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Mechanical and Dielectric Properties of a New Polymer Blend Composed of 1,2-Bis(vinylphenyl)ethane and Thermosetting Poly(phenylene ether) Copolymer Obtained from 2,6-Dimethylphenol and 2-Allyl-6-methylphenol

Jun NUNOSHIGE,[1,2,†] Haruo AKAHOSHI,[2] Yonggui LIAO,[3] Shin HORIUCHI,[3]
Yuji SHIBASAKI,[4] and Mitsuru UEDA[4]

[1]*Japan Chemical Innovation Institute, Tokyo Institute of Technology,*
2-12-1 O-okayama, Meguro-ku, Tokyo 152-8552, Japan
[2]*Hitachi Research Laboratory, Hitachi Ltd., 7-1-1 Omika, Hitachi 319-1292, Japan*
[3]*Nanotechnology Research Institute, National Institute of Advanced Industrial Science and Technology (AIST),*
1-1-1 Higashi, Tsukuba 305-8565, Japan
[4]*Department of Organic and Polymeric Materials, Tokyo Institute of Technology,*
2-12-1 O-okayama, Meguro-ku, Tokyo 152-8552, Japan

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ABSTRACT: A novel low-dielectric-loss thermosetting material was developed by blending poly(2-allyl-6-methylphenol-co-2,6-dimethylphenol) (Allyl-PPE) with 1,2-bis(vinylphenyl)ethane (BVPE). BVPE could be used effectively as a crosslinking agent for Allyl-PPE, decreasing the cured temperature to 250 °C or lower. The cured products exhibited better thermal and thermomechanical properties than those of non-functionalized-PPE/BVPE blends because of the homogeneity of the cured products. The phases-separated morphologies with small domain sizes less than 10 nm could be observed by employing energy-filtering transmission electron microscopy. The effect of the composition of the blends on the dielectric constant and the dielectric loss were also evaluated. [doi:10.1295/polymj.PJ2006280]

KEY WORDS Insulating Material / Low Dielectric Loss / Poly(phenylene ether) / 1,2-Bis(vinylphenyl)ethane / Thermosetting Resin / Polymer Alloy /

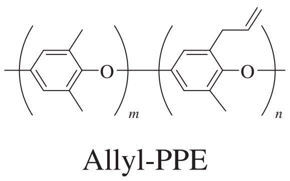
In recent years, an operating frequency at GHz bands has been frequently used for the signals in communication equipments such as portable telephones, and the working frequency (f) is believed to be much higher in the future due to the increasing demands for the communication with large amount of information. Dielectric loss is caused by the capacitive effect of the dielectric material, and it should be kept in low not to lose the electric current. A dielectric loss (α) of an insulating material is expressed with the dielectric constant (ε') and the dielectric loss tangent ($\tan\delta$) by the following equation (1).

$$\alpha \propto \sqrt{\varepsilon'} \cdot \tan\delta \cdot f \qquad (1)$$

To avoid large α, it is necessary to develop a novel insulating material with a low ε' and $\tan\delta$. Many low-dielectric-constant polymers, such as polyimides, poly(aryl ether)s, poly(ether ketone)s, heteroaromatic polymers, fluoropolymers and so on, have been proposed as insulating materials.[1–5] Among them, poly(2,6-dimethyl-1,4-phenylene ether) (PPE) is one of the best candidates because of its excellent dielectric properties, ε' of 2.5 and $\tan\delta$ of 0.002 (at 10 GHz).[6] However, its glass transition temperature is around 210 °C, which is inadequate for a lead-free process.

To improve this property, we previously reported a synthesis of thermosetting PPE resins, poly(2-allyl-6-methylphenol (AMP: 10 mol %)-co-2,6-dimethylphenol (DMP: 90 mol %)) (Allyl-PPE), by oxidative coupling copolymerization of DMP with AMP (Scheme 1).[7] Using large amounts of pyridine, Allyl-PPEs with narrow molecular weight distributions (MWDs) were obtained, which showed low dielectric losses ($\varepsilon' = 2.4$, $\tan\delta = 0.002$ at 10 GHz) than the copolymers with broad MWDs, probably because of the suppression of the branch vibration in the polymers.[8] Allyl cross-linking reaction, however, required high temperature curing around 260–300 °C, and the ε' and $\tan\delta$ of the resulting polymer were still high.

1,2-Bis(vinylphenyl)ethane (BVPE) is a difunction-



Scheme 1. Chemical structures of poly(2-allyl-6-methylphenol-*co*-2,6-dimethylphenol) (10 wt % 2-allyl-6-methylphenole) (Allyl-PPE).

[†] To whom correspondence should be addressed (Tel: +81-3-5734-2128, Fax: +81-3-5734-2128, E-mail: jnunoshige@polymer.titech.ac.jp).

al styrenic monomer that can be cured without curing agents at relatively low temperatures, showing a low dielectric loss ($\varepsilon' = 2.5$, $\tan\delta = 0.0012$ at 10 GHz) with excellent thermal properties.[9] Although a low-dielectric loss material consisting of PPE and BVPE has been reported, the molded compounds had a segregated structure, which spoiled the electric and mechanical properties of the resulting material.[9] We expected that Allyl-PPE could suppress such a phase separation when molded with BVPE because of copolymerization of Allyl-PPE with BVPE. We here report the synthesis of Allyl-PPE, the dielectric loss and thermal properties, and phase-separated morphologies of the blends with BVPE.

EXPERIMENTAL

Materials

DMP was purified by recrystallization from n-hexane. AMP, PPE ($M_n = 23000$, MWD = 2.7), copper chloride (I) (CuCl(I)) were purchased from Sigma-Aldrich Co. Vinylbenzyl chloride (70% m-isomer and 30% p-isomer) (VBC) was purchased from Tokyo Chemical Industry Co., Ltd. Dehydrated toluene, pyridine and tetrahydrofuran were purchased from Wako Pure Chemical Industries, Ltd. Other solvents and reagents were used as received.

Synthesis of Allyl-PPE

Allyl-PPE was prepared by the reported method.[7] A two-necked flask equipped with an oxygen inlet tube and a septum cap was charged with copper (I) chloride (0.04 g, 0.4 mmol), magnesium sulfate (6.0 g, 49.8 mmol), dry pyridine (100 mL 1.2 mol), and dry toluene (100 mL). The mixture was stirred at 25 °C under a stream of oxygen (50 mL/min), yielding a deep-green copper-pyridine complex catalytic solution. To this solution was added a solution of DMP (3.3 g, 27.0 mmol) and AMP (0.45 mL, 3.0 mmol) in toluene (50 mL). The mixture was stirred for 90 min under a stream of oxygen (50 mL/min), and then poured into methanol (1000 mL) containing concentrated 10 M HCl (5 mL) (MeOH/HCl solution). The precipitate was washed with methanol in several times, dissolved in chloroform, and reprecipitated in MeOH/HCl solution. After washing with methanol and drying at 80 °C for 3 h and 110 °C for 6 h under vacuum, a white fibrous polymer was obtained. (Yield: 3.37 g, 91%, $M_n = 24{,}000$, $M_w/M_n = 2.4$).

IR (KBr, ν, cm^{-1}): 1192 (Ar–O–Ar), 914 and 984 (C=C). ^{1}H NMR (CDCl$_3$, δ, ppm): 6.47 (s, 2H, Ar), 5.84 (m, 0.1H, Ar–CH$_2$–**CH**=CH$_2$), 4.99 (m, 0.2H, Ar–CH$_2$–CH=**CH$_2$**), 3.21 (m, 0.2H, Ar–**CH$_2$**–CH=CH$_2$), and 2.09 (m, 5.7H, Ar–**CH$_3$**). ^{13}C NMR (CDCl$_3$, δ, ppm): 16.77, 113.80, 114.41, 114.74, 116.02, 132.51, 132.78, 134.55, 136.17, 144.88, 145.39, 154.69, and 154.91.

Anal. Calcd. for $[(C_8H_8O)_9\text{-co-}(C_{10}H_{10}O)_1]$: C, 92.3%; H, 7.7%; Found: C, 92.2%; H, 7.8%.

Synthesis of BVPE

BVPE was prepared by the reported method.[8] A 500 mL three-necked flask equipped with a nitrogen inlet tube, a 100-mL dropping funnel, and a condenser was charged with magnesium turnings (4.02 g, 0.16 mol) and dry tetrahydrofuran (300 mL). The mixture was stirred and cooled to −5 °C. VBC (45.8 g, 0.30 mol) 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 200 mL of hexane. The hexane solution was then washed with aqueous 1 M 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 the solvent. BVPE was a mixture of *p*,*p*-isomer, *m*,*m*-isomer, and *m*,*p*-isomer. (Yield: 31.8 g, 91%).

IR (KBr, ν, cm^{-1}): 906 and 991 (C=C). ^{1}H NMR (CDCl$_3$, δ, ppm): 7.00–7.35 (8H, multiplet, Ar), 6.69 (2H, Ar–**CH**=CH$_2$), 5.71, 5.21 (2H, Ar–CH=**CH$_2$**), 2.90 (4H, Ar–**CH$_2$**–**CH$_2$**–Ar). ^{13}C NMR (CDCl$_3$, δ, ppm): 141.90, 141.86, 137.59, 137.57, 136.90, 136.63, 135.35, 128.60, 128.50, 127.98, 126.36, 126.19, 123.89, 123.88, 113.66, 113.00, 37.75, 37.56 and 37.49.

Anal. Calcd. for $C_{18}H_{18}$: C, 92.3%; H, 7.7%. Found: C, 92.1%; H, 7.8%.

Molding of Polymer and Polymer Blends

The polymer blends (BVPE and PPE, BVPE and Allyl-PPE) were molded by the following procedure. PPE or Allyl-PPE and BVPE were dissolved in chloroform. The mixture was dried on a PTFE film at room temperature, and at 90 °C for 30 min. The dried mixture was molded by multistage heating (120 °C for 30 min, 150 °C for 30 min, and 230 °C for 60 min) under pressing (1 MPa) in a vacuum condition. Homogeneous PPE and Allyl-PPE resin were molded by single step heating (230 °C for 60 min) under pressing (1 MPa) in a vacuum condition. BVPE resin was molded in spacers with multistage heating (120 °C for 30 min, 150 °C for 30 min and 230 °C for 60 min) under nitrogen atmosphere without pressure. All samples were cooled down with water jacket in the vacuum press. The thickness of these molded films was about 1.0 mm. To measure the tensile strength and the dynamic mechanical properties, the sample was cut out to the width of 5 mm. To measure the dielectric loss, the sample was cut out to the width of 1.5 mm.

IR Measurement

Samples for IR measurement were prepared by the following procedure. Allyl-PPE and the polymer blends were dissolved in toluene (20 wt %). The solution was cast on a Si wafer (1000 rpm, 30 sec) and heated under nitrogen (210–260 °C for 60 min). BVPE was heated on a slide glass under nitrogen (120–260 °C for 60 min). Pulverized fragment of Cured BVPE was mixed with KBr tablet.

Energy-filtering Transmission Electron Microscopy (EFTEM)

An LEO922 in-column-type energy-filtering transmission electron microscope with a LaB6 cathode equipped with an Omega-type energy spectrometer was used at an accelerating voltage of 200 keV. To obtain high-resolution elemental maps and to perform quantitative chemical analysis, we employed the Image-EELS technique. The detailed instrumental setup and the scheme of the process were described in the previous papers.[10–13]

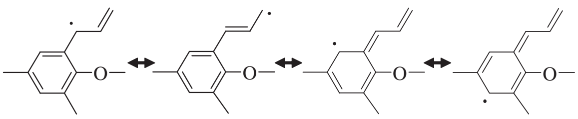
Measurements

Infrared spectra were recorded on a Horiba FT-720 spectrophotometer. ^{1}H and ^{13}C NMR spectra were recorded using a BRUKER DPX300 (300 MHz) spectrometer. Thermogravimetry (TG) and dynamic mechanical analysis (DMA, 0.02 Hz) were performed with a Seiko TG/DTA 6300, TMA/SS 6100, heating rate of 5 °C/min under nitrogen, respectively. Number- and weight-average molecular weights (M_n and M_w) were determined by a gel permeation chromatograph (GPC) on a Jasco GULLIVER 1500 system equipped with a polystyrene gel column (Plgel 5 mm MIXED-C) eluted with chloroform at 40 °C at a flow rate of 1.0 mL/min calibrated by standard polystyrene samples. Tensile strength and elongation were measured with a Shimadzu autograph AGS-100G. 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 at room temperature.

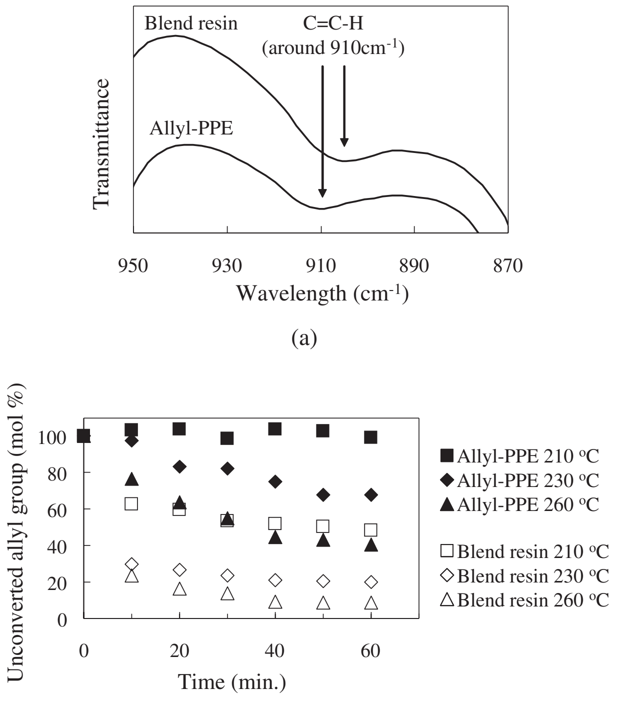
RESULTS AND DISCUSSION

Thermosetting Reaction of Allyl PPE with BVPE

Allyl-hydrogen abstraction occurs thermally, and the produced allyl radical is capable of abstracting hydrogen from hydrocarbons and of adding to olefinic double bonds; thus, Allyl-PPE possesses thermosetting property. However, the high curing temperature was needed for the thermosetting reaction, mainly because of the resonance stabilization of phenylallyl radicals (Scheme 2). To lower the curing temperature, Allyl-PPE was blended with BVPE as a cure promoter. AllyPPE was prepared according to the reported procedure.[8] The progress of thermosetting reaction of Allyl-PPE alone and that blended with BVPE (50 wt %) were monitored by the decrease of the absorption at 910 cm^{-1} corresponding to the C=C stretching in the IR spectrum as shown in Figure 1a, and the temperature dependence of cross-linking reaction is shown in Figure 1b. The cross-linking of Allyl-PPE does not proceed at 210 °C, and the consumption of vinyl groups was less than 60% even at 260 °C for 1 h curing. Meanwhile, because of the high reactivity of styryl group, the absorption rapidly decreases when 50 wt % of BVPE is added to Allyl-PPE. The vinyl groups of 95% is consumed for 1 h in the blended res-



Scheme 2. Resonance structures of intermolecular allyl radical.



(a)

(b)

Figure 1. (a) IR spectrum of Allyl-PPE alone and that blended with BVPE (50 wt %) (Monitored by the absorption at 910 cm^{-1} corresponding to the C=C stretching). (b) Change of cross-linking reaction with time (Allyl-PPE and that blend with BVPE (50 wt %)). The decrease of vinyl group's absorption came from Allyl-PPE and BVPE (around 910 cm^{-1}) and the absorption was corrected by other absorption (1191 cm^{-1} (Ar–**O**–Ar)).

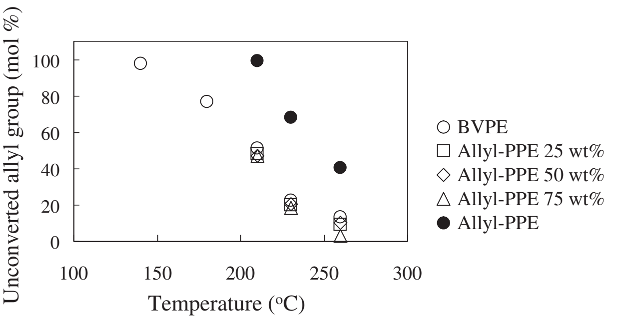


Figure 2. Temperature dependence of crosslinking reaction (molded for 60 min). The decrease of vinyl group's absorption came from allyl group (Allyl-PPE) and styryl group (BVPE) (around 910 cm^{-1}). The absorption was corrected by other absorption (Allyl-PPE and blend resins: 1191 cm^{-1} (Ar–**O**–Ar), BVPE: 713 cm^{-1} (**Ar**)).

in cured at 260 °C, indicating BVPE effectively functions as a cure promoter.

Figure 2 shows the dependence of the thermosetting reaction of blended resins with various compositions on the curing temperature. While the reaction in Allyl-PPE alone is slow, those in all the blended resins quickly proceed. Johansson *et al.* reported that no chain transfer reaction was observed for the free-radical polymerization of styrene in the presence of allyl ethers,[14] from which we could expect that BVPE should be polymerized independently on the amounts of Allyl-PPE. Contrary to what is expected, almost complete consumption of vinyl groups is observed for the blended resin composed of 22 mol % of allyl groups with 78 mol % of styryl groups (Allyl-PPE blended with BVPE(25 wt %)), and the more vinyl groups is remained in the blended resins with less amounts of Allyl-PPE. These results indicate that Allyl group in Allyl-PPE is consumed during the curing with BVPE, and the thermosetting reaction proceeds more effectively with larger amounts of Allyl-PPE, which could act as a diluting agent for the thermosetting of BVPE. Moreover, the molded Allyl-PPE films containing BVPE are insoluble in any organic solvents such as chloroform and heated toluene. The higher vinyl conversion results in higher thermal stability of the resins as shown in Figure 3.

The mechanical properties of the polymer films were first investigated by dynamic mechanical analysis. Figure 4 depicts the dependence of the storage modulus (E') and the storage loss tangent ($\tan\delta$) on the temperature. All samples show softening temperature at 210 °C, corresponding to the glass transition of PPE backbone, which indicates the existence of PPE and cured BVPE domains. The E' of Allyl-PPE homopolymer rapidly decreases just after the T_g, but Allyl-PPE resins blended with BVPE maintains the E' value even above 210 °C. These results clearly indicate that Allyl-PPE resins are reinforced by the addition of BVPE.

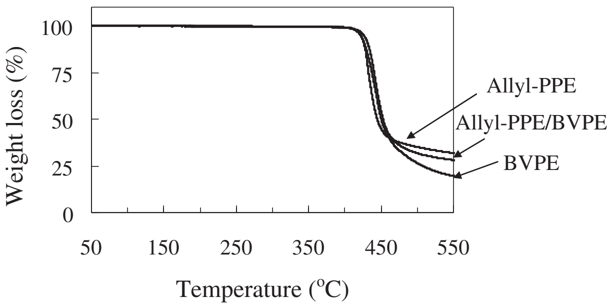


Figure 3. TGA trace for molded Allyl-PPE/BVPE (Allyl-PPE: 50 wt %), Allyl-PPE and BVPE.

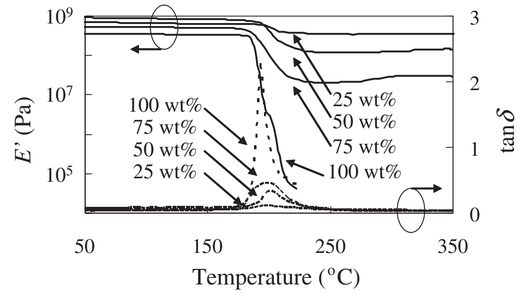


Figure 4. Dynamic mechanical analysis measurement of molded Allyl-PPE/BVPE (Allyl-PPE: wt %).

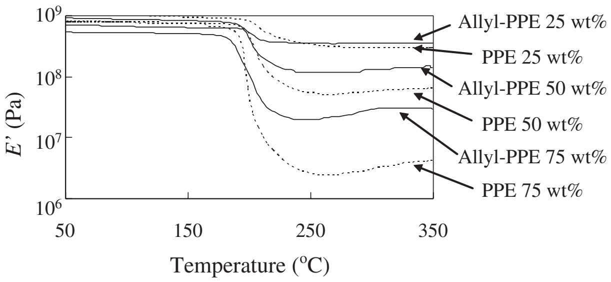


Figure 5. The dynamic mechanical properties of Allyl-PPE/BVPE and PPE/BVPE. (measured by TMA/SS).

The dynamic mechanical properties of Allyl-PPE- and PPE-based resins are shown in Figure 5. In any composition, Allyl-PPE-based resin shows better mechanical properties than PPE-based one. Allyl group gives better miscibility to BVPE resin, which might be caused by the chemical or physical binding between these two resins. Consequently, the segregated domain size in Allyl-PPE resin blended with BVPE could be much smaller than that in the PPE with BVPE because the final E' of the former resin was higher than that of the latter one.

Mechanical Properties of the Molded Resin

Cured BVPE has low mechanical properties and is comparatively fragile. However, BVPE has good

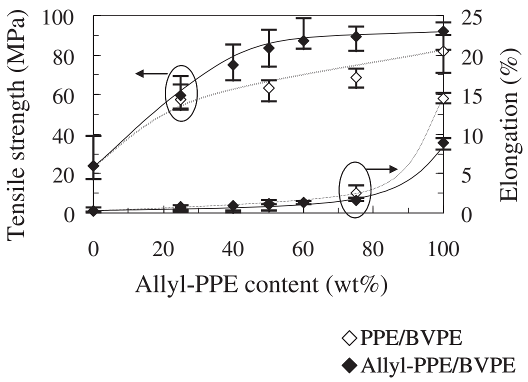


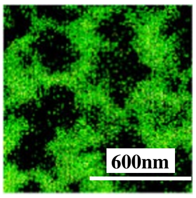
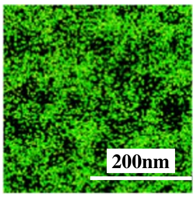
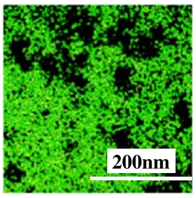
Figure 6. Tensile strength and elongation measurements of molded PPE/BVPE and Allyl-PPE/BVPE.

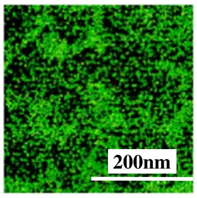
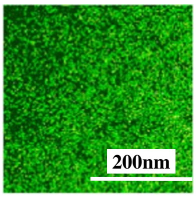
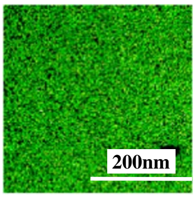
compatibility with PPE resin, so the mechanical properties would be improved by blending with PPE. Further mechanical properties of the films are collected with a tensile instrument as shown in Figure 6. Increasing the amounts of BVPE, the elongation and the tensile strength of the films based on PPE with BVPE are decreased. On the other hands, the tensile strength of Allyl-PPE film containing BVPE below 50 wt % maintains more than 95% of the original strength. This indicates that the two polymers are well miscible each other to form the segregated domains whose size is much smaller than that in PPE with BVPE.

Characterization of the Phase-Separated Morphologies

The blends of PPE/BVPE and Allyl-PPE/BVPE are transparent even after the curing, which suggests the high compatibility or the comparable refractive indices between the components. The phase-separated morphologies of the blends could not be observed by conventional transmission electron microscopy (TEM). However, the oxygen distribution images created by EFTEM clearly reveal the phase separation of the blends, which can be characterized as oxygen-rich and -poor regions. Moreover, the compositional differences in the two phases can be estimated from the integrated intensities of oxygen ionization edges (O K-edges) by EELS acquired from the two regions. The detailed process for acquiring the elemental maps and for estimating the elemental ratios between the two phases by EELS have been shown in our previous papers.[10–13] Table I summarizes the oxygen distribution images and the ratios of the oxygen concentrations of the two blend series obtained by EFTEM. Clear large domains are observed in the films containing PPE and BVPE, where the size of the domains is in the range of 100 to 300 nm. On the other hand, no segregations are observed in Allyl-PPE containing blends when Allyl-PPE content is higher than 50 wt %. And, it was difficult to confirm not only the phase-separated structures but also the differences of the oxygen concentrations. This result indicates a very small phase separation (<10 nm) existed in the blend resin along with the result of the glass transition temperature measured by DMA. The differences in the mechanical properties of the samples seem to be attributed to the appearance of the phase-separated structures. The mechanical properties of the blend resin were improved by the good miscibility and the thermosetting reaction.

Table I. Oxygen maps of molded Allyl-PPE/BVPE and PPE/BVPE, and elemental ratio (O-rich/O-poor)

PPE/BVPE	PPE-25 wt %	PPE-50 wt %	PPE-75 wt %
oxygen map			
O-rich/O-poor ratio	2.23	1.41	1.41

Allyl-PPE/BVPE	Allyl-PPE-25 wt %	Allyl-PPE-50 wt %	Allyl-PPE-75 wt %
oxygen map			
O-rich/O-poor ratio	2.52	(not detected)	(not detected)

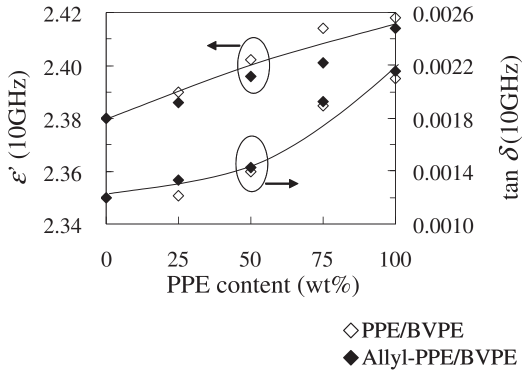


Figure 7. Dielectric properties of molded Allyl-PPE/ BVPE and PPE/BVPE.

Table II. Properties of molded Allyl-PPE/BVPE and PPE/BVPE

BVPE Allyl-PPE	100 0	75 25	50 50	25 75	0 100
ε' (10 GHz)	2.38	2.39	2.40	2.40	2.41
$\tan\delta$ (10 GHz)	0.0012	0.0013	0.0014	0.0019	0.0022
Tensile strength (MPa)	23.7	59.3	83.4	89.2	91.8
Elongation (%)	0.3	0.8	1.1	1.6	8.9
T_g (TMA/SS, °C)	>400	200	201	196	193
T_{d10} (TGA, °C)	428	432	433	430	427

Electric Properties of the Molded Resin

Dielectric constant and the dielectric loss at 10 GHz were measured as the electric properties of Allyl-PPE based samples in Figure 7. These two parameters decrease with increasing the amounts of BVPE because of a lack of heteroatom and of the high cross-linking density, which suppress the vibration of the molecules.

Table II summarized the properties of Allyl-PPE blended with and without BVPE. Cured BVPE possesses poor mechanical strength and toughness, but these properties are improved by blending with Allyl-PPE resin. The blended resins show lower dielectric constant and dielectric loss tangent with excellent thermal stability compared with the other high temperature dielectric loss materials, thus, the blended resin is a good candidate for the next generation insulating material.

CONCLUSIONS

Poly(2-allyl-6-methylphenol-co-2,6-dimethylphenol) (Allyl-PPE) blended with 1,2-bis(vinylphenyl)ethane (BVPE) were molded, and their cross-linking reactions, thermal properties, mechanical properties, phase separations and electric properties were studied. By blending with BVPE, the cross-linking reaction of allyl group in Allyl-PPE efficiently proceeded. The resulting polymer blend showed better thermo-mechanical properties, indicating the better miscibility of the components. The small domain size less than 10 nm was observed by EELS technique. The dielectric constant and dielectric loss were varied by changing the components ratio of Allyl-PPE and BVPE.

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