

# Effects of compositions on shear stress instability in nanoparticle suspensions

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Periodic oscillations in shear stresses have been recently observed experimentally<sup>[1]</sup> and theoretically<sup>[2]</sup> in concentrated nanoparticle suspensions subject to a constant shear rate. Such a time-dependent stress is undesirable in many post-metered coating applications because it can lead to non-uniform liquid film thicknesses. To date, most of previous studies on the stress oscillation have dealt with suspensions at high particle volume fraction of  $\phi \sim 40$  vol% and attributed the origin of stress instability to a hydrodynamic clustering/de-structuring of particle aggregates. In this study, we provide experimental evidence that the stress oscillations emerge at extremely low particle volume fractions of  $\phi < 5$  vol% in toluene-base, co-solvent suspensions of titanium oxide (TiO<sub>2</sub>) nanoparticles containing soluble poly(vinyl acetate)(PVAc) as a binder.<sup>[3]</sup> We examined shear stresses of several suspensions and summarized the effects of compositions oscillation mode maps.

Poly(vinyl acetate) (PVAc, Alfa Aesar Co. USA) with a mass averaged molecular weight (Mw) of 50,000 was dissolved in a mixture of toluene (Tol, Wako Pure Chemical Industries Ltd. Japan) and ethanol (EtOH, Wako Pure Chemical Industries Ltd. Japan). All solvents were used as purchased without any further purification. The mass ratio of ethanol to toluene,  $\beta/(1-\beta)$ , was varied by changing  $\beta$  between 0 and 0.035. The mass ratio of PVAc to solvents was  $\sigma/100$  where  $\sigma$  ranged up to 25. Titanium dioxide (TiO<sub>2</sub>, Ishihara Sangyo Kaisha Ltd. Japan) particles with a mean diameter of 200 nm were added to the polymeric solution and stirred over 24 h. The particle volume fraction in the solution was  $\phi = 4.7$  vol% at  $\beta = 0.035$  and  $\sigma = 5$ . Shear stress measurements of the samples were conducted at  $26 \pm 3$  °C using a HAAKE MARS II (Thermo Scientific Co. Japan) rheometer having cone-plate geometry of 30 mm in radius, 1° in inclination angle, and 0.052 mm in gap. The sample fluids were subject to constant shear rate of  $10 \text{ s}^{-1}$  without pre-shearing. Adsorbed amounts of the polymer on the particle were obtained by measuring the mass of non-adsorbed polymer in supernatants of nanoparticle suspensions after centrifugation at 15000 rpm for 1 h.

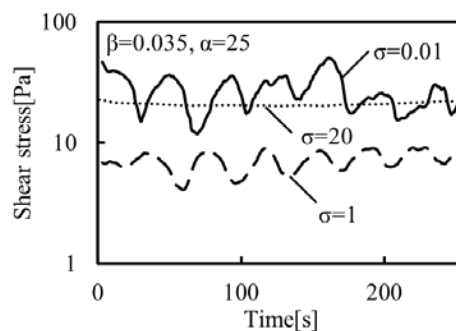


Fig.1 Time evolutions in stresses for different polymer contents at the shear rate of  $10 \text{ s}^{-1}$ .

First, we examined the effect of polymer concentration of stress oscillations in nanoparticle suspension. Figure 1 shows shear stresses of nanoparticle-polymer suspensions at constant shear rate. Stress oscillation appeared at low polymer concentrations of  $\sigma = 0.01$  and 1. The average shear stress decreased with increasing  $\sigma$ . However, a further increase  $\sigma$  led to a non-oscillating shear stress, and an increase in the stress.

To characterize the stress oscillation, we calculated FFT spectra of shear stresses at different polymer and particle contents, and classified the modes as i) oscillation with a single peak at constant frequency  $f_0$  (mode-S), ii) no stress oscillation (mode-N), iii) periodic oscillation with multiple frequency peaks at higher frequencies of  $f_1 > f_0$  (mode- $M_1$ ), and iv) those at lower frequencies of  $f_2 < f_0$  (mode- $M_2$ ). The effects of compositions on the stress instability were systematically examined and summarized as the oscillation mode map (Figure 2).  $M_1$  and  $M_2$  modes appeared at a specific region of low polymer concentrations and high particle concentrations.

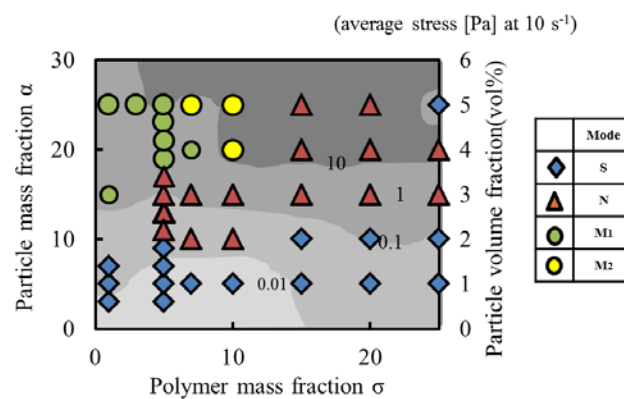


Fig. 2 Time evolutions in stresses for ethanol mass fraction  $\beta=0.035$  at the shear rate of  $10 \text{ s}^{-1}$ .

Next, we examined the adsorbed amounts of polymer on the particle surface. Figure 3 shows amount of adsorbed polymer, and the mass ratio of adsorbed-to-total amounts of polymers at different ethanol contents. The amount of adsorbed polymer showed negligible dependence on ethanol concentration, while the stress showed a transition between mode-S and mode-N. In addition, the mass ratio of adsorbed-to-total amounts of polymer was less than 10 % for any ethanol contents, implying that the stress oscillation is not directly associated to the polymer adsorption on the particle surface. We need further studies to clarify the origin of particle aggregation and the resulting stress instability.

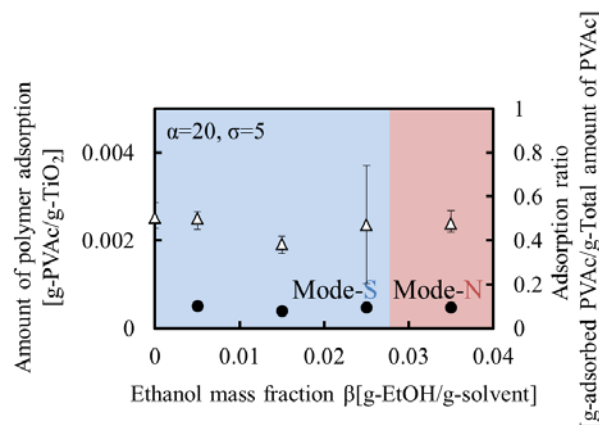


Fig. 3 Amount of adsorbed polymer to particle at different ethanol contents.

## **Conclusions**

We examined rheological behavior of co-solvent solutions of poly(vinylacetate) in ethanol/toluene mixtures. The shear stress shows characteristic non-sinusoidal stress oscillation when the suspension is subjected to a constant shear rate. The corresponding FFT spectra show multiple frequency peaks, implying that nanoparticle aggregates show growth and decay in a sequential manner. An increase in the polymer content led to a stable state with a constant shear stress.

## **References**

- [1] Lootens et al., Phys. Rev. Lett., 90, 178301-1-178303-4 (2003).
- [2] Bashkirtseva et al., J. Appl. Math. Mech., 76, 466-474 (2012).
- [3] Jang et al., Journal of Chemical Engineering of Japan Vol. 49, No. 1 p. 6-9 (2016).

## **Acknowledgement**

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