

PREPARATION OF BISPHENOL A EPOXY RESIN WATERBORNE DISPERSIONS BY THE PHASE INVERSION EMULSIFICATION TECHNIQUE*

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Abstract The phase inversion emulsification technique (PIET) is an effective physical method for preparing waterborne dispersions of polymer resins. Some results concerning the preparation of bisphenol A epoxy resin waterborne dispersions by PIET in our laboratory were summarized. Electrical properties, rheological behavior and morphological evolution during phase inversion progress were systematically characterized. The effects of the emulsifier concentration and emulsification temperature on phase inversion progress and the structural features of the waterborne particles were studied as well. The deformation and break up of water drops in a shear field were analyzed in terms of micro-rheology, while the interaction and coalescence dynamics of water drops were discussed in terms of DLVO theory and Smoluchowski effective collision theory, respectively. Based on the experimental results and theoretical analysis, a physical model of phase inversion progress was suggested, by which the effects of the parameters on phase inversion progress and the structural features of the waterborne particles were interpreted and predicted.

Keywords Phase inversion, Emulsification, Waterborne dispersions, Epoxy resin, Mechanism, Physical model

INTRODUCTION

Waterborne dispersions with low or zero content of volatile organic compounds have gained much attention owing to stringent worldwide environmental regulations. The methods used to prepare waterborne dispersions are classified into two categories: chemical polymerization and physical method. The former one (such as emulsion polymerization) has been extensively investigated for preparation of polymer latex by radical initiation and propagation reaction. However, it is not applicable to preparation of the waterborne system of condensed polymer such as epoxy resin and poly-(ethersulfone). In comparison, the phase inversion emulsification technique, a physical method, is very effective for preparing waterborne dispersions of polymer resins including addition polymers and condensation polymers. In principle, almost all polymers could be emulsified to produce waterborne dispersions. Thus, the polymer dispersions of this sort could be greatly extended.

The term of phase inversion originally refers to the continuous phase transformation from oil to water (or vice versa) in emulsions composed of small molecules. In the vicinity of the phase inversion point, the interfacial tension between oil and water phases reaches a minimum and the emulsion with small size of dispersed phase could be obtained^[1, 2]. A similar idea could be applied to preparation of waterborne dispersions of polymer resins with small particle size. However, the published results concerned are almost all focused on the preparation of the products and their formulations^[3-5]. The studies on phase inversion mechanisms are relatively scarce yet urgently needed.

In this summary, developments in the production of waterborne dispersions of bisphenol A epoxy resin

* This work was supported by the National Key Project for Fundamental Research, "Macromolecular Condensed State" of Ministry of Science and Technology of China and National Natural Science Foundation of China 29774038.

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Received February 25, 1999

undertaken in our laboratory is presented. The variations of electrical properties and rheological behavior with morphological evolution during phase inversion progress were systematically investigated in order to disclose the mechanism of phase inversion progress. A physical model of phase inversion progress was suggested on the basis of the experimental facts and theoretical analysis of the deformation and break-up of water drops in terms of micro-rheology as well as the interactions among the water droplets according to DLVO theory.

RESULTS AND DISCUSSIONS

Characterization of Complete Phase Inversion Progress^[6]

The experimental details could be found in the references^[7, 8]. Briefly speaking, water was added continuously to a mixture of polymer resin and emulsifier under shear field until the electrical resistance of the system dropped abruptly. This means the continuous phase has been inverted from resin to water and the waterborne dispersion could be obtained. It was previously reported that the phase inversion is complete at the phase inversion point (PIP) when emulsification temperature is relatively low (e.g. 73 °C) and the emulsifier concentration (e.g. 10.90%) is high. This part is focused on the relationship between the relevant properties and morphological evolution during complete phase inversion progress. During the emulsification experiment, it was found that both impedance and phase angle dropped abruptly while the speed of the driving motor accelerated suddenly at a critical water content. From Fig. 1 showing the dependence of electrical properties on water content, it is seen that the critical water content is 27.91%. This means the continuous phase has inverted from epoxy resin to water phase at water content 27.91%. This water content is defined as phase inversion point (PIP). The fact that electrical properties are less dependent on water content after PIP indicates that the phase inversion has completely finished at PIP.

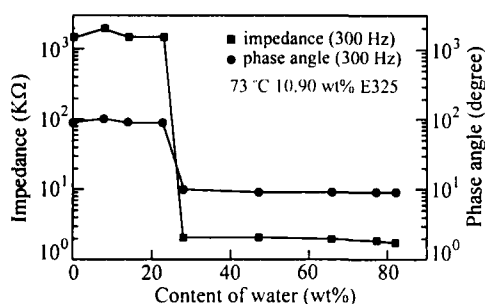


Fig. 1 Changes of the electrical properties with water content during phase inversion progress

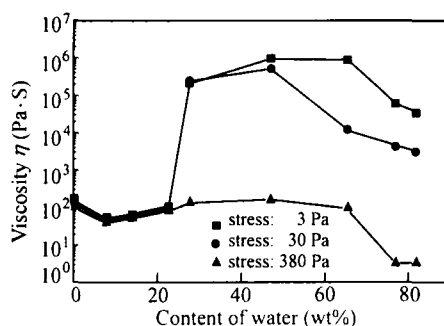


Fig. 2 Dependence of shear viscosity on water content at the three typical stress levels

Figure 2 shows the dependence of shear viscosity on water content at three typical stress levels in stress sweep test during phase inversion progress. The viscosity at lower stress (3 Pa) increases abruptly by 3000 times at PIP and the viscosity at higher stress (380 Pa) decreases profoundly. This is attributed to the formation of a static structure from waterborne particles and the breakup of the static structure at higher stress. The system before PIP is a Newtonian fluid evidenced by the less dependent viscosity on stress. Figure 3 shows the dependence of storage modulus on water content at the three typical frequency levels in dynamic frequency sweep test during phase inversion progress. It is shown that the storage modulus increases abruptly at PIP and the modulus becomes less dependent on frequency. This means that the system at PIP is highly viscoelastic.

In summary, the system before PIP is a Newtonian fluid, and the system is highly viscoelastic at PIP owing to the formation of a static structure from the waterborne particles.

The typical morphological evolution during phase inversion progress is illustrated in Fig. 4. In Fig. 4a) (22.87% water content), there exist small particles in some local regions even before PIP, which have resulted from partial phase inversion due to local fluctuations both in water concentration and in temperature. When the system reaches PIP, all epoxy resin is inverted to the waterborne particles as shown in Fig. 4b). Moreover, it is

found that there exists necklace alike structure composed of waterborne particles. This helps us to elucidate the phase inversion progress, which will be discussed below.

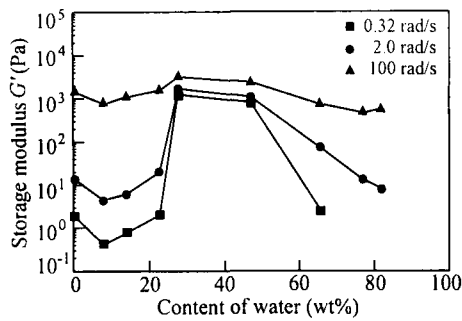


Fig. 3 Dependence of storage modulus on water content at the three typical frequency levels

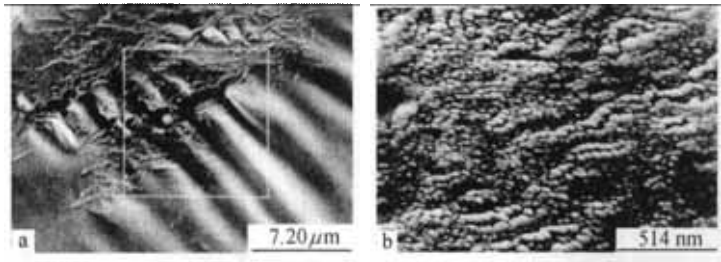


Fig. 4 Morphological evolution with complete phase inversion progress Water content of a) 22.87%, b) 27.91%

Characterization of Incomplete Phase Inversion Progress^[9]

Compared with complete phase inversion progress, the phase inversion is not completely finished at PIP when the emulsifier concentration is lower. As an example, the emulsifier concentration is 2.33% and the emulsification temperature is 80 °C. Figure 5 shows the relation between the electrical properties and water content. When water content reaches the critical value 24.65%, both impedance and phase angle drop abruptly. This means the continuous phase has inverted from epoxy resin to water. This water content 24.65% is defined as PIP. Both impedance and phase angle decrease progressively with water content after PIP. This means the progressive occurrence of partial phase inversion in the system even after PIP. Form this viewpoint, the phase inversion is not completely finished at PIP.

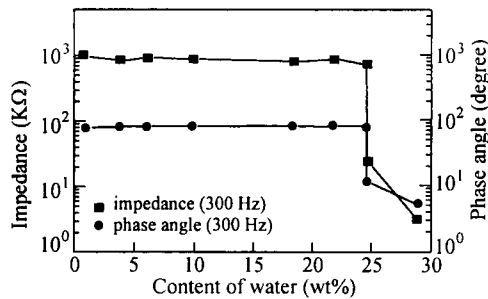


Fig. 5 Changes of the electrical properties with water content during phase inversion progress

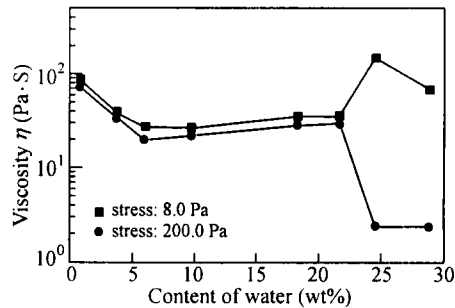


Fig. 6 Dependence of shear viscosity on water content at the two typical stress levels

The dependence of shear viscosity on water content at the two typical stress levels is given in Fig. 6. It can be seen that the viscosity is less dependent on stress before PIP, which is the characteristic of a Newtonian fluid. The viscosity at higher stress decreases pronouncedly at PIP, which is the characteristic of pseudoplasticity. This is consistent with the fact that the speed of the driven motor accelerated suddenly at PIP during the emulsification experiment. The viscosity at lower stress increases slightly at PIP, which is attributed to the weak interaction among the waterborne structure. However, this increase is not so pronounced compared with the complete phase inversion. This could be explained by local lubrication by a large domain of water phase among the waterborne structure.

Figure 7 shows the relationship between storage modulus and frequency in the dynamic frequency sweep test during the phase inversion progress. It can be seen that the storage modulus reaches a minimum at PIP and the storage modulus increases with water content after PIP. This is related with the complicated structure of the inverted system.

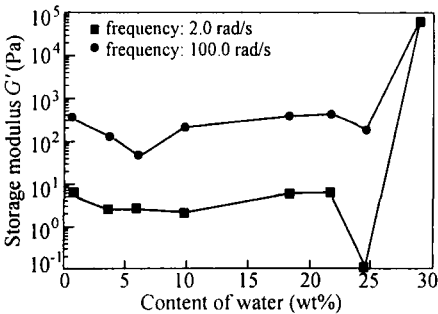


Fig. 7 Dependence of storage modulus on water content at the two typical frequency levels

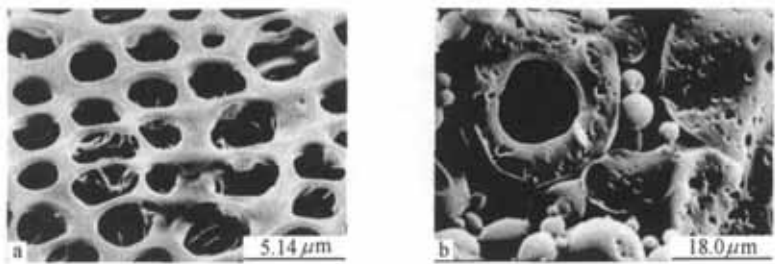


Fig. 8 Morphological evolution with incomplete phase inversion progress
Water content of a) 24.64%, b) 24.65%

When the water content was high enough before PIP, partial phase inversion occurred in local regions (see Fig. 8a)). However, this is completely different from the case of complete phase inversion. In Fig. 8a), an interconnected network could be found in some local regions. In Fig. 8b) at PIP, it can be seen that the inverted system is W/O/W structure of larger size and broad size distribution. This structural feature of the particles helps us to understand the complicated relationship between the electrical properties and the rheological behavior during the phase inversion progress.

The Effects of Some Parameters on Phase Inversion Progress

The effects of emulsifier concentration and emulsification temperature on the critical water content required at PIP are given in Fig. 9 and Fig. 10, respectively. In Fig. 9, the effect of emulsifier concentration on water content is not very pronounced when emulsifier concentration exceeds 5%, which could be explained by the saturation of emulsifier molecules at water/resin interface layers. In Fig. 10, it can be seen that the critical water content increases with temperature, which could be explained by the decrease in attraction with temperature.

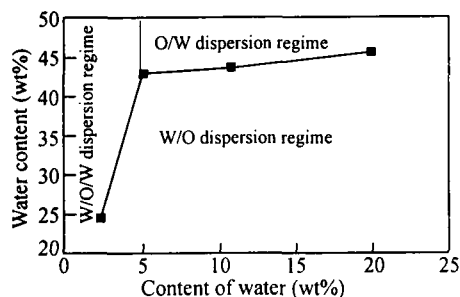


Fig. 9 Dependence of water content at the phase inversion point on the emulsifier concentration

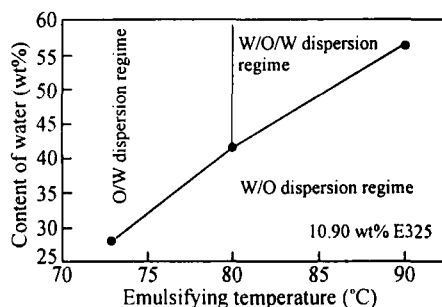


Fig. 10 Dependence of water content at the phase inversion point on emulsification temperature

Besides, the effects of the parameters on structural features of the waterborne particles are also considerable. As indicated in Fig. 9 and Fig. 10, when the emulsification temperature is lower and the emulsifier concentration is higher, the phase inversion progress is completely finished at PIP resulting in a waterborne dispersion of smaller particle size of narrower size distribution. On the contrary, when the temperature is higher and the emulsifier concentration is lower, a complex W/O/W structure is achieved by incomplete phase inversion. This has been confirmed by our experimental results^[10].

Mechanism of Phase Inversion Progress

In terms of Taylor's theorem discussing the deformation and breakup of water drops in a shear field^[11, 12], the water drops become fibril under the shear and extension field in the systems studied herein. When the water fibril structure reaches a critical diameter, surface capillary waves will be developed. Thus, the fibril structure becomes unstable and broken into smaller water droplets promoted especially by an oscillation field. This progress is called Rayleigh break up^[13-15].

Meanwhile, the emulsifier molecules diffuse to the water/resin interface to form an interfacial film. The dynamic coalescence among the water droplets could be impeded owing to the interfacial films. In this case, there exist two opposite courses of coalescence and breakup of the water droplets, which are influenced by many factors such as temperature, shear rate, viscoelasticity of the system. The coalescence dynamics of water droplets covered with emulsifier molecules could be analyzed in terms of the Smoluchowski theory developed by Davis and Rideal^[16]. When the emulsifier concentration is higher and the emulsification temperature is lower, the coalescence could be neglected owing to the stronger interfacial film and the particle size of sub-micron water droplets in a shear field is less influenced. Otherwise, the sub-micron water droplets will coalesce to form larger ones.

Besides the opposite courses of the water droplets, there also exist two opposite interactions: the attraction attributed to van der Waals forces as well as specific strong interaction of hydrogen bond and the entropy repulsion originating from the interfacial film. The attraction increases abruptly with the water content by decreasing the droplet separation when the volume fraction of the effective dispersed phase approaches a critical value while the repulsion is less influenced. When the attraction exceeds the repulsion, the phase inversion takes place. This is the criterion for phase inversion. Since a small amount of water could induce an abrupt increase in attraction when the water content reaches a critical value, the phase inversion takes place suddenly.

When the coalescence of water drops is neglected before the criteria are satisfied, the water drops will coalesce simultaneously to form a continuous phase and the system will be completely inverted to become waterborne particles with small size at PIP. When the coalescence is considerable, the phase inversion is incomplete and a complex w/o/w structure is achieved.

Another mode of driving phase inversion is to change the temperature at a given water content. This is induced by increasing the attraction strength among the water droplets with lowering temperature. Investigations on the mechanism of phase inversion progress, exploitation of this emulsification technique and the applications

of the products are in progress in our research group.

CONCLUSION

Some advances in achieving bisphenol A epoxy resin waterborne dispersions by phase inversion emulsification technique undertaken in our laboratory have been summarized. Electrical properties, rheological behavior and morphological evolution with phase inversion were systematically characterized. The effects of emulsifier concentration and temperature on phase inversion progress as well as the structural features of the waterborne dispersions were investigated. Based on the experimental results and theoretical analysis, a physical model was proposed to predict the phase inversion progress and the structural features of the waterborne particles.

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