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Effects of Final Curing Temperature on the Thermal Expansion Behaviors of Fluorinated Polyimide Films

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Introduction: In recent years, polymer materials have been applied as transparent substrate film exhibiting high thermal stability. One of the challenges for polymer films is suppression of the coefficient of thermal expansion (CTE), which causes peeling or cracking in the device. The CTE of PI films is affected by the preparation procedure. Moreover, although aromatic polyimide (PI) has excellent properties for the substrate, it exhibits a deep yellow color. In this study, we investigated the relationship between thermal expansion behaviors and the free volume size of colorless fluorinated PI films prepared at different imidization temperatures (T_{imd}).

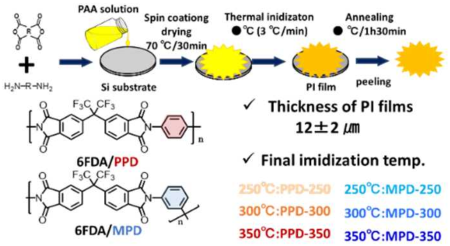

Fig. 1 Preparation and chemical structures of PIs.

Experimental and methods: Fluorinated PI films, 6FDA/PPD and 6FDA/MPD (**Fig. 1**), were formed on a silicon wafer by spin-coating of poly (amic acid) solutions, followed by thermal curing at different T_{imd} (250 – 350 °C). The polyimide films (12±2 µm thick) peeled off from the substrate were annealed at T_{imd} to release residual stress. The out-of-plane and the in-plane thermal expansion coefficient ($\mathrm{CTE}_{\perp}$ and $\mathrm{CTE}_{//}$) were measured in a temperature range from 40 to 230 °C by optical interferometry method [1] and thermomechanical analysis (TMA), respectively. The coefficient of volumetric expansion (CVE) was calculated as $\mathrm{CVE} = 2\,\mathrm{CTE}_{//} + \mathrm{CTE}_{\perp}$. The free volume size and the number density for PI films near "air surface (s)" and " the substrate interface (i)" interfaces were measured by positron annihilation lifetime spectroscopy (PALS) method at room temperature within the range of 1 µm.

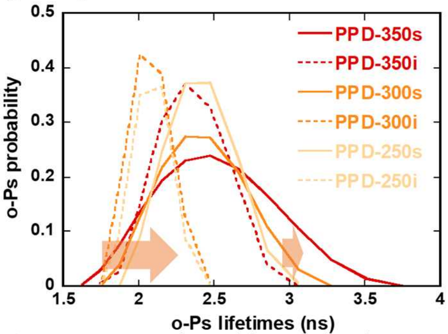

Fig. 2 Variations of o-Ps lifetime distribution.

Results and discussions: $\mathrm{CTE}_{//}$ and $\mathrm{CTE}_{\perp}$ increased with increasing T_{imd}, and the CVE increased by 15%. The distributions of free volume size near the surfaces were broadened either '*s*' and '*i*' with T_{imd} (**Fig. 2**). In other words, films near the interfaces became sparser with increasing T_{imd}. On the other hand, the bulk density estimated from refractive indices increased with increasing T_{imd}. It can be considered that the density near the interface decreases with increasing T_{imd}, whereas the local mobility near PI chain ends is enhanced at higher temperatures, while the density at the bulk state becomes higher because of the increase of ordered structures in bulk. This result indicates that the high T_{imd} films imidized above T_g become equilibrium, while the low T_{imd} films imidized below Tg were stabilized in a non-equilibrium state like pre-physical aging [2], thereby the density inside the sample increased, and free volume expansion is enhanced, leading to a enlargement in $\mathrm{CTE}_{\perp}$ and $\mathrm{CTE}_{//}$ as presented in **Fig. 3**.

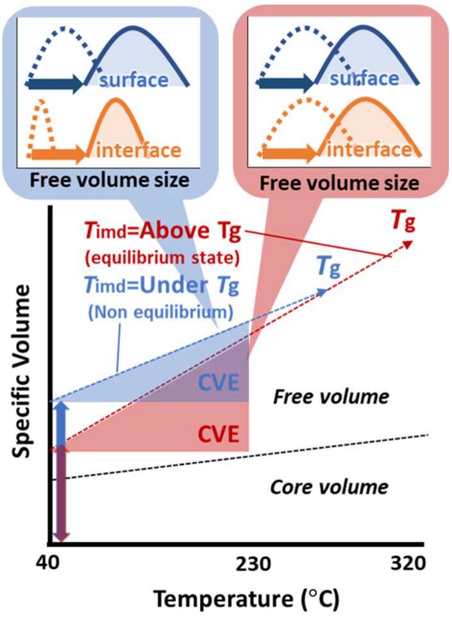

Fig. 3 Schematic images of volumetric thermal expansion behaviors.

Reference: [1] S. Ando, K. Sekiguchi, M. Mizoroki, T. Okada, R. Ishige, *Macromol. Chem. Phys.* 170035 (1-10) (2017). [2] Odegard, G. M, *J. Polym. Sci. Part B Polym. Phys*, **49**, 1695 (2011).

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