INVESTIGATION OF VISCOSITY GRADIENTS IN COATINGS DURING SOLIDIFICATION USING MICRORHEOMETRY

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Introduction

Various coating defects, such as sagging, wrinkling and poor leveling are related to coating viscosity change after the deposition onto a substrate. Controlling coating viscosity during the solidification process is critical to prevent these viscosity related defects in final coating products [1]. A new method is required to characterize such viscosity change during solidification since conventional bulk rheometry cannot be used to follow the viscosity change of coated layers. Information on temporal and spatial gradients in coating viscosity will be useful to design drying or curing process conditions to avoid these defects. In this study, we report results taken with an magnetic microrheometer designed to measure coating viscosity [2] and connect results to defect formation.

Magnetic Microrheometry

In Fig. 1, a schematic diagram of the apparatus, magnetic microrheometer, is shown. In order to calculate coating viscosity, the magnetic particle velocity is measured under an applied magnetic field by observing the positions within a coating as a function of time. Two NdFeB permanent magnets are used to produce magnetic force on Fe_3O_4 superparamagnetic 1 μm diameter probe particles, and optical microscope and particle tracking software (Image J plug-in 1.41) are used for the particle tracking. Heating system with a temperature controller is connected to the sample stage that has air/gas flow channels to produce various drying or curing conditions. The magnetic probe particle motion in coatings is influenced by several forces, such

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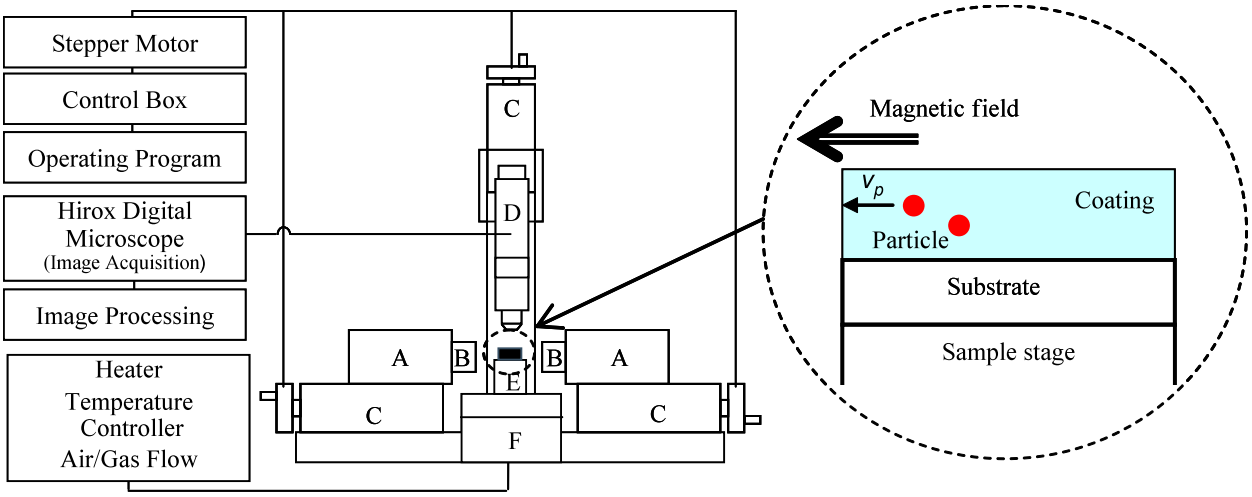

Fig. 1. Schematic of magnetic microrheometer setup and measurement: A: magnet holder and adapter, B: NdFeB permanent magnet, C: stepper motor, D: optical microscope, E: sample stage connected to solidification system, F: micropositioner.

as magnetic force, drag force, gravitational force, thermal fluctuation and interaction between particles. Given the low particle concentration (0.01 wt.%) and Reynold's number ($< 10^{-3}$), the particle velocity in Newtonian coating liquid is governed by the balance between magnetic force (F_m) and drag force (F_{drag}),

$$m\frac{dv_p}{dt} = F_m + F_{drag} = \frac{1}{\mu_0} MV\frac{dB}{dx} - 6\pi\eta R v_p \tag{1}$$

where m and v_p are the particle mass and velocity, respectively, η is the coating viscosity, M is the particle magnetization, dB/dx is the applied magnetic field gradient, and μ_0 is the permeability of free space. Then, the coating viscosity is determined by measured particle velocity [3];

$$v_p = \frac{2MR^2\, dB/dx}{9\mu_0\eta} \qquad \eta = \frac{2MR^2\, dB/dx}{9\mu_0 v_p} \tag{2}$$

Experimental

Polymer coating samples were prepared from aqueous polyvinyl alcohol (PVA) solution (5.08 and 12.1 wt.% PVA, M_w=130,000 g/mol, Aldrich Chemical Co.). A wire-wound coating method was used to apply the coating solution onto the glass substrate, and the expected wet coating thickness was about 230 μm. The effect of drying temperature and time on the PVA

coating viscosity was also investigated. The surfaces of the dried coating samples were observed to check the influence of coating viscosity and drying condition on the final coating surfaces. Samples were dried on a titled stage in a drying oven to induce sagging. Magnetic microrheometer was used to follow the coating viscosity changes during drying at different temperatures. The probe particles in the middle of the coating were tracked for the viscosity measurement to avoid interference from the coating substrate and free surface. The particle velocity data were taken as a function of time at various temperatures from room temperature (RT) to 80°C to measure viscosity-time profile of PVA coatings.

Results and Discussion

Final surfaces of PVA coatings dried on the titled stage were observed. While sagging defects were found in all 5.08 wt.% PVA coatings dried at different temperatures, sagging was observed in 12.1 wt.% PVA coating surfaces dried only at RT and 40^{o}C. Sagging was prevented when the samples were dried at 50 and 60^{o}C, and the surfaces were quite smooth. However, leveling was not sufficient if the drying temperature was 70^{o}C, showing stripes from the rod. Since this film smoothness depends on the drying temperature, the PVA coating viscosity change was also measured at different drying temperatures to check the correlation between them.

Fig. 2 shows the viscosity-time profile of 5.08 wt.% PVA coatings. The coating viscosities show steep increases after a certain drying time, and the time ($t_{build\text{-}up}$) is shorter at higher drying temperature. Sagging can be avoided if the viscosity builds up quickly, so drying temperature needs to be controlled to make $t_{build\text{-}up}$ shorter to avoid sagging in a given coating formulation. This $t_{build\text{-}up}$ also depends on initial coating viscosity and thickness. Since this profile clearly shows the temperature dependence on the time that viscosity starts to show a steep increase, the profile is used to develop a process window that can predict the coating surface property with different drying temperatures, and coating viscosity and thickness.

The magnetic microrheometer can also be utilized to investigate spatial gradients of viscosity in coatings during solidification. Tracking the particle velocities at different positions through coating thickness provides the information needed to detect viscosity gradients during solidification, and skinning which can interfere with drying or curing, causing surface defects,

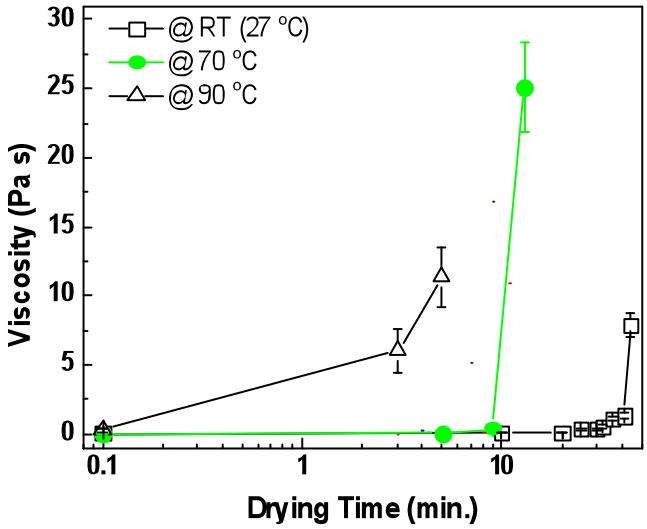

Fig. 2. PVA coating viscosity change from particle velocity measurement at different drying temperatures. Results are shown for a 5.08 wt.% PVA solution.

such as wrinkles. More research is underway to investigate the relation between process condition and the spatial gradients of viscosity within coatings using the data gathered at different coating positions.

References

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