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Rheological Behavior of Epoxy Resin Concentrated Dispersions

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Abstract: For the concentrated dispersions of epoxy resin prepared by phase inversion emulsification technique, the effects of solid content and temperature on the rheological behavior are studied. It is found that there exists reversible structural transition in concentrated dispersions subjected to shearing. The viscosity oscillation correlated with high viscoelasticity at lower stress is remarkable in highly concentrated dispersions. There exists storage modules overshot at higher stress during the dynamic stress time ramp test. This could provide some information on dynamics of structure changes during shear action. Besides, the effects of solid content and temperature on the relationship between tangent delta and frequency are essentially different.

Keywords: Rheological behavior, waterborne dispersion, bisphenol A epoxy resin.

Introduction

Waterborne dispersions of polymer resins with low (or zero) content of volatile organic compounds have received much attention owing to increasingly strict environmental and ecological regulations. Bisphenol A epoxy resin is a condensation polymer of an extensive scope of applications such as in composites, coatings, adhesives. Therefore, the preparation of the epoxy resin waterborne dispersions is very interesting. Recently, we have successfully prepared the epoxy resin waterborne dispersions with high solid content by phase inversion emulsification technique[1]. The particle size is submicron meter if the dispersion is prepared by complete phase inversion[2]. It is important to characterize the rheological behavior of the dispersions in order to provide a guidance to the formulations and applications.

Experimental

The preparation procedure of the waterborne dispersions of epoxy resin was introduced previously[2]. The dispersions of varied solid content were achieved *via* adding water to the inverted system after the phase inversion point at 80^{o}C under stirring. Rheometer DSR-200 (Rheometrics Co.) was used to characterize the rheological behavior of the dispersions. The parallel plates with 25.000 mm diameter and 1.000 mm gap were used. The accuracy of experimental temperature is ±0.1°C. The dispersion loaded between the plates was allowed to stand for 2 min. after adjusting the gap in order to relax the residual stress. The rheological characterizations including dynamic stress at 2 rad/s frequency, dynamic frequency and steady stress ramp tests were performed on the same sample sequentially. The intervals between the two tests are 2 minutes to ensure the structural recovery. The information of the structural dependence on time at varied stress levels could be provided from dynamic time ramp test on a freshly loaded sample**.**

Results and Discussion

It is found that there exists a reversible structural transition in concentrated dispersions of epoxy resin during shear action. **Figure 1** shows the plots of viscosity *vs.* stress at 60°C for the 67.55% concentrated dispersion. From plot S1, obtained from the first stress ramp test, the viscosity at lower stress is high up to 10^5 Pa.S, which is the characteristic of solid behavior. The viscosity at higher stress decreases to 10 Pa.S, which is the characteristic of liquid behavior. At intermediate stress, there exists the transition from solid like state to liquid like state. This transition is attributed to the structural destruction of the concentrated dispersion at higher stress. In order to determine if this transition is reversible, the second dynamic stress ramp test is performed on the dispersion after 2 min. pause following the first test, shown in plot S2. There still exists the solid-liquid like state transition during the second stress ramp test. This means that 2 min. pause is sufficient for the destroyed structure to be recovered. In other words, this structural transition is reversible within 2 min.. In order to study the reversibility dependence on time, the third stress ramp test is performed on the dispersion after 5 min. pause following the second test, shown in plot S3. The viscosity at lower stress in plot S3 is slightly higher than the corresponding value in plot S2. This means that the structure is recovered more completely after longer time. Nevertheless, this recovery is mainly completed within 2 min. It is noted that there exists strong interaction among the waterborne particles *via* hydrogen bond between PEG component of the emulsifier molecules with water[3]. A static structure like network is formed among the waterborne particles in concentrated dispersion[4]. The concentrated dispersion exhibits strong pseudoplasticity at higher stress attributed to the destruction of the static structure. Upon the shear pausing, the destroyed structure starts to be recovered.

Figure 2 shows the effect of temperature on the relationship between viscosity and stress at a given solid content. The viscosity at lower stress decreases with temperature and the critical stress at the transition region decreases as well. This means that the strength of the static structure of the concentrated dispersion decreases with temperature owing to weaker interaction of the hydrogen bond among the waterborne particles.

Figure 3 shows the relationship between tangent delta with frequency in dynamic frequency ramp test. There exists a maximum tangent delta at experimental temperature 40°C. Tangent delta decreases with temperature and increases with frequency. However, the relationship is different at 90°C. Tangent delta decreases with frequency. This complexity is correlated with the complicated physicochemical properties of PEG/water complex with temperature.

Figure 4 shows the effect of solid content on steady shear viscosity. The viscosity and the critical stress at the transition region increases with solid content. It is also found that there exists oscillatory viscosity at lower stress when the solid content is higher (*e.g.* 67.55%), which is interpreted by higher elasticity. It is worthwhile to note that there exists similarity of the relationship between tangent delta and frequency as shown in **Figure 5**. This means that there exists the structural similarity in the dispersions at varied solid content. Tangent delta increases with solid content, which means that the internal friction increases with solid content.

Figure 1. Plots of viscosity *vs.* stress of concentrated dispersions

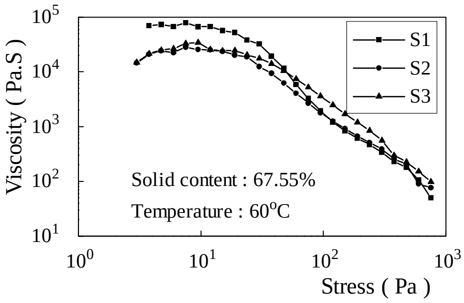


Figure 2. Plots of viscosity *vs.* stress at the typical temperature levels

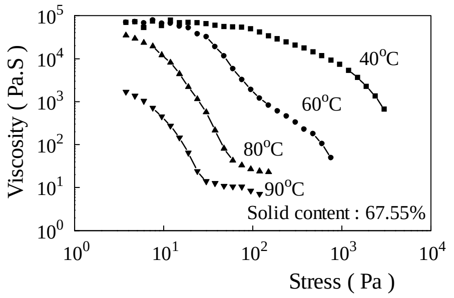


Figure 3. Plots of tangent delta *vs.* frequency at the typical temperature levels

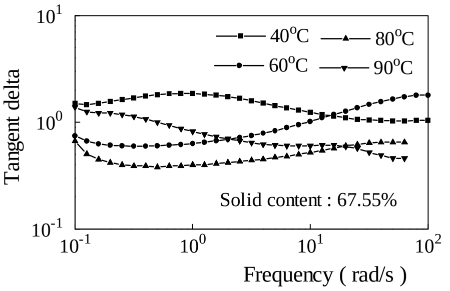
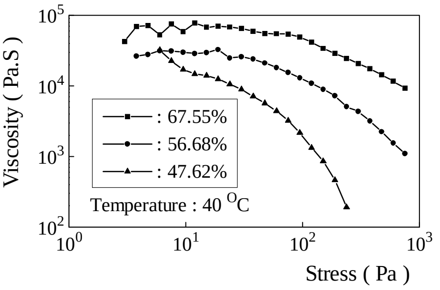


Figure 4. Plots of viscosity *vs.* stress at varied solid contents

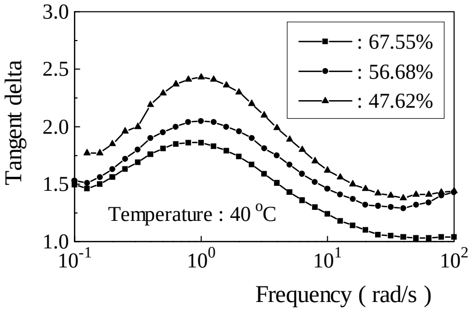


To summarize, the structural density, the network strength and the elasticity of the dispersions increase with solid content and decreasing temperature. At a given temperature, there exists the structural similarity at varied solid content. This similarity will become weak with increasing temperature. All these results reflect that the effect of temperature on the interaction among the waterborne particles is complicated.

Figure 6 shows the result of dynamic stress ramp test for the 56.68% dispersion at 60°C. It is seen that the dynamic rheological parameters drop abruptly when the stress exceeds 200 Pa. This means that the static network is destroyed. This is consistent with the fact that tangent delta increases abruptly with stress, which means that the system becomes more viscose.

Figure 7 shows the dependence of storage modules at 2 rad/s frequency with time of the 56.68% dispersion at 60°C at the three typical stresses. At lower stress (*e.g.* less than 100 Pa), the storage modules is independent on time. This means that the network is mainly sustained. When the stress is higher, the storage modules decreases rapidly with time. After a minimum, the storage modules levels off. This means that the system exhibits modules overshot when the stress is higher corresponding to an nonequilibrium state. The slight decrease in storage modules with stress is ascribed to the structural defects of the concentrated dispersion. Therefore, the strength of the structure and its dependence on time at varied stress levels could be understood from dynamic stress and dynamic time ramp tests, respectively.

Figure 5. Plots of tangent delta *vs.* frequency at varied solid contents



Figrue 6. Results of dynamic stress ramp test of the 56.68% dispersion at 60 °C

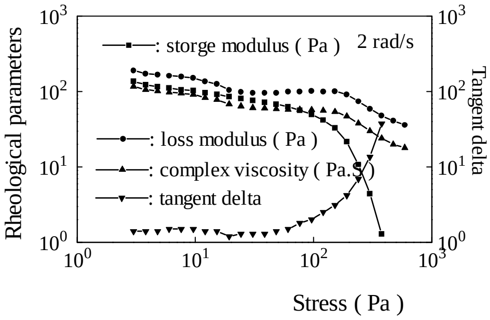
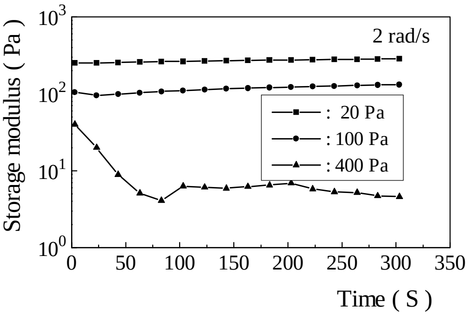


Figure 7. Plots of storage modulus *vs.* time at the three stress levels



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