

Crosslinking Reaction and Properties of Two-Component Waterborne Polyurethane from Terpene-Maleic Ester Type Epoxy Resin

Guo-min Wu,^{1,2,3,4} Zhen-wu Kong,^{1,2,3,4} Cai-feng Chen,^{1,2,3,4} Jian Chen,^{1,2,3,4}
Shu-ping Huo,^{1,2,3,4} Jian-chun Jiang^{1,2,3,4}

¹Institute of Chemical Industry of Forest Products, Chinese Academy of Forestry, Nanjing 210042, China

²Key Laboratory of Biomass Energy and Material, Jiangsu Province, Nanjing 210042, China

³National Engineering Laboratory for Biomass Chemical Utilization, Nanjing 210042, China

⁴Key and Open Laboratory on Forest Chemical Engineering, State Forestry Administration, Nanjing 210042, China

Correspondence to: G.-m. Wu (E-mail: woogm@hotmail.com) or Z.-w. Kong (E-mail: kongzhenwu@yahoo.com.cn)

ABSTRACT: A two-component waterborne polyurethane (2K-WPU) is prepared with the terpene-maleic ester type epoxy resin-based polyol dispersion and a hydrophilically modified hexamethylene diisocyanate tripolymer. Laser particle size analyzer and transmission electron microscopy are used to characterize the particle size distribution and the micromorphology of the 2K-WPU. Crosslinking reaction kinetics of the 2K-WPU is examined by fourier transform infrared spectrometry (FTIR) spectra. In the preliminary stage of the crosslinking reaction, it shows a very good fit with a second order reaction kinetics, and the apparent activation energy is 94.61 kJ mol⁻¹. It is also shown from the FTIR spectra that the complete crosslinking reaction of the 2K-WPU needs 7 h at 70°C. The crosslinked products of the 2K-WPU have good thermal resistant properties, with glass-transition temperatures (T_g) in the range of 35–40°C and 10% weight loss temperatures (T_d) in the range of 275–287°C. The films obtained from the crosslinked products have good water-resistance, antifouling, blocking resistance properties and impact strength of >50 cm, flexibility of 0.5 mm, adhesion of 1 grade, pencil hardness of HB-2H. The pencil hardness and thermal-resistant properties of the crosslinked products increase with the molar ratio of isocyanate (—NCO) group to hydroxyl (—OH) group. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2012

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INTRODUCTION

Two-component solvent polyurethanes have gained an important position in the industrial coatings market. Certainly the success must be ascribed to the high performance that can be achieved with this technology. With the environment criteria becoming stricter, the control of volatile organic compound emissions is increasing the use of waterborne resin-based coatings. Two-component waterborne polyurethanes (2K-WPUs) with high performance just like two-component solvent systems and environmental friendliness, safety just like waterborne system, have been increasingly applied in commercial coatings, adhesives over the last decade.^{1–5}

2K-WPU generally comprises polyisocyanates and polyol dispersions. The commonly used polyol dispersions are acrylic polyol, polyester polyol, and polyurethane polyol dispersions. A waterborne acrylic polyol was crosslinked with polyisocyanates to form 2K-WPU coating.¹ Fast-curing coatings were reported in US patent by mixing a cationic waterborne acrylic resins with secondary

amine groups and a hexamethylene diisocyanate (HDI) biuret.² The commonly used polyester resin may easily be hydrolyzed in water. US patent reported a hydrolytically stable polyester polyol dispersion for preparation of a 2K-WPU coating.^{3,4} Comparing with acrylic polyol and polyester polyol, 2K-WPU prepared with polyurethane polyol had comprehensive properties.⁵ Most of these 2K-WPU were prepared with fossil-based polyols which were complicated in preparation and high cost.

Due to the shortage of fossil resource, it is more desirous of finding renewable nature resource for preparing polymer materials.⁶ Initial bio-based resins development has focused mostly on the use of soybean⁷ and corn oil⁸ as a feedstock, but other natural products are available and can be considered for the elaboration of new sustainable bio-resins. In particular, turpentine is a natural product extracted from pine, which is extensively produced and distributed in China.⁹ Recent studies showed that turpentine could be used for preparing bio-resins. Terpene-maleic ester type epoxy resin (TME), an alicyclic epoxy resin with endocyclic structure, is synthesized from

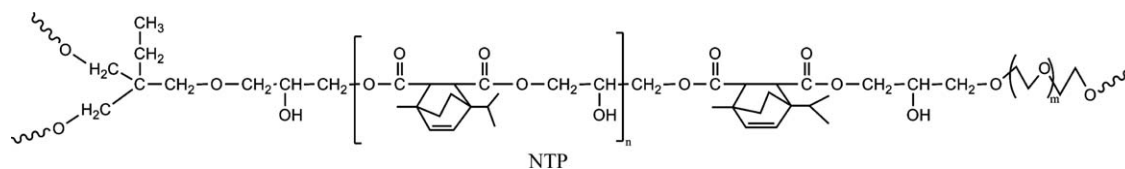


Figure 1. Chemical structure of NTP.

turpentine.^{10,11} TME-based polyols have been synthesized from TME, and their crosslinked polymers have good mechanical and thermal properties.¹² A cationic polyol from TME has been reported to prepare 2K-WPU.¹³ However, the stability of cationic polyol is affected by pH value and it can not be mixed with anionic hydrophilically modified polyisocyanate. Nonionic TME-based polyol (NTP) dispersion has more compatibility with hydrophilically modified polyisocyanate to prepare 2K-WPU, which is synthesized with TME, polyethylene glycol, and trimethylolpropane.¹⁴

In this study, a novel 2K-WPU is prepared with NTP dispersion and a sulfonic hydrophilically modified HDI tripolymer. The particle size distribution, micromorphology, and crosslinking reaction kinetics of the 2K-WPU are examined. And also the mechanical, thermal and water resistance, antifouling resistance, blocking resistance properties of the 2K-WPU crosslinked products are evaluated according to standard test methods. The crosslinked products of the 2K-WPU which combine the rigidity and adhesion of TME with the flexibility and tenacity of the polyurethane, have comprehensive properties.

EXPERIMENTAL

Materials

The base material is NTP dispersion, which was synthesized as described in Ref. 14. The structure of the NTP is shown in Figure 1 and the major technical parameters of NTP and NTP dispersion are shown in Table I. The sulfonic hydrophilically modified HDI tripolymer with —NCO content of 18% and solid content of 100%, technical pure, is supplied by Wuhan Shiquanshi Decorative Coating, China.

Preparation of 2K-WPU with NTP Dispersion and Hydrophilically Modified HDI Tripolymer

2K-WPU is prepared by mixing NTP dispersion with the hydrophilically modified HDI tripolymer and stirring by hand with a glass rod for about 3 min. The relative amounts of each reactive component are adjusted to provide —NCO group to —OH group molar equivalent ratios ranging from 0.8 to 1.4. Total reactant concentrations are typically around 30–35% (by mass) as applied in this work. Following the mixing process, the reactive mixture is held without agitation for 10 min to allow for viscosity reduction and uniform film application, and such mixture is applied to obtain approximately 40 μm (± 3 μm) thick dry films on tinplates or glass slides which are cured in an oven at 70°C for 7 h, and finally kept at room temperature for 4 days.

Measurements

Hydroxyl value of the polyol is obtained by chemical analysis in terms of standard methods GB/T 7383-2007.

Particle size analysis is carried out on a Nano-ZS ZEN3600 Zeta-sizer (Malvern Instrument, UK). The NTP dispersion and

the 2K-WPU dispersion (the mixed system) are diluted with distilled water to 0.5% solid content.

The morphologies of the dispersion particles are characterized by transmission electron microscopy (TEM) performed on a JEM-200CX TEM (JEOL, Japan). To prepare TEM sample, the NTP dispersion and the 2K-WPU dispersion are diluted with distilled water to 2% solid content.

The fourier transform infrared spectrometry (FTIR) samples are prepared by casting the mixed system on BaF₂ pellet. The MAGNA-IR 550 infrared spectrometric analyzer (Nicolet Instrument Co., Madison, Wisconsin) is used to record the spectra in the range of 400–4000 cm^{-1} .

Mechanical properties of the films are evaluated according to standard test methods (impact strength GB/T 1732-93, adhesion GB/T 1720-89, flexibility GB/T 1731-93, and pencil hardness GB/T 6739-96). Water resistance, antifouling, and blocking resistance properties are measured according to standard test method HG/T 3828-2006.

Differential scanning calorimetry (DSC) thermograms are recorded with a PerkinElmer Diamond DSC (Fremont, USA) at a heating rate of 20°C min^{-1} under a nitrogen gas flow of 20 mL min^{-1} .

Thermogravimetric analysis (TGA) is performed with a NETZSCH STA 409 PC/PG thermogravimetric analyzer (Germany) at a heating rate of 10°C min^{-1} under a nitrogen atmosphere.

Kinetics Method

The process of the crosslinking reaction of 2K-WPU is investigated with FTIR spectra. A FTIR spectrum is recorded every hour during the 2K-WPU sample cured at certain temperature. The stretch absorption of —NCO group is strong and acute in

Table I. Technical Parameters of NTP and NTP Dispersion

	Appearance	Yellow transparent solid
NTP (solid resin)	Hydroxyl value (mg g^{-1})	100
	Hydroxyl group content (%)	3.04
	Softening point (°C)	71
	T_g (°C)	4.03
NTP dispersion	Appearance	Milk-white liquid
	Solid content (%)	40
	Viscosity (mPa s , 25°C)	150

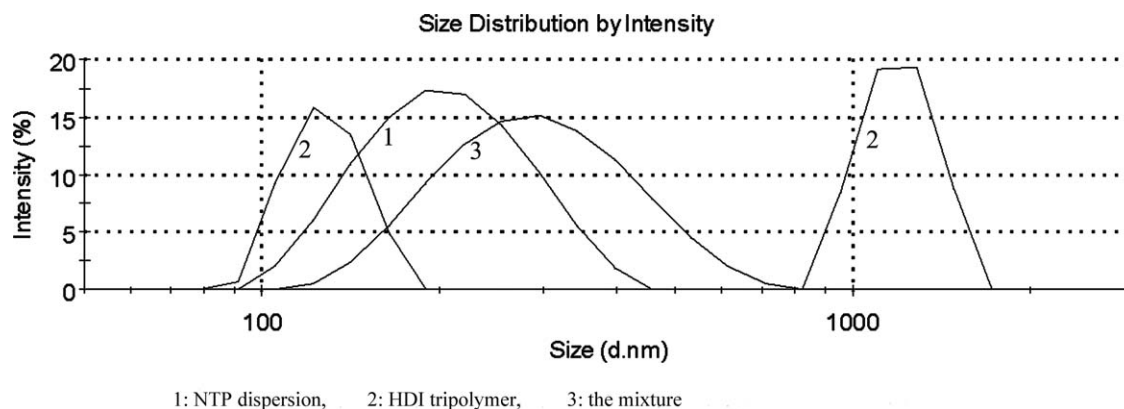


Figure 2. Particle size distribution of NTP dispersion and the mixed system.

FTIR spectra and is not interfered by the other groups during the reaction.¹⁵ So the change of stretch absorption peak area which denotes the change of —NCO group concentration can be used to investigate crosslinking reaction kinetics of the 2K-WPU.

Relation between spectral absorbance and sample concentration can be characterized by Lambert-Beer law as follow [eq. (1)]:¹⁶

$$A = abc \quad (1)$$

where A is sample absorbance, a is absorption coefficient of the sample, b is sample thickness, and c is sample concentration.

The reaction between —NCO group and active hydrogen results from the nucleophilic center of active hydrogen attacking the high positive carbon atom of —NCO group, and it is a nucleophilic addition polymerization. Provided the reaction between —NCO group and —OH group was the second order, the reaction rate equation can be expressed as follow [eq. (2)]:¹⁶

$$-\frac{d[\text{—NCO}]}{dt} = k[\text{—NCO}][\text{—OH}] \quad (2)$$

when $[\text{—NCO}]$ is equal to $[\text{—OH}]$, the equation is as follow [eq. (3)]:

$$-\frac{d[\text{—NCO}]}{dt} = k[\text{—NCO}][\text{—OH}] = k[\text{—NCO}]^2 \quad (3)$$

where k is rate constant. Integral form of the above equation is as follow [eq. (4)]:

$$\frac{1}{[I]} = \frac{1}{[I_0]} + kt \quad (4)$$

where $[I]$ is the molar concentration of —NCO group at reaction time t , and $[I_0]$ is the initial concentration of —NCO group.

The stretch absorption peak of $\text{C}=\text{C}$ group which does not change with reaction process in FTIR spectra can be used as internal standard peak to compensate the change of sample thickness during the reaction. Dividing the absorbance of internal standard peak by that of —NCO group absorbance, the following eq. (5) is obtained,

$$\frac{A_{\text{ref}}}{A_{\text{NCO}}} = \frac{a_{\text{ref}}b[\text{ref}]}{a_{\text{NCO}}b[I]} = \frac{\beta}{[I]} \quad (5)$$

where A_{ref} and A_{NCO} are internal standard peak absorbance and —NCO group peak absorbance respectively, β is $a_{\text{ref}}[\text{ref}]/a_{\text{NCO}}$, a constant, and $[I]$ is —NCO group concentration in the sample.

Then a new eq. (6) can be obtained from eqs. (4) and (5),

$$\frac{A_{\text{ref}}}{A_{\text{NCO}}} = \frac{\beta}{[I]} = \frac{\beta}{[I_0]} + \beta kt \quad (6)$$

If the relation between $A_{\text{ref}}/A_{\text{NCO}}$ and t is linear, it will fit eq. (6), and the 2K-WPU crosslinking reaction is second order.

RESULTS AND DISCUSSION

Particle Size Analysis of the NTP Dispersion and the 2K-WPU Dispersion

The results of particle size tests of the NTP dispersion and the 2K-WPU dispersion are shown in Figure 2. Although the used HDI tripolymer has been hydrophilically modified, directly dispersing it in water is still difficult. The particle size of the hydrophilically modified HDI tripolymer in water is bimodal distribution, and the average particle diameter is 1285 nm. NTP dispersion has an average particle size about 194 nm, and its particle size is unimodal distribution. After mixing these two components and stirring by hand with a glass rod for 3 min, the mixture obtained has an unimodal distribution of the particle size with the average value of about 274 nm, bigger than that of NTP dispersion. These results indicate that NTP dispersion can emulsify the HDI tripolymer and reform new particles when the two components are mixed.

Micromorphologies of the NTP Dispersion and the 2K-WPU Dispersion

To further characterize the dispersibility of the 2K-WPU systems, TEM is used to observe the micromorphologies of the NTP dispersion, the hydrophilically modified HDI tripolymer and their mixed system (Figure 3). NTP dispersion has spherical particles, and their size is distributed in the range of 90–450 nm, most of them about 200 nm (a). The hydrophilically modified HDI tripolymer can not be dispersed very well in water.

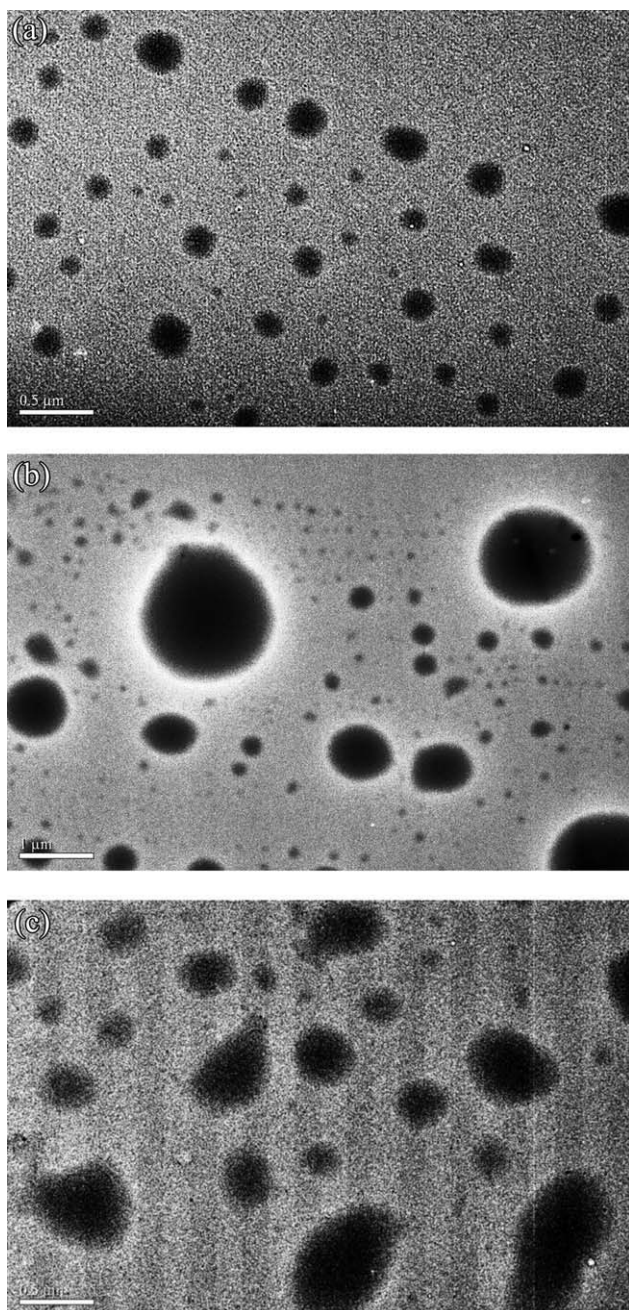


Figure 3. Micromorphologies of the NTP dispersion (a), hydrophilically modified HDI tripolymer (b) and the mixed system (c).

The bigger particles are microsize particles and smaller ones are nanosize (b). When mixing the two components, new shape and size particles are formed, which are bigger than that of NTP dispersion (c). These TEM results correspond to the results from particles size analysis, and indicate that NTP dispersion can emulsify the HDI tripolymer and reform new particles visibly.

Crosslinking Reaction Kinetics of the 2K-WPU

Figure 4 shows the experiment results from FTIR spectra. In the preliminary stage of the crosslinking reaction between NTP and hydrophilically modified HDI tripolymer ($A_{\text{ref}}/A_{\text{NCO}} < 0.1$), it

shows a very good fit with a second order reaction kinetics, and the relation between $A_{\text{ref}}/A_{\text{NCO}}$ and t is linear. Prolonging reaction time, reaction rate constant k (the slope of the $A_{\text{ref}}/A_{\text{NCO}}-t$ line) increases with the proceeding of the crosslinking reaction, and it indicates the reaction deviates from second order kinetics. Latest study shows that this crosslinking reaction follows an auto-catalytic mechanism.¹⁷ The resultant of reaction (urethane $-\text{NH}-\text{CO}-\text{O}-$) can catalyze itself reacting with the $-\text{NCO}$ group and form allophanate.¹⁸ The motion of $-\text{OH}$ group and $-\text{NCO}$ group is easy at the beginning of the reaction when the viscosity is low, and the reaction fits a second order reaction kinetics. With consuming of $-\text{OH}$ group and $-\text{NCO}$ group and forming of the crosslinked network, they can not collide and react with each other easily. Then diffusion turns to control the reaction. While the urethanes encircling the $-\text{NCO}$ group increase with the proceeding of the reaction, they can easily react with $-\text{NCO}$ group. The apparent result is reaction rate constant k increasing. From the Arrhenius eq. (7), we can know k also increases with reaction temperature, just as shown in Figure 4.

In the preliminary stage of the crosslinking reaction between NTP and the hydrophilically modified HDI tripolymer, it fits with a second order kinetics. The initial concentration of $-\text{NCO}$ group $[I_0]$ is known. Rate constant k can be evaluated from the slope of the $A_{\text{ref}}/A_{\text{NCO}}-t$ line. According to the Arrhenius eq. (7), the apparent activation energy of the reaction can be evaluated graphically from the slope of the $\ln k$ vs. $1/T$ line (Figure 5). The data are shown in Table II.

$$\ln k = \ln Z - \frac{\Delta E}{RT} \quad (7)$$

Characterization of the Crosslinking Process with FTIR Spectra

Figure 6 shows the FTIR spectra of the 2K-WPU crosslinking process cured at 70°C with the molar ratio of $-\text{NCO}$ group to $-\text{OH}$ group at 1 : 1. With the proceeding of the reaction

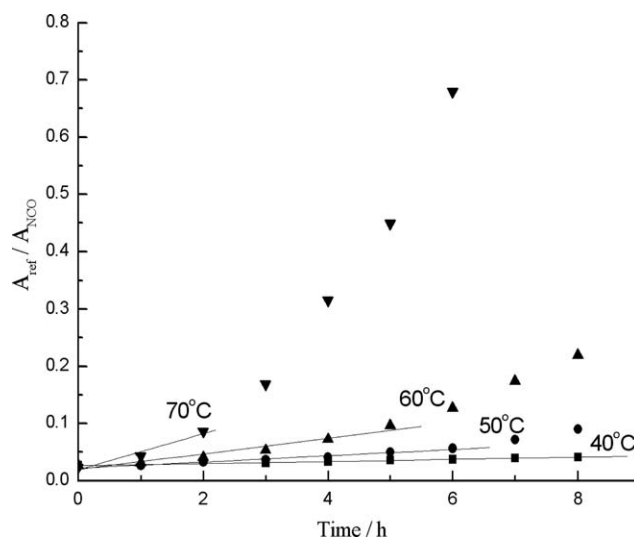


Figure 4. Relation between $A_{\text{ref}}/A_{\text{NCO}}$ and time.

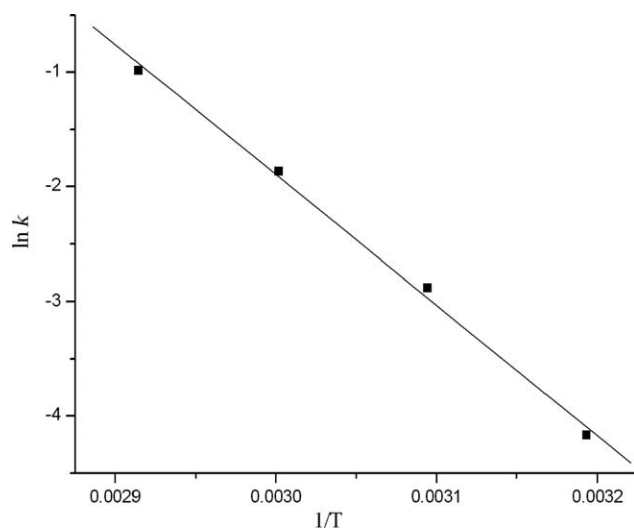


Figure 5. $\ln k - 1/T$ line of the kinetics.

between —NCO group and —OH group, the stretch absorption peak at about 2270 cm^{-1} of —NCO group becomes weaker and eventually disappears obviously, and the characteristic absorption peak of C—N bond of the formed urethane at about 1530 cm^{-1} is strengthened gradually. The formation of N—H bond whose absorption peak is similar to the —OH group's in FTIR spectra, interferes the observed change of —OH group absorption peaks. The region between 3100 and 3600 cm^{-1} does not change a lot with the consumption of —OH group. The FTIR analysis indicates the completion of the 2K-WPU crosslinking reaction at 70°C for 7 h.

Properties of the 2K-WPU Crosslinked Products

The crosslinked products of the 2K-WPU have good impact strength, adhesion, flexibility, water resistance, antifouling, and blocking resistance properties just similar to the commercial product (Table III). Pencil hardness of the crosslinked products can be enhanced by increasing the molar ratio of —NCO group to —OH group. The superfluous —NCO group will react with H_2O and urethane to form urea (—NH—CO—NH—) and allophanate, which can enhance crosslinking density of the products and lead to high rigidity. Considering that the hydrophilically modified HDI tripolymer is more expensive, the suitable molar ratio of —NCO group to —OH group which can result to good properties and low cost of the products is $1.2 : 1$, according to the results in Table III.

Glass transition temperatures (T_g) of the crosslinked products are examined with DSC. As shown in Figure 7, there is only one thermal transition in each DSC curve in the range of scanning temperature from -40°C to 100°C , consequently indicating good compatibility of the NTP and the hydrophilically modified

HDI tripolymer. The crosslinked products are homogeneous phase systems, no major bulk phase separation taking place. T_g of the product increases with the molar ratio of —NCO group to —OH group, because the enhancement of crosslinking density of the products results to small free volume and high T_g of the polymer.¹⁹ As shown in Table III, T_g of the crosslinked product is increased by about 10°C when the molar ratio of —NCO group to —OH group increases from $0.8 : 1$ to $1.4 : 1$.

Figure 8 shows the TGA curves of the 2K-WPU crosslinked products. The crosslinked products have good thermal resistant properties, and the temperatures at 10% weight loss (T_d) are all above 275°C . Increasing the molar ratio of —NCO group to —OH group of the 2K-WPU, which can form urea and allophanate, and enhance crosslinking density of the products, leads to higher T_d of the crosslinked products. When the molar ratio of —NCO group to —OH group increases from $0.8 : 1$ to $1.4 : 1$, T_d of the crosslinked product rises from 275°C to 287°C . As shown as derivative thermogravimetric analysis (DTG) curves, there are three weight loss stages of the crosslinked products in the DTG curves. The first stage degradation with peak temperature 315°C is correlated with the decomposition of HDI tripolymer due to the low breaking energy of C—N bond.²⁰ The second stage degradation with peak temperature 380°C corresponds to thermal decomposition of urethane (—NH—CO—O—), whose thermal resistant property is better than HDI tripolymer, because the N—H bond can form hydrogen bond between the polyurethane chains. This stage gradually disappears with the increase of the mole ratio of —NCO group to —OH group. It indicates the thermal stability of the crosslinked products enhance with the increase of the molar ratio of —NCO group to —OH group, presumably due to the formation of urea and allophanate which enhance crosslinking density of the products. Furthermore, urea (—NH—CO—NH—) with two N—H bonds can form more hydrogen bonds between the polyurethane chains. The third stage with peak temperature 460°C is attributed to the thermal decomposition of epoxy resin (TME) structure.¹²

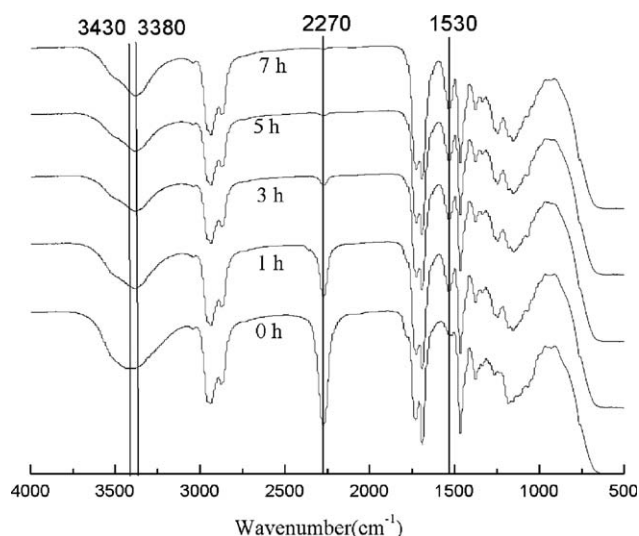


Figure 6. FTIR spectra of the 2K-WPU crosslinking reaction.

Table II. Kinetic Parameters of the 2K-WPU Crosslinking Reaction

	k ($\text{g mol}^{-1}\text{ s}^{-1}$)				ΔE (kJ mol^{-1})
	40°C	50°C	60°C	70°C	94.61
	0.01547	0.05608	0.1547	0.3744	

Table III. Properties of the Crosslinked Products

Items	Molar ratio of —NCO group to —OH group				^a Commercial product
	Crosslinked products of NTP				
	0.8:1	1:1	1.2:1	1.4:1	1.4:1
Appearance	Brilliant, transparent	Brilliant, transparent	Brilliant, transparent	Brilliant, transparent	Brilliant, transparent
T_g (°C)	30.0	33.3	36.4	39.8	38.6
Impact strength (50 cm)	Obversely	Pass	Pass	Pass	Pass
	Inversely	Pass	Pass	Pass	Pass
Adhesion (grade)	1	1	1	1	1
Flexibility (mm)	0.5	0.5	0.5	0.5	0.5
Pencil hardness	HB	H	2H	2H	2H
Water resistance	Water (24 h)	Fail	Pass	Pass	Pass
	Boiling water (15 min)	Pass	Pass	Pass	Pass
Stain resistance (1 h)	Vinegar	Fail	Pass	Pass	Pass
	Tea	Pass	Pass	Pass	Pass
^b Blocking resistance (4 h, 500g, 50°C)	MM:A-O MB:A-O	MM:A-O MB:A-O	MM:A-O MB:A-O	MM:A-O MB:A-O	MM:A-O MB:A-O

^aThe commercial product and its data are supplied by Wuhan Shiquanshi Decorative Coating, China, ^bBlocking resistance: MM means front to front. MB means spoon-fashion. A means free-fall separation. O means no damage.

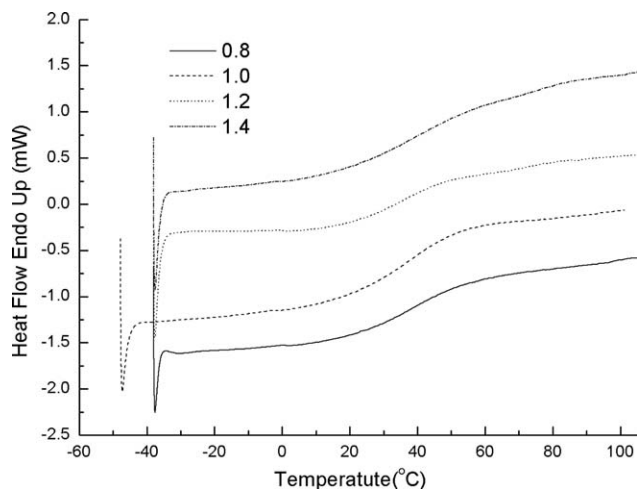


Figure 7. DSC curves of the crosslinked products.

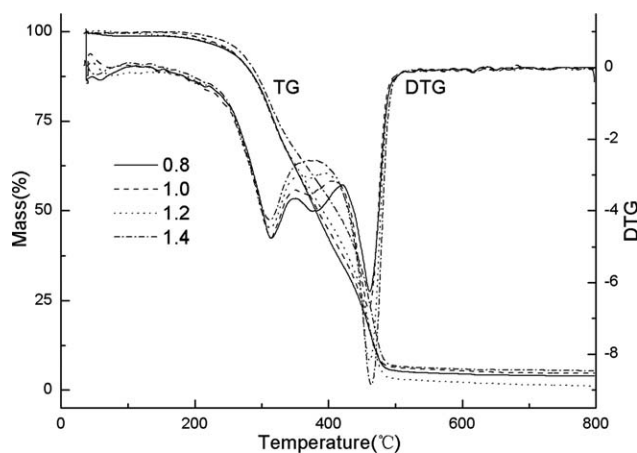


Figure 8. TG and DTG curves of the crosslinked products.

CONCLUSIONS

A 2K-WPU is prepared with the terpene-maleic ester TME-based nonionic polyol dispersion and a hydrophilically modified HDI tripolymer. Laser particle size and TEM are used to characterize the dispersibility of the 2K-WPU. It is shown from the results that NTP particles can enwrap and emulsify the HDI tripolymer and reform new particles. Crosslinking reaction kinetics of the 2K-WPU is examined by FTIR spectra. In the preliminary stage of the crosslinking reaction, it shows a very good fit with a second order reaction kinetics, but with the proceeding of the reaction, it deviates from second order kinetics, presumably due to the forming urethane reacts with $-NCO$ group. It is also shown from the FTIR spectra that the complete crosslinking reaction of the 2K-WPU needs 7 h at 70°C . The

films of the crosslinked products have good water-resistance, antifouling, blocking resistance properties, and thermal stability. The pencil hardness and thermal-resistant properties of the crosslinking products increase with the molar ratio of $-NCO$ group to $-OH$ group owing to the formation of urea and allophanate.

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