Maleopimaric acid-modified two-component waterborne polyurethane for coating applications

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ABSTRACT: Maleopimaric acid (MPA), an important rosin derivative, was used to partially substitute isophthalic acid for the preparation of an anionic polyol (MPP) dispersion. The MPP dispersion was then applied to prepare a novel maleopimaric acid-modified two-component waterborne polyurethane (MPP-2K-WPU). The influences of NCO:OH molar ratio on the thermal properties, water absorption, surface free energy, and application properties of MPP-2K-WPU films were investigated. With increasing NCO:OH molar ratio, the thermal stability, pencil hardness, and ethanol resistance of MPP-2K-WPU films were improved, but the water resistance was enhanced firstly and then weakened. The surface free energy of MPP-2K-WPU films mainly depended on the dispersion interaction which was related to the structure of macromolecules. In addition, compared with the control sample of PP-2K-WPU(1.5:1) film, the MPP-2K-WPU(1.5:1) film exhibited improved thermal stability, water resistance, gloss, pencil hardness, and ethanol resistance. © 2015 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2016**, *133*, 43292.

INTRODUCTION

Due to the shortage of fossil resource, the utilization of biomass resource for fully or partially substituting fossil-based compounds has attracted great interest from scholars.[1,2] Rosin is an abundantly available resin obtained from the exudation of pine, and it consists of 88–90% rosin acid, 2–5% aliphatic acid, and 5–8% neutral substance.[3,4] The present of carboxyl group and double bond imparts a high chemical reactivity to rosin acids, thus numerous rosin derivatives with polyfunctionality can be synthesized.[5,6] The characteristic hydrophenanthrene ring structure of rosin acids is similar in rigidity to some fossil-based cycloaliphatic and aromatic compounds, making rosin and its derivatives as potential substitutes for fossil-based compounds in polymers. Therefore, rosin and its derivatives have been extensively used as raw materials for the preparation of various polymers with specific chemical structures and valuable properties.[7–11]

Waterborne polyurethane (WPU) has a variety of excellent properties, such as good flexibility, environmental friendliness,

fire safety, broad substrate suitability, and so on. These good performances make WPU as an important polymer used widely in automotive finishing, industrial metal coating, wood finishing, and plastics coating.[12,13] Furthermore, the WPU with soft-feel effect can also be used in coatings for flexible substrates, such as car interiors, textiles and rubber.[14,15] WPU coatings mainly involve one-component and two-component waterborne polyurethane coatings. Two-component WPU (2K-WPU) coatings, combining the environment-friendly properties of WPU coatings with the good performances of solvent-based two-component polyurethane coatings, have gained growing attention in scientific research.[16–18] There have been some reports about the preparation and properties of one-component WPU coatings modified by maleopimaric acid (MPA) and other rosin derivatives. The results showed that the introduction of rosin derivatives could improve the thermal stability, water resistance and tensile strength of the one-component WPU coatings.[19–21] Compared with one-component WPU coatings, 2K-WPU coatings exhibit better properties owing to their higher crosslinking density.[22] The introduction of MPA into 2K-WPU coatings

should be an interesting subject. To our knowledge, the investigation of maleopimaric acid-modified 2K-WPU coatings have not been reported.

In this work, a novel maleopimaric acid-modified two-component waterborne polyurethane (MPP-2K-WPU) coating was prepared by the crosslinking reaction between MPP dispersion and polyisocyanate. The influences of NCO:OH molar ratio on the thermal properties, water absorption, surface free energy, and application properties of MPP-2K-WPU films were investigated.

EXPERIMENTAL

Materials
Maleopimaric acid (MPA) with purity of 98.4% was synthesized through the Diels-Alder reaction between rosin acid and maleic anhydride.[23] Isophthalic acid (IPA), adipic acid (AA), neopentyl glycol (NPG), trimethylolpropane (TMP), 5-sulfoisophtalic acid sodium (5-SSIPA), diethylene glycol monoethyl ether acetate, and catalyst Fascat 4100 (butyl stannoic acid with 56.85% Sn) were obtained from Aladdin Industrial, China. Bayhydur® 3100 (Hydrophilic, aliphatic polyisocyanate based on hexamethylene diisocyanate (HDI), 17.4% NCO, 100% solid) was purchased from Bayer, Germany. The leveling agent BYK346 (polyether-modified polydimethyl siloxane) was obtained from BYK, Germany. All reagents were used as received without further purification.

Preparation of Maleopimaric Acid-Modified 2K-WPU
Preparation of Maleopimaric Acid-Modified Polyester Polyol Dispersion. The preparation of maleopimaric acid-modified polyester polyol (MPP) dispersion was described as follows. Firstly, the mixture of 49.2 g NPG, 3.64 g 5-SSIPA (hydrophilic monomer) and 0.122 g catalyst Fascat 4100 was gradually heated to 205°C under N_2 atmosphere, and maintained at this temperature until the mixture was clear. After cooling to 150°C, the hydrophilic polyester intermediate (HPI) was obtained, and then 28.8 g IPA, 8.91 g TMP, 19.1 g MPA and 23.9 g AA were added to HPI at 150°C. Subsequently, the mixture was heated to 230°C and maintained at this temperature for 1 h. After the addition of 4.48 g xylene, the reaction was continued at 230°C for 2.5 h. The xylene was removed under reduced pressure after reaction. The product (MPP) was mixed with 5.60 g diethylene glycol mono ethyl ether acetate (cosolvent), and then dispersed with 44.4 g distilled water (dispersing media) by stirring at 2000 rpm. Finally, the MPP dispersion (MPA 14.3 wt %) with $53 \pm 3\%$ solid content was obtained. The Synthesis of MPP is shown in Scheme 1.

Polyester polyol (PP) dispersion (MPA 0 wt %) as control sample was also prepared using the same method, except for the adding amount of IPA and MPA changing to 38.7 g and 0 g, respectively. The properties of MPP and PP were described in Table I.

Preparation of Maleopimaric Acid-Modified 2K-WPU. Maleopimaric acid-modified 2K-WPU (MPP-2K-WPU) was prepared by mixing MPP dispersion (polyol component), Bayhydur® 3100 polyisocyanate (polyisocyanate component) and 0.3 wt % leveling agent BYK346 together, and stirring by

hand with a glass rod for 5 min. The generated 2K-WPU dispersion was diluted with distilled water to the solid content of about 50 wt %, stirred at 1000 rpm for 10 min and then degassed under vacuum at ambient temperature for 10 min. The formulated MPP-2K-WPU dispersion was applied on clean glass panels or tinplate panels and dried at 80% relative humidity and ambient temperature ($18 \pm 3°C$) for 7 days. By altering the NCO:OH molar ratios in the range of 1.2 : 1, 1.5:1, 1.8:1 and 2.1:1, a series of MPP-2K-WPU films with a thickness of about 40 μm were obtained and denoted as MPP-2K-WPU(1.2:1), MPP-2K-WPU(1.5:1), MPP-2K-WPU(1.8:1) and MPP-2K-WPU(2.1:1), respectively. The synthesis of MPP-2K-WPU is shown in Scheme 2.

Besides, control samples at NCO:OH molar ratios of 1.5:1 and 2.1:1 were prepared with PP dispersion instead of MPP dispersion as polyol component, which were denoted as PP-2K-WPU(1.5:1), PP-2K-WPU(2.1:1), respectively.

Characterization
The molecular weights and molecular weight distributions of MPP and PP were determined by gel permeation chromatography (Viscotek HT-GPC Module 350A, USA). N, N-dimethylformamide (DMF) was used as eluting solvent with a flow rate of 1.0 mL min^{-1} at 60°C.

Hydroxyl values and acid values of MPP and PP were measured by chemical analysis in terms of standard methods HG/T 2709-1995 and HG/T 2708-1995, respectively.

Fourier transform infrared spectroscopy (FTIR) analyses of MPP, polyisocyanate and MPP-2K-WPU were performed on a Nicolet MAGNA-IR 550 FTIR spectrometer (USA).

Transmission electron microscopy (TEM) of MPP-2K-WPU(1.5:1) dispersion was conducted using a JEM-200CX instrument (JEOL, Japan). The TEM sample of MPP-2K-WPU(1.5:1) dispersion after 5 min of mixing was prepared as following: the mixture of MPP dispersion, polyisocyanate and 0.3 wt % leveling agent BYK346 was stirred by hand for 5 min, diluted with distilled water to 0.1 wt % solid content, and then casted on copper grids. To prepare the TEM samples of MPP-2K-WPU(1.5:1) dispersions after 20 and 60 min of mixing, the MPP-2K-WPU(1.5:1) dispersion (50 wt % solid content) after 15 min of mixing was continuously stirred by a magnetic stirrer for about 5 min and 45 min, respectively, diluted with distilled water to 0.1 wt % solid content, and then casted on copper grids. All the TEM samples were measured after freeze-drying at about −35°C for 24 h.

Atomic force microscopy (AFM) image of MPP-2K-WPU(1.5:1) film was recorded with a SPM9600 instrument (Shimadzu, Japan) in phase mode. To prepare the AFM sample, MPP-2K-WPU(1.5:1) dispersion (50 wt % solid content) was casted on mica substrate and dried at ambient temperature.

Thermogravimetric analyses (TGA) of MPP-2K-WPU films were carried out on a NETZSCH STA 409 PC/PG instrument (Germany) with a heating rate of 10°C min^{-1} under N_2 atmosphere.
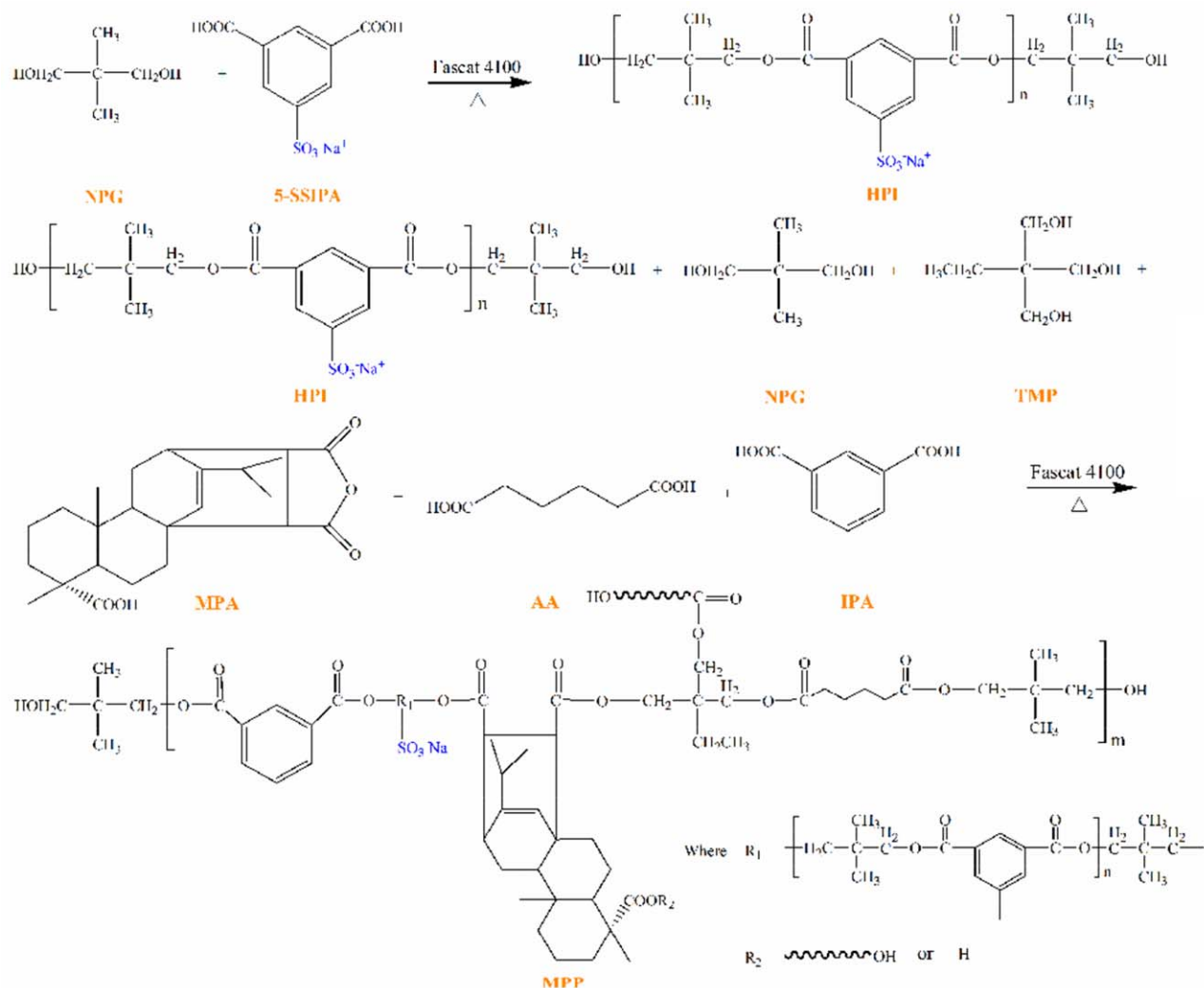
Scheme 1. Synthesis of maleopimaric acid-modified polyester polyol. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Differential scanning calorimetry (DSC) thermograms of MPP-2K-WPU films were recorded on a PerkinElmer Diamond DSC instrument (USA) with a heating rate of 20°C min^{-1} under N_2 atmosphere.

The water absorption of MPP-2K-WPU films with a thickness of about 1 mm was determined according to literature [22]. The MPP-2K-WPU films were cut into 3 cm × 3 cm pieces, dried in a vacuum oven at 70°C for 24 h to determine their dry weight (W_1), and then immersed in distilled water for 72 h at room temperature. The films were weighed immediately when the water attached to the surface was wiped off to obtain their weight (W_2). The water absorption (W%) was then calculated by the following equation:

$$W\% = \frac{W_2 - W_1}{W_1} \times 100\% \qquad (1)$$

Surface free energy (γ_S) of MPP-2K-WPU films was quantified using a contact angle goniometer (Kruss DSA100 instrument, Germany). Water (polar liquid) and diiodomethane (nonpolar liquid) were chosen as testing liquids. Static contact angles of testing liquids were measured at ambient temperature by the sessile-drop method. For each liquid six different surface regions were selected to obtain a statistical result. Based on the measured contact angles for MPP-2K-WPU films, γ_S was determined by Equation of State method and Owens-Wendt-Rabel-Kaelble method.[24–26]

The application properties of the MPP-2K-WPU films were evaluated as follows. The dry time of MPP-2K-WPU film was determined by pushing a cotton ball (1 cm^3) on the film surface

Table I. The Properties of MPP and PP

Properties	MPP	PP
Hydroxyl value (mg KOH g^{-1})	102	103
Acid value (mg KOH g^{-1})	17.4	4.19
Number-average molecular weight (M_n)	2422	2476
Weight-average molecular weight (M_w)	5522	4605
Molecular weight distribution (M_w/M_n)	2.28	1.86
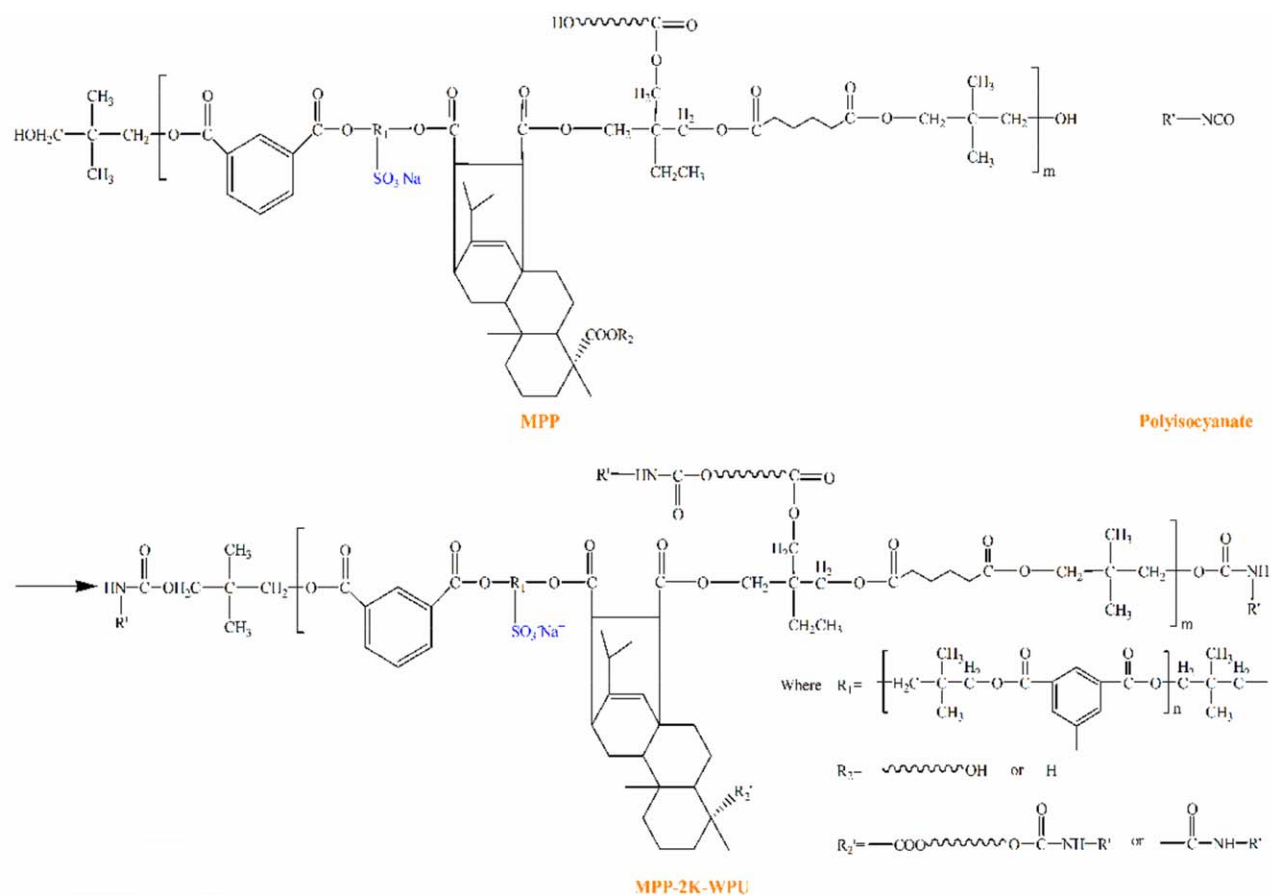
Scheme 2. Synthesis of maleopimaric acid-modified 2K-WPU. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary. com.]

with a weight (200 g and 1 cm^2 bottom area) for 30 s according to GB/T 1728–1989. If there was no trace on the surface of the film after taking away the weight and cotton ball, this testing time was the drying time. The impact resistance was measured by an impact tester with a falling weight (1000 ± 1 g) according to GB/T 1732-1993. The height of striking of MPP-2K-WPU film coated tinplate panel without cracking and peeling was recorded as impact resistance. The gloss of MPP-2K-WPU film was detected at 60° on glass panel using a glossmeter (GB/T 1743-1989). The adhesion of MPP-2K-WPU film on tinplate panel was tested by the circle-cut method according to GB/T 1720-1989, where the best adhesion was grade 1 followed by grades 2, 3, 4, 5, 6, and 7. The flexibility of MPP-2K-WPU film was studied by bending the film coated panel with a conical mandrel at angle of 180°, and expressed by the diameter of conical mandrel for bending film coated tinplate panel without peeling and cracking (GB/T 1731-1993). The pencil hardness of MPP-2K-WPU film was measured by a pencil with different hardness at an angle of 45° and a movement speed of 0.5-1 mm s^{-1} according to GB/T 6739-2006. The antifouling resistance (testing time of 1 h) and blocking resistance (testing time of 4 h) were measured according to standard test method GB/T 23999-2009.

RESULTS AND DISCUSSION

Characterization of Maleopimaric Acid-Modified 2K-WPU

MPP-2K-WPU is composed of MPP dispersion and polyisocyanate. The film formation process of MPP-2K-WPU dispersion mainly involves the following three steps: (i) solvent and water volatilizing, (ii) particles aggregating, merging, (iii) NCO group reacting with OH group.[27] The particles aggregating, merging and chemical reaction processes were characterized by TEM, AFM, and FTIR, respectively.

In order to investigate the particles aggregating process, the TEM images of MPP-2K-WPU reactive dispersions after 5, 20, and 60 min of mixing were recorded (Figure 1). As shown in Figure 1, the MPP-2K-WPU reactive dispersions after 5 min of mixing exhibit good water dispersity, with particle size of about 290 nm. After 20 min of mixing, the particle size of MPP-2K-WPU reactive dispersions increases to about 500 nm and the aggregating phenomena of particles are observed. The results validate that the particles aggregating process is related to the increase in particle size of MPP-2K-WPU system.[28] As mixing progresses, the aggregating phenomena of particles are more evident, which are observed in the TEM image of MPP-2K-

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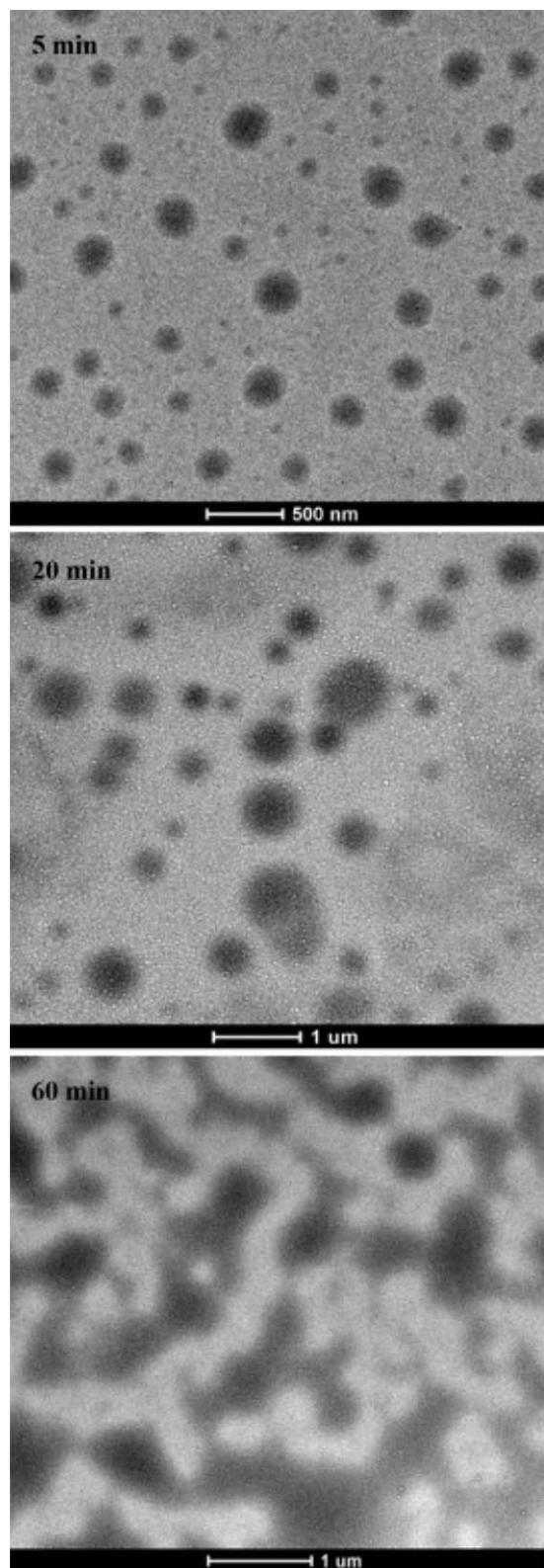
Figure 1. TEM images of MPP-2K-WPU(1.5:1) reactive dispersions after 5 min, 20 min, and 60 min of mixing.

WPU reactive dispersions after 60 min of mixing. The results demonstrate that the aggregation of particles is occurred during the film formation process.
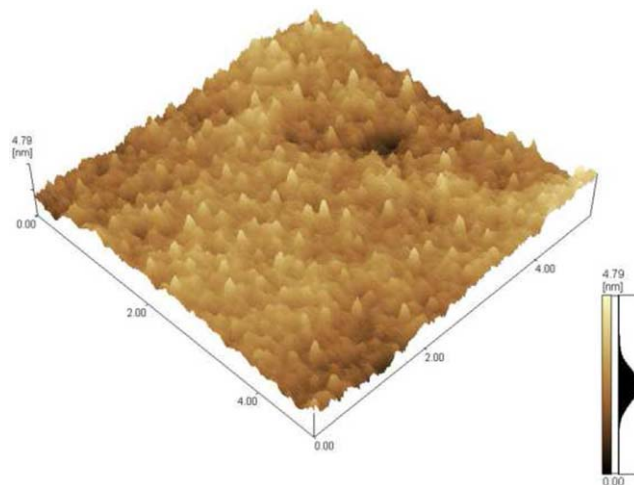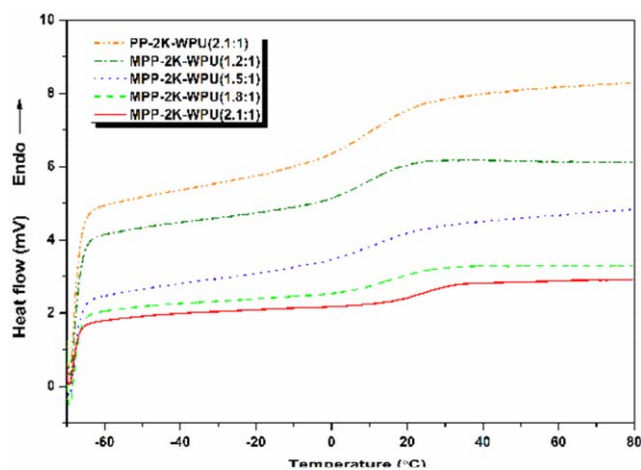

Figure 2. AFM image of MPP-2K-WPU(1.5:1) film. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

The AFM topographic image of MPP-2K-WPU film is presented in Figure 2. It can be observed that there are many cone-shaped hillocks on the surface of MPP-2K-WPU film. When particles of the two reactive dispersions overlap with each other during the film formation process, only the edge parts of the particles can merge together, and the unmerged parts of the particles exposed on the surface of MPP-2K-WPU film are observed as cone-shaped hillocks.[29] The "hillock topography" found on the surface of MPP-2K-WPU film is the trace of merged particles of the reactive dispersions, which validates the particle merging process of the MPP-2K-WPU film formation.

The FTIR spectra of MPP, polyisocyanate and MPP-2K-WPU are shown in Figure 3. The disappearances of absorption peaks at 3527 cm^{-1} (—OH group stretching vibration) and 2260 cm^{-1} (—NCO group stretching vibration) indicate that NCO group of polyisocyanate has reacted with OH group of MPP. The characteristic absorption peaks at 3369 cm^{-1} (N—H
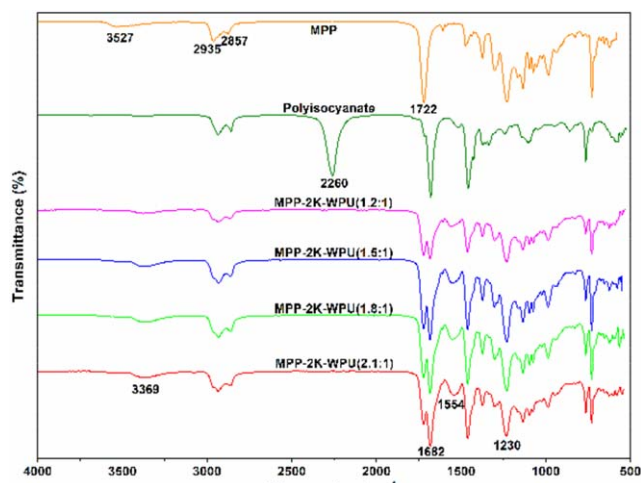
Figure 3. FTIR spectra of MPP, polyisocyanate, and MPP-2K-WPU. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 4. DSC curves of MPP-2K-WPU film. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table II. Thermal Properties of MPP-2K-WPU Films

Sample	T_g (°C)	T_{max1}[a] (°C)	T_{max2}[b] (°C)
MPP-2K-WPU(1.2:1)	10.9	368.4	465.7
MPP-2K-WPU(1.5:1)	12.2	372.3	465.1
MPP-2K-WPU(1.8:1)	16.5	375.6	463.4
MPP-2K-WPU(2.1:1)	22.9	377.7	464.6
PP-2K-WPU(2.1:1)	10.3	378.6	440.2

[a] T_{max1}, the temperature at maximum weight loss rate in the first stage.
[b] T_{max2}, the temperature at maximum weight loss rate in the second stage.

stretching vibration), 1682 cm^{-1} (C=O stretching vibration), 1554 cm^{-1} (N—H out of plane bending and C—N stretching vibration) and 1230 cm^{-1} (the esteric C—O—C stretching vibration) confirm that urethane (—NH—CO—O—) is formed through the addition reaction of NCO group and OH group.[29,30] The other absorption peaks in Figure 3 correspond to the —CH$_3$ and —CH$_2$— stretching vibration (2857–2935 cm^{-1}) and C=O stretching vibration of ester group in MPP (1722 cm^{-1}), respectively.

Thermal Properties of Maleopimaric Acid-Modified 2K-WPU Films

DSC was used to measure the glass transition temperature associated with MPP-2K-WPU films (Figure 4). The values of glass transition temperature (T_g) are list in Table II. As shown in Figure 4, all MPP-2K-WPU films show only one T_g in the temperature range of −70°C to 80°C. The result indicates that MPP component and polyisocyanate component have nice compatibility.[31] The T_g of MPP-2K-WPU film (Table II) increases from 10.9°C to 22.9°C, when the NCO:OH molar ratio increases from 1.2 : 1 to 2.1 : 1. Higher NCO:OH molar ratio results in more content of urethane and urea which is formed through the side reaction between NCO and H$_2$O, and then the crosslinking density and hydrogen bonding from urethane and urea groups are enhanced.[32] Therefore, the T_g of MPP-2K-WPU film shifts toward higher temperature with increasing NCO:OH molar ratio. Furthermore, compared with the control sample of PP-2K-WPU(2.1 : 1), MPP-2K-WPU(2.1 : 1) shows higher T_g. Because MPA with the hydrophenanthrene ring structure is a polyfunctional compound, the introduction of MPA can not only enhance the crosslinking density of MPP-2K-WPU film, but also increase the rigidity of MPP-2K-WPU molecule chain. As a result, the motion of MPP-2K-WPU molecule chain is restricted which leads to a higher T_g.[6,20]

The thermal degradation and stability of MPP-2K-WPU films were investigated by TGA. The TGA curves of MPP-2K-WPU films are shown in Figure 5, and the thermal decomposition data are summarized in Table II. Two thermal degradation

stages of MPP-2K-WPU films are observed in TGA curves. The first stage of degradation in the temperature range of 250°C to 390°C is related to the decomposition of urethane/urea bonds due to the low breaking energy of C—N bond.[12,33] The second stage of degradation in the temperature range of 390°C to 500°C is attributed to the decomposition of MPP molecule chain.[34] For the MPP-2K-WPU films based on different NCO:OH molar ratios, the temperature at maximum weight loss rate in the first stage (T_{max1}) increases from 368.4°C to 377.7°C, while the temperature at maximum weight loss rate in the second stage (T_{max2}) shows almost no change, when the NCO:OH molar ratio increase from 1.2 : 1 to 2.1 : 1. The results indicate that the enhancement of crosslinking density of MPP-2K-WPU film caused by increasing NCO:OH molar ratio can improve the thermal stability of the first stage degradation but cannot affect the decomposition of the second stage degradation. The results are in agreement with other studies.[35] For the 2K-WPU films based on different kinds of polyol component, the T_{max2} of MPP-2K-WPU films are about 465°C, which is higher than that of control samples (about 440°C). The result reveals that the thermal stability of MPP-2K-WPU films is improved by introducing MPA. This is attributed to the introduction of hydrophenanthrene ring structure and the increasing crosslinking density of MPP-2K-WPU film.
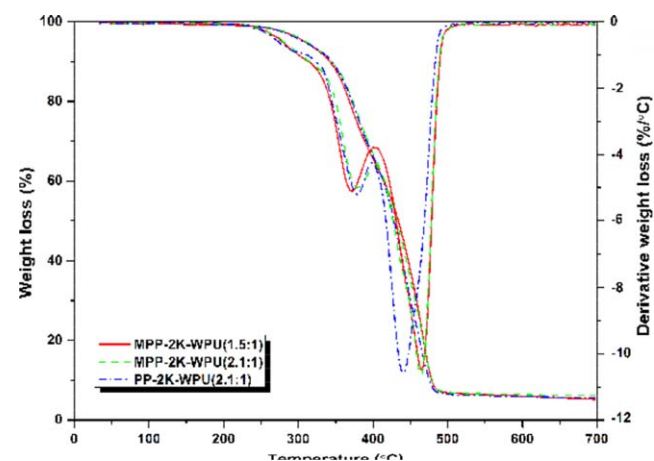
Figure 5. TG curves of MPP-2K-WPU film. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
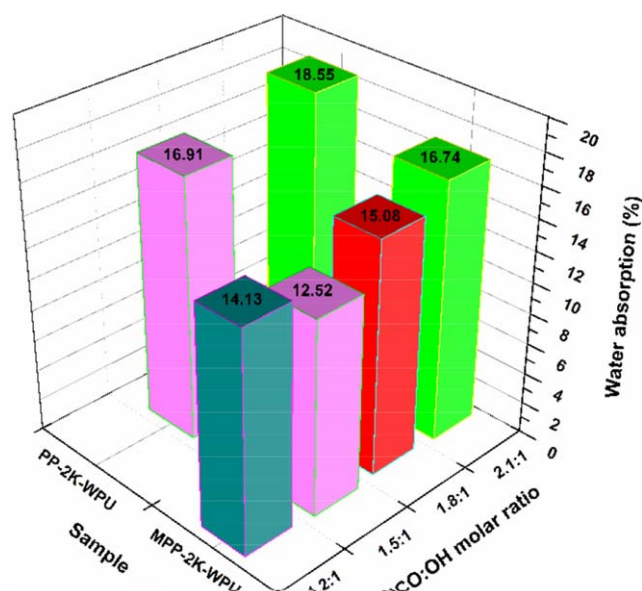
Figure 6. Water absorption of MPP-2K-WPU film. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Water Absorption

The water resistance of MPP-2K-WPU films was characterized by water absorption (Figure 6). As can be seen from Figure 6, the water absorption of MPP-2K-WPU films decreases firstly and then increases with increasing NCO:OH molar ratio. This result indicates that the water resistance of MPP-2K-WPU films is enhanced firstly and then weakened with increasing NCO:OH molar ratio. There are two competitive factors which affect the water resistance of MPP-2K-WPU films. On the one hand, when NCO:OH molar ratio increases, the excess of NCO group is beneficial for the improvement of the crosslinking density and hydrogen bonding interactions in MPP-2K-WPU system. Hence the water resistance of MPP-2K-WPU films improves.[36] On the other hand, the increase in the NCO:OH molar ratio increases the polar groups of urethane and urea, which leads to the enhancement of hydrogen bonding interactions between MPP-2K-WPU and water molecules, thus facilitating the penetration of water into the MPP-2K-WPU films. Therefore the water resistance of MPP-2K-WPU films weakens.[37,38] Because of the above two competitive factors, the water resistance of MPP-2K-WPU films presents a trend of enhancing firstly and then weakening with increasing NCO:OH molar ratio. In addition,

water absorption decrease from 16.91% for PP-2K-WPU(1.5:1) film to 12.52% for MPP-2K-WPU(1.5:1) film. Water absorption of these 2K-WPU films show the same trend at NCO:OH molar ratio of 2.1 : 1. The results indicate that the incorporation of MPA improves the water resistance of MPP-2K-WPU films.

Surface Free Energy of Maleopimaric Acid-Modified 2K-WPU Films

The surface free energy (γ_S) of MPP-2K-WPU films were obtained by measuring the contact angles of testing liquids on their surface. The contact angles of testing liquids were analyzed using Equation of State method and Owens-Wendt-Rabel-Kaelble method. The surface parameters are listed in Table III. The γ_S of studied 2K-WPU films calculated by Owens-Wendt-Rabel-Kaelble method are within the range of 32.72-36.39 mJ·m^{-2}, which are in a good accordance with the γ_S calculated by Equation of State method. Besides, the dispersive component (γ_S^d) and polar component (γ_S^p) of surface free energy are also obtained through Owens-Wendt-Rabel-Kaelble method. It can be seen from Table III that the quantitative contribution of γ_S^d and γ_S^p to surface free energy are about 83% and 17%, respectively. These results suggest that the dispersion interaction depending on the structure of macromolecules makes major contribution to the surface free energy.[39]

When NCO:OH molar ratio increases from 1.2 to 2.1, a trend toward an increasing γ_S^p of MPP-2K-WPU film is observed. The γ_S^p is related to the dipole-dipole, dipole-induced dipole and hydrogen bonding interactions between the solid and liquid.[26,40] More urethane and urea will be formed with increasing NCO:OH molar ratio, which can enhance the hydrogen bonding interaction in MPP-2K-WPU, thus the γ_S^p increases.[41] However, the γ_S and γ_S^d of MPP-2K-WPU film decrease firstly and then increase with increasing NCO:OH molar ratio, which indicates that the surface property of MPP-2K-WPU film is affected by NCO:OH molar ratio. Generally, the higher contact angles, the lower γ_S, which means the stronger resistance of solid surface to liquid wetting.[39,41] The changes in γ_S further confirm that the water resistance of MPP-2K-WPU films is enhanced firstly and then weakened with increasing NCO:OH molar ratio. Furthermore, compared with the control samples of PP-2K-WPU films, the MPP-2K-WPU films exhibit lower γ_S due to the introduction of MPA with hydrophobic hydrophenanthrene ring.

Table III. Surface Free Energy Parameters of MPP-2K-WPU Films

		MPP-2K-WPU				PP-2K-WPU	
Sample		1.2:1	1.5:1	1.8:1	2.1:1	1.5:1	2.1:1
Equation of State method	γ_S (mJ m^{-2})	33.41 ± 0.36	32.83 ± 0.35	33.75 ± 0.42	34.75 ± 0.56	35.34 ± 0.36	35.95 ± 0.58
Owens-Wendt -Rabel-Kaelble method	γ_S (mJ m^{-2})	34.08 ± 0.27	32.72 ± 0.26	34.38 ± 0.29	35.38 ± 0.35	35.49 ± 0.25	36.39 ± 0.36
	γ_S^d (mJ m^{-2})	29.50 ± 0.20	28.14 ± 0.19	29.62 ± 0.22	30.13 ± 0.27	29.75 ± 0.18	30.43 ± 0.29
	γ_S^p (mJ m^{-2})	4.58 ± 0.08	4.59 ± 0.09	4.76 ± 0.09	5.25 ± 0.11	5.74 ± 0.08	5.96 ± 0.11

Table IV. The Application Properties of MPP-2K-WPU Films

Item	MPP-2K-WPU				PP-2K-WPU	
	1.2:1	1.5:1	1.8:1	2.1:1	1.5:1	2.1:1
Drying time						
Surface-dry (min)	50	50	60	65	130	155
Tough-dry (h)	11	12	13.5	15	33	35
Gloss (60°)	93.2	93.7	94.1	93.6	90.2	90.7
Impact strength (kg·cm)	120	120	120	120	120	120
Pencile hardness	H	2H	2H	2H	H	2H
Adhesion (grade)	2	2	2	2	2	2
Flexibility (mm)	0.5	0.5	0.5	0.5	0.5	0.5
Pollution resistance						
Vinegar (1 h)	Unchanged	Unchanged	Unchanged	Unchanged	Unchanged	Unchanged
Tea (1 h)	Unchanged	Unchanged	Unchanged	Unchanged	Whitening	Unchanged
Alkali resistance (1 h) 50 g L^{-1} NaHCO$_3$	Unchanged	Unchanged	Unchanged	Unchanged	Unchanged	Unchanged
Ethanol resistance (1 h)	Whitening	Unchanged	Unchanged	Unchanged	Whitening	Unchanged
Blocking resistance (4 h, 500 g, 50°C)[a]	MM: A-0 MB: A-0	MM: A-0 MB: A-0	MM: A-0 MB: A-0	MM: A-0 MB: A-0	MM: A-0 MB: A-0	MM: A-0 MB: A-0

[a] Blocking resistance: MM means front to front. MB means spoon-fashion. A means free-falling separation. B means separation after slight tapping. 0 means no damage.

The Application Properties of Maleopimaric Acid-Modified 2K-WPU Films

Table IV illustrates the application properties of MPP-2K-WPU films. The MPP-2K-WPU film based on higher NCO:OH molar ratio dries slower. When NCO:OH molar ratio increases, the hydrogen bonding interactions between MPP-2K-WPU and water molecules are enhanced, which reduces the volatilizing rates of bounding water, thus resulting in slower drying.[22] Pencil hardness and ethanol resistance are improved by increasing NCO:OH molar ratio due to the increase in crosslinking density of MPP-2K-WPU film. However, the application properties of MPP-2K-WPU films show almost no changes when the NCO : OH molar ratio is larger than 1.5. Hence, the optimum NCO:OH molar ratio is found to be 1.5 : 1. In addition, compared with the control samples of PP-2K-WPU films, MPP-2K-WPU films exhibit faster drying and higher gloss owing to the presence of the hydrophobic hydrophenanthrene ring in MPP-2K-WPU.[42] Although the other application properties of MPP-2K-WPU(2.1 : 1) film are similar to those of PP-2K-WPU(2.1 : 1) film, the MPP-2K-WPU(1.5:1) film shows enhanced pencil hardness and ethanol resistance in comparison with PP-2K-WPU(1.5:1) film. These results suggest that the introduction of MPA contributes to the improvement in the properties of MPP-2K-WPU films at NCO:OH molar ratio of 1.5 : 1.

CONCLUSIONS

A novel maleopimaric acid-modified two-component waterborne polyurethane (MPP-2K-WPU) coating was prepared by crosslinking of MPP dispersion with polyisocyanate. The film formation process of MPP-2K-WPU dispersion was character-ized by TEM, AFM and FTIR, respectively. The influences of NCO:OH molar ratio on the properties of MPP-2K-WPU films were investigated. When NCO:OH molar ratio increased, the thermal stability, pencil hardness and ethanol resistance of MPP-2K-WPU films were improved, but the water resistance was enhanced firstly and then weakened. Dispersion interaction depending on the structure of macromolecules made major contribution to the surface free energy of MPP-2K-WPU films. The MPP-2K-WPU films had better thermal stability, water resistance, gloss, pencil hardness and ethanol resistance than those of PP-2K-WPU films.

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