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SHORT COMMUNICATION

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Preparation of waterborne dispersions of epoxy resin by the phase-inversion emulsification technique. 2. Theoretical consideration of the phase-inversion process

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Abstract A theoretical consideration of the phase-inversion technique to prepare waterborne particles based on the experimental facts of the phase inversion process given in part 1 of this series is presented. The deformation and breakup of the water droplets dispersed in an epoxy resin phase under shear action are analyzed in terms of microrheology. The interaction and coalescence dynamics among the water droplets stabilized by an interfacial layer formed by the emulsifier molecules are discussed in terms of Derjaguin–Landau–Verwey–Overbeek theory and effective collision theory, respectively. A criterion for the completion of phase-inversion is that the attraction among the water droplets exceeds the entropic repulsion. Thus, a physical model of phase-inversion is proposed to predict the effects of some control variables on the phase-inversion process as well as the structural features of the waterborne particles, by which the experimental results could be well interpreted. It is indicated that the achievement of phase inversion is determined by the dynamic coalescence among the water droplets before the phase-inversion point (PIP). If the dynamic coalescence among the water droplets is ignored, phase inversion is achieved completely and submicron-sized particles are prepared. In comparison, if the dynamic coalescence is significant, phase inversion is achieved incompletely and a large complex water-in-oil-in-water structure is prepared. In the case of complete phase inversion, it is shown that the size of the waterborne particles is comparable with the size of the water droplets before the PIP.

Key words Bisphenol A epoxy resin · Waterborne dispersions · Phase-inversion emulsification · Physical method · Mechanism

Introduction

The phase-inversion emulsification technique is an effective physical method for preparing waterborne dispersions of polymer resins. Recently, we have successfully prepared waterborne dispersions of bisphenol A epoxy resin [1].

In part 1 of this series of papers, an experimental study on the typical features of phase inversion was presented. It was found that the degree of completion of phase inversion is different under different conditions; the emulsifier concentration and the temperature are two main control variables which influence the completion of phase inversion. Phase inversion is accomplished more completely at the phase-inversion point (PIP) when the emulsification temperature is relatively low and the emulsifier concentration is relatively high. In comparison, phase inversion is incomplete when the temperature is high and the emulsifier concentration is low. In the former case, phase inversion is achieved through

simultaneous coalescence among the nearest water droplets, and all water droplets are inverted into the continuous phase at the PIP. The waterborne particles are sub-micron sized with a narrow particle size distribution. In the latter case, there is irreversible coalescence among the water droplets before the PIP and not all the water droplets are inverted into the continuous phase, with small water droplets being trapped in the waterborne structure at the PIP. Thus, a complex water-in-oil-in-water W/O/W structure is obtained.

The phase-inversion emulsification technique is an effective physical method for preparing waterborne dispersions of polymer resins. Almost all the work published in journals and patents has focused on the preparation of waterborne dispersions of polymer resins by phase inversion and their formulation; the mechanism has scarcely been reported. The mechanism of the phase-inversion process needs to be explained urgently in order to understand and utilize this technique better. Here, a theoretical consideration of the phase-inversion process is presented. Firstly, the deformation and breakup of the water phase under shear action are considered in terms of microrheology. Then, the expressions for interaction among the water droplets are given. Finally, a criterion for phase inversion is proposed and a physical model of phase inversion is given to predict the effects of some variables on the phase-inversion process as well as the structural features of the waterborne particles.

Discussions

Deformation and breakup of water phase under shear action

During the experiment, water was continuously added into the mixture of epoxy resin (E-20)/emulsifier (E325) to drive the phase inversion. Before the PIP, the amount of water is small and the water added is dispersed in the viscous mixture continuous phase. The water phase will become a fibril structure subjected to shear action. According to Taylor's theoretical analysis [2, 3], when the characteristic diameter of the fibril structure reaches a critical value, a kind of surface capillary wave is developed. Furthermore, the fibril structure will become unstable and will break into small water droplets owing to the evolution of the surface capillary wave; this is especially promoted by the extensional field [4–9]. This break process is of the Rayleigh type [10–12]. The dimensions and shapes of the small water droplets are related to the reduced capillary number, K^*, which is defined as the ratio of the capillary number to the critical capillary number. The reduced capillary number is dependent on the water-oil interfacial tension and the rheological parameters of the water and oil phases. The water phase continues to break-up until the dimension of the water droplets reaches a critical value [2–4] and the requirement $0.1 < K^* < 1$ is met. In this case, the final water droplets will be deformed to some extent and oriented by $\alpha = \pi/4$ with respect to the shear direction.

Meanwhile, emulsifier molecules diffuse onto the water/resin interfaces to form interfacial layers. This diffusion process is governed by many variables, such as the viscosity of the epoxy resin continuous phase, the molecular weight of the emulsifier, the miscibility of the emulsifier with the epoxy resin phase as well as water phases, the strength of the shear field, etc. It has been shown that some proper amphiphilic molecules with medium molecular weight at the interface can stabilize the dispersed phase [13–15]. In order to ensure enough stability of the dispersed phase, it is required that the rate for the amphiphilic molecules to diffuse onto the interfacial phase is not slower than the formation rate of the fresh interface. A dimensionless parameter, defined as $Pe = t_D/t_{def}$ [16], is used to describe this process, where t_D is the time required for the amphiphilic molecules to diffuse onto the interface and t_{def} is the time for a new interface to form. If $Pe < 1$, the interface freshly formed could be stabilized by the amphiphilic molecules. The molecular weight of the emulsifier is an important factor for determining the diffusion rate [17]: the lower the molecular weight, the faster the diffusion rate. However, the stabilization is not so remarkable as that of a high-molecular-weight emulsifier. In order to ensure sufficient stabilization, it is necessary for the segmental chain length of the emulsifier to reach the entanglement state [18]; however, an extremely high molecular weight will result in opposite effects, such as a slower diffusion rate and microphase separation in the continuous phase [19]. Therefore, it is recommended to use an emulsifier system with a double-peak molecular-weight distribution in order to balance the stabilization and the diffusion rate of the emulsifier. Moreover, the diffusion process could be promoted by increasing the shear rate. In the system studied here, there is a critical emulsifier concentration for the freshly formed surface to be saturated by emulsifier (a kind of amphiphilic molecule). Below this critical concentration, insufficient emulsifier molecules diffuse onto the interface to stabilize the dispersed phase. Therefore, the concentration of the emulsifier should exceed the critical concentration so as to ensure stabilization of the dispersed phase.

There is a dynamic equilibrium between breakup and coalescence among the water droplets under a shear field. The coalescence among the water droplets can be impeded by the interfacial film. The effects of other factors, such as temperature, shear rate, viscosity, on the coalescence are considerable as well. In terms of the Smoluchowski [20–22] theory developed by Davis and Rideal [23], the coalescence dynamics can be expressed by

$$-\frac{dn}{dt} = \frac{2}{3}kTn^2\frac{r}{\eta a}\exp\left(-\frac{E}{kT}\right) \quad , \tag{1}$$

where n is the number of dispersed phases, t is the time, η is the viscosity of the continuous phase, k is Boltzmann's constant, T is the absolute temperature, r is the radius of the dispersed phase, a is the collision radius and E is the energy barrier. A higher emulsifier concentration and a lower emulsification temperature will give rise to a higher energy barrier and a higher viscosity, respectively. According to Eq. (1), the coalescence among water droplets is ignored and the diameter of the water droplets remains unchanged in this case. The attraction among the water droplets will increase with the amount of water phase, thus a "necklace" structure composed of small water droplets is formed owing to their dynamic collision. It is noticed that the spherical contour is kept in the necklace structure as shown in step 3 in Fig. 1. From this viewpoint, the net coalescence is ignored. Otherwise, the coalescence is remarkable and large water drops are formed through the irreversible coalescence among the small water droplets. This dynamic coalescence among the water droplets before the PIP will determine the achievement of phase inversion.

Interactions among water droplets

There are two counteracting interactions among the water droplets: entropic repulsion and van der Waals attraction. The entropic repulsion is mainly determined by the strength of the interfacial film, which originates from the hydrogen bond between the emulsifier and water. The van der Waals attraction is governed by many variables, such as the volume fraction of the dispersed phase, the separation between the dispersed phase and the interaction mode among the dispersed phase (dispersion, polar or hydrogen bond). In terms of the attraction expression for a macrobody [24–27], it is roughly expressed as $\mathrm{Wa} \propto A_{212}D^{-2}$, where A_{212} is Hamaker's constant and D is the separation of the water droplets. According to the geometrical mixture rule, $A_{212} = (\sqrt{A_{11}} - \sqrt{A_{22}})^2$, where A_{11} and A_{22} are Hamaker constants of epoxy resin and the aqueous moieties of the interfacial film, respectively. The effect of temperature and the physicochemical properties of the medium on attraction are reflected by Hamaker constant A_{212}. The attraction decreases with temperature because the strength of the hydrogen bond decreases with increasing temperature.

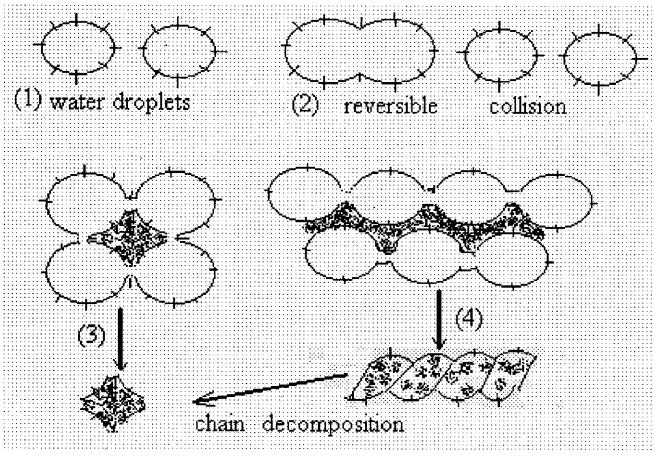

Fig. 1 Illustration of the complete phase-inversion process

Physical model of phase inversion

When the system reaches a critical state, a small change in the control variables, such as increasing water content and decreasing temperature, will result in an abrupt increase in attraction among the water droplets. Meanwhile, the change in entropic repulsion is not so remarkable. Thus, a criterion for the occurrence for phase inversion is proposed; phase inversion will take place when the attraction exceeds the repulsion. If the dynamic coalescence among the water droplets before the PIP is ignored, the size of the submicron water droplets is influenced less. When the requirement for phase inversion is satisfied in this case, complete phase inversion occurs via abrupt simultaneous coalescence of the nearest water droplets, and small waterborne polymer particles are obtained.

The complete phase inversion process is illustrated in Fig. 1. Before the PIP, the collision among the water droplets is reversible owing to stabilization of the strong interfacial film, and the net coalescence is ignored. This corresponds to the process from step 1 to 2. During this collision process, matter exchange among the water droplets takes place and the particle size distribution of the water droplets becomes narrower. When the requirement for phase inversion is satisfied, all the water droplets will simultaneously coalesce at a rapid rate to the continuous phase and small waterborne particles of polymer resin are obtained. It is reasonable to deduce that there are two typical methods to form the waterborne particles: coalescence either among the nearest discrete water droplets (step 3) or among the "necklace" water structure (step 4). In the former case, discrete waterborne particles will be obtained. In the latter case, a corresponding waterborne "necklace" structure composed of waterborne particles is formed. The protruding boundaries between the nearest beads within the "necklace" structure originate from the coalescence among the "necklace" structure of the water droplets. The angle between the bead contact boundary and the axis direction of the necklace structure is related

to the orientation of the water droplets before the PIP, this has been verified by the experimental results [1]. Under shear action, the "necklace" structure is broken up into small waterborne particles. The particle size is determined by the periodicity of the "necklace" structure of the water phase, which is comparable with the size of the water droplets before the PIP. This will be discussed in more detail later. It is worth noting that the water content at the PIP is 20.09 wt% in the case of complete phase inversion [1]. In this case, it is impossible for the water droplets to form a maximum dense state to drive phase inversion. It is reasonable to deduce that there is perforation among the water droplets at the PIP since the attraction among the water droplets is extremely strong. This is consistent with the result of Cazabat et al. [28] that there are the fluctuations both in concentration and connectivity resulting from the perforation at the interfacial film in the vicinity of the critical point when the attraction among the water droplets is sufficiently high. Coniglio et al. [29] correlated the concentration and connectivity in terms of a site-bond percolation model. It is shown that the stronger the attraction, the steeper the conductivity increase at the critical point. Their studies supported the result studied here. There is a length distribution for the "necklace" structure composed of waterborne particles, which results from the coalescence among the "necklace" structure of the water phase. Nevertheless, all the "necklace" structure will be broken up into small particles under shear action after the PIP. In the two methods, it is not requisite for the curvature of the interfacial film to change too much during the phase inversion process; therefore, the waterborne particles are not strictly spherical. This is confirmed by our result that the boundary among the waterborne particles is irregular rather than spherical.

The process of incomplete phase inversion is illustrated in Fig. 2. When the coalescence among the water droplets is significant before the PIP, larger water drops will be formed by the irreversible coalescence among the small water droplets under shear action and will be randomly dispersed in the epoxy resin continuous phase, which corresponds to the process from step 1 to 2. This will result in a broad size distribution of the water droplets. The interfacial film will become weaker when the water droplets become larger. In this case, phase inversion will take place via the coalescence of the deformed larger water droplets to form the waterborne structure as shown in step 3, and the small water droplets are trapped within the waterborne structure. Therefore, a complex water-in-oil-in-water (W/O/W) structure is obtained, as shown in step 4.

According to the aforementioned physical model of phase inversion, we can arrive at a tentative result for the correlation between the morphologies of waterborne particles and the dispersed phase as well as their size dependence.

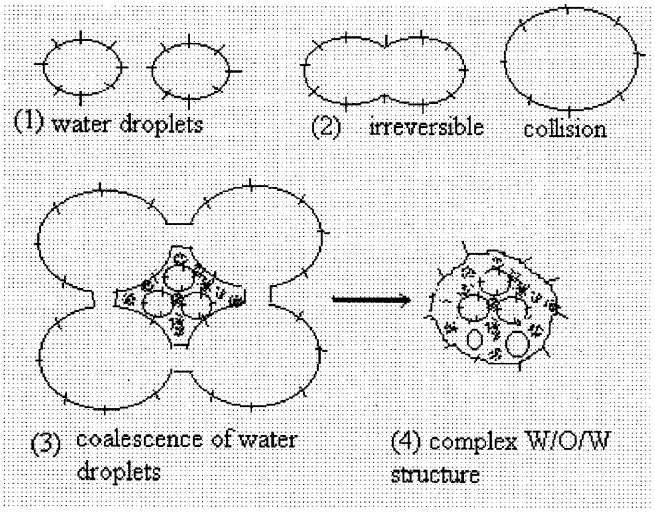

Fig. 2 Illustration of the incomplete phase-inversion process

Size prediction of the waterborne structure

It is important to predict the morphology and the size of the waterborne particles prepared by the phase-inversion emulsification technique. In principle, it is possible to predict the morphology and the size of the dispersed water phase before the PIP on the basis of the aforementioned analysis, though there are some difficulties for the moment partially because of the complication discussed previously. On the other hand, information about the water content at the PIP can be obtained both experimentally and theoretically on the basis of the interactions among the water droplets.

As discussed earlier, the morphology of the waterborne particles is closely related to the dynamic coalescence among the water droplets before the PIP. Generally speaking, discrete waterborne particles are obtained by complete phase inversion at high emulsifier concentration and low emulsification temperature, whilst, a complex W/O/W structure is achieved by incomplete phase inversion at low emulsifier concentration and high emulsification temperature.

It is very interesting to predict the size of the waterborne particles in the case of complete phase inversion. In order to derive the expression for the particle size of the waterborne structure, the following four assumptions are made:

1. There is no net coalescence among the water droplets before the PIP.

2. All nearest water droplets simultaneously coalesce into the continuous phase at the PIP.
3. The characteristic size of the water droplets is uniform.
4. The characteristic size of the waterborne particles is uniform.

According to assumptions 1 and 2, the number of waterborne particles is equivalent to that of the water droplets in the vicinity of the PIP, as expressed in Eq. (2):

$$N_w = N_p \tag{2}$$

where N_w and N_p are the number of water droplets and waterborne particles at the PIP, respectively. The subscripts w and p stand for water and polymer resin, respectively.

According to assumptions 3 and 4, the weights of the dispersed water phase and the waterborne particles of polymer resins in the vicinity of the PIP are expressed as in Eqs. (3) and (4), respectively.

$$W_w = N_w\left(\frac{1}{6}\pi D_w^3\right)\rho_w \ , \tag{3}$$

$$W_p = N_p\left(\frac{1}{6}\pi D_p^3\right)\rho_p \ , \tag{4}$$

where D and ρ are the diameter and the density of the phases, respectively.

The water content at the PIP defined in Eq. (5), can be obtained experimentally.

$$R = \frac{W_w}{W_w + W_p} \tag{5}$$

Equation (6) is obtained by combining Eqs. (2)–(5).

$$R = \frac{W_w}{W_w + W_p} = \frac{N_w D_w^3 \rho_w}{N_w D_w^3 \rho_w + N_p D_p^3 \rho_p} = \frac{D_w^3 \rho_w}{D_w^3 \rho_w + D_p^3 \rho_p} \tag{6}$$

After a simple transformation of Eq. (6), the correlation between the size of the waterborne structure with water content at the PIP and the size of the dispersed water phase is derived as shown in Eq. (7).

$$D_p = \left(\frac{\rho_w}{\rho_p}\frac{1-R}{R}\right)^{\frac{1}{3}} D_w \tag{7}$$

In our study, the densities of water and epoxy resin are comparable, and Eq. (7) is simplified to Eq. (8):

$$D_p = \left(\frac{1-R}{R}\right)^{\frac{1}{3}} D_w \ . \tag{8}$$

According to Eq. (8), the theoretically predicted particle size of the waterborne structure is as shown in Fig. 3.

It is known that the critical water content at the PIP ranges from 20 to 40 wt% in the case of the complete phase-inversion process. In Fig. 3, the diameter ratio, D_p/D_w, ranges from 1.1 to 1.6. Thus, a tentative conclusion is arrived at that the particles size of the waterborne structure prepared by complete phase-inversion is comparable with the size of the dispersed water phase in the vicinity of the PIP; therefore, the dependence of the waterborne particle size on the control variables is predicted by analyzing their effects on the dispersed water phase in the vicinity of the PIP, which is possible as discussed in the aforementioned context. This helps to design and control the size of the waterborne particles prepared by complete phase inversion.

Summary and conclusions

On the basis of the experimental characterization of the phase-inversion process, including electrical properties, rheological behavior and morphological evolution, it is shown that the achievement of phase inversion is different under different conditions. The effects of some control variables, such as emulsifier concentration and emulsification temperature, on the critical water content required at the PIP and the structural features of the waterborne particles are investigated. Complete phase inversion dominates via simultaneous coalescence among the nearest water droplets when the emulsifier concentration is high and the emulsification temperature is low. Small, discrete waterborne particles of polymer resins are prepared. In comparison, a complex W/O/W structure is formed from incomplete phase inversion at low emulsifier concentration and high emulsification temperature. The deformation and breakup of water

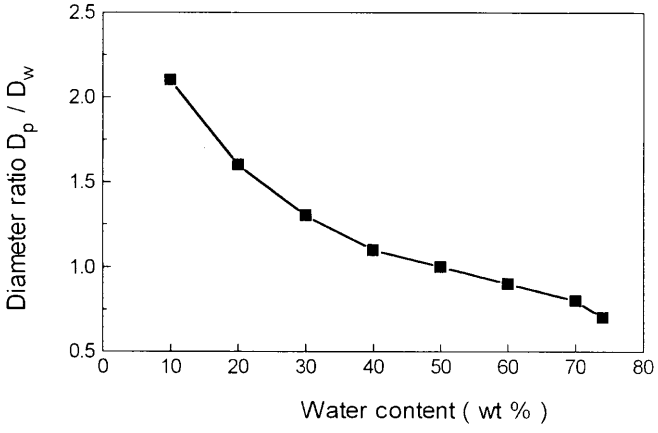

Fig. 3 Theoretical prediction of the size of waterborne particles by Eq. (8)

droplets dispersed in the viscous continuous phase under a shear field is analyzed in terms of microrheology theory. The coalescence dynamics was expressed by an improved Smoluchowski equation to predict the effect of some control variables on dynamic coalescence among the water droplets. There are two counteracting interactions among the water droplets: attraction and repulsion. The criterion for phase inversion is presented according to the coalescence dynamics of the water droplets before the PIP and the balance between the two counteracting interactions. This criterion acts as a guide to understand the effects of the variables on the phase inversion process and the structural features of the waterborne structures. If the dynamic coalescence among the dispersed water phase is ignored in the case of high emulsifier concentration and low emulsification temperature, complete phase inversion occurs and small, discrete waterborne particles of polymer resins are formed. In comparison, if the dynamic coalescence among the dispersed water phase is significant, resulting in the formation of large water drops in the case of low emulsifier concentration and high emulsification temperature, incomplete phase inversion occurs and a complex W/O/W structure is formed. In the case of complete phase inversion, the size of the waterborne particles is comparable with the characteristic size of the dispersed water phase in the vicinity of the PIP; therefore, the size of the resultant waterborne particles can be predicted by analyzing the effects of the control variables on the size of the dispersed water phase.

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