

PREPARATION OF WATERBORNE ULTRAFINE PARTICLES OF EPOXY RESIN BY PHASE INVERSION TECHNIQUE*

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ABSTRACT

Waterborne ultrafine particles of epoxy resin were prepared by phase inversion technique. The results of SEM revealed that the particles diameter was in the range of 50 to 100 nm and the effects on amount of water required at phase inversion point were also discussed.

INTRODUCTION

Waterborne systems of polymer resins, free of organic solvent, could completely fulfill both the requirements of environmental protection and low cost, besides, their operation performance is good even at high concentration of polymer resins owing to low viscosity and strong shearing thinning effect. So, studies on these systems are appealing. The well-known emulsion polymerization method is only effective for preparing the waterborne systems of addition polymers, but it is not applicable to condensation polymers whose properties are better. On the contrary, phase inversion technique for preparing polymer resin waterborne systems is applicable to both addition polymers and condensation polymers.

Phase inversion refers to the continuous phase transformation from oil to water (or vice versa) in emulsions^[1]. In the vicinity of phase inversion point, emulsion with

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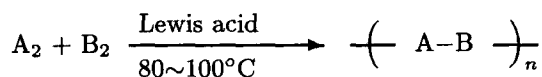
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minimum dispersed phase size could be obtained^[2]. Thus, the emulsifying method to prepare emulsions with minimum dispersed phase size near the phase inversion point is called phase inversion technique which holds for emulsifying polymer resins. So, it is deduced that waterborne systems of polymer resins with small particles could also be obtained by phase inversion technique^[3-4].

EXPERIMENTAL

Synthesis and characterization of polymer emulsifiers

The polymeric emulsifier was synthesized by polycondensation between two bi-functional oligomers containing bifunctional groups, e.g., PEG 10000 (A_2 , hydrophilic component) and Bisphenol A Epoxy Resin E-20 (B_2 , lyophilic component) under action of Lewis acid. The reaction can be represented as follows:



The samples for GPC experiment were dissolved in CH_2Cl_2 , and LC-4A type GPC with ultraviolet detector was used.

Preparation of bisphenol A epoxy resin waterborne system with ultrafine particles by phase inversion technique

The mixture of bisphenol A epoxy resin E-20 (supplied by Chemicals Co. of East Tianjin) and the above mentioned polymeric emulsifier was stirred to be homogeneous at a certain temperature, and deionized water droplet was added to the mixture until the conductance of the system increased abruptly which meant the phase inversion occurred, when the system was dispersible in water. Then, much cold deionized water was added to cool and dilute the inversed systems.

The S-530 SEM was utilized to determine the particles size, and the samples were prepared by air drying the very diluted systems.

RESULTS AND DISCUSSION

Analysis of the polymeric emulsifier

It is well-known that the structural characteristics (e.g. property of hydrophilic-lyophilic balance) of emulsifier play a key role in preparing emulsion. Such is the case in emulsifying polymer resins by phase inversion technique. Appearance contrast test of aqueous solutions of polymeric emulsifier (synthetic product between A_2

and B_2 at 1:1 molar ratio) and A_2/B_2 simple mixture in Table 1 shows that the former aqueous solution exhibits one phase behavior, while the latter one exhibits two phases behavior.

Table 1 Contrast test between emulsifier and mixture

Sample	Water solubility	Foam stability	Centrifugation
Emulsifier (with catalyst)	homogeneous, clear	stable	homogeneous, clear
A_2/B_2 mixture (no catalyst)	milky	unstable	two layers

It is pointed out that the ultraviolet detector is used in GPC, where only the B_2 lyophilic component can be detected. The results of GPC (Figure 1) indicate that the position of peak of the lyophilic component (B_2) in the above-mentioned polymeric emulsifier shifts to lower position (curve a), on the contrary, that one in A_2/B_2 mixture (curve b) is almost similar to that of pure B_2 (curve c). It is clear that the molecular weight of the polymeric emulsifier with B_2 component becomes larger. In another word, the polycondensation between the two oligomers (A_2 and B_2) catalyzed by Lewis acid occurred definitely, therefore the polymeric emulsifier could be synthesized. What is more, it is reasonable to deduce that the property of hydrophilic-lyophilic balance of the polymeric emulsifier could be adjusted by controlling the molar ratio as well as molecular weight of A_2 and B_2 oligomers^[5].

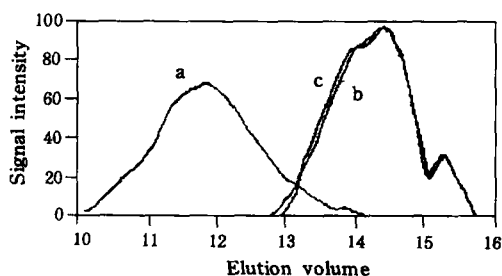


Fig. 1 GPC curve (a) polymeric emulsifier; (b) A_2/B_2 mixture; (c) B_2 oligomer

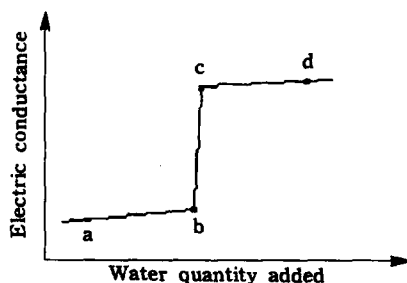


Fig. 2 Effect of quantity of water added on electric conductance

Analysis of the epoxy resin waterborne systems

The relationship between electric conductance and the quantity of water added during preparing the waterborne systems is quantitatively illustrated in Fig. 2. It is indicated that the continuous phase changes abruptly from epoxy resin of lower electric conductance (ab region) to water of higher electric conductance (cd region) with the increase of amount of water added. Thus, the bc region is called phase inversion zone. The systems in region cd are dispersible in water.

The results of SEM (Fig. 3) show that the particles size are very small within the range of 50~100 nm.

The study on the effects of amount of water required at phase inversion point could help to understand the characteristics of the polymeric emulsifier^[6].

The effect of emulsifying temperature on R_w (weight ratio of amount of water required at phase inversion to epoxy resin) is illustrated in Fig. 4. The results that R_w is less than 1 and decreases with lowering of emulsifying temperature show that the polymeric emulsifier is more hydrophilic and the tendency could become more hydrophilic with lowering of temperature due to increasing interaction between water and PEG hydrophilic component in the emulsifier^[7].

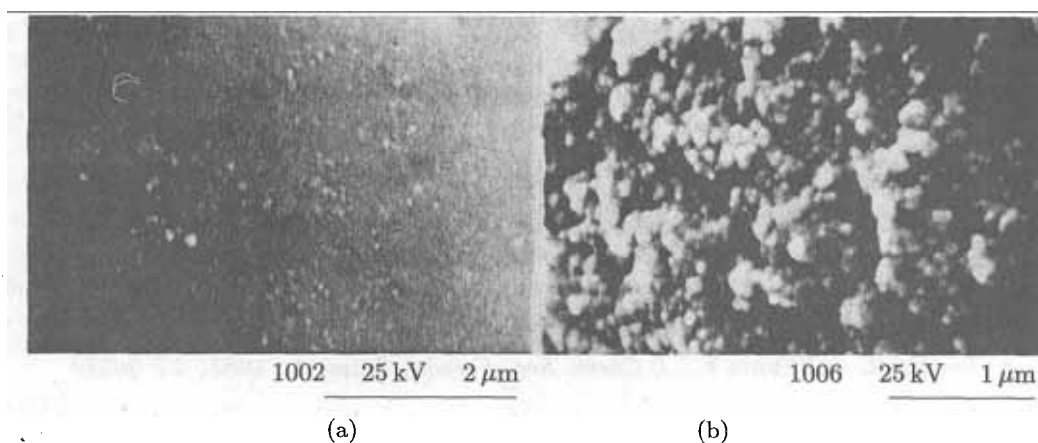


Fig. 3 Morphology of ultrafine particles by SEM
Emulsifying temperature (a) 89.0°C; (b) 82.0°C

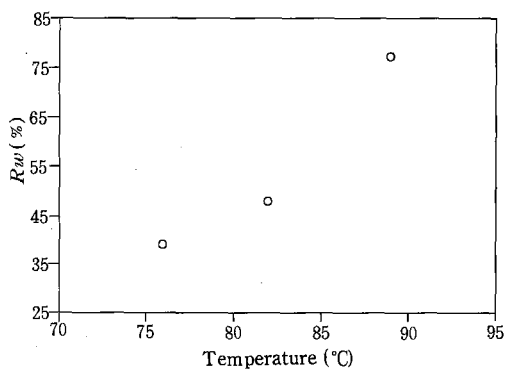


Fig. 4 Effect of emulsifying temperature on R_w

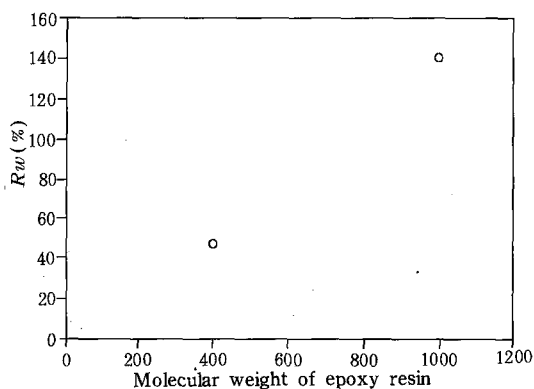


Fig. 5 Effect of molecular weight of epoxy resin on R_w

The effect of M_w of epoxy resin on R_w is illustrated in Fig. 5. The result that R_w

increases with decreasing molecular weight of epoxy resin shows that the polymeric emulsifier becomes more lyophilic owing to more oil molecules acting on the lyophilic component of the emulsifier.

So, it is concluded that the title particles can be prepared by phase inversion technique, and the phase inversion progression of emulsifying polymer resin is affected by many factors, such as the structure of polymeric emulsifier and the characteristics of oil phase (e.g. molecular weight).

Keywords:

Waterborne, Ultrafine particles; Bisphenol A epoxy resin; Phase inversion technique

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