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Uniquely low volumetric thermal expansion of siloxane-containing polyimide copolymers

Atsuto MOMOZE[1], Tomoya HIGASHIHARA[2], Naoki MATSUDA[2], Yoichiro Maruyama[3], Shintaro Fujitomi[3], Shinji ANDO[1], Ryohei ISHIGE[1]

([1]Dept. Chem. Sci. Eng. Tokyo Institute of Technology, [2]Grad. Sch. Org. Mater. Sci., Yamagata University, [3]JSR Corp.)

[**Introdcution**] Polyimides (PIs) are used as an insulating film for electronic circuit boards because of their excellent properties. Block copolyimides with poly(dimethyl siloxane) (PDMS) have been developed to improve the toughness and adhesion properties of PIs. However, copolymerization with PDMS leads to a decrease in thermal stability of the dimension. Contraly, we have found that a multi-block copolymer of a fluorinated fully aromatic PI, PMDA-TFDB, and PDMS (PI/PDMS, **Fig. 1**) shows significantly smaller coefficient of volumetric thermal expansion (CVE) than the PMDA-TFDB homopolymer (Homo-PI). Here, we tried to clarify the mechanism of the low CVE of PI/PDMS by analyzing the structural change during the heating process.

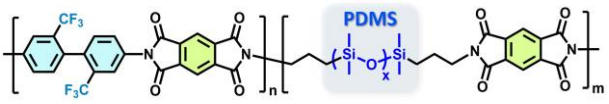

Fig. 1 Chemical structure of PI/PDMS.

[**Experiments**] PAA solutions of the precursor of PI/PDMS_x (molecular weight of PDMS block (x) = 0.8k,1.5k, 2.9k, 4.4k, 5.5k, and 25k, volume fraction of PDMS = 12.6%), were prepared on glass plates, and cured at 400°C. Tensile tests were performed to obtain stress-strain curves. The in-plane and out-of-plane linear thermal expansion coefficients of the film, $CTE_{//}$ and $CTE_{\perp}$, were evaluated and CVE was calculated by $2 \cdot CTE_{//} + CTE_{\perp}$. Changes in the microphase-separated (MPS) structure of PI/PDMS on heating process were investigated by in-situ variable-temperature small-angle X-ray scattering (VT-SAXS) measurements. The weight density of the films was measured by the sink-float method, and the PDMS density in PI/PDMS was estimated from the measured density by assuming the density of PI block is same as that of the Homo-PI.

[**Results and Discisssion**] PI/PDMS_4.4k shows higher breaking-elongation than that of the Homo-PI, even though each Young's modulus is comparable (**Fig. 2**). The CVE of the PI/PDMS decreased with increasing molecular weight (Mw) of PDMS block and smaller than that of the Homo-PI when Mw of PDMS > 4.4k (**Fig. 3**). TEM image of a cross section of PI/PDMS (**Fig. 4**) shows a MPS structure consisting of dark islands (PDMS phase) in a light gray background (PI phase). The temperature dependence of the SAXS intensity curves indicates that the electron-density difference between the PI and PDMS phases decreases with heating while maintaining their structure. The density of PDMS in PI/PDMS decreased with increasing Mw of PDMS block and became lower than that of PDMS homopolymer (0.97) when Mw > 3.0k (**Fig. 5**). From the above results, the low CVE of PI/PDMS would be explainable by a volume reduction on heating induced with partial mixing of both PI and PDMS block and negative thermal expansion of the excessively low-density PDMS block.

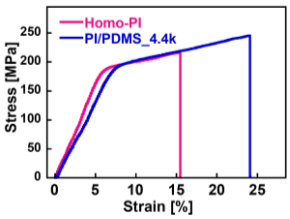

Fig. 2 Mechanical property of Homo-PI and PI/PDMS film.

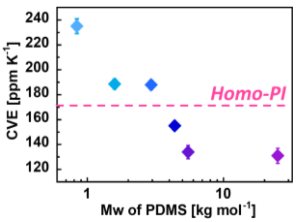

Fig. 3 Mw of PDMS versus CVE of PI/PDMS.

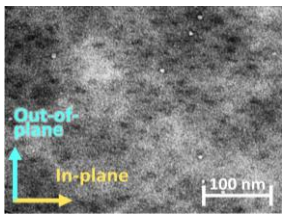

Fig. 4 TEM image of PI/PDMS observed without staining.

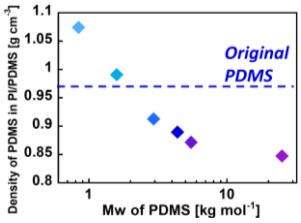

Fig. 5 Mw of PDMS versus density of PDMS in PI/PDMS.

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