

Article

Preparation and Properties of Novel Modified Waterborne Polyurethane Acrylate

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Abstract: A series of novel modified waterborne polyurethane acrylate (WPU-EA) emulsions were prepared with isophorone diisocyanate (IPDI), polycarbonate diol, 2,2-bis-hydroxymethyl-propionic acid (DMPA), 1,4-butanediol (BDO), epoxy acrylate (EA), and pentaerythritol triacrylate (PETA). The structure of WPU-EA was confirmed by FTIR and ¹H NMR spectroscopy. The effects of different dosages of epoxy acrylate on the cured film were investigated by tensile properties, dynamic mechanical analysis and thermogravimetric analysis. The results indicate that with increasing content of epoxy acrylate, the average particle size of the emulsion gradually increases. With the rise in epoxy acrylate concentration from 0%, 3.0%, 6.0% to 9.0%, the gel fraction of the cured film increases from 83.7%, 92.5%, 93.0% to 93.6%, respectively, and the glass transition temperature rises from 90.3 °C, 107.5 °C, 141.9 °C to 146.6 °C. The tensile strength and the thermal stability of the cured film increases, and the elongation at break decreases. Moreover, the WPU-EA emulsions were sprayed on polycarbonate sheets and exhibited the advantages of high hardness, better gloss and good adhesion, which is promising for the application of plastic coatings.

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1. Introduction

In recent years, research and development of environmentally friendly materials has attracted much attention, due to serious environmental pollution [1,2]. UV curing technology, a green coating technology, with the characteristics of: energy saving; high efficiency; empowerment; economic and environmental protection [3]; has proved compatible with the basic requirements of social and economic development, and has been applied to various fields of adhesives, inks and paints [4–6]. Waterborne polyurethane acrylates, combining the advantages of UV curing technology and waterborne materials, have received extensive attention from scholars [7,8]. For the advantages of their high curing rate, low curing temperature and outstanding environmentally friendly characteristics, waterborne polyurethane acrylates have been applied in many fields, such as protective coatings, adhesives, and inks [9]. Li et al. [10] prepared a UV-curable waterborne polyurethane acrylate with acrylated epoxidized soybean oil and pentaerythritol triacrylate, which was used for wood coatings, with a high cure rate and high hardness. Li et al. [11] synthesized a vegetable oil-based UV-curable waterborne polyurethane pigment prints' adhesive, which was used in textiles with good color fastness. Waterborne UV-curable hyperbranched polyurethane acrylate/silica nanocomposites were also prepared and exhibited good abrasion resistance for flexographic ink [12]. However, current waterborne polyurethane acrylates have some shortcomings that limit their practical application, such as poor water-, and heat-resistance, and unsatisfactory mechanical properties [13].

Now several approaches have been developed, to overcome these limitations in expanding its scope of application. The content of photosensitive groups in the existing waterborne polyurethane acrylates is not abundant and has influence on the film

performance [14]. Hence, an effective method for improving the strength and water resistance of polyurethane acrylate materials is to increase the crosslinking degree by introducing large numbers of acrylate double bonds. Wu et al. [4] reported that UV-curable waterborne polyurethane emulsions, prepared with different contents of dipentaerythritol hexaacrylate (DPHA)/dipropylene glycol diacrylate (DPGDA) monomers, exhibited excellent water resistance; Yin et al. [15] synthesized a waterborne hyperbranched polyurethane acrylate, with higher double-bond concentration and tested it, to show that the film possessed better heat-resistance and mechanical properties. Organic/inorganic nanocomposites can be compounded through physical action between the inorganic and organic surfaces, or chemistry, at the nanometer scale level. Nanoparticle reinforcement (nano-silica [12], titania/graphene [16], calcium carbonate [17]) has been used to modify waterborne polyurethane acrylates, to improve the water resistance and hardness of the UV-cured films.

Fluorine-silicone materials can be used to modify waterborne polyurethane acrylates, in order to improve their chemical stability, water resistance and stain resistance, due to their unique properties, for example: low surface energy, high thermal stability, hydrophobicity, and chemical resistance. Shan et al. [18] has reported that a UV-curable waterborne polyurethane, modified by a fluorinated side chain extender, exhibited high tensile strength and low surface free-energy. Li et al. [19] synthesized a series of fluorine-silicon block polyurethane acrylates and found that all the films had good thermal properties, and excellent water-, and chemical-resistance.

Alternatively, bisphenol A-based epoxy resin has good chemical resistance, excellent thermal insulating properties and high tensile strength [20]. It reacted with acrylic acid to obtain an epoxy acrylate containing hydroxyl groups [21], which could be used to modify waterborne polyurethane acrylates by utilizing their superior chemical and physical properties.

In this paper, combining the advantages of epoxy acrylate and waterborne polyurethane, a series of novel modified waterborne polyurethane acrylate resins for plastic coatings were designed and investigated. The introduction of epoxy acrylate, with rigid benzene-ring structure to the main chain of the molecule, could improve the mechanical strength and heat resistance of the UV-cured waterborne polyurethane acrylate film. At the same time, the epoxy acrylate is a common material in the UV curing field and has a wide range of sources. Therefore, it is of great significance to solve the shortcomings of existing waterborne polyurethane acrylates.

2. Materials and Methods

2.1. Materials

The following chemicals were used as received: isophorone diisocyanate (IPDI) purchased from Wanhua Chemical Group Co., Ltd. (Yantai, China), 2,2-bis(hydroxymethyl)propionic acid (DMPA) (99%, Aladdin, Shanghai, China), 1,4-butanediol (BDO) (AR, Aladdin), pentaerythritol triacrylate (PETA) supplied by Eternal Materials Co., Ltd. (Zhuhai, China), di-n-butyltin dilaurate (DBTDL) (AR, Macklin, Shanghai, China), triethylamine (TEA) (AR, Macklin), acetone (AR, Guangzhou Shiji, Guangzhou, China), JRCure 500, blend of 50% 1-hydroxy-cyclohexyl-phenyl-ketone and 50% benzophenone (industrial grade, Tianjin Jiuri New Materials Co., Ltd., Tianjin, China) and 4-methoxyphenol (MEHQ) (AR, Macklin); Photoinitiator 2-Hydroxyl-2-methyl-1-phenyl-1-propanone (Irgacure1173) (AR, Macklin); Ethyl (2,4,6-trimethylbenzoyl) phenylphosphinate (L-TPO) was provided by Hubei Gurun Technology Co., Ltd. (Jingmen, China).

Polycarbonate diol (PCD-621) with number average molecular weight of around 2000 g mol^{-1} and carbonate unit content of 32%, were provided by Guangdong Dazhi Environmental Protection Technology Co., Ltd. (Huizhou, China); epoxy acrylate (EA) was supplied by Nanxiong Sanben Chemical Technology Co., Ltd. (Shaoguan, China).

2.2. Hydroxyl Value of Epoxy Acrylate

Epoxy acrylates containing a certain number of hydroxyl groups were prepared using the ring-opening reaction of acrylic acid with bisphenol A-based epoxy resin [22]. The hydroxyl groups in epoxy acrylates react with isocyanate groups of isophorone diisocyanate (IPDI). To calculate the hydroxyl value, epoxy acrylate was reacted with a large excess of isophorone diisocyanate (IPDI) monomer and the $-NCO$ content of the mixture was measured, based on the di-n-butylamine method [23]. IPDI and epoxy acrylate, corresponding mass: 31.11 g and 28.89 g, were added into a four-necked flask, under constant stirring, with dibutyltin dilaurate as a catalyst (0.1 wt.%), then heated to 85 °C for 1 h. After that, the $-NCO$ content of the mixture was detected every 0.5 h until no further change was observed. The hydroxyl value (H_{OH} : 200.67 mgKOH/g) of epoxy acrylate can be calculated from Equations (1) and (2):

$$W_{NCO} = [(2 \times n_{IPDI} - n_{OH}) \times M_{NCO} \times 100\%]/(m_{IPDI} + m_{EA}) \quad (1)$$

$$H_{OH} = (1000 \times M_{KOH} \times n_{OH})/m_{EA} \quad (2)$$

2.3. Preparation of Modified Polyurethane Acrylate Emulsion

Isophorone diisocyanate (IPDI) and polycarbonate diol (PCD-621) were added into a four-necked flask, with stirring and a thermometer, using dibutyltin dilaurate as a catalyst (0.1 wt.%). The reaction mixture was heated up to 85~90 °C for 1 h. Dimethylolpropionic acid (DMPA), 1,4-butanediol (BDO) and epoxy acrylate were then added into the mixture and the temperature was kept between 85~90 °C until the theoretical $-NCO$ content of the prepolymer was obtained. Pentaerythritol triacrylate (PET3A) and inhibitor (MEHQ) were added for an end-capping reaction at 80~85 °C. The prepolymer was cooled to 50 °C and neutralized by triethylamine (TEA). The viscosity of prepolymer was diluted by adding acetone. After the neutralization, the mixture was poured into cold deionized water and stirred vigorously for 20 min at approximately 2500 rpm. Finally, the modified polyurethane acrylate emulsion (WPU-EA) was obtained. The compositions of WPU-EA with EA content are listed in Table 1. The reaction route for the WPU-EA is illustrated in Figure 1.

Table 1. Composition of each component of WPU-EA.

Samples No.	Polymer Composition (%)							DBC (mmol/g)
	IPDI	PCD	BDO	DMPA	EA	PET3A	TEA	
WPU-EA-0	36.61	29.39	2.30	5.00	0.0	23.11	3.58	2.32
WPU-EA-3	35.66	28.62	1.64	5.00	3.0	22.31	3.58	2.35
WPU-EA-6	34.70	27.85	0.97	5.00	6.0	21.90	3.58	2.41
WPU-EA-9	33.74	27.08	0.30	5.00	9.0	21.29	3.58	2.45

Note: DBC is an abbreviation for double bond content, calculated according to the formula [24].

2.4. Preparation of Film and Coating

As a photoinitiator, 3% of JRCure500 was added into the WPU-EA emulsion and stirred until completely dissolved. Then the mixture was cast into a 50 mm × 15 mm × 1 mm polytetrafluoroethylene mold and dried at room temperature for one day. Finally, the film was cured under an UV curing machine (model: RX300-1; lamp power: 2000 W; distance of the lamp: 10 cm, Dongguan Ergu Optoelectronics Technology Co., Ltd., Dongguan, China) for 10 s, to perform the curing of the film.

Preparation for the plastic coating: the surfaces of the PC sheets were wiped with alcohol. After the alcohol had completely evaporated, the self-synthesized WPU-EA emulsion was evenly sprayed on the surface of the PC sheets and dried in an oven at 50 °C for 6 min. Then, the PC sheets were taken out and irradiated under an UV curing machine (model: RX300-1; lamp power: 2000 W; distance of the lamp: 10 cm) for 10 s. The final thickness of the films was 50~55 μm (measured by the height variation between the

substrate thickness, before and after being coated with film, by the thickness tester (model: SMD-565, TECLOCK, Okaya, Japan). The PC sheets were stored in ambient conditions for 3 days, and then the performance of the plastic coatings was tested.

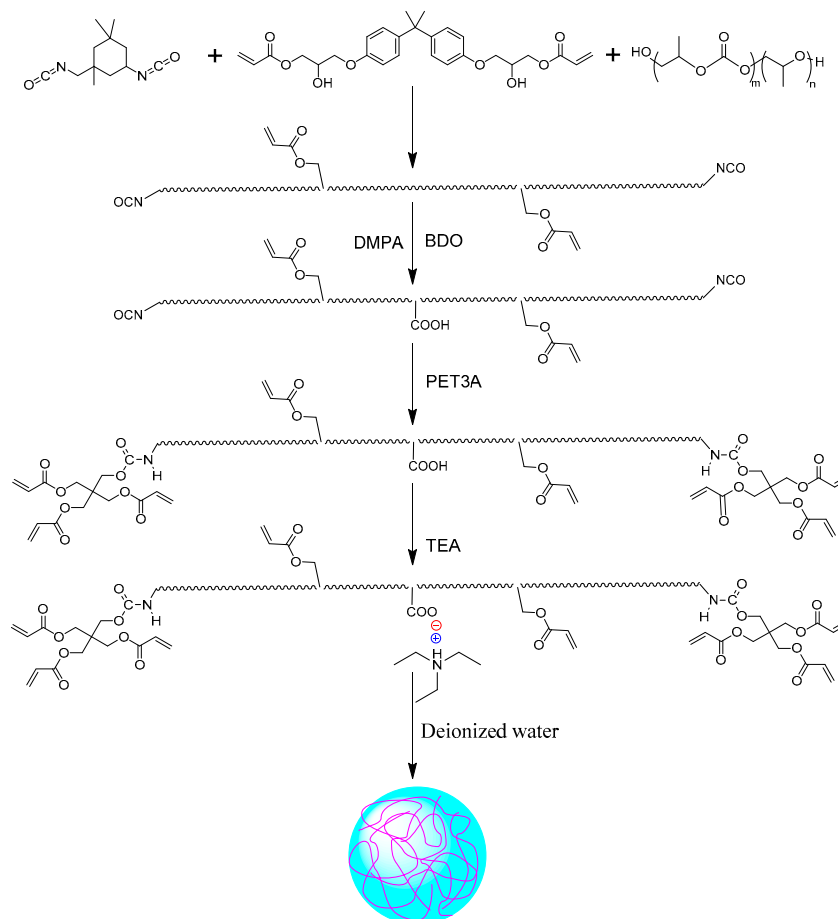


Figure 1. The reaction route of the modified polyurethane acrylate emulsion.

2.5. Characterization

Fourier transform infrared (FTIR) spectroscopy was performed on a Nicolet 560 infrared spectrometer (Thermo Fisher Scientific, Waltham, MA, USA) with a disc of KBr at room temperature. The wavenumber range was $4000\text{--}600\text{ cm}^{-1}$ with a 4 cm^{-1} resolution over 32 scans.

Proton nuclear magnetic resonance spectra ($^1\text{H NMR}$) of the samples were recorded on Bruker AVANCE III HD 400 spectrometer (Bruker, Fällanden, Switzerland), with CDCl_3 as a solvent, at $25\text{ }^\circ\text{C}$.

The WPU-EA emulsion was diluted to a solid content of 1.0 wt.% with deionized water. Particle size and distribution were measured by a submicron particle size and Zeta potential analyzer (Delta Nano C, Beckman Coulter, Inc., Brea, CA, USA) at room temperature.

The conversion of acrylate double bonds during UV irradiation was determined by real-time infrared spectra on a Nicolet iS50 FTIR at room temperature. The WPU-EA emulsions were coated on PP films with a thickness of approximately $50\text{ }\mu\text{m}$ and dried for 15 min in an oven at $40\text{ }^\circ\text{C}$, then irradiated in situ by a M-Ultra violet light source with a dominant wavelength of 365 nm (MUA-165, MEJIRO GENOSSEN, Tokyo, Japan). Each spectrum obtained from the IR spectrometer was an average of 4 scans with a resolution of 8 cm^{-1} . The double bond conversion was calculated from the decay of the absorption peak at 1640 cm^{-1} belonging to the acrylate double bond, and the characteristic absorption peak

of carbonyl group (C=O) at 1730 cm^{-1} was used as the internal standard. The double bond conversion was calculated according to Equation (3) [25].

$$\text{Double bond conversion} = \frac{(A_{1640}/A_{1730})_0 - (A_{1640}/A_{1730})_t}{(A_{1640}/A_{1730})_0} \times 100\% \quad (3)$$

where $(A_{1640}/A_{1730})_0$ and $(A_{1640}/A_{1730})_t$ were the relative peak-area ratio of acrylate double bond to carbonyl group, before and after UV irradiation curing at different time (t), respectively.

Dynamic mechanical analysis (DMA) was conducted with TA Instruments DMA 50 (Metravib Co., Ltd., Limonest, France) in tensile mode at 1 Hz with a heating rate of $3\text{ }^\circ\text{C}/\text{min}$ in temperature scans from $30\text{ }^\circ\text{C}$ to $250\text{ }^\circ\text{C}$.

Tensile properties of the UV-cured film were evaluated using a SANS CMT 6000 Universal Tester (MTS Systems Co., Ltd., Eden Prairie, MN, USA), in accordance with GB/T 528-2009 standard, at room temperature. Dumbbell-shaped specimens, total length: 50 mm, thickness: 1 mm, width of the parallel part: 4 mm, according to GB/T 1040.2-2010, were made for the tensile tests, and a deformation speed of 50 mm/min was employed in the test process. Five measurements were taken for each group, and the results were averaged.

Thermal degradation behavior of the UV-cured film was assessed from thermogravimetric analysis (TGA) with a TGA/SDTA 851 instrument (METTLER, Switzerland) in 20 mL/min N_2 atmosphere from $30\text{ }^\circ\text{C}$ to $600\text{ }^\circ\text{C}$ with a heating rate of $10\text{ }^\circ\text{C}/\text{min}$.

The gel fraction was measured with the Soxhlet extraction method. First, the UV-cured film was cut to a size of $2\text{ cm} \times 2\text{ cm}$ and dried at $40\text{ }^\circ\text{C}$ under vacuum for 12 h. Second, the UV-cured film was placed in the Soxhlet extractor, and then the added acetone was heated to reflux for 24 h. Third, the remaining cured film was dried at $40\text{ }^\circ\text{C}$ under vacuum for 12 h, and the residual mass was compared with the initial mass to obtain the gel fraction, calculated by Equation (4) [3].

$$G = \frac{w_t}{w_0} \times 100\% \quad (4)$$

where G represents gel fraction, w_0 and w_t represent initial mass and final mass, respectively.

Water-absorption behaviors of WPU-EA cured films were assessed by weighing. First, the prepared WPU-EA cured films were cut into specimens with dimensions $10\text{ mm} \times 10\text{ mm} \times 1\text{ mm}$. After being dried at $60\text{ }^\circ\text{C}$ for 4 h, the weight of sample (m_0) was obtained. Then the samples were immersed into deionized water for 24 h, after which time they were taken out and the surface moisture was wiped off, before the weight of sample (m_1) was obtained. The water absorption rate (W) of samples was calculated according to the following equation [26]:

$$W = \frac{m_t - m_0}{m_0} \times 100\% \quad (5)$$

The isocyanate content ($-\text{NCO}\%$) was determined by chemical titration, according to ASTM D5155-01 standard. Pencil hardness of the UV-cured film was estimated in accordance with ASTM D3363 standard. Adhesion force was measured according to ASTM D3359 standard (11 cuts, spaced 1 mm apart). The gloss at 60° was measured, using ASTM D523 standard. The mechanical stability of the emulsion was judged by centrifuging at 3000 rpm for 30 min (TG1650-WS, Shanghai Luxiangyi Centrifuge Instrument Co., Ltd., Shanghai, China) and the thermal stability of the emulsion was evaluated by maintaining for 14 days at $60\text{ }^\circ\text{C}$ to inspect the appearance of the bulk water phase.

3. Results and Discussion

3.1. Hydroxyl Value of Epoxy Acrylate

Figure 2 is the change trend of the $-\text{NCO}$ content. It showed that the content of $-\text{NCO}$ did not change after 2 h. This indicated that the reaction of $-\text{OH}$ and $-\text{NCO}$ was complete and the $-\text{NCO}$ content of the mixture W_{NCO} was 12.36%. The hydroxyl value of epoxy acrylate, calculated from Equations (1) and (2), was 200.67 mg KOH/g, which was used for experimental design. The compositions of materials are listed in Table 1.

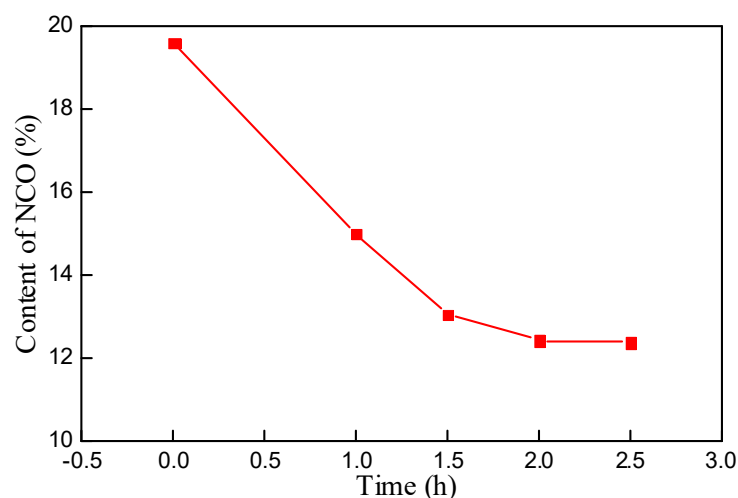


Figure 2. The variation of NCO content.

3.2. Structure Analysis of WPU-EA

Modified waterborne polyurethane acrylate was prepared by excessive isocyanate groups ($-\text{NCO}$) reacting with hydroxyl groups ($-\text{OH}$). The isocyanate group ($-\text{NCO}$) always existed in the prepolymer until deionized water was added for emulsification. Figure 3 is the FTIR spectra of the modified waterborne polyurethane acrylate before and after emulsification. The bands at 3335 cm^{-1} and 1528 cm^{-1} belong to the stretching vibrations of the $-\text{NH}$ and $\text{C}-\text{N}$ bonds, respectively, in the carbamate group ($-\text{NHCOO}-$) [26]. The bands around 2930 cm^{-1} and 2856 cm^{-1} are ascribed to the stretching vibrations of $-\text{CH}_2$ and $-\text{CH}_3$. The characteristic band corresponding to $-\text{C}=\text{O}$ can be observed at around 1730 cm^{-1} . The bands near 1640 cm^{-1} , 1409 cm^{-1} and 810 cm^{-1} are ascribed to the characteristic bands of alkene moieties [27]. The characteristic absorption band of isocyanate group at 2267 cm^{-1} [12], observed before emulsification, disappeared after emulsification, indicating that the isocyanate group had been almost consumed. To sum up, the existence of the characteristic bands of the $-\text{NH}$ and $\text{C}-\text{N}$ bonds demonstrates that WPU-EA has the molecular structure of polyurethane. In addition, the existence of the characteristic band of $-\text{CH}_2=\text{CH}_2$ proves that WPU-EA has the structure of an acrylate group.

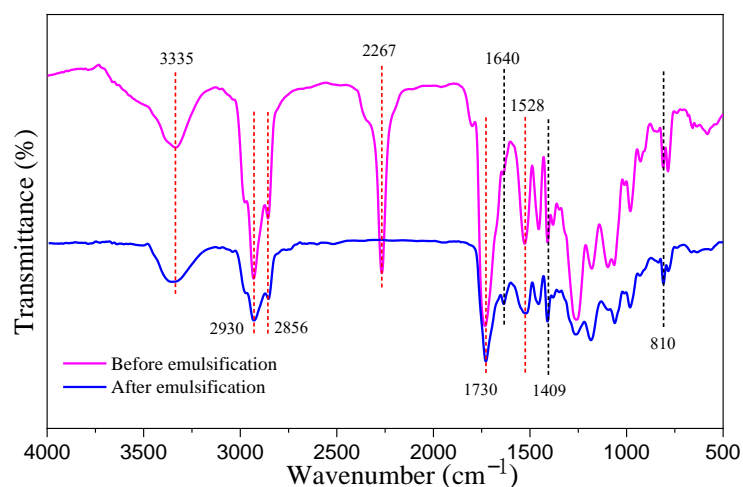


Figure 3. FTIR spectra of the modified waterborne polyurethane acrylate before and after emulsification.

Figure 4a shows the ^1H NMR spectrum of epoxy acrylate. ^1H NMR (400 MHz, chloroform- d) δ (ppm): 7.12 (s , 4H), 6.80 (s , 4H), 6.52~5.79 (m , 6H), 4.59~3.66 (m , 10H), 1.63 (s , 6H). The peaks at 7.12 and 6.80 ppm were assigned as the protons in the benzene

ring from bisphenol A-based epoxy acrylate; the peaks at 5.79~6.52 ppm were attributed to the protons of a carbon-carbon double bond. The peak at 1.63 ppm is ascribed to the proton of the methyl group.

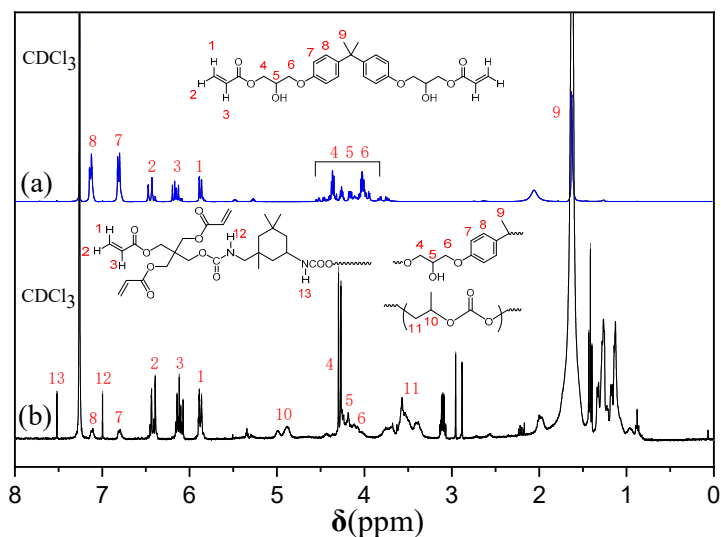


Figure 4. ^1H NMR spectra of bisphenol A-based epoxy acrylates (a) and modified polyurethane acrylate (b).

Figure 4b is the ^1H NMR spectrum of modified waterborne urethane acrylate. ^1H NMR (400 MHz, chloroform-*d*) δ (ppm): 7.52 (s, 1H), 7.12 (s, 2H), 7.00 (s, 1H), 6.80 (s, 2H), 6.42~5.88 (m, 15H), 4.89 (s, 5H), 4.28 (d, 13H), 3.80~3.37 (m, 18H), 3.10 (m, 7H), 1.62 (s, 242H), 1.41 (t, 11H), 1.29~1.20 (m, 21H), 1.20~1.10 (m, 23H). The peaks at 7.12 ppm and 6.80 ppm, attributed to the protons of benzene rings from bisphenol A-based epoxy acrylate, are consistent with Figure 4a, indicating that epoxy acrylate was successfully introduced into the main chain of waterborne urethane acrylate. The signals at 4.89 ppm and 4.28 ppm were assigned as CH and CH_2 in the propylene carbonate unit of polycarbonate diol [28]. The signals at 6.42~5.88 ppm were assigned to the proton of a carbon-carbon double bond in WPU-EA. Combining the analysis of the polymer structure by FTIR and ^1H NMR spectra, the target structure of WPU-EA, as shown in Figure 1, carrying epoxy acrylate and terminal acrylate double bond, was confirmed.

3.3. Particle Size and Distribution of WPU-EA Emulsion

The influence of different epoxy acrylate content on the appearance and the emulsion particle size of WPU-EA are shown in Figure 5. With the increasing content of epoxy acrylate, the appearance of the WPU-EA emulsion is changed from translucent blue to milky white, and the average particle size increases. When the content of epoxy acrylate is zero, the smallest average particle size (45.2 nm) and the narrowest particle size distribution are obtained. The average particle size of the emulsion gradually increases from 45.2 nm, 51.3 nm, 74.7 nm to 123.3 nm with the increase of epoxy acrylate content from 0%, 3.0%, 6.0% to 9.0%, respectively. This is because increasing the content of epoxy acrylates with rigid benzene ring increases the rigidity of the molecular chain, making it difficult for the molecular chains to crimp, which is harmful for emulsification and results in larger average particle sizes.

Emulsion stability includes mechanical stability and thermal stability. After centrifugation and thermal storage experiments, the phase separation of emulsion is not observed, indicating it has good stability with minimal storage periods of 12 months. Table 2 shows the basic properties of emulsions with different epoxy acrylate contents. The emulsions have good stability and the minimal storage periods are over 12 months, except for WPU-EA-9.

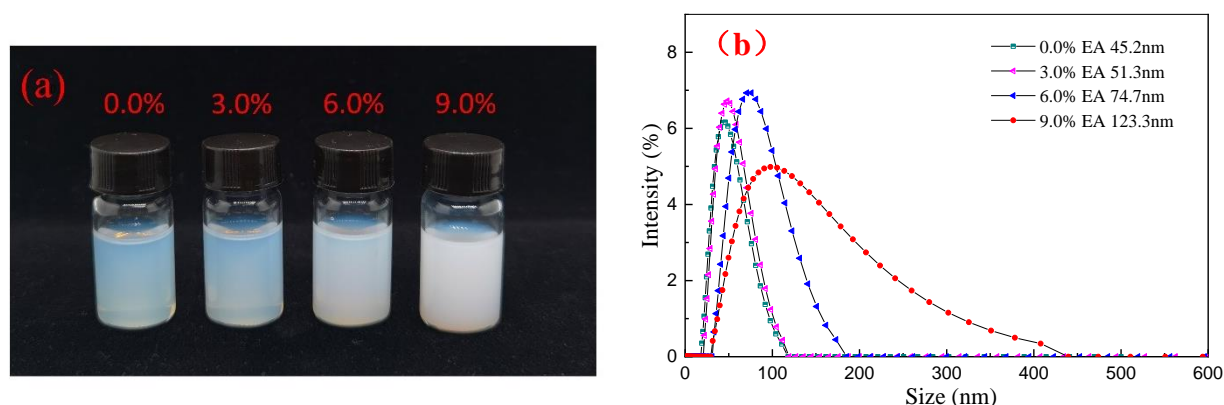


Figure 5. Effect of different EA content on the appearance (a) and the particle size (b) of the WPU-EA emulsion.

Table 2. Properties of WPU-EA emulsions with different contents of EA resin.

Samples No.	EA (%)	Appearance	Centrifugal Stability	Thermal Stability	Storage Duration (Month)
WPU-EA-0	0.0	Blue translucent	Stability	Stability	>12
WPU-EA-3	3.0	Blue translucent	Stability	Stability	>12
WPU-EA-6	6.0	Slight milky	Stability	Stability	>12
WPU-EA-9	9.0	Milky white	Stability	Sedimentation	None

3.4. Photopolymerization Kinetics of WPU-EA Resin

Real time FTIR spectroscopy is a robust means by which to monitor kinetics of polymerization in situ. In our experiment, the photoinitiator concentration is 3 wt.% of the solid content of emulsion, and the UV irradiation intensity is 50 mW cm^{-2} . Due to the limited types of waterborne photoinitiator, liquid photoinitiator (JRCure-500, Irgacure1173 and L-TPO) was chosen for the ease of dispersion. The conversion and rate of photopolymerization, versus irradiation time curves of WPU-EA, with different photoinitiators, are shown in Figure 6. The double-bond conversion of the formulations containing L-TPO, Irgacure1173 and JRCure-500 increases from 76.5%, 87.8% to 93.5%, and JRCure-500 has the maximal rate of photopolymerization. This is mainly because the JRCure-500 has better solubility in water than Irgacure1173 and L-TPO, leading to better dispersion in the emulsion. L-TPO is oil soluble and difficult to disperse in water, leading to a lower conversion and rate of photopolymerization.

3.5. Tensile Properties

Epoxy acrylate, prepared by the ring-opening reaction of bisphenol A-based epoxy resin with acrylic acid, contains rigid benzene ring structure and photo-curable acrylate double bonds. The introduction of epoxy acrylate has a great influence on the tensile properties of the UV-cured film. Figure 7 displays the strain-stress curves of the WPU-EA films with different contents of epoxy acrylate, ranging from 0% to 9.0%. As shown in Figure 7, the WPU-EA film without epoxy acrylate has a tensile strength of 21.1 MPa and an elongation at break of 25.9%. When epoxy acrylate dosage increases to 9.0%, the tensile strength of the WPU-EA film increases to 38.6 MPa and the elongation at break decreases to 8.8%. It can be seen that the tensile strength shows a substantial increase when the content of epoxy acrylate increases from 0% to 9.0%. However, the elongation at break obviously decreases with the increasing content of epoxy acrylate. This is because the introduction of bisphenol A benzene ring structure into the main chain of polyurethane acrylate leads to increased rigidity, and decreased flexibility, of the modified urethane acrylate molecular chain. This trend is more pronounced as the content of epoxy acrylate

increases. In addition, the introduction of epoxy acrylate increases acrylate double bonds in the side chain simultaneously, leading to a higher crosslinking density of the UV-cured film.

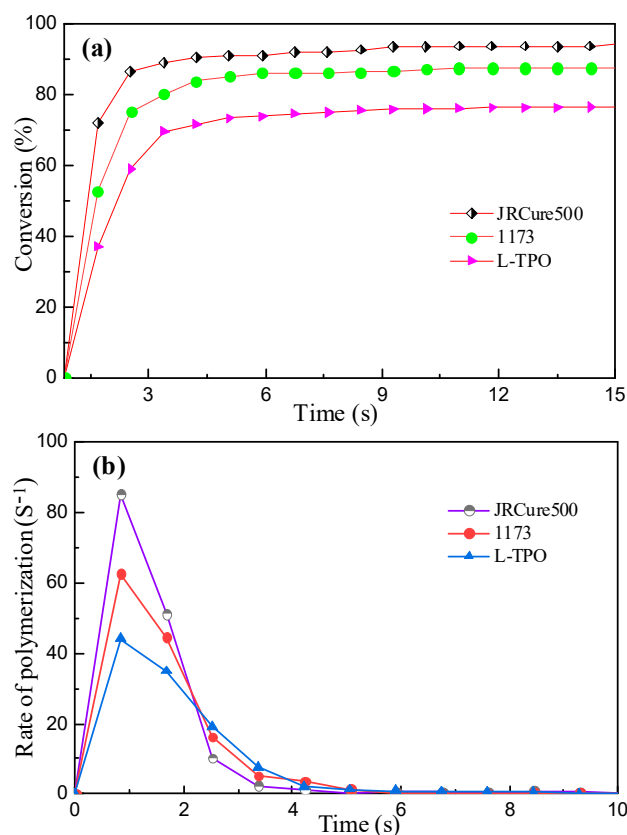


Figure 6. Effect of different kinds of photoinitiators on the photopolymerization kinetics of WPU-EA resin. (a) the kinetic curve of double-bond conversion and (b) rate of photopolymerization with different kinds of photoinitiators as a function of irradiation time, under UV irradiation intensity of 50 mW/cm² and photoinitiator concentrations of 3 wt.%.

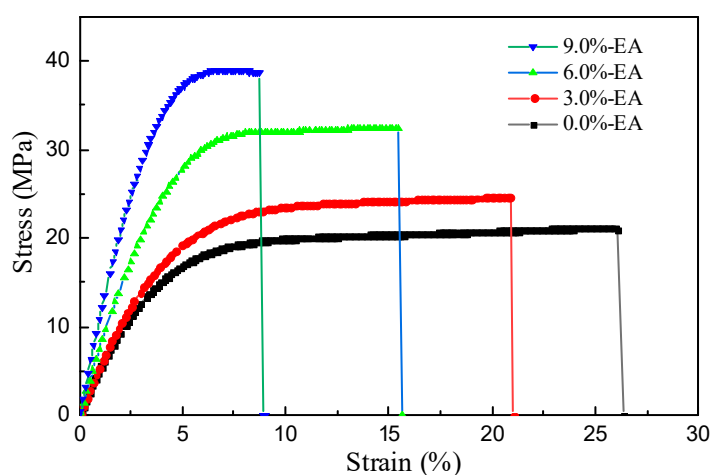


Figure 7. Strain-stress curves of the UV-cured film.

3.6. Dynamic Mechanical Analysis (DMA)

Figure 8 shows the storage modulus (E') and loss factor ($\tan\delta$), respectively, of the UV-cured films as a function of temperature. As shown in Figure 8a, the storage modulus E' of the UV-cured films gradually increases when increasing the content of epoxy acrylate

at the same temperature. The WPU-EA film without epoxy acrylate possesses the smallest storage modulus, while the film with epoxy acrylate content of 9.0% has the maximum storage modulus.

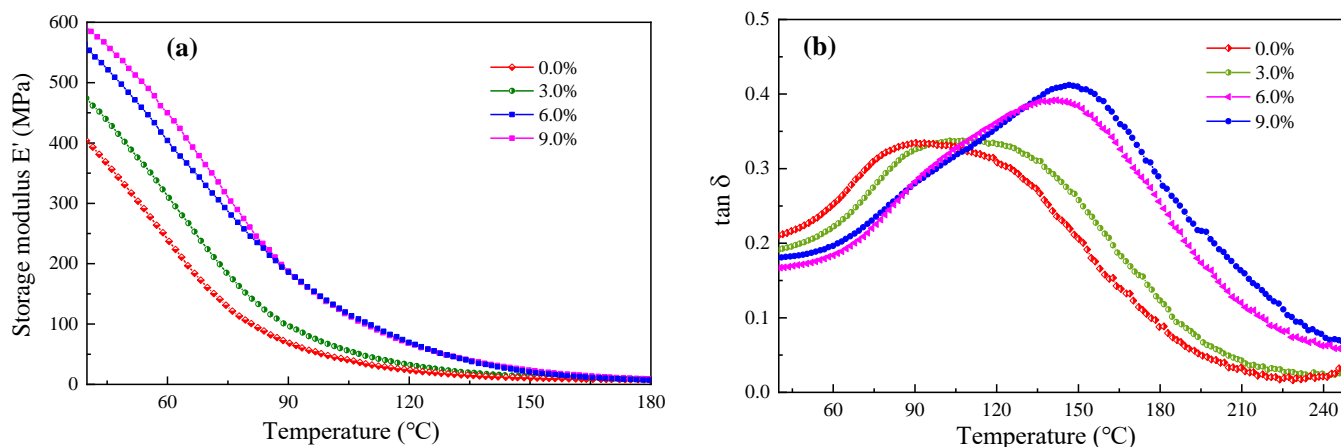


Figure 8. (a) The storage modulus and (b) $\tan \delta$ of the UV-cured films as a function of temperature.

The maximum of the $\tan \delta$ curve signals the glass transition temperature of the UV-cured film [29]. As shown in Figure 8b, with the increasing content of epoxy acrylate from 0.0% to 9.0%, the glass transition of the UV-cured film increases from 90.3 °C to 146.6 °C, respectively. The enhancement can be explained in that the increase of epoxy acrylate not only improves the cross-linking degree of the UV-cured film, causing restriction of the molecular chain movement, but also leads to increased rigidity and decreased flexibility of the modified urethane acrylate.

3.7. Gel Fraction

The gel fraction reflects the cross-linking state of the UV-cured film and the ease of movement of the molecular chain in solution. Figure 9 is the gel fraction versus the content of epoxy acrylate. With the contents of the epoxy acrylate increasing from 0%, 3.0%, 6.0% to 9.0%, the gel fraction of WPU-EA film increases from 83.7%, 92.5%, 93.0% to 93.6%, respectively. There are two reasons for the enhancement of the gel fractions. First, increasing the double-bond content of the WPU-EA, with higher content of epoxy acrylate, leads to higher crosslinking density of the UV-cured film. At the same time, the curable acrylate double bond introduced into the polyurethane side chain, through epoxy acrylate, increased the three-dimensional cross-linking points of the UV-cured film. Second, the epoxy acrylate contains a rigid benzene ring structure, which increases the rigidity and reduces the segment movement of the chain molecules. Therefore, the UV-cured films containing epoxy acrylate possess higher gel fraction. However, the gel fractions of the UV-cured films with different epoxy acrylate content are not significant, due to the minor differences in double bond contents and crosslinking density of the UV-cured films.

3.8. Thermal Stability of the WPU-EA Film

The thermal stability of the UV-cured film was evaluated by observing the weight change of the sample at the heating rate of 10 °C/min under nitrogen atmosphere. Figure 10 shows the TGA curves of the WPU-EA cured film samples. The results are shown in Table 3. The thermal decomposition process of WPU-EA cured films is divided into three main stages.

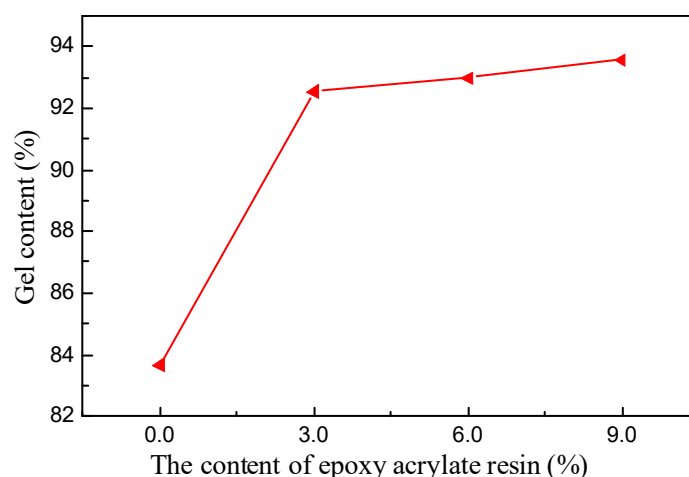


Figure 9. Gel fraction change trend of the UV-cured film affected by the content of epoxy acrylate.

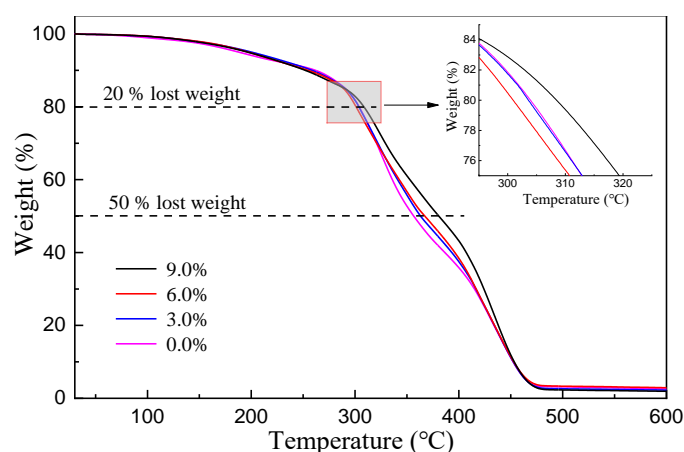


Figure 10. TGA curves of the WPU-EA cured film.

Table 3. Thermal properties of the WPU-EA cured film.

Samples No.	Decomposition Stage			
	T _{5%} (°C)	T _{10%} (°C)	T _{50%} (°C)	T _{Max%} (°C)
WPU-EA-0	188	261	356	326
WPU-EA-3	200	258	363	433
WPU-EA-6	197	255	367	432
WPU-EA-9	196	252	380	434

The first stage occurs before 200 °C, which is mainly due to the small amounts of water and the residual initiator within the UV-cured films. The second stage of degradation occurs between 250 °C and 265 °C, with a mass loss of 10%, approximately. The main reason for the decomposition is the loss of carboxylate, due to the dissociation of ionic bonds. The third stage occurs between 350 °C and 380 °C with a mass loss of 50%, mainly due to the decomposition of the hydrocarbon chain of polycarbonate diol. Due to the presence of epoxy acrylate, the increase of benzene rings and double bonds raises the degradation temperature of the WPU-EA cured films at a weight loss of 20%. In addition, the third stage degradation temperature increases with increasing content of epoxy acrylate, indicating that the thermal stability of the WPU-EA cured films is ameliorated. This is probably because the epoxy acrylate increases the rigidity and reduces the migration of the chain segments.

3.9. Performance of the Coatings

The prepared WPU-EA resins were applied to plastic coatings and the evaluated properties of the plastic coatings with different epoxy acrylate content, such as pencil hardness, adhesion, glossiness and water absorption, are shown in Table 4. The epoxy acrylate content is the key factor affecting the performance of the WPU-EA cured films. With continuously increasing epoxy acrylate content, the rigid benzene ring and double bond content also increases, causing the crosslinking density, pencil hardness and glossiness of the film to increase after UV curing. However, the water absorption decreases, caused, predominantly, by the increased crosslinking density. The adhesion of the WPU-EA coatings on plastic substrate was not noticeably changed.

Table 4. Effect of different components on the performance of the WPU-EA coatings.

Samples No.	Hardness	Adhesion	Gloss/°	Water Absorption (%)
WPU-EA-0	2H	4B	91.2	14.2
WPU-EA-3	3H	4B	92.5	12.3
WPU-EA-6	4H	5B	93.4	11.2
WPU-EA-9	4H	5B	93.6	10.8

4. Conclusions

Waterborne polyurethane acrylate was modified by epoxy acrylate to prepare a series of the WPU-EA emulsions in this study. The structure of WPU-EA was confirmed by FTIR and ¹H NMR. When the content of epoxy acrylate was 6.0%, the emulsion was stable and had relatively good performance. There were no precipitation or stratification phenomena over 12 months. The effects of different kind of photoinitiators on photopolymerization kinetics of WPU-EA were investigated, and the photoinitiator JRCure-500 gave the maximal photopolymerization rate and double-bond conversions. In addition, the effects of different epoxy acrylate content on the properties of the WPU-EA cured film were evaluated. The results show that with increasing epoxy acrylate content, the gel fraction of the WPU-EA cured film increases from 83.7% to 93.6% and the glass transition temperature rises from 90.3 °C to 146.6 °C. The tensile strength of the WPU-EA cured film increases and the elongation at break decreases. The thermal stability of the WPU-EA cured film also improves with increasing epoxy acrylate content. Finally, the WPU-EA UV cured films exhibit the advantages of high hardness, better gloss and good adhesion, which are promising for plastic coatings.

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