3. Polyimide hybrids for reduced dielectric constants

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Abstract: Miniaturized Internet of Things (IoT) devices and next-generation wireless networks (5G/6G) demand high-performance, low-k (<2.5) polymers to ensure high signal transmission rates and integrity. Polyimides (PIs) provide a more cost-effective solution, combining superior thermal stability, mechanical strength, and tunable dielectric properties, which make them ideal for microelectronics and low-dielectric applications. PI hybrids are widely used in high-performance electronic applications to minimize signal delay and power loss[1]. These materials consist of a polyimide matrix modified with organic or inorganic components such as fluorinated groups, POSS, SiO_2, ZrO_2, BN, or porous fillers which help reduce polarizability and increase free volume or porosity. Among various modifiers, polyhedral oligomeric silsesquioxane (POSS) and hexachlorocyclotriphosphazene (HCP)-based hybrids of polyimides (PIs) are particularly advantageous due to their ability to significantly enhance thermal stability, dielectric performance, and flame retardancy. In this presentation, therefore, two typical examples of PI hybrids to possess reduced dielectric constant will be introduced, based on our recent publications, one with POSS [2] and another with phosphazene[3].

Keywords: Polyimide, hybrid, dielectric constan, POSS, phosphazene.

[1] Lee, et al. A Novel Diamine Containing Ester and Diphenylethane Groups for Colorless Polyimide with a Low Dielectric Constant and Low Water Absorption. Polymers 2022, 14, 4504.
[2] S. R. Nagella et al. Fabrication of Aminopropyl POSS End Capped Polyimide Hybrids for Enhanced Hydrophobicity and Reduced Dielectric Properties. Macromol. Chem. Phys. 2025, 2500015
[3] S. R. Nagella et al. Hybrid Films of Novel Fluorinated Polyimides and Hyperbranched Cyclotriphosphazene Polymer for Enhanced Flame Retardancy, Thermomechanical Properties, and Reduced Dielectric Constant. Chem. Commun., 2025, 61, 4824.

4. Vibrational Spectroscopic Analysis on Relative Humidity and Water Sorption Dependence of Dielectric Properties of Polyimides

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Abstract: Water sorption is an intrinsic factor to deteriorates the dielectric properties of polyimides (PIs).[1-3] In this study, the relationships among relative humidity (RH), amount of sorbed water (H_2O), structures of sorbed H_2O molecules, and the dielectric properties measured at 10 GHz were precisely analyzed for 15 types of aromatic and semi-aromatic PIs using a home-built variable-RH infrared (IR) spectroscopy. The absorbance of the IR bands attributable to the O — H stretching (νOH) and H — O — H bending (δHOH) vibrations of H_2O molecules sorbed in PI films gradually increased with an increase in RH, which can be a measure of the concentration of sorbed water (CH_2O). The dielectric constant (D_k) and dissipation factor (D_f) of the PIs also linearly and curvilinearly increased with an increase in CH_2O, respectively, and the rate of increase is almost independent of the chemical structure, which confirms that CH_2O is the dominant factor of the RH-dependent increase of D_k and D_f. In particular, the curvilinear increase of D_f with CH_2O is induced not only by the large D_f of water itself (~60) but also by the plasticization effect of the water absorbed in the PI films which activates the local motion of PI chains resonating at 10 GHz. In addition, the spectral decomposition of the νOH band enables the separation of two types of sorbed water molecules, namely I) H_2O directly forms a hydrogen bond (HB) with an imide carbonyl (C=O), called 'bound water' and II) H_2O forms HBs with other H_2Os, called 'self-associated water (Wassoc)' .[4] Notably, the total amount of the spectral components of Wassoc (Aassoc) increased with an increase in CH_2O in an accelerated manner. Furthermore, the rapid increase in D_f with an increase in Aassoc indicates that Wassoc activates the local motion of PI chains through water plasticization. To reduce the RH dependence on the D_k and D_f of PIs at higher frequencies up to 330 GHz [5], the reduction of Wassoc and the suppression of the local molecular motion caused by water plasticization is essential.

Keywords: Polyimides, IR analysis, Dielectric constant, Dissipation factor, Humidity dependence, Sorbed water, Water plasticization, Hydrogen bond

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