Synthesis and Characterization of Cationic Waterborne Epoxy Acrylic Resin

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Abstract. In this work, a cationic waterborne epoxy acrylic resin (WCEA) was synthesized from bisphenol an epoxy resin, acrylic acid, acrylic acid, hydroquinone as an inhibitor, and N, N-dimethylbenzylamine (DMBA) as a catalyst. The changes of NCO groups and acid value during the synthesis process were measured by chemical titration method, and its Fourier Transform Infrared (FTIR) spectra were investigated. The results indicate that the acidified waterborne resin has great water solubility and storage stability after grafting the half-blocked isocyanate.

Keywords. Synthesis, characterization, waterborne, cationic, epoxy acrylic resin.

1. Introduction
Epoxy resin was widely used in civil engineering, aerospace and other fields with significant advantages such as high modulus, cohesiveness and good chemical stability [1-3]. Traditional epoxy resin is limited by construction conditions, environmentally friendly materials while waterborne oxygen resin has great practical significance for protecting the ecological environment while reducing the cost of use [4,5]. The preparation methods of waterborne epoxy resin are primarily mechanical method, the reverse conversion method, chemical modification method at present [6-8].

In this paper, a hydrophilic modification method is used to connect a hydrophilic amine group and an ether group into an epoxy resin structure to prepare an aqueous epoxy resin, and the WCEA is dissolved in water by an action of a hydrophilic group to form a stable state. Water dispersion system has practical application value.

2. Experimental
2.1. Materials
Epoxy resin (E51, Ep 0.48–0.54), purchased from Jiangyin Wanqian Chemical Co., Ltd. N,N-dimethylbenzylamine Polyethylene glycol, Diethanolamine (DEA), polyethylene glycol (PEG-400), 2-hydroxyethyl acrylate (HEA), acrylic acid (AA), purchased from Shanghai Maclean Biochemical Technology Co., Ltd., Dibutyltin dilaurate (DBTDL), N, N-dimethylbenzylamine (DMBA), 2,4-toluene diisocyanate (TDI), purchased from Siya Reagent. Acetic acid (HAc), phosphoric acid, purchased from Sinopharm Chemical reagent Co. Ltd., All materials in this study were used without further purification.

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2.2. Synthesis

We synthesized three kinds of cationic aqueous resins based on epoxy E51 throughout the experimental procedure (two of which were used for comparison).

(a) Preparation of epoxy acrylate monoester

Epoxy Acrylate Monoester (EAM) was synthesized by monitoring the change of acid value and FT-IR in step a. It is completely mixed according with the mass ratio (epoxy resins to acrylic acid: 49:9). DBMA (0.10 wt%) and hydroquinone (0.05 wt%) are respectively added as a polymerization inhibitor and a catalyst at the start. It slowly heats up to 110 °C and keep this temperature for a while the acid value reaches less than 5 mgKOH/g in a three-necked flask with oil bath, thermometer, condensing device, constant pressure funnel, and PTFE stirring bar.

(b) Synthesis of grafted segments*3

b1: The modified waterborne epoxy resin (E51-0) was synthesized by b1. EAM (1.0mol) as previously described was added to a three-neck bottle with water bath and PTFE stirring bar and heated to 80 °C with a molar ratio of EAM to diethanolamine (DEA) are 1:1. After half an hour of heat preservation, acetic acid (HAc 1mol) added and kept for 30 minutes when the temperature is lowered to 60 °C.

b2: The modified waterborne epoxy resin (E51-A) was synthesized in b1. Briefly, the Single-blocked acrylic isocyanate (SAI) as an intermediate containing the single NCO groups and C=C were synthesized in process of b2. 2, 4-Toluene diisocyanate (TDI, 1.0mol) was added to a 250mL three-necked flask stirred under reflux with a relatively stable environment which keep at room temperature under stable stirring for 2 h. HEA (1.0mol) was added dropwise to the reaction system in 1 h which allowed at about temperature of 80 °C and maintained for 2h in the reaction time. In addition, EAM (1mol), SAI (1mol) and 0.1 wt% to 0.2 wt% DBTDL as catalyst mixed in three-necked flask with water bath until the reaction temperature keeps at 75 °C under constant stirring condition until the content of NCO groups disappeared. Repeat step b1.

b3: 2,4-Toluene diisocyanate (TDI, 2mol) was added to a 500mL three-necked flask with water bath and constant stirring condition and PEG (0.5mol) was mixed by dropped into three-necked flask by dropping funnel within 30 to 40 min. It was kept at about room temperature and maintained for 2h during the reaction while we get dihydrocyanate (DNCO). The reaction system heated to 75 °C and added HEA(1mol) which was containing 0.08 wt% hydroquinone in a closure condition with water bath maintained at 75 °C under constant stirring which was continued 2h we get monohydrocyanate (MNCO) repeat step b2.

The expected molecular structure of waterborne epoxy acrylic resin was shown in figure 1.

2.3. Infrared Spectra

Using Nicolet’s Nicolet 6700 infrared spectrometer to characterize the resin in the synthesis process. The resin of the sample was tested with the scanning wavelength ranged from 4000 to 400 cm\(^{-1}\) and resolution of 4 cm\(^{-1}\).

2.4. Appearance, Water Solubility and Storage Stability

A small amount of prepolymer was placed in the beaker while observing the appearance of the resin. It was recorded the value when water was added in an amount of 1 g/time after weighing until the system become semi-transparent, milky. The resin with water stored in the dark environment after sealing with a wrap film. The appearance of resin is observed after 15 days, 30 days, and 60 days.

3. Results and Discussion

3.1. Infrared Spectroscopy

The FTIR spectra of EMA is shown in figure 2. The characteristic C=C absorption of the unsaturated acrylic groups at 1637.3 cm\(^{-1}\) was used to determine the extent of photopolymerization in this study. Epoxy acrylate monoester (EAM) showed a strong absorption peak at 1727.4 cm\(^{-1}\)and a strong C=O
stretching absorption peak appeared at 1727.4 cm\(^{-1}\) which indicate that the expected product was synthesized successfully. The enhancement of the peak at 3504 cm\(^{-1}\) confirmed that the epoxy acrylate monoester had more hydroxyl groups than E51.

**Figure 1.** The molecular structure of WCEA, E51-0, E51-A.

The epoxy group in resin and the acrylic acid are subjected to ring-opening esterification to obtain a carboxyl group. 1251.1 cm\(^{-1}\), 917.0 cm\(^{-1}\) and 832.6 cm\(^{-1}\) are the absorption peaks of three epoxy groups of E51. In the infrared spectrum of EAM, these three epoxy group absorption peaks still exist, which confirms EAM. Based on the epoxy resin, the epoxy group was retained. From the viewpoint of the intensity of the peak, the absorption peak of E51 at 1251.1 cm\(^{-1}\), 917.0 cm\(^{-1}\), and 832.6 cm\(^{-1}\) was stronger than EAM which indicated E51 was also confirmed.

It can see from figure 3 that 3321 cm\(^{-1}\) is the NH characteristic absorption peak of the carbamate group, and 1720 cm\(^{-1}\) is the characteristic absorption peak of the carbonyl group (\(-\text{C}=\text{O}\)) of the polyurethane. The characteristic absorption peak of the group confirmed that the TDI and polyethylene glycol synthesis of the double-end isocyanate was successful in this experiment; a strong -NCO absorption peak was retained at 2284 cm\(^{-1}\), indicating that the 2,4-TDI was in the 2 position. The -NCO group is largely retained.

Stage 2 is the synthesis of semi-blocked isocyanate, introducing unsaturated double bonds, DNCO is compared with stage 1, and MNCO infrared spectrum shows that 1620 and 811 cm\(^{-1}\) are characteristic peaks of carbon-carbon double bonds, indicating double The terminal isocyanate reacts with the hydroxyl group of HEA to introduce the C=C required for light solidification. At the same time, the absorption strength at 2284 cm\(^{-1}\) was significantly weakened compared to the first stage,
indicating that the -NCO group and the hydroxyethyl acrylate retained a portion of the -NCO group after the formation of the half-blocked isocyanate.

Figure 2. The FTIR spectra of EAM and E51.

Figure 3. The FTIR spectra of DNCO, MNCO, WCEA.
Stage 3 is the reaction of blocked isocyanate with EAM. It is apparent that the -NCO characteristic absorption peak at 2284 cm\(^{-1}\) disappears, indicating that the -NCO group reacts completely with the EAM in the MNCO product; the C=C occurs at 1630 and 810 cm\(^{-1}\). The absorption peak indicates that the absorption peak of C=C is still present, which also indicates that the synthesized product retains the unsaturated double bond required for photocuring, and the prepared PUA prepolymer meets the expected requirements.

3.2. Appearance, Water Solubility, Storage Stability

It can be seen from table 1 that the comparison of the three groups of data shows that after grafting the side chain containing the ether group, the water solubility is 30.15% higher than that of the cationic type. On storage, E51-400 does not stratify at 60d, in the experiment. The added catalyst and polymerization inhibitor can be precipitated to the lower layer at 30 days, and the amount of the carcinogen hydroquinone can be reduced after separation. E51-0 and E51-A are prone to turbidity at 15d.

| Project | E51-400 | E51-0 | E51-A |
|---------|---------|-------|-------|
| Appearance | Light yellow, transparent | Yellow, transparent | Yellow, transparent |
| Water solubility % | 16.01 | 5.21 | 4.94 |
| Storage stability | 15d | No stratification, clarification | Turbid, layered | Turbid, layered |
| | 30d | No delamination, bottom white precipitate | Turbid, layered | Turbid, layered |
| | 60d | No delamination, bottom white precipitate | Turbid, layered | Turbid, layered |

4. Summary

A series of aqueous cationic resins were synthesized from epoxy resin E51, acrylic acid, PEG400, diisocyanate hydroxyethyl acrylate, etc. WCEA resin was characterized by infrared. The water solubility and storage stability of the three resins were compared at the same time. The results show that WCEA has good water solubility and storage stability.

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