Macromol. Rapid Commun. **21**, *574–578 (2000)*

Communication: Micrometer sized multi-hollow spheres of epoxy resin were prepared by a physical method so-called phase inversion emulsification technique. The formation mechanism of the titled spheres was studied by incomplete phase inversion. The requisite for the formation of multi-hollow spheres was that irreversible coalescence among the water droplets under shear action before the phase inversion point existed. This process could be facilitated by a lower emulsifier concentration and a higher emulsification temperature. Moreover, a theoretical explanation of the formation of the titled spheres was presented.

Mechanistic investigation on the formation of epoxy resin multi-hollow spheres prepared by a phase inversion emulsification technique

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(Received: December 1, 1999; revised: February 16, 2000)

Introduction

Micrometer sized multi-hollow polymer spheres have found many potential applications such as in the industrial areas of separation and adsorption, catalysis, electronic, printing and information. Recently, hard latex particles with interior cavities have been found to have potential uses in coatings as opacifiers. The pacification effect originates from multiple scattering and interference contributed to the scattering ability of the internal pores rather than light absorption of such as kaolin or calcium carbonate[1–2]. The study on the opacification mechanism of porous spheres indicates that visible light is scattered more efficiently by voids having diameters of 200–800 nm[3].

Some approaches have been reported to prepare multi-hollow polymer spheres. According to Okubo et al.[4, 5, 6], sub-micrometer sized multi-hollow polymer structures could be obtained via stepwise treatment with alkali followed by acid of emulsion copolymers containing polystyrene and acrylate. Moreover, Okubo has successfully prepared micrometer sized polymer spheres via dynamic swelling seeded polymerization[7, 8]. In order to achieve cavities within the spheres, the post-treatment is similar to the aforementioned procedure. Generally speaking, this method involves many tedious treatment procedures, producing lots of waste. This makes the production more time intensive and thus the products more expensive.

Instead, Schlarb et al. developed a new method to prepare multi-hollow polymer particles, which involved formation of copolymer containing acrylic acid as emulsifier for the second emulsion polymerization in the presence of organic solvents. At the end of the experiments, the residual solvents were removed by distillation and multi-hollow polymer particles were yielded. This method involves residual organic solvents, which obviously brings in many drawbacks[9, 10].

According to Garti, double emulsions are commonly prepared by two-step mode: hydrophobic emulsifier for the W/O inner droplets, and hydrophilic emulsifiers for the external O/W emulsion. However, this process also involves too many procedures[11, 12].

Recently, we have found an easy method to prepare multi-hollow spheres of epoxy resins by incomplete phase inversion progress[13, 14] with the added advantage that no organic solvents are involved in this method. Therefore, from the viewpoint of a practical application, this method is very attractive to achieve multi-hollow polymer spheres owing to its low cost and simplicity. In this paper, we attempt to understand the formation mechanism of the multi-hollow spheres prepared by phase inversion emulsification.

Experimental part

Materials

Bisphenol A epoxy resin E-20 (epoxide equivalent value 0.20 mol/100 g resin) with an average molecular weight $\bar{M}_w$ = 1000, was purchased from Chinese East Tianjin Chemicals

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Co. and used as received. The polymeric emulsifier E325 with an number average molecular weight $\overline{M}_n = 4.6 \times 10^4$, measured by GPC[15], is a multiblock copolymer composed of 10 wt.-% of epoxy resin E-20 as a hydrophobic component and 90 wt.-% poly (ethylene glycol) PEG10000 as the hydrophilic component. Both of the epoxy resin E-20 and the emulsifier E325 are powdery at ambient temperatures.

Description of phase inversion progress

After the powdery bisphenol A epoxy resin E-20 and some amount of emulsifier E325 were charged into a glass emulsification device at ambient temperatures, the mixture was progressively heated until melted. Then, the mixture was kept homogeneous by stirring and keeping the temperature constant, and deionized water was added to the mixture continuously to drive the phase inversion. Meanwhile, the electrical properties were monitored by directly reading the current impedance value measured with a HIOKI 3520 LCR Hi TESTER, which was connected with two well designed parallel rod electrodes fully immersed in the mixture. Once the impedance of the system suddenly dropped accompanied by an acceleration of the motor during the experiment, a continuous phase inversion from the epoxy resin to the water phase had occurred and the system could be dispersed in water. This critical water content is defined as the phase inversion point (PIP). Next, a large amount of water was added in order to cool and dilute the inverted system, and the products were obtained after drying under vacuum.

Characterization

Very diluted dispersions were spread onto a metal plate and dried at ambient temperature under vacuum. The dried powders were sputtered with Au and observed with an Hitachi scanning electron microscopy (S-530).

During the phase inversion process, samples of representative water content were taken off the emulsification device and cooled immediately in an ice/water mixture. The cooled samples were fractured in liquid nitrogen, and the fractured surface was dried at ambient temperature under vacuum. The dried fracture was sputtered with Au in vacuum and then observed under a scanning electron microscopy (S-4200). The water content of the systems, which is defined as the weight ratio of water to epoxy resin, was determined by drying the systems at 140 °C for 30 min and weighing the mass loss under ambient conditions. The emulsifier concentration refers to the weight ratio of the emulsifier to epoxy resin.

Results and discussions

Representative morphology of the multi-hollow spheres

Fig. 1 shows two representative scanning electron micrographs of the multi-hollow particles of epoxy resin prepared by the incomplete phase inversion emulsification technique at 85 °C when the emulsifier concentration is about 5%. The contour of the particles is given in Fig. 1A. It can be seen that the particles are multi-hollow

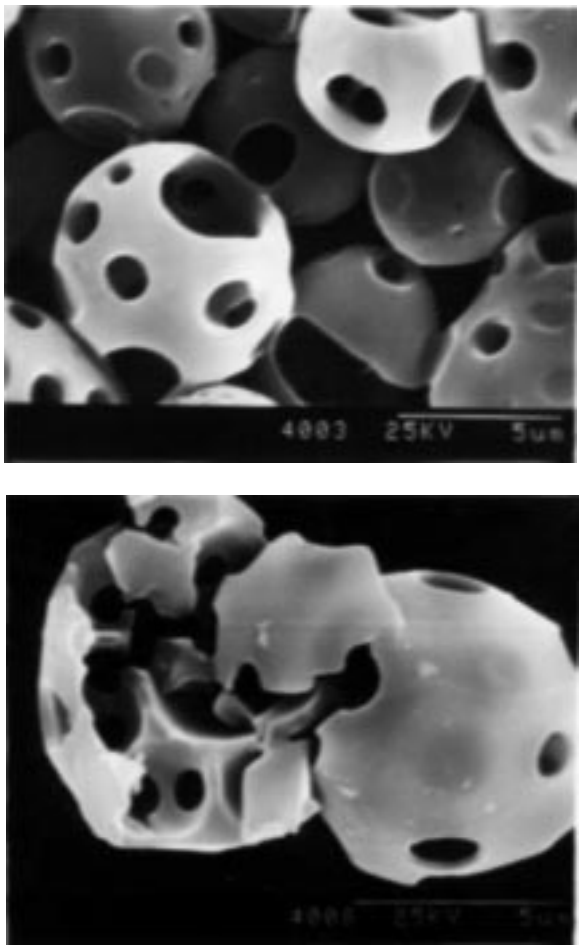

Fig. 1. Representative scanning electron micrographs of the multi-hollow particles prepared at 5% emulsifier E325 and 85 °C (scale bar is 5 μm)
A: Contour of the particles (top), B: Internal structure of the particles (botton)

about 5 μm diameter with the hollows about 1 μm diameter. Fig. 1B shows the internal structure of the particles. It can be seen that the cavities are interconnected within the particles.

Some variables to control formation of the multi-hollow spheres

It is found that the effects of emulsifier concentration and emulsification temperature on the structural features of the waterborne particles prepared by the phase inversion emulsification technique are very pronounced. Fig. 2 shows the dependence of water content at PIP and the structural features of the waterborne particles on the emulsifier concentration. Below the curve, the amount of water is not sufficient to drive phase inversion from epoxy resin into the aqueous phase. Therefore, the system in region 3 is a water dispersed in oil (W/O) system. On the other hand above the curve, phase inversion occurs and the continuous phase of the system is water. There is

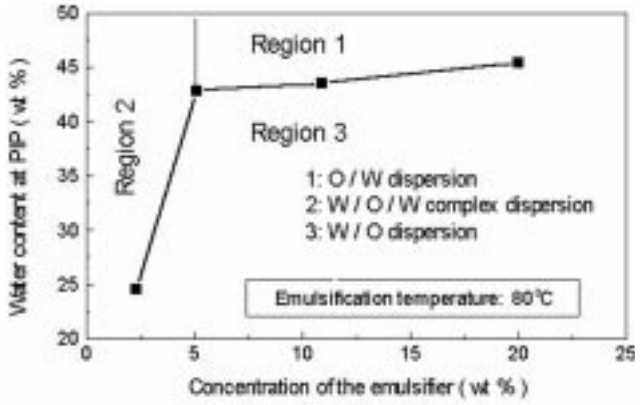

Fig. 2. The dependence of water content at PIP and the structural features of the waterborne particles on the emulsifier concentration

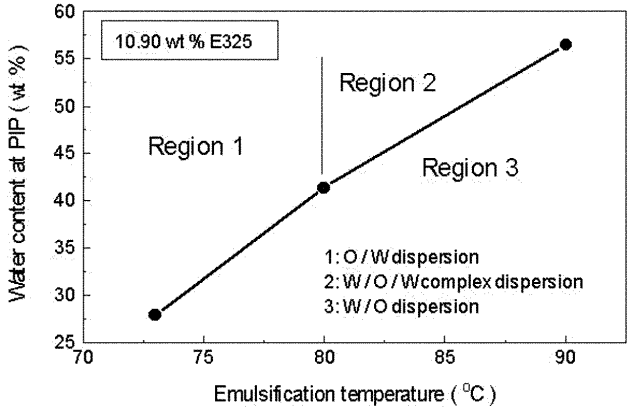

Fig. 3. The dependence of water content at PIP and the structural features of the waterborne particles on emulsification temperature

a transition region simply indicated by a vertical line from region 1 to region 2. In region 1, emulsifier concentration is relatively high and discrete smaller waterborne particles (O/W dispersion) dominate. In region 2, porous particles (W/O/W dispersion) dominate at lower emulsifier concentration. The water content at PIP asymptotes a constant when emulsifier concentration exceeds 5%. This infers that the emulsifier is sufficient to almost saturate the W/O interface before PIP at this critical emulsifier concentration.

Fig. 3 shows the dependence of water content at PIP and the structural features of the waterborne particles on the emulsification temperature. It can be seen that the water content at PIP increases monotonically with temperature. Below the curve, the water content is not sufficient to drive phase inversion and the system in region 3 is a water dispersed in oil (W/O) system. Above the curve, the continuous phase is aqueous. In region 1, the emulsification temperature is low, and discrete smaller particles dominate resulting from the complete phase inversion process. In region 2, when the temperature is higher, a W/O/W complex dispersion dominates. This means that the perfection of phase inversion becomes less with increasing temperature. This is likely to be correlated with the weakening interfacial film with temperature.

Formation process of the multi-hollow spheres by incomplete phase inversion emulsification

In order to understand the formation process of the multi-hollow particles, the morphological evolution was characterized by observing the representative samples with SEM during the phase inversion process, as shown in Fig. 4. It is noted that the emulsifier E325 concentration is fixed at 2.33% and emulsification temperature is 85 °C. In this case, the critical water content at PIP is 24.65%.

As can be seen in Fig. 4A, when the water content is 21.72% before PIP, it is found that some bigger deformed water drops coexist with smaller water droplets. On increasing water content, for example to 24.64%, a local phase inversion occurs and the interconnected structure is formed by the coalescence among the bigger water drops (Fig. 4B). When the water content reaches 24.65% (Fig. 4C), the continuous phase is suddenly inverted from epoxy resin into the aqueous phase, as shown by the abrupt decrease in the electrical resistance. It can be seen that lots of smaller water droplets are trapped in the bigger waterborne structure. Therefore, a W/O/W complex dispersion is obtained in this case. As shown in Fig. 4D, the structure becomes spherical owing to the decrease in surface energy on further addition of water. Some interconnected network within the spheres is also seen in Fig. 4D. This is consistent with the structure shown in Fig. 1.

Theoretical analysis of the multi-hollow spheres formation

Before PIP, the added water is dispersed in the viscose epoxy resin and broken-up into smaller droplets under shear field[16, 17, 18, 19]. Meanwhile, the emulsifier molecules diffuse onto the water/resin interfaces, and interfacial films are formed to stabilize the water droplets. The dynamic coalescence rate R among the water droplets could be impeded owing to the interfacial film, which is in agreement with the Smoluchowski[20, 21, 22] theory developed by Davis and Rideal[23]:

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

where k is the Boltzman constant, T the absolute temperature, n the number fraction of dispersed phase, r the radius of dispersed phase, η the viscosity of the system, a the collision radius, and E is the energy barrier mainly determined by the strength of the interfacial film.

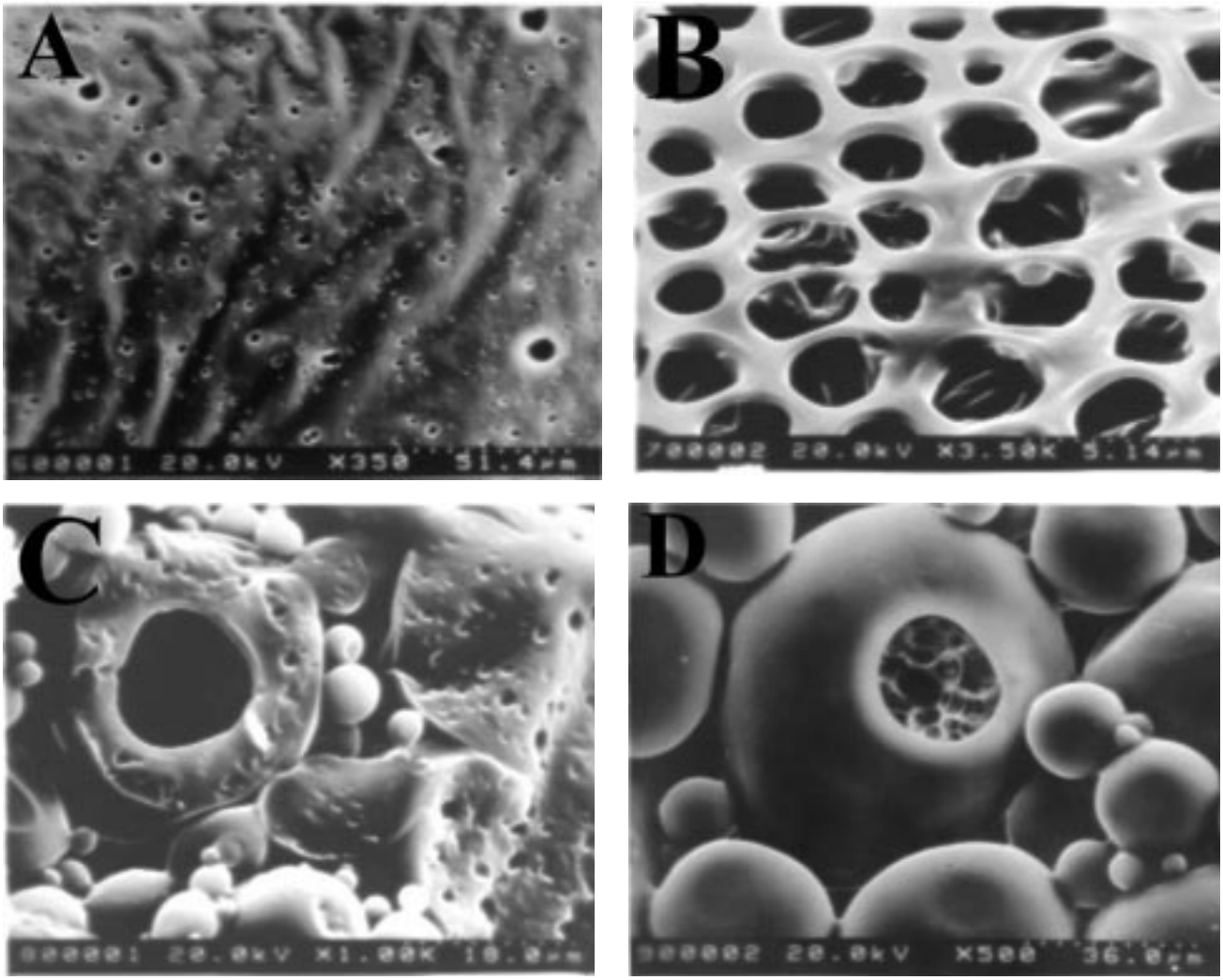

Fig. 4. Morphological evolution during an incomplete phase inversion process (Water content A: 21.72%, B: 24.64%, C: 24.65%, D: 28.85%)

The formation process of the multi-hollow particles by incomplete phase inversion is shown in Fig. 5. At low emulsifier concentrations, the emulsifier molecules are not sufficient to diffuse onto the newly formed water/resin interface and smaller water droplets are poorly stabilized. Therefore, the smaller water droplets coalesce to form larger ones. In this case, the interfacial film is less saturated with the emulsifier molecules. This analysis explains the dependence of phase inversion perfection on emulsifier concentration. Even the interfacial film is saturated, the strength of the interfacial film will also decrease with temperature by weakening the hydrogen bond between PEO units in the emulsifier and water. Therefore, the coalescence among the smaller droplets becomes much more marked with increasing temperature. In these two cases, an irreversible coalescence among the dispersed water droplets to form some larger ones exists. This process corresponds to the change from structure 1 to 2 in Fig. 5. For phase inversion before the requirement is satisfied that the attraction among the water droplets is comparable with repulsion, larger water droplets will be forced into a continuous phase at PIP under shear field, and lots of smaller water droplets are trapped within the larger waterborne structure. This corresponds to structure 3. Therefore, multi-hollow waterborne particles of epoxy resin (W/O/W dispersions) are prepared by an incomplete phase inversion emulsification technique as illustrated by structure 4 in Fig. 5.

To summarize, when coalescence among the water droplets occurs prior to PIP, larger water droplets will be formed via the irreversible coalescence among smaller water droplets under shear field. They are randomly dispersed in the epoxy resin continuous phase. This process results in broad size distribution of the water droplets. The water/resin interfacial film will become further weakened when the water droplets become larger. In this case, the phase inversion will take place via the forced coalescence among the deformed larger water drops sub-

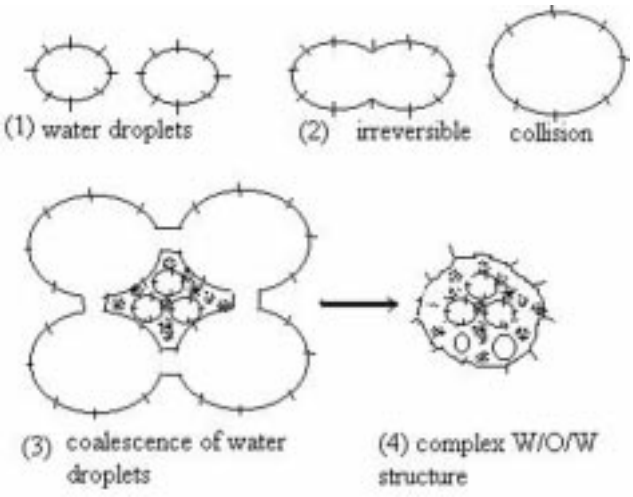

Fig. 5. Illustration of incomplete phase inversion evolution

jected to a shear field, and the smaller water droplets are trapped within the waterborne structure. Therefore, multi-hollow particles of epoxy resin are achieved by an incomplete phase inversion emulsification technique.

Conclusion

The formation mechanism of epoxy resin multi-hollow particles by incomplete phase inversion is investigated. It is found that the formation of larger water droplets by irreversible coalescence among the smaller water droplets before PIP is a requisite condition. This condition is achieved by lowering the strength of the interfacial film by decreasing the emulsifier concentration and increasing the emulsification temperature. At low emulsifier concentration, there are insufficient emulsifier molecules to diffuse onto the freshly formed surfaces, and stabilization of the dispersed water droplets becomes low. In this case, the interfacial film is unsaturated by the emulsifier molecules. With increasing temperature, the strength of the interfacial film becomes less and the irreversible coalescence among the water droplets are remarkable. Therefore, both decreasing the emulsifier concentration and increasing the emulsification temperature could facilitate the formation of epoxy resin multi-hollow particles by an incomplete phase inversion emulsification technique.

Acknowledgement: This work was supported by the National Key Project for Fundamental Research "Macromolecular Condensed State" of the *Chinese Science and Technology Ministry*, and *National Natural Science Foundation of China* under Grant No. 29774038

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