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A generality in stress development of silica/poly(vinyl alcohol) mixtures during drying process

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ABSTRACT

Colloidal dispersions in polymer solution are important material systems in coating and printing applications. Understanding the role of polymers in drying process is important to obtain the desired performance of the solid film. In this study, we investigated the role of polymers in stress development during drying of aqueous silica and poly(vinyl alcohol) (PVA) suspensions, and the microstructure of solid film. Adsorbed polymers were found to affect the spatial organization of silica particles, which reduces the size of aggregates and the increase in stress development. The effect of adsorbed polymers on the stress development was hindered as the amount of non-adsorbed polymer increased. The role of adsorbed and non-adsorbed PVA in stress development was found to be generalized to yield a single master curve independent of polymer concentration.

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1. Introduction

Evaporation of solvent from nanoparticle/polymer mixture to create a thin solid film is an important process in coating and printing applications [1,2]. When drying occurs in the mixtures, they experience a large volume shrinkage and structural evolution. As a result, drying film may result in undesired coating defects such as deformation, crack, aggregation of particles, or non-uniformity [3,4]. Therefore, understanding the evolution of microstructure and physical properties in drying process is critical to obtain required properties of the solid film.

Dispersion stability of particles in the particle/polymer mixtures significantly depends on molecular weight, chemistry, and concentration of polymers. Therefore, it is important to understand the role of polymer not only in the microstructure of the coating liquid but also in the final film performance. Polymers in dispersions exist as a state of adsorbed or non-adsorbed in the suspension. The adsorbed polymers affect the microstructure of the suspension by introducing bridging attraction or steric repulsion, depending on the extent of saturation on the particle surface or the molecular weight of the polymer [5]. Non-adsorbed polymers also affect the microstructure of the suspension by introducing depletion attraction, or depletion repulsion, depending on the concentration of polymer in the medium or the molecular weight [6]. While there

have been extensive studies on the role of polymers in the suspension, the role of polymers on drying process and the properties of the final film has been scarcely understood. It has been a long technical challenge to adequately evaluate the contribution of polymers in drying behavior of particle/polymer mixtures. One of the widely used techniques to evaluate drying behavior is to measure the stress development during drying, particularly by means of the cantilever deflection method [7]. It has been utilized to characterize the drying behavior of various coating liquids, such as polymer solutions [8], polymer lattices [9–12], and ceramic materials [13–17]. Lately, we have studied the drying behavior of aqueous nano-silica and PVA suspension as a model particle/polymer mixture [4,18,19] and showed that the polymer adsorption results in an increased level of drying stresses, because of the improved dispersion of particles in solid film as a result of steric stabilization. However, the results were only obtained from single formulation, which cannot be generalized in the wide range of formulations. In particular, we focused on the amount of adsorbed polymers in our previous study, which cannot address the role of non-adsorbed polymers in stress development and the microstructure of the film.

In this study, we investigate the drying behavior of silica and PVA suspensions by focusing on the role of both adsorbed and non-adsorbed polymers as we vary the amount of adsorbed and non-adsorbed PVA, respectively. The stress development during drying process is measured in-situ by the cantilever deflection method. Small Angle X-ray Scattering (SAXS) and electron microscopy are used to analyze the microstructure of the solid film at the length scales of both spatial arrangement of the particles

and their aggregates. The stress development during drying significantly depends on the adsorbed PVA at low concentration of non-adsorbed PVA, but the effect of adsorbed polymer fades out as the amount of non-adsorbed PVA increases. The microstructure of the solid film is significantly affected by both adsorbed and non-adsorbed polymers, which can explain the dependency of stress development on the polymer concentration. Finally, the dependency of the stress development on both adsorbed and non-adsorbed PVA can be generalized to yield a single master curve.

2. Experimental

2.1. Sample preparation

Aqueous suspensions of silica and poly(vinyl alcohol) were prepared by mixing aqueous poly(vinyl alcohol) (PVA) solution and colloidal silica at different weight ratios. PVA with molecular weight of $(31–50) \times 10^3$ mol/g, degree of hydrolysis of 87% to 88% and density of 1.27×10^3 kg/m^3 was purchased from Aldrich. 20 wt% aqueous PVA solution was prepared by dissolving in DI water at 353 K for 3 h. Colloidal silica of 30 wt% (Ludox® HS-30) was purchased from Aldrich. Silica particles (specific surface area 220 m^2/g and density 2.37×10^3 kg/m^3 according to the supplier) were strongly charge stabilized at pH 10. The average diameter of silica particle was determined to 15 ± 2 nm from SAXS intensity of charge-screened dilute suspension [20]. Aqueous silica/PVA suspensions were prepared by varying PVA concentration (ϕ_{PVA}) from 4 wt% to 10 wt% at constant silica concentration of 10 wt%. pH of prepared silica/PVA suspension was measured as 9.5 after stirring for 30 min at the whole range of ϕ_{PVA}. The suspension was used without changing pH.

In this study, the amount of polymer adsorption was altered by stirring time. We previously observed that the silica/PVA suspension at basic condition (e.g. pH 9.5 in this study) experienced a gradual increase in the amount of adsorbed polymer (Γ) as stirring time increases [18]. We found the increase in Γ was originated from the saponification process of acetate group in PVA during stirring, which provides hydrogen ion in the suspension and finally results in the increase in deionized silanol group on silica surface as a source for hydrogen bonding between silica and PVA [19]. In this study, we employed stirring time as a controllable factor of polymer adsorption. The silica/PVA suspensions were stirred with a magnetic stirrer at 80 rpm up to 120 h at room temperature (25 °C).

2.2. Steady shear viscosity

We measured steady shear viscosity of the silica/PVA suspensions at stirring time (t_s) 24 h and 120 h, respectively, to obtain the hydrodynamic radius of the particles, which increased due to polymer adsorption. The viscosity was measured at 298 K over a range of shear rate from 10^{-1} to 10^2 s^{-1} using a double gap concentric cylinder with 500 μm gap equipped on a stress controlled rheometer (AR-G2, TA instruments, USA).

2.3. Stress development during drying

Stress development during drying process was measured in-situ by means of the cantilever deflection technique, which measures the deflection of one free end of the cantilever with the other end clamped. The stress was calculated from the deflection by the Corcoran equation. Extensive description of the principle, apparatus and equation can be found elsewhere [4,18,19]. Silicon wafer (dimension of 70 mm × 6 mm × 0.5 mm by length × width × thickness) was used as a cantilever. The suspension was coated onto the cantilever with the area of 45 mm long and 6 mm wide by blade coating. The gap between the blade and

the substrate was adjusted to ensure the solid film thickness to 11 ± 1 μm. The deflection was measured in the drying chamber with a relative humidity of $10 \pm 3\%$ and drying temperature of 25 ± 2 °C. We note the measured stress development is in-plain tensile stress which is averaged over the coating area on the beam. The stress development has a distribution due to the non-uniform microstructure throughout the plane of coating film and it is not clear how the stress distribution affects the averaged stress in this study. Nevertheless, the obtained averaged stress is useful to characterize the drying behavior of silica/PVA suspensions.

2.4. Microstructure of solid film

We observed the microstructure of the solid film after drying at both length scales of the particles and the aggregates by means of Small Angle X-ray Scattering (SAXS) and Electron microscopy (JSM-840A, JEOL, Japan). SAXS experiments were performed at an undulated PLS-II 9A beamline of PAL (Pohang accelerator laboratory, Korea). Solid film with a thickness of 100 μm was adhered to the sample stage with a hole of 2 mm diameter. X-ray beam with a wavelength of 1.12 Å passes through the solid film and two-dimensional scattering images were recorded on a CCD detector (Rayonix 2D SX165, USA) located at 4511 mm from the sample. After removing the background intensity and relevant uncertainties around the beamstop, the q range was determined to be 0.15–1 nm^{-1}.

3. Results and discussion

3.1. Suspension microstructure

In this section, we first investigate the microstructure of the suspension and estimate the amount of adsorbed and non-adsorbed polymers in the suspensions of varying ϕ_{PVA}. The amount of adsorbed polymer on the silica surface can be directly determined from the comparison of polymer concentration in medium before and after the sedimentation of particles via centrifugation [4,18,19]. However, it is not easy to employ this method in this particular system due to the increased medium viscosity at high ϕ_{PVA}, which makes sedimentation of particles difficult. Therefore, we evaluate the amount of polymer adsorption from the measurement of hydrodynamic particle radius which increases by polymer adsorption.

The hydrodynamic radius (r_h) of silica particles can be calculated from the viscosity of silica/PVA suspension ($\eta_{silica/PVA}$) and PVA solution (η_{PVA}) based on Krieger–Dougherty equation[21] given by

$$\frac{\eta_{silica/PVA}}{\eta_{PVA}} = \left(1 - \frac{\phi_{eff}}{\phi_m} \right)^{-[\eta]\phi_m} \tag{1}$$

where $[\eta]$ is the intrinsic viscosity of the suspension and ϕ_m is the maximum random packing volume fraction. ϕ_{eff} is the effective hydrodynamic volume fraction of silica particles in the suspension, given by

$$\phi_{eff} = \phi_0 \left(\frac{r_h}{r} \right)^3 = \phi_0 \left(1 + \frac{\delta}{r} \right)^3 \tag{2}$$

where ϕ_0 is volume fraction of core particles, and r_h is hydrodynamic radius of the silica particle, which consists of the radius of silica particle r and the thickness of adsorbed polymer δ. Fig. 1 displays the steady shear viscosity (η) of silica/PVA suspensions as a function of shear rate at $\phi_{PVA} = 4$, 7.5, and 10 wt%. The viscosity measured with both $t_s = 24$ h and 120 h exhibit Newtonian behavior in the whole range of ϕ_{PVA}, with a slight increase in η for $t_s = 120$ h. We previously showed that the silica particles in aqueous PVA solution at $\phi_{PVA} = 5$ wt% are charge-stabilized, which is stable during stirring up to $t_s = 120$ h [18]. The viscosity measurement (Fig. 1) and the