Styrene-terminated polyphenylene oxide and polybutadiene low dielectric reactive blend

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Abstract. Styrene-terminated polyphenylene oxide (SPPO) and low polar thermosetting polybutadiene (PB) resin were employed to obtain a curing system with excellent electrical properties and enhanced thermal properties. By terminal styrenisation, SPPO is cured with PB, forming a continuous phase in the blend. The SPPO/PB blends have excellent solvent resistance and thermal stability, while the good dielectric performance is retained. Especially, when the mass ratio of PB is 0.5, the curing system has a high Tg of 226.5°C and excellent dielectric properties with Dk = 2.46 and Df = 0.0022 at 10 GHz, which is suitable for high frequency electrical applications.

1. Introduction
The rapid development of electronic information requires access to Copper-Clad Laminates (CCLs) with high thermal stability, low dielectric constant (Dk), and loss factor (Df) [1-3]. Thermoset polymers, such as phenolic and epoxy resins, have been widely used as base materials for CCLs. However, their dielectric properties are not able to meet the requirements of high frequency application [4]. PTFE resin is a popular polymeric matrix for high frequency CCLs [5-7] because of its outstanding dielectric properties. However, its disadvantages are also glaring, such as low glass transition temperature, high coefficient of thermal expansion (CTE), difficult processability, poor rigidity, and high cost. Therefore, new materials need to be developed to meet the requirements for high frequency CCLs applications.

Polyphenylene oxide (PPO) resin is known for its low Df, which is the second after PTFE resin in common polymeric matrices of CCLs. Besides, PPO has additional merits, such as high glass transition temperature among the thermoplastic polymers, low CTE, outstanding mechanical properties, and good resistance against acids and alkalis. Therefore, PPO resin is considered as a potential candidate for the matrix of high frequency CCLs. However, PPO is easily corroded by solvents such as halogenated hydrocarbons or aromatic hydrocarbons, used in the clean processing for CCLs. Moreover, the progress of lead-free welding process requires higher thermal stability for high performance CCLs. In order to make PPO meeting these requirements, numerous efforts have been made [8-10]. A general approach is to blend with other thermosetting resins, especially epoxy resins [11], which cross-linked structures can restrain the movement of PPO molecular chains to make PPO insoluble in organic solvents and improve the temperature of its glass transition or degradation. Unfortunately, the polar hydroxy groups, introduced via the curing of the epoxy resins, drastically increase the dielectric constant and loss factor.
of polymeric dielectrics. Hence, it is significant to develop a facile and effective method to improve the solvent resistance and thermal properties of PPO with its electrical properties maintaining.

PB resin has a very weak polarity and cross-linkable groups, making it an effective curing agent to blend with PPO. Thus, it is expected to make polymer matrix for the high-performance CCLs by modifying PPO with PB. However, the structural differences between the two resins lead to poor compatibility of the PPO/PB blend system, especially for the high molecular weight PPO [12,13]. Furthermore, the molecular chain of PPO is only interspersed in the cross-linked network of PB, resulting in bad structural stability of the blend. The compatibility and phase behaviour for the blend of PPO with other resins also have been investigated by several research groups [14-17]. Weng et al. [16,17] have found that the molecular weight of PPO influences its compatibility with other resins and the decrease in PPO molecular weight leads to the improvement of its compatibility and processability.

Previously, compatibilisers were widely used to promote blending of incompatible polymers through reducing the interfacial energy between different phases. It is reported that copolymeric compatibilisers were introduced into the PPO/PB blends to construct the blends with good compatibility [18]. These non-reactive compatibilisers only make the blend components finer and enhance dispersion uniformity upon blending, that is, they act only as a general emulsifier. Compared with the utilization of compatibilisers, reactive blending by chemical functionalization of polymer chains is a more effective way for preparing polymer with better compatibility and structural stability with incompatible raw materials. The reactive functional groups can react to form cross-linked structure at the interface, which can reduce the interfacial tension and stabilize the morphology of blends [19]. Grafting the functional groups such as allyl and methacrylate to PPO’s backbones or chain ends was also reported [20,21]. However, in these works, the synthesis process of allylated PPO is too complicated, while the telechelic PPO oligomers with methacrylate end group contain polar ester bonds, which are harmful to the dielectric properties. Compared with above functional groups, introduction of styrene, which structure is similar to the main chain structure of PPO, will retain the high symmetry of PPO molecular chain and its dielectric properties. Therefore, it would be an ideal modification group of PPO for high-performance CCLs. However, as far as we know, the blend of styrene-terminated PPO and PB has rarely been explored and its curing reaction mechanism is still far from being well understood. Moreover, the effects of terminal modification of PPO on the curing behaviour and phase morphology of PPO/PB blends have been scarcely investigated.

In this study, the styrene-terminated low-molecular-weight PPO was synthesized and reactively blended with low polar thermosetting PB resin. PPO curing system with good compatibility and structural stability was obtained. The curing behaviour, phase morphology, solvent resistance, thermal and dielectric properties of cured SPPO/PB blends were investigated.

2. Experimental

2.1. Materials
PPO was purchased from SABIC Innovative Plastics Co., Ltd. PB with Mn of 4000 g/mol was purchased from Toyo Soda Manufacturing Co., Ltd. The terminating agent 4-Chloromethylstyrene (≥ 95.0%) was purchased from Saen Chemical Technology Co., Ltd. The phase transfer catalyst Tetrabutylammonium bromide (TBAB) (99.0%), Sodium hydroxide, and Dicumyl peroxide initiator were purchased from Sinopharm Chemical Reagent Co., Ltd. All reagents were used without further purification.

2.2. Synthesis of styrene-terminated PPO
Figure 1 illustrates the synthetic procedure of styrene-terminated PPO (SPPO). PPO was dissolved in a mixture of toluene and isopropanol. TBAB and 4-Chloromethylstyrene were added and the reaction mixture was heated to 80℃ under mechanical stirring. Then 50% aqueous NaOH solution was added dropwise over a period of 30 min and the mixture was kept at 80℃ for 5 h. After the reaction, the mixture was poured into a mixed solvent containing methanol and deionized water. The filtrated product was dried at 80℃ for 24 h under vacuum.
SPPO was thermally curing with PB, and the PPO/PB blends were also prepared for the investigation of terminal modification effects on the curing behaviour and phase morphology of PPO/PB blends. The chemical structures of PPO, SPPO, PB, and curing agent DCP are illustrated in Figure 2. SPPO (or PPO), PB, and DCP with the predetermined mass fraction (Table 1) were dissolved in toluene. The solvent was removed under ventilating cabinet at room temperature for 48 h and under vacuum at 40°C for 24 h. Then the blends were heated in a quartz tube furnace at 200°C for 30 min and then at 220°C for 10 min. The blends were named as SPPO/PB-x or PPO/PB-x, where x corresponds to mass fraction of PB.

| Sample        | Mass fraction (%) | PPO/SPPO | PB  | DCP |
|---------------|-------------------|----------|-----|-----|
| SPPO          | 100               | 0        |     |     |
| SPPO/PB-0.1   | 90                | 10       |     |     |
| SPPO/PB-0.3   | 70                | 30       |     |     |
| SPPO/PB-0.5   | 50                | 50       |     |     |
| PPO/PB-0.1    | 90                | 10       |     |     |
| PPO/PB-0.3    | 70                | 30       |     |     |
| PPO/PB-0.5    | 50                | 50       |     |     |

a Relative to the total mass of the resin.

2.3. Preparation and blends of SPPO

Figure 1. Synthetic route of SPPO.

Figure 2. Chemical structures of PPO, SPPO, PB, and DCP.
2.4. Characterization

$^1$H-NMR spectra were recorded on a 300 MHz Bruker AVANCE II nuclear magnetic resonance spectrometer (Bruker Biospin Corp., Switzerland) using CDCl$_3$ as the solvent. Gel permeation chromatography (GPC) was performed by a Hitachi L2400 (Hitachi, NY, USA) in tetrahydrofuran (THF), using polystyrene as a standard. Fourier transform infrared (FTIR) spectroscopic analysis was carried out on a NICOLET 6700 spectrometer (Thermo Electron Corp., USA) with KBr pellets at room temperature. Differential scanning calorimetric (DSC) analysis was recorded on a TA-DSC2500 instrument, the sample was heated from 30 to 350°C at a heating rate of 10°C/min. The peak areas in the DSC curing curves were taken as the curing enthalpy. The phase morphology of blends was examined with a JSM-IT300 scanning electron microscope (JEOL Corp., Japan). The cryofracture surface of blends was obtained by quenching fracture in liquid nitrogen. Thermogravimetric analysis (TGA) was performed with a Discovery TGA (Waters Corp., USA) at a heating rate of 10°C/min in an atmosphere of nitrogen. Dynamic mechanical analysis (DMA) was performed using a PE-DMA8000 instrument (Perkin-Elmer Corp., USA). The tan δ and storage modulus were determined under the bending mode at a frequency of 1 Hz and a heating rate of 5°C/min. Dielectric properties were performed with an Agilent 8722ET network analyser (Agilent, Santa Clara, CA, USA) at 10 GHz at room temperature.

3. Results and discussion

3.1. Synthesis and characterization of SPPO

SPPO was prepared from the electrophilic substitution of PPO and 4-chloromethylstyrene (Fig. 1). PPO in the organic phase interacts with sodium hydroxide in the aqueous phase at the interface to generate aromatic oxygen anion, which forms ion pair with TBAB cation and transfers to the organic phase for alkyl reaction with 4-chloromethylstyrene. Figure 3 shows the $^1$H-NMR spectra of PPO and SPPO. The signals of phenolic OH at 4.0–4.5 ppm [22, 23] are observed in PPO. However, new signals of the vinyl group at 5.0–6.0 ppm [24] appear for SPPO, whereas no phenolic OH signals are observed, suggesting the successful modification of PPO chain terminals to styrene through the completion of the alkyl reaction. Furthermore, as shown in Table 2, the molecular weight of PPO increases and its distribution remains narrow after the terminal modification, indicating the successful transformation of chain terminals.

3.2. Curing behaviour

Styrene-terminated PPO and PB can be cured with peroxides. In this work, we used high-vinyl polybutadiene with the 1,2-structure content more than 70%, which can provide a large amount of reactive vinyl groups and improve the cross-linking density during curing [25]. The reaction of vinyl modified PPO and PB is generally considered as addition polymerization, which follows the mechanism of free radical crosslinking [26-28]. Figure 4 shows the curing procedure of SPPO/PB blend based on the widely proposed reaction mechanism. At first, the homolytic cleavage of the curing agent DCP occurs and forms two alkoxy radicals. The subsequent addition reaction of the alkoxy radicals to the carbon-carbon double bond takes place, and then two adjacent polymer chain radicals combine. These elementary reactions repeat successively to give the thermosetting SPPO/PB blend.

The actual curing process of SPPO/PB blend was investigated by FTIR analysis. All the blends show similar curing behaviours, thus SPPO/PB-0.5 is taken as an example to depict the IR spectrum, TGA and DSC curves. Figure 5 shows the FTIR spectra of SPPO/PB blend before and after curing. As shown, the characteristic absorption peaks at 1640 and 910 cm$^{-1}$ corresponding to the vinyl group stretching and

| Table 2. Molecular weights of PPO and SPPO. |
|-----------------|-----------------|-----------------|
| Sample         | $M_n$           | $M_w$           | PD   |
| PPO            | 3186            | 5271            | 1.65 |
| SPPO           | 3359            | 5848            | 1.74 |
Figure 3. $^1$H-NMR spectra of (a) PPO and (b) SPPO in CDCl$_3$.

Figure 4. Supposed procedure for the synthesis of SPPO/PB blend.
Figure 5. FT-IR spectra of SPPO/PB blend before and after curing.

Figure 6. Corrected procedure for the synthesis of SPPO/PB blend.
distorting [24] still exist after curing, while absorption peak at 2970 cm$^{-1}$ attributed to the stretching vibration of the methine [29] disappears. The $\alpha$-H, which is bonded to the carbon-carbon double bond of pendant vinyl group in the polybutadiene, belongs to methine hydrogen, and its activation energy required for the substitution reaction with the radical is very small [30]. Thus, the transfer of methine hydrogen easily occurs from polybutadiene to the alkoxy radicals generated by DCP split during curing (Fig. 6).

To further examine the curing process of SPPO/PB blend, DSC and TGA analysis was employed to determine the thermal behaviour of the blend. As shown in the Figure 7, the SPPO/PB blend with 3 wt% of DCP starts to form cross-linked structures under the temperature of ~120°C, and experiences an unobvious weight loss process in the range 120–200°C. This can be ascribed to the formation of small molecules (2-phenylisopropanol) through the substitution reaction between the alkoxy radical and methine hydrogen. When the temperature is elevated to 220°C, a wide exothermic peak appears, indicating that the cross-linking reaction is further carried out. This could be explained by the complicated curing reactions in the SPPO/PB curing system. The alkoxy radicals not only capture the methine hydrogen of PB, but also add to the terminal styrene groups of SPPO, which leads to the appearance of multiple curing peaks. In addition, the DSC trace of the cured SPPO/PB blend exhibits no obvious exothermic peak, reflecting the curing reaction of SPPO/PB is completed.

The effects of terminal modification of PPO on the curing process of the blend were studied via DSC. Figure 8 shows the DSC curves of unterminated PPO/PB blends and styrene-terminated PPO/PB blends recorded during the heating process. All curves show one major exothermal curing peak in the temperature range of 120-220°C. The major peak temperature ($T_p$) and curing enthalpy ($\Delta H$) were evaluated in Figures 9a,b, respectively. As seen in Figures 8 and 9a, SPPO/PB blend presents a lower $T_p$ than the corresponding PPO/PB blend under the same blend composition, suggesting a reduced curing temperature. For the SPPO/PB blends, the tail-end styrene group of the SPPO reacts with the vinyl groups of PB to extend the network chain. Thus, the DSC curves appear as relatively sharp peaks and the curing peaks shift to lower temperature in contrast to the unterminated PPO/PB blends. This result indicates the faster curing rate of the SPPO/PB blends. Moreover, obvious shoulder peaks appear at high temperature for the SPPO/PB blends, which could be attributed to the self-crosslinking reaction of SPPO. As shown in Figure 9b, due to introducing reactive styrene groups in PPO, the $\Delta H$ of the blending of SPPO/PB blend, which is proportional to the degree of curing, is much higher than that of PPO/PB blend with the same composition. In addition, the $T_p$ of blends decreases with an increase in the fraction

![Figure 7. TGA and DSC curves of SPPO/PB blend before (solid line) and after (dotted line) curing.](image-url)
Figure 8. DSC curves of (a) PPO/PB and (b) SPPO/PB blends with different compositions.

Figure 9. (a) Peak temperature and (b) curing enthalpy of PPO/PB and SPPO/PB blends with different compositions.

of PB and the opposite one appears to the ΔH change, which can be more clearly observed in the SPPO/PB blends. High-vinyl polybutadiene contains many active sites for crosslinking, the higher PB content contributes to promote the reaction between the blend components and increase the crosslinking density of curing system.

3.3. Phase morphology

The effects of terminal modification of PPO on phase morphology of the blends were investigated via SEM. Figure 10 shows the SEM images of cryofracture surfaces of PPO/PB and SPPO/PB blends. For the PPO/PB blends, although the low-molecular-weight PPO can partly improve the compatibility of blends, the obvious granular structure and phase interface are observed with different compositions due to the difference in molecular structure [18]. Comparatively, the SPPO/PB blends give rise to the novel morphological features due to the reaction between the blend components in curing. As seen in the SEM images, PB phase is dispersed throughout the SPPO matrix as the irregular-shaped islands, while the phase interface is fuzzy at a very low PB concentration (10%). The reaction between the styrene-terminated PPO and PB is difficult due to low amount of reactive groups, thus the transfer of PB phase is restrained by the cross-linked structure of SPPO. As the PB content increases, no obvious phase interface and an evenly continuous morphology is formed on the whole. The unique morphology of SPPO/PB blends can be ascribed to the reaction between the blend components, PB can be involved in the cross-linked structure of SPPO matrix and a continuous phase is ultimately formed at a high PB content.
3.4. Solvent resistance

Table 3 presents the solvent resistance of PPO/PB blends with different compositions before and after PPO modified. All the cured blends show good resistance against acids and alkalis. The cured SPPO/PB blends are insoluble in the common organic solvents, in contrast to the blends of unterminated PPO and PB that show bad resistance against these organic solvents due to their poor structural stability. This indicates that the solvent resistance of PPO/PB is improved, which is a result of the formation of cross-linked networks between the blend components by introducing styrene groups to the PPO chain ends. The good solvent resistance makes the SPPO/PB blend ready for cleaning process in the copper clad laminate industry.

3.5. Thermal properties

The thermal properties of cured SPPO/PB blends were investigated by TGA and DMA. Figure 11a shows the TGA curves of original SPPO and its reactive blends with PB. Both SPPO and PB have a good thermal stability, because they bear the high-density benzene ring structure and cross-linked structure, respectively. As depicted in Figure 11b, SPPO exhibits 5-wt% loss temperature (Td5%) of 365.8°C, higher than that of PB (346.2°C). The Td5% values of SPPO/PB bends with 0.1, 0.3, and 0.5 PB fractions are 421.5, 432.2, and 415.8°C, respectively, which are higher than that of the original SPPO. First, it increases and then decreases as the content of PB increases. At a relatively low PB content, the increase in Td5% of SPPO/PB blends with an increase in the PB content is due to the increased degree of curing under this condition, proved by the increases in the weight residues of SPPO/PB blends. However, when the PB content is increased to 50%, since the thermal stability of PB is inferior to that of SPPO, the Td5% values of SPPO/PB blend decreased at high PB content.

Table 3. Solvent resistance of PPO/PB and SPPO/PB blends with different compositions.

| Sample      | Toluene | THF   | Chloroform | Acid   | Alkali  |
|-------------|---------|-------|------------|--------|---------|
| PPO/PB-0.1  | Soluble | Soluble| Soluble    | Insoluble | Insoluble|
| PPO/PB-0.3  | Soluble | Soluble| Soluble    | Insoluble | Insoluble|
| PPO/PB-0.5  | Soluble | Soluble| Soluble    | Insoluble | Insoluble|
| SPPO/PB-0.1 | Insoluble| Insoluble| Insoluble | Insoluble | Insoluble|
| SPPO/PB-0.3 | Insoluble| Insoluble| Insoluble | Insoluble | Insoluble|
| SPPO/PB-0.5 | Insoluble| Insoluble| Insoluble | Insoluble | Insoluble|

Figure 10. SEM images of PPO/PB blends with (a) 0.1, (b) 0.3, and (c) 0.5 PB fractions and SPPO/PB blends with (d) 0.1, (e) 0.3, and (f) 0.5 PB fractions.
It is notable that high performance PPO should have high $T_g$, which can be identified by the tan $\delta$ peak of DMA curves. Figure 12a shows the tan $\delta$ values versus temperature of SPPO/PB blends as a function of PB content, with the $T_g$ of all reactive blends increased, and the $T_g$ of original PB and SPPO occurring at 144.8 and 171.7°C, respectively. The copolymerization between SPPO and PB restricts dynamic motion, resulting in the great increase in $T_g$. Meanwhile, the higher PB content promoted the reactivity of tail-end styrene groups and led to less spacing between the crosslink networks, also resulting in a higher $T_g$ as well. Remarkably, the cured SPPO/PB blends with 0.3 and 0.5 PB fractions exhibit relatively high $T_g$ (214.6 and 226.5°C) compared with other PPO, demonstrating that enhancing thermal properties of PPO are archived successfully in this work. In addition, the DMA curve of SPPO/PB blend has two peaks at a very low PB concentration (10%), while increasing the PB content results in the appearance of relatively sharp single peaks in DMA curves, indicating that the reactive blends have a relatively uniform phase structure. These are consistent with the results observed by SEM. Based on rubber elasticity theory, the crosslinking density of cured resins can be estimated from rubbery plateau modulus [31,32]. The temperature dependent storage modulus of cured SPPO/PB blends with different PB contents is shown in Figure 12b. The increase of the storage modulus suggests that the crosslinking density increases with increasing PB content. This can be explained by the functionality of SPPO and high reactivity of PB, which leads to a more densely crosslinked network.

**Figure 12.** DMA curves of temperature dependent (a) tan $\delta$ and (b) storage modulus of SPPO/PB blends with different PB contents.
3.6. Dielectric properties

Figure 13 shows the dielectric constant (Dk) and loss factor (Df) of the blends with different compositions. As seen in this figure, all the cured blends have low Dk and Df, and those are lower than original SPPO. The Dk and Df values generally decrease with increasing the PB content, which is due to the fact that PB has a very low polarity. However, the Df values decrease more slowly with respect to the Dk, when the PB fraction increases from zero to 0.3, which is considered to be attributed to the multiphase morphology of the blends. In the case of a multiphase material, the dielectric properties are mainly dominated by the polarity of each phase, but the dielectric loss is dominated not only by composition, but also by phase morphology [33]. The compatibility between SPPO and PB is poor at a low PB concentration, and the appearance of the second phase increases the quantity of the accumulated charge due to an additional contribution of the polarization at phase interfaces [19]. As the PB content further increases, the compatibility of the resin system is improved, leading to the Df of the blend decreasing significantly.

4. Conclusion

In this study, the terminally styrene-modified PPO is cured with PB to form SPPO/PB blends successfully. The results show that higher PB content promotes the reactivity of tail-end styrene groups and leads to a higher degree of curing. The terminal styrenisation of PPO enhances the compatibility of SPPO and PB, and thus continuous phase is formed in the blend at high PB contents. The cross-linked network enhances organic solvent-resistance of the blends, and the high density of the benzene ring structure and cross-linked structure provide excellent thermal properties with good dielectric performance retained. Especially, when the mass ratio of PB in the blend is 0.5, the curing system has a high $T_g$ of 226.5 °C, and simultaneously extremely low Dk (2.46) and Df (0.0022) at 10 GHz, indicating that the reactive blend of styrene-terminated PPO can meet the requirements of matrix resins for the fabrication of printed circuit board in electronic industry.

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