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Viscoelasticity of Onion Phase Composed of Complex Surfactant Bilayers

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Onion (multilamellar vesicles) has a quite fascinating structure organized by amphiphilic bilayer membranes. According to the unique structure, a decrease in the onion radius is considered to be a serial event induced by peeling off the outer shell. However, it is not well known how onion grows up, when a shear rate is changed. We studied its mechanism by viscoelastic measurements. When the shear rate is quenched with a large depth, onion structure is degraded with exponential decay in the viscosity, followed by onion reformation. However, small quench depth in the shear rate does not cause exponential decay. Threshold shear rate for this mechanism is determined by the viscosity of lamellar phase in Newtonian region.

Key words: Viscoelasticity, Onion phase, Vesicle, Lamellar phase, Shear-induced phase transition

1. INTRODUCTION

Multilamellar vesicles, so-called onion phase, can be prepared by applying shear flow on the surfactant lyotropic lamellar phases(1). Onion phase has so fascinating structure, in which smaller vesicles are enveloped in larger one. Many researchers try to understand the physics underlying this shear-induced non-equilibrium phase transition experimentally and theoretically, respectively. Using of the small angle neutron scattering under shear (Rheo-SANS) and viscoelastic measurements shed light on its mechanism(2). We have recently shown that the size of the onion particles changes reversibly as a function of the shear rate(3). When the shear rate is increased, onion size starts to be small. On the other hand, onion size starts to be larger by decreasing shear rate. Then, our question at this stage is how onion grows up from smaller to larger one and what parameter controls the growth of onion size.

In this study, we try to understand the mechanism how and from where onion gets outer shell to increase its size. We mainly report here the viscoelastic behavior when the onion grows up after shear-jump method.

2. Experimental

Surfactant lamellar phase was prepared by nonionic surfactant, $C_{10}E_3$, purchased from Nikko Chemicals co. ltd. $C_{10}E_3$ was dissolved in H_2O with the concentration of 40wt.%. For the viscoelastic measurements in this study, we used ARES-LS, Rheometrics. Geometry used here was a couette shear cell. Every measurement has done at 25°C.

2. Results and Discussion

2.1 Flow curve at steady state

Figure 1 shows a flow curve, viscosity vs. shear rate, at steady state. Each data points were obtained from plateau value of the time dependent measurements of the viscosity. Dynamic viscoelastic measurements were performed after the plateau is reached. In figure 1, storage modulus obtained at frequency of 1Hz is also shown. We can clearly see that the flow curve is classified into three shear rate domains. First, in the low shear rate region, 1-3s^{-1}, where the structural transition is not appeared yet, this system shows a Newtonian behavior. In the intermediate shear rate region, the viscosity starts to increase remarkably as a function of the shear rate, referred as a shear-thickening viscosity. In this region, shear modulus also increases significantly. This second region corresponds to the start of the onion formation and regarded as lamellar-to-onion transition region. Further increase in the shear rate causes the shear-thinning viscosity, where the viscosity decreases as a function of the shear rate. Here, the shear modulus increases gently. This third shear rate region corresponds to the Onion phase.

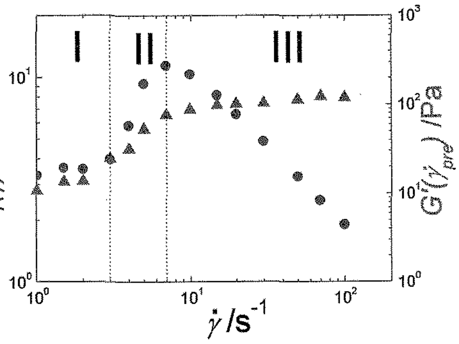

Figure 1. Flow curve for $C_{10}E_3$ lyotropic lamellar phase.

2.2 Degradation of onion phase

On the basis of the flow curve, shear jump tests were preformed by changing the shear rate from fixed initial (high) shear rate to final (low) one, which was controlled, and visa versa. As a typical example of the measurements, figure 2 shows decay curves of viscosity as a function of time elapsed after shear jump. Here, the final shear rate was fixed at 2s^{-1}, where lamellar

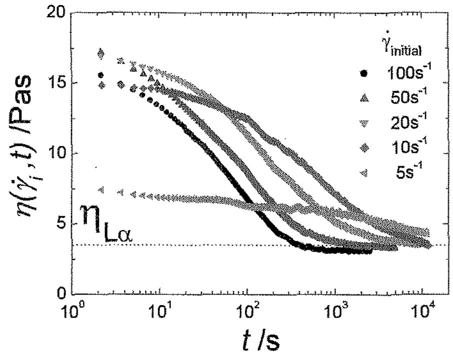

Figure 2. Decay curve of the viscosity after shear jump.

structure only exists, and initial shear rate was controlled from 100 to 5s^{-1}, where onion exists. After the shear jump from 100 to 2s^{-1}, shear viscosity decays like a single exponential function. Eventually, the viscosity reaches to the same value as that of the lamellar phase in the Newtonian region. Since onion structure was not observed at 2s^{-1}, the single exponential like decay shows a degeneration process from onion to lamellar structure. The decay rate clearly depends on the initial shear rate. The lower the initial shear rate, the slower the decay rate. Degeneration process of the onion structure depends on the initial shear rate.

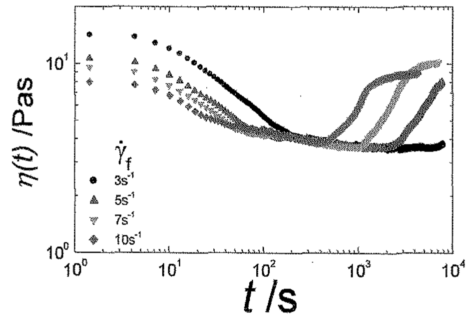

Figure 3. Decay curve of the viscosity after shear jump.

Figure 3 also shows the decay curve of the viscosity as a function of time. Here, the initial shear rate was fixed at 100s^{-1} and the final shear rate was controlled. When the shear rate is jumped from 100 to 3s^{-1}, the shear viscosity decays like a single exponential function as shown in figure 2. When the shear rate is jumped into regions II or III, however, viscosity decays like a double exponential like function followed by increase through the viscosity minimum. This unique behavior is attributed to onion reformation after degeneration to lamellar structure. Fast mode in the decay curve of the viscosity will be corresponding to the rupture of the onion structure as shown in figure 2. It is not sure yet what the slow decay mode is. Induction time for the onion reformation depends on the final shear rate. Thus, reformation properties of onion structure will be determined by the final shear rate.

2.3 Summarized flow curve

Summarizing the shear jump tests shown in figure 2 and 3, three viscosity values are plotted as a function of shear rate in figure 4. Here, the initial viscosity, η_0, and the minimum one, η_m, correspond to the initial (at t=0) and minimum values of the viscosity in the decay curve, respectively. In figure 4, η_0 follows the steady viscosity in the region III. In the Newtonian and shear-thickening regions, η_0 shows the Newtonian like behavior. Apparent Newtonian and shear-thinning behavior of η_0 might be the same as a typical character of suspension systems. Thus, the Peclet number would describe the critical shear rate for the shear-thinning viscosity(4). After the degradation process of onion structure, viscosity reached to the same value as that of lamellar phase in the Newtonian region (region I). The same viscosity of η_m as the lamellae suggests that the onion is collapsed and goes back to lamellae when the shear rate is reduced. Since we could see that onion was reformed again after the degradation in figure 3, we would be able to say that size change process of onion was dominated by complicated path way.

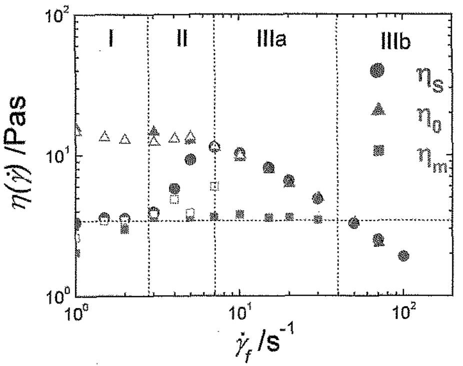

Figure 4. η_S, η_0, and η_m as a function of the final shear rate. Open and filled symbols show the results from different initial shear rates of 15 and 100s^{-1}, respectively.

3 Summaries

First, onion prepared at high shear rate was collapsed into lamellae when shear rate was reduced. Then, the lamellae transformed the structure to onion at low shear rate. This anomalous onion-lamellae-onion transformation would be attributed to elastic bending energy of bilayer membrane, which depends on a curvature. At high shear rate regions, viscous stress applied by shear flow is balanced with elastic bending energy of membrane. However, unbalance between the viscous stress and bending modulus being appeared by reducing shear rate will induce instability of bilayer membrane because elastic bending modulus becomes larger when shear rate is reduced. This instability will cause the degradation of membranes resulting in rupture of onion structure.

4 References

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