Shear stress oscillation in co-solvent nanoparticle suspensions: instability mode map

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Nanoparticle-polymer composites such as fuel cell electrode, green sheet, and optical films are produced by coating and drying of nanoparticle suspensions. Time-dependent stress variations are undesirable in these applications since the liquid film thickness in a post-metered coating is determined by a balance between the shear stress and the liquid surface tension. However, periodic oscillations in shear stresses have been recently observed experimentally [1] and theoretically in concentrated nanoparticle suspensions at particle volume fractions of φ~ 40 vol %.

In this study, we provide experimental evidence that the stress oscillations emerge at extremely low particle volume fractions of φ< 7 vol% in toluene-base, co-solvent suspensions of titanium oxide (TiO₂) nanoparticles containing soluble poly(vinyl acetate)(PVAc) as a binder.

We prepared toluene and toluene-ethanol co-solvent polymeric suspensions containing TiO₂ particles of 200 nm in diameter. The toluene suspension behaved as a viscous liquid (Fig. 1a), whereas the co-solvent suspension was an elastic gel without showing a fluidity (Fig. 1b).

The stress-controlled rheometer (HAAKE MARS II) was used to measure the time variations in shear stress in suspensions subject to a constant shear rate. The ethanol-to-toluene mass ratio (β) was ranged between 0 and 0.035. The shear stress showed a non-sinusoidal oscillation at high ethanol contents. Fourier spectrum analyses of the time-evolving stress signals showed a sharp primary peak at low β, whereas the higher-order peaks evolved at high frequencies at high β values. 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. Based on the FFT spectra, we classified the oscillation modes as i) mode-S with a single frequency peak, ii) mode-M with multiple peaks, and iii) mode-N without showing stress oscillation. The effects of compositions were systematically examined and summarized as the oscillation mode maps (Fig. 2(b)).

Fig. 1 (a) toluene suspension (b) toluene-ethanol co-solvent suspension.

Fig. 2 (a) Time evolutions in stresses for different ethanol content at the shear rate of 10 s⁻¹. (b) oscillation mode maps at β=0.035 for different contents of polymer and particle.

References