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# Studies on particle size of waterborne emulsions derived from epoxy resin

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**Abstract**

The bisphenol type epoxy resin has been modified by *p*-aminobenzoic acid, that leads to the formation of a product with both hydrophilic and lipophilic properties. The factors influencing the emulsion particle size of the modified resins were investigated, namely, neutralization value, solvent polarity, dripping speed of water and initial solid content. The particle morphology of the waterborne emulsion was also studied. Another aspect surveyed was the conductivity variation during the emulsification process. © 2001 Elsevier Science Ltd. All rights reserved.

*Keywords:* Epoxy resin; Waterborne emulsion; Particle size; Morphology; Conductivity

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## 1. Introduction

With the environmental criteria becoming stricter, waterborne coating has been gaining importance in the modern coating industry. The use of waterborne coatings has made it possible to control pollution, to reduce risks of fire, and to improve aspects of occupational health and safety [1]. Epoxy resin is one of the most important materials in coating industry. The manufacture of its waterborne emulsion has received considerable attention in industrial field.

There are two ways to produce waterborne epoxy emulsion [2]. One is dependent on the external emulsifier to make the resin dispersed in water. The other is by way of chemical modification to introduce polar groups which confer water dispersibility to the resin. The former technology is simpler and cheaper, while the latter one can achieve very fine and well distributed emulsion (nm particles).

This paper intends to discuss the factors influencing particle size and the morphology of waterborne emulsion of epoxy resin by chemical modification.

## 2. Experimental

### 2.1. Materials

The epoxy resin used was a liquid bisphenol-A-type epoxy resin (E44, Wuxi Resin Factory, China, weight of epoxy equivalent is 459 g/eq), *p*-aminobenzoic acid, AR, Wulian Chemical Industry, China. Ethanolamine, CP, and ethylene glycol monobutyl ether, CP, Guangzhou Xingang Chemical Factory; DMF, CP, Guangzhou Xingang Chemical Factory.

### 2.2. Modification reaction [3]

A 500 ml four-necked flask equipped with stirrer, nitrogen blanket, thermometer, condenser and heating mantle was charged with E44. Ethylene glycol monobutyl ether and ethanol (2/1, v/v) are also added. The temperature is raised to 80°C until the resin is dissolved. Equivalent amount of *p*-aminobenzoic acid is then added. The temperature is maintained at 80°C for 13.5 h for the reaction to complete. The product was washed with a mixed solvent of ethanol and water (1/5, v/v). Then it was dried in a vacuum for 48 h before characterization.

The epoxy resin and the modified epoxy resin were assigned as EP and PABA-EP respectively.

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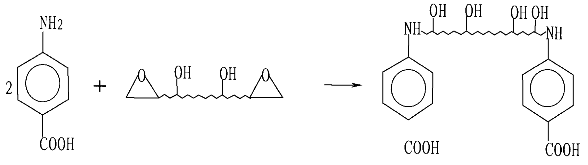

### 2.3. Emulsification procedure

The modified resin was dissolved in DMF. Then the solution was neutralized by a certain amount of ethanolamine. Emulsification was carried out by dropping deionized water slowly to the solution of the modified resin at ambient temperature with constant agitation.

### 2.4. Measurements

The particle size of the emulsions was obtained by using MALVERN Autosizer Lo-C. The 670 nm of laser wavelength and the 90° scattering angle were used. TEM studies were made by using JEM-1010 electron microscope. The conductivity variations during the emulsification process were measured by utilizing DDS-11A at ambient temperature.

## 3. Results and discussion

### 3.1. Factors influencing particle size

Research has been conducted on the factors influencing the particle size. In summary, the particle size was related to the neutralization value of carboxylic acid groups in PABA-EP, the solvent polarity, the dripping speed of water, and the initial solid contents. The results were illustrated in Figs. 1–4.

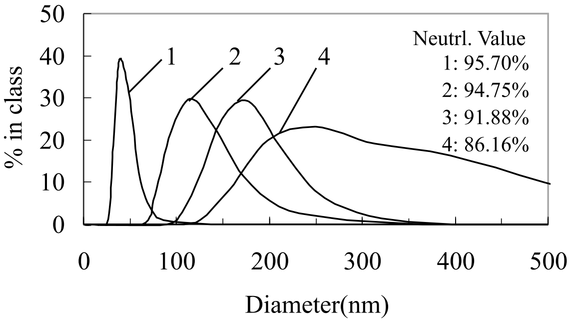

Fig. 1. The influence of neutralization value on particle size. With the amount of the neutralizer (ethanolamine) increasing, the particle size of the waterborne emulsion ranged from large to small.

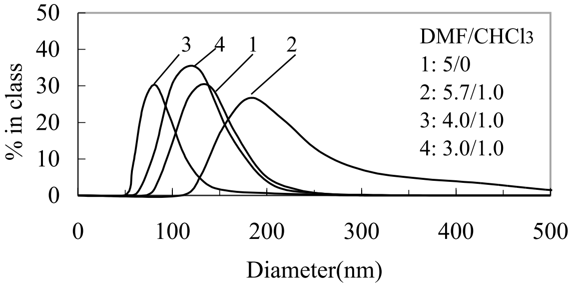

Fig. 2. The influence of solvent polarity on particle size – the finest particles were obtained for the solvent system of DMF/$CHCl_3$, 4.0/1.0, it seems an optimum polarity existing for the molecular chain in the state of isolated but relatively expanded which was conducive to form smaller particle during emulsification process.

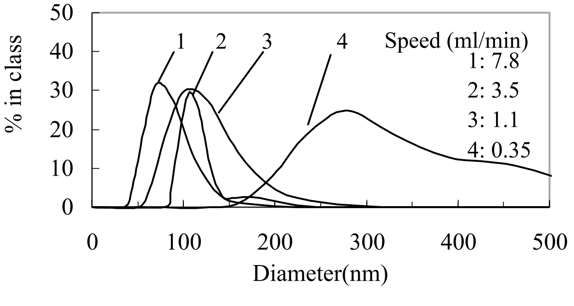

Fig. 3. The influence of the dripping speed of water on particle size – during the emulsification process, the faster the water dripped, the smaller the particle size.

The hydrophilicity of the carboxylic acid groups in the modified resin was greatly enhanced after neutralization because of the dissociation between the carboxylic groups on the modified epoxy resin chains. So with the amount of the neutralizer (ethanolamine) increasing, the modified resin displayed different morphology in water, ranging from opaque cream to semi-transparent emulsion and the particle size in emulsion corresponded from large to small. The solvent polarity influenced the state of the molecular chains in solvent. From Fig. 2, it seems an optimum polarity existing for the molecular chain in the state of isolated but relatively expanded which was conducive to form smaller particle during emulsification process, thus the finest particles were obtained for the solvent system of DMF/$CHCl_3$, 4.0/1.0. And during the emulsification process, the faster the water dripped, the smaller the particle size. The explanation is that the molecular chain will agglomerate with time during the emulsification process. Higher initial solid contents produced smaller particle size in 4–6% of initial solid content solution. The modified resins with

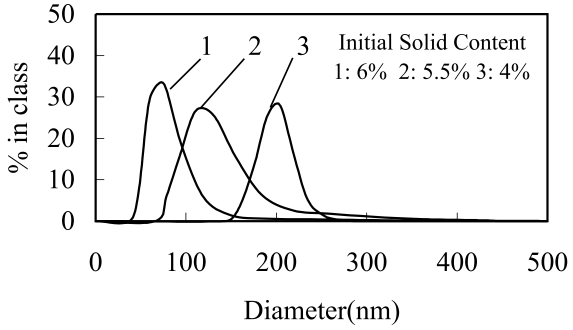

Fig. 4. The influence of the initial solid contents on particle size – higher initial solid contents produced smaller particle size in 4–6% of initial solid content solution.

different proportion of *p*-aminobenzoic acid had similar regularity in these aspects.

### 3.2. Morphology of emulsion particle

Fig. 5 shows the TEM images of the waterborne epoxy resin particles in different neutralization value systems. The particles of lower neutralization value system are more spherical and larger, while the shape of the smaller particles of the higher neutralization value system is not so regular and they are easy to undergo aggregation. And the particles in different solvent polarity system had the same regularity which was demonstrated in Fig. 6. The finest particles were produced in the solvent system of DMF/$CHCl_3$, 4.0/1.0.

### 3.3. Conductivity variation during emulsification process

The conductivity variations were extensively studied under different emulsification process. It was proposed in previous studies [4,5] on waterborne emulsion that the emulsification will undergo phase-inversion process. The system will change from water-in-oil condition to oil-in-water condition as the water content increasing.

Fig. 7 illustrated the conductivity variations during the emulsification process of different neutralization value system. Higher neutralization value leads to higher ion concentration. The ions tend to distribute at the surface of the particle and spread into the water phase. So with the water content of the system increasing, the ions dissociate gradually, which results in the increase of conductivity. At a certain ratio of water content, the system turned into oil-in-water condition and the dissociation of the ions reached equilibrium. Therefore, the conductivity of the system was nearly stable after the phase-inversion point.

In solvent system of lower polarity, the polar groups tend to extend more completely into the water phase. So

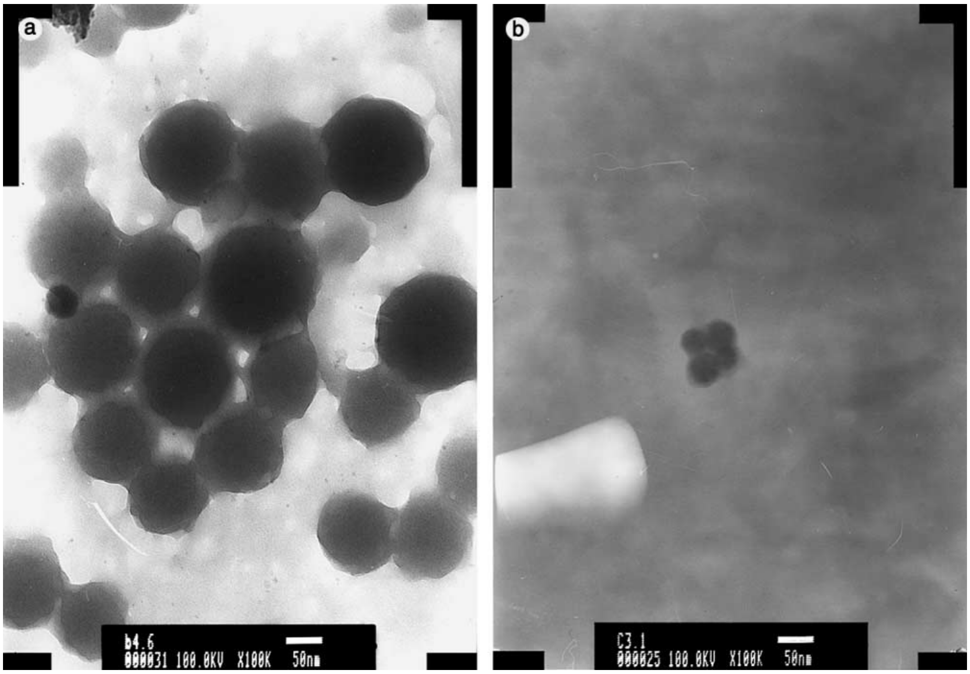

Fig. 5. Transmission electron micrograph of the waterborne epoxy emulsion of different neutralization value system. Neutralization value: (a) 91.88%, (b) 95.70%. The particles of lower neutralization value system are more spherical and larger, while the shape of the smaller particles of the higher neutralization value system is not so regular and they are easy to undergo aggregation.

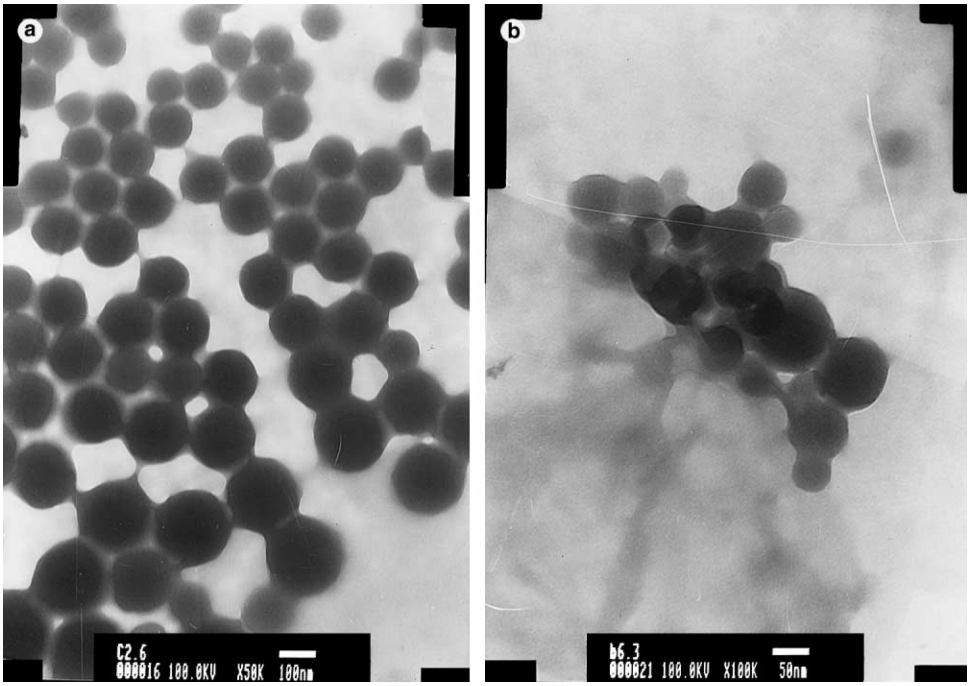

Fig. 6. Transmission electron micrograph of the waterborne epoxy emulsion of different solvent polarity system. DMF/$CH_3Cl$: (a) 4.25/0.75, (b) 4.0/1.0. The finest particles were produced in the solvent system of DMF/$CHCl_3$, 4.0/1.0.

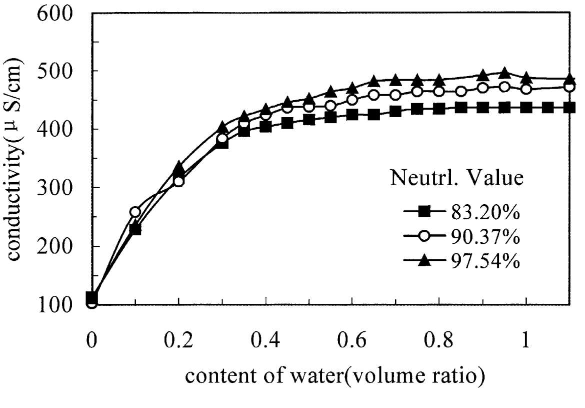

Fig. 7. Conductivity variations during the emulsification process of different neutralization value system – with the water content of the system increasing, the ions dissociate gradually, which results in the increase of conductivity. At a certain ratio of water content, the conductivity of the system was nearly stable after the phase-inversion point.

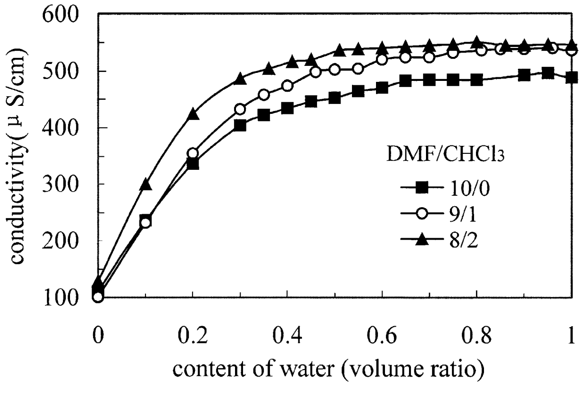

Fig. 8. Conductivity variation during the emulsification process of different solvent system – the conductivity of lower polarity system was higher than that of the higher polarity system. The difference became smaller as the solvent polarity decreasing.

its conductivity was higher than that of the higher polarity system. But the difference became smaller as the solvent polarity decreasing. This was demonstrated in Fig. 8.

Fig. 9 shows the relationship between conductivity variation and initial solid content. Higher initial solid content produced higher ion concentration. So after reaching the equilibrium, the conductivity is directly proportional to the initial solid content.

During the emulsification process, the particles formed with water content increasing. And they will undergo aggregation with time. At lower water content system, there weren't enough dissociated ions on the surface to stabilize the particle in water. So it would aggregate with time at a faster rate and the amount of ions at the surface of the particle declined because of

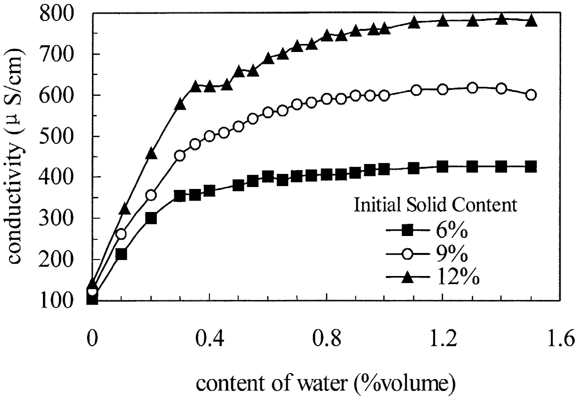

Fig. 9. Conductivity variation during emulsification process of different initial solid content system – after reaching the equilibrium, the conductivity is directly proportional to the initial solid content.

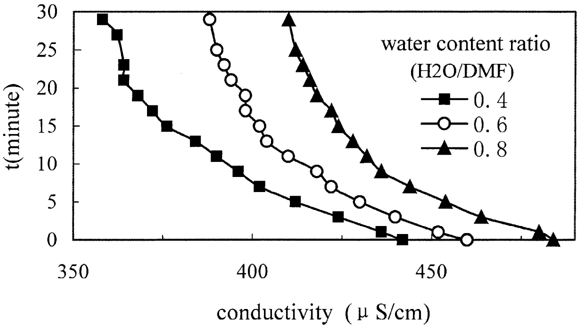

Fig. 10. Conductivity variation with time of different water content ratio system – at lower water content system, there weren't enough dissociated ions on the surface to stabilize the particle in water. So it would aggregate with time at a faster rate and the amount of ions at the surface of the particle declined. The decrease of ions brought about the lowering of conductivity.

burying. The decrease of ions amount brought about the lowering of conductivity as was showed in Fig. 10. This was also in good agreement with the phenomena that high dripping speed produced finer particle, which was demonstrated in Fig. 3.

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