IUPAC 2015- A20150527-6067

Effect of Hyperbranched Polyimide on Nanoscale Dispersion of SiO_2 in Linear Polyimides

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It is of particular interest in developing organic-inorganic composites based on polyimides (PIs) for improving the insulating, dielectric, and optical properties of flexible wiring boards.[1, 2] However, inorganic particles in micron-scale usually cause opaqueness and has not shown a strong demand for application as functional transparent composites.

The hyperbranched polymers have received much attention in a variety of fields, because of the unique properties, such as low solution viscosity, high solubility, increasing free volume, as compared with their linear analogues. [1, 3, 4] Therefore, we synthesized a hydroxyl terminated hyperbranched polyimide[1, 2] as a component to satisfy the requirements for cutting-edge insulators with low dielectric constants and high thermal stability as well as to reduce inorganic particle sizes by controlling the interactions between polyimide backbone and silica phase for transparency. Then, based on the hydroxyl-terminated hyperbranched polyimide ($HBPI_{BPADA\text{-}TAP(OH)}$), we successfully fabricated hybrid ternary composites which comprised of a linear polyimide ($PI_{6FDA\text{-}APB}$), $HBPI_{BPADA\text{-}TAP(OH)}$, and inorganic SiO_2 component by traditional 'Sol-Gel' method. It is complementary to improve the dielectric and thermal resistant drawbacks of unary systems and the dielectric and optical drawbacks of binary systems. [1, 2]

For an optimized composition, the dielectric constant (D_k) of the $PI_{6FDA\text{-}APB}$_$HBPI_{BPADA\text{-}TAP(OH)}$-30%_$SiO_2$-20% composite reaches the lowest value of 2.24 at 100 kHz. Moreover, the optical transparency is significantly improved with the increase of the $HBPI_{BPADA\text{-}TAP(OH)}$ content in the composite. Compared with the binary composite ($PI_{6FDA\text{-}APB}$_SiO_2), the optical transmittance increases from 1 % to 75 % at the wavelength of 450 nm. Without the hyperbranched component, the aggregated silica particles can be clearly seen as spherical beads with smooth surface. By using the hyperbranched PI, the particle size of SiO_2 is significantly reduced, from an average diameter around 1500 nm to 100-200 nm. The incorporation of SiO_2 can preserve the good thermal properties of the hybrid composites containing $HBPI_{BPADA\text{-}TAP(OH)}$. By adding

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10% of $HBPI_{BPADA\text{-}TAP(OH)}$ to the $PI_{6FDA\text{-}APB}$_SiO_2-20% system, the coefficient of thermal expansion (CTE) of the hybrid ternary composite is 20.9 ppm $°C^{-1}$ in the temperature range of 100–150 °C, which is significantly smaller than that of the linear polyimide (37.1 ppm $°C^{-1}$ for $PI_{6FDA\text{-}APB}$). Owing to these optimized properties, hybrid ternary composites can show potential applications in the micro-electronic insulator applications such as interlayer dielectrics in advanced electronic devices.

Keywords: low dielectric constant, ternary composite, hyperbranched polyimide, PI/Silica hybrid, reduced size particles.

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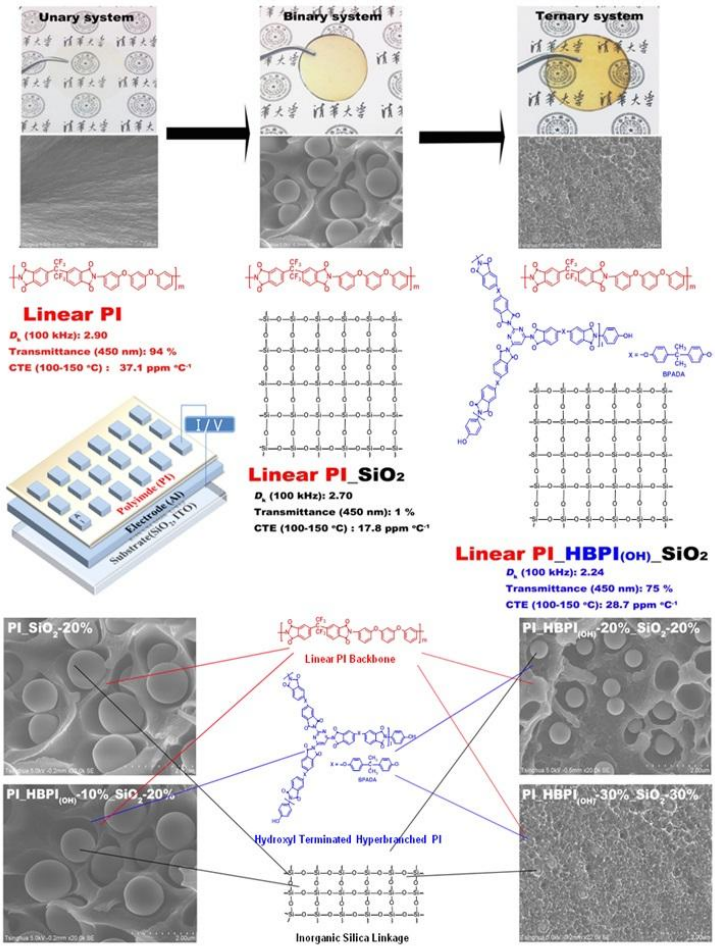

Figure 1 The graphical images, properties of unary, binary, and ternary system, and the SEM image of reduced silica particle size with increasing $HBPI_{BPADA\text{-}TAP(OH)}$. Scale bar: 2㎛