

RHEOLOGICAL BEHAVIOR OF EPOXY RESIN WATERBORNE DISPERSIONS*

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Abstract The waterborne dispersions of epoxy resin were prepared by the phase inversion emulsification technique. Rheological behavior and its relationship with the structural change of the systems were studied. It was shown that the concentrated dispersions were highly viscoelastic and pseudoplastic, which was attributed to the formation of a physical network among the waterborne particles *via* hydrogen bond. The dilute dispersions were Newtonian fluids. The discrete clusters composed of small waterborne particles were found in diluted dispersions. With increasing solid content, there existed a structural transition *via* percolation through a cluster-cluster aggregation mode to form the physical network, which was qualitatively evidenced by the TEM morphologies.

Keywords Epoxy resin waterborne dispersion, Rheological behavior, Cluster-cluster aggregation, Percolation transition

INTRODUCTION

Nowadays, waterborne dispersions of polymer resins with low or zero content of volatile organic compounds (VOCs) have received increasing attention owing to strict environmental and ecological regulations. Most polymeric waterborne dispersions are manufactured by chemical means, such as emulsion or suspension polymerization. It is noted that these methods mainly involve the polymerization of vinyl group by radical initiation and chain growth. Therefore, it is difficult to prepare waterborne dispersions of condensation polymer resins. Alternatively, the so-called phase inversion emulsification technique^[1] proved to be very easy and effective to prepare waterborne dispersions of both addition polymers and condensation polymers from our recent results. The latter method is a physical one and no solvents are involved. Therefore, it is environmentally friendly, and is one of the most favorable methods. Recently, we have successfully employed the phase inversion emulsification technique to prepare bisphenol A epoxy resin waterborne dispersion of sub-micron particle size^[2]. It is expected that this dispersion could find an ample scope of applications^[3]. In order to understand the structure-performance relationship as a guide to practical formulations, it is necessary to characterize the rheological behavior of the dispersions. In this paper, we are mainly concerned with the rheological behavior and its relationship with the morphology of the dispersions.

EXPERIMENTAL

Preparation of the Waterborne Dispersions

Bisphenol A epoxy resin E20 (epoxide molar equivalence 0.20) with an average molecular weight of about 10^3 , was purchased from Chinese East Tianjin Chemicals Co. and used as received. The emulsifier denoted as E325

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composed of E20/PEG10⁴ (weight ratio 1/10) was a self-prepared multiblock copolymer with average molecular weight about 4.6×10^4 measured by GPC. The waterborne dispersion of E20 was prepared with an emulsifier E325 concentration of 10.90% and at 80°C by the phase inversion emulsification technique^[2]. The dispersions of varied solid content were prepared by adding water to the inverted system under stirring.

Characterization of Rheological Behavior

Rheometer DSR-200 (Rheometrics Co.) with parallel plates of 25.00 mm diameter was used to characterize the rheological behavior of the concentrated dispersions. The gap was fixed at 1.00 mm and the temperature during the characterization was accurate to $\pm 0.1^\circ\text{C}$. After the concentrated dispersion was loaded between the parallel plates and the gap between the parallel plates was adjusted to be 1.00 mm, the dispersion was allowed to stand for 2 min in order to relax the residual stress. Dynamic stress at 2 rad/s angular frequency, dynamic frequency and steady stress ramp tests were performed on the same sample sequentially after an interval of 2 min. From the first test, the linear viscoelasticity region was determined. The dynamic rheological behavior of the dispersion was obtained from the second test. From the third test, the structural dependence on stress was obtained. In order to study the structural dependence on time at varied stress levels, a dynamic time ramp test was performed on a freshly loaded sample.

When the solid content of the dispersions was very low, the yield stress was so low that DSR-200 was not applicable to characterize the rheological behavior. Instead, rheometer Low Shear-30 (Contraves Co.) with concentric cylinder rotator was used. The dependence of viscosity on solid content and temperature was also investigated.

Morphological Observation by TEM

A small amount of the relatively dilute dispersion was homogeneously spread onto a carbon coated copper grid and quickly dried in vacuum at ambient temperature. Afterwards, a very thin film was formed from the dispersions on the grid to be observed with transmission electron microscope (JEOL TEM-100 CXII). It was noted that the morphology of the dried film provided the information about the dispersions since the thickness of the spread dispersion was very small and the drying rate was extremely fast.

RESULTS AND DISCUSSIONS

Reversible Structural Transition in Concentrated Dispersions

The relationship between viscosity and stress of the concentrated dispersion with 67.55% solid content at 60°C was shown in Fig. 1. Curve S1 was obtained from the first stress ramp test. It can be seen that the viscosity at lower stress is as high as $10^5 \text{ Pa} \cdot \text{s}$, which is the characteristic behavior of solid-like. The viscosity at higher stress decreases to $10^1 \text{ Pa} \cdot \text{s}$, which is the characteristic behavior of liquid-like. At intermediate stress, there exists the transition from solid-like state to liquid-like state. This transition is attributed to the structural destruction at higher stress. In order to determine whether this transition is reversible, a second stress ramp test was performed on the same sample after standing for 2 min following the first test. The result is shown as curve S2. It is indicated that the solid-liquid like transition during the second test still exists. This means that the destroyed structure was recovered within 2 min. In order to study the time dependent reversibility, a third stress ramp test was performed after standing for 5 min following the second test. The result is shown as curve S3. The viscosity at lower stress shown in curve S3 is slightly higher than that in curve S2. This means that the structure is more completely recovered after longer time.

It is noted that there exists strong hydrogen bond interaction among the waterborne particles covered with the emulsifier containing PEG^[4]. A physical network is formed among the waterborne particles at high concentrations^[5]. The dispersion displays strong pseudoplasticity with increasing stress due to the destruction of the physical network. During the pause of stress action, the destroyed structure could be recovered reversibly.

Effect of Temperature on Rheological Behavior

Figure 2 shows the curves of viscosity versus stress at a given solid content and different temperature. The

viscosity at lower stress and the critical stress at the transition region decrease with temperature. This means that the strength of the physical network decreases with increasing temperature owing to the weakening of the hydrogen bond interaction among the waterborne particles.

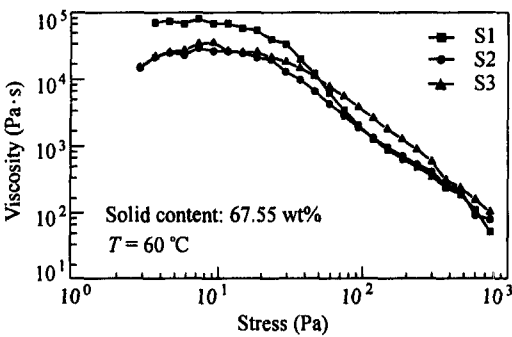


Fig. 1 Relationship between viscosity and stress of concentrated dispersions

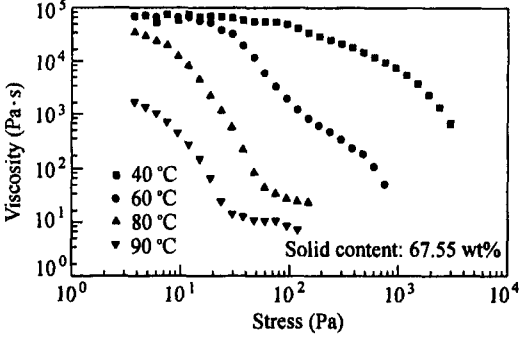


Fig. 2 Dependence of viscosity on stress at the typical temperature levels

The relationship between storage modulus and stress during the dynamic stress ramp test at 2 rad/s angular frequency is shown in Fig. 3. Both the storage modulus and the critical stress, where the storage modulus drops, decrease with temperature. This means that the elasticity of the concentrated dispersion and the strength of the network decrease with temperature. Especially, the storage modulus decreases rapidly in the stress range of 10^1 – 10^2 Pa at a high temperature between 80–90 °C, which is closely correlated with the weaker structure at high temperature.

Figure 4 shows the variation of storage modulus with frequency obtained from the dynamic frequency ramp test at different temperatures. It can be seen that the storage modulus decreases with temperature. This means that the elasticity of the system decreased with temperature. In Fig. 5 showing the dependence of loss modulus on frequency at different temperatures, the loss modulus increases with lowering temperature. This means that the interaction among the waterborne particles decreases with temperature.

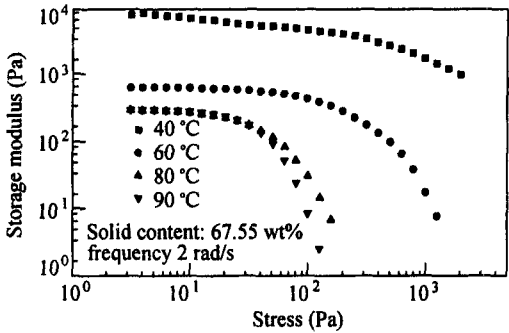


Fig. 3 Relationship between storage modulus and stress at various temperatures

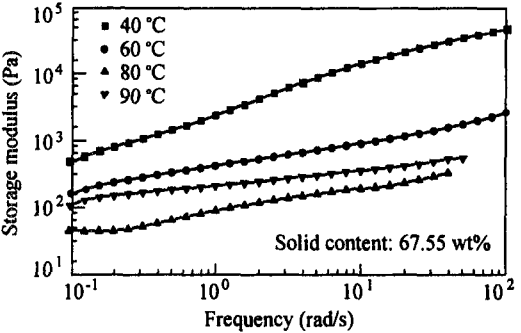


Fig. 4 Variation of storage modulus with frequency at various temperatures

The effect of temperature on the relationship between loss tangent $\tan\delta$ and frequency, as shown in Fig. 6, is very complicated. At 40 °C, $\tan\delta$ reaches a maximum at the frequency 10^0 rad/s, which is probably corresponds to a structural transition. The peak is relatively broad, inferring that the relaxation time of the units involved in the transition has a broad spectrum. On increasing the temperature to 80 °C, $\tan\delta$ decreases, which can be attributed to the decrease in the interaction among the waterborne particles. It is consistent with the strength dependence of the hydrogen bond of PEG/water complex on temperature^[4, 5]. The abnormal increase of $\tan\delta$ at 90 °C is not well understood yet.

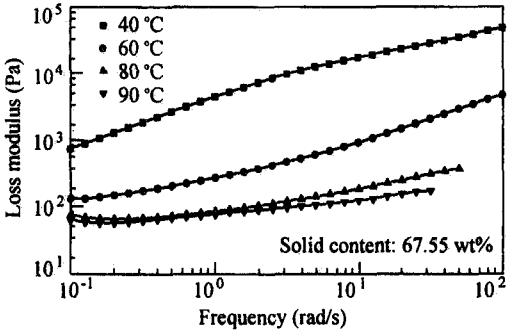


Fig. 5 Dependence of loss modulus on frequency at various temperatures

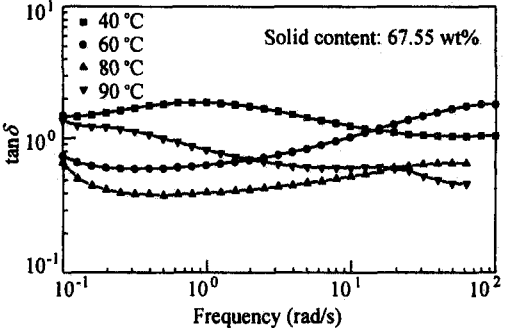


Fig. 6 Relationship between $\tan\delta$ and frequency at various temperatures

Effect of Solid Content on Rheological Behavior

The effect of solid content on steady shear viscosity is shown in Fig. 7. Both the viscosity and the critical stress at the transition region increase with solid content. In addition, there exists viscosity oscillation in the low stress region when the solid content is high (e.g. 67.55%), which is interpreted by the high elasticity in this case. This is explained by the strength weakening of the static structure with decreasing solid content.

The effects of solid content on storage modulus and loss modulus at 40 °C are shown in Fig. 8 and Fig. 9, respectively. It can be seen that the corresponding parameters increase with solid content because the systems become more compacted. It is also interesting to find the curves of $\tan\delta$ versus frequency are similar, as shown in Fig. 10. This indicates structural similarity at varied solid contents, which is completely different from the effect of temperature on this parameter. The increase of $\tan\delta$ with the solid content means that the internal friction increases with solid content.

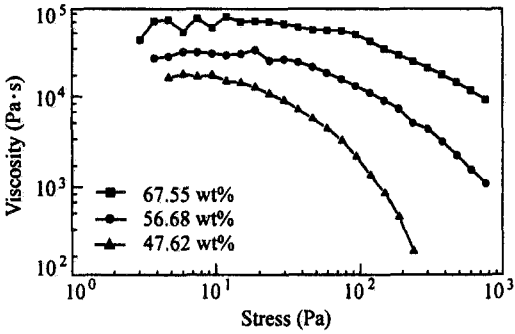


Fig. 7 The effect of solid content on viscosity of the concentrated dispersions

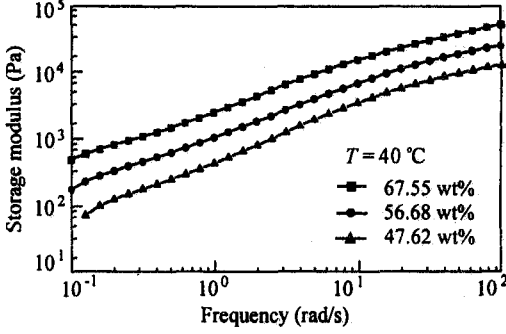


Fig. 8 The effect of solid content on storage modulus of the concentrated dispersions

To sum up, the structural density and strength of the network increase with increasing solid content and falling temperature. At a given temperature, there exists structural similarity at varied solid contents. This similarity becomes less with increasing temperature. All these results reflect that the effect of temperature on the interaction among the waterborne particles is rather complicated.

Rheological Behavior of the Dilute Dispersions

Figure 11 shows the dependence of viscosity on shear rate of the dilute dispersions at 60 °C, the viscosity is only slightly dependent on the shear rate. This is characteristics of Newtonian fluids. Besides, the viscosity increases with solid content and with decreasing temperature as shown in Fig. 12. Moreover, it is also found that plots of logarithmic viscosity versus shear rate at different solid contents are linear with almost the same slope. This

means that the dispersed phase in the dispersions exists in a self-similar mode.

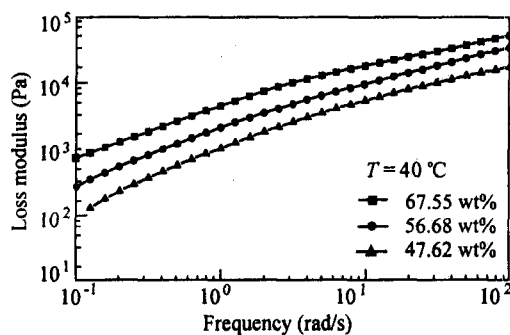


Fig. 9 The effect of solid content on loss modulus of the concentrated dispersions

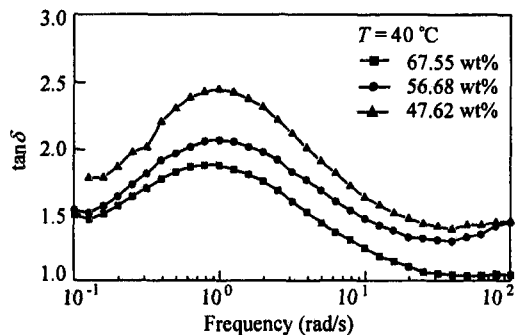


Fig. 10 Variation of $\tan \delta$ with solid content of the concentrated dispersions

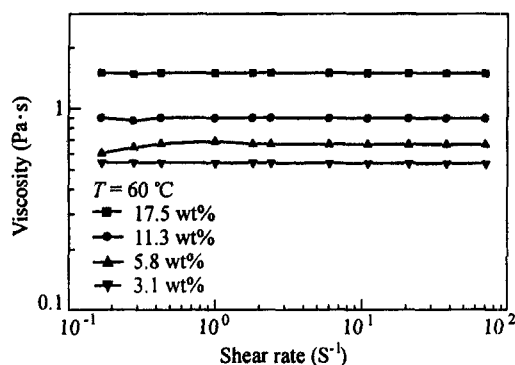


Fig. 11 Dependence of viscosity on shear rate of the dilute dispersions

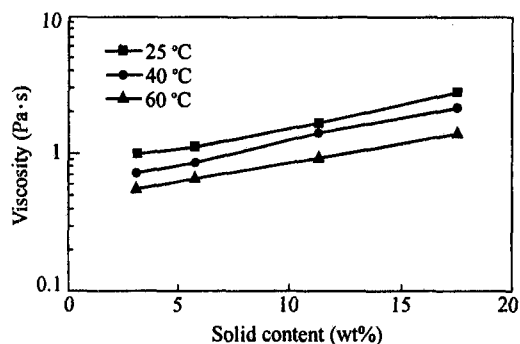


Fig. 12 Dependence of viscosity on shear rate at the typical temperatures

It can be concluded that the effects of solid content on the rheological behavior are pronounced in the waterborne epoxy resin dispersions. The concentrated systems are highly viscoelastic and highly pseudoplastic, which is attributed to the formation of a three-dimensional network from the waterborne particles. In contrast, the dilute dispersions are Newtonian fluids. It is deduced that a structural transition occurs on changing the solid content in the range of 18%–47.6% of the dispersions. This is consistent with Ploehn's finding^[6] that there exists a phase transition with increasing solid content in the PEG grafted polystyrene dispersions attributed to the formation of a static structure.

It was found that the dispersion with 34.90% solid content is more fluidic even at room temperature, and it is difficult to perform the rheological measurement by using the DSR-200 rheometer. However, during the measurement with Low Shear-30 rheometer at 40–60 °C, the rotator is inevitably eccentric and away from the equilibrium position. This means that there exists some viscoelasticity in this case. Therefore, the critical solid content for the structural transition is estimated to be about 35%. The determination of the critical solid content and its temperature dependence is under investigation.

The transmission electron micrographs of the dilute dispersion as shown in Fig. 13(a) indicate that there exist some clusters composed of smaller particles in the dispersion. This result has also been confirmed by light scattering experiments^[7]. When the solid content of the dispersion is high, a network structure composed of the clusters is observable as shown in Fig. 13(b). From Fig. 13(a) to Fig. 13(b) with increasing solid content, there exists a structural transition *via* percolation in the form of cluster-cluster aggregation^[8, 9], which probably originates from the irreversible aggregation by a short range collision sticky mode^[10].

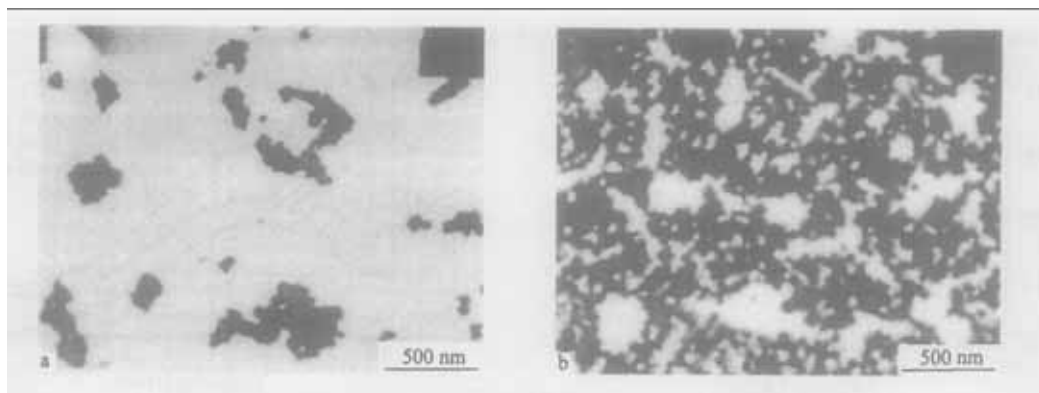


Fig. 13 Transmission electron micrographs of the dispersed phase
a) Diluted dispersion; b) Concentrated dispersion

SUMMARY

In this paper, the relationship between rheological behavior and structure of epoxy resin waterborne dispersions was studied. The effects of solid content and temperature on the rheological behavior were also discussed. It was shown that the concentrated dispersions were highly viscoelastic and pseudoplastic especially at lower temperature, while the dilute dispersions belong to Newtonian fluids. There existed structural transition *via* percolation in cluster-cluster aggregation mode with varying solid content, which was evidenced by TEM results.

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