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# Composition-Dependent Stress Oscillations in a Dilute Suspension under Shear

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**This study presents empirical evidence that dilute particle-polymer suspensions exhibit composition-dependent stress oscillations at constant shear rate. In ethanol/toluene co-solvent suspensions, an increase in the ethanol concentration promoted a transition of the particle-polymer suspension from a stable state, through an oscillating state with well-defined periodicity, toward an unstable mode with multiple frequency peaks. This transition corresponded to increases in the gyration radii of the polymer chains in the fluids. Furthermore, the opposite transition from an unstable state to stable states was observed with increasing polymer concentrations. In contrast, the extent of the transition was curtailed in cyclohexane/toluene suspension, in which both the shear stress and gyration radius remained constant with negligible dependence on the fluid composition. These facts indicate that the non-hydrodynamic depletion attractions among particles play a significant role in influencing the stress instability of polymer-particle suspensions.**

## Introduction

Periodic oscillations in shear stresses have been observed experimentally (Lootens *et al.*, 2003) and theoretically (Bashkirtseva *et al.*, 2012) in nanoparticle suspensions subjected to a constant shear rate. Such a rheological response has so far been attributed to particle clusters (Bender and Wagner, 1995; Bossis and Brady, 1989; Gopalakrishnan and Zukoski, 2004) that form and destruct under shear, and is recognized as a unique fluid property of concentrated suspensions with particle volume fractions of  $\phi \sim 40$  vol %. However, we recently demonstrated that co-solvent nanoparticle-polymer suspensions exhibited a distinct stress oscillation at extremely low volume fractions of  $\phi < 6$  vol% (Yamamura *et al.*, 2013). Since local lubrication forces between neighboring particles decrease with decreasing particle volume fraction, the stress instability in such low  $\phi$  fluids leads to the hypothesis that non-hydrodynamic attractive forces may play a role in building non-permanent particle clusters. In addition, the

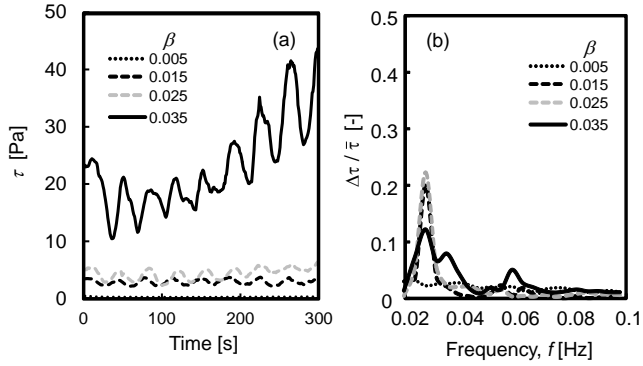
short-range non-hydrodynamic forces may lead to the formation of spatially heterogeneous clusters that undergo partial destruction during shearing, resulting in non-sinusoidal stress signals with multiple wavelengths. Despite the practical utility of particle-polymer suspensions in many coating industries, understanding of which forces dominate the fluid system and how they promote the transition between stress instability modes is far from complete. In this article, we examine the stress oscillation in dilute suspensions in terms of depletion forces that are caused by the exclusion of non-adsorbing polymer chains from gaps between particles (Vincent *et al.*, 1986). The effects of the mass fractions of the polymers, the effects of a secondary poor solvent, and of the solvent species were evaluated by variation of these parameters in order to tune the radius of the polymer chains, and thus the magnitude of the depletion attractions. The Fourier spectra of time-evolving stress signals indicated that an increase in the chain radius led to a mode transition from stable, though an unstable state with well-defined periodicity, toward an unstable stress mode having multiple frequency peaks.

## 1. Experimental

Poly(vinyl acetate) (PVAc, Alfa Aesar Co.) with a mass averaged molecular weight ( $M_w$ ) of 50,000 was dissolved in a

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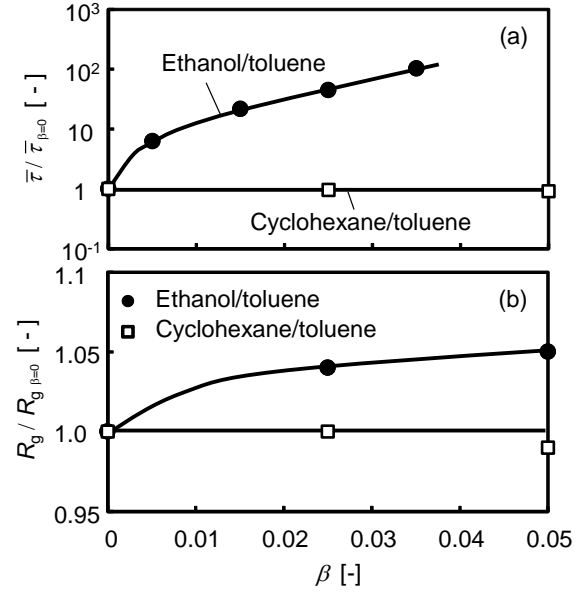


**Fig. 1** (a) Time evolution of stress and (b) frequency spectra of PVAc/TiO<sub>2</sub> in solvent mixtures with different ethanol contents at the shear rate of  $10\text{ s}^{-1}$ . The shear stresses were measured 97 h after adding particles in polymeric solutions at  $\delta = 5$ .

mixture of toluene (Wako Pure Chemical Industries Ltd.) and ethanol (EtOH, Wako Pure Chemical Industries Ltd.), or a mixture of cyclohexane (Wako Pure Chemical Industries Ltd.) and ethanol. All solvents were used as purchased without any further purification. The mass ratio of ethanol or cyclohexane to toluene is described as  $\beta/(1-\beta)$ , where  $\beta$  varied between 0 and 0.035. The mass ratio of PVAc to solvent was  $\delta/100$ , where  $\delta$  ranged between 5 and 25. Titanium dioxide (TiO<sub>2</sub>, Ishihara Sangyo Kaisha Ltd.) particles with a mean diameter of 200 nm were added to the polymeric solution and stirred over a period of 24 h. The particle volume fraction ( $\phi$ ) in the solution was  $\phi = 4.7$  vol% at  $\beta = 0.035$  and  $\delta = 5$ , and 4.1 vol% at  $\delta = 25$ . Shear stress measurements of the samples were conducted at  $26 \pm 3$  °C with a 1 s interval using a HAAKE MARS II (Thermo Scientific Co.) rheometer having a cone-plate geometry with a 30 mm radius and  $1^\circ$  inclination angle. The sample fluids were subjected to a constant shear rate of  $10\text{ s}^{-1}$  or  $40\text{ s}^{-1}$  without pre-shearing. We used the values measured within 300 s as the stress data in order to reduce the effect of drying at the sample edge.

## 2. Results and Discussion

**Figure 1(a)** shows the stress evolution in ethanol/toluene mixtures with different ethanol contents,  $\beta$ , ranging from 0.005 to 0.035. The measured shear stress ( $\tau$ ) was low and almost constant at  $\beta = 0.005$ , whereas the shear stress showed a remarkable near-sinusoidal oscillation at  $\beta = 0.015$ . A further increase in  $\beta$  resulted in an increase in the stress and its oscillation amplitude, leading to complex stress evolution with a sharp growth and subsequent slow decay. Similar stress instability was observed in

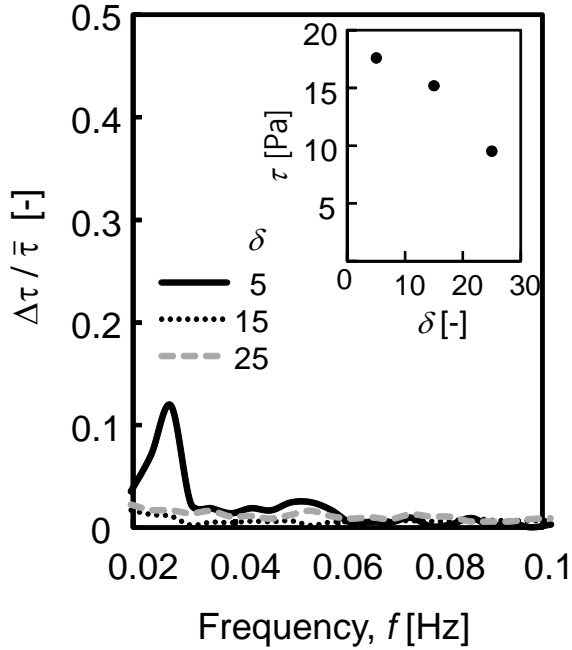


**Fig. 2** (a) Mean stresses in suspensions and (b) gyration radius of PVAc in polymeric solutions normalized by those at  $\beta = 0$ . The shear stress in cyclohexane/toluene suspensions was measured at  $40\text{ s}^{-1}$ .

our supplementary measurements using a rheometer with a parallel-plate geometry having a 0.5 mm gap (data not shown).

For detailed quantification of the stress oscillation, Fourier analyses of the time-evolved stress signals were performed. **Figure 1(b)** shows the frequency spectra for different  $\beta$  values, corresponding to the stress variations in Figure 1(a). The oscillation amplitude ( $\Delta\tau$ ) was normalized by the mean stresses ( $\bar{\tau}$ ) within the measurement time of 256 s for each  $\beta$ . The spectra showed a sharp primary peak at the frequency of  $f_1 = 0.0273\text{ Hz}$  for different ethanol contents of  $\beta = 0.015$  and  $0.025$ . In contrast, in the case of  $\beta = 0.035$ , the intensity of the primary peak declined and higher-order peaks with lower amplitudes evolved at high frequencies. These facts indicate that an increase in the ethanol content resulted in an oscillation transition from a well-defined periodicity toward an instability with multiple characteristic wavelengths.

The frequency of the  $i$ -th peak allows us to calculate the characteristic time scale of the oscillation as  $\lambda_i = 1/f_i$ ; we thus obtained  $\lambda_1 = 37$  s. The time scale corresponding to the primary peak agreed with that required for the one-cycle cone rotation ( $\lambda_r$ ) as  $\lambda_r/\lambda_1 \sim 1$ . In fact, the feedback process to maintain a constant shear rate may be one cause of the stress oscillations, particularly in dilute suspensions with low stress levels. However, the time scales for the higher-order oscillations did not match  $\lambda_r$  and show



**Fig. 3** Frequency spectra of PVA/TiO<sub>2</sub> in ethanol/toluene suspensions with different polymer contents at  $\beta = 0.035$ . The inset shows the decrease in the mean stress with an increase in  $\delta$ . The shear stress was measured 24 h after adding particles to the polymeric solutions.

non-harmonic features of  $\lambda_1/\lambda_2 \sim 1.3$  and  $\lambda_1/\lambda_3 \sim 2.1$ , implying that the stress oscillation is due to the rheological response of the sample fluids.

We estimated the relaxation time ( $T$ ) of the fluid by dividing the steady-state shear viscosity ( $\mu$ ) by the elastic modulus ( $G'$ ) as  $T = \mu/G'$ . The modulus was measured using small-amplitude oscillatory shearing in cone-plate geometry. For the typical sample composition of  $\phi = 4.7 \text{ vol.}\%$ ,  $\beta = 0.035$ , and  $\delta = 5$ , the modulus had an almost constant value of  $G' \sim 10 \text{ kPa}$  over the wide frequency range of 0.1 to 100 Hz. The corresponding relaxation time was  $T = 0.2 \text{ ms}$ , which is much shorter than the characteristic time scale of the stress oscillation.

To examine the physical factors underlying the increase in the shear stress with increasing ethanol content, similar stress measurements were conducted by utilizing cyclohexane as the secondary solvent. As shown in **Figure 2(a)**, the stresses in the polymer-particle suspensions in the cyclohexane/toluene mixture remained constant, whereas those of the ethanol/toluene mixtures increased exponentially by two-orders of magnitude with an increase in  $\beta$  over a narrow composition range between 0 and

0.035. The difference in the rheological responses between two fluids can be understood by considering the radii of gyration ( $R_g$ ) of PVAc in the fluids. **Figure 2(b)** shows the variations of  $R_g$  for the particle-free ethanol/toluene and cyclohexane/toluene mixtures at different  $\beta$ , determined from the measured intrinsic viscosities (Larson, 1999). Polymer coils in a liquid medium overlap above the critical overlap concentration,  $c^*$ , which is related to the radius of gyration as  $c^* \sim 1/R_g^3$ . On the other hand, the intrinsic viscosity of the polymer solution ( $[\eta]$ ) can be related to  $c^*$  by the Einstein formula when we assume a hard sphere of radius equal to the radius of gyration of the coil. The expression  $[\eta] = 10 N_A R_g^3 / (3M)$  was used to estimate  $R_g$  from the shear viscosity data at the limit of dilution, where  $N_A$  and  $M$  denote Avogadro's number and the molecular weight of the polymer, respectively.

The chain radius increased monotonically with increasing  $\beta$  in the ethanol/toluene mixture but remained constant in the cyclohexane/toluene mixture, showing the same trend as the stress variations. As neighboring particles move closer to each other, the freely suspended polymers located among the particles are excluded and move outside the region of chain overlap. The resulting difference in the polymer concentrations between the overlap region and the bulk medium increases the osmotic pressure, which induces flocculation of the particles driven by the depletion force. Since the depletion potential is proportional to  $R_g^2$  when the particle radius is much larger than the chain radius, the increase in  $R_g$  in the ethanol/toluene suspensions possibly induces stronger depletion attractions between neighboring particles, resulting in particle clustering. This is consistent with the significant rise in stress, as well as the transition in the stress oscillation modes with increasing ethanol content.

To further prove the importance of the depletion forces in influencing the stress, we varied the polymer concentrations while maintaining the solvent composition and the particle-to-solvent mass ratio constant. **Figure 3** shows the Fourier spectra of the stress signals for different PVAc to solvent mass ratios, i.e.,  $\delta$ . The spectrum showed a distinct peak at  $\delta = 5$ , whereas the intensity of the peak declined, leading to oscillation-free stresses, at higher polymer contents of  $\delta = 15$  and 25. The same trend was observed in the case of longer mixing times (not shown). In addition, the mean stress values decreased monotonically with increasing  $\delta$  (shown in the inset), indicating the opposite scenario in the particle-free polymeric solutions. Generally, the gyration radius of polymer chains decreases with increasing polymer concentration when the polymer chains overlap in concentrated solutions. Reduction of the chain radius leads to weaker depletion attractions

between particles, and hence, less clustering of particles. This is consistent with the lower stresses observed at higher polymer concentrations and the mode transition from oscillating mode to the steady stress state. Indeed, the supplementary steady shear viscosity measurement of the particle-free PVAc solutions revealed that the viscosity increased slightly with increasing polymer concentration in the dilute unentangled regime, whereas the viscosity increased exponentially in the entangled regime. The viscosity data at a constant shear rate of  $10\text{ s}^{-1}$  fit well to the power law  $\eta \sim \delta^n$  in both regimes; however, the exponent  $n$  apparently changed at the critical overlap concentration of  $\delta^* = 8\text{--}9$ . This is consistent with the present stress spectrum that showed a distinct peak at  $\delta = 5$ , whereas the intensity of this peak diminished at higher polymer contents of  $\delta = 15$ , supporting the postulate that overlapping of the polymer chains at  $\delta > \delta^*$  is the physical source of the decay in the stress oscillation at high polymer concentrations.

Although we have not yet succeeded at direct measurement of  $R_g$  in the present particle-polymer suspensions because of inherent difficulties in the light scattering experiments for concentrated systems, the present results support the hypothesis that the depletion forces play a significant role in the stress evolution in suspensions, possibly by competing against the shear-induced destruction of particle clusters to promote the stress instability.

## Conclusions

We compared the rheological behavior of poly(vinylacetate) in two co-solvent solutions comprising ethanol/toluene and cyclohexane/toluene mixtures. In the former, an increase in the ethanol content led to an increase in the gyration radius of the polymer in dilute polymeric solutions, and an exponential increase in the stress in the polymer-particle suspensions, accompanying a transition from a stable state, though an oscillating state with well-defined periodicity, toward an unstable mode with multiple frequency peaks. On the other hand, the gyration radius and stress remained constant in the cyclohexane/toluene solutions, irrespective of the cyclohexane content. This good correlation between the stress response and the gyration radius of the polymer indicated that depletion attraction

among the particles is one of the physical sources promoting stress instability in the ethanol/toluene suspensions.

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