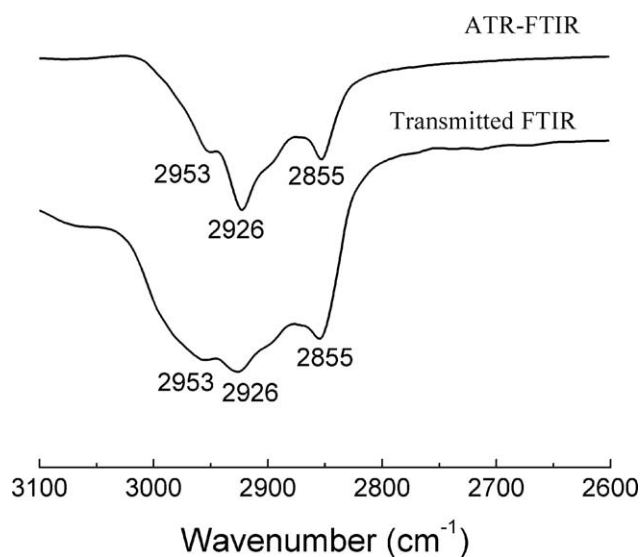


Figure 3 The enlarged ATR FT-IR and transmitted FT-IR spectra of CWPU with branched straight hexadecyl chains.

obvious influence on the ATR-FTIR spectrum and transmitted FTIR spectrum of CWPU film. The stretching vibration peaks of N–H bond and C=O bond are located at 3320 and 1700 cm^{-1} in ATR-FTIR spectrum of CWPU, respectively. Notably, the two peaks shifts to 3336 and 1715 cm^{-1} in

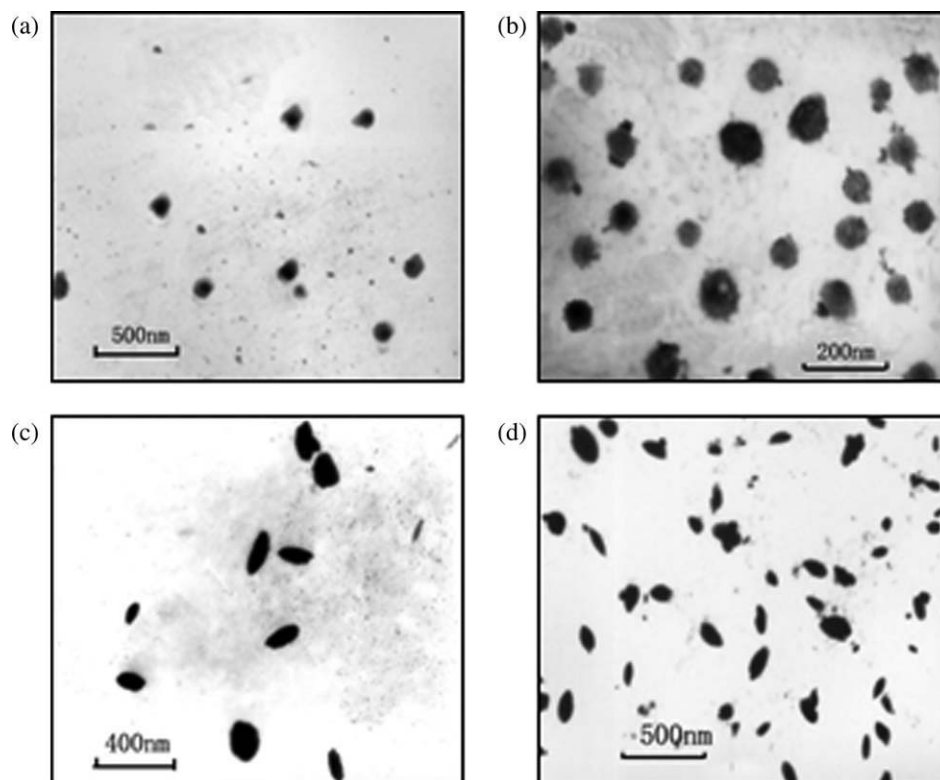


Figure 4 TEM photo of CWPU emulsion with branched straight aliphatic chains: (a) content of branched straight hexadecyl chains: 0%; (b) content of branched straight hexadecyl chains:1.5 mol %; (c) content of branched straight hexadecyl chains:7.5 mol %; (d) content of branched straight octyl chains: 7.5 mol %.

TABLE I
The Data of the Shape and Size of CWPU Emulsion Particle Versus Aliphatic Chain Length

Aliphatic chain		CWPU emulsion	
Type	Content/mol %	Shape	Particle size
No	0	Round	About 100 nm
Hexadecyl	1.5	Round	About 100 nm
Hexadecyl	7.5	Spindle	About 80 nm × 200 nm
Octyl	7.5	Spindle	About 80 nm × 200 nm

transmitted FT-IR spectrum of CWPU, respectively. The stretching vibration peaks of N—H bond and C=O bond are strongly dependent on the strength and kinds of hydrogen bond in polyurethane.^{16,17} The hydrogen bond is formed only between N—H and C=O of urethane group on the surface of CWPU film, which results in the lower band of C=O stretching vibration. In the bulk of CWPU film, N—H can form hydrogen bond with both C=O of urethane group and —O— linkage in structure of polyols, which reduces the strength of hydrogen bond derived from C=O of urethane group, therefore, the stretching vibration of C=O of urethane group in bulk CWPU film shift to higher band 1715 cm⁻¹.

TEM analysis of CWPU emulsion

Figure 4 shows the TEM photos of CWPU emulsion. Obviously, the increase in content of branched straight hexadecanyl chains leads to the variation of morphology of CWPU emulsion particles. The data of morphology and size of CWPU emulsion particle versus aliphatic chain length from Figure 4 were showed in Table I. The pristine WPU emulsion [shown in Fig. 4(a)] and CWPU emulsion with 1.5 mol % branched straight hexadecyl chains

[shown in Fig. 4(b)] have the round particle and their sizes are about 100 nm. When the molar content of branched straight hexadecyl chains reaches to 7.5 mol % [shown in Fig. 4(c)], the particles size of CWPU emulsion exhibits 80 nm × 200 nm and its shape looks as spindle. The strong hydrophobic property of branched straight hexadecyl chains is responsible for the variation of shape and size of CWPU emulsion particle as content of branched straight hexadecyl chains. In Figure 4(d), the particles size and shape of CWPU emulsion with 7.5 mol % branched straight octyl chains are the same as that of CWPU emulsion with 7.5 mol % branched straight hexadecyl chains, which indicates that the length of aliphatic chains has little influence on the morphology of CWPU emulsion particle when the content of aliphatic chains is constant.

Effect of branched straight aliphatic chains on hydrophobic property of CWPU film

WPU usually exhibits strong hydrophilic property due to the pendant hydrophilic functional groups, which leads to the weak water-resistance of WPU film. In this article, CWPU were prepared by grafting hydrophobic long aliphatic chains on polyurethane main chains, and contact angle was used to

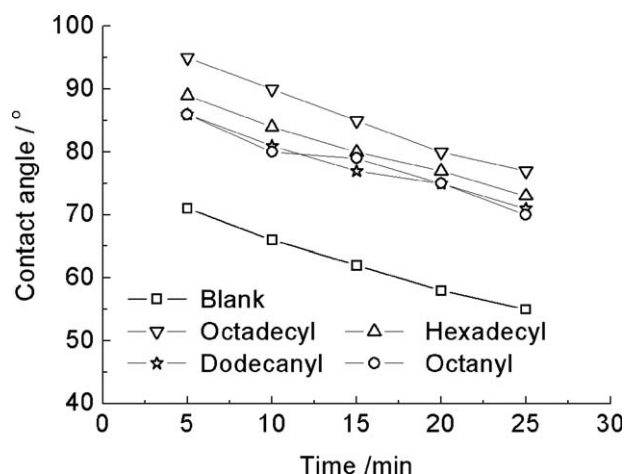


Figure 5 Effect of length of branched straight aliphatic chains on hydrophobic property of CWPU.

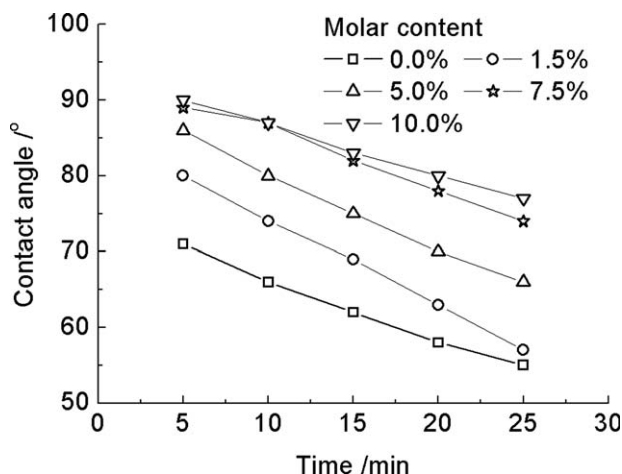


Figure 6 Effect of content of branched straight hexadecyl chains on hydrophobic property of CWPU.

evaluate the surface property of CWPU film. The effect of length and content of branched straight aliphatic chains on contact angle of CWPU film are shown in Figures 5 and 6, respectively. In Figure 5, the contact angle on surface of CWPU film is sharply increased with increasing length of branched straight aliphatic chains when content of branched straight aliphatic chains is 7.5 mol %. Contact angle on surface of CWPU film containing branched straight octadecyl chains is more than 90° in comparison with 71° of blank WPU film when contact time is 5 min. The sharp increase in contact angle on surface of CWPU film shows the obvious improvement on hydrophobic property of CWPU film. It is attributed to the hydrophobic layer of aliphatic chains enriched on the surface of CWPU film. The branched straight aliphatic chains are longer, surface of CWPU film has more hydrophobic. The variation of contact angle of CWPU film as the molar content of branched straight hexadecyl chains is shown in Figure 6. Obviously, contact angle of CWPU film rises with the increase of molar content of branched straight hexadecyl chains, but contact angle slowly increases when the content of branched straight hexadecyl chains is more than 7.5 mol %. The reason is that the surface of CWPU film is composed of branched straight hexadecyl chains basically and has no space to hold more branched straight hexadecyl chains when the content of branched straight hexadecyl chains is more than 7.5 mol %. So, more than 7.5 mol % branched straight hexadecyl chains is not helpful for the increase in contact angle on surface of CWPU film. In each case from Figures 5 and 6, contact angle of CWPU film decreases with increasing contact time due to the migration of polar urethane group from bulk to surface to decrease surface tension.

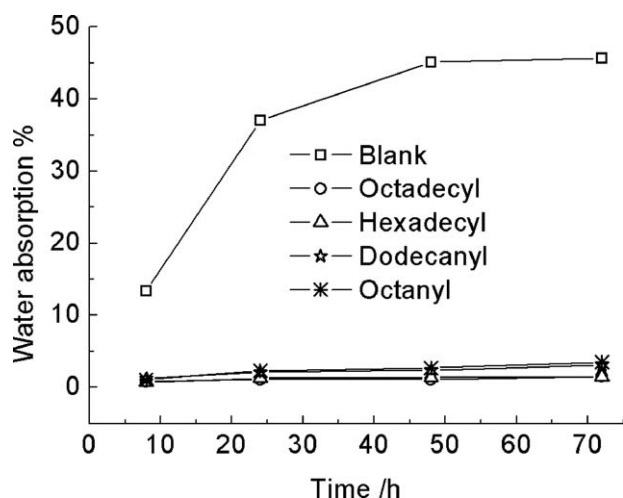


Figure 7 Effect of length of branched straight aliphatic chains on water-resistance of CWPU.

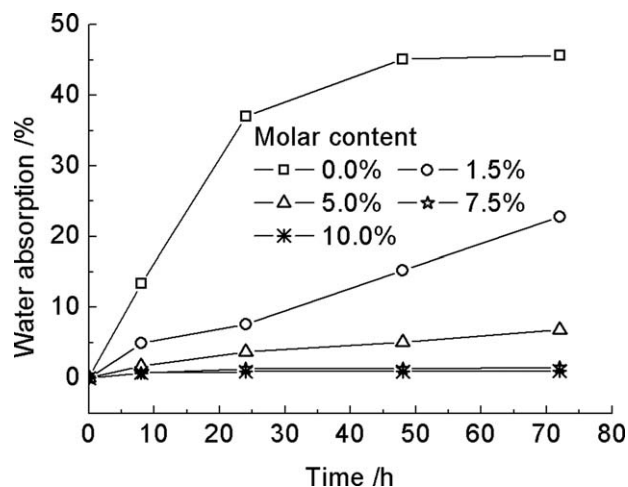


Figure 8 Effect of content of branched straight hexadecyl chains on water-resistance of CWPU.

Effect of branched straight aliphatic chains on water-resistance of CWPU film

Figure 7 shows the function of water absorption of CWPU film with different length of branched straight aliphatic chains as soak time. Water absorption of blank WPU film increases from 13.4 to 45.7% with increasing soak time from 8 to 72 h, which shows the weak water-resistance of blank WPU film. Whereas, water absorption of CWPU film is lower than 5.0% and decreases with increasing length of branched straight aliphatic chains at the same soak time. It indicates that the branched straight aliphatic chains grafted on polyurethane main chain reduce water absorption of CWPU film remarkably. Furthermore, effect of molar content of branched straight hexadecyl chains on water absorption of CWPU film was investigated and the results are shown in Figure 8. Water absorption of CWPU film sharply decreases with increasing molar content of branched straight hexadecyl chains at the same soak time. The water absorption is lower 5.0% when the content of branched straight hexadecyl chains is no less than 7.5 mol %, which exhibits excellent water-resistance of CWPU film. It is also attributed to the hydrophobic layer of branched straight aliphatic chains enriched on the surface of CWPU film.

CONCLUSION

CWPU emulsion was prepared by grafting the hydrophobic aliphatic chains on polyurethane main chain. The results show that the hydrophobic aliphatic chains are enriched on the surface of CWPU film, which is helpful for the improvement of hydrophobic property and water-resistance of CWPU. With increasing of content of branched straight aliphatic chains, the particle size of CWPU emulsion

increases and the round particle turns into the spindle-shaped particle. However, the particle size of CWPU emulsion is not sensitive to the increases of length of branched straight aliphatic chains.

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