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主论坛报告摘要 / Main-Forum Abstract

1.Physico-chemical Mechanisms Underlying the Humidity and Frequency Dependence of the Dielectric Properties of Polyimides

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Abstract: The origin of RH dependence and effects of sorbed H_2O on the dielectric properties (D_k and D_f) of 15 types of polyimides (PIs) were elucidated through quantitative structural analyses of sorbed H_2O using variable relative-humidity (RH) FT-IR spectroscopy.[1] A distinct RH dependence of the absorbance (A) of ν(OH) stretching and δ(HOH) bending bands was observed for all PIs in their difference spectra between the wet and dry states. As $A_{\delta(HOH)}$ is proportional to the concentration of water sorbed in PI films, D_k and D_f measured at 10 GHz significantly increased owing to the increase in the water absorption of PIs at elevated RH.[2] In contrast to the linear and proportional increase of D_k, the increase in D_f gradually deviated from linearity and increased upward at larger $A_{\delta(HOH)}$ values; this is attributable to the large D_f of water as well as the water-induced plasticization effects and activation of local relaxation motions of dipoles in the PI chains. Notably, a_{Dk} and a_{Df}, which represent the sensitivity to water absorption of D_k and D_f, were almost independent of the chemical structures of the PIs; this is totally different from those of RH (h_{Dk} and h_{Df}). This result confirms that the dominant factor contributing to the significant changes in D_k and D_f caused by RH was H_2O sorbed onto the PIs. In particular, D_f is strongly affected by the increase in the content of 'self-associated water'[3], which interacts with at least one bound water.

Furthermore, the thermal, optical, and dielectric properties up to 330 GHz were systematically characterized for a series of highly fluorinated PIs (HFPIs) derived from 6FDA or 10FEDA dianhydrides and various fluorinated diamines.[4,5] All PI films showed significantly low D_k and low D_f across wide humidity and frequency ranges, enabling quantitative evaluation of the structure-property relationships. It was revealed that the D_f in HFPIs originates from two structurally distinct mechanisms: 1) humidity-induced dissipation, which is primarily governed by water uptake and influenced by the fluorine and imide contents, and 2) frequency-dependent dissipation, which arises from vibrational relaxation and is influenced by the skeletal structures and substitution patterns of −F and $-CF_3$ groups. By introducing two descriptors, humidity sensitivity (h_{Df}) and frequency sensitivity (k_{Df}), a structure-property framework for the rational design of low-dissipation polymers across the 10−330 GHz range can be established.

Key words: Polyimides, IR analysis, Dielectric constant, Dissipation factor, Humidity dependence, Water plasticization, Hydrogen bond, Frequency dispersion

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