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# Origin of Residual Stress and Ways to Reduce It in Solvent Cast Polymer Film

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## INTRODUCTION

Nowadays, solvent cast method is becoming increasingly attractive for the production of films with high quality requirements because of its advantage of transparency, isotropy and uniform thickness distribution. For these features, solvent cast films have been widely applied to optical films and micro interlayer devices. However, residual stress which is generated during solvent cast process could cause defects such as crease, curling, interface delaminating and folds [1]. In order to reduce residual stress, revealing its origin is desired to develop a theoretical strategy which can apply to a lot of polymer solution systems.

In general, solvent cast method consists of two processes: one is ‘drying process’ to evaporate solvent at drying temperature ( $T_{dry}$ ) and the other is ‘cooling process’ to cool the film from drying temperature to use temperature ( $T_{use}$ ). Residual stress ( $\sigma_r$ ) is the sum of the dry stress ( $\sigma_d$ ) caused by volume shrinking during the drying process and thermal stress ( $\sigma_T$ ) caused by difference of coefficient of thermal expansion between a film and a substrate during the cooling process:

$$\sigma_r = \sigma_d + \sigma_T. \quad (1)$$

Thermal stress simply depends on mechanical constant, coefficient of thermal expansion of a film and a substrate and difference between  $T_{dry}$  and  $T_{use}$  [2], while it is considered that dry stress is affected by numerous factors. To simplify those factors, we examined stress development based on Croll’s idea [3-5]. Croll stated that dry stress arises from the time that film solidifies when its glass transition temperature ( $T_g$ ) is equal to the  $T_{dry}$ , and is due solely to the difference between the volume fraction of solvent at which the film solidifies and that of retained solvent in the dry film. By paraphrasing this idea, we make a simple assumption focusing on *uprising* and *growth* of dry stress as below.

- *Uprising*: dry stress uprises at the glass transition point of solution as polymer chain is pinned by a substrate.
- *Growth*: the volume of solvent at uprising (glass transition) point shrinks isotropically and it generates dry stress.

In this study, we will investigate the origin of residual stress especially from the view point of influence of  $T_{dry}$  on *uprising* and *growth* of dry stress.

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<sup>1</sup> Unpublished. ISCST shall not be responsible for statements or opinions contained in papers or printed in its publications.

## EXPERIMENTAL

Polystyrene (PS: Styron G8102, Asahi-Kasei Co.)/toluene solution with  $\phi = 0.88$  ( $\phi$  is volume fraction of toluene) was prepared. The solution was coated on a glass substrate by a glass bar, and dried at constant drying temperature ( $T_{dry} = 20 \sim 80$  °C: drying process). The film thickness after drying was approximately 15  $\mu\text{m}$ . After keeping  $T_{dry}$ , the sample was cooled slowly to use temperature ( $T_{use} = 20$ °C: cooling process). During the processes, the strain of a substrate ( $\varepsilon_s$ ) generated by bending was *in situ* monitored by strain gage which was attached to back side of the substrate. Film stress was evaluated from  $\varepsilon_s$  using the bending beam equation [6]:

$$\frac{E_s}{1-\nu_s} \varepsilon_s = \frac{E_f}{1-\nu_f} \varepsilon_f = \sigma \quad (2)$$

where  $E$  and  $\nu$  are Young's modulus and Poisson's ratio, and subscripts f and s mean a film and a substrate, respectively. The change of  $\phi$  was estimated with an electric balance.

## RESULTS AND DISCUSSION

### *Drying temperature dependence of residual stress, dry stress and thermal stress*

In Fig.1, residual stress ( $\sigma_r$ ), dry stress ( $\sigma_d$ ), and thermal stress ( $\sigma_T$ ) as a function of  $T_{dry}$  are plotted, and  $\sigma_r$  takes a minimum value at  $T_{dry} \approx 50$ °C. It shows that 50°C is approximately an optimum temperature to minimize  $\sigma_r$  in this system. It is because that  $\sigma_T$  increases linearly to  $T_{dry}$  and  $\sigma_d$  decreases with  $T_{dry}$  monotonically.

In this system, biaxial modulus of the PS film is smaller enough than that of the glass substrate, thus  $\sigma_T$  can be evaluated by Eq.3 [7,8]:

$$\sigma_T \approx \frac{E_f}{1-\nu_f} (\alpha_f - \alpha_s) (T_{use} - T_{dry}) \quad (3)$$

here  $\alpha$  is coefficient of thermal expansion and  $E_f = 1.64$  GPa,  $\nu_f = 0.34$  [9],  $\alpha_f = 9.15 \times 10^{-5}$  K<sup>-1</sup> and  $\alpha_s = 7.2 \times 10^{-6}$  K<sup>-1</sup>, respectively.  $E_f$  is determined by tensile

test (2.0 mm/min) and  $\alpha_f$  by Pressure-Volume-Temperature data. Calculated  $\sigma_T$  ( $\sigma_T(\text{cal.})$ ) is shown as the broken line in Fig.1. It almost agrees with experimental value  $\sigma_T$ . Since  $\alpha$  and  $E$  are the specific parameter of the materials,  $\sigma_T$  depends on the choice of materials, that is,  $\sigma_T$  is dominated only by  $T_{dry}$  in this system and predicted easily. On the other hand, the mechanism of generation of  $\sigma_d$  is unclear. From Eq.1,  $\sigma_r$  is the sum of  $\sigma_d$  and  $\sigma_T$ , therefore we can see the key point to minimize  $\sigma_r$  is reducing  $\sigma_d$  by revealing its mechanism to optimize dry condition.

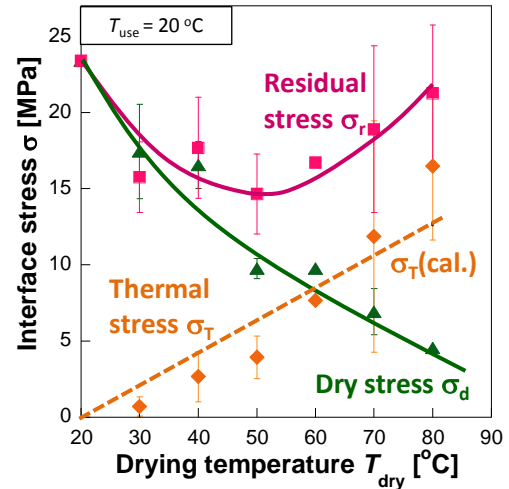


Fig.1 Residual stress  $\sigma_r$ , thermal stress  $\sigma_T$  and dry stress  $\sigma_d$  as a function of drying temperature  $T_{dry}$

### Uprising point of dry stress

Fig.2 shows the change of  $\varepsilon_s$  and  $\phi$  during drying process at  $T_{dry} = 70^\circ\text{C}$ . At the beginning of the drying process,  $\varepsilon_s$  monotonically decreases and after  $t = 4$  min  $\varepsilon_s$  starts increasing. Taking into account of bending of the substrate by the own weight of solution, the decrease of  $\varepsilon_s$  until 4 min is caused by the loss of solvent weight during evaporation. The increase of  $\varepsilon_s$  which starts at  $t = 4$  min is due to the *uprising* of dry stress ( $\phi = \phi_c$ ), which means that polymer chain is pinned by a substrate.  $T_{dry}$  dependence of  $\phi_c$  is plotted in Fig.3.

To confirm whether the *uprising* point is glass transition point or not, we evaluated the volume fraction of toluene at glass transition point of polymer solution ( $\phi_{T_g}$ ) by DSC measurement. Completely sealed samples with different solvent content  $\phi$  (0.03-0.22) were prepared and  $T_g$  of each sample was measured (cooling rate:  $10^\circ\text{C}/\text{min}$ ). The relationships between  $\phi_{T_g}$  and  $T_g$  and between  $\phi_c$  and  $T_{dry}$  are shown in Fig.3. From another view point,  $\phi_{T_g}$  shows the amount of solvent with which the solution transfers to glassy state when  $\phi$  decreases at a constant temperature. For instance,  $T_g$  of the solution with  $\phi_{T_g} = 0.2$  is approximately  $40^\circ\text{C}$ , whereas it can be considered that the solution with  $\phi = 0.2$  vitrifies when it is dried at  $40^\circ\text{C}$ . In Fig.3, the behavior of  $\phi_c$  and  $\phi_{T_g}$  are similar. It indicates  $\phi_c$  corresponds to the glass transition point of solution, as assumption of *uprising*.

### Growth of dry stress

Employing the assumption of *uprising* and *growth* by Croll model, dry stress ( $\sigma_{d,c}$ ) can be estimated from  $\phi_c$ . Suppose that the all volume of solvent corresponding to  $\phi_c$  shrinks isotropically,  $\sigma_{d,c}$  is estimated by substituting  $\varepsilon_f = \phi_c/3$  to Eq.2 as below:

$$\sigma_{d,c} = \frac{E_f}{1-\nu_f} \varepsilon_f = \frac{E_f}{1-\nu_f} \frac{\phi_c}{3} \quad (4)$$

In Fig. 4,  $\sigma_{d,c}$  and  $\sigma_d$  are plotted, and we can see the big difference between  $\sigma_{d,c}$  and  $\sigma_d$  at each  $T_{dry}$ . As

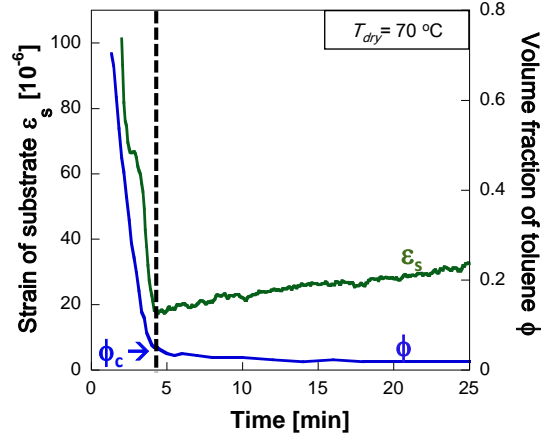


Fig.2 Time variation of strain of a substrate ( $\varepsilon_s$ ) and volume fraction of toluene at  $70^\circ\text{C}$

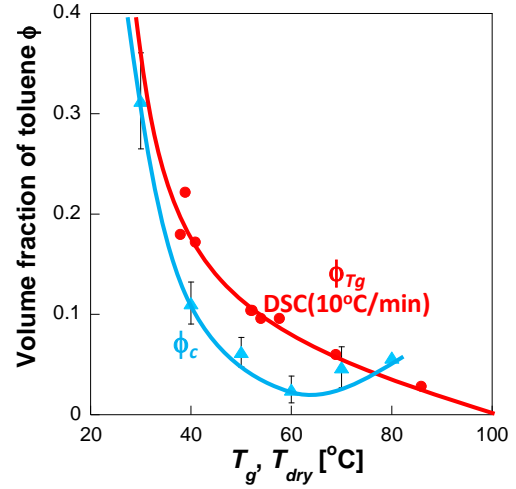


Fig.3 Volume fraction of toluene at  $T_g$  ( $\phi_{T_g}$ ) and at uprising point of dry stress ( $\phi_c$ ) as a function of  $T_g$  and  $T_{dry}$

discussed in the previous part, *uprising* point of dry stress corresponds to glass transition point. Therefore, the gap should be due to some errors in assumption of *growth* of dry stress. It means that not all volume corresponding to  $\phi_c$  generates  $\varepsilon_f$ , in other words, contributes to  $\sigma_d$ . It should be because that nevertheless the solution vitrifies at *uprising* point, stress relaxation occurs. Moreover, as can be seen in Fig.4, the stress relaxation ( $\sigma_{d,c} - \sigma_d$ ) during *growth* process has a strong influence on the final value  $\sigma_d$ .

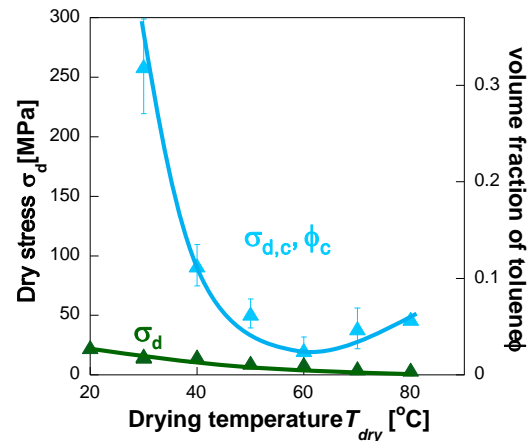


Fig.4 Dry stress ( $\sigma_d$ ) and volume fraction of toluene at *uprising* point of dry stress ( $\phi_c$ ) as a function of  $T_{dry}$ .

## CONCLUSION

Experimental behavior of residual stress, thermal stress and dry stress as a function of  $T_{dry}$  had shown that thermal stress depends on the choice of the materials and the key point to reduce residual stress is reducing dry stress by optimizing dry condition. Through *in situ* monitoring of dry stress and volume fraction of toluene at various drying temperature, we experimentally investigated *uprising* and *growth* of dry stress. As a result, it was revealed that the *uprising* point of dry stress corresponded to glass transition point of the polymer solution. Whereas, in *growth* process, all volume of solvent corresponding to  $\phi_c$  did not contribute to dry stress and stress relaxation after *uprising* occurred. Stress relaxation strongly affected the final value of dry stress, that is to say, to enhance stress relaxation is a strategy to reduce dry stress, and finally, to minimize residual stress.

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