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Ternary Composites of Linear and Hyperbranched Polyimides with Nanoscale Silica for Low Dielectric Constant, High Transparency, and High Thermal Stability

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A new series of ternary polyimide-silica composites was developed to obtain polymer films with low dielectric constant, high optical transparency, and good thermal stability. By using a linear polyamic acid with triethoxysilane termini and a hyperbranched polyimide with peripheral hydroxyl groups (HBPI₁BPADA₆TAP(OH)₈), the ternary composites were fabricated through in situ imidization and sol-gel reaction with tetraethoxysilane. The results show that the composite films exhibit significantly improved properties due to the strong silica cross-linkages between organic-inorganic phases. The triethoxysilane termini can effectively enhance transparency because of the homogeneous dispersion of the inorganic phase in the PI matrices and the improved dispersibility through their strong covalent and partial hydrogen bonding with inorganic silica networks. With an appropriate content of 30% HBPI₁BPADA₆TAP(OH)₈ and 20% SiO₂ in the linear polyimide (PI₆FDA-APB(Si))₉, the dielectric constant ($Dk$) can reach the lowest value of 2.19 at 100 kHz. The highest transmittance of 96% at 450 nm is obtained for a ternary hybrid containing 20% SiO₂ and 10% HBPI₁BPADA₆TAP(OH)₈. The incorporation of HBPI₁BPADA₆TAP(OH)₈ does not cause negative effects on the thermal stability. The ternary hybrid containing 20% SiO₂ and 10% HBPI₁BPADA₆TAP(OH)₈ also exhibits the lowest coefficient of thermal expansion (CTE) of 27.8 ppm °C⁻¹, when compared with 29.9 ppm °C⁻¹ for the binary composite as PI₆FDA-APB(Si)₉ with 20% SiO₂. These properties can well match the requirements for potential applications in the microelectronic insulator fields as interlayer dielectric of advanced electronic devices.

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Introduction

The insulating interlayer materials possessing low dielectric constant, high transparency, and thermal stability are urgently demanded in microelectronic industry. The low dielectric constant is required to accelerate signal transmission by reducing resistance capacitance (RC) delay time among the chips in large integrated circuit or multilayer printed circuit board, and to alleviate power dissipation by reducing capacitance between interconnection conductor lines. For improving the insulating and electronic transmission properties of flexible wiring boards, it is of particular interests in developing organic-inorganic composites. Based on polyimides (PIs) with the reduced dielectric constant, organic-inorganic binary composites have been reported as a promising system for possible applications in high-speed, high-frequency circuits in electric material fields.

Since it was reported by Kim and Webster in 1990, 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. Their highly branched structures with a large number of terminated functional groups are highly characteristic features for some specific application fields. Particularly, it can be used as an efficient component to enhance the interaction between the organic and inorganic phases through covalent and hydrogen bonding.
In the past decade, hyperbranched polyimides (HBPIs) have been studied from various aspects, such as synthesis, characterization, gas permeability, hydrogen storage, nonlinear optics, and optoelectronics. One unique feature of the hyperbranched structures is the existence of many open and accessible cavities (typically several angstroms in size) in a rigid branched structure. This unique feature can result in air gap or pore voids systems, low polarizability, increased free volume, and high optical transparency and thermal stability.

In our previous studies, we have synthesized a hydroxyl-terminated hyperbranched polyimide (HBPI$_{BPADA-TAP(OH)}$) and developed a series of ternary composites by using a typical linear polyimide, HBPI$_{BPADA-TAP(OH)}$ and SiO$_2$. Owing to particular features of hyperbranched polymers, such as a large number of end groups, high solubility, increased free volume and high reactivity, the ternary composites show significantly improved properties, such as low dielectric constant, high optical transparency and thermal stability. However, the linkage between the linear PI and inorganic particles has not been considered for the composites.

In this work, we developed a way to enhance the interaction between polyimide backbone and silica phase. We used a linear poliimide with triethoxysilane-terminated group, which has been developed in our recent study for a binary system. To further improve the properties, we fabricated a series of new ternary hybrid composite, P$_{6FDA-APB(Si)}$$_{6FDA-APB(Si)}$$_{BPADA-TAP(OH)}$$\_SI0$_2$, by the typical sol-gel method. The structures and properties of the composites were carefully characterized. The ternary hybrid composites not only show significantly reduced dielectric constants, but also exhibit other improved performances such as high transmitance and good thermal properties.

**Experimental Section**

**Materials**

4,4’-(Hexafluoroisopropylidene) dipthalic anhydride (6FDA, 95%), 2,6-triaminopyrimidine (TAP, 98%), 1,3-bis(3-aminophenoxy)benzene (APB, 98%), and (3-aminopropyl) triethoxysilane (APTEOS, 98%) were purchased from Adamas-Reagent Co. Ltd. 4,4’-Bis(4,4’-isopropylidene diphenoxy) bis(phthalic anhydride) (BPADA 97%) was purchased from Sigma-Aldrich Corporation. 4-Amino-phenol was purchased from Tianjin Chem. Eng. Lab. N, N-Dimethylacetamide (DMAc, 98%), N, N-dimethylformamide (DMF, 98%), tetrahydrofuran (THF, 98%), and toluene, used as the reaction media, were purchased from Beijing Chemical Works and Alfa Aesar. The solvent N-methyl-2-pyrrolidone (NMP, 97%) was purchased from Beijing Modern Eastern Fine Chemical. Hydrochloric acid (HCl) and tetraethoxysiliane (TEOS, 98%) were purchased from Alfa Aesar and used without further purification. If it is not mentioned specifically, the reactants and solvents were used as received without further purification.

**Synthesis**

The synthetic routes of the materials are shown in Scheme 1-2, which show preparations of PAA$_{6FDA-APB(Si)}$ and its binary composite with silica network (Scheme 1), and the hybrid ternary P$_{6FDA-APB(Si)}$$_{6FDA-APB(Si)}$$_{BPADA-TAP(OH)}$$\_SI0$_2$ composite films (Scheme 2). The hydroxyl terminated hyperbranched polyimide (BPADA-TAP(OH)) was synthesized by the A$_2$ + B$_1$ polycondensation, which has been described in our previous report. The preparation details are described below.

**Linear polyamic acid with triethoxysilane termini (PAA$_{6FDA-APB(Si)}$).** Polyamic acid (PAA) was synthesized by a typical two-step condensation process at 0 °C. Then, APTEOS was added into the PAA solution to obtain a triethoxysilane terminated PAA, 1.3-Bis(3-aminophenoxy)benzene (APB, 0.526 g, 1.8 mmol) was dissolved in NMP (10 wt%) and cooled in an ice bath, followed by adding 4,4’-(hexafluoroisopropylidene) dipthalic anhydride (6FDA, 1 g, 2.25 mmol) under stirring. Then, (3-aminopropyl) triethoxysilane (APTEOS, 0.199 g, 0.9 mmol) was slowly dropped into the mixture. The molar ratio of 6FDA: APB: APTEOS was controlled to be 5: 4: 2. After stirring at 40 °C for 12 h, the PAA solution with silica terminated groups (PAA$_{6FDA-APB(Si)}$$_{APB(Si)}$$_{6FDA-APB(Si)}$$_{6FDA-APB(Si)}$$_{BPADA-TAP(OH)}$) was obtained. FT-IR (KBr, cm$^{-1}$): 3450 cm$^{-1}$ (–CONH); 2920 cm$^{-1}$ (C–CH$_3$–C); 1690 cm$^{-1}$ (C=O, –COOH); 1629 cm$^{-1}$ (C=O, –CONH); 1021 cm$^{-1}$ (Si–O–C$_2$H$_5$). P$_{6FDA-APB(Si)}$$_{6FDA-APB(Si)}$$_{SI0$_2$}-20%$ binary composite (SF-1). SF-1 was prepared by hydrolysis reaction with TEOS (theoretical SiO$_2$ content of 20 wt%) and heated through several steps up to the highest temperature to obtain the binary composites. The preparation of the binary composite is given here as a typical example. Stoichiometric quantities of TEOS in DMAc (10 wt%, 1.38 g), and HCl in deionized water (0.1 N, 0.048 g) were mixed and stirred at room temperature for 0.5 h to form the SiO$_2$ sol. Then, the SiO$_2$ sol was added to the PAA$_{6FDA-APB(Si)}$ solution (10 wt%, 2 g) by droplets under stirring. The mixture was then stirred at room temperature for 6 h and PAA$_{6FDA-APB(Si)}$$_{6FDA-APB(Si)}$$_{SI0$_2$}-20%$ precursor was obtained. In the second stage, the PAA$_{6FDA-APB(Si)}$$_{6FDA-APB(Si)}$$_{SI0$_2$}-20%$ precursor solution was casted on the glass plate and heated at 80 °C for 2 h. The film was then thermally imidized by step-wise heating at 150 °C (1 h), 200 °C (1 h), and 300 °C (1 h) to afford the P$_{6FDA-APB(Si)}$$_{6FDA-APB(Si)}$$_{SI0$_2$}-20%$ binary composite. FT-IR (KBr, cm$^{-1}$): 2920 cm$^{-1}$ (C–CH$_3$–C); 1776 cm$^{-1}$ (C=O sym. str. imide); 1716 cm$^{-1}$ (C=O asym. str. imide); 1587 cm$^{-1}$ (C=O str. Ar); 1477 cm$^{-1}$ (C–CH$_2$–C); 1443 cm$^{-1}$ (C=C str. Ar); 1364 cm$^{-1}$ (C–N str. imide.); 1296 cm$^{-1}$ (Si–O–Ar); 1125 cm$^{-1}$ (–CF$_3$); 1096–1067 cm$^{-1}$ (Si–O–Si); 964 cm$^{-1}$ (Subst. Ar); 888 cm$^{-1}$ (Si–OH); 845–718 cm$^{-1}$ (Subst. Ar); 680 cm$^{-1}$ (–CF$_3$); 3500–3300 cm$^{-1}$ and 1300 cm$^{-1}$ (Non amine structure band, –NH$_2$); 3350 cm$^{-1}$ (Non amide band, –NH–); and 1690–1629 cm$^{-1}$ (Non PAA structure band).

P$_{6FDA-APB(Si)}$$_{6FDA-APB(Si)}$$_{BPADA-TAP(OH)}$$_{10–40%}$ SiO$_2$-20% hybrid ternary composites. The ternary hybrid composite films were prepared by a typical sol-gel method (Scheme 2). The preparation procedures for a composite SF-3 (P$_{6FDA-APB(Si)}$$_{6FDA-APB(Si)}$$_{BPADA-TAP(OH)}$$_{20%}$ SiO$_2$-20%) is given here as a typical example. Stoichiometric quantities of TEOS in DMAc (10 wt%, 1.38 g), and HCl in deionized water (0.1 N, 0.048 g) were mixed and stirred at room temperature for 0.5 h to form the SiO$_2$ sol. Then, the SiO$_2$ solution was added dropwise into the mixture solution of linear PAA$_{6FDA-APB(Si)}$ (10 wt%, 2 g) and HBPI$_{BPADA-TAP(OH)}$ (0.04 g) under stirring. The solution was stirred at room
the precursor solution was casted on the glass plate and heated at 80 °C for 2 h. The film was then thermally imidized by stepwise heating at 150 °C (1 h), 200 °C (1 h), and 300 °C (1 h).

The hybrid ternary composites with different compositions were prepared by a similar method by adjusting the composition of the PI_{6FDA-APB(Si)} and silica. The film formation property of the hybrid ternary composite depended on the contents of the HBPI_{BPADA-TAP(OH)}%TEOS. By using the linear PAA(Si) and hyperbranched polyimide, the hybrid ternary composites were prepared successfully. The films are named as SF-2 to SF-5 (PI_{6FDA-APB(Si)}_{HBPI_{BPADA-TAP(OH)}}=10–40% SiO$_2$-20%). The percentage given in the generic abbreviations are the weight percentage. The hybrid films exhibit similar spectra, the characteristic IR absorption bands are listed below.

\[\text{SF-2–SF-5 FTIR (KBr, cm}^{-1}\text{): 2920 cm}^{-1} (\text{C–CH}_2–\text{C}); 2911 \text{ cm}^{-1} (\text{C–CH}_3 \text{ sym. str. Al.}); 1766 \text{ cm}^{-1} (\text{C=O sym. str. imide.}); 1716 \text{ cm}^{-1} (\text{C=O asym. str. imide.}); 1587 \text{ cm}^{-1} (\text{C=C str. Ar.}); 1504 \text{ cm}^{-1} (\text{asym. tri-subst. Ar.}); 1477 \text{ cm}^{-1} (\text{C–CH}_3–\text{C}); 1443 \text{ cm}^{-1} (\text{C=O str. Ar.}); 1364 \text{ cm}^{-1} (\text{C–N–C str. imide.}); 1356 \text{ cm}^{-1} (\text{–CH}_3 \text{ Al.}); 1296 \text{ cm}^{-1} (\text{–CF}_3); 1235–1192 \text{ cm}^{-1} (\text{Ar.–O–Ar.}); 1125 \text{ cm}^{-1} (\text{–CF}_3); 1096–1067 \text{ cm}^{-1} (\text{Si–O–Si}); 1012 \text{ cm}^{-1} (\text{Para-di subst. Ar.}); 964 \text{ cm}^{-1} (\text{Subst. Ar.}); 888 \text{ cm}^{-1} (\text{Si–OH}); 845 \text{ cm}^{-1} (\text{Subst. Ar.}); 680 \text{ cm}^{-1} (\text{–CF}_3); \text{ and 1690–1629 cm}^{-1} (\text{Non PAA structure band}).\]

**Characterization**

Fourier transform infrared (FTIR) spectroscopic measurements were performed using a Magna-IR Nicolet 560 in the range 4000–450 cm$^{-1}$ at a resolution of 0.35 cm$^{-1}$ by incorporating samples in KBr disks. The phase transitions and thermal properties were characterized by differential scanning calorimeter (DSC), thermal gravimetric analysis (TGA), and dynamic mechanical analysis (DMA). TGA was performed with a TGA 2050 analyzer (TA instrument Co.) at a heating rate of 20 °C from room temperature to 900 °C under nitrogen. Thermal phase transitions of the polymers were scanned by DSC 2910 (TA Instrument Co.) with a heating rate of 20 °C min$^{-1}$ under nitrogen. The dielectric constants were measured using a NOVOCOOL Alpha-ANB (Novocontrol Technologies GmbH & Co. KG) dielectric analyzer with silver paint electrode. The measurements were carried out at the room temperature with scan frequencies from 1 Hz to 10$^6$ Hz by a reference of commercial Kapton® HN film ($D_k = 3.81$ at 100 kHz). The thickness of specimens was controlled to be 17-24 µm. The coefficients of thermal expansion (CTE) parallel to the film surfaces were measured using a DMA Q800 dynamic mechanical analyzer (DMA, TA Instrument Co.) in extension mode over a temperature range from 25 to 320 °C with a force of 0.01 N. The size of samples was 14 mm in length, 5 mm in width, and 2227 µm in thickness. UV-visible absorption spectra of films were measured on a Lambda Bio-40 spectrometer (Perkin–Elmer). A silica glass plate was used as a reference, and the thickness of specimens was below 10 µm. Cross-sectional images of the PI hybrid films were obtained by scanning electron microscopy (SEM) using a SU5500 microscope (Hitachi) operating at an acceleration voltage of 5.0 kV. The cross-sectioned samples were prepared by breaking films in liquid nitrogen and sputtered with carbon nanoparticles.

![Fig. 1 FTIR spectra of the hydroxyl terminated hyperbranched polyimide, PI_{6FDA-APB(Si)}, SiO$_2$-20% binary composite (SF-1), and PI_{SiO$_2$-20% hybrid ternary composites (SF-2–5).}](image-url)
Table 1 Dielectric, optical, and thermal properties of P(6FDA-APB(Si))/SiO$_2$-20% (SF-1) and P(6FDA-APB(Si))HBPI$_{6FDA-TAP(OH)}$-10–40% (SF-2–5) hybrid ternary composite films.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Thickness $^a$ $\mu$m</th>
<th>$D_a$ $^b$</th>
<th>$\lambda_{max}$ nm</th>
<th>Transmittance $^c$ %</th>
<th>$T_d^a$ / $^\circ$C</th>
<th>$T_{s-d}^b$ / $^\circ$C</th>
<th>$T_{w 800}^c$ / %</th>
<th>$R_{w 800}$ / %</th>
<th>CTE $^d$ / ppm $^\circ$C$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>SF-1 P(6FDA-SiO$_2$)-20%</td>
<td>24</td>
<td>2.67</td>
<td>326</td>
<td>87</td>
<td>68</td>
<td>203.3</td>
<td>529</td>
<td>545</td>
<td>72.9</td>
</tr>
<tr>
<td>SF-2 P(6FDA-HBPI$_{6FDA}$-10%)-SiO$_2$-20%</td>
<td>17</td>
<td>2.28</td>
<td>326</td>
<td>96</td>
<td>92</td>
<td>207.4</td>
<td>527</td>
<td>546</td>
<td>72.8</td>
</tr>
<tr>
<td>SF-3 P(6FDA-HBPI$_{6FDA}$-20%)-SiO$_2$-20%</td>
<td>20</td>
<td>2.22</td>
<td>326</td>
<td>94</td>
<td>86</td>
<td>206.6</td>
<td>513</td>
<td>540</td>
<td>51.2</td>
</tr>
<tr>
<td>SF-4 P(6FDA-HBPI$_{6FDA}$-50%)-SiO$_2$-20%</td>
<td>20</td>
<td>2.19</td>
<td>325</td>
<td>94</td>
<td>86</td>
<td>210.8</td>
<td>494</td>
<td>531</td>
<td>52.7</td>
</tr>
<tr>
<td>SF-5 P(6FDA-SiO$_2$)-40%</td>
<td>21</td>
<td>2.39</td>
<td>326</td>
<td>88</td>
<td>75</td>
<td>203.8</td>
<td>492</td>
<td>526</td>
<td>51.3</td>
</tr>
</tbody>
</table>

$^a$ The thickness of specimens for dielectric constant measurement.

$^b$ Measured dielectric constant at a frequency of 100 kHz.

$^c$ Temperatures at which 5% and 10% weight loss occurred, respectively, measured by TGA at a heating rate of 20 $^\circ$C min$^{-1}$ and a $N_2$ gas flow rate of 25 cm$^3$ min$^{-1}$.

$^d$ Residual weight percentages at 800 $^\circ$C.

The coefficients of thermal expansion (CTE) at the temperature range from 100 to 150 $^\circ$C with a force of 0.01 N.

Results and Discussion

Synthesis and Characterization

In this study, a series of hybrid nano-composites was prepared. To facilitate the comparison and discussion, the binary composite (P(6FDA-APB(Si))/SiO$_2$-20%) is referred to as SF-1, and abbreviations SF-2–SF-5 are used to denote the hybrid ternary composites P(6FDA-APB(Si))HBPI$_{6FDA-TAP(OH)}$-10–40% SiO$_2$-20%.

FT-IR spectra of HBPI$_{6FDA-TAP(OH)}$ and SF-1 and ternary hybrid composites SF-2–SF-5 are shown in Fig. 1. In the spectra of HBPI$_{6FDA-TAP(OH)}$ and all the composites, the absorption bands assignable to imide structure are clearly observed at 1785, 1766 cm$^{-1}$ for the symmetric and anti-symmetric stretching vibrations of the carbonyl groups, and there are no obvious absorption bands of polyamic acid (PAA) between 1690 and 1629 cm$^{-1}$. All composites clearly exhibit typical spectral characteristics related to the SiO$_2$ network formation. A very weak absorption at 888 cm$^{-1}$ (Si–OH) and strong absorption at 1096-1067 cm$^{-1}$ (Si–O–Si, symmetric stretching vibrations) in all the composites indicate that only tiny amount of Si–OH groups still remains and dominant Si–O–Si networks form during the hydrolysis of alkoxy groups. In Fig. 1 and 2, the absorption bands of –CH$_2$–CH$_2$– linkage from APTEOS are clearly observed at 2920 and 1477 cm$^{-1}$. There are no obvious absorption bands of amine (–NH$_2$) at 3500-3300 cm$^{-1}$ and 1300 cm$^{-1}$, and –NH– at 3450 cm$^{-1}$ after the terminal reaction with APTEOS. It proves that the linkage is successfully introduced between linear PI backbone and silica network.

The FT-IR spectra of SF-1 to SF-5 show significant shifts for the absorption bands related with the transformation during the synthesis of the hybrid ternary composites. The absorption bands of C=O are shifted from 1785 and 1731 cm$^{-1}$ for HBPI$_{6FDA-TAP(OH)}$ to 1766 and 1716 cm$^{-1}$ for the hybrid ternary composites. The absorption band of C–N is also shifted from 1384 cm$^{-1}$ for HBPI$_{6FDA-TAP(OH)}$ to 1364 cm$^{-1}$ for the hybrid ternary composites. These band-shifts are related with the hydrogen bonding and hydrolysis reactions with TEOs, which effectively enhance the intermolecular interactions. Therefore, with the increase of the HBPI$_{6FDA-TAP(OH)}$ percentage, the characteristic bands of C=O and C–N are gradually shifted to lower wavenumbers. Moreover, the intensities of the absorption bands around 1776, 1716 (C=O stretching vibrations), 1504 (tri-substituted aromatic benzene), 1364 cm$^{-1}$ (C–N stretched imide), 1356 cm$^{-1}$ (aliphatic methyl groups), and 1012 cm$^{-1}$ (para-di-substituted aromatic benzene) increase with the increase of the HBPI$_{6FDA-TAP(OH)}$ amount by using the intensity of SiO$_2$ as the standard.

Above results all verify that, not only the PAA precursor is completely converted to PI, but also SiO$_2$ networks are formed in the organic-inorganic composite through the sol-gel process.

Dielectric properties of hybrid binary and ternary composites

The dielectric constants of the unary PI (S-1), composites (SF-1–5) and commercial Kapton® HN as a control are shown in Fig. 3 and also listed in Table 1. The dielectric constants ($D_a$) of the composite films and related materials were measured in the frequency range from 1 Hz to 10$^6$ Hz at a fixed frequency (100 kHz).

The dielectric constants show an increase with decreasing frequency, which is a typical frequency dependence of dielectric properties. It can be described by Cole-Cole equation,

$$\varepsilon^* - \varepsilon_\infty = (\varepsilon_0 - \varepsilon_\infty) [1 + (i\omega\tau_0)^{-\alpha}]$$

where $\varepsilon^*$ is the complex dielectric constant, $\varepsilon_0$ and $\varepsilon_\infty$ are the dielectric constants at “static” and “infinite frequency”, $\omega = 2\pi$ times the frequency, and $\tau_0$ is a generalized relaxation time. The exponent parameter $\alpha$ can assume a certain value between 0 and 1, in which the former case corresponds to the result by Debye for polar dielectrics.
promote the homogeneous dispersion, and miscibility through HBPI and enhance the effect of 6FDA%APB significantly lower than that of the linear PI 4 exhibits the lowest hybrid ternary composites (SF%1). Under the optimized conditions, SF% the binary composite (SF%1). The low dielectric constants of the films prepared in this study are significantly lower than that of the linear PI HBPI BPADA%TAP(OH) 6FDA%55%20% (SF%1), and PI matrix due to the terminated linkages on PI 6FDA%APB(Si) and PI other series SF composites are obviously reduced, and they are also less dependent on the frequency. Especially, the decrease of Dk in the 1 Hz to 10 Hz range shown in Fig. 3(a) could be related to a decrease in space charge polarization between organic and inorganic phases.\cite{23,24} It verifies in comparison to series SA that the series SF composites has good adhesion between the silica and PI matrix due to the terminated linkages on PI and reaction of HBPI BPADA%TAP(OH) with TEOS. The Dk values of hybrid ternary composites (SF-2-SF-5) are smaller than that of the binary composite (SF-1). Under the optimized conditions, SF-4 exhibits the lowest Dk of 2.19, which is slightly smaller than SA-4 (a typical specimen in SA series, Dk = 2.24).\cite{23} It can be attributed to that the terminated linkage of PI to promote the homogeneous dispersion, and miscibility through their strong covalent bonds. And it enhances the effect of HBPI BPADA%TAP(OH) on reducing Dk by forming Si–O–Si with the inorganic phase. The low dielectric constants of the system are also related with the fundamental characters of monomers, i.e., the high fluorine content of 6FDA,\cite{31,32} the flexible and bent structure of APB,\cite{33,34} and the bulky side groups of BPADA.\cite{35,36,37} Moreover, the introduction of inorganic silica effectively reduces the moisture absorption of the material and expands the free volume.\cite{29} The improved phase dispersion of HBPI BPADA%TAP(OH) and PI plays a very important role to result in the reduced dielectric constant in hybrid ternary composite films.

Fig. 4 shows typical SEM images of the representative composite films. It is confirmed by the SEM observation that HBPI BPADA%TAP(OH) can reinforce the binding between PI and SiO2 and promote the dispersion of SiO2 in the matrices. Fig. 4(a) and 4(c) show the SEM images of SA-1 (PI BPADA%TAP(OH)%20%, and SF-1 (PI BPADA%TAP(OH)%20% without the existence of HBPI BPADA%TAP(OH)). Compared with SA-1, which has been reported in our previous study, the SF-1 still displays aggregated silica particles but shows obviously reduced size of spherical beads with smooth surface. The average size of partially aggregated silica particles reduces from 1500 nm for SA-1 (Fig. 4(a)) to around 100-200 nm for SF-1 (Fig. 4(c)). When the triethoxysilane termini are introduced to the PI, dispersion of SiO2 in matrices is dramatically improved. This result is consistent with our previous study for optically transparent polyimide.\cite{25}
without the inorganic phase. Compared with SA-1 and SA-4 of our previous study (Fig. 4(a) and (b)), the synergy of HBPI_{BPADA-TAP(OH)} and PI_{6FDA-APB(Si)} can effectively reduce the aggregation of silica and suppress phase separation between heterogeneous organic-inorganic phases. Moreover, the hyperbranched structure can introduce the nano-scaled cavities, which are beneficial for reducing the dielectric constants the hybrid ternary composites. As discussed in the following sections, owing to the reduced phase separation, the transmittance of the composites can be significantly improved by incorporating HBPI_{BPADA-TAP(OH)} into the PI_{6FDA-APB(Si)}-SiO_2 binary composite. The decrease in D_k in the frequencies between 1 and 10^4 Hz range, which is mainly form the space charge polarization, can also be attributed to the effective reduction in phase separation.

### Optical properties of hybrid binary and ternary composites

The optical transparency of SF-1 and hybrid ternary composites (SF-2-5) was characterized with UV-Vis spectroscopy. Fig. 5 shows the UV-Vis transmission spectra of the composite films. The cutoff wavelengths (absorption edge, λ_{cutoff}) and the transmittance at 450 nm and 400 nm estimated from these spectra are listed in Table 1.

![Image](image.png)

**Fig. 5** (a) UV-Vis spectra of the PI_{6FDA-APB(Si)}-SiO_2-20% binary composite (SF-1), and PI_{6FDA-APB(Si)}-HBPI_{BPADA-TAP(OH)}-10-40%, SiO_2-20% ternary hybrid composites (SF-2-5). The film thickness was under 10 µm on the glass substrates. (b) commercial Kapton film (25 µm) and (c) SF-2 film (28 µm).

The optical transparency of the series SF composites is obviously improved by incorporating HBPI_{BPADA-TAP(OH)} into the PI_{6FDA-APB(Si)}-SiO_2 system. On the other hand, the effect of triethoxysilane termini in PI_{6FDA-APB(Si)} is also observed from the improved transparency compared with those of the series SA composites reported by us before. The SF-1 composite exhibits a transmittance of 87% at 450 nm. By incorporating HBPI_{BPADA-TAP(OH)}, SF-2 shows the highest transmittance of 96% at 450 nm. The transmittance of SF-1 is also improved in comparison to SA-1. The composite with the lowest D_k (SF-4) in the series also shows a transmittance of 94% at 450 nm, which are also obviously higher than that of SA-4 (PI_{6FDA-APB-HBPI_{BPADA-TAP(OH)}}-10%-SiO_2-20%).

Fundamental characters of monomers, i.e., the high fluorine content of FDA, the flexible and bent structure of APB, and the bulky side groups of BPADA are important for the colorless feature. On the other hand, this effect is also attributed to the synergy effect of HBPI_{BPADA-TAP(OH)} and PI_{6FDA-APB(Si)} components to reduce the phase separation between PI matrices and silica particles, which improves the dispersibility and reduces the size of silica particles. Therefore, it can reduce the light scattering from the aggregated inorganic silica phase in the visible wavelength scale.

### Thermal properties of hybrid binary and ternary composites

The thermal phase transition behavior of the hybrid ternary composites and related materials was investigated by DSC. The results are shown in Fig. 6(a) and summarized at Table 1.

All the hybrid ternary composites and related materials show glass transitions, which means the PI components exist in the amorphous phase. The SF series composites show the glass transition temperatures (T_g) ranging from 203.3 to 210.8 °C. After incorporating HBPI_{BPADA-TAP(OH)} into the binary system, the T_g of the hybrid ternary composites become slightly higher in a few degree scale than that of SF-1, which is attributed to the covalent cross-linkages and partial hydrogen linkages in the composites networks. It causes enhanced interaction between PI and inorganic silica phase. However, the differences in T_g from SF-2 to SF-5 are only few degrees. The T_g of SF-5 is 203.8 °C, which is the lowest in the series. HBPPI_{BPADA-TAP(OH)} has a hyperbranched structure with low molecular weight. The lower T_g of SF-5 can be attributed to the large free volume and low T_g of the hyperbranched polymer. On the other hand, as long as its concentration is below the critical value, HBPI_{BPADA-TAP(OH)} does not separate from the matrices or affect the T_g significantly. The effect for reducing T_g is not obvious for the binary composites. The addition of HBPI_{BPADA-TAP(OH)} does not show an obvious effect to decrease T_g in the ternary composite system, which has also been observed in our previous study.

The thermal decomposition temperatures of the hybrid ternary composites and related materials measured by TGA analysis are shown in Fig. 6(b) and summarized in Table 1. It can be observed for the SF series, the residual weights of the composites are nearly 100% below 450 °C, which are higher than those of the SA, SB, and SC series reported by us before.

The 5% and 10% weight loss temperatures (T_{d,5%} and T_{d,10%}) of SF-1 are 529 and 545 °C, respectively. The ternary hybrid composites (SF-2-5) show the T_{d,5%} ranging from 527 to 492 °C and T_{d,10%} from 546 to 526 °C. These are significantly higher than those for the SA series (T_{d,5%}: 487 to 481 °C).

It can be attributed to cross-linked silica networks with HBPI_{BPADA-TAP(OH)} and PI_{6FDA-APB(Si)} The T_d values decrease with the increase in the HBPI_{BPADA-TAP(OH)} content in the systems, which might be caused by the elimination of water molecules from Si-OH and hydroxyl groups of HBPI_{BPADA-TAP(OH)} at the high temperatures and lower T_d of HBPI_{BPADA-TAP(OH)}-.
The coefficient of thermal expansion (CTE) was characterized by DMA in the direction of film surface of the ternary hybrid composites and related materials. The CTE curves are shown in Fig. 6(c) and the CTE values in the temperature range from 100 to 150 °C are listed in Table 1.

The CTE values of the SF series change from 32.9 to 27.8 ppm °C⁻¹. By comparing the CTE values below the Tg, the hybrid composites exhibit significantly smaller CTEs than that of the pristine PI (S%1, 37.1 ppm °C⁻¹). The smallest CTE value was obtained for SF-2 (27.8 ppm °C⁻¹) in the series. It can be attributed to cross-linkages between the hydroxyl groups of HBPADA-TAP(OH) and silica termini in the P_{6FDA-APBSi}_2%_20%. However, compared to the CTE of 17.8 ppm °C⁻¹ for SA-1 (P_{6FDA-APB-SiO_2-20%}) in the ternary system, the triethoxysilane termini of PI_6FDA%APB(Si)_20% and SiO_2%20% did not show favorable effect to further decrease CTE values.

Above the results indicate that these hybrid ternary composites show significant improvements in dielectric properties and high transparency, which are attained by introducing HBPADA-TAP(OH) in the P_{6FDA-APBSi}_2%_20% and SiO_2 composite. Although the CTE is reduced by introducing the inorganic silica networks in the ternary system, the triethoxysilane termini of PI_{6FDA-APBSi} do not favorably further decreasing CTE values.

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Reference