

Mechanical and Dielectric Properties of Cured 1,2-Bis(vinylphenyl)ethane Resin Modified with Poly(phenylene oxide)

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ABSTRACT: 1,2-Bis(vinylphenyl)ethane (BVPE) could be cured without curing agents at relatively low temperatures ($\sim 180^\circ$) in a nitrogen atmosphere. Cured BVPE (CBVPE) resin showed exceptionally low dielectric constant ($\epsilon = 2.50$ at 10 GHz) and low dielectric loss tangent ($\tan \delta = 0.0012$ at 10 GHz), and had excellent thermal resistance. Its 5 wt % weight-loss temperature was 425°C in a nitrogen atmosphere and glass transition temperature was over 400°C . Poly(phenylene oxide) (PPO) was used to improve the toughness of CBVPE resin. PPO was an effective modifier to

toughen CBVPE resin: when using 30 wt % of the modifier, the tensile strength and elongation of the modified CBVPE resin were 75 MPa and 26%, respectively. The modified CBVPE resin also showed excellent dielectric properties ($\epsilon = 2.45$ at 10 GHz, $\tan \delta = 0.0015$ at 10 GHz). © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 92: 1252–1258, 2004

Key words: crosslinking; dielectric properties; high performance polymers; poly(phenylene oxide); morphology

INTRODUCTION

Polystyrene derivatives are commercially interesting because of their very low dielectric constant, moisture resistance, and good thermal stability. Polystyrene derivatives are thought to be well suited to become insulators for electronic devices. Many research groups have an interest in polystyrene derivatives and have been studying their synthesis and various properties. For example, Mathias et al.¹ investigated thermal properties of polymers derived from bis(vinylbenzyl) ethers and bis(vinylbenzyl) thioethers. They described the excellent physical and thermal properties of carbon fiber composites prepared with these polymers. Ohtani et al.² reported on heat resistance of copolymers derived from bis(vinylbenzyl) ether compounds and bismaleimide resins. Bismaleimide resins were effective for improving heat resistance of cured bis(vinylbenzyl) ether compounds. Liao and Wang³ showed that polymers derived from vinylbenzyl ether compounds had low moisture absorption and high heat resistance. We have investigated copolymerization and thermal properties of styrene derivatives having unsaturated imide groups; for example, *N*-(4-vinylphenyl) maleimide (VPMI) yields linear polymers containing unsaturated pendants by ionic polymerizations and poly(VPMI)s show good heat resistance.⁴ However, these polystyrene compounds were not op-

timal structures to obtain the desired dielectric properties, showing relatively high ϵ and $\tan \delta$ compared to polystyrene because their structures contained heteroatoms such as nitrogen and oxygen. For this article, we investigated the dielectric and thermal properties of cured 1,2-bis(vinylphenyl) ethane (BVPE) resin, which does not include heteroatoms in the structure. Cured BVPE (CBVPE) resin is expected to show excellent dielectric properties equal to those of polystyrene.

The toughening of cured resins by blending of various polymers has been studied by many researchers. For examples, engineering thermoplastics like polyetherimides,⁵ poly(aryl ether ketone)s,⁶ poly(phenylene oxide) (PPO),⁷ and aromatic polyesters⁸ have been reported as effective modifiers for epoxy resins. We therefore studied the toughening of CBVPE resin by modification with engineering thermoplastics. We selected PPO as a modifier for CBVPE resin on the basis of the excellent dielectric properties of PPO. We expected that CBVPE resin modified with PPO would show low ϵ , low $\tan \delta$, and good mechanical properties.

EXPERIMENTAL

Materials

The vinylbenzyl chloride (VBC) used was a mixture of 70% *m*-isomer and 30% *p*-isomer (Tokyo Chemical Industrials Co., Tokyo, Japan). VBC was distilled under reduced pressure. The following were all used as

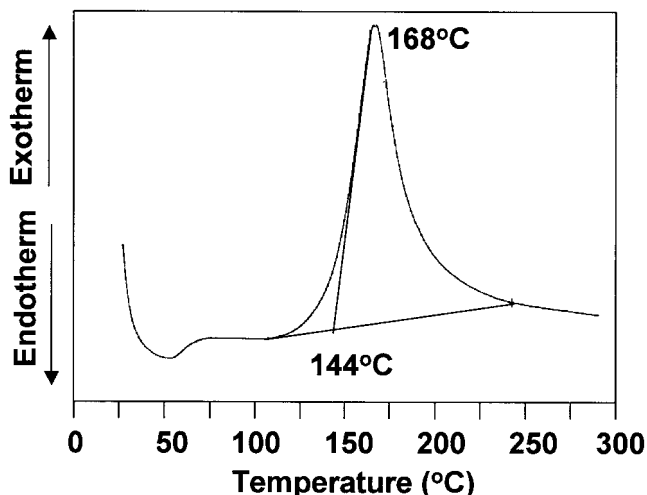


Figure 1 DSC curve of BVPE without curing agent.

received: magnesium turnings (Kanto Chemical Co., Tokyo, Japan), anhydrous tetrahydrofuran (THF, Kanto Chemical Co.), chloroform (Kanto Chemical Co.), 2-butynyltetramethylenesulfonium hexafluoroantimonite (Asahi Denka Kogyo K.K., Tokyo, Japan), cobalt naphthenate (Kanto Chemical Co.), 2,5-dimethyl-2,5-di(t-butylperoxy) hexyne-3 (25B, NOF Co., Tokyo, Japan), poly(phenylene oxide) (PPO, Sigma-Aldrich, Tokyo, Japan; Mw = 47500, Mn = 15100, D = 3.1), polystyrene (Gasukuro Kogyo Inc., Tokyo, Japan; Mw = 171900, Mn = 167900, D = 1.03), 1,1-bis(4-cyanatophenyl)ethane(Arocy L10, Asahi-Ciba Ltd., Tokyo, Japan), 2-propenoic acid(octahydro-4,7-methano-1H-indenediyl)bis(methylene)ester(R684, Nippon Kayaku Co., Tokyo, Japan), bisphenol A diglycidyl ether (Ep828, Japan Epoxy Resins Co., Ltd., Tokyo, Japan), 3,4-epoxycyclohexyl-3,4-epoxycyclohexane carboxylate (CL2021A, Dicel Chemical Industries, Ltd., Osaka, Japan).

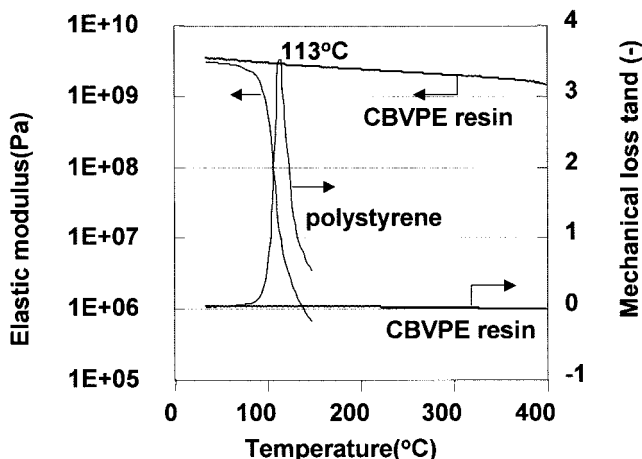


Figure 2 Dynamic mechanical analysis for CBVPE resin and polystyrene.

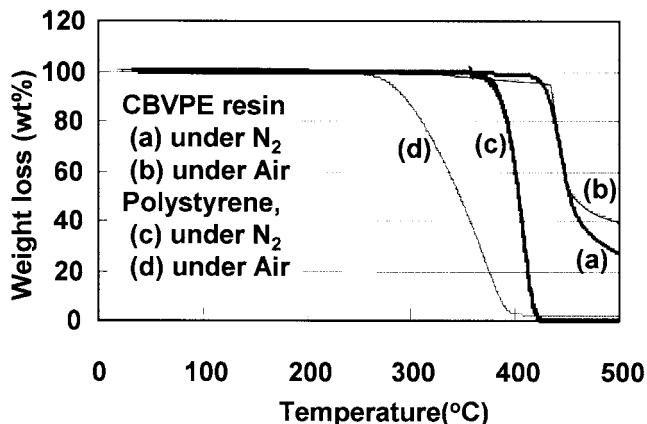


Figure 3 TGA curves of CBVPE resin and polystyrene.

Measurements

¹H-NMR spectra were recorded on a JEOL JNM-GX-400 FT-NMR spectrometer using chloroform-d as a solvent. The gel permeation chromatograms (GPCs) were measured with a Waters 150CV that joined Shodex AT-G and AT-806MS columns using dichlorobenzene as an eluent (flow rate 1.0 mL/min) at 145°C. DSC and TGA measurements were carried out with a DuPont 910 differential scanning calorimeter and a DuPont 951 thermogravimetric analyzer, under a nitrogen atmosphere and an air atmosphere at heating rates of 10 and 5°C/min, respectively. The dielectric constants (ϵ) and the dielectric loss tangent ($\tan \delta$) were measured with an Agilent Technology type 810 network analyzer connecting cavity resonators of Kanto Densi Ouyou. The peel strength between rough

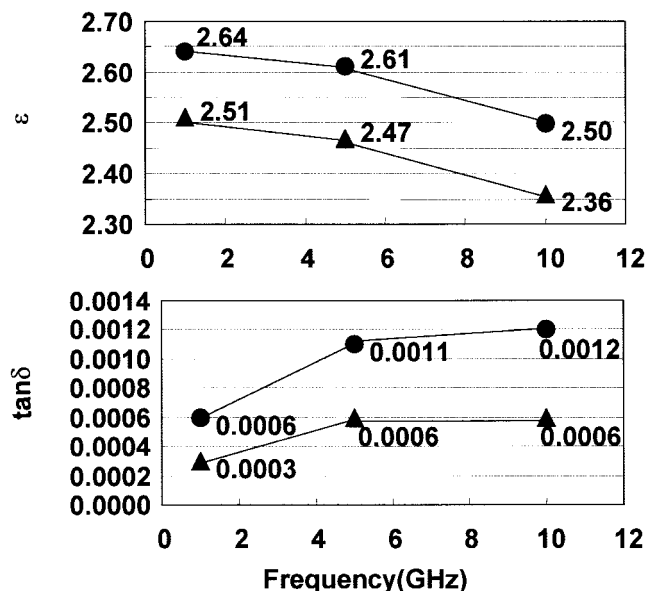


Figure 4 Dielectric constants (ϵ) and dielectric loss tangents ($\tan \delta$) of cured CBVPE resin (●) and polystyrene (▲).

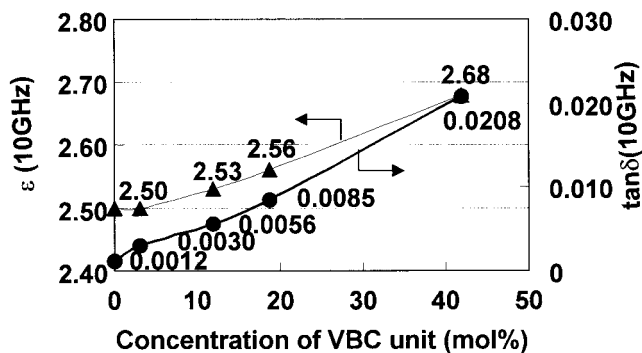


Figure 5 Dielectric constants (ϵ) and dielectric loss tangents ($\tan \delta$) of CBVPE resin containing vinylbenzylchloride (VBC).

face copper foil and cured resins was investigated by the following procedure: the spacer on the rough face copper foil was filled with a resin. The resin was molded by heating and pressing. Then the peel strength was measured. The molding conditions are described later.

Synthesis of 1,2-bis(vinylphenyl)ethane (BVPE)

BVPE was prepared by the reported method.⁹ The procedure is shown below. The synthesis of BVPE was done under a nitrogen atmosphere. Magnesium turnings (0.32 mol; 8.04 g) and 600 mL of dry THF were placed in a 1-L three-neck flask equipped with a 100-mL dropping funnel, a condenser, and a dry nitrogen flow tube. The mixture was stirred and cooled to -5°C . VBC (0.60 mol; 91.6 g) was added slowly into the mixture and the reaction system was stirred at 0°C for 20 h. The reaction mixture was filtered and the solvent was evaporated. The residue was dissolved in 300 mL of hexane. The hexane solution was then washed with aqueous 3.6% HCl once and with water twice, using a separatory funnel. The solution was dried over MgSO_4 and the solvent was evaporated. The product was dissolved in hexane and the solution was passed through a short column packed with silica gel. The purified product was obtained by removal of

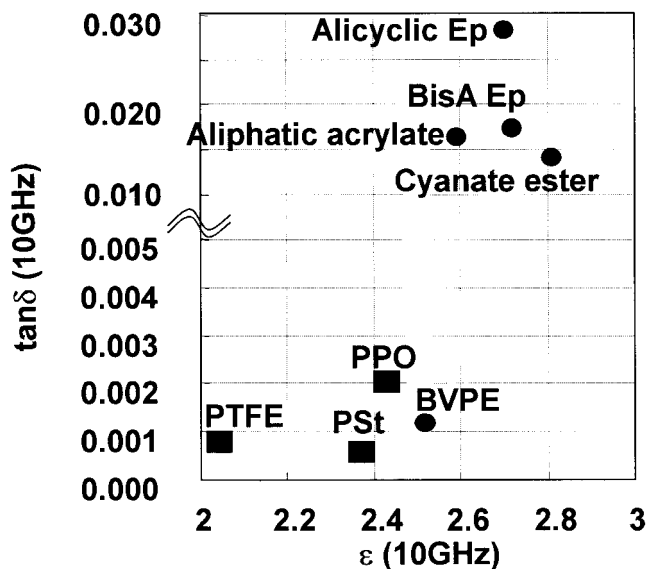


Figure 6 Dielectric constants (ϵ) and dielectric loss tangents ($\tan \delta$) of crosslinked (solid black circle) and linear (solid black square) resins. PTFE (polytetrafluoroethylene); PSt (polystyrene); PPO (poly(phenylene oxide)); Cyanate ester (1,1-bis(4-cyanatophenyl) ethane with 2% cobalt naphthenate); Aliphatic acrylate (2-propenoic acid(octa-hydro-4,7-methano-1H-indenediyl)-bis(methylene)ester); BisA Ep (bisphenol A diglycidyl ether(Ep828) with 2% 2-butynyl-tetramethylene sulfonium hexafluoro antimonate(acid catalyst)); Alicyclic Ep (3,4-epoxy-cyclohexyl-3,4-epoxycyclohexanecarboxylate with 2% acid catalyst).

the solvent. BVPE was a mixture of *p,p*-isomer, *m,m*-isomer, and *m,p*-isomer. The yield was 63.3 g (90%).

ANAL. Calcd. for $\text{C}_{18}\text{H}_{18}$: C, 92.3%; H, 7.7%. Found: C, 92.0%; H, 7.7%. $^1\text{H-NMR}(\text{CDCl}_3)$: σ 6.7 ppm (2H, vinyl- α H), 5.7, 5.2 ppm (2H, vinyl- β H), 7.1–7.35 ppm (8H, arom), \sim 2.9 ppm (4H, ethylene).

Molding procedure

CBVPE resins modified with PPO were molded by the following procedure. Poly(phenylene oxide) (PPO) was dissolved in chloroform. BVPE and the curing agent were mixed with the polymer solution. The

TABLE I
Properties of CBVPE Resin Modified with PPO

	100	70	50	30	0
BVPE	100	70	50	30	0
PPO	0	30	50	70	100
25B ^a	0	1	1	1	0
ϵ (10 GHz)	2.50	2.45	2.43	2.43	2.41
$\tan \delta$ (10 GHz)	0.0012	0.0015	0.0019	0.0020	0.0022
Tensile strength (MPa)	32	75	79	78	79
Elongation (%)	<2	26	27	47	123
Peel strength (kN/m)	0.3	0.8	1.0	1.2	1.5
Tg (DMA, $^{\circ}\text{C}$)	>400	219	222	219	229

^a 2,5-dimethyl-2,5-(*t*-butylperoxy)hexyne-3

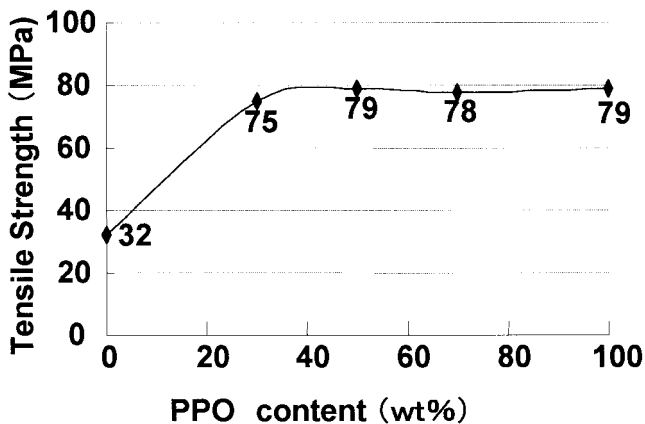


Figure 7 Tensile strength of modified CBVPE resin.

mixture was coated on a polyimide film and then dried by multistage heating at room temperature/120 min and 90°C/30 min. The dried mixture was peeled from the polyimide film and filled into a spacer. The mixture was molded by multistage heating (120°C/30 min, 150°C/30 min, and 180°C/100 min) and pressing (1.5 MPa) *in vacuo*.

CBVPE resins and other thermosetting resins were molded in spacers with multistage heating at 120°C/30 min, 150°/30 min, and 180°C/100 min under nitrogen atmosphere without press pressure. The molding conditions of PPO were 280°C and 1.5 MPa *in vacuo*. The resulting molded resins were about 1.0 mm thick.

RESULTS AND DISCUSSION

Thermal properties of cured BVPE resin

Figure 1 shows the DSC curve of BVPE monomer without curing agent. The monomer is a mixture of *p,p*-isomer, *m,p*-isomer, and *m,m*-isomer. The melting

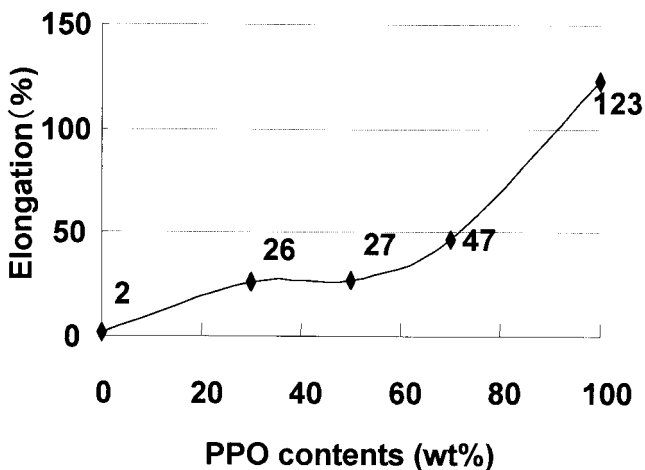


Figure 8 Elongation of modified CBVPE resin.

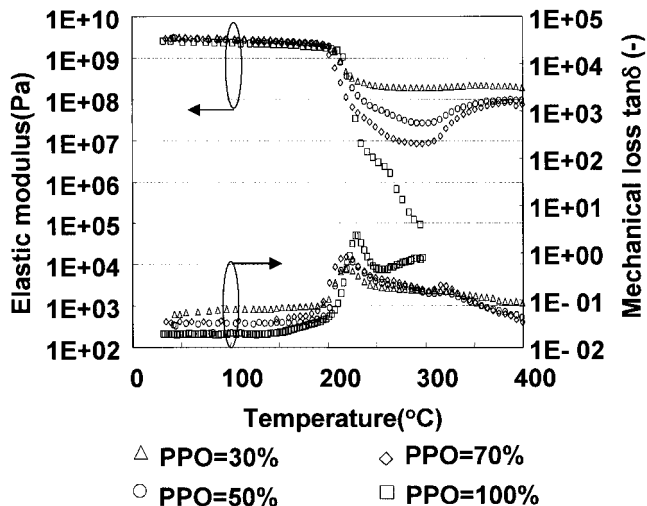


Figure 9 Dynamic mechanical analysis of modified CBVPE resin.

point of the *p,p*-isomer is about 93°C.⁹ The *m,p*- and *m,m*-isomers are liquids at room temperature. The DSC curve of BVPE showed a broad endothermic peak at about 50°C. It is considered that this endothermic temperature, which corresponds to the melting point of BVPE, was lower than that of the *p,p*-isomer because the *m,p*- and *m,m*-isomers acted as a solvent for the *p,p*-isomer. The onset point and the exothermic peak for the thermal cure of BVPE were observed at about 145°C and 170°C, respectively. These results suggest that BVPE may be a suitable molding material, because it was cured at a comparatively low temperature and there was a wide range between the melting point and the onset point for the thermal cure. This monomer was a low-viscosity liquid at 50°C to 145°C, and therefore it can be molded into any form.

CBVPE resin showed excellent thermal resistance. Figure 2 shows the elastic modulus and mechanical loss of CBVPE resin and polystyrene. While the Tg of

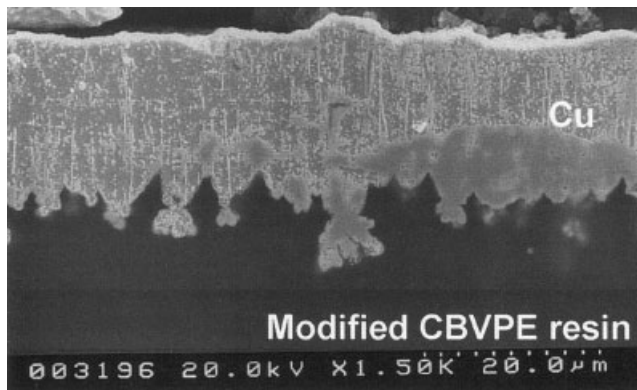


Figure 10 SEM of the interface between copper foil and CBVPE resin modified with 50 wt % PPO.

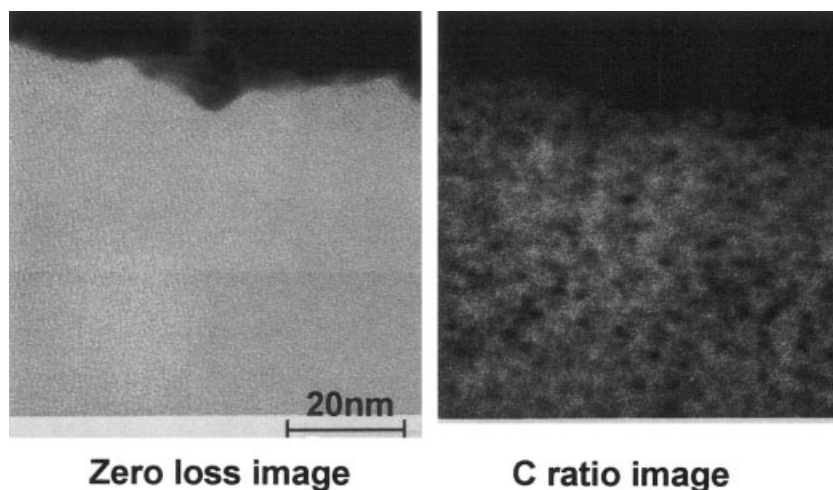


Figure 11 Transmission electron micrograph of modified CBVPE resin modified with 50 wt % PPO.

polystyrene was observed at 113°C, that of CBVPE resin was above 400°C. Figure 3 shows the TGA curves of CBVPE resin and polystyrene: 5 wt % weight-loss temperature of CBVPE resin was about 425°C under a nitrogen atmosphere, while that of polystyrene was about 380°C. The cured resin showed excellent thermal resistance even in an air atmosphere, and 5 wt % weight-loss temperature was about 425°C. CBVPE resin has a structure composed of two crosslinking points per monomer unit, and the depolymerization of the resin is considered to be retarded, resulting in higher thermal stability compared to linear polystyrene. We believe that the thermal properties are sufficiently good values for use as insulation materials for electronic parts.

Dielectric properties of BVPE

The dielectric constants (ϵ) and the dielectric loss tangents ($\tan \delta$) at various frequencies for CBVPE resin without curing agent are shown in Figure 4. The values of ϵ for CBVPE resin and polystyrene decreased with an increase in measurement frequency, while the $\tan \delta$ increased. The values of ϵ and $\tan \delta$ were 2.50–2.64 and 0.0004–0.0012, respectively. These values of CBVPE resin were somewhat higher than those of polystyrene. This result may originate from differences in the amount of impurities and the density between CBVPE resin and polystyrene. The density of crosslinked BVPE resin might be higher compared to that of linear polystyrene. We studied impurities that influence the dielectric properties. Hardly any impurities, metal salts such as MgCl_2 and multistage heating VBCMgSO_4 , were detected by elemental analysis in CBVPE resin. VBC, as a contaminant in BVPE monomer, was presumed to influence the dielectric properties of CBVPE resin. The influence of concentrations of VBC in CBVPE resin on the dielectric prop-

erties is shown in Figure 5. The ϵ and $\tan \delta$ of CBVPE resin increased with an increase in VBC concentrations. The $\tan \delta$ of CBVPE resin increased 0.0012 to 0.0208 with 42 mol % VBC content. The average increment of $\tan \delta$ with 1 mol % VBC content was 0.0005. Increased VBC content gave more influence to $\tan \delta$ than to ϵ . This result suggests that the $\tan \delta$ of CBVPE resin increased by a small amount of impurity: careful purification of BVPE monomer is necessary to improve the dielectric properties of CBVPE resin. However, even the $\tan \delta$ (0.0012) of CBVPE resin under the present conditions was sufficiently low compared with other crosslinked resins. Figure 6 shows the dielectric properties of various linear and crosslinked resins at 10 GHz. CBVPE resin showed the lowest $\tan \delta$ among other crosslinkable resins examined. Such a low $\tan \delta$ of CBVPE is concluded to be induced by the resin structure containing no heteroatoms.

Modification of CBVPE resin

CBVPE resin had low mechanical properties: the tensile strength and elongation of the resin were 32 MPa and <2%, respectively. We studied toughening of CBVPE resin using poly(phenylene oxide) (PPO) as a modifier. PPO has good compatibility with polystyrene and good dielectric properties. It was expected that BVPE monomer and CBVPE resin, having a structure similar to polystyrene, would show good compatibility with PPO. The ϵ and $\tan \delta$ of PPO at 10 GHz were 2.41 and 0.0022, respectively. Various properties of CBVPE resins modified with PPO are summarized in Table I. PPO was an effective modifier for toughening of CBVPE resin. The tensile strength and elongation of the modified resin—75–79 MPa and 26–47%, respectively—are shown in Figures 7 and 8. The mechanical properties of CBVPE resin were greatly improved by modification with PPO. Modified CB-

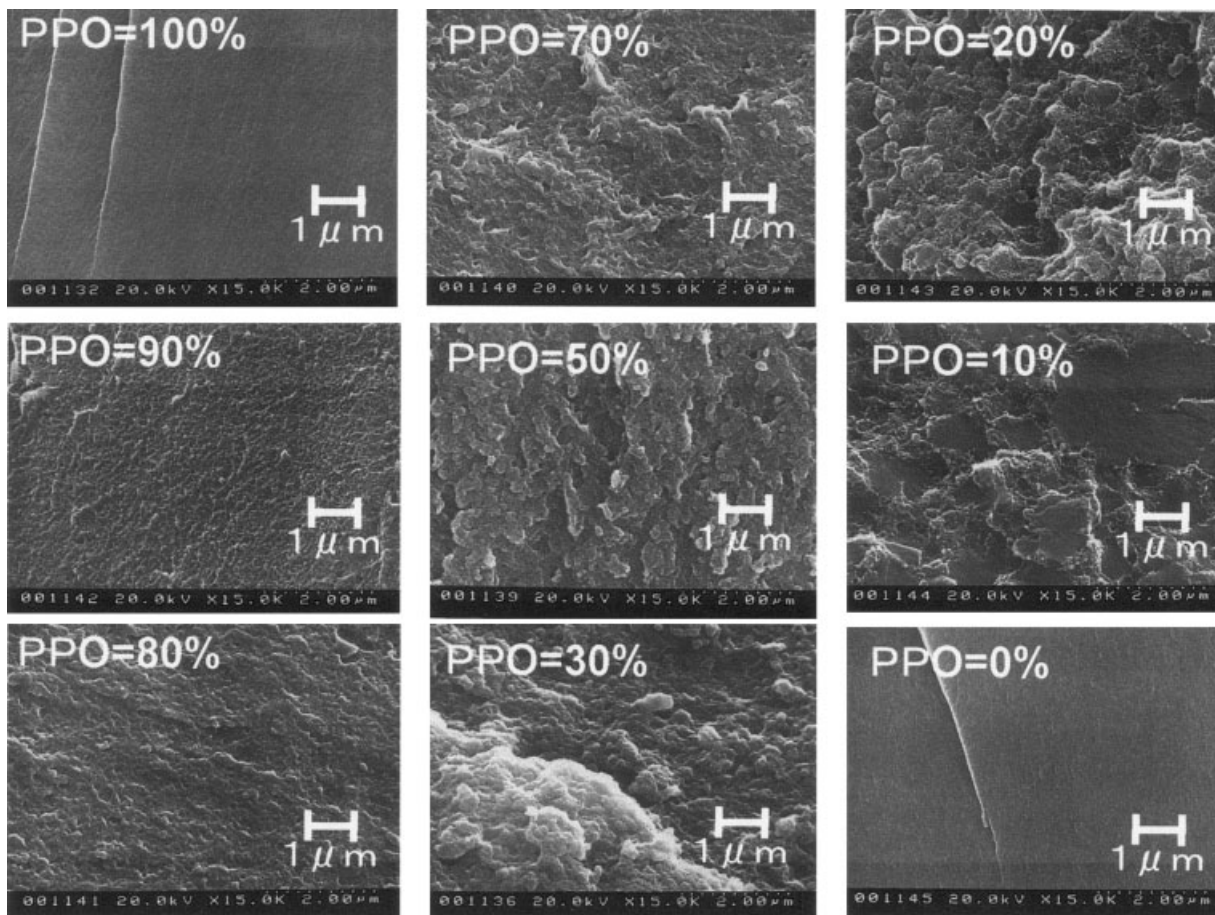


Figure 12 SEMs of fracture surfaces of modified CBPVE resin.

VPE resin showed tensile strength near that of PPO and an intermediate value in elongation between unmodified CBVPE resin and PPO. It seemed that the increased tensile strength of modified CBVPE resin was brought about by the high tensile strength of PPO.

Figure 9 shows the DMA curves of modified CBVPE resins. The T_g of the modified resin was about 220° without depending on the content of PPO. The T_g of the modified resin was lower compared to the T_g ($>400^\circ\text{C}$) of the unmodified resin and, moreover, was somewhat lower than that of PPO (229°C). An increase in elastic modulus for the resin modified with 50 to 70 wt % of PPO was observed over 300°C . The increased elastic modulus at high temperature suggests that reaction intermediate BVPE oligomers or BVPE monomer remain in the modified CBVPE resin. The polymerization and/or crosslinking of BVPE monomer or BVPE oligomers may be retarded in the latter half of the reaction, which proceeds in the solid phase containing PPO. The decreased T_g of modified CBVPE resin is attributed to remaining BVPE monomer and oligomers, which work as a plasticizer for PPO. Furthermore, it is conceivable that remaining BVPE monomer and oligomers contribute to the improvement of the elongation of modified CBVPE resin.

The peel strength between copper foil and modified CBVPE resin increased with increasing PPO concentration. The peel strength ($0.8\text{--}1.2\text{ kN/m}$) was intermediate between that of CBVPE resin and PPO. A sectional photograph between the interface of the copper foil and modified CBVPE resin is shown in Figure 10. The moderate peel strength is considered to originate from the physical connection between the resin and the rough-face of the copper foil and the peel strength became high as the elongation of the modified resin became high.

Modified CBVPE resin was light yellow and transparent. But we presumed the modified resin had a continuous phase structure of PPO because the tensile strength and T_g of the modified resin was dependent on those of PPO even at low PPO concentration (30 wt %). If PPO were dispersed as fine spherical particles in CBVPE matrix, no significant improvement of the strength of the modified resin would be expected. Also, it is conceivable that the T_g of modified CBVPE resin would be intermediate between that of CBVPE resin and PPO, if the modified resin had a completely homogeneous phase and an IPN (interpenetrating polymer network) structure. It is also conceivable that the separated phase was nanometer level in size be-

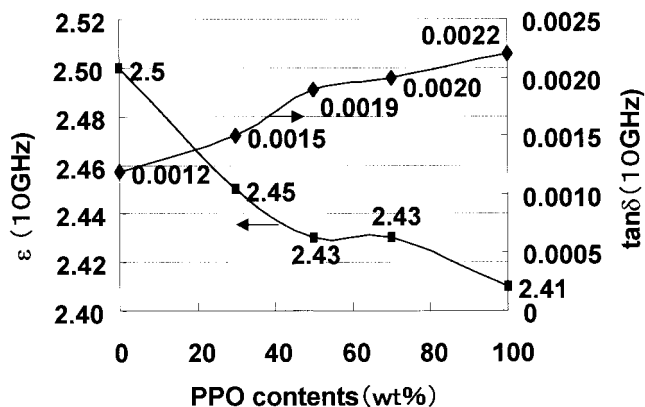


Figure 13 Dielectric properties of modified CBVPE resin.

cause the modified resin was transparent. Figure 11 shows zero loss image and C ratio image of CBVPE resin modified with 50 wt % PPO, analyzed by transmission electron micrography. The C ratio image shows distribution of carbon atoms in the modified resin: the white parts are carbon-rich phases and the black parts are oxygen-rich phases. This figure confirms that the oxygen-rich phases, that is, PPO-rich phases, are dispersed in the carbon-rich phases (CBVPE resin phases) at the nanometer level. The fracture surfaces of modified CBVPE resin are shown in Figure 12. Rough phases were observed at the fracture surfaces of the modified resin, while the fracture surfaces of the unmodified resin and PPO showed smooth phases. This result also showed that the modified resin had a heterogeneous phase structure.

The electric properties of modified CBVPE resin are shown in Figure 13 and summarized in Table I. The modified resin showed slightly higher $\tan \delta$ (0.0015–0.002 at 10 GHz) and slightly lower ϵ (2.43–2.45 at 10 GHz) than those of the unmodified resin. The modified resin had excellent dielectric properties, which were intermediate between those of CBVPE resin and

PPO. CBVPE resin modified with PPO showed not only excellent dielectric properties but also good thermal stabilities and practical toughness.

CONCLUSION

1,2-Bis(vinylphenyl)ethane (BVPE) could be cured at 180°C without curing agents. Cured BVPE (CBVPE) resin had an extremely low dielectric constant ($\epsilon = 2.50$ at 10 GHz) and low dielectric loss tangent ($\tan \delta = 0.0012$ at 10 GHz), compared with conventional thermosetting resins. CBVPE resin had good thermal resistance: The thermal decomposition (5 wt % weight loss) temperature of CBVPE resin under nitrogen atmosphere and air atmosphere was 425°C. The glass transition temperature of the resin was over 400°C. The mechanical properties of the resin could be improved by modification with PPO. The tensile strength and Tg of CBVPE resin modified with PPO were compared to those of PPO. On the other hand, the dielectric properties, elongation, and peel strength of modified CBVPE resin were intermediate between those of unmodified CBVPE resin and PPO.

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