

Effect of polymer adsorption on film formation of silica/PVA suspension

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1. Abstract

Understanding the polymer adsorption in particle/binder/solvent system is important to achieve successful film products. While most of the reported work has dealt with the suspension microstructure, a few studies have focused on film formation. We investigated the effect of adsorption on film formation through measurement of adsorption amount in suspension and stress development in drying film with respect to mixing time (t_m). All of the adsorption amount (PVA), characteristic stress (σ_{ch}) exhibited similarities expressed by the form of $1 - e^{-t_m/\tau}$. The porous and non-uniform dried film at short t_m became close-packed and uniform with longer t_m . We found that polymer adsorption plays the key role in film formation as it introduces steric repulsion in suspension and suppresses the flocculation during solvent evaporation. We also found that the mixing time for the saturated polymer adsorption is the important variable to acquire the consolidated and uniform film microstructure.

2. Introduction

Particle/binder/solvent system is ubiquitous in various kinds of coating and printing process to produce battery, LCD display and electronic components. More often than not, a number of coating defects such as delamination, crack

and particle coagulation occurs during drying. In order to overcome the coating failure during drying process, many attempts have been carried out, for example, to control the suspension structure in order to satisfy the required property of final products. Widely used methods to control suspension microstructure are to incorporate additives like electrolyte or polymer to incorporate electrostatic repulsion or steric repulsion. While most of the reported work has dealt with the suspension microstructure, a few studies have focused on film formation. In particular, understanding the stress development during drying is important because it leads to severe coating defects such as crack, curl and deformation. In this presentation, we investigate the effect of polymer adsorption on the microstructure of suspension of silica/PVA suspension and its drying behavior by changing suspension mixing time(t_m). We characterized the suspension structure with measuring particle size, zeta potential, viscosity and amount of adsorption. Stress development during drying and film microstructure was characterized as a function of drying time and the evolution of the film microstructure during drying was discussed in the association of particle interactions influenced by adsorbed polymer.

3. Experimental Section

10 wt% poly(vinyl alcohol)(PVA, Aldrich) which is molecular weight 31 - 50103mol/g, degree of hydrolysis 87-89% and density 1.27103 kg/m³, was dissolved in DI water at 353K for 3 h. Commercialized 30 wt% silica suspension (Ludox HS-30, Aldrich) stabilized at pH 9.8 was used. Silica particle with average diameter of silica particle 12 nm, specific surface area 220m²/g and density 2.37103 kg/m³ was negatively charged (-30 mV) from zeta potential measurement. Silica/PVA suspension was prepared with the volume fraction of silica / PVA / DI water to 4.3 / 4.3 / 91.4 and measured to pH 9. Suspension was mixed on magnetic stirrer with 80 rpm up to 200 h under the room

temperature (25°C). Zeta potential and particle size measurement of suspension were carried out with dynamic light scattering (Zetasizer nano zs, Malvern instruments Ltd, UK). Steady shear viscosity was measured at 298K over a range of shear rates from 10⁻¹ to 10² s⁻¹ using double gap concentric cylinder with 500 μ m gap in conjunction with stress control rheometer (AR-G2, TA instruments Ltd, USA). The amount of PVA adsorption on silica surface was quantified using total organic carbon analyzer (TOC analyzer, Apollo 9000, Teledyne Instruments, CA, USA). Stress development of silica/PVA suspension film was quantified at each mixing time based on the measurement of the deflection of cantilever¹⁾. Surface image of coating layer after drying were observed using scanning electron microscope (JSM-840A, JEOL, Japan).

4. Results and discussion

Zeta potential of suspension is around - 25mV initially and doesn't change during mixing. Particle diameter was between 13nm and 18 nm all over t_m which means that particles are well dispersed during mixing. Viscosity, measured at the shear rate 1s⁻¹ shows viscosity was around 10cP and constant over t_m . It also supports that suspension doesn't exhibit considerable structure change during mixing. However, adsorption increases with stirring time in Figure 1, displaying the amount of PVA adsorption on silica surface during mixing.

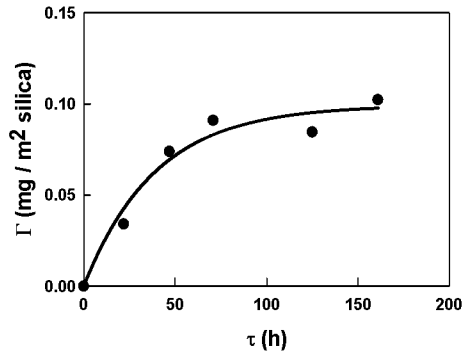


Figure 1. Amount of PVA adsorption on silica surface with mixing time. Measured value(●) and its regression curve(-)

Characteristic stress(σ_{ch}) defined the maximum value of stress development was plotted in terms of t_m and displayed in Figure 2. σ_{ch} increases with t_m and approaches constant value over 100 h. The trend of maximum stress that is dependent to t_m is exactly same as the trend of adsorption.

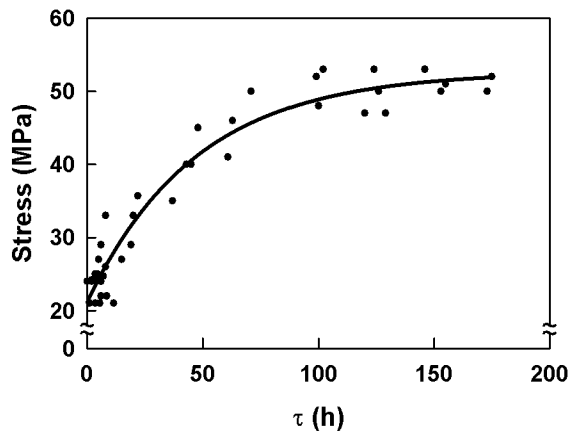


Figure 2. Maximum stress of Silica / PVA suspension with mixing time. measured value (●)and its regression curve(---)

Dried film in Figure 3 prepared from silica/PVA suspension shows porous structure at 18 h, suggesting flocculation is severely formed during drying.

However, film microstructure becomes consolidated as t_m increases. Finally, film surface prepared from suspension at 134 h displays well close-packed microstructure of flocculation, which is much smaller than that of the suspension prepared at 18 h.

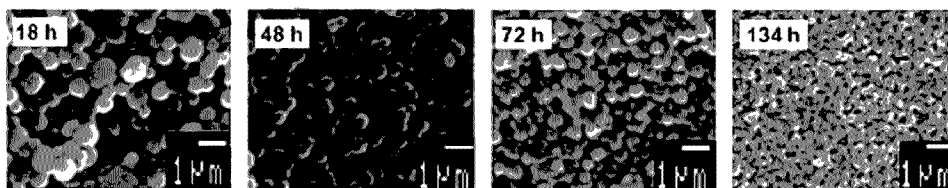


Figure 3. SEM image of dried silica/PVA suspension film surface at different t_m .

As the presence of polymer affects suspension stability, we evaluated the total potential energy (V_{tot}) expressed by $V_{tot} = V_s + V_{dep} + V_{vdw} + V_e$ as a function of d at different t_m as shown in figure 4.

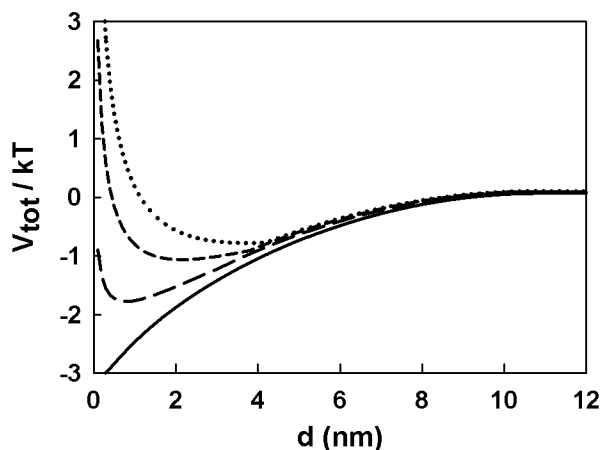


Figure 4. Total potential energy (V_{tot}) as a function of d at various t_m . (---) 24 h, (- · -) 47 h, (—) 71 h, (···) 161 h

When $t_m = 24$ h, V_{tot} shows positive value which implies that the particles seldom approach each other because of electrostatic repulsion. As d reduces,

short range forces (e.g. V_{dep} and V_s) occur and V_{tot} becomes negative due to the effect of depletion attraction in addition to bridging attraction. In the association with film formation, approaching particles due to solvent evaporation are likely to form flocculation, resulting in flocculated and open microstructure in dried film. On the other hand, at $t_m = 161$ h, V_{tot} also shows positive value. Although V_{tot} becomes negative as d reduces due to depletion attraction, it becomes positive where d is shorter than 1.5 nm due to steric repulsion. In the conjunction with film formation, adsorbed polymers induce steric repulsion and suppress flocculation as solvent evaporation, leading to close-packed film microstructure.

5. Acknowledgement

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6. References

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