

Properties and Origins of High-Performance Poly(phenylene oxide)/Cyanate Ester Resins for High-Frequency Copper-Clad Laminates

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ABSTRACT: A high-performance matrix is the key base for the fabrication of high-frequency copper-clad laminates. A high-performance resin system based on commercial poly(phenylene oxide) (PPO) and 2,2'-bis(4-cyanatophenyl) isopropylidene (BADCy), coded as PPO-*n*/BADCy (where *n* is the weight parts of PPO per 100 weight parts of BADCy), was developed. The effect of PPO on the key properties, including the dielectric and thermal properties, water resistance, and toughness, of the cured resins was investigated extensively. The results show that PPO not only catalyzed the curing reaction of BADCy but also reacted with BADCy to form a single-phase structure. Furthermore, compared with the cured

BADCy resin with 1 phr epoxy resin as a catalyst, the cured PPO-*n*/BADCy resins had significantly increased impact strengths and decreased dielectric constants, loss, and water resistance. The reasons behind these desirable improvements are discussed from the view of structure-property relationships. These results suggest that the PPO-*n*/BADCy system has great potential to be used as a matrix for high-frequency copper-clad laminates or other advanced composites. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 121: 1675–1684, 2011

Key words: polyphenylene oxide; structure-property relations; thermosets

INTRODUCTION

Copper-clad laminates (CCLs) are the key base material for the electrical industry and are needed by almost all electric products. Since the beginning of this century, high-frequency CCLs have been the trend for the development of the CCL market because faster speeds and larger capacities for delivering information have been increasingly demanded by modern information-related electrical products.^{1–3}

CCLs are a kind of polymeric composite, so their key properties, including processing characteristics and thermal and dielectric properties, are greatly dependent on the performance of the matrix. The key properties of high-frequency CCLs mainly include a high thermal stability [glass-transition temperature (T_g) > 250°C], excellent dielectric properties (low dielectric constant and loss), good processing

characteristics, and an acceptable price. Currently, the resin matrices used for high-frequency CCLs are engineering plastics, such as polyimide,⁴ poly(phenylene oxide) (PPO),⁵ and polytetrafluoroethylene;⁶ one of their biggest disadvantages is their poor processing features.

It is well known that at present, about 80% of polymeric composites employ thermosetting resins as their matrices because of their attractive merits of good processing and the reactivity of thermosetting resins. Therefore, it is interesting to develop high-frequency CCLs based on high-performance thermosetting resins.

Cyanate ester (CE) resin is representative of high-performance thermosetting resins and has excellent integrated properties, such as outstanding dielectric properties (low dielectric constant and loss), high thermal resistance, good processing, and so on, so CE resin has been regarded as the candidate with the greatest competition to fabricate advanced functional/structural materials for many cutting-edge fields, such as microelectronics, aerospace, and transportation fields in the 21st century,⁷ so it holds potential way for the development of high-performance matrixes (based on CE resin) for high-frequency CCLs.

However, as a thermosetting resin, a low impact resistance is an intrinsic disadvantage of CE resin.^{8–13} In addition, CE resin needs to be cured at very high temperatures. Generally, a high curing

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temperature not only causes a high energy consumption but also results in a bigger internal stress and defects in the cured resin; it, thereby, deteriorates the overall integrated properties of the resulting materials. These two key disadvantages greatly limit the use of CE resin in applications requiring outstanding overall properties, especially for the microelectric industry.

Many efforts have been made to develop modified CE resins for high-performance CCLs, of which BT resin made up of CE and bismaleimide may be the most representative example,¹⁴ but its dielectric properties, moisture resistance, and toughness need to be further improved. Our research group has conducted a lot of studies on the development of high-performance matrix resins for CCLs^{15–20} and has found that a thermoplastic polymer with very good dielectric properties and thermal and moisture resistance is a more effective modifier for the development of CE-based resins.

PPO is an amorphous thermoplastic polymer with excellent dielectric properties (extremely low dielectric constant and loss), outstanding moisture and thermal resistance, and a desirable toughness,^{21–25} however, few studies have focused on PPO/CE systems. Wu and Mi²⁶ studied the curing kinetics of a blend made up of a multifunctional CE ("PrimasetTM PT Resins" (number average molecular weight (Mn)) = 320–420 g mol⁻¹, Ciba-Geigy, USA) and PPO and found that there was an autocatalytic curing mechanism in the blend. Peters et al.²⁷ synthesized unique poly(phenylene oxide) telechelic copolymers (PPOTCs) with low molecular weight, which were then used to modify CE; the results show that the PPOTC/CE system had improved toughness, moisture resistance, and dielectric properties. These suggested great potential for high-frequency CCLs. However, the synthesis of PPOTC is so complex that it is still far away from industrial production, so the PPOTC/CE system will be difficult to be applied in the CCL market in the near future.

The aim of this study was to develop a new kind of high-performance resin for high-frequency CCLs. A commercial amorphous thermoplastic polymer, poly(2,6-dimethyl-1,4-phenylene oxide), was used to modify 2,2'-bis(4-cyanatophenyl) isopropylidene (BADCy), and the effect of PPO and its contents on the integrated properties, including the dielectric and thermal properties, water resistance, and toughness, of the resulting resins were investigated extensively.

EXPERIMENTAL

Materials

BADCy, with a molecular weight of 278 g/mol, was made at Zhejiang Shengda Chemicals Co., Ltd.

(Hangzhou, Zhejiang, China). Poly(2,6-dimethyl-1,4-phenylene oxide) (PPO), with a weight-average molecular mass of 1500 g/mol, was bought from General Electric Co., Ltd. (Shanghai China). Bisphenol A diglycidyl ether (E51) was made by Sanmu Group of Jiangsu (Yixing, Jiangsu, China); its epoxy value was 0.48–0.54 equiv/mg. Dichloromethane was an analytical-grade commercial product and was used without further purification.

Preparation of the PPO/BADCy blends

Appropriate amounts of PPO and BADCy were dissolved in dichloromethane at room temperature, and then, the resulting polymer solution was heated at 80°C for 1 h with stirring to evaporate most of the solvent. After that, the liquid mixture was poured into a preheated mold and degassed at 120°C for 1 h in a vacuum oven to remove the rest of solvent and entrapped air; this was followed by curing via the conditions of 140°C for 2 h, 160°C for 2 h, 180°C for 2 h, 200°C for 2 h, and postcuring at 220°C for 3 h in an air oven. The resulting resin was transparent and was coded as PPO-*n*/BADCy, where *n* is the weight parts of PPO per 100 weight parts of BADCy.

Preparation of the BADCy resin

Because it is difficult for pure BADCy to be cured with good quality without the addition of catalysts, a small amount of epoxy resin is usually used to catalyze the curing of BADCy. This method was also used in this study to compare the performance of the PPO-*n*/BADCy system.

Appropriate amounts of BADCy and 1-phr epoxy resin were heated at 80°C for 1 h with stirring to obtain a clear liquid, which was then poured into a preheated mold and degassed at 120°C for 1 h in a vacuum oven. After that, the mold was moved into an air-circulating oven, followed by curing and postcuring per the procedures for the preparation of cured PPO-*n*/BADCy resins. The resulting resin was called the BADCy-E resin.

Measurements

The gel time of each resin was measured on a temperature-controlled hot plate by a standard knife method.^{28,29} The resin was spread on a plate that was preheated to a set temperature and maintained at this temperature with stirring for a period of time. The time required for the resin to stop legging and forming filaments, that is, for the resin to become elastic, was recorded as the gel time.

Differential scanning calorimetry (DSC) analyses were done with a DSC 200 F3 (Netzsch, Selb, Bavaria,

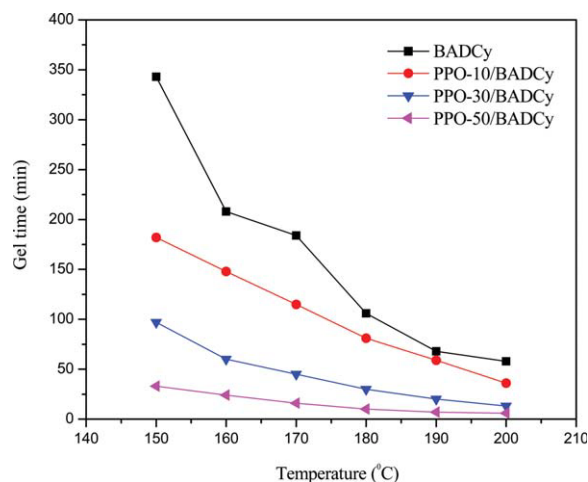


Figure 1 Overlay curves of the gel time versus temperature for uncured BADCy and PPO-*n*/BADCy. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Germany) at a heating rate of 10°C/min under a nitrogen atmosphere.

Fourier transform infrared (FTIR) spectra were recorded between 400 and 4000 cm⁻¹ with a resolution of 2 cm⁻¹ on a Nicolet FTIR 5700 spectrometer (Nicolet, Madison, Wisconsin, USA).

Dynamic mechanical analysis (DMA) scans were measured with a TA Q800 (TA Instruments, New Castle, Pennsylvania, USA) dynamic mechanical analyzer in a single-cantilever bending mode. DMA tests were carried out from room temperature to 320°C at a heating rate of 3°C/min at 1 Hz. The dimensions of the sample were (35 ± 0.02) × (13 ± 0.02) × (3 ± 0.02) mm³.

Thermogravimetry (TG) analysis was performed with a PerkinElmer TGA-7 (PerkinElmer, Manhattan, USA); instrument at a heating rate of 10°C/min under a nitrogen atmosphere from 50 to 800°C.

The impact strength was tested with an impact machine tester XJJ-40 (Shenzhen Kaiqiangli Testing Instruments Co., Ltd, Shenzhen, Guangdong, China); according to GB/T1043-1993; at least 10 samples with dimensions of (50 ± 0.02) × (6 ± 0.02) × (4 ± 0.02) mm³ were measured for each resin to calculate the average value.

A scanning electron microscope Hitachi S-4700 (Hitachi, Japan) was used to observe the morphology of the fractured surfaces of the cured samples.

The water absorption was measured according to GB/1034-86. Three samples for each resin were tested to calculate the average value.

The dielectric constant and loss were tested with a broadband dielectric spectrometer Novocontrol Concept 80 analyzer (Novocontrol Technologies GmbH & Co. KG, Hundsangen, Germany.) at room temperature over a frequency range from 1 to 10⁶ Hz. The dimensions of each sample were (25 ± 0.02) × (25 ± 0.02) × (3 ± 0.02) mm³.

RESULTS AND DISCUSSION

Reactivity of the PPO-*n*/BADCy resins

Figure 1 shows the relationship between the gel time and temperature of different resins. In the whole temperature range, the gel time of each PPO-*n*/BADCy resin was obviously shorter than that of the neat BADCy, especially at a relatively low temperature. Furthermore, the larger the content of PPO was, the shorter the gel time was. For example, the gel times at 150°C of PPO-10/BADCy and PPO-50/BADCy were only about 53 and 10% of that of BADCy, respectively; this suggested that PPO was an effective catalyst for the thermal curing of BADCy.

To further evaluate the catalytic role of PPO in the whole curing process of BADCy, DSC analyses for BADCy and PPO-*n*/BADCy were carried out, and the corresponding DSC curves are depicted in Figure 2. We observed that each system showed two peaks: one was an endothermic peak, attributed to the melting of BADCy, and the other was an exothermic peak. Compared with the whole exothermic peak of BADCy, the peak of each PPO-*n*/BADCy system appeared at a significantly lower temperature; this was closely dependent on the content of PPO. Specifically, the PPO-*n*/BADCy system, with a larger content of PPO, tended to have an exothermic peak appearing at a lower temperature; this further confirmed the catalyzing effect of PPO on the curing of BADCy.

As stated before, the poor curing characteristics were one main disadvantage of CE; that is, to obtain a desirable performance, CE needed to be cured at a high temperature. Moreover, the curing of CE was very sensitive to the materials around. The catalytic effect of PPO on the curing reaction of BADCy was

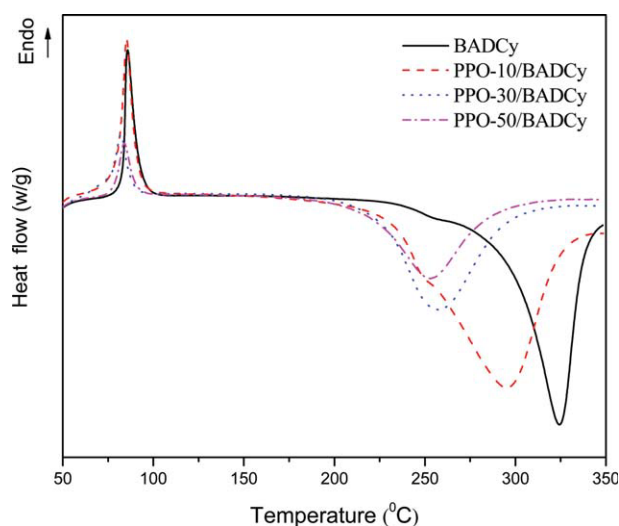
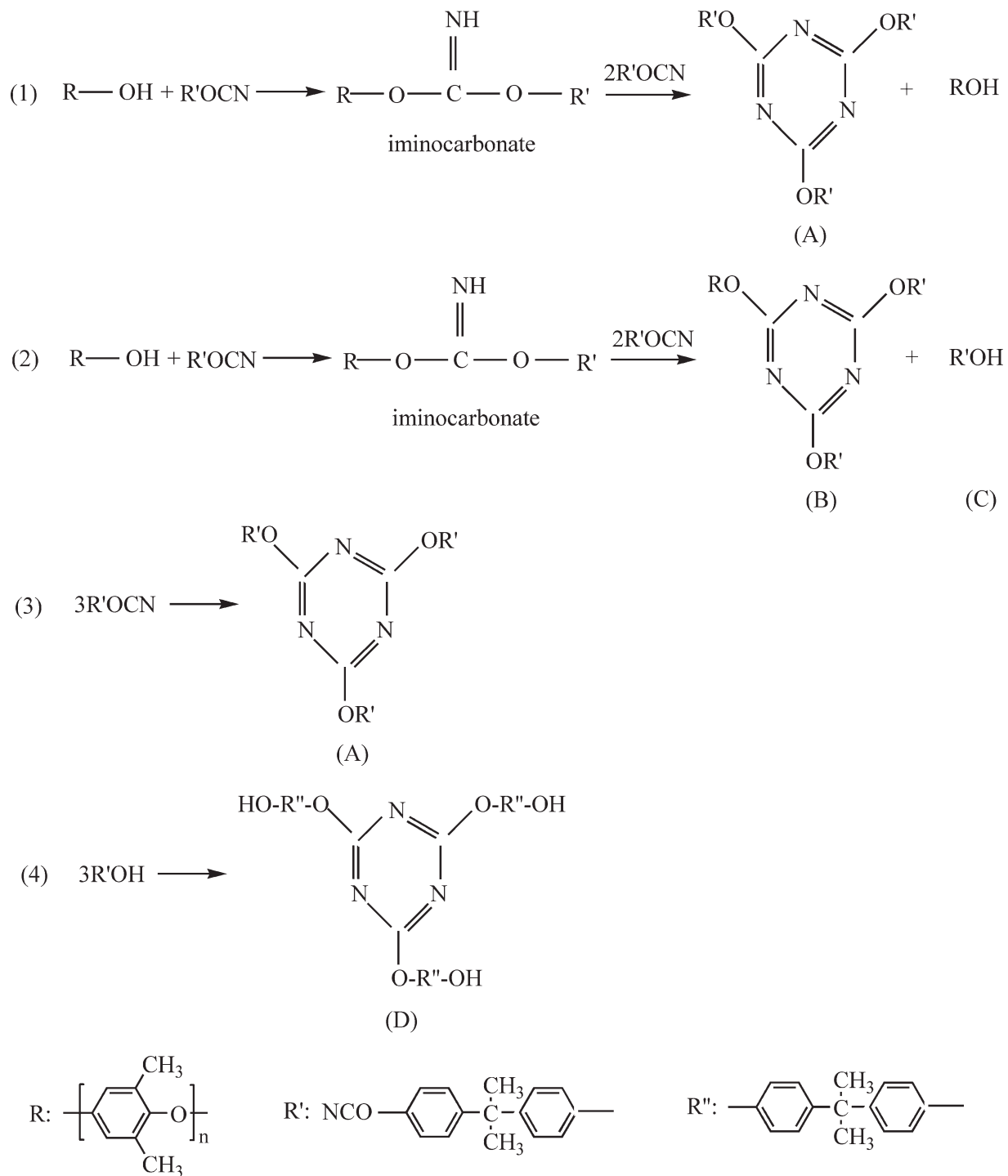


Figure 2 DSC curves of uncured BADCy and PPO-*n*/BADCy. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]



Scheme 1 Curing mechanism of PPO-*n*/BADCy resins.

attributed to the phenolic hydroxyl ($-OH$) groups in the molecule of PPO. The catalytic mechanism is illustrated as path 1 in Scheme 1. Specifically, the $-OCN$ group of BADCy reacted with the $-OH$ group of PPO under the heating conditions to form the iminocarbonate, a reactive intermediate product, which further reacted with more molecules of BADCy to generate triazine ring **A** (Scheme 1) and expelled one phenol group.^{30,31}

Generally, four major reactions accounted for the curing mechanism of the PPO-*n*/BADCy system. In addition to the previous catalytic reaction, the $-OCN$ group in the BADCy molecule reacted with the $-OH$ group in the PPO molecule via an iminocarbonate intermediate to form molecule **B** (Scheme 1), so the PPO chain was trapped into triazine rings at the chain end (path 2, Scheme 1). Obviously, path 2 was beneficial for getting a blend with good

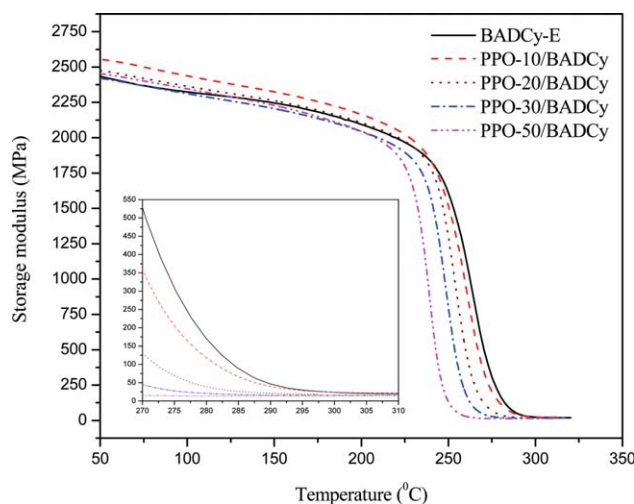


Figure 3 Dependence of the storage modulus on temperature for cured BADCy-E and PPO-*n*/BADCy resins. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

miscibility and that also decreased the crosslinking density of BADCy. Another major reaction in the PPO-*n*/BADCy system was the polycyclotrimerization of BADCy (path 3, Scheme 1) at high temperatures. Furthermore, there was still a —OCN group in molecule C (Scheme 1), and three of these molecules formed triazine ring D with three —OH end groups (path 4, Scheme 1); this reaction also decreased the crosslinking density of BADCy without decreasing the conversion of the —OCN group.

To further confirm the previous statement, the crosslinking densities of the cured BADCy-E and PPO-*n*/BADCy resins were calculated with a semi-empirical equation³¹ based on the storage modulus of the resins (Fig. 3):

$$\lg G' = 7 + 293X_{\text{density}} \quad (1)$$

where G' is the storage modulus of each cured resin in the rubbery plateau region above T_g (i.e., $T_g + 20^\circ\text{C}$) and X_{density} is the crosslinking density. The corresponding data are summarized in Table I.

As shown in Table I, the cured PPO-10/BADCy resin had a larger crosslinking density than the cured BADCy-E resin, whereas all of the other PPO-*n*/BADCy resins showed lower crosslinking densities

TABLE I
Crosslinking Densities of the Cured BADCy-E and PPO-*n*/BADCy Resins

Sample	Crosslinking density (mol/m ³)
BADCy-E	4449
PPO-10/BADCy	4629
PPO-20/BADCy	4367
PPO-30/BADCy	4228
PPO-50/BADCy	3933

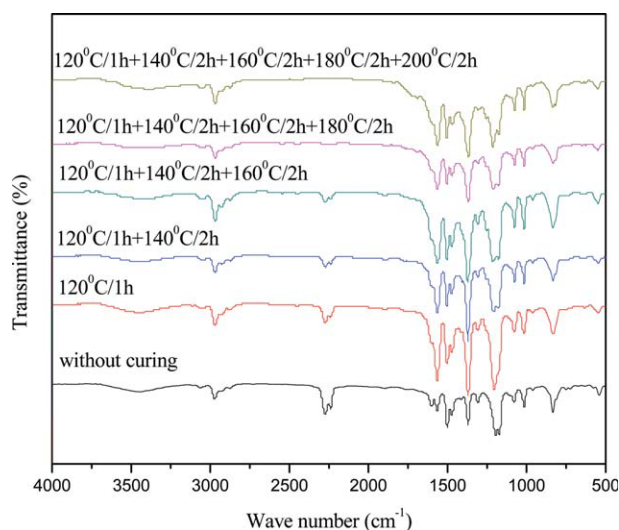


Figure 4 FTIR spectra of PPO-30/BADCy after curing via different procedures. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

than the cured BADCy-E resin. In addition, with regard to the PPO-*n*/BADCy system, its crosslinking density gradually decreased with increasing content of PPO. These data demonstrated that when the content of PPO was small, PPO mainly played a catalytic role in the polycyclotrimerization of BADCy, and this led to the increase of the crosslinking density. However, with increasing content of PPO, the reaction between PPO and BADCy may have become the predominate one and, thus, resulted in a decreased crosslinking density. This viewpoint was proven by the FTIR spectra of PPO-30/BADCy (Fig. 4). Specifically, with the progress of curing, the absorption peak at 2200–2300 cm⁻¹, attributed to the —OCN group,^{32,33} disappeared finally, whereas the crosslinking density of the PPO-30/BADCy resin decreased compared with that of the BADCy-E resin. These data not only suggested that —OCN groups completely transformed into triazine rings but also indicated the existence of the reactions, as shown in paths 2 and 4 because, if only the reactions shown in paths 1 and 3 existed, the crosslinking density of the PPO-*n*/BADCy system would not be smaller than that of the cured BADCy-E resin.

Impact strength of the PPO-*n*/BADCy resins

The impact resistance of a resin is the ability of the material to absorb the energy of a rapidly applied load and is related to the toughness of the resin.³⁴ Figure 5 shows the relationship between the impact strength and the content of PPO for the cured PPO-*n*/BADCy resins. All of the PPO-*n*/BADCy resins had higher impact strengths than the BADCy-E resin. Moreover, with increasing the content of PPO, the impact strength increased and reached the maximum value (18.1 kJ/

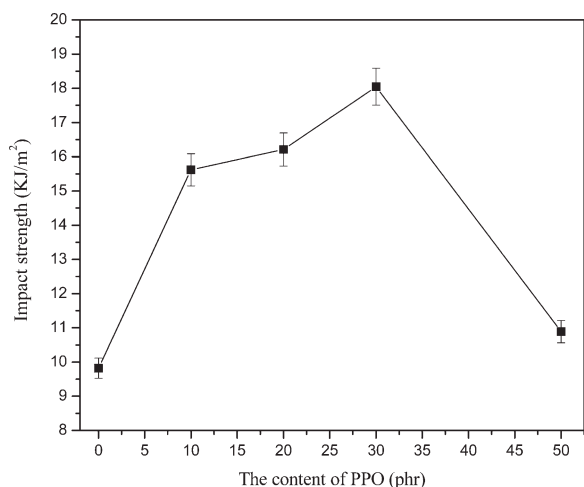


Figure 5 Impact strengths of cured PPO-*n*/BADCy resins with different contents of PPO.

m²) when the content of PPO was 30 wt %. The maximum impact strength of PPO-30/BADCy was almost two times of that of the neat BADCy-E resin.

The dependence of the impact strength on the content of PPO was also reflected by the variety of morphologies of the PPO-*n*/BADCy resins with increasing content of PPO. From the SEM micrographs shown in Figure 6, one can see that the fractured surface of the BADCy-E resin was smooth and glassy; this indicated that there was less plastic energy dissipation accompanying the fracture process, whereas the PPO-*n*/BADCy resins showed much rougher fractured surfaces with the appearance of dimples, which reflected a tough feature.

The toughening effect of PPO on the BADCy resin came from the changed network structure. First, there were a large number of flexible ether bonds in the PPO chain, so the introduction of the PPO chain

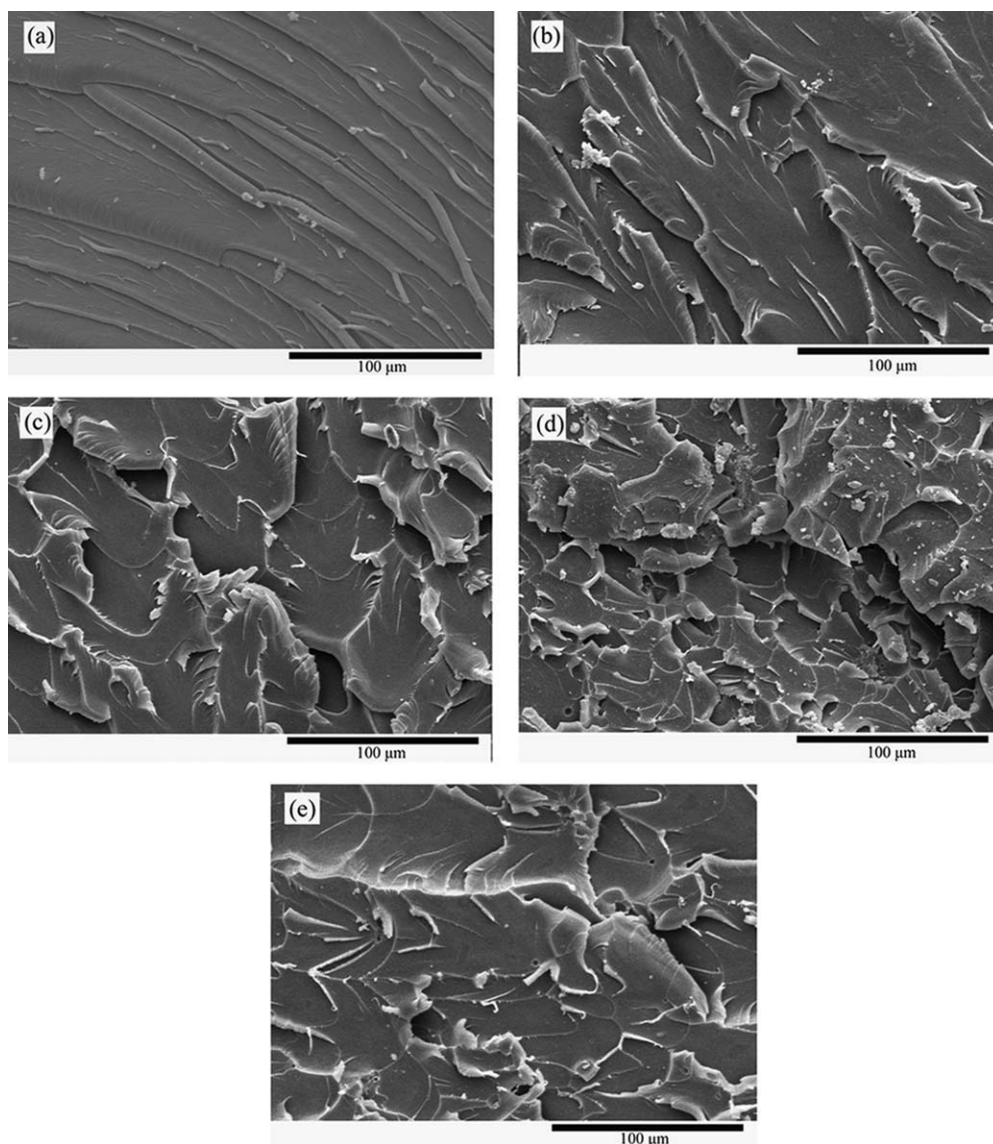


Figure 6 SEM micrographs of (a) cured BADCy-E, (b) PPO-10/BADCy, (c) PPO-20/BADCy, (d) PPO-30/BADCy, and (e) PPO-50/BADCy resins.

into the rigid triazine matrix enhanced the flexibility of the structure; this was the major toughening mechanism for these PPO-*n*/BADCy resins. Second, as discussed previously, the addition of PPO to the BADCy resin led to a reduced crosslinking density, which also improved the toughness of the resins.

However, according to the previous analyses, it seemed that the impact strength of the PPO-*n*/BADCy resin increased with increasing content of PPO, but in fact, there was an optimum content of PPO required to get the maximum impact strength. This was because it was difficult for a very large amount of PPO to be homogeneously dispersed in the BADCy resin; this led to a poor morphology and, thus, poor macroproperties.

Thermal resistance of the PPO-*n*/BADCy resins

For a thermosetting resin, the thermal resistance includes many aspects, of which T_g and thermal stability are two key ones. T_g is the maximum application temperature of the resin, which can be tested by some methods; however, the one that defines T_g as the peak (maximum) temperature in the $\tan \delta$ /temperature plot from DMA measurement has been proven to be most effective³⁵ and was also used in this study.

Figure 7 shows overlay $\tan \delta$ /temperature curves from the DMA tests of the cured BADCy-E and PPO-*n*/BADCy resins. One single and sharp damping peak was detected for all of the resins, indicating that the PPO-*n*/BADCy resins had a homogeneous and single-phase structure; otherwise, even if the phase domains existed, their sizes were so small that the whole morphologies of PPO-*n*/BADCy resins looked molecularly homogeneous, at least up to the scale of the DMA test.³⁶

Figure 7 also shows that the T_g values of all of the PPO-*n*/BADCy resins were lower than that of the BADCy-E resin, and the PPO-*n*/BADCy resin, with a larger content of PPO, tended to have a lower T_g . This was not a surprise result because the T_g value of PPO was only 210°C, which was much lower than that of the BADCy-E resin (287°C). However, it was interesting that when the content of PPO was not large, for example, 10 phr, the resultant modified resin showed an almost similar T_g value (283°C), as did the BADCy-E resin. This was because the crosslinking density of the PPO-10/BADCy resin was higher than that of the BADCy-E resin. This had a positive effect on increasing the T_g value and counteracted the negative effect induced by the low T_g value of PPO. Furthermore, generally, for totally incompatible polymer blends or copolymers, each phase maintains the properties (e.g., T_g) of the pure homopolymer. As molecular mixing occurs, whether because of altered thermodynamic equilibrium conditions or because of mechanical entrapment, the

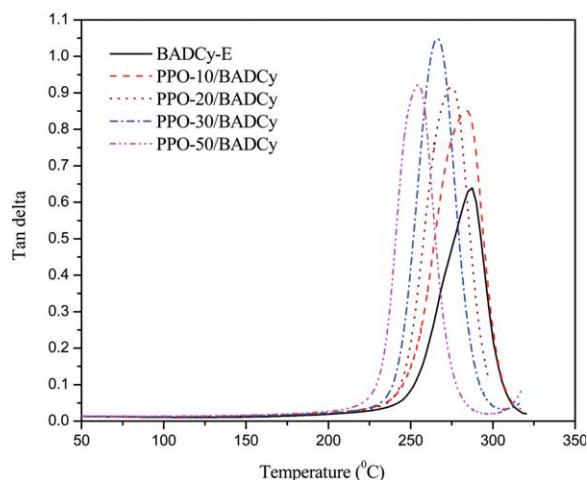


Figure 7 Overlay plots of $\tan \delta$ versus temperature for cured BADCy-E and PPO-*n*/BADCy resins. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://www.interscience.wiley.com).]

glass-transition peaks shift inward between two individual ones and broaden. In the case of the PPO-*n*/BADCy resins, the co-reactions between PPO and BADCy restricted the molecular motion, so their T_g values tended to be near that of the BADCy-E resin. Even when the T_g value of the PPO-50/BADCy resin decreased to 254°C, this value is still high enough for actual applications in the field of high-frequency CCLs.

From the view of molecular structure, the intensity of the damping peak reflects the rigidity of materials: the greater the damping peak is, the less rigid the system structure is.³⁶ Because of the flexible molecular chain of PPO, we expected to find that the damping peaks of all of the PPO-*n*/BADCy resins would be bigger than that of the BADCy-E resin. The intensity of the damping peak for the PPO-*n*/BADCy resin was also affected by the content of PPO; this tended to increase with increasing content of PPO; however, the former reached the highest value when the content of PPO was 30 wt %. This phenomenon was in accordance with the impact strength, as discussed in a previous part of this article.

The thermal stabilities of the cured BADCy-E and PPO-*n*/BADCy resins were evaluated by TG analyses under a nitrogen atmosphere. Figure 8 shows the corresponding TG and differential thermogravimetry (DTG) curves, and Table II summarizes the typical data, such as the initial decomposition temperature (T_{di} ; the temperature at which the weight loss was 5 wt %), the temperature of the maximum degradation rate (T_{max}), and the char yield (Y_c) at 700°C.

PPO had a similar T_{di} value as the BADCy-E resin, so the decomposition of PPO was expected to have little negative influence on the T_{di} value of the PPO-*n*/BADCy resin; however, all of the PPO-*n*/BADCy

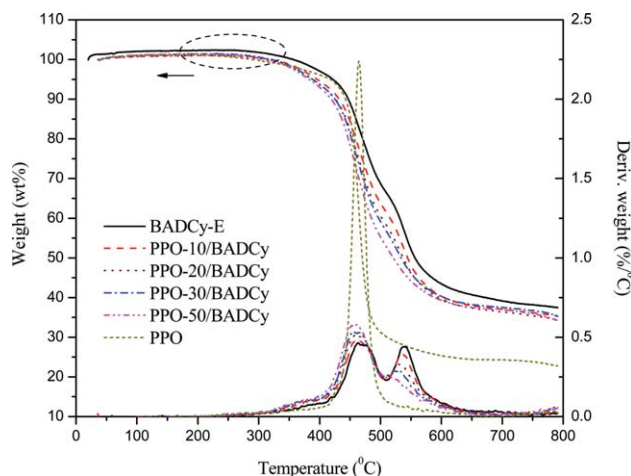


Figure 8 TG and DTG curves of PPO, cured BADCy-E, and PPO-*n*/BADCy resins. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

resins had decreased T_{di} values compared to the BADCy-E resin. The reasons behind this phenomenon may have been the effect of PPO on the curing network. As discussed previously, compared with the crosslinked network of the BADCy-E resin, those of the PPO-*n*/BADCy resins not only had smaller amounts of triazine rings with excellent thermostability but also showed decreased crosslink densities; this, therefore, led to deteriorated thermal stability.^{37,38} Interestingly, the Y_c value of PPO at 700°C was 24.3 wt %, which was much lower than that of the BADCy-E resin. If the PPO-*n*/BADCy resin was a simple blend of the two individual components, its Y_c value would be smaller than that of the cured BADCy-E resin or close to the average value of the cured BADCy-E resin and PPO, but the Y_c value of each PPO-*n*/BADCy resin developed herein was close to that of the BADCy-E resin, as shown in Table II; this suggests that the crosslinked network of the PPO-*n*/BADCy system was completely different from the mixture of the two independent components.³¹

Figure 8 also shows that either the PPO or BADCy-E resin had a peak at about 465°C, whereas the BADCy-E resin exhibited an additional peak at about 539°C. This showed that the PPO and BADCy-E resin had different degradation mechanisms. The

TABLE II

Typical Thermal Degradation Data for the PPO, Cured BADCy-E, and PPO-*n*/BADCy Resins from TG Analyses

Sample	T_{di} (°C)	T_{max1} (°C)	T_{max2} (°C)	Y_c at 700°C (wt %)
BADCy-E	422	477	538	39.2
PPO-10/BADCy	396	462	535	37.1
PPO-20/BADCy	388	461	533	36.4
PPO-30/BADCy	388	456	520	37.5
PPO-50/BADCy	382	459	513	37.0
PPO	418	465	—	24.3

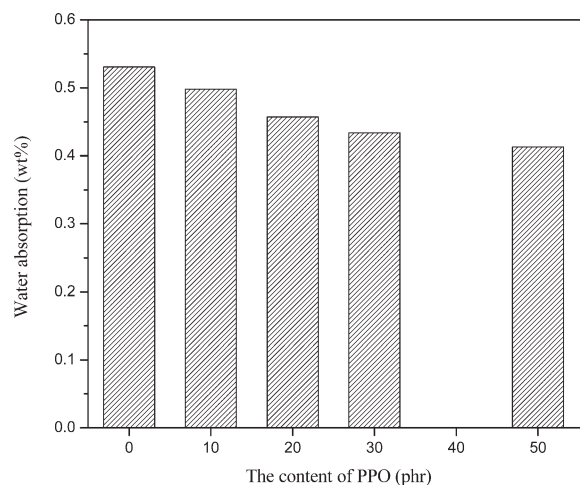


Figure 9 Dependence of water absorption on the content of PPO for cured PPO-*n*/BADCy resins.

PPO-*n*/BADCy resins also showed two peaks appearing at similar temperatures as those of the cured BADCy-E resin. At about 465°C, the degradation rate of PPO was significantly larger than that of the BADCy-E resin; however, that of the latter was similar to those of the PPO-*n*/BADCy resins. This interesting phenomenon showed that there were reactions between PPO and BADCy, and thus, the degradation rate of the resultant resin slowed down.

Water absorption of the PPO-*n*/BADCy resins

Generally, absorbed water has a negative effect on almost all of the properties of a polymer, mainly relating to the thermal, mechanical, and dielectric properties. Hence, low water absorption is a necessary property for developing high-performance resins for high-frequency CCLs.

The water absorptions of the PPO-*n*/BADCy and BADCy-E resins were investigated and are depicted in Figure 9. The water absorptions of all of the PPO-*n*/BADCy resins were significantly lower than that of the BADCy-E resin, and the former decreased with increasing content of PPO. When the content of PPO reached 50 phr, the water absorption decreased to 0.413 wt %, about 22% less than that of the BADCy-E resin (0.531 wt %); this demonstrated that the addition of PPO improved the water resistance of the BADCy-E resin because of the nonpolarity of PPO.

Dielectric properties of the PPO-*n*/BADCy resins

A material with a low dielectric constant and loss will enhance the signal propagation speed and reduce the signal propagation loss,³⁹ so the matrix for high-frequency CCLs should have a low dielectric constant and loss.

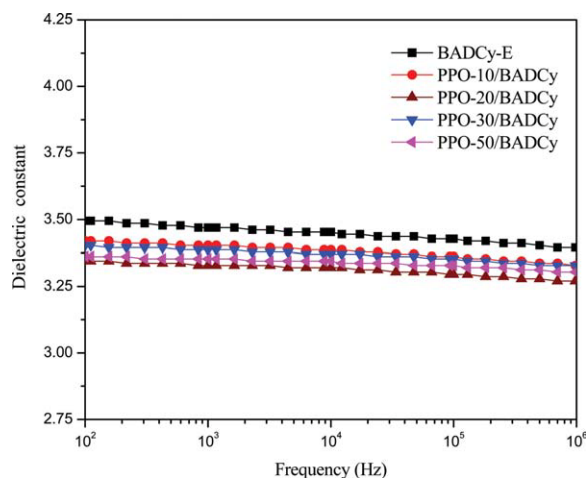


Figure 10 Dependence of the dielectric constant on the frequency for cured BADCy-E and PPO-*n*/BADCy resins. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 10 gives the dielectric constant of the cured BADCy-E and PPO-*n*/BADCy resins over a frequency range from 1 to 10^6 Hz. The dielectric constants of all of the PPO-*n*/BADCy resins retained excellent stability over the tested frequency range, as those of the BADCy-E resin did. Interestingly, the former was slightly lower than the latter; this suggested that the PPO-*n*/BADCy resins had better dielectric properties than the BADCy-E resin.

The dielectric constant had a close relationship with the polarity.⁴⁰ PPO had two opposite effects on the dielectric constant. First, PPO is a nonpolar material with very low dielectric constant (ca. 2.45), so the addition of PPO to the BADCy resin reduced the polarity of the modified resin and, thus, led to a decreased dielectric constant. However, second, as discussed previously, the addition of PPO to BADCy changed the curing mechanism and, thus, the chemical structure of the network. Specifically, the most important feature of the BADCy homopolymer (polycyanurates) was that a high degree of polar symmetry tended to balance the pull of the electrons; this resulted in a short dipole moment and low energy storage in an electromagnetic field. On the other hand, there were appreciable percentages of oxygen and nitrogen in the polycyanurates, but their symmetrical arrangement around a central carbon atom resulted in weak polarity. This could have also been responsible for the observed low dielectric constant and loss for the cured BADCy resin. However, with regard to the cured PPO-*n*/BADCy resin, there were reactions between PPO and BADCy. Particularly, when the PPO chains were trapped to the triazine rings to form molecule **B** (Scheme 1), the degree of polar symmetry was partly destroyed; this led to increased polarity and, thus, an increased

dielectric constant. These two effects counteracted each other to make the PPO-*n*/BADCy resins have a slightly decreased dielectric constant.

Figure 11 shows overlay dielectric loss versus frequency curves of all of the resins. Except for the PPO-10/BADCy resin, the other resins had similar dependence of the dielectric loss on the frequency; in addition, the PPO-*n*/BADCy resins possessed an attractively lower dielectric loss than the cured BADCy-E resin. With regard to the PPO-*n*/BADCy resins, a larger content of PPO was beneficial for getting a resin with a lower dielectric loss. For example, the dielectric loss of PPO-50/BADCy was 0.0038; this was only about 61% of that of the BADCy-E resin, this is very attractive for applications in the microelectric industry. The desirable decreased dielectric loss was attributed to the extremely low dielectric loss of PPO (ca. 0.0007). However, as stated previously, for totally incompatible polymer blends or copolymers, each phase maintained the properties, including the dielectric loss. Hence, from the view of this point, it is reasonable to state that the co-reactions between PPO and BADCy also made a contribution to the decreased dielectric loss.

In the case of PPO-10/BADCy, its dielectric loss was bigger than that of the BADCy-E resin at a low frequency ($<10^4$ Hz), but it showed a better stability on frequency than the other resins. This phenomenon could be interpreted by its chemical structure. As analyzed before that, when the content of PPO was as low as 10 phr, PPO mainly played a catalytic role in the polycyclotrimerization of BADCy; that is, the phenolic hydroxyl group tended to be free rather than connected with other groups, so PPO-10/BADCy showed a large polarity and, thus, a bigger dielectric loss.

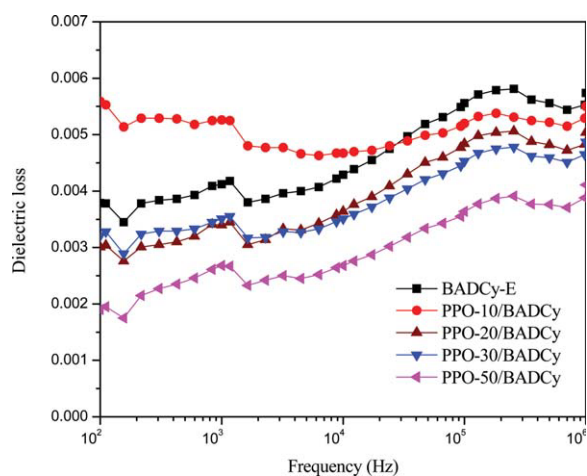


Figure 11 Dependence of the dielectric loss on the frequency for cured BADCy-E and PPO-*n*/BADCy resins. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

CONCLUSIONS

When the content of PPO was as low as 10 phr, PPO mainly played a catalytic role in the polycyclotrimerization of BADCy; with increasing content of PPO, the reaction between PPO and BADCy became the predominate one. The different curing mechanism between BADCy and the PPO-*n*/BADCy system led to different chemical structures and, thus, macroperformances. In addition, the outstanding properties of PPO also made a reasonable contribution to the properties of the PPO-*n*/BADCy system.

Compared with cured BADCy-E resin, the cured PPO-*n*/BADCy resin showed a significantly increased impact strength, decreased dielectric constant and loss, and improved water resistance. It showed great potential to be used as the matrix for high-frequency CCLs. The properties were closely related to the content of PPO because of the variety of the curing mechanism with increasing content of PPO.

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