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Volumetric Thermal Expansion Behaviors of Thermally and Photo-Crosslinkable Polyimide Films

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ABSTRACT:

Fully aromatic polyimides (PIs) have been utilized in a variety of industrial fields because of their high thermal stability and excellent dielectric properties. Minituarization of recent electronic circuits causes an increase of heat generation (Fig. 1). Accordingly, large difference in the coefficients of thermal volumetric expansion (CVE) between low-CVE inorganic materials such as silicon or copper, which are generally used as a substrate or wiring, and high-CVE polymer films as insulating layers can cause problems such as bending, crack, and peeling. Therefore, development of PIs with low CVE is one of the important key issues. In this study, we introduced intermolecular covalent bonds by incorporating thermal- and photo-crosslinking groups in the main chain of PIs to reduce the CVEs.

The chemical structure of the PIs used in this study are shown in Fig. 2. The PI films containing a thermally-crosslinkable phenylethynyl group (EBPA-PIs) cured at variable temperature (330, 350, 380, 400 °C) and a photo-crosslinkable benzophenonediimide group (BTDA-PIs) irradiated with variable time (5, 10, 20, 30 min) were prepared. The conversion of crosslinking reaction was evaluated by Far-IR or Mid-ATR-IR absorption spectra. Coefficients of thermal expansion in the in-plane ($CTE_{//}$) and out-of-plane directions ($CTE_{\perp}$) were evaluated by thermal mechanical analyses (TMA) and optical interferometry, respectively.

The degrees of crosslinking (D_c) increased with increasing the curing temperature from 300 to 400 °C or increasing the UV-irradiation time from 0 to 30 min. Assuming that the conversion ratio of phenylethynyl groups and benzophenonediimide groups is taken as D_c, the D_c of BTDA/DAD was limited to 26 %, while those of the other PIs reached at 42~54 % (Fig. 3). The isomeric structures of diamine moiety and the difference in crosslinking reactions affect the chain orientation and aggregation states after crosslinking. The CVE of thermally-crosslinkable EBPA-PIs was more effectively reduced with increasing the D_c than that of photo-closslinkable BTDA-PIs. The CVE of BTDA/DAD was gradually increased with increasing the UV irradiated time, which may indicates that the benzophenonediimide group of BTDA/DAD causes side reactions such as oxidation rather than formation of crosslinking. The introduction of flexible interchain bonds only restricts the increment of free volume, while that of rigid interchain bonds effectively reduce the CVE by restricting the increment of free volume as well as the local molecular motion. These results strongly suggest that the formation of rigid interchain covalent bonds by thermal cross-linking can effectively reduce the CVE of PI films.

Keywords: Polyimide, Volumetric thermal expansion, Thermal-crosslinking, Photo-crosslinking

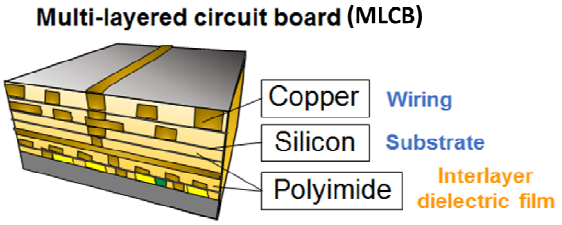

Fig.1 Application of PI films for insulating layers in MLCB.

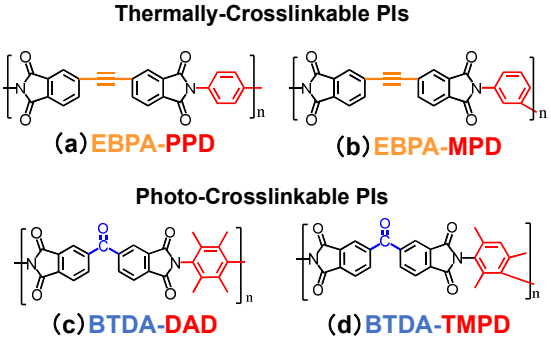

Fig.2 Chemical structures of PI films.

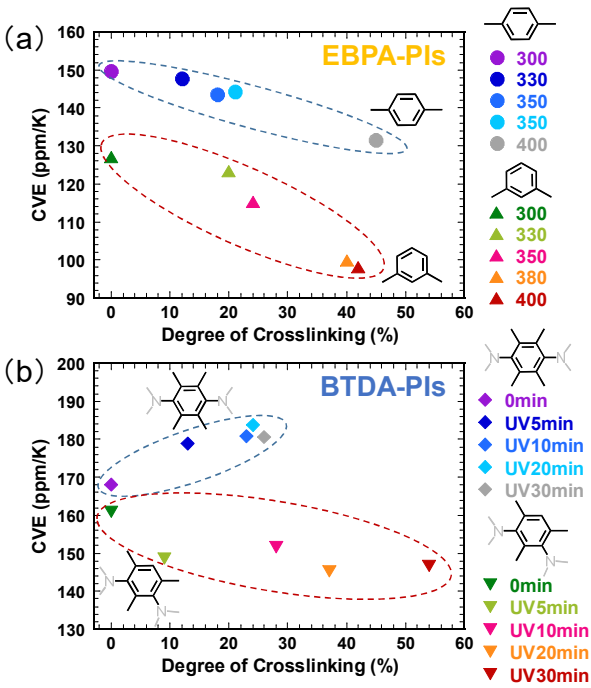

Fig.3 Degree of crosslinking versus coefficients of volumetric thermal expansion for (a) thermally- (b) photo-crosslinkable PI films.