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

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, sub-micron-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% hydrophilic component E-20 and 90 wt% hydrophobic component PEG10000. The number-average molecular weight of E325 was $4.6 \times 10^4$ 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](image-url)