Study on Properties of Waterborne Polyurethane Acrylate Modified Epoxy Acrylate Resin

Hongbo Liu, Xiaowu Xue, Jingjing Wei, Wangdong Xiao and Jing Bai*

School of Applied Chemistry and Biological Technology, Shenzhen Polytechnic, Shenzhen 518055, People’s Republic of China

*Corresponding author email: baijing@szpt.edu.cn

Abstract. Polyurethane acrylate modified epoxy acrylate resin with high solid content and great mechanical properties was synthesized by addition of polyethylene glycol in this work. The conversion process from liquid to solid was confirmed by comparing the FT-IR of oligomer and film. The disappearance of the carbon-carbon double bond absorption peaks at 1639 cm$^{-1}$ and 819 cm$^{-1}$ indicates that the oligomer is cured completely. In addition, the thermal analysis of the resin was characterized by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). According to the experimental data, it can be seen from that the resin started to decompose at 293.31°C until it is almost completely decomposed at 481.73°C which indicated that the stability of the film was better and the decomposition temperature was higher. In addition: Compared with the thermosetting resin E51 and the modified resin, the glass transition temperature is reduced by about 31 °C, which solves the problem of brittleness and hardness.

Keyword: Polyurethane; Modified; Waterborne epoxy acrylate; UV-curable; Properties.

1. Introduction
Epoxy resin is thermosetting resin material with some characteristics like high hardness, good adhesion and good chemical resistance. It was synthesized in 1947 and has been extensively used in various fields until now. It is commonly used in composite materials, adhesives, steel anticorrosion and other industries. Solvent-based epoxy resin emulsion refers to a stable system constituted by the uniform distribution of epoxy resin in organic solvents. A large number of organic compounds in this emulsion are easily volatile into the atmosphere which will cause atmospheric pollution. With the strengthening of people's environmental awareness and national policies, solvents Type epoxy resin can no longer meet the current need, at this time, waterborne epoxy resin came into modern society [1-6].

Aqueous epoxy resin refers to a stable state obtained by uniformly dispersing epoxy resin in the form of droplets or particles in a system where the dispersion medium is water. Waterborne epoxy resin is a nontoxic, harmless and pollution-free environmentally friendly coating. Depending on different preparation methods, the preparation methods of waterborne epoxy resin are mainly divided into mechanical method, chemical modification method and reverse conversion method. The advantages of mechanically preparing water-based epoxy resin emulsion are simple process and low emulsifier content, but the disadvantages of emulsion are also obvious, such as a large particle size, irregular particle shape, poor stability, and poor film-forming performance [6-8]. The size of the dispersed phase particles in the aqueous epoxy resin emulsion prepared by the chemical modification method is unimportant, but the disadvantage is that the preparation steps are difficult to control and the cost is high. With the improvement of environmental awareness and national environmental regulations, ordinary coatings can no longer meet people's needs and special coatings gradually appear in people's field of vision [2,3].

Published under licence by IOP Publishing Ltd
UV-curing technology has been widely used in the coatings industry because of its advantages of energy saving, environmental protection and high efficiency [4-8]. As a special coating, UV-curable waterborne resin and its coatings are gradually appearing in people's lives. Considering the issues of energy conservation, environmental protection, UV-curing conductive coatings have received extensive attention from scientists and become one of the hot research topics in the coatings industry [7-11]. In this paper, epoxy resin E51 is used as the main body, and it is modified by polyurethane acrylate with a hydrophilic segment to obtain an environmentally friendly water-based resin with a lower glass transition temperature and good thermal stability.

2. Experimental

2.1. Materials

Epoxy resin (EP-E51, g/eq 210-244), Baling Petrochemical Branch of Sinopec Group Asset Management Co., Ltd. N, N-dimethylbenzylamine (DMBA), DaMao Chemical Reagent Factory, polyethylene glycol (PEG), Sinopharm Chemical Reagent Co., Ltd. Diethanolamine (DEA), polyethylene glycol (PEG-400), 2-hydroxyethyl acrylate (HEA), acrylic acid (AA), Shanghai Maclean Biochemical Technology Co., Ltd. Dibutyltin dilaurate (DBTDL), Dongguan Sparta Chemical Co., Ltd. 2,4-toluene diisocyanate (TDI), photoinitiators (Darocur 1173) IRGACURE BASF, 1-hydroxycyclohexyl phenyl ketone (photoinitiators 184) IRGACURE BASF. Acetic acid (HAc), phosphoric acid, Nanjing Chemical Reagent Co., Ltd. 4A Molecular Sieves were used to remove water from polyethylene glycol in this study.

2.2. Synthesis of Waterborne Resin

Initially, PEG 400 (1 mol) and 2,4-TDI (2 mol) reacted using dibutyltin oxide as catalysis at room temperature under nitrogen atmosphere without any solvent. The content of -NCO during the reaction of PEG and TDI was measured through anti-titration, which could help us know that the help us to know the advancement of the entire experiment. In the first stage we get double-ended polyurethane (T1-P4). The 1:1 mole ratio of HEA/ T1-P4 was used to obtain mono-terminated line like mono-isocyanate (T-P4) and monitor the progress of reaction using the same method as when synthesizing T1-P4. Lastly, the reaction mixture with T1-P4 and EAM (Obtained by EP-E51 and acrylic to 1:1) in the molar ratio of 1:0.8:1, dibutyltindilaurate as the catalyst for this step. The mixture was kept at 75℃ for 1.5-2.0 h until the -NCO cannot be found and the nonionic waterborne resin (TP-EP) was obtained. However, Due to the poor hydrophilicity of TP-EP, further operation to be made by mixed with DEA in 80℃ (0.5-1h) and HAc in 60 ℃ (0.5h) in sequence, the target resin of waterborne polyurethane acrylate modified epoxy acrylate resin (WTP-EP) was obtained[12,13]. Theoretically, the solid content of the resin reaches 80% before being water-based and the solid content reaches 65% after using water as a solvent to reduce viscosity.

2.3. Preparation of UV-cured Films

The waterborne resin WTP-EP was synthesized through the previous section 2.2. Mix the synthetic resin and photoinitiator according to Table 1 and add water to reduce viscosity. Apply the waterborne resin mixture to the surface of the polytetrafluoroethylene plate, remove water from the resin after flashing, and then irradiate the resin on the polytetrafluoroethylene plate for 8-10 s under ultraviolet light [13].

Table 1. The composition of UV-curable liquid formulations (wt.%).

| Sample  | WTP-EP | H2O   | Darocur 1173 | 184 |
|---------|--------|-------|-------------|-----|
| E51-400 | 65     | 30    | 4           | 1   |

2.4. Infrared Spectra

The blank background was prepared by KBr tableting method and scanned as a background file, the sample was coated evenly on the KBr wafer and dried under dried at low temperature environment. The Nicolet 6700 Fourier Infrared Spectrometer (FT-IR) was used for testing, with a scanning range of 4000 cm⁻¹ to 400 cm⁻¹.
2.5. Gel Content
The cured film is made into a 3cm*3cm*1mm size and record the mass of the cured film. It was immersed in acetone for 48h and then dried in a vacuum oven at 90°C for 6h, and weighed the quality. Calculate the resin gel rate according to calculation formula 1.

\[ \omega(\%) = \frac{m_1}{m_0} \times 100\% \]

\( \omega \) the gel content
\( m_0 \) the resin weight before experiment
\( m_1 \) film weight after extraction and drying

2.6. Thermogravimetry (TG)
The thermodynamics of the coating film were analysed using a TA-Q50. Take about 7-13 mg of sample in a platinum crucible and heat to 480°C at a rate of 8°C/min under nitrogen environment.

2.7. Differential Scanning Calorimeter (DSC)
The glass transition temperature of the film is analysed by TA-Q200. Under a nitrogen atmosphere at a heating rate of 5°C/min, the temperature is increased from -20°C to 300°C, and the cycle is repeated twice.

3. Results and Discussion
3.1. Infrared Spectroscopy

![FTIR spectra of oligomer (a), UV-cured film (b).](image)

Figure 1. The FTIR spectra of oligomer (a), UV-cured film (b).
The FTIR spectra of the oligomer before UV-cured (a) and UV-cured film after radical UV-cured (b) are shown in Figure 1 respectively. After the addition of the free radical photoinitiators Darocur 1173 and 184, the unsaturated double bond radical polymerization of the epoxy acrylate is initiated after brief UV irradiation. In the final product synthesis, an epoxy bond is subjected to a ring-opening reaction with a diethanolamine epoxy group to introduce a hydrophilic group (hydroxyl group, amino group), and to retain as much epoxy group as possible in each resin molecule. It can be seen from Figure 1 that the prepolymer has a characteristic peak of epoxy at 981 cm\(^{-1}\) and 773 cm\(^{-1}\), which indicates that DEA retains a small amount of epoxy bond after reacting with the remaining epoxy bond, avoiding the occurrence of DEA excess phenomenon. It can be seen from the comparison of the infrared spectrum of the prepolymer and the photocurable coating film that the characteristic absorption peak of the double
bond of the cured film at 1639 cm\(^{-1}\) and 819 cm\(^{-1}\) disappears obviously, which indicates that the free radical photoinitiator initiates the prepolymer. After the polymerization, the prepolymer is sufficiently polymerized; after the addition of the radical photoinitiator 184, the ring-opening polymerization of the epoxy group occurs in the action of the epoxy group, which also indicates the synergistic effect of the two photoinitiators. Since the polymerization is enough, the curing speed is fast and sufficient under the action of the two photoinitiators. The characteristic absorption peak of the double bond disappeared at 1639 cm\(^{-1}\) and 819 cm\(^{-1}\), and the characteristic absorption peak of the epoxy group at 981 cm\(^{-1}\) disappeared, indicating that the curing was complete.

3.2. Thermal Decomposition

Figure 2 shows the results of thermal decomposition test of the aqueous resin cured film. At 273.31°C to 315°C, the weight loss caused by the residual moisture and volatilization of small molecules in this stage. The quality decrease between 314 and 400°C is mainly caused by the decomposition of the hard segment in the polymer side chain and the range of quality decrease is caused by the decomposition of the soft segment in the polyether polyol and the breakage of the molecular main chain; after 400°C The thermal weight loss is mainly the decomposition of crosslinks. At a temperature of 481.73, the cured film is almost completely decomposed. The film shows better thermal stability because the maximum weight loss temperature of the cured film is higher than 370°C.

![Figure 2. Thermal decomposition temperature curve of waterborne resin.](image)

3.3. Glass Transition Temperature

Figure 3 show the differential scanning calorimetry (DSC) of cured films of the modified epoxy resin WTP-EP and EP-51. We can explain as follows: Due to the flexible urethane acrylate segment on the side link of the rigid epoxy acrylate monoester, compared with the rigid epoxy acrylate cured film, the aqueous resin cured film of this test has reduced brittleness, enhanced flexibility, and cured film. The glass transition temperature also decreased and the cured film had a glass transition temperature of 58.74°C.
Figure 3. Glass transition temperature curve of cured films of EP-E51(a) and WTP-EP (b).

3.4. Gel Fraction
The photoinitiator was added to the water-based resin, and a solid film was formed after irradiation under ultraviolet light. The gelation rate of the cured film reached 96.65%, which indicates that the aqueous resin can be effectively crosslinked under the action of the photoinitiator, forming a relatively complete Network cross-linking structure.

4. Conclusion
The polyurethane acrylate modified epoxy acrylate waterborne resin with great physical properties was successfully synthesized from EP-E51, 2,4-TDI, PEG400 and HEA in this study. The pre-polymer was utilized in preparation of green environment-friendly UV/energy-saving quickly curing with great properties. After compared the cured film conforms with intended design, the resin is in line with the expected results in the FT-IR. The cured coating film has a great thermal decomposition temperature, a lower glass transition temperature compared with the EP-E51.
Acknowledgements
This paper was financially supported by the Shenzhen Basic Research Project (JCYJ20170818 114324998).

References
[1] Yuan X, Zhu B, Cai X, et al. 2017 Journal of Applied Polymer Science 17 134
[2] Sheng J G, Zeng P, Shan Y D. 2013 Advanced Materials Research 815 547
[3] Qiu S, Cheng C, Cui M, et al. 2017 Applied Surface Science 407 213
[4] Liu T, Li Y, Li X Y, et al. 2019 Progress in Organic Coatings 128 137
[5] Gu Y, Huang Y, Liao B, et al. 2000 Journal of Applied Polymer Science 76 690
[6] Zhang J, Xu H, Hu L, et al. 2017 ACS Omega 2 7546
[7] Krylova I 2001 Progress in Organic Coatings 42 119
[8] El-Ghaffar M, Kantouch F A, Hashem A I, et al. 2014 Pigment and Resin Technology 43 84
[9] Krylova I. 2001 Progress in Organic Coatings 42 119
[10] Wang Y, Liu F, Xue X. 2015, Progress in Organic Coating 78 404
[11] Arsu N, Davidson R S, Holman R.1995 Journal of Photochemistry and Photobiology A Chemistry 87 169
[12] Liu H B, Zhang Y Y, Lin f, et al. 2013 Applied Mechanics & Materials 447 1169
[13] Liu, H B, Xue X W, Zhang W Y, et al. 2020 Materials Science and Engineering 770 012062