Volumetric Thermal Expansion Behaviors of Polyimide Films Analyzed by Optical Interferometry and VT Refractive Index Measurement

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Control of coefficients of linear (CTE) and volumetric (CVE) thermal expansion of materials is crucial for dimensional stability of integrated components and circuits. In particular, CTE mismatch between polymer film and inorganic substrate causes cracks or delamination due to thermal stress. In this study, CTE, CVE, and three dimensional chain orientation were investigated for *a*) free-standing and *b*) as-cast PI films based on near-infrared optical interferometry and variable temperature refractive index measurements.

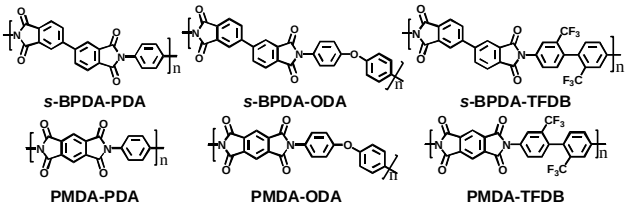

Fig. 1 Structures of aromatic polyimides (PIs)

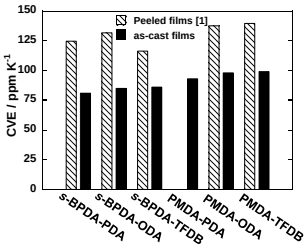

Fig. 2 CVEs estimated for free-standing and as-cast PI films on Si.

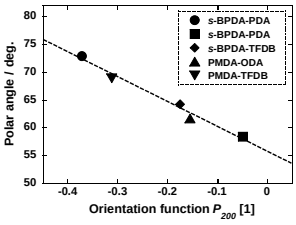

Fig. 3 Relationship between polar angle and orientation function.

Six kinds of PI films (Fig. 1) were prepared by thermal imidization of poly(amic acid)s under N_2 at 350°C for 90 min. In-plane and out-of-plane refractive indices (n_{TE} and n_{TM}) of the films were measured with a prism coupler (Metricon, PC-2010) equipped with a home-built temperature controller [2] between 60°C and 150°C. Near-IR interferometry was conducted with JASCO 4200 FT-IR spectrometer between 50°C and 300°C. Anisotropic molecular polarizability was calculated based on the density functional theory [3], and the degree of chain orientation is expressed by a polar angle between the axis normal to the film surface and that along the PI main chain.

Anisotropy in thermal expansion of free-standing PI films exhibited linear relation with the molecular chain orientation function (P_{200}) estimated from in-plane/out-of-plane birefringence. The molecular structure dependence of CVE of the PIs was examined in terms of local molecular motion of the main chains using dynamic mechanical analysis (DMA). The DMA indicated that the PIs having local relaxation motion at lower temperatures (50~150°C) tend to exhibit larger CVEs. On the other hand, CVEs and polar angles of as-cast PI films were estimated based on the Lorentz-Lorenz and Vuks equations using the refractive indices. Fig. 2 indicates that all as-cast films formed on Si substrates exhibited remarkably smaller CVEs than the free standing PI films, which is caused by residual tensile stress due to CTE mismatch between the PIs and Si substrate. Moreover, the PIs having rigid structures with dense molecular packing exhibited smaller CVEs than those having bent linkages or bulky side chains. Fig. 3 shows that the estimated polar angles are in linear relation with P_{200}.

[1] S. Sekiguchi, S. Ando, *Polym. Prep. Jpn*, **60**, 665 (2011). [2] Y. Terui, S. Ando, *Proc. SPIE*, **5724**, 336 (2005). [3] Y. Terui, S. Ando, *J. Polym. Sci. Part B, Polym. Phys.*, **42**, 2354 (2004).