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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 (σ_r) is the sum of the dry stress (σ_d) caused by volume shrinking during the drying process and thermal stress (σ_T) caused by difference of coefficient of thermal expansion between a film and a substrate during the cooling process:

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

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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[1] 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 ϕ = 0.88 (ϕ 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} = 20~80 ^{o}C: drying process). The film thickness after drying was approximately 15 μm. 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 (ε_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 ε_s using the bending beam equation [6]:

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

where E and ν are Young's modulus and Poisson's ratio, and subscripts f and s mean a film and a substrate, respectively. The change of ϕ 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 (σ_r), dry stress (σ_d), and thermal stress (σ_T) as a function of T_{dry} are plotted, and σ_r takes a minimum value at $T_{dry} \approx 50^o$C. It shows that 50°C is approximately an optimum temperature to minimize σ_r in this system. It is because that σ_T increases linearly to T_{dry} and σ_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 σ_T can be evaluated by Eq.3 [7,8]:

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

here α is coefficient of thermal expansion and E_f = 1.64 GPa, ν_f = 0.34 [9], α_f = 9.15×10^{-5} K^{-1} and α_s = 7.2×10^{-6} K^{-1}, respectively. E_f is determined by tensile

Fig.1 Residual stress σ_r, thermal stress σ_T and dry stress σ_d as a function of drying temperature T_{dry}

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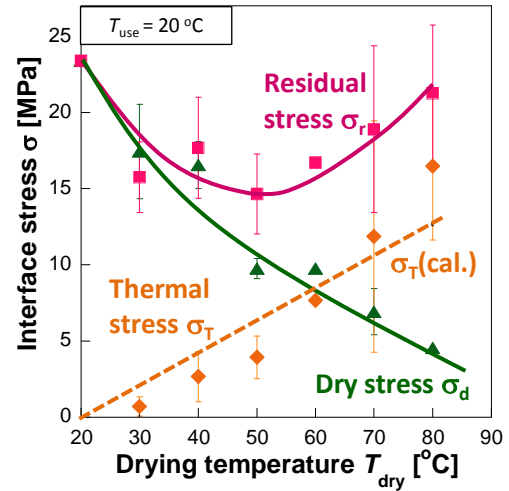
Uprising point of dry stress

Fig.2 shows the change of ε_s and ϕ during drying process at $T_{dry} = 70^{\circ}$C. At the beginning of the drying process, ε_s monotonically decreases and after t = 4 min ε_s starts increasing. Taking into account of bending of the substrate by the own weight of solution, the decrease of ε_s until 4 min is caused by the loss of solvent weight during evaporation. The increase of ε_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 ϕ_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 (ϕ_{Tg}) by DSC measurement. Completely sealed samples with different solvent content ϕ (0.03-0.22) were prepared and T_g of each sample was measured (cooling rate: 10°C/min). The relationships between ϕ_{Tg} and T_g and between ϕ_c and T_{dry} are shown in Fig.3. From another view point, ϕ_{Tg} shows the amount of solvent with which the solution transfers to glassy state when ϕ decreases at a constant temperature. For instance, T_g of the solution with $\phi_{Tg} = 0.2$ is approximately 40°C, whereas it can be considered that the solution with $\phi = 0.2$ vitrifies when it is dried at 40°C. In Fig.3, the behavior of ϕ_c and ϕ_{Tg} are similar. It indicates ϕ_c corresponds to the glass transition point of solution, as assumption of *uprising*.

Fig.2 Time variation of strain of a substrate (ε_s) and volume fraction of toluene at 70°C
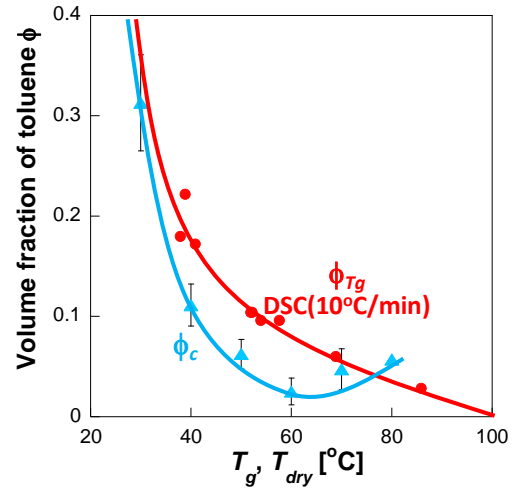
Fig.3 Volume fraction of toluene at T_g (ϕ_{Tg}) and at uprising point of dry stress (ϕ_c) as a function of T_g and T_{dry}

Growth of dry stress

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

$$\sigma_{d,c} = \frac{E_f}{1 - \nu_f} \varepsilon_f = \frac{E_f}{1 - \nu_f} \frac{\phi_c}{3}. \tag{4}$$

In Fig. 4, $\sigma_{d,c}$ and σ_d are plotted, and we can see the big difference between $\sigma_{d,c}$ and σ_d at each T_{dry}. As
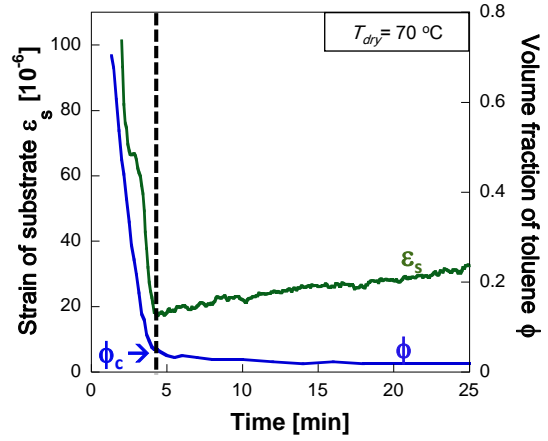
discussed in the previous part, *uprising* point of dry stress corresponds to glass transition point. Therefore, the gap should be due to some errors in assumption of *growth* of dry stress. It means that not all volume corresponding to ϕ_c generates ε_f, in other words, contributes to σ_d. It should 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 σ_d.
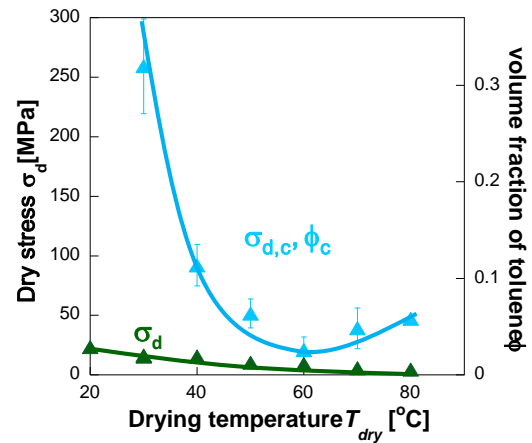

Fig.4 Dry stress (σ_d) and volume fraction of toluene at uprising point of dry stress (ϕ_c) as a function of T_{dry}.

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 ϕ_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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