

Synthesis and Physical Properties of Low-Molecular-Weight Redistributed Poly(2,6-dimethyl-1,4-phenylene oxide) for Epoxy Resin

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ABSTRACT: Low-molecular-weight poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) was prepared by the redistribution of regular PPO with 4,4'-isopropylidenediphenol (bisphenol A) with benzoyl peroxide as an initiator in toluene. The redistributed PPO was characterized by proton nuclear magnetic resonance, mass spectra, and Fourier transform infrared spectroscopy. The redistributed PPO oligomers with terminal phenolic hydroxyl groups and low molecular weights (weight-average molecular weight = 800–4000) were used in the modification of a diglycidyl ether of bisphenol A/4,4'-diaminodiphenylmethane network system. The curing behaviors were investigated by differential scanning calorimetry and Fourier transform infrared spectroscopy. The effect of molecular weight and the amount of redistributed PPO oligomers incorporated

into the network on the physical properties of the resulting systems were investigated. The thermal properties of the cured redistributed PPO/epoxy resins were studied by dynamic mechanical analysis, thermal mechanical analysis, thermogravimetric analysis, and dielectric analysis. These cured redistributed PPO/epoxy resins exhibited lower dielectric constants, dissipation factors, coefficients of thermal expansion, and moisture absorptions than those of the control diglycidyl ether of bisphenol A based epoxy. The effects of the composition on the glass-transition temperature and thermal stability are discussed. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 110: 1880–1890, 2008

Key words: crosslinking; curing of polymers; dielectric properties; poly(phenylene oxide); thermal properties

INTRODUCTION

Conventional electronic circuit boards are made from glass-fiber-reinforced 4,4'-isopropylidenediphenol [i.e., bisphenol A (BPA)] epoxy resins. However, epoxy resin has an undesirably high dielectric constant for high-frequency applications and also an unsatisfactory dimensional stability at higher temperature. With current trends toward increased circuit densities, shorter propagation delays, elevated operating temperatures, and higher reliability, advanced materials with high thermal stabilities and glass-transition temperatures (T_g), low thermal expansions, moisture resistance, and low dielectric properties are required.^{1–5}

Poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) has excellent physical properties, including excellent mechanical properties, high dimensional stability, low moisture uptake, high thermal stability, low flammability, and exceptional electrical properties, including a low dielectric constant and a low dielectric dissipa-

tion factor. In view of these characteristics, PPO would be an excellent candidate as a material for high-frequency substrates.^{6–10}

Many reported studies have used the nonreactive high-molecular-weight thermoplastic PPO to improve the fracture toughness of thermosetting epoxy networks.^{11–13} Furthermore, several works have revealed the addition of PPO-containing functional groups or compatibilizers into the epoxy/PPO blends to facilitate the miscibility and enhance the mechanical properties.^{14–19} However, the presence of high-molecular-weight PPO might result in phase separation in the blend. Redistribution (depolymerization) is an elegant method for obtaining low-molecular-weight PPO with a phenolic tail-end group.²⁰ Most of the previous redistribution studies of PPO have emphasized the understanding of the redistribution mechanism and the screening of potential initiators and phenols.^{21–27} Few researchers have studied the effects of low-molecular-weight redistributed poly(2,6-dimethyl-1,4-phenylene oxide) (rPPO) with a terminal phenolic group on the physical properties of the epoxy network.

To improve the deficiencies of epoxy resin in high-frequency electronic applications, in this study, a phenol-terminated rPPO was prepared by a

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redistribution reaction between commercially available PPO and BPA in the presence of the radical initiator benzoyl peroxide (BPO). The rPPO with lower molecular weight [weight-average molecular weight (M_w) < 4000 g/mol] and terminal phenolic hydroxyl groups was further chemically bonded with epoxy groups. The low-molecular-weight PPO combined with diglycidyl ether of bisphenol A (DGEBA) at various weight ratios was cured with a stoichiometric amount of 4,4'-diaminodiphenylmethane (DDM) as a curing agent and 2-ethyl-4-methylimidazole (2E4MI) as a curing promoter. The physical properties of these cured resins were evaluated with a dynamic mechanical analyzer (T_g), a thermogravimetric analyzer (thermal stability), a thermal mechanical analyzer (thermal expansion coefficient), a dielectric analyzer (electrical properties), and moisture absorption testing. The resulting rPPO/epoxy resins were expected to have lower dielectric constants, dissipation factors, thermal expansions, and moisture absorptions than the control DGEBA-based epoxy resin, and they were also expected to retain their attractive thermal and mechanical properties.

EXPERIMENTAL

Materials

PPO [number-average molecular weight (M_n) = 13,177, M_w = 27,800, M_w/M_n = 2.1] was provided by Chang Chung Chemical Co. Taiwan (Pilot Plant product), and DGEBA with an epoxide equivalent weight of 187 g/equiv was kindly supplied by Nan Ya Plastics. BPO (Lancaster, Windham, NH), BPA (Acros, Somerville, NJ), DDM (Acros), and 2E4MI (Acros) were all used as received. Toluene and methanol were purchased from Tedia (Fairfield, OH). All other solvents were obtained from various commercial sources and were used without further purification.

Monomer synthesis: General procedure for the redistribution of PPO with BPA²⁰

PPO (40 g) was dissolved in 100 mL of toluene at 90°C in nitrogen. Subsequently, 4 g of BPA was added, and then, 4 g of BPO was added portionwise over 15 min. After maintaining the reaction at 90°C for another 3 h, the mixture was allowed to cool to room temperature and was added to methanol to precipitate the product. The pale yellow precipitate was collected by filtration, washed with a Na₂CO₃ aqueous solution to remove excess BPO, and then dried in a vacuum oven at 110°C. The dried product was ground to powder, washed with methanol several times, and finally dried at 70°C *in vacuo*. The aforementioned procedure was repeated with various amounts of BPA and BPO. The M_n and M_w

values of the rPPO were determined with gel permeation chromatography (GPC).

Measurements

The molecular weights of the modified PPO diagrams were obtained with a Shimadzu (Kyoto, Japan) gel permeation chromatograph at 30°C with three TSK gel (G4000HXL/G3000HXL/G2500HXL) columns with tetrahydrofuran as an eluent solvent system.^{26,28} The flow rate was 1 mL/min, detection was by refractive indexing, and M_n and M_w values of the samples were calculated on the basis of polystyrene standards. ¹H-NMR spectra were registered with a Bruker (Rheinstetten, Germany) AMX-400 spectrometer. Fourier transform infrared (FTIR) spectra were recorded on a Nicolet (Madison, WI) Magna-520 spectrometer. We obtained spectra in the optical range 400–4000 cm⁻¹ by averaging 16 scans at a resolution of 4 cm⁻¹. Mass spectrometric analyses were performed on a VG70-250GC/MS spectrometer (Altrincham, Germany). Differential scanning calorimetry (DSC) scans were obtained from samples of about 5–10 mg in a nitrogen atmosphere at a heating rate of 10°C/min with a PerkinElmer (Norwalk, CT) DSC 7 instrument. Dynamic mechanical analysis (DMA) was carried out with a PerkinElmer DMA 7e instrument. The tan δ was determined from a sample subjected to temperature scan mode at a programmed heating rate of 10°C/min from ambient to 250°C at a frequency of 1 Hz and an amplitude of 6 μ m. A sample 15 mm long, 10 mm wide, and approximately 1.5 mm thick was used. The test method was performed in three-point bending mode with a tension ratio at 110%. TGA was performed with a PerkinElmer TGA 7 at a heating rate of 20°C/min under nitrogen and from 30 to 800°C. The coefficient of thermal expansion was measured with the thermal mechanical analysis (TMA) mode of the PerkinElmer DMA-7, with a specimen 5 mm in length used at a heating rate of 10°C/min. The thermal expansion increased with temperature, and the values were calculated from the slope. Dielectric measurements were performed with an Agilent (Palo Alto, CA) 4291B measurement system at a temperature of 30°C in the two-parallel-plate mode at 1 GHz. The applied voltage was 1 V. Before testing, the samples (1 \times 1 cm² and 0.3 cm thick) were dried *in vacuo* at 100°C for 8 h. Moisture absorption was tested as follows. Samples 1 \times 1 cm² and 0.1 cm thick were dried *in vacuo* at 120°C until the moisture had been expelled. After it was cooled to room temperature, the sample was weighed, then placed in 100°C water for 48 h, and weighed again. The moisture absorption was calculated as follows:

TABLE I
GPC Results for rPPO with Various Quantities of Initiator BPO in Toluene at 90°C for 3 h

PPO (g)	40	40	40	40	40	40
Initiator BPO (wt % based on PPO)	1.25	2.5	6.25	10	15	30
BPA (wt % based on PPO)	10	10	10	10	10	10
M_n (g/mol)	12,151	7245	4921	571	562	559
M_w (g/mol)	11,928	6785	5239	3735	3882	3651

$$\text{Weight gain (\%)} = (W/W_0 - 1) \times 100\%$$

where W is the weight of sample after it was placed in 100°C water for 48 h and W_0 is the weight of sample before it was placed in water.

Preparation of the resin formulations and their curing procedure

On the basis of the DSC analyses, various compositions of rPPO/DGEBA were mixed with a stoichiometric amount of curing agent (DDM) and then heated on a hot plate at about 90°C with continuous stirring until a homogeneous solution was obtained. Finally, 0.2% 2E4MI (by weight of epoxy resin) was added as an accelerator, and the mixture was stirred by hand until a homogeneous solution was obtained. The homogeneous mixture was poured into aluminum trays and cured in oven under atmospheric pressure at 130°C for 3 h and 150°C for 2 h and was further postcured at 160°C for 2 h. The molecular weight of PPO over 5000 g/mol could not dissolve in the hot epoxy melt during mixing. Various rPPOs with M_w 's less than 5000 were formulated at various concentrations to study their effects on the physical properties of the cured products. Three different molecular weights of rPPO (3735, 1955, and 855 g/mol) at five concentrations (15, 20, 25, 30, and 40 wt % based on DGEBA) were examined. The curing conditions for these formulations were the same as described previously.

RESULTS AND DISCUSSION

Monomer synthesis

Low-molecular-weight PPO was prepared when bisphenols were brought into a reaction with regular PPO in the presence of a suitable initiator.^{21,22,25–27} On the basis of the free-radical redistribution reac-

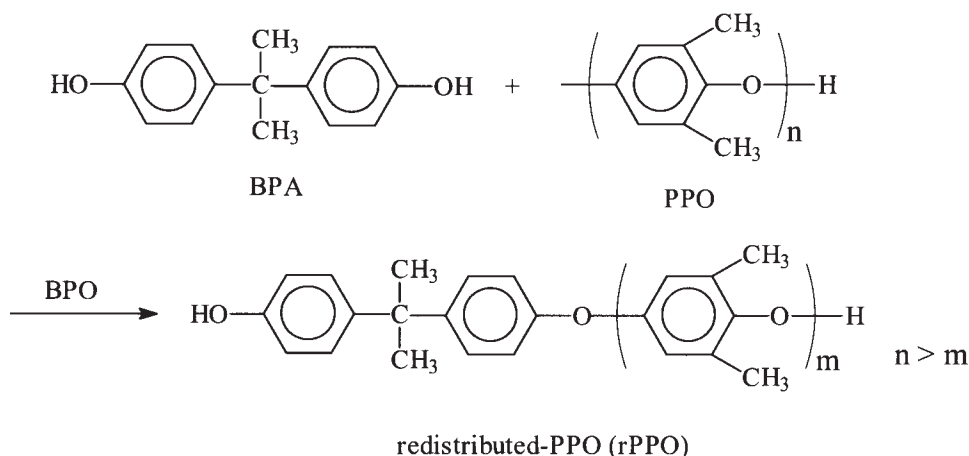
tion, BPO was one of the effective initiators reported by White and others.^{23,29} First, we examined the molecular weight of rPPO when various amounts of the initiator (BPO) and BPA were reacted with PPO in toluene at 90°C. The decrease in molecular weight during the redistribution reaction was traced by GPC. When the amount of BPO was less than 6.25 wt %, the peak of BPA still remained even after 6 h of reaction, which indicated that BPA had not completely reacted. With 10 wt % BPO and 10 wt % BPA, the M_w of rPPO was reduced to 3735 g/mol with no remaining BPA. A further increase in BPO content over 10 wt % (15 or 30 wt %) did not affect the molecular weight ($M_w \sim 3700$ g/mol) of rPPO, which indicated that the redistribution reaction seemed to reach an equilibrium state. Table I lists the M_n and M_w values of the product after redistribution with 40 g of PPO with 0.5–12 g (1.25–30 wt % based on PPO) BPO and 4 g (10 wt % based on PPO) BPA.

Furthermore, the influence of the BPA content (2.5–30 wt % based on PPO weight) on the molecular weight of rPPO was investigated and is listed in Table II. The molecular weight tendency was similar to that shown in Table I for BPA contents below 10 wt %. The molecular weight (M_w) of rPPO was effectively reduced to even less than 1000 g/mol by an equal weight ratio of BPA and BPO over 10 wt % (15 or 30 wt % based on PPO). The molecular weight (M_w) of rPPO was 3735 (g/mol) for 10 wt % BPA and BPO, 1955 (g/mol) for 15 wt % BPA and BPO, and 855 (g/mol) for 30 wt % BPA and BPO, respectively (Table II). The main object of this study was to produce low-molecular-weight PPO (<5000 g/mol) to be cured with a DGEBA-based epoxy to modify the physical properties of epoxy resin.

The desired rPPO was synthesized in one step, as shown in Scheme 1. The structure of the rPPO was confirmed by ¹H-NMR spectroscopy, FTIR spectroscopy, and mass spectrometry. The typical ¹H-NMR spectra of neat PPO and the rPPO by BPA are

TABLE II
GPC Results for rPPO with Various Quantities of BPA in Toluene at 90°C for 3 h

PPO (g)	40	40	40	40	40	40
Initiator BPO (wt % based on PPO)	2.5	5	6.25	10	15	30
BPA (wt % based on PPO)	2.5	5	6.25	10	15	30
M_n (g/mol)	7241	6341	4489	571	336	202
M_w (g/mol)	6745	6289	5147	3735	1955	855



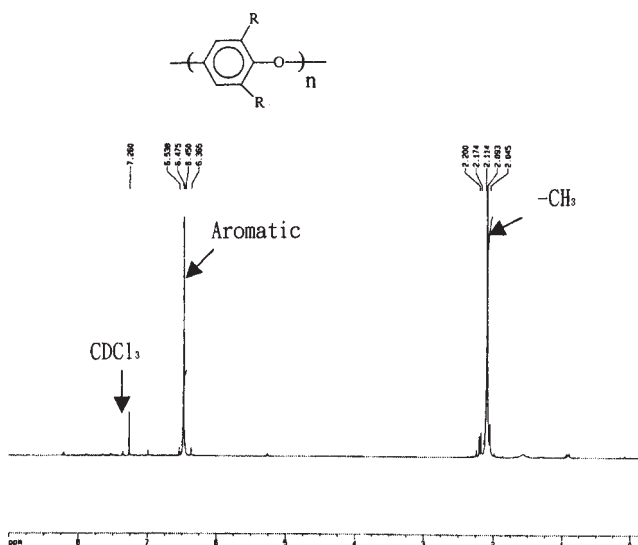
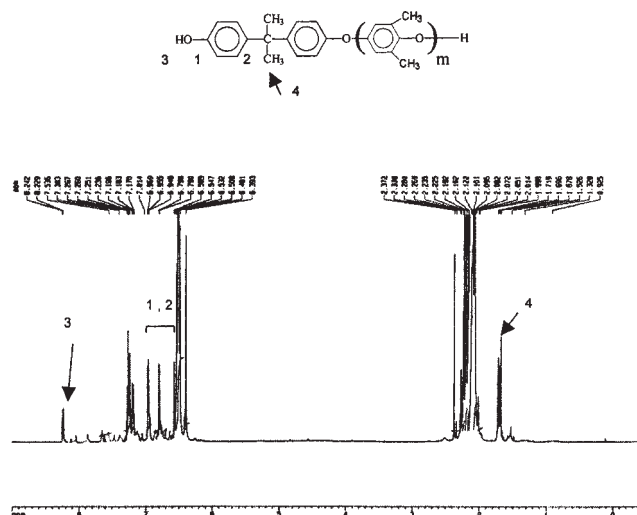
Scheme 1 Synthetic equation of rPPO.

shown in Figures 1 and 2, respectively. Peaks at $\delta = 2.11$ for the methyl protons and $\delta = 6.45$ for the aromatic ring of neat PPO and the rPPO were observed. Furthermore, the methyl proton ($-\text{CH}_3$), the phenolic hydrogen ($\text{Ar}-\text{H}$), and OH proton at $\delta = 1.70$, 6.8–7.0, and 8.2, respectively, for the BPA tailed end group of the rPPO were also observed.

Figure 3 shows FTIR spectra of neat PPO and rPPO. These PPOs possessed two characteristic bands of the phenylene ether at 1020 and 1180 cm^{-1} , which corresponded to $\text{C}-\text{O}$ stretching. The aromatic ring stretching of these PPO showed an absorption at 1602 cm^{-1} . When the FTIR spectrum of rPPO was compared with that of the neat PPO, the absorption peaks were similar. The smaller difference around 3500 cm^{-1} for OH groups and 1740 and 1725 cm^{-1} for carbonyl absorptions were observed. Their intensity depended on the content of the group. The increase in hydroxyl absorption at 3500 cm^{-1} corresponded to an increase in terminal

phenolic groups from the incorporated BPA. The absorptions around 1740 and 1725 cm^{-1} were assigned to the benzoate ester.²⁹ The ester linkage might have been due to the incorporated BPO at the para site of 2,6-dimethylphenol and might also have been derived from the initial reaction of BPO with the methyl group ortho to the PPO phenolic end group to form a benzoyloxymethyl group. The likely chemical structure of the possible product containing a benzoate ester group from the redistribution reaction is shown in Scheme 2.

Molecular fragment ion peaks for neat PPO and rPPO were observed at 107, 135, 154, 289, and 307 by the fast atom bombardment method (as shown in Fig. 4). The scission of the BPA group led to the intense m/z 214 [BPA ($M_w = 228$) - methyl ($M_w = 15$) + 1] fragment ion peak, which was observed in the fast atom bombardment mass spectra of BPA-modified rPPO. Consequently, this reaction could be monitored by means of these absorptions.

Figure 1 ^1H -NMR spectrum of neat PPO.Figure 2 ^1H -NMR spectrum of the rPPO.

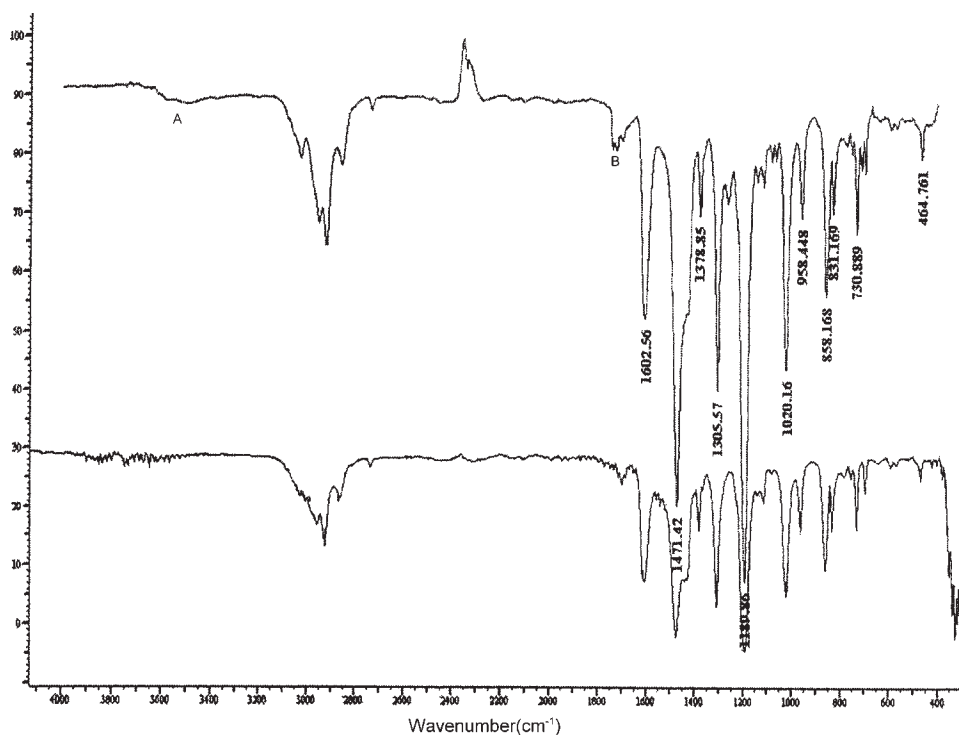
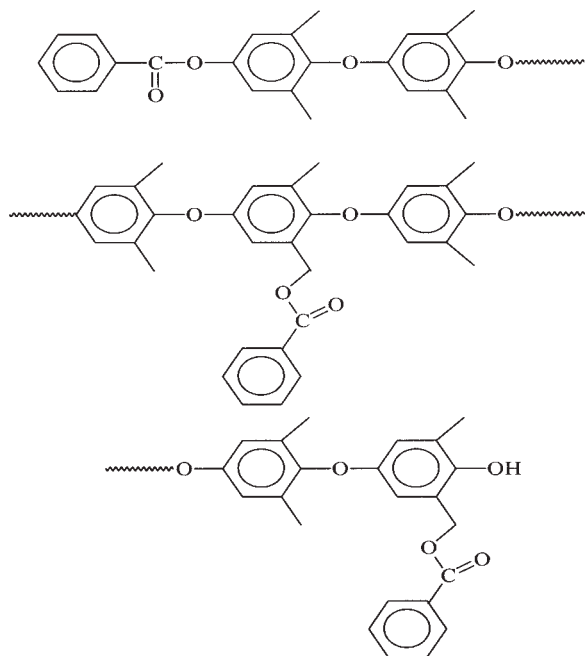


Figure 3 IR spectra of the rPPO (top) and neat PPO (bottom).

Thermal behavior

Figure 5 shows the typical DSC curves for the neat epoxy system and for the mixtures containing various amount of the rPPO copolymer. The onset exothermic temperature (T_i), the maximum exothermic



Scheme 2 Chemical structure of a possible product containing a benzoate ester group from the redistribution reaction.

peak temperature (T_{exo}), and the final exothermic peak temperature (T_f) were 92, 129, and 162°C, respectively, for the control DGEBA and 90, 150, and 190°C, respectively, for rPPO-15A. The DSC scans of these typical compositions (15, 20, and 25 wt %) had similar exothermic peaks. The melting of DDM was not observed clearly in the DSC scans; perhaps DDM had already dissolved in the DGEBA. The exothermic peak of the rPPO/epoxy was broadened. T_{exo} and T_f shifted to a higher temperature region by the introduction of a long phenyl ether linkage of modified PPO. Apparently, the curing rate of rPPO/DGEBA was slower than that of the control DGEBA resin. This was attributed to the steric hindrance of the long-chain rPPO, which reduced the mobility and the reactivity of the OH end group. During the thermal polymerization, the lower diffusion rate resulted in the slower polymerization and formation of crosslinked cured product. The epoxy aliphatic amine curing usually started around 90°C with 2E4MI initiation. The initial stages of curing should have predominantly occurred via the reaction of epoxy with the primary amine. As the curing temperature gradually increased, the tail-end OH group of rPPO, the secondary amine, and the secondary alcohol of the epoxy resin participated in the curing and led to the thermosets. The chemical structure and the related reactions involving rPPO, DGEBA, and DDM are shown in Schemes 3 and 4. In addition, there was a large processing window ($T_{\text{exo}}-T_i$ or T_f-T_i) for curing with rPPO/DGEBA. Therefore, these

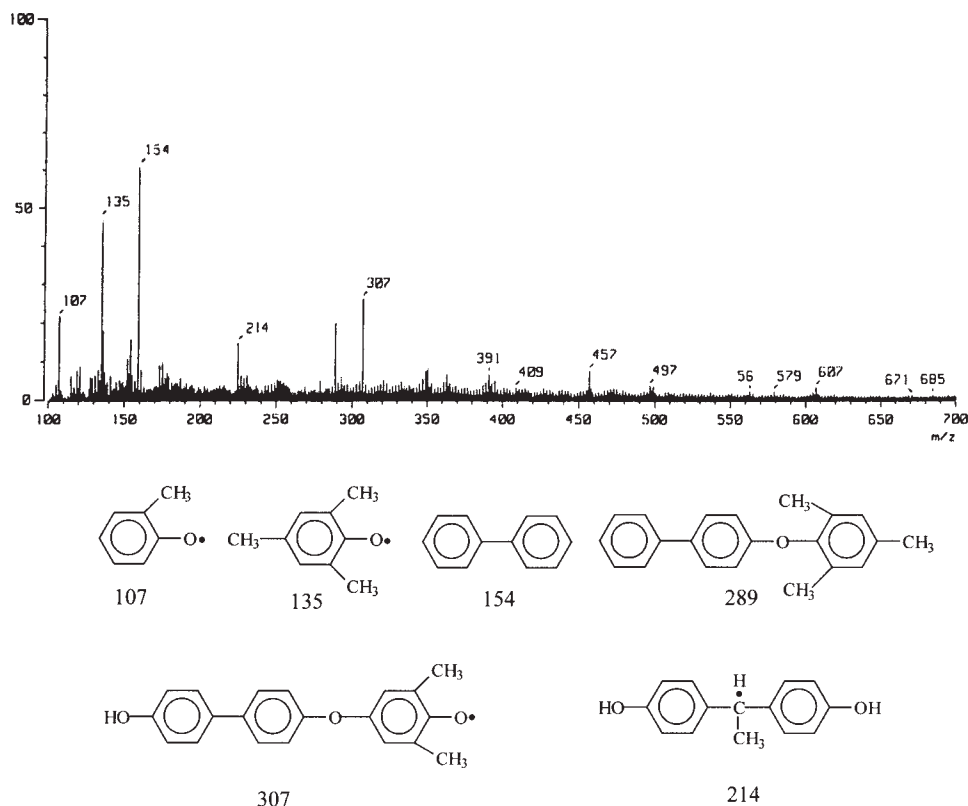


Figure 4 Mass spectrum of rPPO.

rPPO/DGEBA systems had better fluidity and processability during curing than the control DGEBA.

The infrared (IR) spectra of the rPPO/DGEBA mixture before and after curing exhibited several distinctive differences, as shown in Figure 6. The epoxide group absorption at 917 cm^{-1} and the peak assigned to NH_2 for DDM around $3500\text{--}3300\text{ cm}^{-1}$ decreased and the broad absorption of the OH band around 3600 cm^{-1} increased with time.

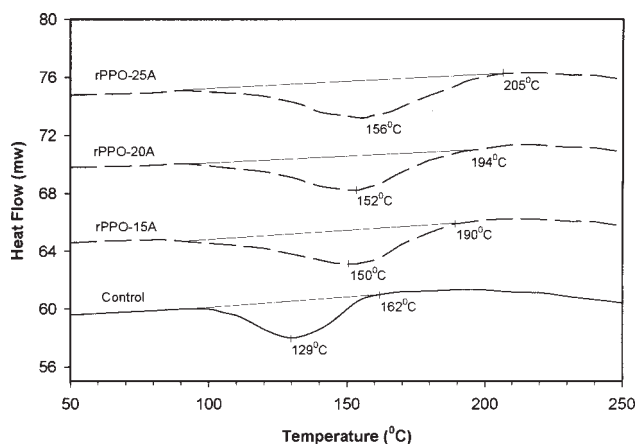
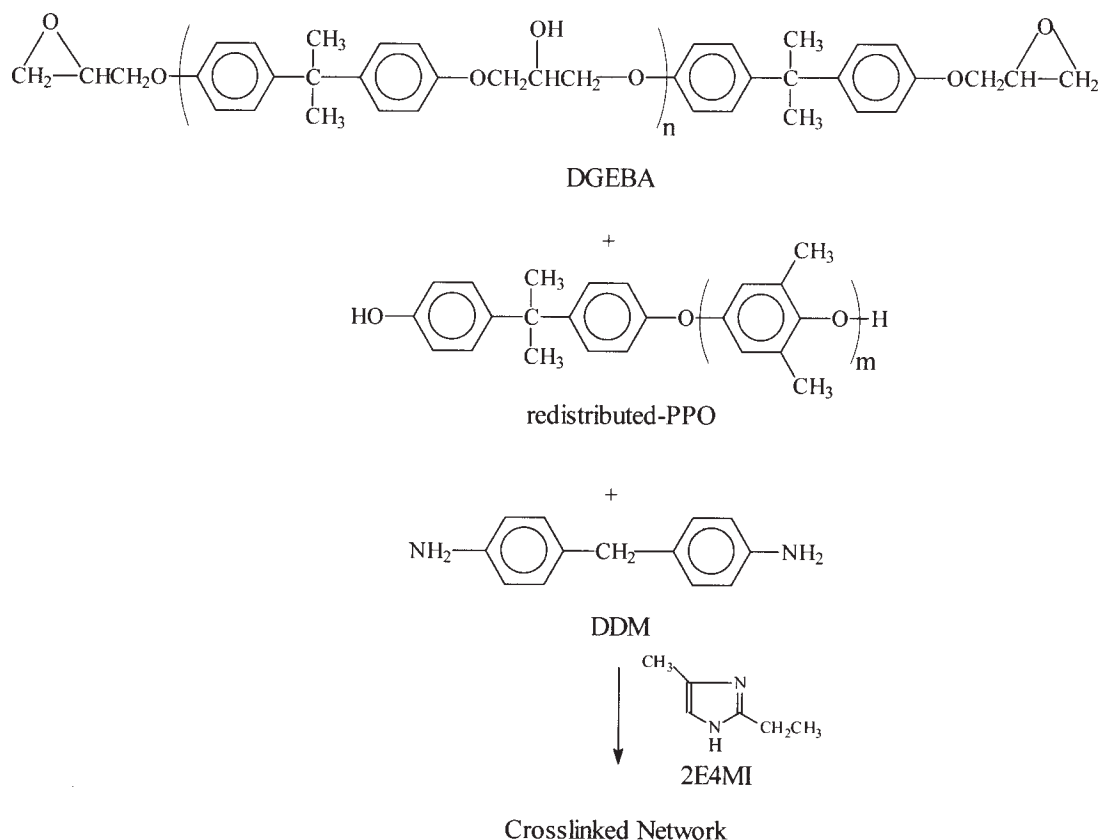


Figure 5 DSC traces of rPPO/DGEBA mixtures with various weight ratios.

Dynamic mechanical properties of the polymers

The peak of $\tan \delta$ was identified as the T_g because a large decrease in the storage modulus occurred at that point. T_g of the cured modified PPO/DGEBA resins with various molecular weight rPPOs or weight ratios were examined, and the results are listed in Table III. The typical dynamic mechanical properties of the cured modified PPO/DGEBA resins are indicated in Figure 7. The T_g of modified PPO/DGEBA ranged between 158 and 169°C . The T_g of the cured modified PPO/DGEBA resins slightly decreased with increasing modified PPO content; the same trend was observed by Shyu,¹² especially for curing systems containing high-molecular-weight rPPO ($M_w = 3735$). Although the T_g of the rPPO/epoxy was slightly lower than that of the control DGEBA resin, it still remained more than 160°C . During curing process, the active tail-end OH group of the rPPO also reacted with the epoxy group to extend the network chain. The higher rPPO content led to more spacing between the crosslink networks and resulted in a lower T_g .

At the same weight ratio, increasing the molecular weight of rPPO also slightly decreased T_g . This was attributed to two factors: First, the higher molecular weight increased the size of bridging group between two crosslinked points. Second, the higher molecular



Scheme 3 Chemical structures of the materials used in this study.

weight reduced the mobility and reactivity of the tail-end OH group. During the thermal copolymerization, the lower diffusion rate at the final curing stage resulted in the lower T_g .

Thermal stability of the polymers

The relative thermal stability of the cured resins was compared by the temperature of 5% weight loss ($T_{5\%}$) and the percentage char yield at 800°C. The TGA data of the cured resins with various weight ratios and molecular weights of rPPO/DGEBA are listed in Table III. The cured resins with various weight ratios exhibited $T_{5\%}$ values ranging between 418 and 386°C in nitrogen. The rPPO modified resin systems showed better thermal stabilities than the control DGEBA-based epoxy. The reason was the higher thermal stability of rPPO, even through the crosslink density was decreased by the introduction of rPPO. For PPO-containing systems, lower $T_{5\%}$ values were noted for higher molecular weight rPPO systems ($M_w = 3735$), and this was consistent with the results of T_g . No significant relation was found between $T_{5\%}$ and the amount of the rPPO.

The char yields increased with the rPPO content, which was much higher than that of the control DGEBA-based epoxy. Upon burning, the aromatic structure of the rPPO improved charring, which

may serve as a heat- and mass-transfer barrier to retard fire propagation. Therefore, the introduction of the rPPO inherently provided a certain degree of flame retardancy.²⁸ Furthermore, the char yield slightly decreased in the following order $M_w = 1955$ series > $M_w = 3735$ series > $M_w = 855$ series. However, too much low-molecular-weight PPO consequently reduced the thermal stability and char yield, as shown in Figure 8.

TMA

The thermally induced dimensional changes of these cured modified PPO/DGEBA resins were investigated with a thermal mechanical analyzer. According to the results listed in Table IV, the coefficients of thermal expansion (between 30 and 150°C, before T_g) of the modified PPO/DGEBA systems were about 56–67 ppm/°C (Table IV), and they decreased with increasing content and molecular weight of rPPO. Although the modified PPO with a longer chain length between two reactive OH groups increased the free volume of the cured resin, the rigidity of phenylene rings and the steric hindrance of *ortho*-methyl groups may have compensated for the effect. Therefore, the modified PPO/DGEBA system had a coefficient of thermal

TABLE III
DMA and TGA Results for rPPO Cured with DGEBA Resin

M_w of rPPO (g/mol)	Sample	PPO (wt % based on DGEBA)	T_g ($^{\circ}$ C)	$T_{5\%}$ ($^{\circ}$ C)	Char yield at 800 $^{\circ}$ C (%)
3735	DGEBA/DDM control	0%	176	387	2.46
	rPPO-15A	15%	162	394	5.86
	rPPO-20A	20%	161	402	8.85
	rPPO-25A	25%	161	386	11.47
	rPPO-30A	30%	159	390	13.67
1955	rPPO-40A	40%	158	392	17.70
	rPPO-15B	15%	165	395	6.12
	rPPO-20B	20%	163	405	9.61
	rPPO-25B	25%	162	414	11.65
	rPPO-30B	30%	161	413	14.58
855	rPPO-40B	40%	160	397	17.89
	rPPO-15C	15%	169	392	5.94
	rPPO-20C	20%	168	408	8.72
	rPPO-25C	25%	166	405	11.38
	rPPO-30C	30%	165	418	13.29
	rPPO-40C	40%	164	414	16.26

rPPO-30C at 1 GHz were 0.0204, 0.0126, 0.0127, and 0.0128 U, respectively. No matter how large the weight ratio of rPPO was, the dielectric constant and dissipation factor of the modified PPO/DGEBA systems were significantly lower than that of the control DGEBA resin (Table IV). The dielectric constant and dissipation factor decreased in the following order at the same content : rPPO-C ($M_w = 855$) series > rPPO-B ($M_w = 1955$) series > rPPO-A ($M_w = 3735$) series. The dielectric constant was reduced when the free volume of the molecule increased or when polarization decreased.³⁰⁻³² The higher rPPO molecular weight led to more spacing between the polymer molecules, and this resulted in less efficient

chain packaging and an increase in the free volume of the polymer, which reduced the dielectric constants and dissipation factors of the modified PPO/epoxy systems.³³ Furthermore, the presence of bulky *ortho*-methyl groups may have shielded interchain electronic interactions and increased hydrophobicity, which would have thus decreased the dielectric constants and dissipation factors.

As shown in Table IV, the higher the rPPO content in the formulation was, the lower the dielectric constants and dissipation factors of the cured rPPO/DGEBA resins were. This was attributed not only to the low polar and hydrophobic structure of PPO chain but also to the increase in free volume.

Moisture resistance

The absorbed moisture acted as a plasticizer, which reduced the mechanical and thermal properties of the cured resins and also had a detrimental effect

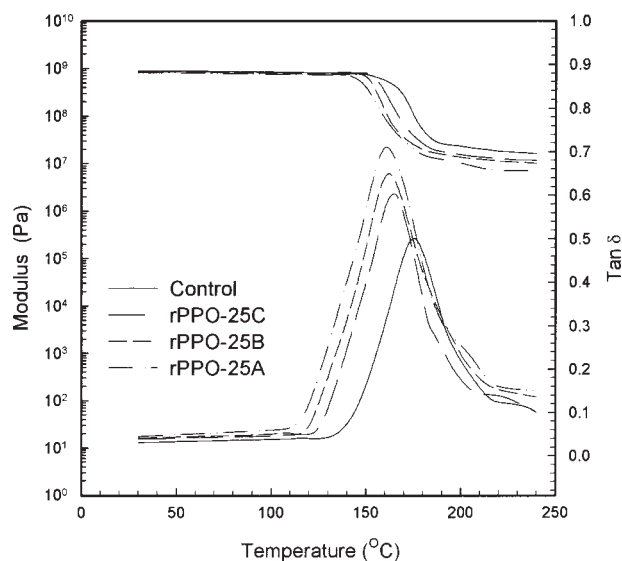


Figure 7 Typical DMA scans of rPPO/DGEBA mixtures cured with various weight ratios.

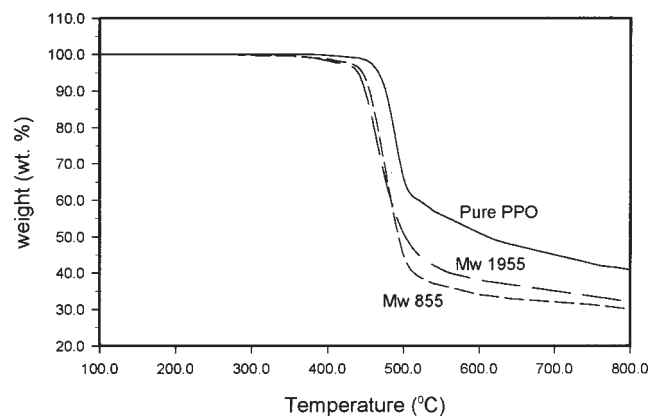


Figure 8 Typical thermogravimetric thermograms of rPPOs with different molecular weights.

TABLE IV
TMA, Dielectric Properties, and Moisture Absorption of rPPO Cured with DGEBA Resin

M_w of rPPO (g/mol)	Sample	PPO (wt % based on DGEDA)	Coefficient of thermal expansion (ppm/°C)	Moisture absorption (%)	Dielectric constant (U) at 1 GHz	Dissipation factor (U) at 1 GHz
3735	DGEBA/DDM control	0	68.03	1.98	3.70	0.0204
	rPPO-15A	15	62.96	1.98	3.20	0.0171
	rPPO-20A	20	62.73	1.92	3.10	0.0163
	rPPO-25A	25	61.10	1.84	3.05	0.0158
	rPPO-30A	30	57.30	1.76	2.82	0.0126
1955	rPPO-40A	40	56.57	1.70	2.73	0.0115
	rPPO-15B	15	65.68	1.98	3.20	0.0172
	rPPO-20B	20	64.92	1.92	3.12	0.0164
	rPPO-25B	25	63.92	1.86	3.07	0.0160
	rPPO-30B	30	62.09	1.77	2.84	0.0127
855	rPPO-40B	40	60.63	1.72	2.78	0.0119
	rPPO-15C	15	67.60	1.98	3.23	0.0179
	rPPO-20C	20	66.99	1.92	3.14	0.0174
	rPPO-25C	25	64.76	1.87	3.12	0.0163
	rPPO-30C	30	63.24	1.74	2.85	0.0128
	rPPO-40C	40	62.09	1.71	2.80	0.0120

on the dielectric properties. Moisture absorption reduces the T_g of a laminate material and may cause the popcorn phenomenon when there is contact with solder at a high temperature. Moisture absorption will also ionize the ionic impurities (e.g., Cl^-) and, therefore, corrode the integrated circuits. Furthermore, the absorption of even a small quantities of water (dielectric constant = 78) in thermoset resins can affect their dielectric properties quite markedly. For these reasons, low moisture absorption is necessary for laminate materials.^{33,34} As shown in Table IV, all of the cured modified PPO/DGEBA resins showed lower moisture absorption than the control DGEBA epoxy. The lower moisture absorption may have been due to the hydrophobic nature of the rPPO structure in the polymer chain. As shown in Table IV, the higher the modified PPO content in the formulation was, the lower the moisture absorption of the cured rPPO/DGEBA resins was. The data indicated no obvious tendency between the molecular weight and moisture absorption.

CONCLUSIONS

Low-molecular-weight PPO with M_w values in the range 800–4000 g/mol and with phenolic end groups were successfully synthesized by the redistribution reaction of high-molecular-weight PPO with more than 10 wt % BPA and BPO on the basis of PPO. The average molecular weight of the rPPO decreased with increasing amount of BPA. Furthermore, the low-molecular-weight rPPO was used to cure DGEBA. The rigidity of phenylene rings and the steric hindrance of *ortho*-methyl groups belong-

ing to rPPO contributed to better thermal dimensional stability. Because of a higher free volume and low polarity of rPPO linkages, the modified PPO/epoxy resins exhibited a low dielectric constant and dissipation factor. Because of the hydrophobic effect of the rPPO structure, rPPO showed lower moisture absorption than that the control DGEBA-based epoxy resin. All modified PPO-containing cured epoxy resins still retained good thermal properties. The combination of a lower dielectric constant, dissipation factor, and moisture absorption and better thermal dimensional stability makes these rPPO/epoxy resins attractive candidates for printed circuit board applications.

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