

Synthesis and adhesion properties of waterborne polyurethane dispersions with long-branched aliphatic chains

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ABSTRACT: In this study, a series of waterborne polyurethanes (WPU) with different contents of long-branched aliphatic chains were synthesized through variation of the amount of diol chain extender trimethylol propane monooleate (TMPM). The effects of the TMPM content on the adhesion properties of the WPU were investigated in terms of their surface tension, interfacial tension, contact angle, and adhesion strength. Fourier transform infrared and $^1\text{H-NMR}$ spectra demonstrated the successful incorporation of TMPM into the polyurethanes. An increase in the TMPM content produced decreases in the surface tension of the WPU and the interfacial tension and contact angle between the WPU and plastic films. This indicated that the wetting properties of the WPU on the plastic films was improved. The improved wettability enhanced the adhesion strength of the WPU, and this showed that the long-branched aliphatic chains could effectively improve the adhesion performance of the WPU on the plastic films. Moreover, TMPM, with its hydrophobic aliphatic chains, increased the hydrophobicity and thermal stability of the WPU films. © 2014 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2015**, *132*, 41688.

KEYWORDS: applications; polyurethanes; synthesis and processing

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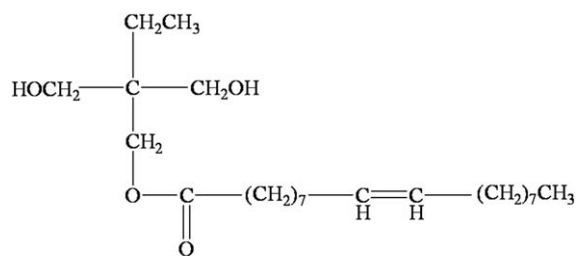
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INTRODUCTION

Presently, gravure printing inks for food packaging are mainly solvent-based polyurethane (PU) inks. The emission of organic solvents is a severe problem. It is mandatory that we decrease the level of volatile organic compounds to protect the environment and our health. Waterborne polyurethanes (WPU) have attracted increasing attention because they are environmentally friendly and have the excellent elasticity, abrasion resistance, flexibility, adhesion, and broad substrate suitability.^{1–5} In the field of flexible packaging printing inks, WPU can offer an efficient alternative to solvent-based PU binders.⁶

The plastic films used for food packaging are mainly poly(ethylene glycol terephthalate) (PET), nylon, oriented polypropylene (OPP), casting polypropylene (CPP) films, and so on. The printing quality is determined by many factors, one of which is the wetting properties of inks on the plastic films,⁷ especially for waterborne inks on low-energy plastic film surfaces. To achieve satisfactory wetting and adhesion, it is necessary to carry out a surface treatment to increase the surface energy of the plastic films. One commonly used method is corona discharge treatment, which increases the polar characteristics of the plastic film surface by introducing new oxidized functionalities (esters, ethers, carboxylic acids, ketones, aldehydes, peroxides, etc.) onto the surface.^{8,9}

In addition to plastic film surface treatment, it is also necessary to decrease the surface tension of the WPU dispersion to achieve satisfactory wetting properties and adhesion. The surface tension greatly depends on the bulk, amount, and volume of the polar groups on the molecular chains¹⁰ and the alignment of the molecules at the air–water interface. In recent years, some approaches have been developed to decrease the surface tension of WPU. Waterborne poly(urethane–acrylate) (PUA) hybrid dispersions possess a lower surface tension than pure WPU dispersions because they have fewer polar groups in the polyacrylate molecular chains.^{10,11} Polydimethylsiloxane belongs to nonpolar soft segments and tends to be aligned on the surface of the WPU dispersion; it offers a low surface tension.¹² WPU with polydimethylsiloxane as a soft segment has a lower surface tension than ester-type WPU and ether-type WPU.¹³ Fluorocarbon chains possess an extremely low surface free energy and have been incorporated into PUs by fluorinated poly(ether glycol),^{14–16} chain extenders,^{17,18} and fluorinated acrylics.^{19,20} The surface tension of waterborne fluorinated poly(urethane–acrylate) is smaller than that of pure waterborne poly(urethane–acrylate) and decreases with increasing fluorine content. However, the synthesis procedure of waterborne PUA is cumbersome and time-consuming and may produce an acrylate monomer residue problem. Silicone-modified WPU may



Trimethylol propane monooleate (TMPM)

Scheme 1. Chemical structure of TMPM.

cause poor recoating, and the cost of organic fluorine-modified WPU is very high; this is not conducive to its wide application.

It has been reported that the alkyl side groups in diols or polyols can improve the hydrophobicity and water resistance of WPUs.^{21,22} The side-chain methyl group ($-\text{CH}_3$), with its hydrophobic nature, can render a low surface tension to poly(propylene glycol) (PPG)-based WPUs.^{1,13,23} However, little attention has been paid to the effects of long-branched aliphatic chains on the adhesion property of WPUs on plastic films; this is one of the most important properties of WPU binders. In this study, trimethylol propane monooleate (TMPM; as shown in Scheme 1), containing two hydroxyl groups and a long aliphatic side chain, was used as a diol chain extender to prepare a series of WPUs with long-branched aliphatic chains. The effects of the TMPM content on the adhesion properties of WPUs on PET and OPP films were investigated.

EXPERIMENTAL

Materials

PPG (weight-average molecular weight = 2000 g/mol, Bluestar, China) was used as a macroglycol and was dried at 120°C *in vacuo* for 2 h to remove residual water. Isophorone diisocyanate (IPDI; BASF Corp, Germany), 2,2-dimethylolpropionic acid (DMPA; Perstorp Corp, Sweden), and TMPM (Qianwei, China) were used without further purification. Acetone (Lingfeng, China), 1-methyl-2-pyrrolidinone (Fuchen, China), triethylamine (Lingfeng, China), 1,4-butanediol (BDO; Kermel, China), and ethylenediamine (Lingfeng, China) were analytically pure and were used without purification. Deionized water was prepared in our laboratory and was used as the dispersing phase.

Synthesis of WPU Dispersions

The WPU dispersions were prepared by the prepolymer mixing process. The molar ratio of the $-\text{N}=\text{C}=\text{O}$ (NCO) group to $-\text{OH}$ group was 1.25, the DMPA content was 5.5 wt % (with respect to the total solid content), and the neutralization degree of $-\text{COOH}$ group was 100%. First, stoichiometric amounts of PPG-2000, TMPM, and DMPA dissolved in 1-methyl-2-pyrrolidinone were added to a four-necked flask equipped with a mechanical stirrer, thermometer, condenser, and nitrogen gas inlet. The mixture was stirred at 70°C for 30 min to obtain a homogeneous mixture. IPDI was then added to the homogeneous mixture and stirred until the amount of residual $-\text{NCO}$ reached the desired value (determined by dibutylamine back-titration). Then, BDO was added dropwise to the reactor for 30 min, and the reaction proceeded at a constant temperature until

the theoretical $-\text{NCO}$ group content was reached. Afterward, the obtained NCO-terminated prepolymer was cooled down to 60°C, diluted by a small amount of acetone, and neutralized by triethylamine. Subsequently, the prepolymer solution was emulsified with a certain amount of deionized water, and ethylenediamine was added as a diamine chain extender to obtain the WPU dispersion. Acetone was removed from the previous dispersion under reduced pressure at 50°C, and the WPU dispersion with a solid content of about 40 wt % was obtained.

Preparation of the WPU Films

We obtained the WPU films by pouring the WPU dispersions onto a Teflon disk to dry at room temperature for 7 days and then at 50°C in a vacuum-drying oven for 24 h to completely remove the solvent and then stored in a desiccator to avoid moisture.

Characterization

The IR spectra of the TMPM and WPUs were obtained with a PerkinElmer 2200 Fourier transform infrared (FTIR) spectrophotometer in the range from 4000 to 400 cm^{-1} .

The $^1\text{H-NMR}$ (400-MHz) spectra of the TMPM and WPUs were recorded in deuterated dimethyl sulfoxide solution with a Bruker Avance digital spectrometer (Germany). The chemical shifts (δ s) are reported in parts per million with tetramethylsilane as the standard.

The average particle size of the WPU dispersions was measured with a Malvern Nano-ZS laser particle sizer (United Kingdom). The WPU dispersion was first diluted in deionized water to 0.5 wt %; this was followed by ultrasonic wave treatment to homogenize the dispersion.

The viscosity of the WPU dispersions with a total solid content of 40 wt % was measured with a Nirun DV-2+PRO rotational viscometer (China) at 25°C.

The surface tension of the WPU dispersions with a total solid content of 40 wt % was determined by a pendant drop method with a Powereach JC2000C1 contact angle goniometer (China) at 25°C. The result was the mean of five replicates.

The static contact angles of the WPU dispersions on the PET and OPP films and the static contact angles of deionized water and ethylene glycol on the surfaces of the WPU films were measured by the sessile drop method with the Powereach JC2000C1 contact angle goniometer at 25°C. The result was the mean of five replicates.

The surface free energies of the WPU films and plastic films (PET and OPP film) were evaluated by static contact angle measurement on the surface of the samples with two liquids (distilled water and ethylene glycol) and were calculated with the following formulas:^{24,25}

$$(1 + \cos \theta_1) \gamma_1 = 4 \left(\frac{\gamma_1^d \gamma_s^d}{\gamma_1^d + \gamma_s^d} + \frac{\gamma_1^p \gamma_s^p}{\gamma_1^p + \gamma_s^p} \right) \quad (1)$$

$$(1 + \cos \theta_2) \gamma_2 = 4 \left(\frac{\gamma_2^d \gamma_s^d}{\gamma_2^d + \gamma_s^d} + \frac{\gamma_2^p \gamma_s^p}{\gamma_2^p + \gamma_s^p} \right) \quad (2)$$



Figure 1. Sketch of the PET/CPP laminated film. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

$$\gamma_s = \gamma_s^d + \gamma_s^p \quad (3)$$

where θ_1 and θ_2 are the contact angles of distilled water and ethylene glycol, respectively, on the surface of the sample; γ_s , γ_s^p , and γ_s^d are the surface free energy, the polar component of the surface free energy, and the dispersion component of the surface free energy, respectively, for the sample; γ_1 , γ_1^p , and γ_1^d are the surface tension of water, the polar component of the surface tension of water, and the dispersion component of the surface tension of water, respectively ($\gamma_1^p = 51.0$ mN/m, $\gamma_1^d = 21.8$ mN/m); and γ_2 , γ_2^p , and γ_2^d are the surface tension of ethylene glycol, the polar component of the surface tension of ethylene glycol, and the dispersion component of the surface tension of ethylene glycol, respectively ($\gamma_2^p = 19.0$ mN/m, $\gamma_2^d = 29.3$ mN/m).

The water absorption measurements were performed by initial immersion of a known weight (W_1) of the dried WPU films (20×20 mm²) in water for 24 h at room temperature. After the residual water was removed from the films with a filter paper, the weight (W_2) of the wet film was immediately measured. The water absorption (A ; %) was obtained with the following equation:

$$A(\%) = [(W_2 - W_1)/W_1] \times 100\%$$

The glass-transition temperatures (T_g 's) of the WPU films were measured with a TA Instruments Q20 differential scanning calorimeter analyzer. Weights of 3–8 mg of the WPU films hermetically sealed in an aluminum pan were heated up to 150°C with a heating rate of 10°C/min and kept there for 3 min to maintain a consistent thermal history for the melting process. Then, the samples were cooled to –80°C at a cooling rate of 10°C/min. The nonisothermal measurement was done from –80 to 200°C with a heating rate of 10°C/min.

The thermal stability of the WPU films was measured with a Netzsch STA-449C-Jupiter thermogravimetric analyzer (Germany) at a constant heating rate of 10°C/min over a temperature range of 30–600°C and under a nitrogen atmosphere with a gas flow rate of 20 cm³/min.

The T-peel strength was determined with a Labthink XLW tensile tester (China) at $23 \pm 2^\circ\text{C}$ and $50 \pm 5\%$ relative humidity. The tests were performed with a 90° angle and a crosshead speed of 300 mm/min. The PET and OPP film, first coated with a WPU binder 10 μm in thickness and then with the PU adhesive, was laminated with the CPP film, respectively, to obtain the laminated film, which was used to measure the T-peel strength. Figure 1 shows a sketch of the PET/CPP laminated film. The peel strength value was the average pull value obtained during the peeling of the tape, and the initial peel values were disregarded.

The high-temperature storage stability of the WPU dispersions was determined by observation of whether the dispersion pre-

cipitated or not after the WPU dispersions sealed in a plastic can were heated at 60°C for 2 weeks. The freeze–thaw stability of the WPU dispersions was obtained by observation of whether the WPU dispersion precipitated or not after the process in which the WPU dispersion was cooled to –20°C for 18 h and then kept at ambient temperature for 6 h. The same operation was repeated five times.

RESULTS AND DISCUSSION

Characterization of the WPU's

The chemical structures of the TPM and WPU's were investigated by FTIR and ¹H-NMR spectroscopy. Figures 2 and 3 show the FTIR spectra of the TPM and WPU's with different TPM contents, respectively. In Figure 2, the absorption peaks at 3445, 1740, 1058, and 720 cm^{–1} were assigned to –OH, C=O, C–O, and (CH₂)_n ($n \geq 4$), respectively, of TPM. The small weak peak at 3010 cm^{–1} was assigned to C–H of the CH=CH group. The absorption peaks centered at 2850 and 2930 cm^{–1} were attributed to the stretching vibrations of the –CH₃ and –CH₂– groups, respectively. The intensity of the –CH₂– stretching vibration peak was higher than that of the –CH₃ stretching vibration peak because of the higher content of –CH₂– compared to that of –CH₃. In Figure 3(a), WPU-0 and WPU-6 stand for the TPM-free WPU and the WPU with 6 wt % TPM, respectively. There were no obvious differences between the spectra of WPU-0 and WPU-6. The peaks at 3338, 1710, and 1537 cm^{–1} corresponded to the –NH, C=O, and –CNH stretching vibrations and showed the formation of urethane groups. There was a clear absorption peak of the ether group (–O–) at 1104 cm^{–1}. For WPU-6, there existed a low-intensity absorption peak at 720 cm^{–1}. Figure 3(b) shows the magnified spectra of WPU-0 and WPU-6 from 750–500 cm^{–1}. For WPU-6, there was an obvious shoulder peak at 720 cm^{–1}, which indicated that TPM was incorporated into the WPU molecular chains.

The ¹H-NMR spectrum of TPM is shown in Figure 4. The peak at 0.8–0.86 ppm was assigned to the CH₃ protons. The CH₂ protons were observed at 1.14–1.52 ppm. The peaks at 1.99 and 3.27 ppm were attributed to the H–C=C and

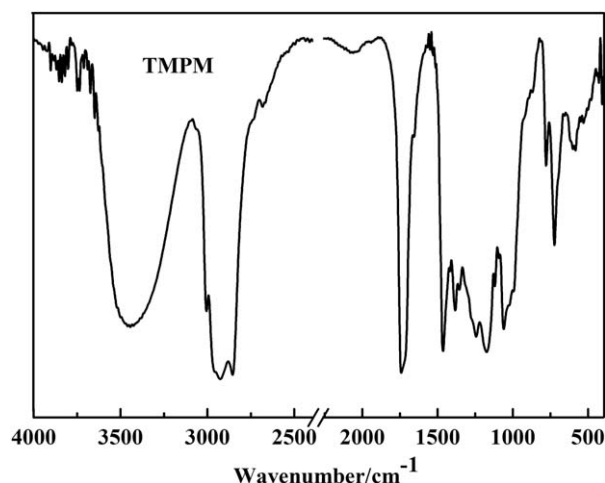


Figure 2. IR spectra of TPM.

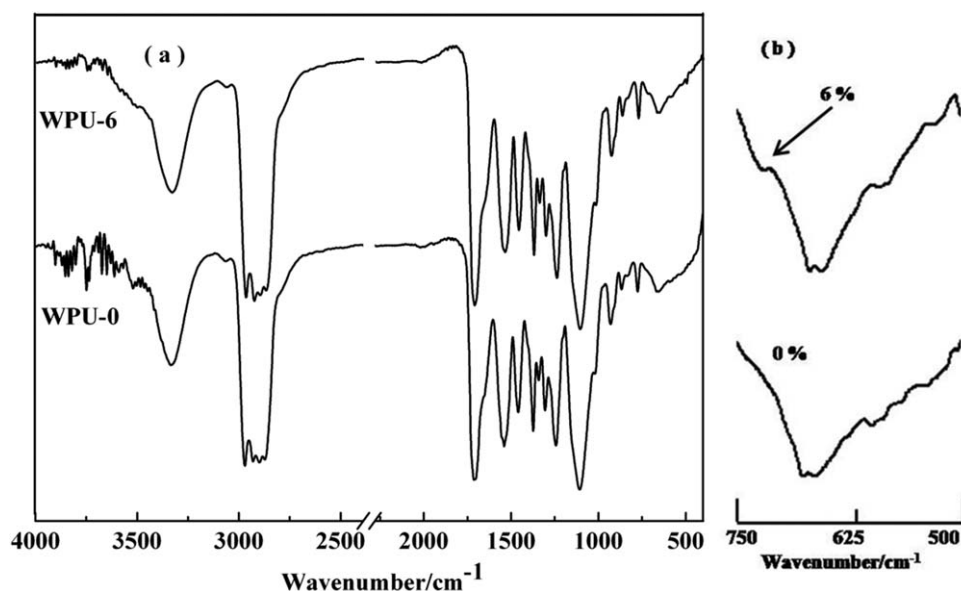


Figure 3. IR spectra of WPU without TPM and WPU with a TPM content of 6 wt %: (a) spectra from 4000–400 cm^{-1} and (b) magnified spectra from 750–500 cm^{-1} .

CH_2O protons, respectively. The appeared peak at 4.37 ppm was ascribed to the OH protons. The C–H protons of C=CH were observed at 5.33 ppm.

Typical $^1\text{H-NMR}$ spectra of the neat WPU and WPU with TPM show several characteristic peaks, as shown in Figure 5. As shown in Figure 5(a), the TPM-free PU was characterized by the appearance of the weak peak at 6.92–7.06 ppm, which was attributed to the N–H proton of urethane groups. The protons of the urethane CH_2 groups of PPG, DMPA, and BDO were observed at 3.94–4.05 ppm. The methyl protons of IPDI appeared at 0.79–0.93 ppm. The observed peaks at 0.93–1.11 ppm were assigned to the methyl group of DMPA and some methylene groups of IPDI. The ethyl groups of tertiary ammonium were observed at 1.45–1.58 ppm. The signals of the $-\text{CH}_3$ group (at $\delta = 1.04$ –1.11), $-\text{CH}_2$ group (at $\delta = 3.45$ –3.48) and $-\text{CH}$ group (at $\delta = 1.45$ –1.58) of PPG were observed.

The $^1\text{H-NMR}$ spectrum of WPU with 6.0 wt % TPM is shown in Figure 5(b). The peaks at 5.29 and 1.96–2.09 ppm were the most important new peaks in the spectrum of PU with TPM and were attributed to the C=CH and H–C–C=C protons of TPM, respectively. Moreover, compared with the TPM-free PU, the PU with the TPM had higher peak intensity at 1.23 ppm, which was ascribed to the increase in the CH_2 group content. As mentioned previously, both the FTIR and $^1\text{H-NMR}$ results revealed that the TPM was successfully incorporated into the PUs.

Average Particle Size and Viscosity of the WPU Dispersions

Figure 6 shows the average particle size and viscosity of the WPUs with various TPM contents. We found that the mean particle size of the WPUs gradually increased with increasing TPM content. The particle size of WPU was affected by several factors, such as the prepolymer viscosity, the amount and position of ionic groups,²⁶ and the flexibility of the macromo-

lecular chains.²⁷ The long-branched aliphatic chains could wrap hydrophilic ionic groups and decrease the dispersity of the PU prepolymer in water and thereby tended to form a large particle. Moreover, because of the hydrophobicity of long-branched aliphatic chains, more TPM caused the PU molecular chains to be more hydrophobic, and the particle size increased. It is known that ionic groups are mainly located on the surface of the particles and interact with water molecules to form hydrated ions. Under the same DMPA content, the thickness and volume of the electric double layer of hydrated ions decreased with increasing particle size; this decreased the hydrodynamic volume

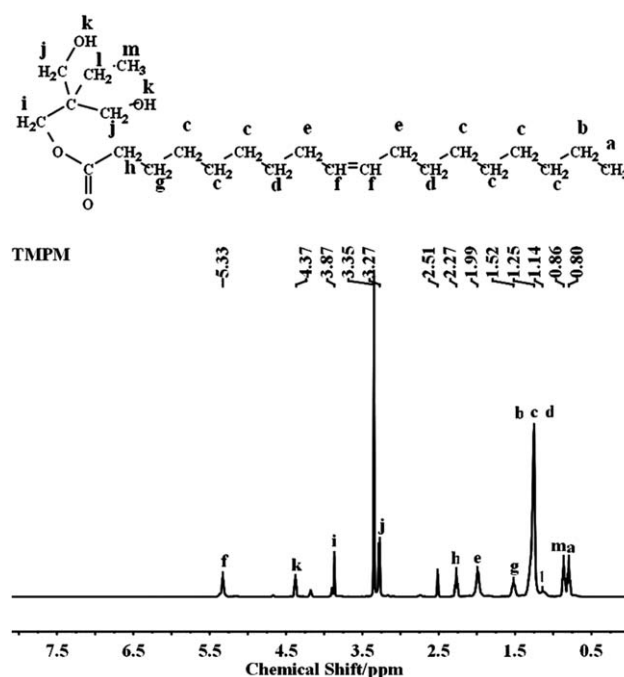


Figure 4. $^1\text{H-NMR}$ spectrum of TPM.

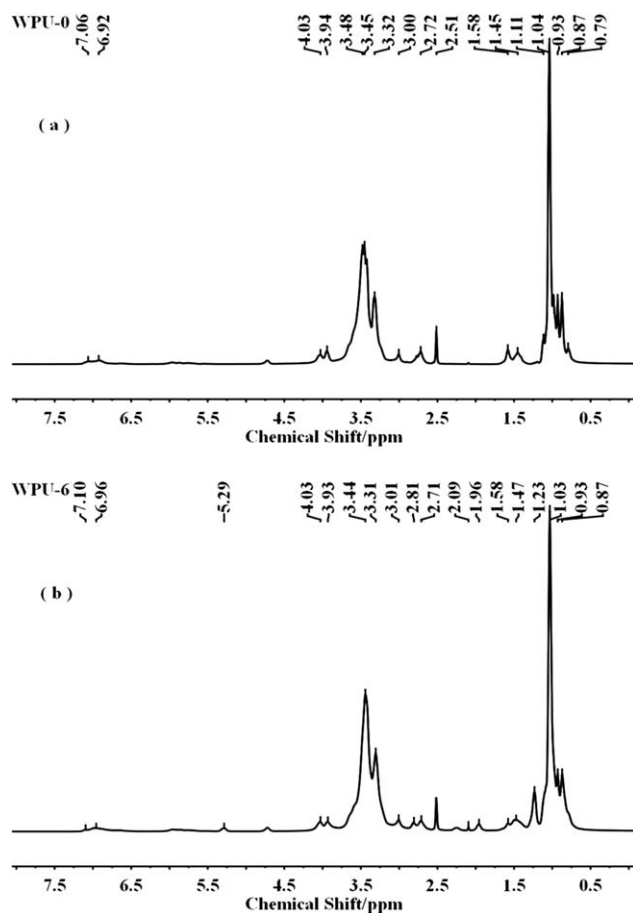


Figure 5. $^1\text{H-NMR}$ spectra of (a) neat WPU and (b) WPU with 6 wt % TMPM.

of particles. As a result, the viscosity of the WPU dispersion decreased. All of the WPU dispersions did not precipitate after high-temperature storage and freeze-thaw stability tests. This phenomenon is very important for applications in industry.

Adhesion Properties of the WPUs on the PET and OPP Films

It is well known that the adhesion strength of WPU is mainly related to the wetting properties of the WPU on the substrates;

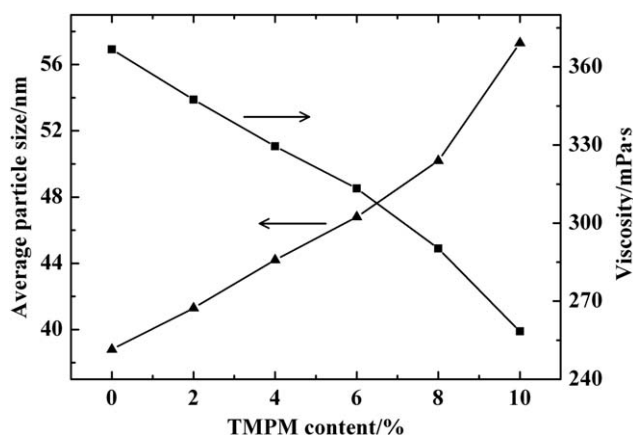


Figure 6. Average particle size and viscosity of the WPU with various TMPM contents.

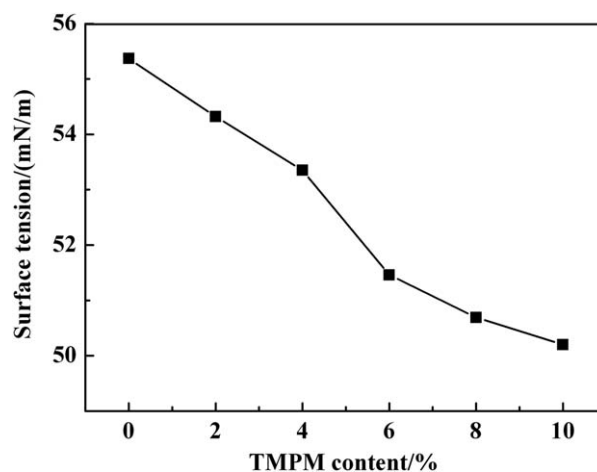


Figure 7. Surface tensions of the WPU with different amounts of TMPM.

this is determined by the surface tension of WPU and the contact angle and interfacial tension between the WPU and substrates.

The surface tension is a phenomenon caused by the cohesive forces between liquid molecules. It can be used to determine the quality of numerous industrial products, such as paints, inks, detergents, cosmetics, and food products. Surface tension is a significant physical property parameter for the application performance of WPU. The smaller the surface tension is, the better the infiltration performance is. The surface tension depends on the number and size of the polarity base in the molecular chains. Figure 7 shows the surface tension of the WPU dispersions with different TMPM contents. The WPU with TMPM had a lower surface tension than the WPU without TMPM because of the hydrophobic nature of the long-branched aliphatic chains. The surface of the aqueous PU dispersion could be occupied by more hydrophobic branched aliphatic chains; this resulted in the lowering of the surface tension. It was also revealed that the surface tension of the WPU gradually decreased with increasing TMPM content. The increase in the TMPM content increased the amount of hydrophobic long aliphatic side chains; this led to a decrease in the amount of polar group in the PU molecular chains. The decrease in the surface tension of WPU with increasing TMPM contents enhanced its wetting ability on the surface of the substrates and would benefit its further applications, such as in waterborne inks.

The wetting properties of the WPU on the substrates could be quantified by the interfacial tension: a lower interfacial tension indicates better wettability. According to the Shell–Nauman empirical formula [eq. (4)],²⁵ the interfacial tension between WPU and plastic films (PET and OPP films) can be calculated as follows:

$$\gamma_{SL} = \frac{(\gamma_S^{0.5} - \gamma_L^{0.5})^2}{1 - 0.015(\gamma_S \gamma_L)^{0.5}} \quad (4)$$

where γ_L , γ_S , and γ_{SL} are the surface tension of the WPU, the surface tension of the plastic films, and the interfacial tension between the WPU and plastic films, respectively. In this study,

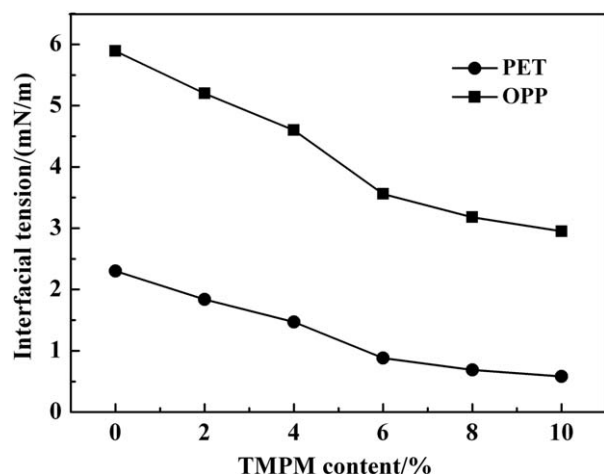


Figure 8. Interfacial tensions between WPU with different TMPM contents and plastic films (PET and OPP films).

the surface free energies of the PET and OPP film treated by corona discharge were 44.56 and 36.73 mN/m, respectively.

The results of γ_{SL} are shown in Figure 8. We found that the interfacial tension between the WPU and PET film was smaller than that between the WPU and OPP film because of the higher surface free energy of the PET film compared to that of the OPP film. Moreover, with increasing TMPM content, γ_{SL} decreased continuously; this showed that the wettability of the WPU on the plastic films was improved. The improvement of the wettability was conducive to the formation of a good adhesion interface.

The wettability could be also directly determined by the static contact angle of the WPU on the plastic films: a smaller contact angle implied better wettability. Figure 9 shows the static contact angles of the WPU with different TMPM contents on the PET and OPP films. The variation trends of the contact angles are similar. With the increase of TMPM content, the contact angle gradually decreases, which indicates that the wettability of WPU on the PET and OPP films is gradually improved. It is because the surface tension of WPU gradually decreases with the increase of TMPM content. The contact angle of the WPU on the PET film was smaller than those of the WPU on the OPP film because of the higher surface free energy of the PET film compared to that of the OPP film.

We investigated the effects of the TMPM concentration on the adhesion properties of the WPU on the PET and OPP films by testing the T-peel strength. The T-peel strength values are shown in Figure 10. It was clear that the peel strength of the WPU to the PET film was much higher than that of the WPU to the OPP film. Compared with the OPP film, the PET film, with a higher surface free energy, was more easily wetted by the WPU, and the PET film surface had more polar groups, which could form hydrogen bonds with the PU molecules. The formed hydrogen bonds were conducive to the formation of good joints. It was also revealed that the T-peel strength value of the WPU initially increased up to a certain value and then decreased as the TMPM content increased. The adhesion strength mainly depended on the wettability and interaction

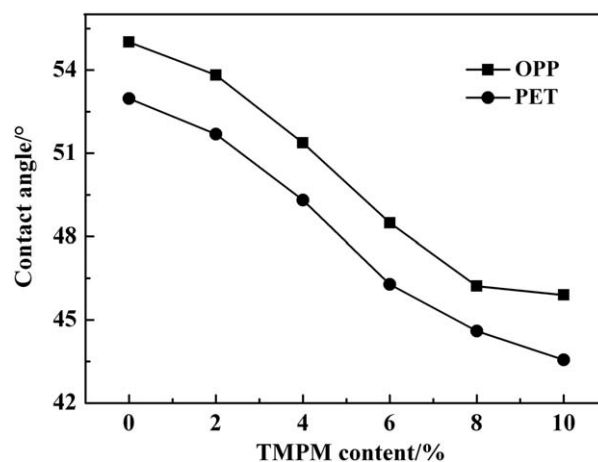


Figure 9. Static contact angles of the WPU with different TMPM contents on PET and OPP films.

between the WPU and plastic films. An increase in the TMPM content reduced the surface tension of the WPU, increased the contact area of the WPU with the PET and OPP films, and thereby enhanced the adhesion strength of the WPU. However, when the amount of TMPM exceeded 6.0 wt %, the substantial branched nonpolar aliphatic chains may have reduced the interaction between the WPU and plastic films, and therefore, the peel adhesion decreased.

Properties of the WPU Films

Table I lists the surface properties and water absorption of the WPU films with different TMPM contents. We found that with increasing TMPM content, the contact angle of the water on the WPU film increased, and the surface free energy of the WPU film decreased. This showed an obvious improvement of the hydrophobic properties of the WPU film. The hydrophobic long aliphatic chain with a low polarity migrated easily to the surface of the WPU film, and thereby, the surface free energy of the WPU film decreased, and the film could not be easily wetted. This phenomenon was also reported in previous literature.^{22,28,29} The water absorption is an important parameter for the practical applications of a polymer. With increasing TMPM content from 0 to 10 wt %, the water absorption decreased

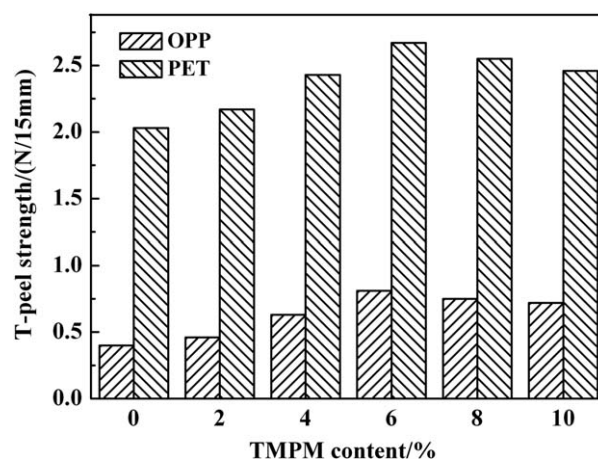


Figure 10. T-peel test results of WPU with different TMPM contents.

Table I. Properties of the WPU Films with Different TMPM Contents

TMPM content (%)	Contact angle (°)			γ^d (mN/m)	γ^p (mN/m)	γ (mN/m)	Water absorption (%)
	H ₂ O	Ethylene glycol					
0	68.3	60.32		8.16	30.26	38.42	14.54
2	70.12	62.54		7.66	29.57	37.24	13.03
4	71.56	64.01		7.4	28.86	36.26	11.74
6	72.52	64.84		7.3	28.30	35.6	10.89
8	72.98	65.32		7.21	28.08	35.29	10.46
10	73.34	65.72		7.13	27.93	35.06	10.25

from 14.54 to 10.25%; this indicated that the long-branched aliphatic chains introduced into PU backbone chain improved the water resistance of the WPU film. This may have been due to the hydrophobic layer of long aliphatic chains enriched on the surface of the WPU film; this decreased the penetration and diffusion of water molecules. Moreover, the large steric hindrance of long-branched aliphatic chains also hindered the interactions between the hydrophilic groups and water molecules.

The glass transitions of all of the samples were investigated by differential scanning calorimetry (DSC). The DSC thermograms are shown in Figure 11. The T_g of the soft segment was observed in each sample and decreased from -49.6 to -56.5°C with increasing TMPM content. This may have been due to the plasticizing effect of long side chains.^{30–32} The long-branched aliphatic chains hindered the close aggregation of soft segments and facilitated the movement of the chain segments. Thus, the increase in the TMPM content increased the free volume of the PU chains, reduced the interaction between backbone chains, and therefore, made the T_g of the soft segment shift to a low temperature.

Ink binders for laminated soft package films should have excellent adhesion strength, water resistance, and thermal stability.

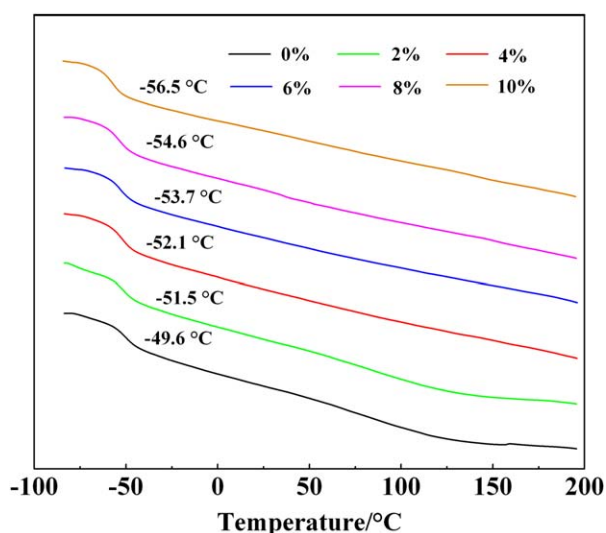


Figure 11. DSC thermograms of the WPU dispersions with different TMPM contents. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

The thermal stability of the WPU films was evaluated with thermogravimetric analysis under a nitrogen atmosphere. The thermogravimetric analysis curves are shown in Figure 12, and the decomposition temperatures corresponding to different weight losses are summarized in Table II. It is known that the hard segment is more prone to thermal decomposition than the soft segment. As a result, the thermal stability of the WPU films was mainly dependent on the thermal stability of the hard segment. $T_{5\%}$ represents the corresponding temperature when the weight loss was 5%. The thermal stability of the samples was obtained by a comparison of the $T_{5\%}$ values. Figure 12 shows that the decomposition of all of the samples started at approximately 180°C and ended at 450°C . The magnified curves from 250 to 350°C showed that the thermal stability of the TMPM-modified WPU was higher than that of the WPU without TMPM, and the thermal stability of the WPU film with a TMPM content of 6 wt % was the highest. This indicated that TMPM enhanced the thermal stability of the WPU films. As shown in Table II, $T_{5\%}$ first increased and then decreased with increasing TMPM content. The decrease was due to the fact that the substantial long nonpolar aliphatic dangling chains were capable of screening the polar groups and thereby decreased the hydrogen-bonding interactions between the polymer main chains and intermolecular attractions.³³

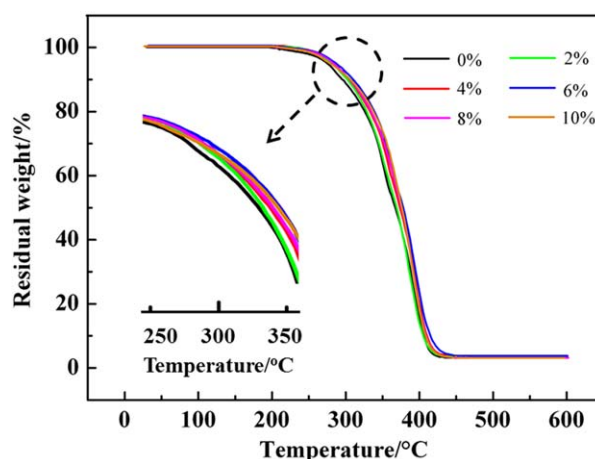


Figure 12. TG curves of the WPU films with different TMPM contents. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table II. Main Decomposition Temperature of the WPU Samples

TMPM content (%)	$T_{5\%}$ (°C)	$T_{10\%}$ (°C)	T_{onset} (°C)	$T_{\text{inflection}}$ (°C)	T_{end} (°C)
0	275.1	295.3	182.4	390.4	442.8
2	279.8	300.8	185.1	391.3	443.4
4	285.3	306.7	186.1	391.8	444.2
6	286.5	309.3	186.7	394.7	445.1
8	284.2	306	183.6	393.7	442.8
10	281.4	305	183.2	393.2	441.6

$T_{10\%}$, the temperature of 10% thermal weight loss; T_{onset} , the initial decomposition temperature; $T_{\text{inflection}}$, the temperature of maximum weight loss rate; T_{end} , the final decomposition temperature.

CONCLUSIONS

In this study, WPU dispersions with long-branched aliphatic chains were prepared by chain extension with TMPM, and the effects of the TMPM content on the properties of the WPU dispersions were investigated. FTIR and $^1\text{H-NMR}$ spectra revealed that TMPM was successfully incorporated into the PUs. As the TMPM content increased, the mean particle size of the WPUs increased, and the viscosity of the WPUs decreased. The increase in the TMPM content improved the wetting properties of the WPUs on the PET and OPP films, increased the hydrophobicity of the WPU films, and decreased the glass-transition temperature of the WPU films. The adhesion strength and thermal stability of the WPUs initially increased and then decreased with increasing TMPM content. The WPU with 6 wt % TMPM had the highest adhesion strength and thermal stability. To summarize, the introduction of long-branched aliphatic chains into WPU molecular chains was an effective way to improve the wetting and adhesion property of WPU on the plastic films.

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