

Synthesis and Characterization of Epoxy Resins-Modified Waterborne Polyurethane Emulsion

Chenhan Zhuang¹, Weilan Xue^{1*} and Zuoxiang Zeng¹

¹School of Chemical Engineering, East China University of Science and Technology, 200237 Shanghai, China.

Authors' contributions

This work was carried out in collaboration among all authors. All authors read and approved the final manuscript.

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ABSTRACT

Aqueous polyurethane emulsion was prepared with diphenylmethane diisocyanate (MDI), polybutylene adipate diol (PBA-1000) as main raw materials and 2, 2-dihydroxymethyl propionic acid (DMPA) as hydrophilic chain extender. On this basis, epoxy resin E-44 was introduced to modify the polyurethane prepolymer, and epoxy resin modified waterborne polyurethane emulsion was obtained. In order to obtain better performance waterborne polyurethane, the effect of DMPA content, the amount of epoxy resin added and modification method on the properties of polyurethane was discussed. The results show that when the DMPA content is 4wt%, the overall performance of the emulsion and the film is the best. And the addition of epoxy resin significantly improves the water resistance, solvent resistance and tensile strength of the waterborne polyurethane film, and its hardness and thermal stability are also improved to a certain extent. When the amount of epoxy resin added is 8wt%, the storage stability decreases significantly, the suitable amount of epoxy resin added is 6wt%. The overall performance of the film obtained by chemical modification is better than that of physical modification.

Keywords: Waterborne polyurethane; epoxy resin; modification.

*Corresponding author: Email: wxue@ecust.edu.cn;

1. INTRODUCTION

Waterborne polyurethane is synthesized with polyurethane resin as the base material and water instead of organic solvent as the dispersion medium. It has the advantages of product safety, environmental friendliness and low cost, and is widely used in coatings, adhesives, textiles, leather processing and other industries [1-3]. However, due to its poor water resistance and weak mechanical properties, the application range of waterborne polyurethane is limited [4-5].

In order to improve these shortcomings, people use epoxy resin, acrylic ester, organic silicon, organic fluorine, nanomaterials to modify waterborne polyurethane [6-10]. Epoxy resin has many excellent properties, such as easy curing, high mechanical strength, strong adhesion, low cost and good thermal stability. At the same time, the structure of epoxy resin contains hydroxyl ether bond and epoxy end group, which can be directly involved in the synthesis of waterborne polyurethane [11-14]. The mechanical properties, water resistance and solvent resistance of waterborne polyurethane film can be improved significantly by modifying it with epoxy resin [15]. Zhan Biao [16] reduced the water absorption rate of the film from 11.46% to 8.23% and enhance the tensile strength from 10.47MPa to 15.61MPa by introducing E-44. Wang Jian et al. [17] reduced the water absorption rate of the film from 33.1% to 14.1% and enhance the pencil hardness from B to HB by introducing E-51. In order to obtain a waterborne polyurethane with better mechanical properties, water resistance and solvent resistance, it is necessary to optimize its synthesis process (basic formula and modifier).

Diphenylmethane diisocyanate (MDI) is cheap and has a special symmetrical structure, which makes it highly reactive [18,19]. In this paper MDI was used as the main raw material to prepare waterborne polyurethane. Epoxy resin e-44 was introduced to prepare waterborne polyurethane emulsion modified by epoxy resin. The influence of the amount of epoxy resin and the modification method on the properties of emulsion and adhesive film was discussed.

2. EXPERIMENTAL AND CHARACTERIZATION

2.1 Materials

Diphenylmethane diisocyanate (industrial-grade)

and Polybutanediol adipate diol (industrial-grade, Mn=1000) was supplied by Yantai Wanhua Polyurethane Co.Ltd. Acetone(99.5wt%)、Dimethylol propionic acid (industrial-grade)、N-methyl pyrrolidone (99.5wt%)、Dibutyltin dilaurate (99.5wt%) and 1, 4 - butanediol (99.5wt%) was supplied by Shanghai Titan Technology Co. Ltd. Triethylamine(99.5wt%)、Epoxy E-44(industrial-grade)、Anhydrous ethanol(99.5wt%)、and Sodium hydroxide(industrial-grade) was supplied by Shanghai Macklin Biochemical Co. Ltd.

2.2 Synthesis Process

2.2.1 Preparation of epoxy resin modified waterborne polyurethane (EWPU) by chemical modification

Chemical modification is to prepare EWPU by reacting the -OH group of epoxy resin with the -NCO group of MDI. The steps are as follows.

(1) Polybutanediol adipate diol and dimethylol propionic acid were dehydrated by vacuum drying, Put them in a blast oven at 110°C for 12 hours, Before the reaction, the polybutanediol adipate diol was quickly moved into a three-port flask and vacuumized at 110°C and 0.08MPa for 1 hour.

(2) Add polybutanediol adipate diol、diphenylmethane diisocyanate (N-methyl pyrrolidone dissolved)、4 drops of dibutyltin dilaurate to a three-port flask, and reacted at 80°C for 90 minutes. Cool to 75°C, add dimethylol propionic acid (N-methyl pyrrolidone dissolved) and react for 90 minutes. Add 1, 4 - butanediol and increase the stirring rate for one hour, adding an appropriate amount of acetone to adjust the viscosity.

(3) Cool to 70°C, add epoxy resin E-44, stir and react for 90 minutes.

(4) Cool to 25°C, add triethylamine and react for 30 minutes. Deionized water was added and emulsified at high speed for 30 minutes to obtain EWPU emulsion. The final product is obtained by vacuum distillation.

2.2.2 Preparation of epoxy resin modified waterborne polyurethane (EWPU) by physical modification

Physical modification is used to prepare EWPU by means of mechanical blending. The preparation process is divided into four steps too.

The three steps ((1), (2) and (4)) are the same as those of the chemical modification process. The step (3) changes to: cool to 40°C, add epoxy resin E-44, stir and react for 15 minutes.

Without adding epoxy resin, the DMPA content was changed to 3, 4 and 5wt% to obtain three water-based polyurethane samples, named WPU-1, WPU-2, and WPU-3 respectively. The amount of epoxy resin added was 4wt%, and an epoxy resin modified waterborne polyurethane sample was prepared by physical modification, named EWPU-P. Four waterborne polyurethane samples modified by epoxy resin were obtained by chemical modification with the addition amount of epoxy resin being 2, 4, 6 and 8 wt% respectively. They were named as EWPU-C1, EWPU-C2, EWPU-C3 and EWPU-C4.

2.2.3 The emulsion film

In order to test the comprehensive properties of the waterborne polyurethane, it is necessary to make the film by casting method. The specific steps are as follows.

Pour the emulsion onto a polytetrafluoroethylene (PTFE) board and bulldoze the emulsion evenly with a scraper rod. The PTFE board was left at room temperature for 24 hours.

The PTFE board was dried in a constant temperature oven at 80°C for 6 hours.

By taking out the PTFE board at room temperature for 12 hours, a waterborne polyurethane film with a thickness of about 0.3mm can be obtained.

2.3 Analysis and Characterization

2.3.1 Infrared spectrum

The characteristic peaks of the molecular structure of the waterborne polyurethane film were characterized by the Fourier transform infrared spectrometer NICOLET6700 produced by thermo fisher scientific Co.Ltd. And the scanning range was 400-4000cm⁻¹.

2.3.2 Thermogravimetric analysis

The STA 6000 manufactured by Perkin Elmer Instruments Co.Ltd was used for thermogravimetric analysis of the polyurethane film. The heating rate was 20°C/min, the temperature span was 30°C to 700°C, and N₂

protection was introduced to measure the thermal weight loss of the film.

2.3.3 Storage stability

If there is no sediment after centrifugation and sedimentation at 3 000r/min in a centrifuge for 15 minutes, its storage stability can be considered as 6 months.

2.3.4 Viscosity

High temperature rheometer MCR302 was used to determine the viscosity of waterborne polyurethane emulsion. Take about 20mL emulsion into the instrument, set the temperature at 25°C, shear rate of 100s⁻¹.

2.3.5 Tensile strength and elongation at break

The waterborne polyurethane film was cut into a rectangular sample of 100mmx20mm, and the average thickness of the film was measured with a helical micrometer. Test with universal testing machine (Shanghai Xinbiao Testing Instrument Manufacturing Co.Ltd) at room temperature, set the stretching speed of the machine to 100mm/min.

2.3.6 Water and solvent resistance

The film was cut into a regular square and weighed (M_1) at room temperature after drying. Then it was soaked in water, 5wt% sodium hydroxide solution and anhydrous ethanol for 24 hours respectively. After taking out the film and absorbing the moisture on its surface, weigh it again (M_2 , M_3 , M_4). The water absorption rate α and swelling rate β of the film are calculated according to the following formula:

$$\alpha = \frac{(M_2 - M_1)}{M_1} \times 100\% \quad (1)$$

$$\beta_{\text{NaOH}} = \frac{(M_3 - M_1)}{M_1} \times 100\% \quad (2)$$

$$\beta_{\text{EtOH}} = \frac{(M_4 - M_1)}{M_1} \times 100\% \quad (3)$$

2.3.7 Hardness

Place the prepared film horizontally, take different types of pencils with the length of 5-6mm of the exposed pencil lead and press them on the film, keeping the Angle between the pencil and film at 45°.

3. RESULTS AND DISCUSSION

3.1 Infrared Analysis

In order to determine the effectiveness of the physical and chemical modification of the epoxy resin to the waterborne polyurethane, the samples WPU-2, EWPU-P and EWPU-C2 were analyzed by infrared, and the results are shown in Fig. 1.

The characteristic absorption peak of -NCO group of MDI is about 2200cm^{-1} , while the infrared spectrum of WPU-2 shows no obvious absorption peak near 2200cm^{-1} , indicating that all -NCO groups are almost completely involved in the reaction. The stretching vibration peak of hydrogen-bonding N-H appeared near 3340cm^{-1} , and the characteristic absorption peak of carbonyl C=O of carbamate was found near 1728cm^{-1} , indicating that the carbamate group was generated by the reaction of -OH and -NCO groups. These peaks indicate the synthesis of waterborne polyurethanes. The curve of EWPU-C2 shows a characteristic absorption peak of para-substituted benzene ring near 830cm^{-1} , and there is no characteristic peak of E-44 hydroxyl group at 3517cm^{-1} , indicating that the epoxy resin was successfully introduced into the main chain of waterborne polyurethane. The EWPU-P curve still has a characteristic peak of E-44 at 3517cm^{-1} , indicating that -OH is not involved in the reaction. In addition, the curves of EWPU-C2

and EWPU-P have no characteristic absorption peaks of epoxy groups near 910cm^{-1} , indicating that both have a ring-opening reaction during the process of epoxy resin modification of waterborne polyurethane.

3.2 Thermogravimetric Analysis

Samples WPU-2, EWPU-P, EWPU-C2 and EWPU-C4 were taken for thermogravimetric analysis, and the results were shown in Fig. 2.

$T_{d, 1/2}$ is the temperature at which the polymer loses 50% of its mass during the heating process, which can indicate the heat resistance of the film. As can be seen from Fig. 2, $T_{d, 1/2}$ of WPU-2, EWPU-P, EWPU-C2 and EWPU-C4 samples are about 386.4°C , 402.2°C , 401.4°C and 415.9°C , respectively. The data combined with the curve of the graph show that the thermal stability of waterborne polyurethane adhesive film modified by epoxy resin is improved. Under the premise of adding the same amount of epoxy resin, different modification methods have little difference in improving the thermal stability.

3.3 The effect of DMPA Content on the Properties of Emulsion and Film

The effects of DMPA content on the properties of waterborne polyurethane emulsion and film were investigated with other conditions unchanged. The results are shown in Table 1.

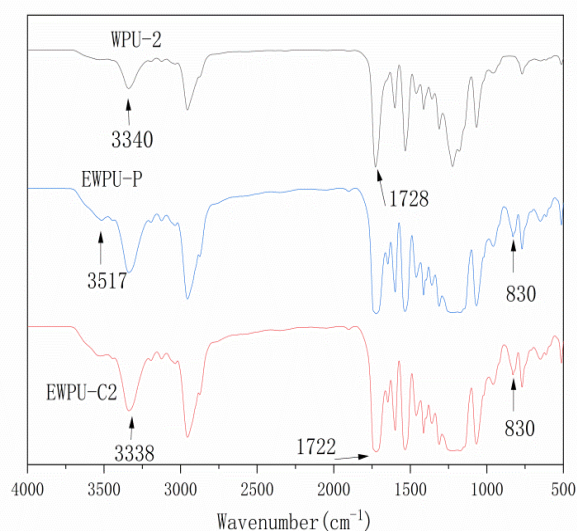


Fig. 1. Infrared spectra of waterborne polyurethane modified by epoxy resin

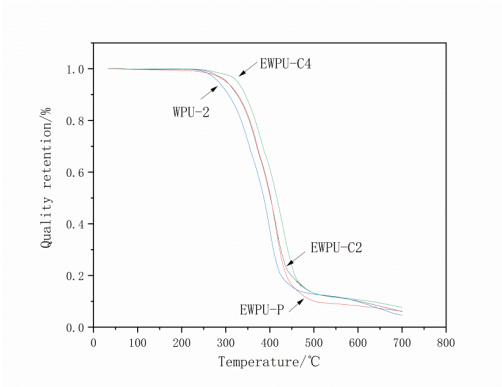


Fig. 2. TG curve of waterborne polyurethane modified by epoxy resin

Table 1. The effect of DMPA content on the properties of emulsion and film

Sample	WPU-1	WPU-2	WPU-3
The content of DMPA / wt%	3	4	5
α / %	8.68	11.97	19.26
Hardness	HB	HB	H
Storage stability	>6 month	>6 month	>6 month
Tensile strength /MPa	6.42	8.66	10.2
Elongation at break /%	745.69	615.78	549.31

Table 2. Effect of epoxy resin modification methods on properties of emulsion and film

Sample	WPU-2	EWPU-P	EWPU-C2
Modification	None	physical	chemical
Hardness	HB	H	H
Storage stability	>6 month	>6 month	>6 month
α /%	11.97	10.85	9.16
Water resistance (48h)	A small amount of white	Mild white	Mild white
β_{NaOH} /%	13.56	11.06	9.21
Alkali resistance (48h)	Part of the white	Part of the white	A small amount of white
β_{EtOH} /%	20.58	14.36	12.82
Resistance to organic solvents (48h)	A small amount of white	A small amount of white	No white

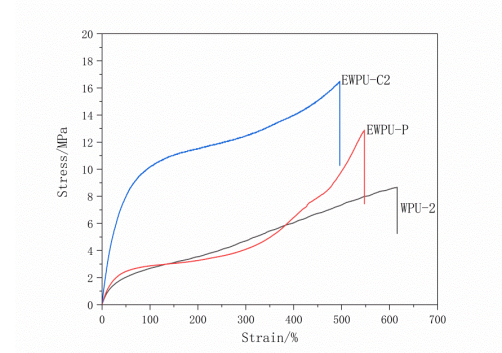


Fig. 3. Effect of modification methods of epoxy resin on mechanical properties of adhesive film

It can be seen from the table that when DMPA content is 4wt%, the comprehensive performance of waterborne polyurethane emulsion and film is the best.

3.4 Effect of Epoxy Resin Modification Methods on Properties of Emulsion and Film

The content of DMPA is 4wt%, and the addition of E-44 is 4wt%, keeping other conditions unchanged. Physical modification and chemical modification were adopted to add epoxy resin E-44, and the results are shown in Table 2.

Samples WPU-2, EWPU-P and EWPU-C2 were taken for mechanical properties test, and the results were shown in Fig. 3.

It can be seen from Table 2 that both chemical modification and physical modification increased the hardness of the film from HB to H. The water absorption of the film was reduced from 11.97% to 10.85% and 9.16%, the swelling rate of NaOH was reduced from 13.56% to 11.06% and 9.21%, and the swelling rate of ethanol was reduced from 20.58% to 14.36% and 12.82%. The water resistance, alkali resistance and organic solvent resistance of the film prepared by chemical modification are better than that of physical modification. According to Fig. 3, the tensile strength of the film was increased from 8.66MPa to 12.88MPa and 16.49MPa by physical and chemical modification, and the elongation at break was decreased from 615.78% to 547.26% and 496.07%. In general, the overall performance of the film prepared by chemical modification is better than that of physical modification.

3.5 Effect of Epoxy Resin Dosage on Properties of Emulsion and Film

The waterborne polyurethane emulsion modified by epoxy resin was prepared by chemical modification, and the influence of the amount of

epoxy resin added on the properties of emulsion and adhesive film was investigated. The results are shown in Table 3.

With the increase of the amount of epoxy resin added, the viscosity of the prepolymer becomes more and more viscous, and excessive deionized water is needed to produce reverse transformation, which makes emulsification more and more difficult. As can be seen from the table, with the increase of the amount of epoxy resin added, the hardness of the film is getting better and better, the viscosity of the emulsion is getting more and more viscous, but the stability becomes worse. Wang Jian et al. [17] enhance the pencil hardness from B to HB by introducing E-51. This is because the epoxy groups on the epoxy resin are ring-opened under the catalysis of the neutralizer TEA, and the slow reaction between them leads to cross-linking, resulting in the decline of emulsion stability [20].

The mechanical properties of WPU-2, EWPU-C1, EWPU-C2, EWPU-C3 and EWPU-C4 were tested.

As can be seen from the figure, when the epoxy resin content increases, the tensile strength of the film increases significantly, and the elongation at break decreases significantly, from the initial 8.66MPa and 615.78% to 24.24MPa and 349.99%. Zhan Biao [16] enhance the tensile strength from 10.47MPa to 15.61MPa by introducing E-44. This is because the introduction of epoxy resin rigid chain and the increase of molecular branch chain improve the degree of cross-linking of the whole system, and the increase of benzene ring content increases the content of polyurethane hard segment and the rigidity [21].

Samples WPU-2, EWPU-C1, EWPU-C2, EWPU-C3 and EWPU-C4 were tested for water resistance and solvent resistance.

Table 3. Effect of epoxy resin dosage on properties of emulsion and film

Sample	E-44 content /wt %	Hardnes	Viscosity /MPa.S	Appearance	Storage stability
WPU-2	0	HB	93.55	Translucent (Y ^a)	>6 month
EWPU-C1	2	HB	112.84	Translucent (W ^b)	>6 month
EWPU-C2	4	H	127.29	Translucent (W ^b)	>6 month
EWPU-C3	6	H	148.53	Milky	>6 month
EWPU-C4	8	2H	165.36	Milky	<6 month

^a Y means yellow; ^b W means white

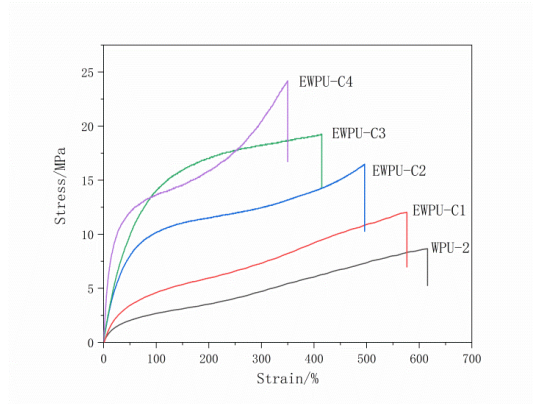


Fig. 4. Effect of epoxy resin dosage on mechanical properties of adhesive film

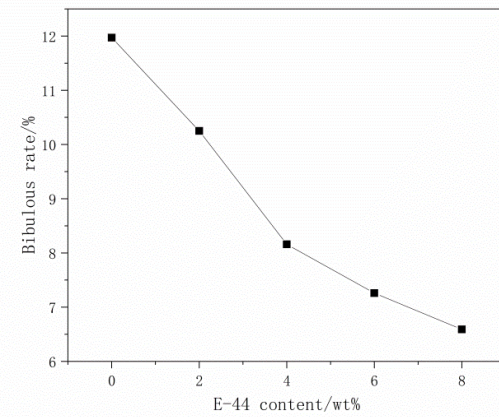


Fig. 5. Effect of epoxy resin dosage on water absorption

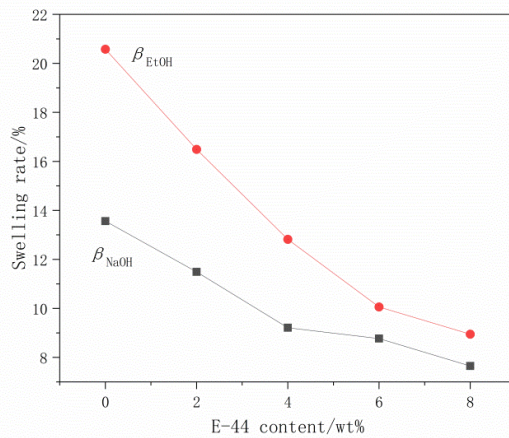


Fig. 6. Effect of epoxy resin dosage on swelling rate

As can be seen from Figure 5, the water absorption rate of the film decreased from 11.97% to 6.59%. As can be seen from Figure 6, the swelling rate of sodium hydroxide of the film decreased from 13.56% to 7.65%, and the swelling rate of ethanol decreased from 20.58% to 8.95%. Zhan Biao [16] reduced the water absorption rate of the film from 11.46% to 8.23% and Wang Jian et al. [17] reduced the water absorption rate of the film from 33.1% to 14.1% by introducing E-51. With the increase of epoxy resin dosage, the water absorption rate, NaOH swelling rate and ethanol swelling rate of the film decreased significantly, and the trend slowed down with the increase of epoxy resin dosage. This is because the cross-linked structure formed makes it more difficult for the liquid to penetrate and diffuse into the film, and when the amount of epoxy resin increased to 8wt%, the cross-linked structure gradually became saturated.

4. CONCLUSION

In this paper, waterborne polyurethane emulsion and epoxy resin modified waterborne polyurethane emulsion were synthesized, and the effects of DMPA content, epoxy resin E-44 addition amount and modification method on the properties were systematically studied. When the DMPA content is 4wt%, the comprehensive performance of waterborne polyurethane emulsion and film is the best. The water resistance, alkali resistance, organic solvent resistance and tensile strength of the film prepared by chemical modification are better than those of physical modification, and the hardness and thermal stability have no obvious difference. The overall performance of the film prepared by chemical modification is better than that of physical modification. With the addition of epoxy resin, the hardness, water resistance, solvent resistance, thermal stability and tensile strength of waterborne polyurethane film were increased to a certain extent, while the elongation at break was decreased. When the addition of epoxy resin was 8wt%, the storage stability was decreased obviously. The optimum dosage of epoxy resin is 6wt%.

DISCLAIMER

The products used for this research are commonly and predominantly use products in our area of research and country. There is absolutely no conflict of interest between the authors and producers of the products because we do not intend to use these products as an avenue for

any litigation but for the advancement of knowledge. Also, the research was not funded by the producing company rather it was funded by personal efforts of the authors.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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