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Synthesis and characterization of 1 K waterborne non-isocyanate polyurethane epoxy hybrid coating

Zichen Ling, Cheng Zhang, Qixin Zhou

Department of Chemical, Biomolecular, and Corrosion Engineering, The University of Akron, 264 Wolf Ledges Parkway, Akron, OH 44325, United States

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ABSTRACT

Non-isocyanate polyurethanes (NIPU) attract more attention these days due to the increasing environmental concerns from the traditional polyurethanes that involve isocyanates in the synthesis. Herein we prepared a novel one-package (1 K) waterborne non-isocyanate polyurethane in this study. A series of 1 K waterborne epoxy hybrid coatings were synthesized from bio-based amine, cyclic carbonate, internal emulsifier, and epoxy resin. Different formulations of the 1 K waterborne NIPU epoxy hybrid coatings were designed including different ratios of soft and hard segments, different urethane contents, and different functionalities and structures of the hybridized epoxy. The chemical structure of the NIPU polymers was analyzed by Fourier transform infrared spectroscopy and nuclear magnetic resonance. The thermal stability and mechanical property of the 1 K waterborne NIPU coatings were investigated by thermogravimetric analysis and tensile tests, respectively. One glass transition temperature studied by differential scanning calorimetry was found for each coating which demonstrated that the soft segments and the hard segments were mixed well in the 1 K waterborne NIPU coating systems. The coatings with different formulations can achieve a broad range of thermal and mechanical properties. In addition, the general coating properties, such as hardness, adhesion, and chemical resistance, were evaluated to demonstrate the practical application of the 1 K waterborne NIPU in coatings.

1. Introduction

Polyurethanes were first discovered by Otto Bayer in 1937 which have become one of the most widely used polymers in many fields including automotive, footwear, textile, packaging, adhesives, and coatings [1–6]. The traditional synthesis method for polyurethane is the polyaddition reaction between polyol and di- or multifunctional isocyanate. However, the usage of isocyanate brings environmental and health issues because of its severe toxicity. Furthermore, phosgene, which is the main raw material to synthesize isocyanate, is a lethal gas that can cause serious diseases such as pulmonary edema [7,8]. Therefore, it is needed to explore an isocyanate-free method to produce polyurethane.

Non-isocyanate polyurethane (NIPU) is the polyurethane produced from the isocyanate-free route. Several green and safe methods have been developed to acquire NIPU such as the transurethanization method and cyclic carbonate/amine reaction [9–12]. Among them, cyclic carbonate/amine reaction is considered as one of the promising pathways because of the low reaction temperature and various choices of raw

materials from bio-based or petroleum-based sources [13–17]. Furthermore, the ring-opening reaction of cyclic carbonate forms the side hydroxyl groups which not only increase the hydrolytic resistance due to the intramolecular hydrogen bonding but also can be further functionalized for the special purpose of applications [18,19]. Besides the green NIPU approach to produce polyurethanes, volatile organic components (VOCs) used in coatings also bring environmental concerns that need to be avoided. Thus, waterborne polyurethane (WPU) has attracted much attention because of its low VOCs and low flammability [20–22]. Combining the features of NIPU and WPU, waterborne non-isocyanate polyurethane can be prepared by using non-ionic, cationic, or anionic dispersion agents [23–25].

Although the research on the synthesis of NIPU has made significant progress, the low reactivity of cyclic carbonate/amine reaction still impedes further development. Usually, a high synthesis temperature and a long reaction time are required to acquire high molecular weight NIPU polymers. To overcome this issue, many efforts have been made such as using high reactive cyclic carbonates. It has been studied that the 6-, 7-, and 8-membered cyclic carbonates have much higher reactivity than 5-

E-mail address: qzhou@uakron.edu (Q. Zhou).

^{*} Corresponding author.

membered cyclic carbonates (5CC), but the synthesis of these 6-, 7-, and 8-membered cyclic carbonates usually involves hazardous chemicals [26–28]. So, the 5CC is still considered as the ideal cyclic carbonate to produce NIPU. Another way to overcome the low reactivity is the synthesis of hybrid NIPU by incorporating the groups with a high reactivity such as epoxy groups. For example, Cornille et al. synthesized NIPUs hybridizing with different epoxies [29]. The reaction was reported to be accelerated with high conversion of hybrid NIPUs because the reactivity between epoxy and amine is much higher than that between cyclic carbonate and amine. Our research group has synthesized a two-package (2 K) waterborne NIPU hybridizing with epoxy groups to increase the reactivity [30]. The waterborne amine-terminated NIPU prepolymer and waterborne epoxy chain extender were the two packages to produce waterborne NIPU. So far, these hybrid coatings were synthesized from two-package methods. The one-package (1 K) coating is the future direction and in demand in the market since it can simply the coating preparation process, eliminate the two-package ratio calculations and errors in the actual application, and facilitate material storage. In the meanwhile, it is very challenging to generate a stable 1 K coating system. To the best of our knowledge, there is no published work related to 1 K waterborne NIPU coatings so far.

Herein, based on our previous work of a 2 K waterborne NIPU, we developed a 1 K waterborne NIPU epoxy hybrid coating. In this work, the waterborne NIPU hybrid coatings were prepared from cyclic carbonate, bio-based fatty acid amine (FDA), 3,3'-diamino-N-methyl-dipropylamine (DMDPA), and commercially available epoxy resins including bisphenol A diglycidyl ether (DGEBA) and trimethylolpropane triglycidyl ether (TTE). The chemical structure of amine-terminated NIPU prepolymer was characterized by Fourier transform infrared spectroscopy (FTIR) and ¹H and ¹³C nuclear magnetic resonance spectroscopy (NMR). The glass transition temperatures of 1 K waterborne NIPU coatings were measured by differential scanning calorimetry (DSC). The thermal stability and mechanical property of 1 K waterborne NIPU coating films were studied by thermogravimetric analysis (TGA) and tensile tests, respectively. General coating properties such as hardness, solvent resistance, impact resistance, and adhesion were also

evaluated for the newly developed 1 K waterborne NIPU coatings.

2. Experimental section

2.1. Materials

3,3'-diamino-*N*-methyldipropylamine (DMDPA, 96%, 145.25 g mol $^{-1}$), tetrabutylammonium bromide (TBAB, \geq 98%), bisphenol A diglycidyl ether (DGEBA, 340.41 g mol $^{-1}$), trimethylolpropane triglycidyl ether (TTE, technical grade, 302.36 g mol $^{-1}$), and acetic acid (\geq 99.7%) were purchased from Sigma-Aldrich. Ethanol (200 proof) was purchased from Fisher Scientific. PRIAMINE 1075-LQ (GD) dimer fatty acid diamine (FDA) was kindly provided by CRODA. All the materials were used as received without further purification. The chemical structures of these raw materials are shown in Scheme 1.

2.2. Synthesis of DGEBA cyclic carbonate

The DGEBA cyclic carbonate was synthesized from DGEBA by adding carbon dioxide and catalyzed by TBAB as according to the previous report [31]. The synthesis procedure is shown in Scheme S1. Firstly, 150.0 g DGEBA and 5.0 g TBAB were added into a 500 ml three-neck round-bottom reaction flask equipped with a $\rm CO_2$ inlet. Then the temperature was increased to 130 °C and reacted for 96 h with magnetic stirring under atmospheric pressure. After the reaction was finished and cooled to room temperature, the final product was collected. The DGEBA cyclic carbonate was a transparent yellow brittle solid. The chemical structure of DGEBA cyclic carbonate was characterized by FTIR, $^1\rm H$ NMR, and $^{13}\rm C$ NMR.

 1 H NMR (400 MHz, CDCl₃, ppm): δ 1.63(CCH3), 4.09–4.20 (C₆H₄OCH₂), 4.45–4.65 (CH₂O, cyclic carbonates), 5.00 (CHO, cyclic carbonates). 13 C NMR (400 MHz, CDCl₃, ppm): 154.84 (C=O, cyclic carbonates).

3,3'-diamino-N-methyldipropylamine

Fatty acid diamine

Bisphenol A diglycidyl ether

Trimethylolpropane triglycidyl ether

Scheme 1. Chemical structures of 3,3'-diamino-N-methyldipropylamine, fatty acid diamine, bisphenol A diglycidyl ether, and trimethylolpropane triglycidyl ether.

2.3. Synthesis of waterborne epoxy hybrid NIPU

The synthesis of a waterborne epoxy hybrid NIPU consists of four steps as shown in Scheme 2: synthesis of amine-terminated NIPU prepolymer, chain extension by epoxy resins, neutralization, and dispersion. Firstly, the DGEBA cyclic carbonate, DMDPA, and fatty acid diamine were dissolved in ethanol and well mixed by magnetic stirring under N₂ purge. Then, the mixture was heated to 75 °C for 8 h to synthesize the amine-terminated NIPU. Secondly, after the sample was cooled to room temperature, an epoxy resin was added into the flask under magnetically stirred for 1 h. Thirdly, an equivalent amount of acetic acid based on the amount of DMDPA was added into the mixture to neutralize the product under stirring for 1 h. Finally, the NIPU polymer was dispersed in water under vigorous stirring, followed by solvent removal by a rotary evaporator. The solid content of the waterborne NIPU was controlled to around 20 wt%.

Two different epoxy resins were chosen in the third synthesis step as mentioned above to generate different waterborne epoxy hybrid NIPUs. These epoxy resins were DGEBA and TTE. The formulations of different waterborne NIPUs are listed in Table 1. The mole ratio of cyclic

Table 1
The composition details of 1 K waterborne epoxy hybrid NIPU (wt%).

	DMDPA	Cyclic carbonate	FDA	DGEBA	TTE	Hard segment ^a
DGEBA-5	5	27	47	21	-	53
DGEBA-	10	30	37	23	-	63
10						
TTE-5	5	29	52	-	14	48
TTE-10	10	33	41	-	16	59

 $^{\rm a}$ The hard segment content = weight of (DMDPA + cyclic carbonate + DGEBA/TTE) / total weight.

carbonate group/epoxy group/amine group is 1:1:2. The samples are named by the type of epoxy resin used and the weight percent of DMDPA used. For instance, DGEBA-5 is waterborne NIPU hybridized with DGEBA epoxy containing 5 wt% DMDPA. The hard segment content can be calculated by dividing the weight of DMDPA, DGEBA cyclic carbonate, and epoxy resins by the total weight.

Amine-terminated NIPU prepolymer

Scheme 2. The synthesis procedures of 1 K waterborne epoxy hybrid NIPU.

Waterborne epoxy hybrid NIPU

2.4. Preparation of 1 K waterborne NIPU epoxy hybrid coatings

After the synthesis of the different waterborne NIPUs, the polymers were applied on the steel substrates (Q-Lab Corporation, QD-36) by a drawdown bar with a wet film thickness of 120 um. The samples were dried at room temperature for 12 h of water evaporation to form mechanically strong dry films. To achieve better film formation, the tackfree films were baked in an oven at 120 $^{\circ}\text{C}$ for 2 h. Finally, the testable coatings were obtained with a dry film thickness of around 45 μm after placing in the air at room temperature for 7 days.

2.5. Characterization methods

FTIR spectra were obtained by a Nicolet iS10 FT-IR Spectrometer with transmission mode at room temperature. The data was collected from 64 scans with a resolution of 4 cm $^{-1}$. 1 H and 13 C NMR spectra were performed from a Varian INOVA 300 instrument at room temperature using CDCl $_{3}$ as the solvent.

The glass transition temperature (T_g) of waterborne NIPU films was determined by the differential scanning calorimetry (DSC, TA Instruments Q200). The weight of samples was around 5 mg. The temperature was increased from -40 to $140\,^{\circ}\text{C}$ under a nitrogen atmosphere (40 ml min $^{-1}$) and the rate was $10\,^{\circ}\text{C}$ min $^{-1}$. The thermal stability of waterborne NIPU coatings was characterized by the thermogravimetric analysis (TGA, TA Instruments Q500). The weight of samples was around 10 mg. The temperature of the sample was raised to $600\,^{\circ}\text{C}$ at a steady rate of $10\,^{\circ}\text{C}$ min $^{-1}$ under nitrogen purge (10 ml min $^{-1}$) and then kept at $600\,^{\circ}\text{C}$ for 10 min.

The mechanical properties of waterborne NIPU coatings were measured by an Instron 5567 testing machine (Instron Corp) at room temperature. The self-standing films were peeled off from the substrates and cut into the desired dimensions for mechanical testing. The dimension of samples was around 30 mm in length and 10 mm in width. The moving speed of the test frame was 5 mm min⁻¹. The average data was obtained by five duplicable tests for each sample. The waterborne NIPU coating samples (coatings on the steel substrates) were also evaluated for their general coating properties. The general coating properties including pendulum hardness, pencil hardness, solvent resistance, impact resistance, crosshatch adhesion, and pull off adhesion were investigated based on the standards of ASTM D4366, ASTM D3363, ASTM D4752, ISO 6272-2, ASTM D3359, and ASTM D4541, respectively.

3. Results and discussion

3.1. Analysis of DGEBA cyclic carbonate

DGEBA cyclic carbonate was synthesized from the insertion of $\rm CO_2$ into the epoxy group under the catalysis of TBAB. The conversion process was monitored by FTIR. As shown in Fig. 1, DGEBA had an absorption peak at 914 cm⁻¹, which was attributed to the C—C vibrations of the epoxy group. For DGEBA cyclic carbonate, the strong peak at 1794 cm⁻¹ was associated with the C—O stretching of the cyclic carbonate group [31]. The appearance of the cyclic carbonate peak and the disappearance of the epoxy group peak demonstrated the successful synthesis of the DGEBA cyclic carbonate.

The chemical structure of the synthesized DGEBA cyclic carbonate was further characterized by $^{1}\mathrm{H}$ and $^{13}\mathrm{C}$ NMR. The chemical shifts at 5.00 ppm and 4.45–4.65 ppm of $^{1}\mathrm{H}$ NMR were associated with the cyclic carbonate group (e and f, Fig. 2). In addition, no peaks of epoxy groups were observed in the range of 2.5–3.1 ppm suggesting that all epoxies were completely consumed [32]. The chemical shift of $^{13}\mathrm{C}$ NMR spectra at 154.84 ppm corresponded to the carbonyl of the cyclic carbonate group (j, Fig. S1). The $^{1}\mathrm{H}$ and $^{13}\mathrm{C}$ NMR results of the DGEBA cyclic carbonate are consistent with the previously reported which confirmed the successful synthesis of the DGEBA cyclic carbonate [31,33].

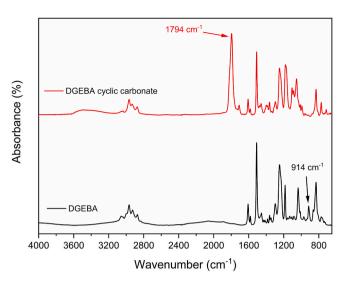


Fig. 1. FTIR spectra of DGEBA and DGEBA-cyclic carbonate.

3.2. Analysis of amine-terminated NIPU prepolymer and waterborne NIPU epoxy hybrid coatings

The amine-terminated NIPU prepolymer was synthesized from the bio-based fatty acid amine, DGEBA cyclic carbonate, and DMDPA. FTIR was utilized to monitor the changes of chemical groups during the synthesis of amine-terminated NIPU prepolymer. The FTIR of DGEBA-5 was chosen as an example to represent other cyclic carbonates during the synthesis. As shown in Fig. 3, after 8 h reaction, the absorption peak of C=O stretching at 1800 cm⁻¹ disappeared which suggested that all the cyclic carbonates completely reacted with amines. Also, the appearance of the signal at 1710 cm⁻¹ was assigned to C=O stretching in the urethane group. Furthermore, for the final product, the broad peak at 3600-3000 cm⁻¹ was assigned to the O—H stretching and N—H stretching [34,35]. The two closed peaks at 2925 and 2854 cm⁻¹ were assigned to the C—H stretching of — CH_3 and — CH_2 - groups [30,36]. The absorption band at 1248 cm⁻¹ was assigned to the asymmetric stretching of N-CO-O and stretching of C-O-C [31,37]. The appearance of typical absorption bands of polyurethanes suggested the successful synthesis of NIPU prepolymer. In addition, the chemical structure of NIPU prepolymer was also confirmed by ¹H NMR and ¹³C NMR as illustrated in Figs. 4 and S2, respectively. From ¹H NMR, the strong peaks at 7.10 and 6.79 ppm suggested the formation of the urethane group, and the peaks at 5.05 and 4.90 ppm were attributed to the hydroxyl group formed by the reaction between cyclic carbonate and amine [24,38]. Therefore, the amine-terminated NIPU was successfully synthesized based on the chemical structure characterizations.

After the curing of waterborne NIPU epoxy hybrid coatings, the functional groups of coating films were characterized by the infrared spectrum. As illustrated in Fig. 5, the appearance of the C=O stretching further verified the existence of the urethane group in the cured coating films.

3.3. Glass transition temperature measured by DSC

DSC was utilized to measure the glass transition temperature (T_g) of 1 K waterborne NIPU epoxy hybrid coatings. The DSC curves of these coating films are demonstrated in Fig. 6 (a) and the T_g values are listed in Table 2. Only one T_g of each coating was observed that indicating the coating was homogeneous without micro-phase separation which means the soft segments and the hard segments of the waterborne NIPU films were well mixed [39–41]. For the coatings hybridized with the same type of epoxy, the coating contained 10 wt% DMDPA had a higher T_g than that synthesized from the same epoxy but contained 5 wt%

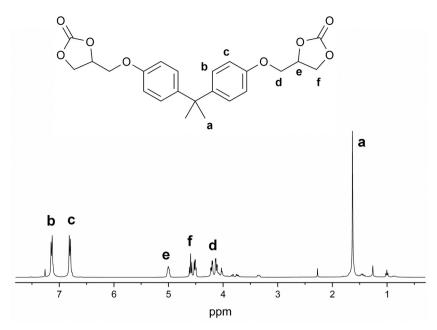


Fig. 2. ¹H NMR spectra of DGEBA-cyclic carbonate.

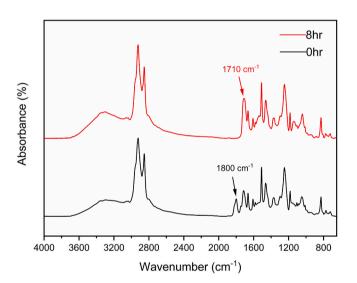


Fig. 3. FTIR spectra of amine-terminated NIPU prepolymer at 0 h and 8 h reaction stages.

DMDPA. For instance, the T_g of DGEBA-5 was 14 °C and the T_g of DGEBA-10 was 19 °C. The different values of T_g are due to the different weight percent of soft segment and hard segment in the coatings. In general, the soft segment has a lower T_g , in contrast, the hard segment comes to a higher T_g due to its immobility [42,43]. In this study, the FDA acts as the soft domain while DMDPA, cyclic carbonate, and epoxies are considered as the hard segments. The coating with 5 wt% DMDPA had a lower hard segment content than that of 10 wt% DMDPA listed in Table 1. Therefore, the coating with 5 wt% DMDPA had a lower T_g than the one of 10 wt% DMDPA.

Additionally, when the content of DMDPA was the same, the coating hybridized with DGEBA had a higher T_g than that with TTE. This is because the aromatic ring within the DGEBA makes DGEBA more rigid. Fig. 6 (b) describes the derivative DSC heat flow curves, which confirm that there is only one T_g for each coating. Also, no obvious melting or exotherm signal was observed within this testing temperature range, which suggested that the structure of 1 K waterborne NIPU films was amorphous, and all the functional groups were fully reacted after curing.

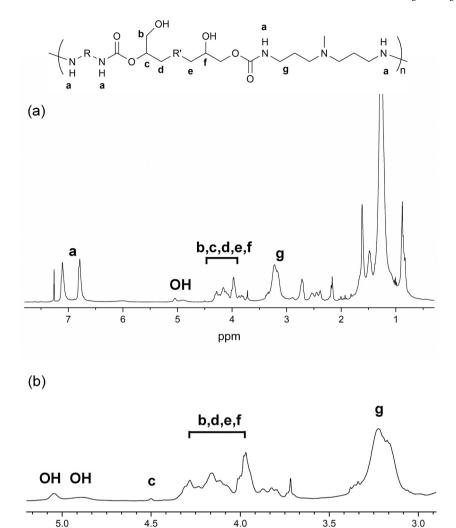
3.4. Thermal stability

TGA was used to analyze the thermal stability of the 1 K waterborne NIPU coating films. The TGA and DTG traces are shown in Fig. 7 and the temperatures of 10% and 20% weight loss (T_{10} and T_{20}) are summarized in Table 2. All the NIPU films showed a similar trend that they began to decompose at around 200 °C and all the NIPU hybrid coatings fully decomposed above 500 °C.

From the DTG curves, two obvious peaks were observed. The first peak at 350–400 °C was associated with the decomposition of the urethane bond, and the second peak at about 480–530 °C suggested the degradation of the other parts of the NIPU coatings [44]. Also, the T_{10} of DGEBA-5 was 374 °C which was the largest among all the coatings. The highest T_{10} of DGEBA-5 could be explained by the lower urethane content in the coating composition. The urethane bonds always tend to decompose firstly during the thermal degradation, so the coating sample with a higher concentration of urethane bonds can be easier decomposed, which comes to a lower decomposition temperature [45]. The order of T_{10} value was DGEBA-5 $\,$ TTE-5 $\,$ DGEBA-10 $\,$ TTE-10 from Table 2, which is exactly inverse to the order of urethane content, DGEBA-5 $\,$ TTE-5 $\,$ DGEBA-10 $\,$ TTE-10 based on the formulation listed in Table 1. A similar trend was also observed for T_{20} .

3.5. Mechanical properties

The mechanical properties of 1 K waterborne NIPU epoxy hybrid coatings were evaluated by the tensile test. The elongation-at-break (ϵ), tensile strength (σ), and Young's modulus (E) are listed in Table 2. The tensile strength and Young's modulus were higher for 10 wt% DMDPA NIPU coatings hybridized with the same type of epoxy. For example, tensile strength and Young's modulus of DGEBA-5 were 1.7 and 33.2 MPa, respectively. However, those for DGEBA-10 were 3.5 and 102.5 MPa, respectively. On the other hand, the elongation-at-break of 5 wt% DMDPA NIPU coatings was higher than that of 10 wt% DMDPA NIPU coatings. For instance, elongation-at-break of DGEBA-5 was 79.5%, which was 56.1% higher than that of DGEBA-10. The higher content of the soft segment in the 5 wt% DMDPA NIPU coatings caused the polymer more flexible to present a higher elongation. In other words, due to a higher content of hard segment in the 10 wt% DMDPA NIPU coatings, the polymer chains were tougher that came to higher Young's modulus



ppm

Fig. 4. ¹H NMR spectra of amine-terminated NIPU: (a) full range; (b) in the range of 5.2–2.9 ppm.

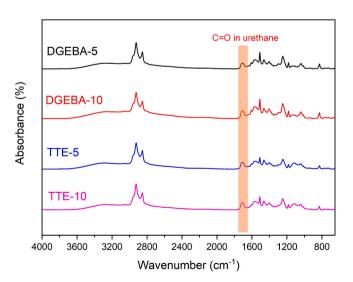


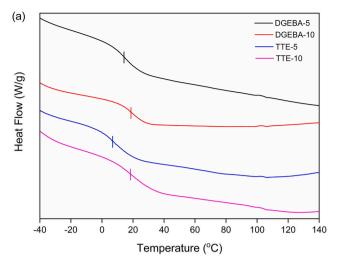
Fig. 5. FTIR spectra of 1 K waterborne epoxy hybrid NIPU films. Different formulations refer to the composition details as listed in Table 1.

and tensile strength.

For coatings with different types of epoxies, functionality, structure of epoxy, and hard segment content all affect the mechanical properties of waterborne NIPU. For example, TTE-5 and TTE-10 had higher tensile strength than that of DGEBA-5 and DGEBA-10, respectively. The higher tensile strength of TTE hybrid coatings may be because of the greater functionality of TTE (3) than that of DGEBA (2). Meanwhile, due to the existence of the rigid aromatic rings in DGEBA and higher hard segment content in DGEBA hybrid coatings, they showed lower elongation at break. Based on the combination of these factors, these waterborne epoxy hybrid coatings had different Young's modulus. For instance, DGEBA-5 showed a higher Young's modulus than TTE-5 but DGEBA-10 and TTE-10 have comparable Young's modulus. In general, the mechanical properties of the waterborne NIPU epoxy hybrid coatings are influenced by the functionality and the structure of the hybrid epoxy resins, and the content of soft/hard segments.

3.6. General coating properties

Table 3 shows the general properties of the 1 K waterborne NIPU epoxy hybrid coatings. It is obvious that the pendulum hardness and pencil hardness of 10 wt% DMDPA NIPU coatings were higher than 5 wt % ones since more hard segments were incorporated into the 10 wt% DMDPA NIPU coatings. Also, the 10 wt% DMDPA NIPU coatings showed better solvent resistance which indicated a higher crosslinking. Finally,



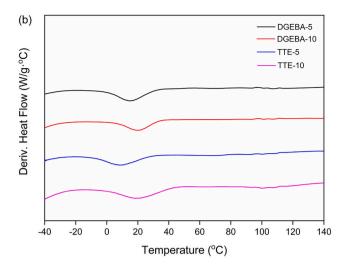


Fig. 6. (a) DSC curves of 1 K waterborne NIPU epoxy hybrid coating films; (b) Derivative DSC curves of 1 K waterborne NIPU epoxy hybrid coating films.

Table 2Thermal and mechanical properties of 1 K waterborne NIPU epoxy hybrid coating films.

	DSC (°C)	TGA (°C)		Tensile test ^a		
	T_g	T ₁₀	T ₂₀	ε (%)	σ (MPa)	E (MPa)
DGEBA-5	14	338	374	79.5 ± 6.4	1.7 ± 0.2	33.2 ± 6.6
DGEBA- 10	19	312	363	56.1 ± 8.0	3.5 ± 0.4	102.5 ± 20.4
TTE-5	7	337	371	$167.3 \pm \\31.3$	$\begin{array}{c} \textbf{3.2} \pm \\ \textbf{0.4} \end{array}$	23.9 ± 2.2
TTE-10	18	302	352	85.8 ± 22.5	4.4 ± 0.4	$102.9 \pm \\21.4$

^a ε is elongation-at-break; σ is tensile strength, and E is Young's modulus.

all the coatings showed similar and excellent impact resistance, crosshatch adhesion, and pull-off adhesion.

4. Conclusions

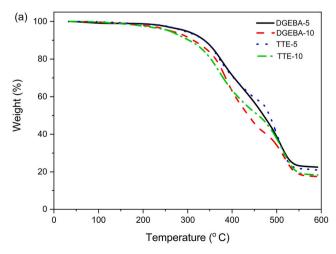
In this study, a series of one-package waterborne NIPU epoxy hybrid coatings were prepared from DGEBA-based cyclic carbonate, bio-based diamine (FDA), amine-based internal emulsifier (DMDPA), and epoxy

resin (DGEBA/TTE) through a facile method. The coatings with different ratios of hard/soft segments, urethane contents, and epoxy types and structures were designed and analyzed. The soft segments and hard segments were mixed well in the 1 K waterborne NIPU coating systems demonstrated by one T_g for each coating from DSC analysis. The higher content of soft segments brought to a lower T_g . In addition, the waterborne NIPU coatings with more content of urethane groups showed lower thermal stability because urethane groups decomposed firstly. Besides the tunable thermal properties, the mechanical properties of the 1 K waterborne NIPU coatings can be adjusted by the functionality and the structure of the hybrid epoxy resins and the content of soft/hard segments. The new synthesis method for the 1 K waterborne NIPU coatings is not only the green process without utilizing isocyanates to produce polyurethanes, but also a practical process to produce tunable properties of waterborne polyurethanes for coating application.

CRediT authorship contribution statement

Zichen Ling: Conceptualization, Methodology, Validation, Formal analysis, Investigation, Writing - Original Draft, Writing - Review & Editing. Cheng Zhang: Conceptualization, Methodology, Investigation. Qixin Zhou: Conceptualization, Writing - Review & Editing, Supervision, Project administration, Funding acquisition.

All authors have read and agreed to the published version of the manuscript.



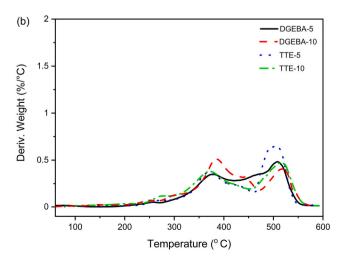


Fig. 7. TGA curves of 1 K waterborne NIPU epoxy hybrid coating films (a) TGA traces and (b) DTG curves.

Table 3General coatings properties of 1 K waterborne NIPU epoxy hybrid coating films.

	Pendulum hardness (s)	Pencil hardness	Solvent resistance ^a	Impact resistance (kg·cm)	Crosshatch adhesion	Pull-off adhesion (MPa) ^b
DGEBA-5	20	4B	46	100+	4B	1.8 ± 0.2
DGEBA-10	34	HB	96	100+	5B	1.8 ± 0.1
TTE-5	14	5B	62	100+	4B	1.8 ± 0.1
TTE-10	25	4B	100+	100+	4B	1.9 ± 0.2

^a The unit of solvent resistance is the number of MEK double rubs.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

The supporting information is available free of charge. Synthesis procedure of DGEBA cyclic carbonate, ¹³C NMR spectra of DGEBA-cyclic carbonate, and ¹³C NMR spectra of amine-terminated NIPU. Supplementary data to this article can be found online at https://doi.org/10.1016/j.porgcoat.2022.106915.

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^b Failure type is the mix of cohesive failure and adhesive failure.

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