

Interfacial design and property regulation of modified poly(phenylene oxide)/silica dielectric composites

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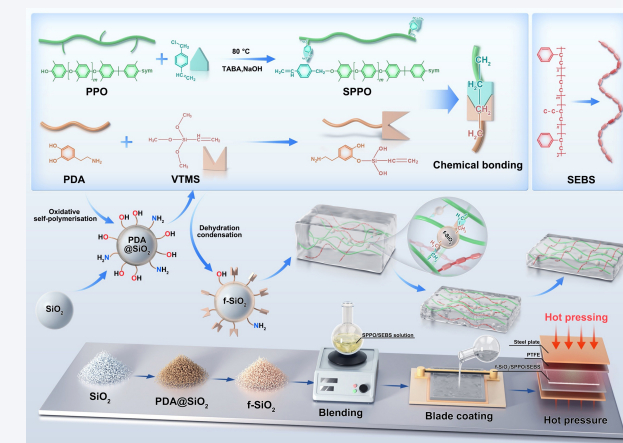
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ABSTRACT: Poly(phenylene oxide) (PPO) is a promising resin matrix for high-frequency packaging, owing to its outstanding dielectric properties and high glass transition temperature ($\sim 210^\circ\text{C}$). However, the abundant rigid phenyl ring structures restrict chain segment mobility, resulting in intrinsic brittleness and inferior processability. Furthermore, PPO exhibits a relatively high coefficient of thermal expansion (CTE, $76\text{ ppm}/^\circ\text{C}$), which restricts its application in advanced dielectric composites demanding high thermal dimensional stability. Although hydrogenated styrene-butadiene-styrene block copolymer (SEBS) and inorganic fillers have been incorporated into PPO to improve toughness and reduce CTE, respectively, weak interfacial bonding in such ternary systems often causes increased dielectric loss and degraded mechanical performance. Herein, we proposed an interfacial regulation strategy based on carbon-carbon double-bond reactions. PPO was first end-capped with styryl groups to obtain crosslinkable styryl-terminated poly(phenylene oxide) (SPPO), and vinyl groups were grafted onto the silica surface to produce functionalized silica (f-SiO₂). During curing, free-radical polymerization of the double bonds generated covalent linkages between the SPPO/SEBS matrix and f-SiO₂. Consequently, a stable chemically bonded interface and a three-dimensional crosslinked network were constructed between the resin phase and the filler phase, thus effectively resolving the interfacial mismatch issue in the ternary composite system. The as-fabricated dielectric composites exhibited a low dielectric constant ($D_k = 2.65$) and low dielectric loss ($D_f = 2.58 \times 10^{-3}$) at 10 GHz, as well as a low z-direction coefficient of thermal expansion (CTE = $27\text{ ppm}/^\circ\text{C}$) and excellent thermal stability.

KEYWORDS: poly(phenylene oxide), dielectric composites, interfacial bonding, functionalized silica

1 Introduction

With the rapid development of 5G/6G communications and high-performance computing, electronic devices are evolving toward higher frequencies, higher power densities, and higher



integration [1, 2]. These evolving trends impose increasingly stringent requirements on dielectric composites. As the core functional layer for signal transmission and chip interconnection, dielectric composites must simultaneously possess a low dielectric constant (D_k) and a low dielectric loss (D_f) to minimize signal delay and transmission loss [3], as well as high thermal resistance and dimensional stability to ensure thermo-mechanical reliability under high-density integration scenarios. Furthermore, in heterogeneous integration and multi-layer stacked packaging, the dimensional stability and process compatibility of dielectric composites during multi-step thermal processing have become critical factors for packaging yield. Therefore, developing polymer-

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based composites that integrate low Dk, low Df, high thermal resistance, low coefficient of thermal expansion (CTE), and good processability has become an important direction in dielectric composites.

Poly(phenylene oxide) (PPO) is a promising resin matrix for high-frequency and high-speed electronic devices owing to its polytetrafluoroethylene (PTFE)-comparable dielectric properties ($D_k \approx 2.5$ and $D_f \approx 0.002$ at 10 GHz), high glass transition temperature ($T_g \approx 210^\circ\text{C}$), and relatively low CTE ($\approx 76\text{ ppm}/^\circ\text{C}$) compared with conventional high-frequency polymer matrices (e.g., polytetrafluoroethylene, $\text{CTE} \approx 160\text{ ppm}/^\circ\text{C}$) [4]. However, its rigid phenyl-rich backbone restricts chain segment mobility, resulting in intrinsic brittleness, high melt viscosity, and poor processability. To address these inherent drawbacks, previous studies have mainly focused on modifying PPO via end-group functionalization and blending modification [5–8]. For example, Hu et al. blended styryl-terminated PPO with polybutadiene (PB), constructing a multi-component crosslinked network to enhance compatibility and thermal stability [9]. Guo et al. incorporated styrene-butadiene-styrene block copolymer (SEBS) into methacrylate-terminated PPO (MPPO) based on their molecular structural similarity, thereby improving the processability of MPPO and yielding a blend system with excellent compatibility [10]. End-group functionalization converts PPO from a thermoplastic into a thermosetting resin, enabling the formation of a stable three-dimensional crosslinked network after curing, which enhances thermal resistance and solvent resistance. In contrast, blending modification enhances toughness by introducing an elastomeric phase. These modification strategies not only enhance the intrinsic properties of PPO, but also facilitate blending with other resins to construct interpenetrating or semi-interpenetrating networks, thereby further enhancing interfacial adhesion and thermal stability. However, regarding the stringent requirements of 5G/6G heterogeneous integration packaging and the matching demand with adjacent functional layers (e.g., copper circuits, silicon chips), the CTE of PPO matrix is still inherently high, which remains a critical unresolved challenge. Under high-power operating conditions, this large CTE induces significant volumetric mismatch between the resin and adjacent functional layers, leading to interfacial delamination, solder joint fatigue, and ultimately device failure—thereby failing to satisfy stringent reliability requirements for advanced electronic devices applications.

To further reduce the CTE and improve dimensional stability, low-CTE inorganic fillers such as SiO_2 ($\text{CTE} = 0.5\text{ ppm}/^\circ\text{C}$) are widely incorporated into polymer matrices [11, 12]. However, the silica surface is abundant in hydrophilic silanol groups, and its significant polarity mismatch with hydrophobic polymer matrices causes surface-energy incompatibility. This incompatibility tends to induce filler agglomeration and interfacial defects. These issues increase dielectric loss and degrade the mechanical properties of organic–inorganic composites [13, 14]. Although conventional silane coupling agents moderately improve interfacial compatibility, insufficient surface-energy matching, limited interfacial wettability, and poor dispersion stability at high filler loadings remain unresolved [15, 16]. Previous studies have demonstrated that surface modification of inorganic fillers via polydopamine (PDA)-assisted functionalization or silane coupling agents can improve the interfacial compatibility between inorganic fillers and polymer matrices to some extent [17, 18]. Specifically, the PDA layer serves as an interfacial transition layer; meanwhile, amidation between

pentafluorobenzoyl chloride (FPBC) and the amino groups on PDA@SiO_2 allows the introduction of fluorinated moieties onto the SiO_2 surface, thereby reducing its surface energy and improving its compatibility with low-surface-energy fluoropolymers [17]. In contrast, silane coupling agent modification typically proceeds via reactions with hydroxyl groups on the SiO_2 surface and the introduction of low-polarity organic segments, thereby reducing the surface polarity of the fillers, enhancing their dispersion in the low-polarity or hydrophobic resins. Overall, the aforementioned strategies are effective for improving the interfacial compatibility of inorganic filler/resin systems and optimizing filler dispersion. However, the improvement in interfacial performance achieved by these methods still largely depends on surface-energy similarity and non-covalent interactions (e.g., hydrogen bonding), whereas the formation of stronger inorganic–organic interfacial coupling remains limited. Therefore, how to further enhance the inorganic–organic interfacial interactions while maintaining good filler dispersion, thereby maintaining the excellent mechanical strength of the dielectric composites and reducing their CTE under high filler loading, remains a significant challenge in this field.

Building on these insights, we developed a synergistic interfacial modification strategy based on carbon–carbon double bonds for the preparation of high-performance dielectric composites. Styryl-terminated poly(phenylene oxide) (SPPO) and SEBS served as the organic matrix, whereas silica dual-functionalized via PDA pre-coating and vinyltrimethoxysilane (VTMS) treatment (f-SiO_2) acted as the reinforcing filler. The thermosetting crosslinked SPPO network and flexible SEBS chains together formed a semi-interpenetrating network, while the vinyl groups on f-SiO_2 copolymerized with the styryl groups of SPPO during curing to form stable covalent bonds at the organic–inorganic interface. Based on this, f-SiO_2 /SPPO/SEBS composites were fabricated via doctor-blade coating and hot pressing. At an f-SiO_2 loading of 50 wt.%, the composites achieved exceptional comprehensive performance: A dielectric constant of 2.65 and a dielectric loss of 2.58×10^{-3} at 10 GHz, a low CTE of $27\text{ ppm}/^\circ\text{C}$ and a 5% weight loss temperature ($T_{\text{d}5\%}$) of 407.4°C , as well as a tensile strength of 10.5 MPa and an elongation at break of 115%. These results clearly demonstrate the feasibility and superiority of the proposed interfacial modification strategy, thus providing a viable approach for the development of high-performance dielectric composites.

2 Results and discussion

2.1 Structural and performance characterization of SPPO/SEBS resin substrates

In this work, SPPO was synthesized by styryl end-group modification of PPO, and SEBS was introduced as a toughening phase to address the poor processability caused by the intrinsic brittleness of PPO. This design effectively constructed a three-dimensional semi-interpenetrating network structure. The chemical structure and molecular weight distribution of SPPO were characterized by Fourier transform infrared (FTIR) spectroscopy, nuclear magnetic resonance (NMR), and gel permeation chromatography (GPC), as shown in Figs. S1 and S2 and Table S1 in the Electronic Supplementary Material (ESM). The results demonstrate that styryl groups were successfully introduced at both ends of the PPO chains, providing reactive sites for subsequent curing and crosslinking.

Figures 1(a)–1(i) compare the fracture cross-sectional morphologies of the PPO/SEBS and SPPO/SEBS systems. Compared with the unmodified PPO/SEBS system, the SPPO/SEBS composites exhibit smoother fracture surfaces, lower cross-sectional roughness, and less distinct phase interfaces, indicating that styryl end-capping and subsequent curing alter the phase morphology of the blend and strengthen interfacial bonding between the two phases. Furthermore, with the SEBS content increasing, fracture surfaces of SPPO/SEBS composites gradually roughen and exhibit distinct dimple structures, indicating increased plastic deformation during fracture and a gradual transition in fracture behavior from brittleness- to toughness-dominated with increasing SEBS contents.

Figures 1(j) and 1(k) compare tensile strength and elongation at break of PPO/SEBS and SPPO/SEBS systems. With the SEBS content increasing from 40 wt.% to 80 wt.%, both systems showed increased tensile strength and elongation at break, indicating SEBS introduction effectively enhances composite mechanical properties. For the SPPO/SEBS system, increasing the SEBS content from 40 wt.% to 80 wt.% results in a 28% increase in tensile strength and

a 351% increase in elongation at break relative to the sample with 40 wt.% SEBS content. At the same SEBS content, however, SPPO/SEBS composites show higher tensile strength but lower elongation at break than PPO/SEBS counterparts. This result indicates that the chemically crosslinked network formed during SPPO curing not only strengthens SEBS chain constraints, but also improves load transfer across the two-phase interface, thereby reducing tensile deformation under applied stress.

Dynamic mechanical analysis (DMA) results further support the above structural evolution. As shown in Fig. 1(l), composite storage modulus (E') decreases with increasing SEBS contents, mainly because elastomeric phase introduction increases flexible chain fraction and reduces overall system rigidity. At the same SEBS content, the SPPO/SEBS system shows higher E' than the PPO/SEBS system. This is attributed to the three-dimensional crosslinked network formed during SPPO curing, which provides higher structural stability than PPO system chain structure and thus enhances high-temperature stiffness retention and thermomechanical stability.

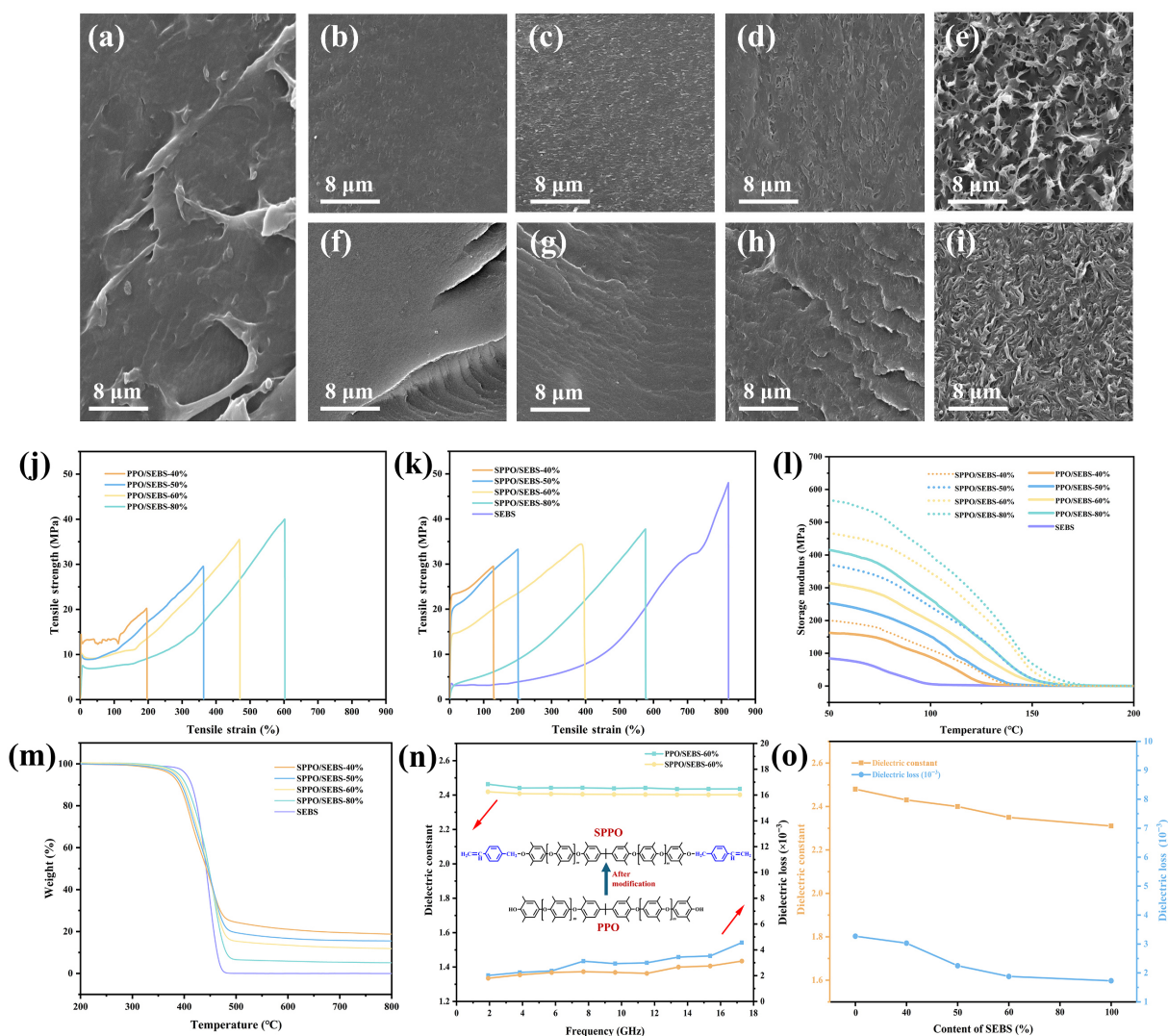


Figure 1 (a) SEM image of the fracture cross-section of SEBS. (b)–(e) SEM images of the fracture cross-sections of PPO/SEBS- x composites ($x = 40\%$, 50% , 60% , and 80% , respectively). (f)–(i) SEM images of the fracture cross-sections of SPPO/SEBS- x composites ($x = 40\%$, 50% , 60% , and 80% , respectively). (j) and (k) Stress-strain curves of PPO/SEBS and SPPO/SEBS composites, respectively. (l) Temperature dependence of the storage modulus of PPO/SEBS and SPPO/SEBS composites. (m) Thermogravimetric curves of SPPO/SEBS composites. (n) Comparison of the dielectric properties of PPO/SEBS-60% and SPPO/SEBS-60% composites. (o) Dielectric properties of SPPO/SEBS composites at 10 GHz.

Figure 1(m) shows thermogravimetric analysis (TGA) results of composites. With the SEBS content increasing from 40 wt.% to 80 wt.%, the 5% weight loss temperature ($T_{d5\%}$) increases from 373.7 to 389.7 °C, indicating improved thermal stability with increasing SEBS contents. This is mainly attributed to the slightly higher intrinsic thermal stability of SEBS than that of SPPO. In contrast, char yield under inert atmosphere gradually decreases with the increase in SEBS content, suggesting that the SPPO-derived crosslinked network favors stable char layer formation at elevated temperature and thus suppresses further degradation and volatilization of polymer chains. Thus, the incorporation of SEBS endows the system with excellent thermal stability, while the crosslinked structure of SPPO enhances the high-temperature morphological retention and flame-retardant properties of the material. Furthermore, thermomechanical analysis (TMA) was employed to investigate the effect of SEBS content on the *z*-direction thermal dimensional stability of SPPO/SEBS composites, as shown in Fig. S3 in the ESM. The CTE of the composites increases with increasing SEBS contents. This can be attributed to the fact that as the SEBS content increases, the proportion of flexible chain segments in the composite system increases significantly, while the density of the SPPO crosslinked network decreases relatively, which weakens the constraining effect of the SPPO crosslinked network on the thermal motion of SEBS flexible chain segments. When the temperature rises, the unconstrained flexible chain segments undergo intense thermal motion, leading to an increase in molecular spacing and a significant enhancement of the thermal expansion effect of the composite, thus resulting in the increase of CTE with the increase of SEBS contents.

The dielectric properties of PPO/SEBS-60 wt.% and SPPO/SEBS-60 wt.% were further compared. As shown in Fig. 1(n), the SPPO/SEBS system shows lower dielectric constant (*Dk*) and dielectric loss (*Df*) than the PPO/SEBS system over a wide frequency range. This improvement is mainly attributed to two factors. First, the polar hydroxyl end groups of PPO are markedly reduced after styryl end-group modification. Second, the interfacial compatibility between SPPO and SEBS is improved, which effectively suppresses dielectric loss associated with interfacial defects and interfacial polarization. Figure S4 in the ESM shows the dielectric constant and dielectric loss of the SPPO/SEBS composites in the 1–18 GHz range. Figure 1(o) further shows the effect of SEBS content on the dielectric properties of SPPO/SEBS system at 10 GHz. With increasing SEBS contents, *Dk* decreases from 2.48 to 2.30 and *Df* decreases from 3.27×10^{-3} to 1.73×10^{-3} . This is mainly because SEBS consists of nonpolar saturated hydrocarbon chains with intrinsically low polarizability, a feature that reduces dipolar response under a high-frequency electric field and thus further enhances the high-frequency dielectric performance of the composites.

2.2 Preparation and structural verification of modified fillers

To improve the dispersion stability of SiO₂ in the SPPO/SEBS matrix, a dual surface functionalization strategy involving PDA precoating and silane grafting was adopted, as illustrated in Fig. 2(a). In this design, the vinyl groups on functionalized silica (f-SiO₂) can covalently react with the styryl groups of SPPO during thermal curing, thereby forming a stable chemically bonded interface between the inorganic filler and the organic matrix, as shown in Fig. 2(b).

To verify the evolution of silica surface chemistry during modification, FTIR spectra of pristine SiO₂, PDA@SiO₂, vinyl-silanized SiO₂ (V-SiO₂), and f-SiO₂ were comparatively analyzed, as shown in Fig. 3(a). For V-SiO₂, a new absorption peak emerges at 1637 cm⁻¹, which corresponds to the stretching vibration of the vinyl group (–C=C–), confirming the successful introduction of VTMS onto the SiO₂ surface [19, 20]. For PDA@SiO₂, the broad absorption band around 1620 cm⁻¹ is attributed to the bending vibration of N–H and the skeletal vibrations of aromatic rings in the PDA layer [21]. In the FTIR spectrum of f-SiO₂, the characteristic absorption peak of the vinyl groups at 1628 cm⁻¹ is retained, accompanied by distinct absorption bands at 2847 and 2920 cm⁻¹, which are assigned to the symmetric stretching vibration of –CH₃ and the asymmetric stretching vibrations of –CH₂–, respectively [16]. The coexistence of these characteristic peaks indicates the successful grafting of VTMS onto the PDA-coated SiO₂ surface via hydrolysis-condensation reactions, thus introducing vinyl groups capable of participating in curing crosslinking.

Figure 3(b) shows the X-ray photoelectron spectroscopy (XPS) results for the elemental composition and chemical states of the filler surface. Compared with PDA@SiO₂, f-SiO₂ (VTMS-modified PDA@SiO₂) mainly introduces two elements, C and Si, among which C is the dominant one. Specifically, the introduction of C usually leads to an increase in the relative content of C in f-SiO₂ (from 7.46 at.% to 9.53 at.%) as well as a decrease in the relative content of other elements (e.g., O, from 31.26 at.% to 29.38 at.%). However, because VTMS molecules themselves contain Si atoms, the Si content does not decrease compared with that before modification, but rather slightly increases (from 15.11 at.% to 15.19 at.%). This is consistent with the successful introduction of carbon-containing and silicon-containing groups from VTMS molecules via hydrolysis-condensation reactions [16], as reported in previous studies on silane-modified silica. High-resolution Si 2p spectra are shown in Figs. 3(c)–3(f), where all samples exhibit a typical Si–O–Si characteristic peak at ~ 103.8 eV. After peak deconvolution and fitting, new peaks assigned to Si–C bonds appear in the lower binding energy region for both V-SiO₂ and f-SiO₂. The Si–C peak of f-SiO₂ shifts to a higher binding energy relative to that of V-SiO₂, indicating a change in the local electronic environment of Si atoms due to interaction with the PDA layer. These results indicate that VTMS is hydrolyzed to form silanol groups, which react with the active functional groups on the PDA layer and are grafted onto the PDA-coated SiO₂ surface, thereby modifying the surface chemical environment. Meanwhile, the high-resolution C 1s and N 1s spectra of PDA@SiO₂, V-SiO₂, and f-SiO₂ are presented in Fig. S5 in the ESM. The above results confirm the successful grafting of VTMS onto the PDA@SiO₂ surface.

High-resolution transmission electron microscopy (HRTEM) further reveals the microstructure of f-SiO₂. As shown in Fig. 3(g), the modified particles retain an intact spherical morphology and are uniformly coated with a continuous and dense shell layer of ~ 15.3 nm. Combined with the dual-functionalization modification process of f-SiO₂, this shell layer is identified as a PDA-VTMS composite shell layer, where the inner layer is the PDA coating and the outer layer is the silane layer formed by VTMS hydrolysis and condensation. The shell layer exhibits a clear boundary and intact interface, indicating that the subsequent VTMS grafting does not disrupt the preformed PDA interlayer.

Figure 3(h) compares static water contact angles of samples at

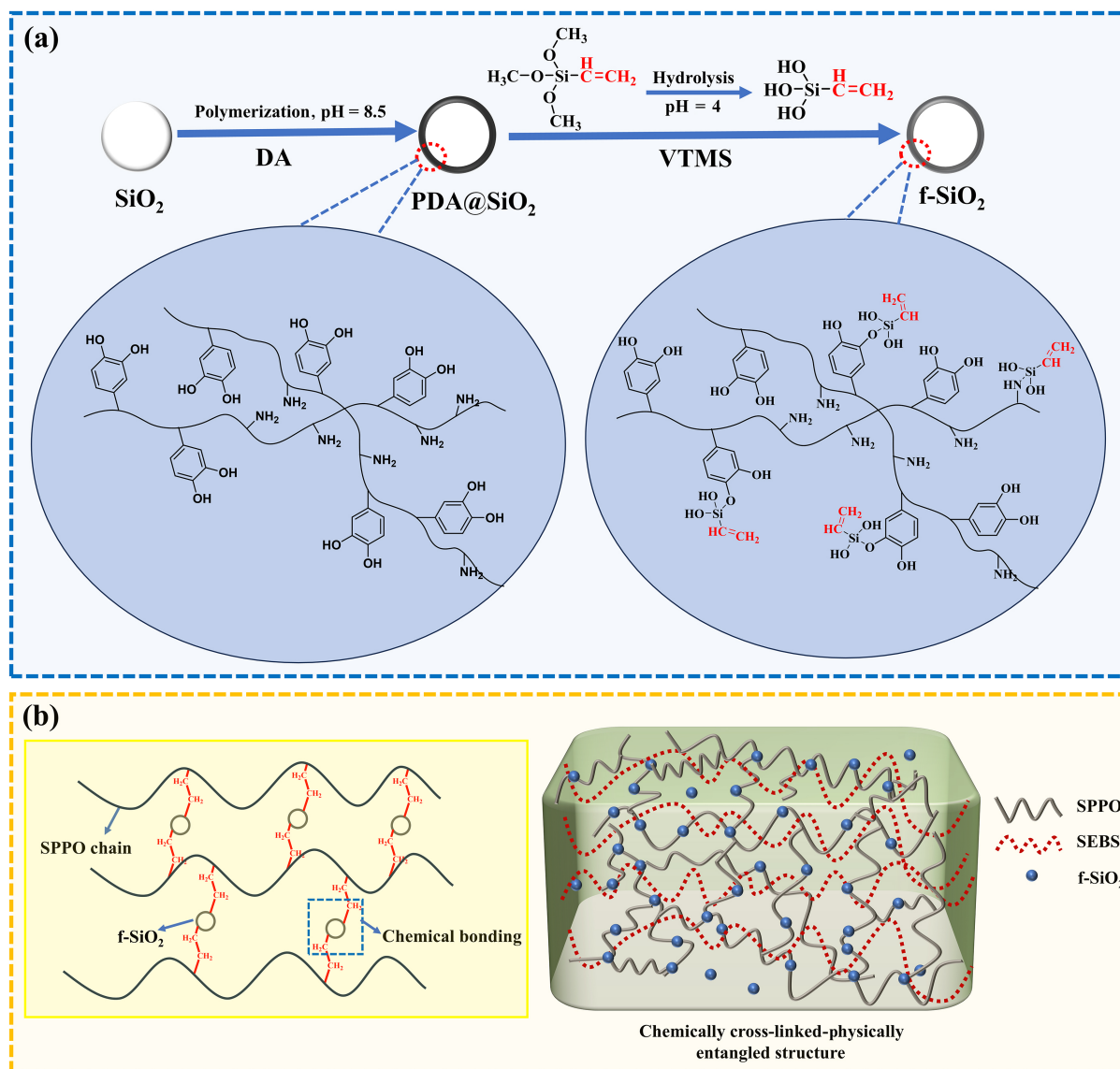


Figure 2 (a) Schematic illustrations of the preparation of f-SiO₂ and (b) the chemically crosslinked/physically entangled structure of the f-SiO₂/SPPO/SEBS composites.

different modification stages. Exposed silanol groups on pristine SiO₂ impart pronounced hydrophilicity, with a contact angle of only 13.5°. After sole silanization, V-SiO₂ contact angle increases markedly to 155°, showing superhydrophobicity. This confirms the successful grafting of VTMS onto SiO₂ surfaces via hydrolysis and condensation, introducing low-polarity organic moieties and significantly altering surface wettability. In contrast, PDA@SiO₂ exhibits a contact angle of 27.8°, as the PDA coating partially shields the underlying silanol groups but retains the surface phenolic hydroxyl and amino groups, endowing the particles with relatively high polarity. After further VTMS modification, f-SiO₂ contact angle increases to 86.5°, showing moderate wettability and a pronounced decrease in surface polarity. Combined with the aforementioned chemical characterization results, this change originates from the participation of some polar sites on the PDA layer in VTMS grafting and the introduction of low-surface-energy organosilane chains. Since the SPPO/SEBS matrix exhibits a static water contact angle of 90.1° (Fig. S6 in the ESM), close to that of f-SiO₂, this surface modification is expected to reduce the filler-matrix wettability mismatch and improve interfacial compatibility [22].

The sedimentation behavior of the fillers in the SPPO/SEBS resin solution further reflects their dispersion stability, as shown in Fig. 3(i). After standing for 6 h, the suspension containing pristine SiO₂ has completely sedimented, and the supernatant becomes nearly clear. The suspensions containing PDA@SiO₂ and V-SiO₂ also exhibit partial sedimentation, indicating limited dispersion stability in the resin system. In contrast, the slurry containing f-SiO₂ still exhibits a distinct Tyndall effect after standing, with little sediment at the bottom, demonstrating excellent suspension stability. These results indicate that synergistic PDA/VTMS modification not only optimizes filler surface energy, facilitating wetting and dispersion in the resin solution, but also effectively suppresses particle agglomeration and gravitational sedimentation via enhanced interfacial adhesion and steric hindrance, thereby improving filler dispersion in the SPPO/SEBS system.

2.3 Structural and performance characterization of f-SiO₂/SPPO/SEBS composites

Figures 4(a)–4(e) show cross-sectional scanning electron

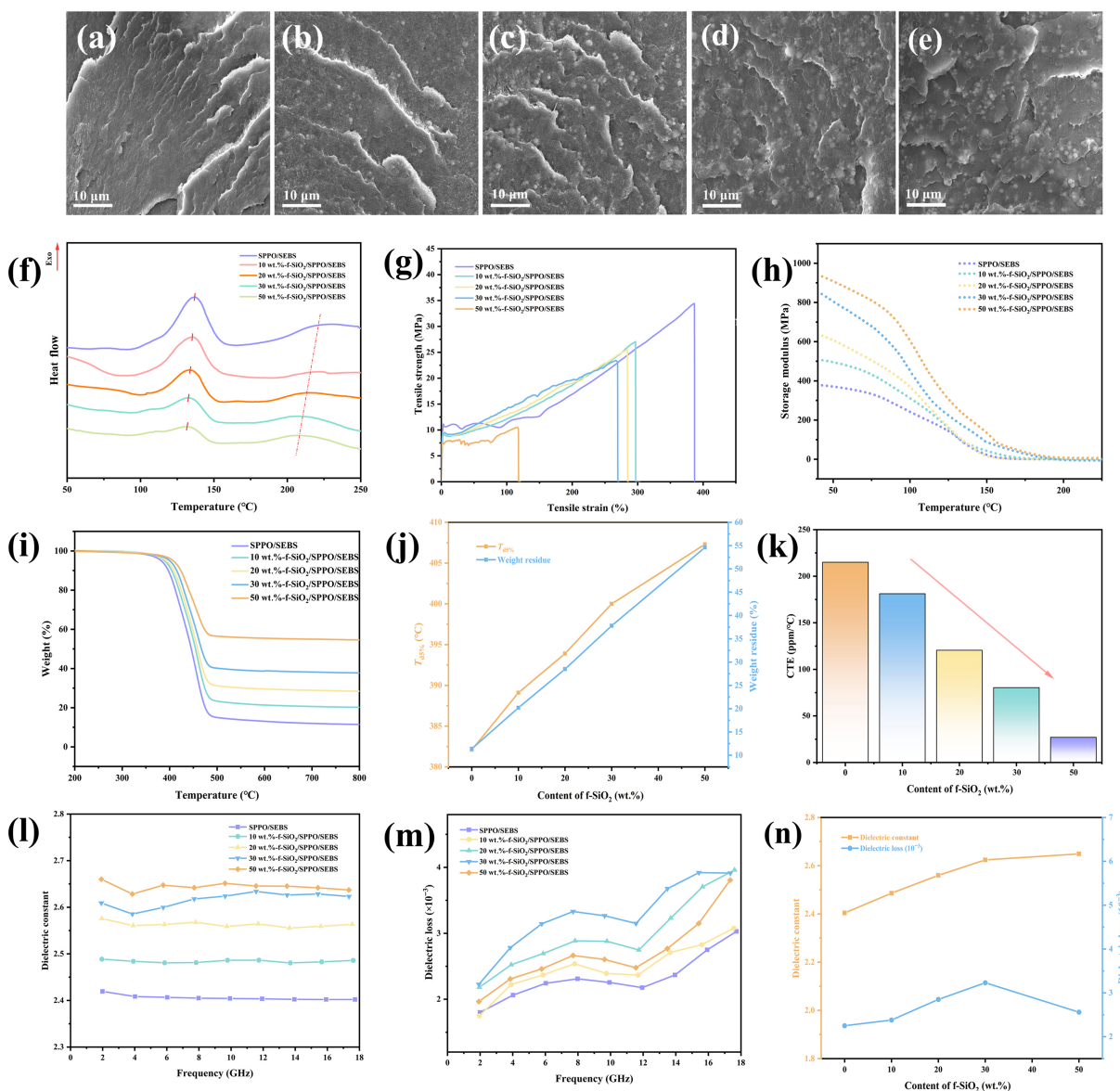


Figure 4 (a)–(e) Cross-sectional SEM images of SPPO/SEBS and x -f-SiO₂/SPPO/SEBS composites (x = 10 wt.%, 20 wt.%, 30 wt.%, and 50 wt.%). (f) DSC curves of f-SiO₂/SPPO/SEBS composites before curing. (g) Stress–strain curves of f-SiO₂/SPPO/SEBS composites. (h) Temperature dependence of storage modulus for f-SiO₂/SPPO/SEBS composites. (i) TGA curves of f-SiO₂/SPPO/SEBS composites. (j) $T_{d5\%}$ and residual weight of the composites. (k) CTE of f-SiO₂/SPPO/SEBS composites in the z -direction at 100 °C. (l) Frequency dependence of dielectric constant for f-SiO₂/SPPO/SEBS composites. (m) Frequency dependence of dielectric loss. (n) Dielectric constant and dielectric loss at 10 GHz.

indicates that f-SiO₂ acts as a rigid reinforcing phase to enhance the modulus of the system. In addition, surface vinyl groups participate in SPPO curing, thereby enhancing filler/resin interfacial interactions. At relatively high filler loadings, the combined effects of rigid-filler constraint and interfacial interactions further restrict polymer chain motion, leading to enhanced storage modulus and thermomechanical stability.

TGA results are shown in Figs. 4(i) and 4(j). With increasing f-SiO₂ contents, the thermal decomposition temperature of the composites generally increases, indicating enhanced thermal stability. The $T_{d5\%}$ increases from 384.1 °C for the unfilled SPPO/SEBS matrix to 407.4 °C at an f-SiO₂ loading of 50 wt.%. This enhancement is mainly attributed to the intrinsic thermal stability of SiO₂, together with its barrier effect against heat transfer and volatile diffusion in the polymer matrix. These effects retard the

release of small-molecule decomposition products and thus delay matrix degradation.

Figure 4(k) shows the coefficient of thermal expansion of the f-SiO₂/SPPO/SEBS composites in the z -direction. The CTE decreases continuously with increasing f-SiO₂ contents. At 50 wt.% filler loading, the CTE decreases from 215 ppm/°C for the unfilled SPPO/SEBS matrix to 27 ppm/°C, corresponding to an 87.4% reduction. This pronounced decrease is mainly attributed to two factors. First, rigid SiO₂ particles physically restrict the thermally induced volumetric expansion of the polymer network. Second, the surface vinyl groups of f-SiO₂ participate in SPPO curing, thereby restricting local chain motion. The combined effect enhances interfacial constraint on thermal chain motion and suppresses the thermal expansion response of the composites. These results indicate excellent thermal dimensional stability, highlighting the

potential of the composites for high-frequency/high-speed electronic packaging.

Figures 4(l)–4(n) summarize the dielectric response of the composites over the 1–18 GHz range. As the f-SiO₂ content increases from 0 to 30 wt.%, the dielectric constant (Dk) gradually increases, mainly due to the higher intrinsic dielectric constant of f-SiO₂ compared to the SPPO/SEBS matrix. Notably, the dielectric loss (Df) of all samples remains low ($< 3.5 \times 10^{-3}$). More importantly, the composite with 50 wt.% filler loading exhibits a lower Df than the 30 wt.% counterpart. This phenomenon is primarily attributed to the increased fraction of the low-loss f-SiO₂ phase at high filler loading, which in turn enhances its contribution to the overall dielectric response. Additionally, the reduced interparticle distance, together with the insulating PDA/VTMS-modified interfacial layer, improves the barrier effect for inhibiting charge carrier migration, thus effectively suppressing conduction loss [23].

Figures 5(a) and 5(b) compare the overall performance of the 50 wt.% f-SiO₂/SPPO/SEBS composite prepared in this work with those of previously reported similar PPO-based composites and commercial composite dielectric materials (e.g., GL102 and GZ30) [10, 17, 24–32]. The results demonstrate that this composite simultaneously maintains low dielectric loss and exhibits excellent thermomechanical properties and thermal dimensional stability, highlighting significant application potential in the fields of microwave communication and advanced electronic packaging.

3 Conclusions

In this study, an interface regulation strategy based on the synergistic effect of chain-end functionalization and filler surface functionalization was proposed, which successfully constructs low-interface-loss nonpolar strong chemical bonding between the filler and matrix interfaces, thereby effectively optimizing the interfacial bonding performance of the composites. Specifically, styryl end-capping modification converts PPO into a thermosetting resin; meanwhile, SEBS with excellent toughness is introduced as a toughening phase to synergistically construct a three-dimensional semi-interpenetrating polymer network structure, which effectively overcomes the poor processability and low toughness of pristine PPO (elongation at break $< 5\%$), with the elongation at break of the composites reaching 115% as demonstrated in the study. Furthermore, the dual-functionalized f-SiO₂ optimizes its surface energy matching with the SPPO/SEBS matrix, which significantly improves the dispersion uniformity of the filler in the matrix and

thus effectively suppresses the agglomeration behavior under high filler loading.

The surface vinyl groups of f-SiO₂ can copolymerize with the styryl groups of SPPO during curing, thereby constructing a robust chemically bonded organic–inorganic interface and enhancing interfacial bonding and stress transfer. As a result, the composites achieve a synergistic enhancement in dielectric, thermomechanical, and thermal dimensional properties. At an f-SiO₂ loading of 50 wt.%, the composite maintains a low dielectric constant (Dk = 2.65) and low dielectric loss (Df = 2.58×10^{-3}) at 10 GHz, while the z-direction CTE decreases to 27 ppm/°C, corresponding to an 87.4% reduction relative to the neat matrix. In addition, the $T_{d5\%}$ increases to 407.4 °C, with a tensile strength of 10.5 MPa retained. This study provides a novel theoretical basis and technical route for the design, fabrication, and industrial application of next-generation dielectric materials for high-frequency/high-speed electronic packaging.

4 Experimental

4.1 Materials

Poly(phenylene oxide) (grade SA90) was purchased from SABIC. Hydrogenated styrene-butadiene-styrene block copolymer (grade G1652) was purchased from Kraton, supplied through Zhejiang Changhong. Spherical silica (SiO₂, average particle size: 1 μm) was purchased from Suzhou Bisley New Materials. 4-Chloromethylstyrene (CMS, 98% purity) and VTMS were purchased from Adamas-Beta. Dibenzoyl peroxide (BPO, 98% purity), tetrabutylammonium bromide (TBAB), dopamine hydrochloride, and conventional solvents were purchased from Sinopharm Chemical Reagent Co., Ltd. All reagents were used as received without further purification.

4.2 Preparation of SPPO and SPPO/SEBS composites

PPO was dissolved in an appropriate amount of toluene. Once completely dissolved to form a clear solution, an appropriate amount of aqueous NaOH was added to establish an alkaline reaction environment, and the system was heated to 80 °C. Subsequently, 0.56 g TBAB and 2.6 g 4-chloromethylstyrene were added sequentially, and the reaction was maintained under constant-temperature continuous stirring for 6 h. After the reaction was completed, the reaction mixture was centrifuged, and the supernatant was slowly added dropwise into a methanol/deionized water mixed precipitant to precipitate the product. The resulting precipitate was collected via vacuum filtration and then vacuum-

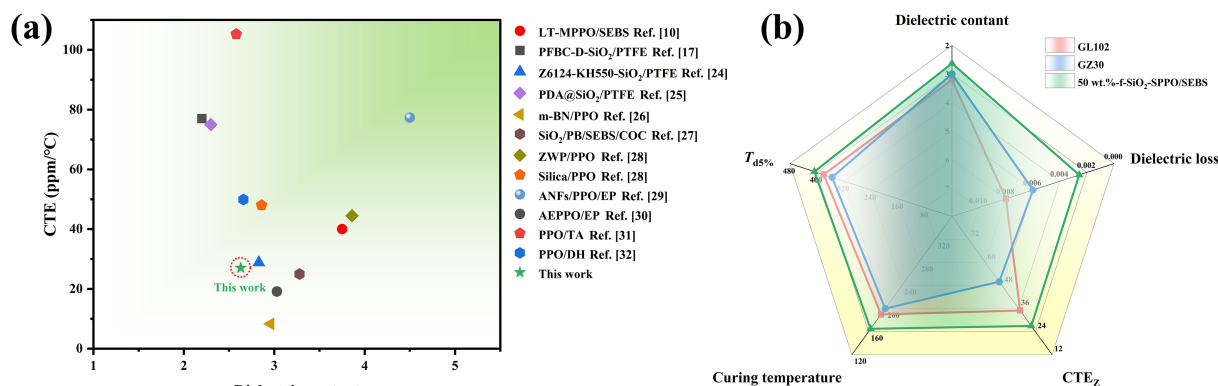


Figure 5 (a) Comparison of CTE and dielectric constant between this work and previously reported results. (b) Performance comparison of 50 wt.% f-SiO₂/SPPO/SEBS with commercial substrate materials (GL102 and GZ30).

dried at 80 °C for 24 h to finally obtain SPPO. The synthetic route is shown in Fig. S7 in the ESM.

SPPO and SEBS were co-dissolved in toluene at the preset mass ratio; subsequently, 3 wt.% benzoyl peroxide (BPO) was added as the initiator, followed by stirring for 4 h to obtain a homogeneous mixed solution. The resulting system was magnetically stirred at room temperature until a transparent slurry was formed, after which the slurry was uniformly coated onto a glass substrate via the doctor-blade method. After sufficient solvent evaporation, the obtained composite precursor was placed between two polytetrafluoroethylene release films and subjected to stepwise hot-press curing to finally prepare SPPO/SEBS composites. Experiments showed that when the SEBS content was below 40 wt.%, the rigid PPO phase dominated the system; due to insufficient flexible chain segments to effectively relax processing-induced local stresses, the resin was prone to brittle fracture during doctor blading and subsequent molding. Therefore, considering processability and mechanical reliability, the SEBS content investigated in this study was set at 40 wt.%–80 wt.%.

4.3 Preparation of functionalized silica (f-SiO₂) and f-SiO₂/SPPO/SEBS composites

SiO₂ (6.0 g) was dispersed in Tris-HCl buffer (pH = 8.5), after which dopamine (0.3 g) was added. The mixture was stirred at room temperature for 24 h, during which a PDA coating was formed on the SiO₂ surface via oxidative self-polymerization. After centrifugation and washing, the obtained PDA@SiO₂ was redispersed in acetate buffer (pH = 4.0); subsequently, 4 wt.% VTMS was added. The silanization reaction was then carried out in a water bath at 50 °C for 2 h. The product was then collected via centrifugation and dried to obtain gray powdery f-SiO₂.

Based on the experimental comparison of comprehensive properties of SPPO/SEBS-*x* composites, SPPO/SEBS-60 wt.% was selected as the matrix for subsequent filler incorporation due to its favorable mechanical properties and thermal stability. SPPO and SEBS were mixed at a mass ratio of 4:6 and dissolved in toluene;

afterward, BPO was added, followed by magnetic stirring for 1 h. Subsequently, f-SiO₂ powder was gradually added at the designed loadings and continuously dispersed at room temperature for 4 h to obtain a homogeneous and stable composite slurry. The subsequent molding and curing procedures were identical to those for SPPO/SEBS composite preparation, and the complete fabrication process is shown in Fig. 6. Therefore, considering slurry processability, composite moldability, and mechanical reliability, the f-SiO₂ loading was set at 0–50 wt.% in this study.

4.4 Characterization

Chemical structures of resins and fillers were analyzed by Fourier transform infrared spectroscopy (Nicolet 6700, Thermo Electron, USA) in the 400–4000 cm⁻¹ mid-infrared range. ¹H nuclear magnetic resonance (¹H NMR) spectra of resins were recorded on a Bruker Avance III 400 MHz spectrometer (Bruker Biospin Corp, Switzerland) with CDCl₃ as solvent. Average relative molecular weights of materials were determined by gel permeation chromatography (GPC, Agilent 1260) with polystyrene as standard, tetrahydrofuran as mobile phase, and a flow rate of 1 mL/min. Surface chemical information of fillers was obtained by XPS (ESCALAB 250Xi, Waltham, MA, USA) with an Al K α radiation source ($h\nu = 1253.6$ eV). Core-shell structure and filler surface elemental distribution were characterized by field-emission high-resolution transmission electron microscopy (JEM-2100F) equipped with an EDAX Elite T energy-dispersive X-ray spectroscopy (EDS) system. Static contact angles of inorganic fillers were measured using a DSA30S contact angle analyzer (Krüss, Germany). Curing thermal behavior of resins was analyzed using a differential scanning calorimeter (TA DSC 2500) from room temperature to 250 °C at a heating rate of 10 °C/min under N₂ atmosphere. Resins were cryogenically fractured in liquid nitrogen, and fracture surface morphologies were observed by scanning electron microscopy (JSM-IT300). Mechanical properties of materials were measured using an Instron 5967 universal testing machine with a test area of 20 mm × 5 mm. Thermogravimetric

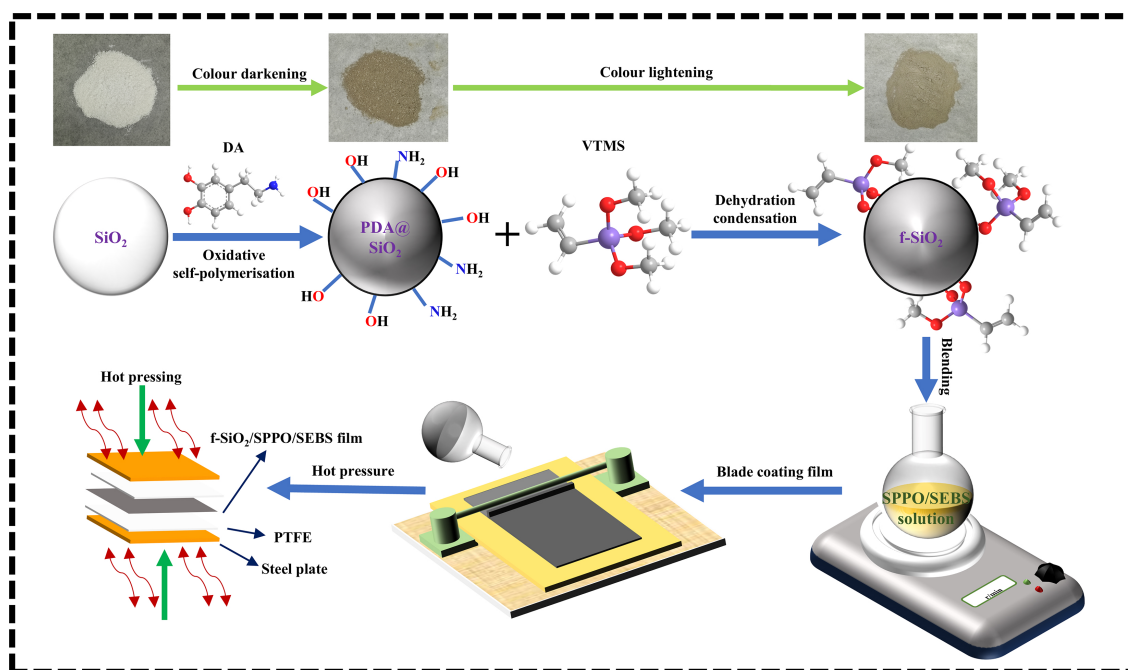


Figure 6 Flow chart for the preparation of the f-SiO₂/SPPO/SEBS composites.

analysis was performed on a NETZSCH STA 449 F3 instrument at a heating rate of 10 °C/min under nitrogen atmosphere. According to IPC-TM-650 2.5.5, dielectric properties of composites were measured via microstrip line method using a microwave network analyzer (HP 8722ET, Palo Alto, CA, USA) in the 1–18 GHz frequency range, with all test samples having dimensions of 30 × 50 mm. Based on IPC-TM-650 2.4.41, CTE of composites in the z-direction was measured using a thermomechanical analyzer (TMA 202, Selb, Germany) with a sample size of 5 mm × 5 mm, a load of 2 N, 25–150 °C test temperature range, and 5 °C/min heating rate. Temperature dependence of composite storage modulus was measured using a dynamic mechanical analyzer (DMA 8000, Waltham, MA, USA) from 30 to 250 °C at a heating rate of 5 °C/min.

Electronic Supplementary Material: Supplementary material (supplementary experimental characterizations to verify chemical structures and fundamental properties of as-synthesized styrene-terminated polyphenylene oxide (SPPO) and SPPO/SEBS-based dielectric composites; Fig. S1 presents FT-IR spectra confirming successful styryl end-capping of PPO; Fig. S2 shows ¹H-NMR spectra and Table S1 lists GPC molecular-weight data for pristine PPO and SPPO, verifying end-group functionalization without obvious chain degradation; supplementary TMA (Fig. S3), broadband dielectric (Fig. S4), XPS (Fig. S5), water-contact-angle (Fig. S6) spectra and schematic synthetic route (Fig. S7) further supply baseline thermal-dimensional, high-frequency dielectric, filler-surface and wettability data for different SEBS and filler fractions) is available in the online version of this article at <https://doi.org/10.26599/NR.2026.94908910>.

Data availability

All data needed to support the conclusions in the paper are presented in the manuscript and the Electronic Supplementary Material. Additional data related to this paper may be requested from the corresponding author upon request.

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Declaration of competing interest

The authors declare no competing financial interest.

Author contribution statement

L. L.: Writing original draft, performing experiments, methodology, formal analysis, conceptualization. J. Y. Z.: Original draft revision, investigation, formal analysis. Z. Z. X.: Graphic design and beautification for the pictures. J. S.: Review & editing, supervision, methodology, conceptualization. J. Z. and W. C.: Review & editing, supervision. All authors have approved the final manuscript.

Use of AI statement

None.

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