Elucidating the Mechanism of Water Sorption Dependence in Dielectric Properties at GHz Region of Polyimides by Quantification and Analysis of Water Sorption and Its Behavior Using Infrared Spectroscopy

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Abstract

Polyimides (PIs) are highly functional polymers with excellent thermal stability, chemical stability, electrical insulation, and mechanical strength. For the next-generation (5G and 6G) wireless communication devices, lower values of dielectric constant (D_k) and dissipation factor (D_f) are demanded for PIs in the high-frequency range.[1] Recently, we have clarified that the D_k and D_f of PIs (**Fig. 1**) at 10 GHz are highly sensitive to the relative humidity (RH) of the environment.[2] In this study, the principle of the water sorption dependence of D_k and D_f was investigated by quantifying the water concentration (C_w) in PI films using *in-situ* RH-variable Fourier-transform infrared (FT-IR) spectroscopy. The RH-dependent IR spectra of Kapton-H are shown in **Fig. 2(a)**, in which the OH stretching (ν(OH)) and HOH bending (δ(HOH)) vibrations of a water molecule are detected. **Figs. 2(b)** and **(c)** display the difference spectra between the dry and wet conditions in the range of (b) 3700–3200 cm^{-1} for ν(OH) and (c) 1680–1600 cm^{-1} for δ(HOH), respectively. Since an integrated area of δ(HOH) band is linearly proportional to C_w in PI films,[3,4] **Fig. 2(b)** indicates that the C_w in PIs gradually increases with RH. **Fig. 3** shows the relationships between δ(HOH) band intensity and D_k and D_f. Notably, the slopes of linear approximation in **Fig. 3**, which reflect the sensitivity to C_w, are almost independent of PI structures. This indicates that an increase in D_k and D_f with RH is almost solely caused by sorbed water in PI films. However, the dependence of D_f on C_w is slightly different from that of D_k. The D_k linearly correlates to C_w over the entire range, while the D_f deviates from a linearity at high C_w. Note that D_f is significantly affected by local molecular motion with a phase delay at 10 GHz. The upward deviation of D_f could be caused by the activated local motion enhanced by 'plasticization effect' of water molecules attached to PI chains as well as the direct effect of large D_f of water (≈ 0.5). Consequently, PIs containing plural fluorine groups (–CF_3, –F) effectively reduce both water sorption and variations in dielectric properties, and the increase in D_k and D_f of the PIs caused by water sorption was precisely quantified by combining dielectric measurements and RH-variable FT-IR spectroscopy.

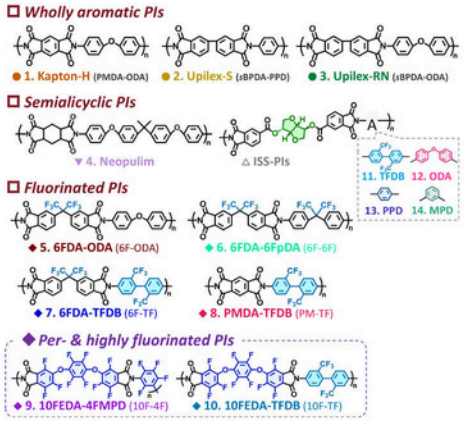

Fig. 1 Chemical structures of PIs.

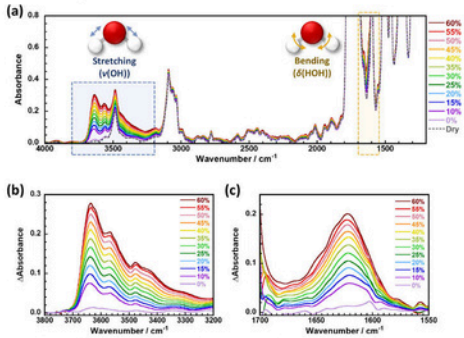

Fig. 2 (a) FT-IR and (b, c) difference spectra of Kapton-H under variable RH conditions.

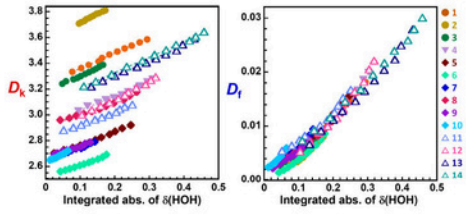

Fig. 3 Water sorption dependence of D_k and D_f.

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