

DETERMINATION OF PHASE INVERSION POINT IN THE EMULSIFICATION OF POLYMERS *

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ABSTRACT

Phase inversion emulsification technique is a recently developed method to achieve waterborne dispersions of polymer resin. It is found that the electrical and rheological properties of the system experience abrupt changes in the vicinity of the phase inversion point (PIP). Before PIP, the system is a Newtonian fluid. At PIP, the continuous phase transforms from polymer resin to water phase with the result that the electrical resistance of the system drops abruptly. Meanwhile, the system at PIP exhibits high viscoelasticity originated from the formation of a physical gel like structure among the waterborne particles. Besides, the morphology evolution is observed by Scanning Electron Microscopy (SEM).

INTRODUCTION

The term of phase inversion originally refers to the transformation of the continuous phase from oil to water phase (or vice versa) in emulsions composed of small molecules. In the vicinity of the phase inversion point, the interfacial tension between oil and water reaches a minimum value and the emulsion with small size of dispersed phase could be obtained^[1-2]. Recently, the phase inversion technique has been extensively exploited in a wide range of research areas such as multiphase polymer materials and polymer dispersions^[3-5]. By means of this technique, almost all polymer resins could be emulsified to be dispersions with small waterborne particles. Therefore, the scope of the polymer emulsions can be greatly broadened. It is clear that this study is of theoretical and practical significance. However, the published

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papers on emulsifying polymer resin by phase inversion technique are almost focused on the preparation of the products and their applications, the research work on the mechanism of phase inversion are relatively scarce and urgently needed. In this communication, we try to determine the PIP accurately as a start point to investigate the mechanism of phase inversion evolution systematically.

EXPERIMENTAL

Materials

Bisphenol A epoxy resin E-20 was purchased from East Tianjin Chemicals Co. and used as received. The polymeric emulsifier used is a multiblock copolymer consisted of E-20 and Poly (ethylene glycol) 10,000 (1 : 10 weight ratio), the average number molecular weight is 46,000 measured by GPC.

Phase inversion description and characterization

After E-20 and the emulsifier (10.90 wt%) was mixed homogeneously at a temperature (80°C) in a glass bottle, deionized water was added to the mixture continuously. When the electrical resistance of the system dropped abruptly, the phase inversion from epoxy resin to water phase occurred and the system could be dispersed in water. Then much water was added in order to cool and dilute the system.

The electrical resistance of the system was measured with HIOKI 3520 LCR Hi TESTER at 500 Hz. The steady and dynamic rheological properties during phase inversion were characterized by DSR-200 (Dynamic Stress Rheometer, Rheometrics Co.) with parallel plate holding device. The diameter of the parallel plates was 25.000 mm, and the gap between the plates was 1.000 mm. The samples were taken off the glass bottle at a regular interval with adding water continuously and were cooled immediately in ice water mixture. The cooled samples were fractured in liquid nitrogen, the fracture was sprayed with Au in vacuum and observed with SEM (S-530).

RESULTS AND DISCUSSION

Changes of the electrical properties during phase inversion progress

It is well known that the conductivity of epoxy resin is much lower than that of water. So, the electrical resistance of the system will drop greatly when the continuous phase transforms from epoxy resin to water content. Fig.1 shows the variation of electrical properties with water content during phase inversion evolution. It is seen that the impedance reaches a maximum value at about 10% water content, then decreases gradually with water content. At 41.408% water content, both impedance

and phase angle drop abruptly to low values respectively. This means the phase inversion from epoxy resin to water phase has occurred. The fact that the system at 41.408% water content becomes dispersible in water is another evidence of the phase inversion. Therefore, the 41.408% water content can be defined as phase inversion point (PIP).

Rheological behavior of the system during phase inversion progress

While the electrical properties of the system change abruptly at PIP, the rheological behavior also undergoes abrupt changes.

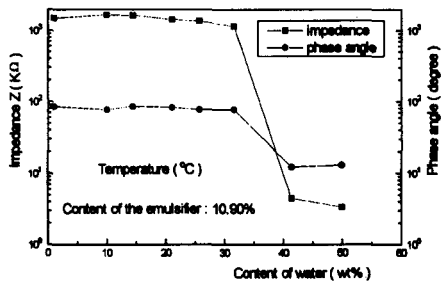


Fig.1 Variation of electrical properties with water content during phase inversion evolution

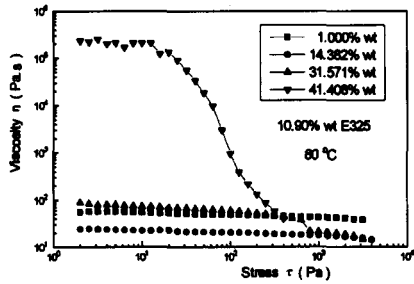


Fig.2 Typical curves of viscosity vs. stress during phase inversion evolution

Fig.2 shows four typical curves of viscosity vs. stress at different water contents. The viscosity of the system before PIP at a fixed water content keeps almost the same value, that is, the system exhibits the behavior of Newtonian fluid. The viscosity at low stress of the system at PIP increases suddenly by 3000 times, and it decreases at relatively high stress. It is clear that the system at PIP exhibits strong pseudoplasticity. Fig.3 shows the relationship of viscosity vs. water content under the three typical levels of stress. It is seen that the viscosity of the system at 10% water content reaches a minimum value, which corresponds to the maximum impedance in Fig.1. Then, the viscosity increases gradually with water content, until it increases suddenly at 41.408% water content. The viscosity at the stress levels lower than 20 Pa increases by 3000 times after PIP. However, the viscosity increase at high stress levels is not so great as that at low stress, which means the pseudoplasticity of the system. It is accepted that the dependence of viscosity on volume fraction of the dispersed phase can be described by Dougherty-Krieger formula^[9]:

$$\eta = \eta_0(1 - \phi/\phi_m)^{-[\eta]\phi_m}$$

where η_0 is the viscosity of the continuous phase, ϕ is the volume fraction of the

dispersed phase, ϕ_m is the maximum packing volume fraction, $[\eta]$ is the characteristic viscosity. It is pointed out that D-K formula is only applicable to the emulsions in which the excluded volume effect dominates. It is predicted from the D-K formula that the viscosity η increases monotonously with the volume fraction. However, it is inconsistent with this experimental results that there exists the minimum viscosity at 10 wt% water content. The minimum viscosity is probably attributed to the state transition of the polymeric emulsifier from loose state to reversed micelle structure. In this case, the small amount of free water in epoxy resin continuous phase is driven into the core zone of the reversed micelles, and the enforcement of the hydrophilic component PEG in the emulsifier is screened by the lyophilic component E-20 of the emulsifier at interface.

From 10% to 41.081% water content, the trend that viscosity increases with water content due to the effect of excluded volume agrees with D-K formula. What is more, the viscosity of the system within 41.408~50% water content keeps high up to 10^5 Pa.s. If the effect of excluded volume rather than other strong interaction between dispersed phase dominated after PIP, the viscosity would drop abruptly because the restriction of maximum packing was released. So, it is proposed that a new static structure has formed among the waterborne particles after PIP. In fact, the hydrophilic component of the emulsifier PEG can form strong interaction through hydrogen bond^[6-7]. Therefore, the waterborne particles of epoxy resin may be bridged through hydrogen bond to cause the formation of the three dimensional crosslinked gel alike structure. The pseudoplasticity behavior of the system is due to the break up of the static structure at high stress.

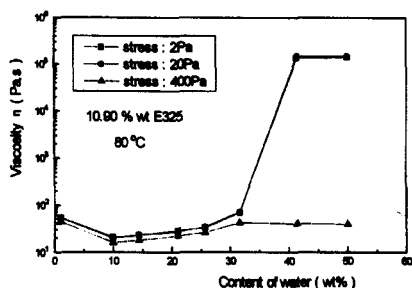


Fig.3 Dependence of viscosity on water content at the three typical stress levels

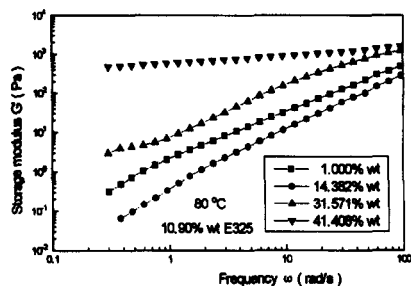


Fig.4 Typical curves of storage modulus vs. frequency during phase inversion evolution

According to the hypothesis that a new static structure is formed, it is predicted that the system after PIP will exhibit high elastic state. In order to confirm the prediction above, the dynamic frequency sweep test is performed in which 20 Pa

stress is applied to avoid the destruction of the static structure of the system. Fig.4 shows four typical curves of storage modulus vs. frequency during phase inversion progress. It is clear that storage modulus of the system at PIP is high up to 10^3 Pa, and the slope of the curve is small close to zero which indicates that the storage modulus is almost independent on frequency. So, it is concluded that the system at PIP exhibits high elastic state. On the contrary, the storage modulus of the system before PIP is low and increases rapidly with frequency, which is the characteristics of liquid state.

Observation of the morphology development during phase inversion progress

Besides the changes of the electrical and rheological properties, observation of the morphology development of the system during phase inversion can help to well understand the structure transformation of the system during phase inversion evolution.

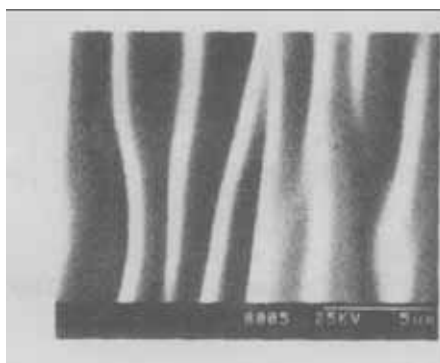


Fig.5 The morphology of the system before PIP



Fig.6 The morphology of the system at PIP



Fig.7 The magnified image of Fig.6

The typical morphology of the system (14.382%) before PIP is shown in Fig.5. It is clear that epoxy resin is the continuous phase with the formation of a stripe texture. Fig.6 shows the typical morphology of the system at PIP, the stripe structure is not so clear as that in Fig.5, and it seems that there is another fine structure in the stripes. In order to disclose the fine structure of the stripes, the magnified image is shown in Fig.7. It indicates that the

stripe is composed of small particles, and a static structure like crosslinked network is formed among particles. This is the origin of high viscoelasticity for the system at PIP.

In conclusion, the phase inversion point (PIP) was determined by the abrupt changes of electrical and rheological properties. Before PIP, the system possesses a high electrical resistance and exhibits the Newtonian behavior. At PIP, the system possesses a low electrical resistance and exhibits high viscoelastic state, and the formation of a crosslinked network structure alike among the waterborne particles can be observed by scanning electron microscopy.

Keywords:

Phase inversion; Rheological behavior; Morphology development; Waterborne dispersions

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