Synthesis of waterborne polyurethane acrylate–modified epoxy resin

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Abstract. This study aimed to synthesize a cationic waterborne polyurethane acrylate–modified epoxy acrylic resin (CWEA) from bisphenol A epoxy resin, acrylic acid, 2,4-toluene diisocyanate, polyethylene glycol 400 (PEG-400), 2-hydroxyethyl acrylate, and hydroquinone as inhibitors and N,N-dimethylbenzylamine as a catalyst. The changes in the NCO groups and the acid value during the synthesis process were measured using the chemical titration method. This method was considered as the best method for synthesizing epoxy acrylate monoesters, with optimal reaction conditions for polyurethane acrylate–modified epoxy resin.

1. Introduction
The development of economy and technology has led to solvent pollution, one of the important issues in the environment [1, 2]. Reducing the use of volatile organic solvents in coatings, inks, and adhesives has become an inevitable trend. The ultraviolet (UV) curing technology is one of the best ways to solve this problem.

Usually, the UV-curing systems consist of photoactive resins, monofunctional or polyfunctional diluent monomers, photo initiators, and auxiliaries [3]. The photoactive oligomer becomes a three-dimensional network structure of the polymer after UV curing, which plays a decisive role in the physical and chemical properties of the cured film. Monofunctional or polyfunctional diluent monomers are mainly used to replace organic solvents, adjusting the viscosity of the system to suit industrial coating needs. However, this also causes the following problems: some of the diluent monomers are harmful to the human body; on some porous substrates, the diluent easily diffuses into the pores and cannot be cured, and the coated object has a long-term odor; and the diluent monomers strongly affect the cured film [4, 5]. The increasing application of UV-curable coatings demands a technologically more environment friendly and safer UV-curing coating to overcome the aforementioned drawbacks of the large use of reactive diluents. The water-based UV-curing resin is considered to solve these problems in a better way, and hence is a hot research topic [6, 8].

In this study, the epoxy group was partially esterified with acrylic acid (AA), and then the half-block isocyanate synthesized from the branched polyethylene glycol (PEG), 2,4-toluene diisocyanate (TDI), and 2-hydroxyethyl acrylate (HEA) was obtained by side linking to obtain a modified epoxy acrylate (MEA). The hydrophilic group was introduced into the molecular chain by the reaction of diethanolamine with an epoxy group, and the aqueous UV epoxy acrylate resin was synthesized by neutralization with an organic acid. The synthesis process was tested stepwise.

2. Experimental
2.1. Materials
The epoxy resin (EP; E51, Ep 0.48–0.54) was purchased from Jiangyin Wanqian Chemical Co., Ltd. (China). N, N-dimethylbenzylamine (DMBA), PEG, diethanolamine, PEG-400, HEA, and AA were purchased from Shanghai Maclean Biochemical Technology Co., Ltd. (China). Dibutyltin dilaurate (DBTDL), DMBA, and 2,4-TDI were purchased from Siya Reagent. Acetic acid (HAc) and phosphoric acid were purchased from Shanghai Aladdin Bio-Chem Technology Co., Ltd. (China).

![Figure 1. Reaction scheme of CWEA resin.](image)

### 2.2. Synthesis
The waterborne resin was synthesized using the following steps, as illustrated in Figure 1. The optimized reaction conditions were monitored through the titration of acid, and the NCO concentration remaining the mixture.

Step 1: EP was mixed completely with AA (the mass ratio of EP to AA was 49:9), 0.10 wt% DBMA, and 0.05 wt% hydroquinone at room temperature. The reaction mixture was gradually heated to 110°C in 1 h and kept at 110°C for at least 2 h when the acid value keeps not more than 5 mg NaOH/g. The acid value of the reaction system was determined by a quick method as showed in 2.3. The idealized molecular structures are shown in figure 1; the epoxy acrylate monoester is denoted as EAM.

Step 2: The diisocyanate (DNCO) containing the double NCO groups and the ether bond chain segments were synthesized. Then, 2.4-TDI (1 mol) was added to a 500-mL three-necked flask under constant-stirring condition. PEG (200 g, hydroxyl content about 0.5 mol) was mixed drop by drop in 1 h. It was kept at room temperature and maintained for 2 h in the reaction system.

Step 3: The semi-blocked isocyanate acrylate (SNCO) containing single NCO groups and carbon–carbon double bonds was prepared in step 2. The SNCO was synthesized by mixing DNCO and HEA, containing 0.08 wt% hydroquinone (the molar ratio of DNCO to HEA was 1:1) in a closure condition at 75°C with constant stirring, which was continued for 2 h.

Step 4: The MEA containing carbon–carbon double bond and no NCO groups was synthesized. The EAM, SNCO, and 0.1–0.2 wt% DBTDL as a catalyst were mixed in a three-necked flask. The reaction temperature was kept at 75°C under constant-stirring condition until the content of NCO groups disappeared.

Step 5: The cationic waterborne epoxy acrylic resin (CWEA) was prepared. The prepolymer of step 3 was heated to 80°C under stable-mixing status in a 500-mL flask with three necks. DEA was added dropwise. The resultant mixture was heated to 80°C and maintained for 0.5–1 h. After 1 h, the HAc was added and then the mixture was cooled down to 60°C and maintained for 0.5 h.

In steps 2–4, the method named acetone-di-n-butylamine titration was monitored the content of NCO groups of the product whenever the reaction is carried out in ten minutes. The reaction scheme of the waterborne epoxy acrylic resin is shown in figure 1.

2.3. Determination of acid value and NCO groups

About 0.5–1 g of resin was taken in a conical flask, and the resin was accurately weighed. Acetone–ethanol (5:2) was added to the Erlenmeyer flask and shaken after micro-heating until the resin was completely dissolved. Two to three drops of phenolphthalein indicator were added to the Erlenmeyer flask. A red color developed within 1 min was compared with the calibrated sodium hydroxide solution. The acid value was calculated via equation (1):

\[
\text{Acid value} = \frac{40 \times (V_1 - V_0)N}{m}
\]  (1)

where \(V_0\) is the amount of sodium hydroxide used in the parallel blank test calibration, \(V_0\) is the amount required before the experiment (mL), \(V_1\) is the amount of sodium hydroxide used, which was calibrated (mL), \(N\) is the concentration of NaOH (mol/L), and \(m\) is the resin quantity (g).

The content measurement of NCO groups in the preparation process of DNCO, SNCO, and MEA was monitored using the method of acetone-di-n-butylamine titration. Specific details about the process are described as below: The specimen was precisely weighed (about 1.0000 g) in a dry iodine measuring flask such that it completely dissolved in acetone (10 mL). Then, 20.00 mL of di-n-butylamine-acetone solution was added to the iodine volumetric flask and shaken to fully mix the solution, which was maintained for at least 15 min. Finally, 2–3 trickle of the indicator was added to the iodine measuring flask and titrated with 0.1 mol/L HCl standard solution to the endpoint (bromoresol green as indicator dropped while system colour become blue and titrated until yellow). The blank comparison group experiment was conducted applied the consistent titration method. The content of NCO groups in the preparation was calculated using equation (2):

\[
\text{Content of NCO (\%)} = \frac{(V_0 - V_1) \times c \times 42}{1000m} \times 100\%
\]  (2)
where $V_0$ is the mass consumption of HCl of the blank comparison group (mL), $V_i$ is the mass consumption of HCl of the specimen (mL), $c$ is the molar concentration of HCl specimen (mol/L), $m$ is the weight of specimen (g), 42 is the molar weight of NCO (g/mol).

3. Results and discussion

3.1. Determination of the acid value

Figure 2 shows that the acid value of the system decreased slowly before the temperature increased to the temperature required for the experiment. The acid value decreased and became uniform when the temperature reached 108°C, and then decreased slowly after 180 min. The AA was added at one time during the synthesis of epoxy acrylate monoester, which reduced the time of the reaction and the amount of the polymerization inhibitor at the same time. The temperature increased after mixing at room temperature to avoid local overheating caused by sudden exothermic heat during the experiment. Figure 2 shows that the reaction was slow because the change rate of acid value was low before 60 min, which effectively avoided the violent mixing reaction of AA and E51 in the early stage. The acid value was less than 5 mg NaOH/g in 180 min and close to 0 mg NaOH/g in 220 min. The reaction continued, and the acid value continued to decrease after 180 min. The optimal reaction time to reduce the loss of the double bond was defined as 180 min.

![Figure 2](image-url)

Figure 2. Acid value change in the synthesis process of EAM.

3.2. Titration of the NCO groups

The change in the content of NCO was shown the reaction degree of the preparation process of the intermediate product. In this study, the traditional chemical titration method with necessary improvement was used to determine the content of NCO in the preparation process. The graph in figures 3–5 indicated the correlation between the NCO content and the time in the three stages during steps 2–4.

The PEG was added to 2,4- TDI in stage 2 (figure 3). The angular coefficient of curve demonstrated that the NCO groups of TDI fast reacted with the oxhydryl of PEG during the reaction. The content of NCO groups was almost invariant in conditions a and b after 2 h and almost invariant after 1 h in conditions c and d. The content of NCO groups was 2-fold that of oxhydryl, suggesting that the oxhydryl of PEG reacted anticipatively. In addition, PEG was added dropwise to the superfluous amount of TDI to ensure that the maximum demand of the synthesized product was the expected prepolymer.
In the absence of phosphoric acid to adjust the acidity and alkalinity, the content of \(-\text{NCO}\) decreased sharply after 1 h until it was close to zero in 2 h (condition A). The reaction required $\geq 6$ h for completion, which indicated that the reaction rate was slow when the temperature of the ice water cold bath was $0^\circ\text{C}$ and $25^\circ\text{C}$ in an acidic environment. The heat generated in the reaction dissipated in time, which could avoid the side reactions, and reached the reaction endpoint in $\leq 2.2$ h at $60^\circ\text{C}$. Therefore, the optimal reaction conditions were defined as condition C.

The polyurethane acrylates containing the single NCO group and carbon–carbon double bond were prepared in step 3 (figure 4). The content of NCO groups decreased from 5 to 2.5%. Subsequently, the value was kept invariant. It was concluded that the reaction between HEA and NCO groups in the prepolymer was complete. Three sets of comparisons of reaction conditions (figure 4) were made in step 2. Comparing the three sets of reaction conditions, it was found that the NCO value reached the required value in 140 min with an extremely small amount of phosphoric acid, in 100 min with the addition of
DBTDL, a catalyst, and an extremely small amount of phosphoric acid, and in 30 min with only 0.1% of the catalyst. Based on this, 0.1% DBTDL and 0.04% H₃PO₄ were the optimum conditions for stage 3 at 75°C.

![Figure 5. Content of NCO group in step 4.](image)

The polyurethane acrylates containing the carbon–carbon double bond and no NCO groups were prepared in step 4 (figure 5). A small amount of the catalyst could accelerate the progress of the reaction, and the reaction rate was slow without adding a catalyst, as shown in figure 5. A small probability of gelation was found with 0.2% DBTDL, which could speed up the reaction. The molecular weight distribution of the experimental product was wider when the temperature of the system increased rapidly, leading to higher viscosity that was difficult to control.

4. Conclusions

A new CWEA resin was prepared from epoxy resin, AA, 2,4-TDI, HEA, and PEG. The standard chemical titration method identified the change in NCO groups during the synthesis of CWEA.

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