

# Solidification Process in Film Formation from Polymer Solution

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In order to study the film formation process during evaporation of solvent in polymer solution, the solidification process along thickness direction was measured by *in situ* monitoring the weight, the shrinkage stress and the out-of-plane birefringence of polycarbonate (PC)/1,2-dichloroethane and polystyrene (PS)/toluen (or 1,2-dichloroethane) solutions coated on a glass under a fixed drying condition (20 °C). As shown in Fig.1, we analyzed the change of solution weight and found some bending points of its changing rate corresponding to the changing point of rate-determining step from fluid dynamic state of the drying air to internal-diffusion-controlling process ( $t_0$ ), the solidification point of the solution in surface region ( $t_1$ ) and the time when the evaporation rate was dramatically depressed ( $t_2$ ). On the other hand, the solidification point at the interfacial region between the film and the substrate was evaluated as the starting point of the shrinkage stress development ( $t_{\text{stress}}$ ). The value of  $t_{\text{stress}}$  becomes bigger or smaller than  $t_2$  depending on the evaporation rate [1]. The relationship between  $t_2$  and  $t_{\text{stress}}$  has an influence on the homogeneity of the formed film. The simultaneous measurement of the solution weight and retardation during drying process was also performed so as to estimate the relationship between the solidification process and the development of out-of-plane birefringence to be caused by the planar orientation of the polymer chain with the solidification. It was found that the value of retardation when light was incident at 60 degree ( $\text{Re}(60)$ ) has begun to increase in  $t_1$  as shown in Fig.1. As for our knowledge, these are the first data which confirm experimentally the fact that the out-of-plane birefringence during evaporation of solvent starts to develop at the solidification point of the solution surface. From these results, we proposed a model of solidification process during evaporation of solvent in polymer solution under the condition of this study. The effects of drying condition on solidification process were also studied.

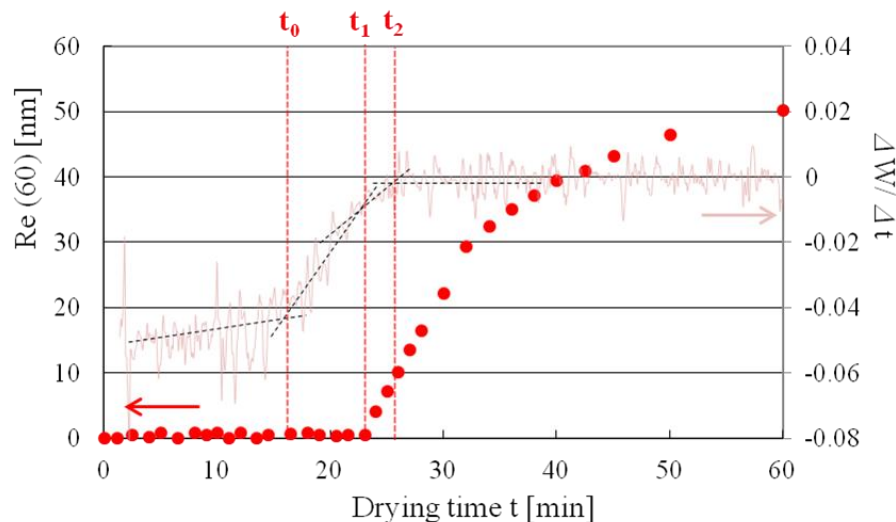


Fig. 1. Time variation of retardation (filled circle) and temporal differentiation of weight change (solid line) of PC film. Final film thickness is 28  $\mu\text{m}$ .

## Reference

1. R.Katsumata, S.Ata, K.Kuboyama, and T.Ougizawa, *J. Applied Polymer Science*, **128**, 60-65(2013).