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

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Introduction: In recent years, application of polymer materials as heat-resistant transparent substrate film is desired, but one of the challenges is the need to suppress the volume coefficient of thermal expansion (CVE), which causes peeling and cracking. Although conventional aromatic polyimides (PIs) exhibit excellent properties required for insulating substrates, but they exhibit deep yellow coloration. On the other hand, polymer thin films have been reported to show different thermal expansion coefficients depending on the preparation conditions. In this study, PI films with optically transparent and colorless properties were prepared at different imidization temperatures, and in addition to their aggregation state and molecular chain orientation, local mobility and free volume size were evaluated. The purpose of this study is to elucidate the effects on thermal expansion characteristics of the PI films.

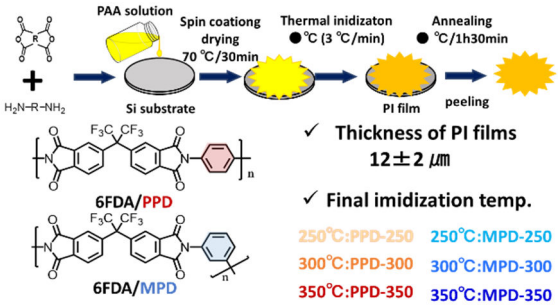

Fig. 1 Preparation method and chemical structures of PI films.

Experimental and methods: Poly(amic acid) solutions of 6FDA/PPD and 6FDA/MPD derived from two kinds of diamines were spin-coated on Si substrates and thermally imidized at different imidization temperatures of 250 to 350 °C to prepare PI thin films (**Fig. 1**). After PI films were peeled off from the substrates, heat treatment was performed at the final imidization temp. to remove residual stress. Out-of-plane thermal expansion coefficient ($CTE_{\perp}$) was measured by optical interferometry [1-3], and the in-plane thermal expansion coefficient ($CTE_{//}$) was measured by thermomechanical analysis (TMA). The free volume size was measured by positron annihilation lifetime measurement (PALS) at room temperature.

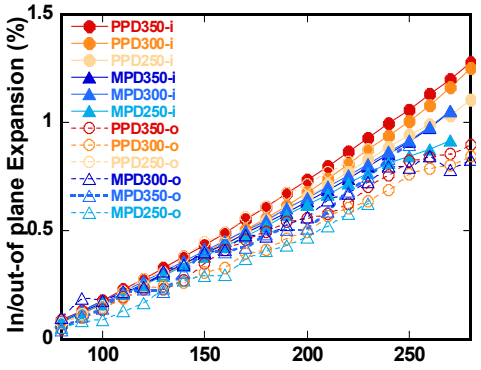

Fig.2 Variations of thermal expansion behavior of PI films.

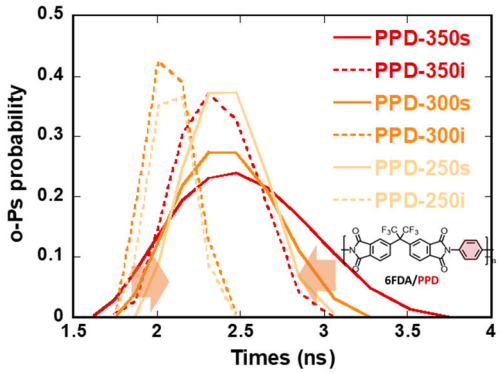

Fig.3 Variations of o-Ps lifetime distribution of PI films.

Results and discussions: As the imidization temperature increased, the thermal expansion increased, even though the characteristic temperatures such as T_g and T_β increased (**Fig. 2**). This is because the T_g and T_β was increased due to the enhanced structural rigidity with the high imidization temperatures. It was suggested that a decrease in volumetric thermal expansion was observed by reducing the expansion of the free volume by enhanced deviations in free volumes between the surface and the substrate-interface during imidization processes at lower imidization temperatures.

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