Preparation and Properties of Autocatalytic Biobased Waterborne Polyol from Rosin Based Epoxy Resin

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Abstract

Due to the complex heterogeneous film forming process of two-component waterborne polyurethane (2K-WPU), the crosslinking reaction rate of 2K-WPU cannot meet the demand of efficient application in coatings. In order to improve the crosslinking reaction rate of 2K-WPU, a waterborne polyol containing tertiary amine groups was synthesized from rosin based epoxy resin and secondary amine compound, and then autocatalytic 2K-WPU was prepared by crosslinking the rosin based waterborne amino polyol with polyisocyanate. The structure of the polyol from rosin based epoxy resin was characterized with Fourier infrared (FT-IR) and nuclear magnetic resonance (NMR). The crosslinking kinetics and the crosslinked product of the rosin based waterborne amino polyol were also compared with a commercial acrylic polyol. It was shown from the results that the crosslinking reaction rate of the rosin based waterborne amino polyol was faster than that of the commercial acrylic polyol, which indicated the tertiary amine groups chemically bonded in the rosin based polyols could autocatalyze the crosslinking reaction of 2K-WPUs with catalysts free. The film of the rosin based waterborne amino polyol had excellent impact strength, adhesion, flexibility, hardness, gloss, fullness and solvent resistance, showing a good application prospect in the field of waterborne coatings.

Introduction

Two-component polyurethane coatings have the merits of low film forming temperature, strong adhesion, good wear resistance, high hardness, and good chemical resistance, and are widely used as industrial protection, wood furniture and automotive coatings [1-2]. However, most two-component polyurethane coatings need to be diluted with organic solvent. With the increasingly stringent emission limits of volatile organic compounds (VOCs), the development of two-component waterborne polyurethane (2K-WPU) coatings with water instead of organic solvents has attracted much attention [3-5]. 2K-WPU coatings combine the high performance of two-component solvent based polyurethane coatings with the environment friendly of waterborne coatings, which have replaced solvent based coatings in the fields of surface decoration and protection of automobile [6], wood [7], plastic [8], furniture. In recent years, multinational enterprises such as Costron, Pasteur and Mitsui have been committed to promoting the development and application of 2K-WPU coatings.

2K-WPU is composed of waterborne polyol containing hydroxyl groups (-OH) and polyisocyanate containing isocyanate groups (-NCO). The film formation process of 2K-WPU is a complex heterogeneous film forming process involving a series of physical and chemical processes among latex particles, which results to a common problem of slow film-forming rate [9]. The crosslinking reaction of 2K-WPU can be accelerated by metal organic compounds and tertiary amines. Rosthauser et al. [10] synthesized sulfur-containing organotin catalyst. Most tin catalysts are sensitive to water, but sulfur-containing tin catalysts are stable to the presence of water. Compared with dibutyltin dilaurate (DBTDL), it was found that the catalytic activity of sulfur-containing tin was slightly lower than that of DBTDL, but the water resistance was better than that of DBTDL. Blank et al. [11] found that the catalytic effect of zirconium chelates in 2K-WPU could replace organotin compounds to catalyze the reaction between -NCO and -OH. Arenivar et al.

[12] studied the catalytic mechanism of bismuth carboxylate and zinc carboxylate compounds for the reaction of -NCO and -OH by using kinetic theory. It is found that the catalytic mechanism of bismuth carboxylate and zinc carboxylate for the reaction of -NCO and -OH was different from that of organotin compounds. However, with the increasing requirements of environmental protection and human health, organometallic compounds catalysts have been restricted in many application fields of coatings, especially in food packaging and children's toys. Tertiary amines are another kind catalyst for catalyzing the crosslinking reaction of 2K-WPU. Because the activity of tertiary amines in catalyzing the reaction of -NCO and H_2O is higher than that of -NCO and -OH, small molecular tertiary amines are generally not used alone as catalysts, but combined with metal catalysts in the film formation of 2K-WPU coatings [13]. Moreover, most small molecular tertiary amines do not take part in the crosslinking reaction of 2K-WPU. They are easy to volatilize into the environment, which not only produces unpleasant odor, but also increases the emission of toxic VOC.

At present, the main kinds of waterborne polyols used to prepare 2K-WPU are waterborne acrylic polyol dispersion, waterborne polyurethane polyol dispersion and waterborne polyester polyol dispersion, most of which are synthesized from fossil resources. Replacing fossil resources with renewable biomass resources have been considered as one of the most promising renewable feedstocks to prepare green compounds with low environmental load [14-15]. Rosin is a characteristic forestry resource in China, with an annual output of about 400-thousand tons. In recent years, the technology for rosin deep processing and utilization had developed rapidly [16-17]. Rosin has been used as the raw material to prepare epoxy resin. In the 1970s, Penczek et al. prepared rosin based epoxy resin by reacting maleic rosin with epichlorohydrin in 30% KOH solution [18]. The rosin based epoxy resin had similar physical and mechanical properties to bisphenol A epoxy resin. Wang et al. reduced the carboxyl group of rosin acid to hydroxyl by $LiAlH_4$, and then reacted hydroxyl with epibromohydrin to prepare rosin based glycidyl ether epoxy resin [19], which had better hydrolysis stability and heat resistance than rosin based glycidyl ester epoxy resin. Li et al. prepared rosin based glycidyl amine epoxy resin by the reaction of dehydrogenated rosin amine and epichlorohydrin [20]. The cured product had excellent heat resistance, and the glass transition temperature reached 167 °C. Mantzaridis et al. synthesized an epoxy resin with two rosin fused rings structure by using rosin dimer, and studied the curing reaction with isophorone diamine and the thermodynamic properties of the cured product [21]. Introducing the rigid structure of rosin based epoxy resin into the molecular chain of waterborne polyurethane could improve the mechanical property of polyurethane materials [22-23].

In this paper, a novel rosin based waterborne polyol containing tertiary amine group was synthesized by the reaction between rosin based epoxy resin and secondary amine compound, and then rosin based 2K-WPU with autocatalytic property was prepared by crosslinking the polyol with polyisocyanate. By introducing sterically hindered tertiary amine group into the molecular structure of polyol, the film-forming efficiency of 2K-WPU was improved as a result of the catalysis of tertiary amine on the crosslinking reaction between hydroxyl group and isocyanate group. The rosin alicyclic structure was also introduced into the main chain of 2K-WPU in the form of epoxy resin to control the rigidity and hardness of waterborne coatings. The characteristics of crosslinking reaction and the properties of crosslinked product of the rosin based waterborne polyol were compared with a commercial acrylic polyol.

1 Experimental

1.1 Materials

The rosin based epoxy resin named as maleopimaric acid epoxy resin (MPE) (Scheme 1) with epoxy value of 3.2 mmol g^{-1} was synthesized from rosin, maleic anhydride and epichlorohydrin [24]. N-benzylethanolamine, dimethylol propionic acid (DMPA), 1,6-hexanediisocyanate (HDI) were purchased from Macklin Inc., Shanghai, China. Acetone and N, N-dimethylethanolamine (DMEA) were purchased from Nanjing Chemical Reagent, Co., Ltd., China. Acrylic polyol dispersion (Antkote® 2703), solid content 42%, hydroxyl content 3.6 % (solid resin), was obtained from Wanhua Chemical Group Co., Ltd. Hydrophilic modified polyisocyanate (D100), solid content 100%, was obtained from Wuhan Shiquanxing New Material Technology Co., Ltd.

1.2 Preparation of waterborne polyol from rosin based epoxy

Waterborne polyol from rosin based epoxy resin (WMPP) was prepared through the following steps. (1) MPE, N-benzylethanolamine and acetone were put into a four port flask with heating device, thermometer, stirrer and condenser tube. The reaction was heated to acetone reflux temperature and maintained for 5h. Then a yellow transparent product polyol from rosin based epoxy resin (MPP) (Fig. 1) was obtained. (2) DMPA and HDI were reacted with MPP in acetone solution for 5 hours at reflux temperature. Then the product was neutralized with DMEA and dispersed with water. After evaporating acetone under reduced pressure, waterborne polyol from rosin based epoxy resin (WMPP) (Fig. 2) with solid content of 35 % and hydroxyl content of 3.7 % (solid resin) was obtained.

1.3 Preparation of 2K-WPUs

2K-WPUs were prepared by mixing WMPP dispersion and antkote® 2703 dispersion with polyisocyanate curing agent D100, respectively, with the molar ratio of hydroxyl group to isocyanate group at 1:1.4. After mixed equably, 2K-WPUs were coated on the surface of tinplate, and maintained at room temperature for 7 days.

1.4 Characterization

1.4.1 FT-IR

The samples were measured on an ALPHA-II Fourier infrared (FT-IR) spectrometer (Bruker, Germany) with attenuated total reflection method. The scanning range was $4000 \text{ cm}^{-1} \sim 500 \text{ cm}^{-1}$ with an average of 32 scans.

1.4.2 NMR

NMR measurements were recorded on an AVANCE 500 MHz DRX nuclear magnetic resonance (NMR) spectrometer (Bruker, Germany). The samples are solved in CDCl_3 . Chemical shifts are calculated relative to TMS for NMR control.

1.4.3 Laser particle size analysis

The particle size distribution of the polyol dispersions was measured on a ZS ZEN3600 nano particle size analyzer (Malvern Instrument Co., UK). WMPP dispersion and Antkote® 2703 dispersion were distilled with deionized water to a solids content of 0.5%-1%, and 1 mL of the distilled sample was placed in a cuvette to measure the particle size.

1.4.4 Rotational rheology analysis

HAAKE Mars III rotary rheometer (Thermo Fisher, USA) was used to test the variation of storage modulus during the crosslinking reaction of 2K-WPUs. The reaction temperature rised from 30 °C to 150 °C at a heating rate of 2 °C·min⁻¹ and the vibration frequency is 2 Hz.

1.4.5 DSC characterization of crosslinking reaction

The samples of 2K-WPUs was frozen and dried in a vacuum freezing machine for 24 hours to remove water (Cold well temperature is -55 °C). About 10 mg of sample was taken in aluminum crucible. The exothermic process of the crosslinking reaction of the sample was determined by a diamond differential scanning calorimetry (DSC) (PerkinElmer, USA) at four different temperature rise rates of 5, 10, 15 and 20 °C min⁻¹. The test was played at nitrogen atmosphere and the temperature ranges from -10 °C to 180 °C.

1.4.6 Glass transition temperature

The glass transition temperature (T_g) of the crosslinked products of 2K-WPUs was measured on a diamond DSC analyzer (PerkinElmer, USA) at the heating rate of 20 °C·min⁻¹ and nitrogen flow of 50 ml/min. About 6 mg sample was weighted accurately and put into a closed aluminum crucible. Pure indium was used for calibration and an empty crucible was used as the reference. The scanning temperature range was -50~150 °C.

1.4.7 TG analysis

The thermal stability of the crosslinked products of 2K-WPUs was carried on a STA 409 PC/PG thermogravimetric analyzer (Netzsch, Germany) under nitrogen atmosphere at the heating rate of 10°C·min⁻¹. The scanning temperature range was 25 °C to 800 °C.

1.4.8 DMA analysis

The dynamic thermomechanical analysis (DMA) of the crosslinked products of 2K-WPUs was measured on a Q800 dynamic thermomechanical analyzer (Thermo Fisher, USA) at the heating rate of 2 °C·min⁻¹ and vibration frequency of 1 Hz. The scanning temperature range was -50 °C to 150 °C. The sample size was 40×6.5×0.5 mm³.

1.4.9 Film properties

The properties of films from 2K-WPUs were determined according to the Standard (GB/T 23999-2009) "Waterborne wood coatings for interior decoration".

2 Results And Discussion

2.1 Characterization of polyols from rosin based epoxy resin

2.1.1 FT-IR

FT-IR spectra of the polyols from rosin based epoxy resin were shown in Fig.3. Compared with the spectra of epoxy resin MPE, the characteristic absorption peaks of epoxy group at 908 cm^{-1} in the spectra of MPP and WMPP polyols disappeared, while the characteristic absorption peaks of hydroxyl group at $3100\sim 3700\text{ cm}^{-1}$ and C-O at 1040 cm^{-1} were significantly enhanced. This result indicated that amine group had reacted with epoxy group, and the ternary ring of epoxy group was opened to produce C-OH group. Due to the introduction of N-benzylethanolamine to the structure of MPP polyol, the characteristic peaks of benzene ring in the spectrum of MPP appeared at 1600 cm^{-1} and 1500 cm^{-1} . The characteristic peak of isocyanate group at 2272 cm^{-1} completely disappeared in the WMPP spectrum, indicating that the reaction between isocyanate group and hydroxyl group was complete. Due to the formation of urethane, the carbonyl characteristic peak was enhanced at 1700 cm^{-1} , and the amide II band characteristic peak appeared at 1530 cm^{-1} , which was consistent with the structural characteristics of polyurethane formed by the reaction of hydroxyl group and isocyanate group [25]. Other strong absorption peaks in the spectra mainly included 2955 cm^{-1} methyl stretching vibration absorption peak, 2874 cm^{-1} methylene stretching vibration absorption peak, 1716 cm^{-1} carbonyl stretching vibration absorption peak of ester bond, 1456 cm^{-1} methylene bending vibration absorption peak, 1380 cm^{-1} methyl bending vibration absorption peak, 1240 cm^{-1} and 1165 cm^{-1} -C-O-C stretching vibration absorption peak of ester bond.

2.1.2 NMR

Fig. 4 (a) showed the ^1H -NMR spectra of rosin based epoxy resin (MPE) and its polyol product (MPP). Compared with the spectrum of MPE, the chemical shift of methylene hydrogen of epoxy group at $\delta\ 4.32$ disappeared in MPP spectrum. After the ring-opening addition reaction between epoxy group and amine group, the chemical shift of this methylene hydrogen moved to high field and appeared at $\delta\ 2.05$ in MPP spectrum. The chemical shift at $\delta\ 7.26$ was the characteristic peak of hydrogen on the carbon-carbon double bond in the rosin ring in MPE spectrum, and this peak was significantly enhanced in the MPP spectrum. Because after the addition of N-benzylethanolamine, the benzene ring was introduced into the MPP structure, leading to the increase of the hydrogen on the carbon-carbon double bond.

Fig. 4 (b) showed the ^{13}C -NMR spectra of MPE and MPP. Compared with the spectrum of MPE, the chemical shift of secondary carbon and tertiary carbon of epoxy group at $\delta\ 44.6$ and $\delta\ 49.8$ disappeared in MPP spectrum [26]. After the ring opening addition reaction of epoxy group and amino group, the chemical shifts of the two carbons moved to the low field and appeared at $\delta\ 55.9$ and $\delta\ 66.8$, respectively. The

characteristic peaks of $\underline{\text{C}}\text{-N}$ and benzene ring in the N-benzylethanolamine appeared at δ 59.3 and δ 127.9, respectively.

2.2 Particle size analysis of the dispersion

The particle size distribution of polyol dispersion affects the storage stability and film-forming properties of 2K-WPU [9]. The particle size distribution of WMPP dispersion was compared with that of commercial acrylic polyol dispersion (Antkote® 2703). As shown in Fig. 5, the particle size distributions of the two polyol dispersions were almost the same, with particle size distribution range of 40-250 nm and average particle size about 100 nm. Both of them had good storage stability and film-forming ability.

2.3 Crosslinking reaction of the polyols

The variation of storage modulus during the crosslinking reaction of polyol dispersions was investigated by rotating rheometer (Fig. 6). During the crosslinking reaction of WMPP and Antkote®2703, the storage modulus increased first and then decreased with an increase of temperature. In the initial stage of heating up, the crosslinking reaction rate accelerates and the crosslinking density of the crosslinked product increased with an increase of temperature. When the crosslinking reaction completed, the storage modulus of the crosslinked product reached the maximum. Then when the temperature continued to rise, the polymers turned from glass to rubber state, and the storage modulus decreased sharply. In contrast with that of Antkote®2703, the storage modulus of WMPP increased rapidly in the crosslinking stage, which indicated that the crosslinking reaction activity of WMPP was higher than that of the ordinary hydroxyacrylic polyols. Because the tertiary amine group introduced into the WMPP structure could catalyze the reaction between hydroxyl and isocyanate group and improve the crosslinking reaction rate [27].

2.4 Kinetics of the crosslinking reaction of the polyols

According to Arrhenius formula, the reaction rate constant has an exponential relationship with activation energy (E_a). Low E_a value of crosslinking reaction is conducive to increasing the reaction rate constant and accelerating the reaction speed. A large number of reaction models have been developed for the polymerization of thermosetting resin [28], among which Kissinger and Friedman are two classical methods to calculate E_a . Both of them can calculate E_a value through equation without specific model.

Kissinger method is based on the following two assumptions [29]: (1) the exothermic peak temperature T_p changes with the heating rate; (2) Maximum reaction rate da/dt occurs at the peak temperature. Equation can be expressed as Equation 1.

$$\ln(\beta / T_p^2) = \ln(A R / E_a) - E_a / R T_p \quad (1)$$

Where β is the heating rate, T_p is the peak temperature of DSC curves, A is the pre exponential factor, and R is the gas constant (8.314 J/mol K).

Linear regression curve of $\ln(\beta/T_p^2)$ vs $1/T_p$ was calculated by least square method (Fig. 7). E_a of crosslinking reaction could be calculated from the slope of the curve.

Table 1 T_p of the DSC curves and E_a obtained by Kissinger method

samples	T_p (K)				E_a (kJ/mol)	R^2
	5 K/min	10 K/min	15 K/min	20 K/min		
WMPP	361.96	373.64	380.75	387.92	69.43	0.9999
Antkote® 2703	372.14	382.91	389.19	395.85	79.38	0.9999

Table 1 listed T_p of the DSC exothermic curves of WMPP dispersion and Antkote®2703 crosslinked with polyisocyanate at different heating rates and E_a calculated by Kissinger equation. T_p increased with an increase of heating rate. Because the reaction time to the same temperature was shortened with an increase of heating rate, resulting in the incompleteness of crosslinking reaction and the hysteresis of T_p . This hysteresis showed that T_p moved towards high temperature. E_a of crosslinking reaction of WMPP dispersion calculated by Kissinger equation was lower than that of Antkote®2703, indicating that the crosslinking reaction rate of WMPP dispersion was faster than that of commercial product Antkote®2703. Because WMPP could auto-catalyze the crosslinking reaction between hydroxyl group and isocyanate group.

Kissinger method is a model free method, but it assumes that E_a is constant with the change of reaction transformation process. In fact, E_a will change with the progress of crosslinking reaction. E_a measured by the equal conversion method can overcome the shortcomings of Kissinger method. The average value is obtained from E_a at different conversion rates measured by equal conversion method. Friedman method is the most common differential equal conversion method in kinetic analysis, evaluating E_a as a function of conversion (α) [30]. According to Friedman's method, E_a is determined by the logarithmic form of the kinetic reaction rate (Equation 2).

$$\ln\left(\beta \frac{d\alpha}{dT}\right) = \ln \frac{d\alpha}{dt} = \ln[Af(\alpha)] - \frac{E_a}{RT} \quad (2)$$

By integrating the area under the exothermic peak of DSC exothermic curves at different heating rates, the relation curves of the crosslinking conversion (α) vs temperature (T) and α vs time (t) were obtained. From the α - t curves (Fig. 8), it could be seen intuitively that the crosslinking reaction rate of WNPP containing tertiary amine group was significantly faster than that of Antkote®2703 whether at 5 °C/min or at 20 °C/min.

The crosslinking reaction rate da/dt can be obtained by differentiating the α - t curve. Assuming that da/dt is a function of α and T , $\ln(da/dt)$ can be described by Equation (2). Then $\ln(da/dt)$ and $1/T$ with the same α on DSC curves at different heating rates can be approximately fitted into a straight line with a slope of $-E_a/R$ (Fig. 9). Repeat this process to obtain E_a at different α , and then calculate the average value to obtain the activation energy of crosslinking reaction [31].

Table 2 E_a (kJ/mol) obtained from Friedman method

Samples	α									Average
	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	
WMPP	59.65	59.25	58.63	58.44	57.82	57.52	58.09	59.79	64.30	59.28
Antkote® 2703	63.02	60.19	61.61	61.80	61.72	62.65	63.75	66.98	73.53	63.92

E_a values at different conversion of crosslinking reaction calculated by Friedman method were shown in Table 2. E_a decreased first and then increased during the conversion ranging from 0.1 to 0.9. Carbamate (-NH-CO-O-) which formed from the reaction between -NCO group and -OH group can catalyze the reaction between -NCO group and -OH group [32]. With the process of crosslinking reaction, the content of carbamate group increased gradually, and the catalytic effect was more obvious. This effect made E_a decrease with an increase of α . On the other hand, with the process of crosslinking reaction, the active functional groups (-NCO group and -OH group) in the crosslinking matrix gradually consumed, and the crosslinked network gradually formed. The unreacted active groups were trapped in the crosslinked network. More activation energy was needed to overcome the larger steric effect in order to continue the reaction. This effect resulted to an increase of E_a with an increase of α . The above two opposite factors worked together causing E_a value of the crosslinking reaction to decrease first and then increase with an increase of α . E_a of the crosslinking reaction of WMPP dispersion calculated by Friedman method was smaller than that of Antkote® 2703 dispersion, which was consistent with the result obtained by Kissinger method.

2.5 Thermal Properties of the crosslinked products

The DSC curves of the crosslinked products were shown in Fig. 10(a). The glass transition temperatures (T_g) of the crosslinked product of WMPP dispersion was slightly higher than that of the crosslinked product of Antkote® 2703 dispersions. The hydroxyl group contents of WMPP and Antkote® 2703 were almost the same, but the chemical structure of WMPP contained rosin alicyclic rings, which increased the rigidity of the molecular chain and improved the T_g of the crosslinked product.

Fig. 10(b) showed the thermogravimetric analysis curves of the crosslinked product. The thermogravimetric curves of the crosslinked products of WMPP and Antkote® 2703 were typical thermal degradation curves of polyurethane [33]. There were two rapid thermal degradation stages. The first rapid degradation stage was the thermal decomposition of C-N bond in polyurethane, because the bond energy

of C-N bond is smaller than those of C-C bond and C-O bond [34]. The second rapid degradation stage was the thermal decomposition of C-C and C-O bond in polyurethane. In the first thermal degradation stage, the thermal stability of the crosslinked product of WMPP was significantly worse than that of the crosslinked product of Antkote® 2703. The fastest weight loss temperature of the crosslinked product of WMPP in the first stage was 296 °C, while the fastest weight loss temperature of the crosslinked product of Antkote® 2703 in the first stage was 353 °C. Because benzylaminoethanol was introduced into WMPP structure, its crosslinked product had more C-N bond than that of the crosslinked product of Antkote® 2703, resulting in the reduction of thermal stability in the first stage. The carbon residue rate of the crosslinked product of WMPP was slightly higher than that of the crosslinked product of Antkote® 2703, because WMPP contained rosin fused rings structure, and the thermal degradation residue was easier to form dense carbon layer [35].

2.6 DMA of crosslinked products

Fig. 11(a) showed the curves of storage modulus (E') and loss modulus (E'') of the crosslinked products with temperature. When the temperature was lower than the glass transition temperature (T_g), the crosslinked product was in the glass state and the molecular motion energy was low. The rigidity and the storage modulus of the material reached the maximum when the internal chain segment was in a "frozen" state [36]. With an increase of temperature, the motion of molecular segments intensified, and the molecular chains stretched from the curled state. The material showed deformation, and the storage modulus of crosslinked products decreased. Meanwhile, in the initial stage of heating up, the increase of temperature weakened the internal tension of the crosslinked polymer and increased the flexibility of molecular chain. Under the action of external force, the chain segment movement resistance decreased, so the loss modulus decreased. As the temperature continued to rise, the polymer chains obtained enough energy and started to move violently, generating more heat. The mechanical loss occurred inside and between the molecular chains, and the loss modulus of the crosslinked products increased gradually. When the temperature was higher than T_g of the crosslinked product, the crosslinked product was in rubber state, and its storage modulus and loss modulus decreased sharply. Before glass transition, the storage modulus and loss modulus of WMPP crosslinked products were higher than those of Antkote® 2703 crosslinked products at the same temperature, because WMPP contained rosin fused rings with strong rigidity and poor flexibility. At the end of glass transition, the storage modulus and loss modulus of WMPP crosslinked products were lower than those of Antkote® 2703 crosslinked products under the same temperature, because the hydroxyl arrangement in Antkote® 2703 obtained by free radical polymerization was more regular than WMPP, and the regular crosslinked network slowed the chain segment movement of the crosslinked products after glass transition [37]. The decrease of storage modulus and loss modulus was not as sharp as that of WMPP crosslinked products.

Fig. 11(b) showed the loss factor ($\tan \delta$) of the crosslinked product. DMA defines the temperature range of $\tan \delta$ as the glass transition zone. There is a relaxation process in this temperature range, which is caused by the thermal softening of the chain segments in the amorphous region of the polymer and the micro Brownian motion of the polymer molecules [38]. T_g (68 °C) of the WMPP crosslinked product obtained by

DMA was slightly higher than that of the Antkote® 2703 crosslinked product (66 °C), and this result was consistent with that obtained by DSC. The dispersity of chain segment motion affects the width of Tan δ peak. Large dispersity of segment motion leads to wide peak of Tan δ , indicating the chain segments have poor regularity and long relaxation process [37]. The width of Tan δ peak of Antkote® 2703 crosslinked product was narrower than that of WMPP crosslinked product, which also indicated the crosslinked network of Antkote® 2703 was more regular.

2.7 Film properties of the 2K-WPUs

Table 3 Properties of the films from 2K-WPUs

Items		WMPP	Antkote® 2703
Gloss@60° ¹	0h	94	85
	3h	90	81
	4h	83	79
Adhesion (grade)		0	0
Pencil hardness		2H	H-2H
Flexibility@mm		0.5	0.5
Blocking resistance@MM		A-0	A-0
Transparency ²		5	4
Fullness ²		5	4
Water resistance@24 h		Pass	Pass
Alcohol resistance@50 % alcohol@1 h		Pass	Pass
Alkali resistance@50 g/L NaHCO ₃ @1 h		Pass	Pass
Resistant to red wine@1 h		Pass	Pass
Vinegar resistance@1 h		Pass	Pass
Tea resistance@1 h		Pass	Pass

Note¹gloss at different pot life; ²“5” represents the best, “1” represents the worst.

The film properties of WMPP crosslinked product and Antkote® 2703 crosslinked product were listed in Table 3. The results showed that the film from WMPP had excellent impact strength, adhesion, flexibility, hardness, gloss, fullness and liquid medium resistance, as a result of the introduction of rosin based epoxy resin into two-component waterborne polyurethane coatings. The hardness, transparency, gloss and fullness of the film prepared from WMPP were better than those of the film from the common commercial Antkote® 2703. The high performance of the film from WMPP was almost the same as that of the solvent

based two-component polyurethane [39]. Because the rosin fused rings introduced into the polyurethane main structure improved the hardness, fullness and gloss of the crosslinked film.

3 Conclusions

Rosin based epoxy resin and N-benzylethanolamine were used to prepare autocatalytic 2K-WPU. The particle size distribution and hydroxyl content of WMPP dispersions were almost the same as those of the commercial acrylic polyol dispersion (Antkote® 2703), while the crosslinking reaction rate of WMPP was faster than that of Antkote® 2703. Activation energy calculated by Kissinger method and Friedman method both showed E_a of the crosslinking reaction of WMPP was lower than that of the crosslinking reaction of Antkote® 2703, indicating the crosslinking reaction rate of WMPP was improved by the introduction of tertiary amine group into the polyol structure. By introduction of the rigid rosin alicyclic rings into the 2K-WPU crosslinked product, glass transition temperatures, hardness, fullness and gloss of the WMPP crosslinked film were higher than those of the Antkote® 2703 crosslinked product. The performance of the film from WMPP was almost the same as that of the solvent based two-component polyurethane, exhibiting significant potential in many applications.

Declarations

Conflict of interest: There are no conflicts to declare.

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Figures

Figure 1

Synthesis of polyol from rosin based epoxy resin

Figure 2

Synthesis of waterborne polyol from rosin based epoxy resin

Figure 3

FT-IR spectra of polyols from rosin based epoxy resin

Figure 4

^1H -NMR (a) and ^{13}C -NMR (b) spectra of MPE and MPP

Figure 5

Particle size distribution of polyol dispersions

Figure 6

Variation of storage modulus during the crosslinking reaction of polyol dispersions

Figure 7

Linear regression curve of $\ln(\beta/T_p^2)$ vs $1/T_p$

Figure 8

α - t curves

Figure 9

$\ln(da/dt)-1/T$ fitting curves (a: Antkote® 2703; b: WMPP)

Figure 10

DSC (a) and TG (b) curves of crosslinked products

Figure 11

The storage modulus, loss modulus (a) and loss factor (b) of the crosslinked products