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ORIGINAL CONTRIBUTION

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Preparation of waterborne dispersions of epoxy resin by the phase-inversion emulsification technique. 1. Experimental study on the phase-inversion process

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Abstract Waterborne dispersions of bisphenol A epoxy resin were prepared by the so-called phase-inversion emulsification technique. The electrical properties, rheological behavior and morphological evolution during the phase inversion process were characterized systematically. It was shown that both emulsifier concentration and emulsification temperature play great roles in controlling the phase inversion process as well as the structural features of the waterborne particles. A high emulsifier concentration, i.e. 10.90 wt% and a low emulsification temperature, i.e. 73 °C, facilitate complete phase inversion, in which all water droplets in the system are simultaneously transformed into the continuous phase at the phase-inversion point (PIP). In this case, submicron-sized, discrete waterborne particles were formed. In contrast, a complex water-in-oil-in-water structure was achieved by incomplete phase inversion at a low emulsifier concentration, i.e. 2.33 wt%, and a high temperature of 80 °C. The morphological evolution observed by scanning electron microscopy revealed that not all the water droplets in the system were converted into the continuous phase at the PIP and that some small water drops were trapped within the waterborne structure.

Key words Bisphenol A epoxy resin · Waterborne dispersions · Phase-inversion emulsification · Electrical properties · Rheological behavior

Introduction

The study of waterborne dispersions of polymer resins with low or zero content of volatile organic compounds has received much attention owing to increasing worldwide environmental and ecological regulations. The methods to prepare waterborne dispersions of polymer resins are roughly classified into chemical polymerization and physical emulsification. The former (e.g. emulsion polymerization) is almost restricted to preparing dispersions of addition polymer resins formed by the radical polymerization mechanism. It is difficult to apply to condensation polymers such as bisphenol A epoxy resin. Nowadays, much effort is being made to prepare dispersions of condensation polymers because of their high performance. A physical method called the phase-inversion emulsification technique is proposed to prepare waterborne dispersions of polymer resins. It has been proved to be highly effective in that almost all polymers (addition polymers and condensation polymers) can be emulsified to form waterborne dispersions; therefore, the scope of polymer waterborne dispersions is greatly extended [1, 2].

The term phase inversion originally referred to transformation of the continuous phase from the oil to the water phase (or vice versa) in emulsions composed of small molecular species. In the vicinity of the phase-inversion point (PIP), interfacial tension between the oil and the water phases reaches a minimum and an emulsion of small particle size is obtained [3, 4]. More recently, the phase-inversion technique has been applied extensively in a range of research areas, such as multiphase polymer materials and polymer dispersions [5–8]. In principle, almost all polymer resins can be emulsified into waterborne dispersions using the phase-inversion technique; however, published work concerning emulsifying polymer resins by the phase-inversion technique has almost always focused on the preparation of the products and their formulations. The characterization of the phase-inversion process and the investigation of the mechanism are relatively scarcely reported but yet are urgently needed.

Experimental

Materials

Bisphenol A epoxy resin, denoted as E-20, with a weight-average molecular weight of 1000 was purchased from Chinese East Tianjin Chemicals Co. and was used as received. Poly(ethylene glycol) (PEG10000) with a weight-average molecular weight of 10000 was provided by Beijing Donghuan Chemical Factory and was also used as received. The polymeric emulsifier denoted as E325 is a self-prepared, multiblock copolymer composed of 10 wt% hydrophobic component E-20 and 90 wt% hydrophilic component PEG10000. The number-average molecular weight of E325 was 4.6×10^4 as measured by gel permeation chromatography [9, 10]. Epoxy resin E-20 and emulsifier E325 are powders at ambient temperature.

Description of the phase-inversion process

Powdery bisphenol A epoxy resin E-20 and some emulsifier E325 were charged into a glass emulsification device at ambient temperature and then the system was heated to a relatively high temperature so as to melt the raw materials. While maintaining the temperature, the mixture was stirred so as to become homogeneous in 20 min. Afterwards, deionized water was continuously added into the mixture to drive the continuous phase inversion from the epoxy resin into the aqueous phase. The PIP was determined by monitoring the amplitude and the phase angle of the impedance measured at 300 Hz using a Hioki 3520 LCR Hi Tester connected with a couple of parallel rodlike electrodes fully immersed in the melt mixture. When the amplitude and the phase angle of the impedance dropped abruptly accompanying the sudden acceleration of the stirrer during the experiment, phase inversion occurred and the system was dispersible in water. Then much water was added in order to cool and dilute the inverted system.

Characterization

The amplitude and the phase angle of the impedance during the phase-inversion process were measured with a Hioki 3520 LCR Hi Tester at 300 Hz to ensure the accuracy of the signal. Since the inversion of the continuous phase was the main concern, the reading from the instrument connected with the rod electrodes was sufficient to qualitatively determine which phase was the continuous one. From this viewpoint, it was unnecessary to know the absolute values of the impedance of the system. Samples for rheological characterization were taken from the emulsification device with a preheated stainless spade and loaded between the parallel plates attached to a dynamic stress rheometer (DSR-200, Rheometrics Co.). The diameter of the parallel plates was 25.000 mm, and the gap between the plates was 1.000 mm. The measurement temperature was kept the same as the emulsification temperature. The residual stress in the sample caused by adjusting the gap was relaxed in 2 min. In the case of a high emulsifier concentration, a dynamic frequency ramp test was performed at the angular rate range of 0.1–100 rad/s at 80 Pa stress (in the linear viscoelasticity region determined by a dynamic stress ramp test at 2 rad/s). After pausing for 2 min following the dynamic frequency ramp test, a steady stress ramp test was performed on the same sample in the stress range 0.1–4000 Pa to obtain static structural information at a lower stress and the dependence on shear stress. In the case of a low emulsifier concentration, the stress applied during the dynamic frequency sweep test was 20 Pa. Meanwhile, the samples were taken off the emulsification device and cooled immediately in an ice/water mixture in order to freeze the morphology of the samples. The cooled samples were fractured in liquid nitrogen, and the fracture was dried and sputtered with Au in a vacuum. The Au-sputtered fracture was observed with scanning electron microscopy (Hitachi S-4200). The water content of the samples, defined as the weight fraction of water at different intervals, was determined by the mass-loss method after drying the systems at 140 °C for 30 min.

Results and discussion

Electrical properties during the phase-inversion process

It is well known that the conductive capability of epoxy resin is much lower than that of water. The amplitude

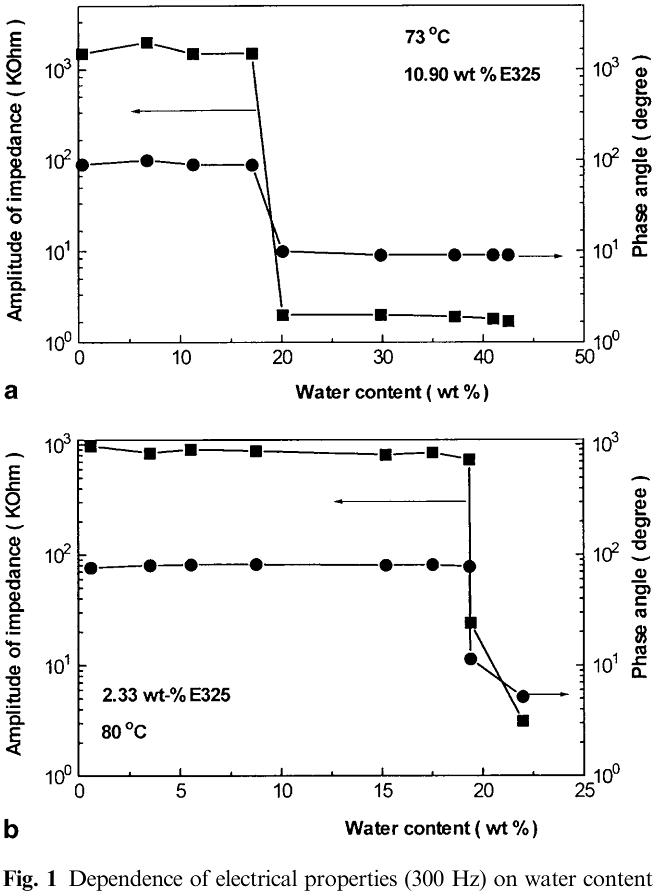

Fig. 1 Dependence of electrical properties (300 Hz) on water content during phase inversion: **A** complete phase inversion; **B** incomplete phase inversion

and the phase angle of the impedance are expected to drop when the continuous phase is inverted from epoxy resin to water. The dependences of the amplitude and the phase angle of the impedance measured at 300 Hz on water content during phase-inversion at 10.90 wt% emulsifier E325 and 73 °C are shown in Fig. 1A.

Both the amplitude and the phase angle of the impedance are higher when the water content is lower than 20.09 wt% because the epoxy resin is in the continuous phase. In the vicinity of 20.09 wt%, they decrease abruptly, which has been verified by our result [11]. This means that the continuous phase has inverted from epoxy resin into water. This critical water content is defined as the PIP. After the PIP, the electrical properties are less dependent on the water content. This infers that phase inversion is achieved completely at the PIP; therefore, this case is defined as complete phase inversion.

In comparison, at a low emulsifier concentration, i.e. 2.33 wt%, and a high emulsification temperature, i.e. 80 °C, the electrical properties differ, as shown in Fig. 1B. It is seen that the critical water content at the PIP is 19.43 wt%. The electrical properties change progressively with water content after the PIP, which means that phase inversion is still in progress. This infers that phase inversion is not completely accomplished at the PIP. This case is defined as incomplete phase inversion.

Rheological behavior during phase inversion

Steady stress ramp test

It was found that the stirrer suddenly accelerated with the occurrence of the abrupt changes in the electrical properties at the PIP, which correspond to the changes in rheological behavior. The relationship between shear viscosity and stress at the typical water contents during complete phase inversion is shown in Fig. 2A. When the water content is low (6.71 wt%) before the PIP, the viscosity is about 10^2 Pas, independent of the stress. This

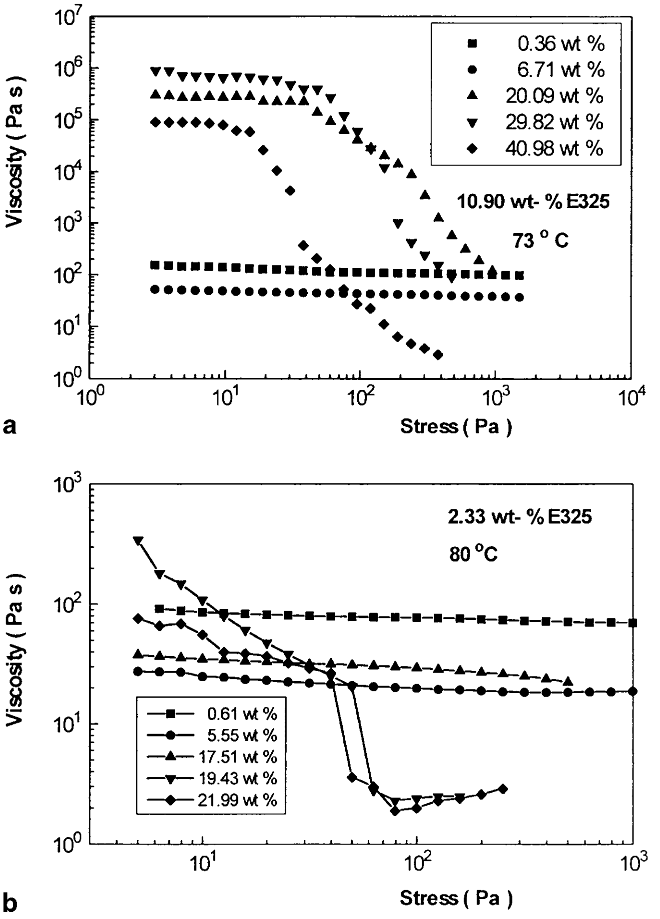

Fig. 2 Typical curves of viscosity versus stress at various water contents during phase-inversion: **A** complete phase inversion; **B** incomplete phase inversion

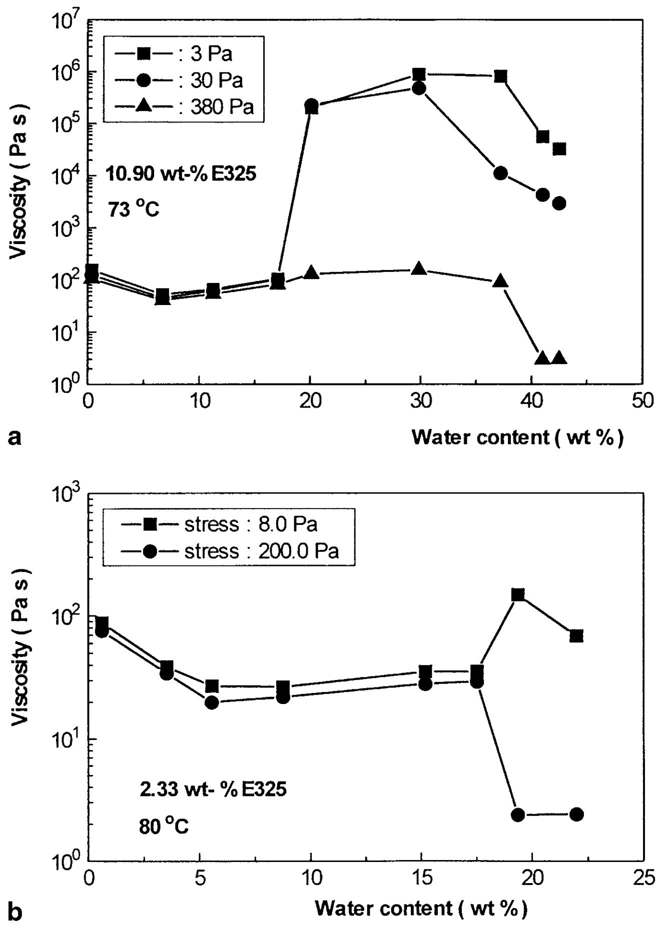

Fig. 3A, B Dependence of viscosity on water content at two stress levels is a characteristic of Newtonian fluids. In comparison, the viscosity–stress curve at the PIP (20.09 wt%) differs considerably from that before the PIP. The viscosity at the lower stress of up to 5×10^5 Pas is about 3000 times that before the PIP. It decreases to an extremely low value at higher stress. This indicates that the inverted system is highly pseudoplastic, which is attributed to the formation of a static structure due to the strong interaction among the waterborne particles via hydrogen bonds between the PEG moiety of the emulsifier covered on the particle surface and the continuous water phase [12, 13].

In comparison, typical plots of shear viscosity versus stress during incomplete phase inversion are shown in Fig. 2B. When the water content is low (17.51 wt%) before the PIP, the system is a Newtonian fluid. Although the plot exhibits a reversed "S" shape at the PIP (19.43 wt%), it is greatly different from that of complete phase-inversion. In the latter case, the viscosity at lower stress increases by 3000 times at the PIP, which is attributed to the formation of a static structure. In the former case, the increase in viscosity at the lower stress is not so remarkable, which is probably due to weak interaction in the inverted system and lubrication by the local water phase.

The relationship between viscosity and water content at the typical stress levels in the case of complete phase inversion is shown in Fig. 3A. When the water content is low before the PIP (6.71 wt%), the viscosity is independent of stress, which is the characteristic of a Newtonian fluid. After the PIP, the viscosity decreases remarkably at higher stress, which is explained by the destruction of the static structure. The viscosity at lower stress (3 Pa) increases abruptly by 1000 times at the PIP. The viscosity reaches a maximum, followed by a decrease with more water after the PIP, which is attributed to hydrogen-bond interaction.

In the case of incomplete phase inversion, the relationship between viscosity and water content at the two typical stress levels is shown in Fig. 3B. When

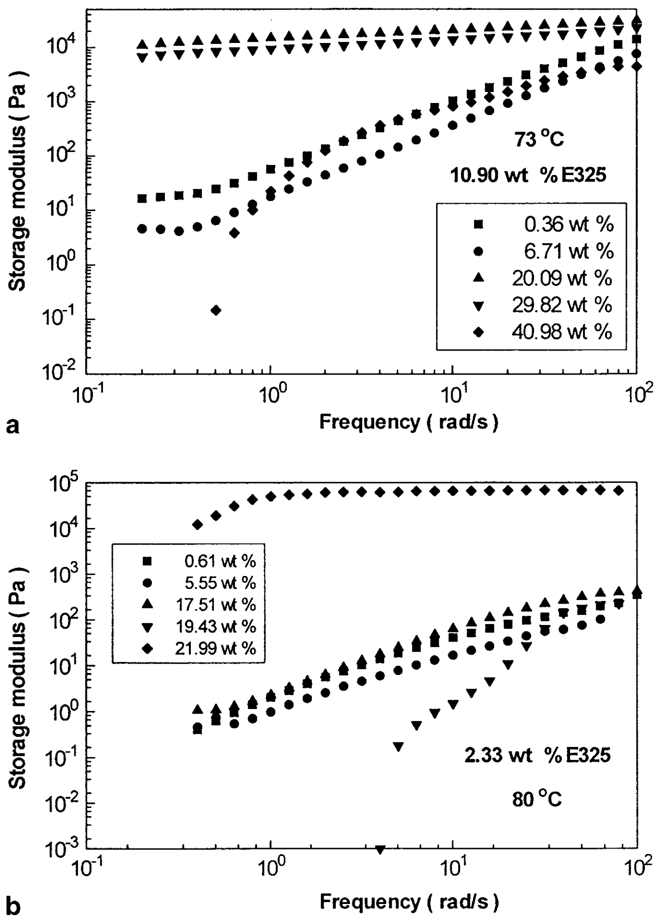

Fig. 4 Typical curves of storage modulus versus frequency at various water contents during phase inversion: **A** complete phase inversion; **B** incomplete phase inversion

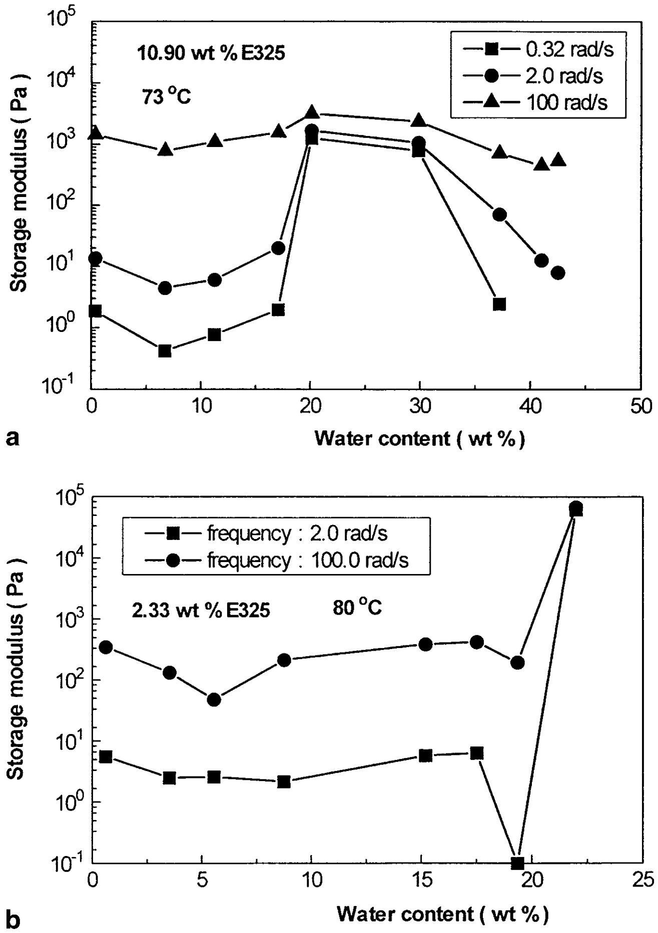

Fig. 5 Dependence of storage modules on water content at two frequency levels: **A** complete phase inversion; **B** incomplete phase inversion

the water content is low (17.51 wt%) before the PIP, the viscosity is less dependent on stress. This indicates that the system is a Newtonian fluid. At the PIP (19.43 wt%), the viscosity at a lower stress (8.0 Pa) suddenly increases to some extent. This can be explained by weak interaction in the system. However, the increase is not so great, which is probably due to the lubrication by the large water domains in the inverted system. The viscosity at higher stress (380 Pa) decreases remarkably. This is evidence for pseudoplasticity.

Dynamic frequency ramp test

Typical curves of storage modulus versus frequency during complete phase inversion are shown in Fig. 4A. When the water content is low (6.71 wt%) before the PIP, the storage modulus increases considerably with frequency, which means that the system is fluidlike. At the PIP (20.09 wt%), the storage modulus is higher and is less dependent on frequency. This means that the inverted system is highly elastic. With addition of more water, the system becomes fluidlike again.

The relationship between the storage modulus and the frequency during incomplete phase inversion is shown in Fig. 4B. When the water content is low (17.51 wt%) before the PIP, the storage modulus increases remarkably with frequency. This means that the system is fluidlike. At the PIP (19.43 wt%), the storage modulus is lower at a low frequency and increases rapidly with frequency. Besides, the curve is complex. This can be explained by the complicated morphology of the inverted waterborne system and by lubrication by the larger domain of the water phase. After the PIP (21.99 wt%), the storage modulus increases greatly and changes slightly with frequency.

The relationship between storage modulus and water content in the case of complete phase inversion is given in Fig. 5A. At lower frequency, the storage modulus increases abruptly at the PIP (20.09 wt%) and decreases with increasing water content. This reflects the fact that the inverted system is highly viscoelastic, which is correlated with the change in morphology.

The dependence of the storage modulus on water content in the case of incomplete phase inversion is shown in Fig. 5B. At the PIP (19.43 wt%), the storage modulus reaches a minimum, which means that the structure is complex. After the PIP, the storage modulus increases greatly owing to progressive partial phase inversion.

Morphological evolution during phase inversion

The morphological evolution during complete phase inversion was observed by scanning electron microscopy.

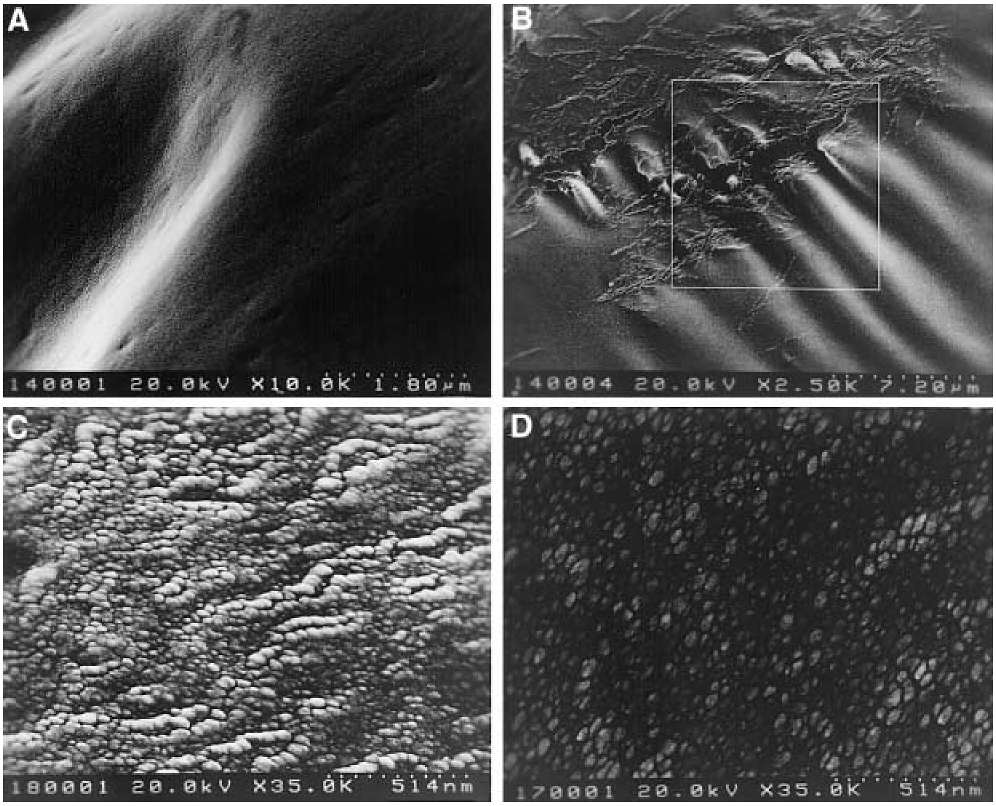

Fig. 6 Morphological evolution during complete phase inversion: **A** 11.25 wt%; **B** 17.08 wt%; **C** 20.09 wt%; **D** 37.18 wt%

Before the PIP (11.25 wt%), the typical morphology of the system is as given in Fig. 6A. It is found that sub-micron-sized water droplets and the deformed fibril of water drops coexist in the system. With increasing water content (17.08 wt%) before the PIP, the typical morphology is as given in Fig. 6B. Although the continuous phase remains an epoxy resin, a necklacelike structure composed of small particles could be found in some local regions originating from local phase inversion. This is probably due to fluctuations in the control variables, such as temperature and water content. The morphology at the PIP (20.09 wt%) is given in Fig. 6C. It is found that all the water phase is inverted to a continuous phase and that the waterborne structure of the epoxy resin exists in two forms: sub-micron-sized discrete particles and a necklace-like structure composed of smaller particles. In the necklacelike structure, an angle of about 45° is found between the particle contact plane and the axis direction of the necklacelike structure. With more water, the necklace structure is broken into sub-micron-sized particles as shown in Fig. 6D. It is found that the particles are not regularly spherical and that they have some irregular boundaries. This is essentially correlated with the physical mechanism of the phase-inversion process.

The morphological evolution during incomplete phase inversion was observed by scanning electron microscopy, as shown in Fig. 7. Before the PIP (17.51 and 19.41 wt%), water drops of large size and broad size distribution were observed, as shown in Fig. 7A and B,

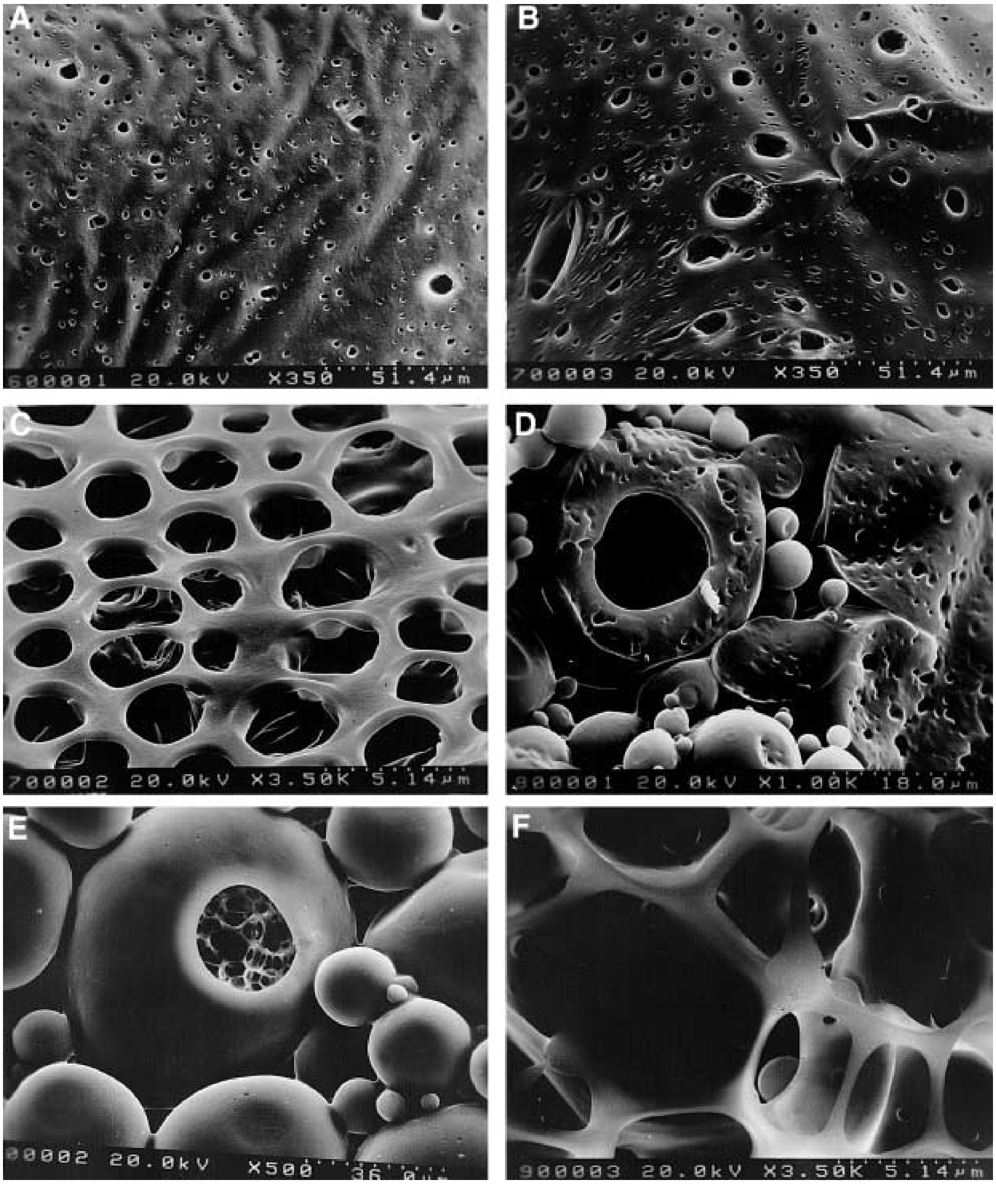

Fig. 7 Morphological evolution during incomplete phase inversion: **A** 17.51 wt%; **B** 19.41 wt%; **C** 19.41 wt%; **D** 19.43 wt%; **E** 21.99 wt%; **F** 21.99 wt%

respectively. Meanwhile, an interconnected network could be found in local regions in the system of 19.41 wt% water content as shown in Fig. 7C, which is attributed to partial phase inversion. In comparison, the morphology caused by partial phase inversion in this case is completely different from that of complete phase inversion. In the latter case, the morphology of the partial phase inversion is a necklacelike structure composed of small waterborne particles. In the former case, the structure resulting from partial phase inversion is a network with a characteristic large size. At the PIP (19.43 wt%), the oil-in-water (O/W) structure achieved by phase inversion is very complicated, as shown in Fig. 7D. Some small water droplets are entrapped in the O/W structure. The waterborne structure is big with a broad size distribution. This is consistent with the complicated rheological behavior at the PIP. After the PIP, the outer surface of the waterborne structure becomes smooth, as shown in Fig. 7E. In Fig. 7F, the internal porous structure of the same system as in Fig. 7E can be observed. From the morphological results, it is concluded that not all the water droplets are inverted into the continuous phase at the PIP in the case of incomplete phase-inversion. These findings help us to understand the mechanism of the phase-inversion process.

Some variables to control phase inversion

The effect of emulsifier concentration on phase inversion

The effects of emulsifier concentration on the critical water content required at the PIP and the achievement of phase inversion are given in Fig. 8. It is shown that the water content at the PIP is low when the emulsifier concentration is low. At 5 wt% emulsifier concentration, the water content at the PIP reaches a maximum. With increasing emulsifier concentration, the water content levels off. The effect of emulsifier concentration on structural features of the waterborne particles is also noticeable. There is a transition concentration window, simply indicated by the vertical line, where the structural features of the waterborne particles are different. In the upper right region, the emulsifier concentration is high, complete phase inversion dominates at the PIP and a waterborne epoxy resin dispersion of small particle size and narrow size distribution is achieved. In the upper left region, when the concentration of the emulsifier is low, a complex water-in-oil-in-water (W/O/W) structure is obtained by incomplete phase inversion. This has been confirmed by our experimental results [14]. Below the curve, the water content is insufficient to drive phase-inversion and the system is mainly a water-in-oil (W/O) structure.

The effect of emulsification temperature on phase inversion

The effects of emulsification temperature on phase inversion as well as the structural features of the waterborne particles are shown in Fig. 9. The water content required at the PIP increases with temperature owing to weakening interaction among the dispersed water phase. In the upper right region, when the temperature is relatively high, a complex waterborne W/O/W structure dominates. In the upper left region, when the temperature is low, a small O/W waterborne structure dominates. Below the curve, the water content is insufficient to drive phase inversion and the system is mainly a W/O structure.

From Fig. 9, it is also interesting to note that there are two methods to drive phase inversion: increasing the

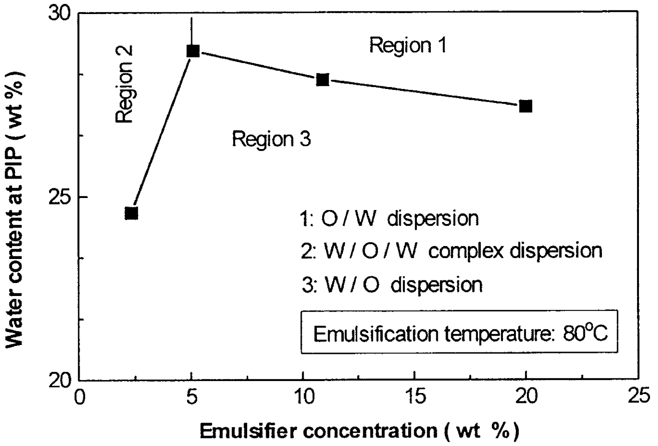

Fig. 8 Dependences of the water content at the phase-inversion point (*PIP*) and the structural features of the waterborne particles on emulsifier concentration

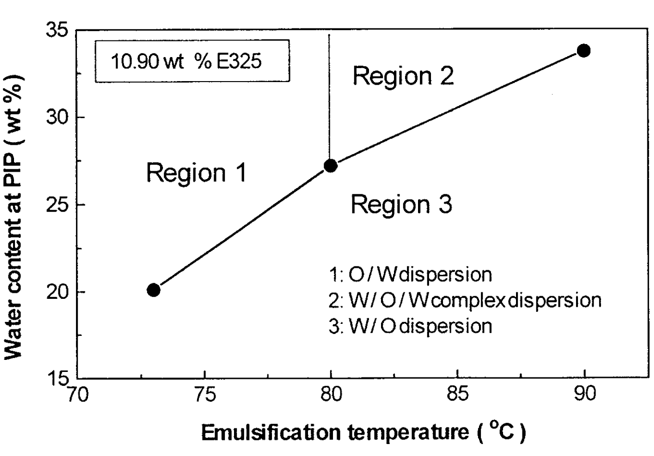

Fig. 9 Dependences of the water content at the PIP and the structural features of the waterborne particles on emulsification temperature

water content at a fixed temperature and lowering the temperature at a fixed water content. The combination of these two methods will make this technique more flexible for preparing waterborne dispersions of polymer resins.

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