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High-performance bio-based thermosetting resins based on bismaleimide and allyl-etherified eugenol derivatives

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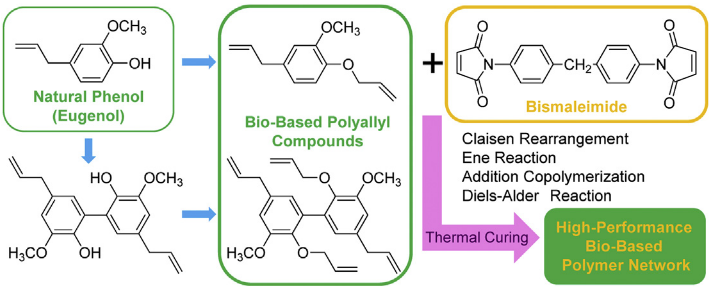
HIGHLIGHTS

- New bio-based thermosetting resins were prepared from eugenol.
- The structure of pyrolyzed allyl-etherified eugenol derivatives was characterized.
- The cured resins showed glass transition temperatures higher than 350 °C.
- The cured resins showed 5% weight loss temperatures higher than 450 °C.
- The cured resins showed superior mechanical properties.

GRAPHICAL ABSTRACT



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ABSTRACT

In this study, eugenol (EG) and bieugenol (BEG) were reacted with allyl bromide in the presence of sodium hydroxide to produce allyl-etherified EG and BEG (AEG and ABEG), respectively. The AEG and ABEG were prepolymerized with 4,4′-bismaleimidodiphenylmethane (BMI) at 160–200 °C and then compression-molded at 250 °C for 5 h to produce cured AEG/BMI (EB) and ABEG/BMI (BB) resins with allyl/maleimide unit ratios of 1/1, 1/2 and 1/3. FT-IR analysis of the cured resins showed that the original allyl and maleimide groups were almost completely consumed during the process and that hydroxy groups were newly formed upon polymerization. Pyrolysis of AEG and ABEG revealed the hydroxy group formation to be caused by the Claisen rearrangement of AEG and out-of-ring Claisen rearrangement of ABEG. Both types of cured resins showed superior glass transition temperatures and 5% weight loss temperatures higher than 350 °C and 450 °C, which are much higher than those of already reported EG/BMI and BEG/BMI cured resins with the same allyl/maleimide ratios. The flexural moduli (2.6–3.1 GPa) of the cured resins were also higher than those of the already reported materials (0.78–2.8 GPa).

1. Introduction

Bismaleimide resins are an important class of high-performance thermosetting polymers that are used as matrices for advanced composites in the aerospace and electronics industries. Cured BMI resins have excellent thermal stability, are flame retardant, and possess electronic properties that are relatively constant over a wide range of temperatures [1]. However, the aromatic nature and the high crosslink density of the cured networks make these materials brittle. Researchers have investigated a range of methods aimed at improving the ductility of BMIs, from blending them with elastomers [2] and engineering thermoplastics [3–5], to co-reacting bismaleimide with multifunctional allyl [6–10], amino

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[11,12] and cyanate [13,14] compounds. Among the techniques investigated, the co-reaction of bismaleimide with polyallyl compounds has become the most reliable method for decreasing brittleness without deteriorating the inherent heat resistance and good processing characteristics of BMI resins. The most popular allyl-compound-modified bismaleimide resin to date is Matrimid 5292 (Ciba–Geigy, Basel, Switzerland), which is composed of a 2,2′-diallylbisphenol A (DABA)/4,4′-bismaleimidodiphenylmethane (BMI) mixture [6]. FT-IR analysis of cured DABA/BMI resin has shown its formation to proceed by an ene reaction followed by chain polymerization [15,16].

In recent years, renewable resource-derived (bio-based) thermosetting resins have attracted a great deal of attention not only as a viable alternative to polymers derived from limited petroleum sources but also because of their unique functional groups and framework characteristics, low cost and possible biodegradability [17–19]. Eugenol (EG, 4-allyl-2-methoxyphenol) is the main component (80 wt%) of clove oil [20]. The fact that EG is relatively cheap (ca. \$5 kg^{-1}) makes it an economically feasible feedstock for the synthesis of bio-based alternatives to DABA [21]. Recently, we reported new bio-based thermosetting bismaleimide resins made with eugenol (EG) and bieugenol (BEG: 3,3′-dimethoxy-5,5′-diallyl-1,1′-biphenyl-2,2′-diol) [22]. The cured EG/BMI and BEG/BMI resins showed higher glass transition temperatures (T_g) and significantly lower flexural strengths and moduli than cured DABA/BMI. It is thought that the higher concentration of allyl functionalities within the eugenol structure, compared to DABA, leads to a higher cross-linking density when reacted with BMI, thereby improving the resin's thermal and mechanical properties. In past studies, Luo et al. reported an improvement of the thermal properties of a cured resin made from allyl-etherified phenol novolac and BMI and attributed it to an increase in the degree of allylation [23]. Gu et al. also reported that cured materials made from allyl-etherified polyaralkylphenolic resin (Xylok) and BMI exhibit superior thermal and mechanical properties [24]. Allyl chloride, which is generally used for allyl-etherification, is industrially produced by the free-radical halogenation of petroleum-based propylene with chlorine. Currently, several strategies, including the fermentation of bio-ethanol and bio-butanol, gasification of biomass to form syngas as a precursor, and the cracking of biomass are being pursued to produce propylene via a renewable and sustainable pathway [25,26]. Therefore, in the near future, it will be possible to utilize allyl halides generated from biologically derived propylene sources in the formation of cured resins. For this reason, the reaction products of EG and BEG with allyl halide, which offer an improvement in the material properties of resins formed from them, also have the potential to be synthesized exclusively using bio-derived reagents.

In this study, allyl-etherified EG (AEG) and allyl-etherified BEG (ABEG) were prepared by the reaction of allyl bromide with EG and BEG, respectively, and the thermal and mechanical properties of the cured resins that resulted from reaction with BMI (AEG/BMI and ABEG/BMI) were investigated (Fig. 1). Several types of reactions, including Claisen rearrangement, ene reaction, Diels–Alder reaction and addition polymerization, have been reported as contributing to the curing mechanism of allylated phenols and maleimides [15,16,22,27–32]. Regarding the Claisen rearrangement of allyl aryl ethers during the curing reaction, it is known that the migrant allyl group preferentially moves to the *ortho*-position or to the *para*-position if both the *ortho*-positions are blocked; migration to a *meta*-position, however, has not been observed [33,34]. The present study also addresses the structural analysis of the pyrolyzed products of AEG and ABEG to address the interesting question of whether the two *ortho*- and one *para*-blocked ABEG undergoes Claisen rearrangement during curing.

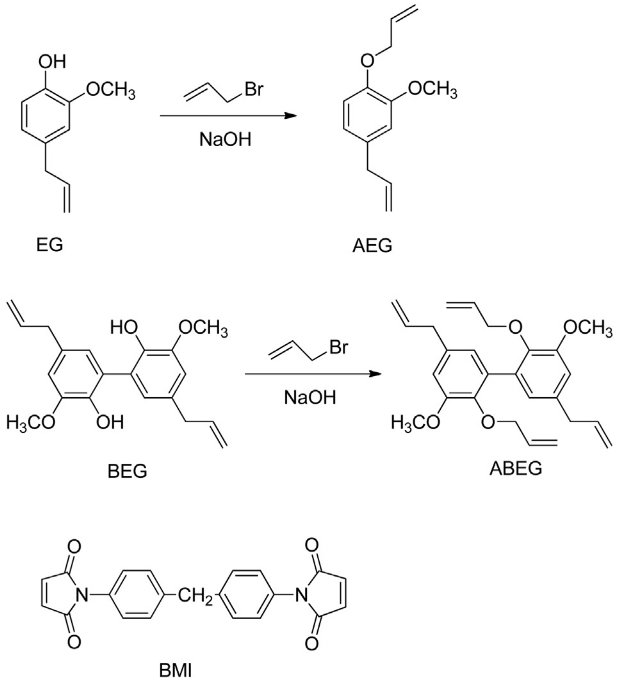

Fig. 1. Synthetic scheme of AEG and ABEG, and structure of BMI.

2. Experimental

2.1. Materials

Eugenol (EG, purity > 98.0% by gas chromatography) and 4,4′-bismaleimidodiphenylmethane (BMI) were purchased from Tokyo Kasei Kogyo Co. Ltd. (Tokyo, Japan). Allyl bromide, sodium hydroxide and dimethyl sulfoxide (DMSO) were purchased from Kanto Chemical Co., Inc. (Tokyo, Japan). BEG was synthesized by an oxidative coupling reaction of EG using potassium hexacyanoferrate, as previously reported [22,35]. All commercially available reagents were used without further purification.

2.2. Synthesis of 1-allyl-4-allyloxy-3-methoxybenzene (allyl-etherified eugenol: AEG)

To a solution of EG (3.28 g, 20.0 mmol) in DMSO (10 mL), pulverized sodium hydroxide (0.880 g, 22.0 mmol) was added, and the resulting mixture was stirred for 10 min. Allyl bromide (2.66 g, 22.0 mmol) was then added dropwise over a period of 1 h at 40 °C. After the addition, the mixture was stirred at 40 °C for 3 h and then at 70 °C for 30 min. The reaction mixture was poured into water and then extracted with chloroform. The organic layer was washed with water twice, dried over sodium sulfate and concentrated in vacuo to yield AEG as a yellow liquid (3.92 g): Yield 96%; ^{1}H NMR (CDCl$_3$, δ) 6.89 ppm (m, 1H, H-*b*), 6.78 (m, 2H, H-*a*, *c*), 6.17 (m, 1H, H-*j*), 6.02 (m, 1H, H-*e*), 5.45 (m, 1H, H-*k*), 5.30 (m, 1H, H-*l*), 5.14 (m, 2H, H-*f*, *g*), 4.66 ppm (m, 2H, H-*i*), 3.95 (s 3H, H-*h*), 3.42 (m, 2H, H-*d*); FT-IR (ATR) 3074, 3028, 2898, 2827, 1637, 1589, 1508, 1464, 1420, 1258, 1229, 1140, 1026, 993, 914, 802, 752 cm^{-1}.

2.3. Synthesis of 3,3′-diallyl-6,6′-diallyloxy-5,5′-dimethoxy-1,1′-biphenyl (allyl-etherified bieugenol: ABEG)

To a solution of BEG (6.52 g, 20.0 mmol) in DMSO (300 mL), pulverized sodium hydroxide (1.76 g, 44.0 mmol) was added, and the mixture was stirred for 10 min. Allyl bromide (5.32 g, 44.0 mmol) was then added dropwise over a period of 1 h at 40 °C. After the addition, the mixture was stirred at 40 °C for 3 h and then at 70 °C for 15 min. The reaction mixture was poured into water and then extracted with chloroform. The organic layer was washed with water two times, dried over sodium sulfate and concentrated in vacuo to give ABEG as a yellow liquid (6.18 g): Yield 76%; ^{1}H NMR ($CDCl_3$, δ) 6.89 ppm (m, 4H, H-*b*, *c*), 6.10 (m, 2H, H-*e*), 5.91 (m, 2H, H-*j*), 5.20 (m, 8H, H-*f*, *g*, *k*, *l*), 4.43 (m, 4H, H-*i*), 4.00 (s, 6H, H-*h*), 3.48 (m, 4H, H-*d*); FT-IR (ATR) 3076, 3001, 2932, 2899, 2831, 1687, 1637, 1580, 1450, 1418, 1265, 1217, 1142, 1047, 989, 914, 750 cm^{-1}.

2.4. Pyrolysis of AEG

AEG (0.910 g, 4.45 mmol) was stirred at 200 °C for 3 h using a Q-Tube pressure reactor (Sigma–Aldrich Corp., St Louis, MO) to give rearranged AEG (rAEG: 2,4-diallyl-6-methoxyphenol) as a yellow oil in a quantitative yield. ^{1}H NMR ($CDCl_3$, δ) 6.60 ppm (s, 1H, H-*b*, *c*), 6.02 (m, 2H, H-*e*, *j*), 5.60 (s, 1H, O*H*), 5.09 (m, 4H, H-*f*, *g*, *k*, *l*), 3.89 (s 3H, H-*h*), 3.44 and 3.33 (m, 4H, H-*d*, *i*); FT-IR (ATR) 3514, 3072, 3001, 2978, 2903, 2843, 1637, 1602, 1495, 1435, 1285, 1230, 1213, 1148, 1074, 995, 908, 843, 756 cm^{-1}.

2.5. Pyrolysis of ABEG

ABEG (0.905 g, 2.23 mmol) was stirred at 200 °C for 3 h in a 30-mL beaker to give rearranged ABEG (rABEG) as a viscous dark brown oil. FT-IR (ATR) 3504, 3444, 3074, 2995, 2931, 2840, 1724, 1637, 1582, 1489, 1460, 1421, 1254, 1219, 1142, 1047, 991, 912, 842, 746 cm^{-1}.

2.6. Preparation of cured resin from AEG and BMI

A mixture of AEG (18.2 g, 89.0 mmol) and BMI (31.9 g, 89.0 mmol) was stirred at 160 °C for 1 h, 180 °C for 1 h, and finally at 200 °C for 1 h to produce a gelatinous material. The pre-polymer that was obtained was compression-molded at 210 °C/8 MPa for 1 h, 220 °C/8 MPa for 2 h, and finally 250 °C/8 MPa for 5 h using a Mini Test Press-10 (Toyo Seiki Co., Ltd, Tokyo, Japan) to produce a cured AEG/BMI with allyl/maleimide ratio of 1/1 (EB11). In a manner similar to the preparation of EB11, the cured resins of AEG/BMI with allyl/maleimide ratios of 1/2 and 1/3 (EB12 and EB13) were also prepared.

2.7. Preparation of cured resins from ABEG and BMI

A mixture of ABEG (18.1 g, 44.5 mmol) and BMI (31.9 g, 89.0 mmol) was melt-mixed at 170 °C and then gradually heated to 200 °C over 1 h to produce a gelatinous material. The pre-polymer that was obtained was compression-molded at 210 °C/8 MPa for 1 h, 220 °C/8 MPa for 2 h, and finally 250 °C/8 MPa for 5 h using a Mini Test Press-10 to produce cured ABEG/BMI with an allyl/maleimide ratio of 1/1 (BB11). Cured resins of ABEG/BMI with allyl/maleimide ratios of 1/2 and 1/3 (BB12 and BB13) were prepared in the same manner.

2.8. Measurements

Proton nuclear magnetic resonance (^{1}H NMR) spectra were recorded on a Bruker AV-400 (400 MHz) NMR (Madison, WI) using $CDCl_3$ as a solvent. FT-IR spectra were measured on an FTIR 8100

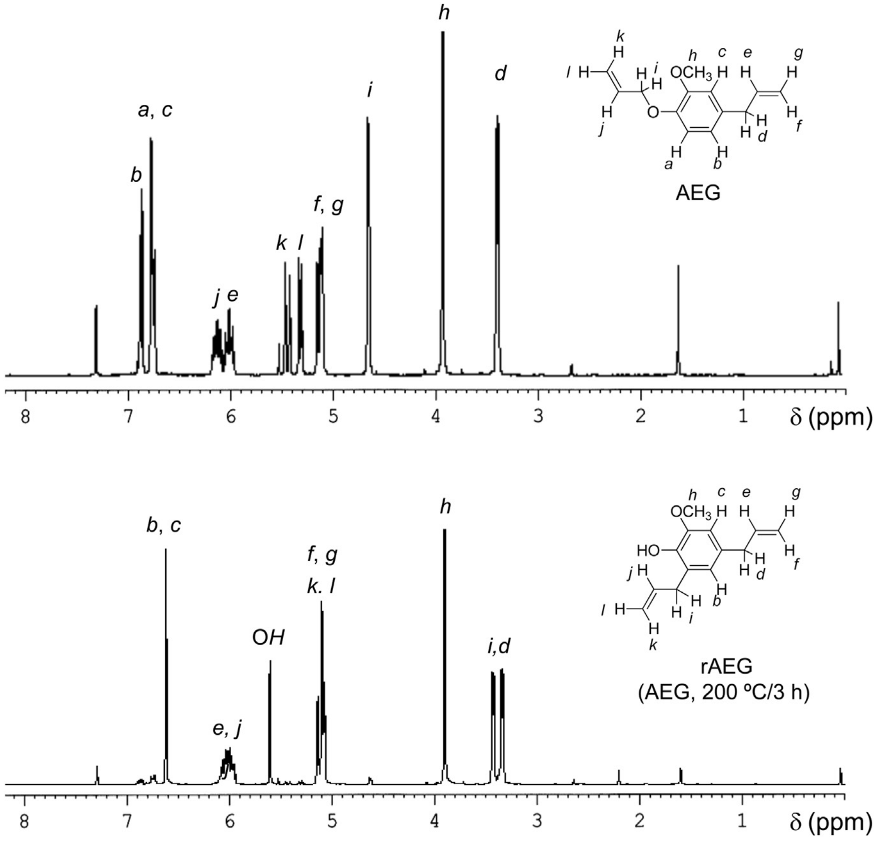

Fig. 2. ^{1}H NMR spectra of AEG and rAEG in $CDCl_3$.

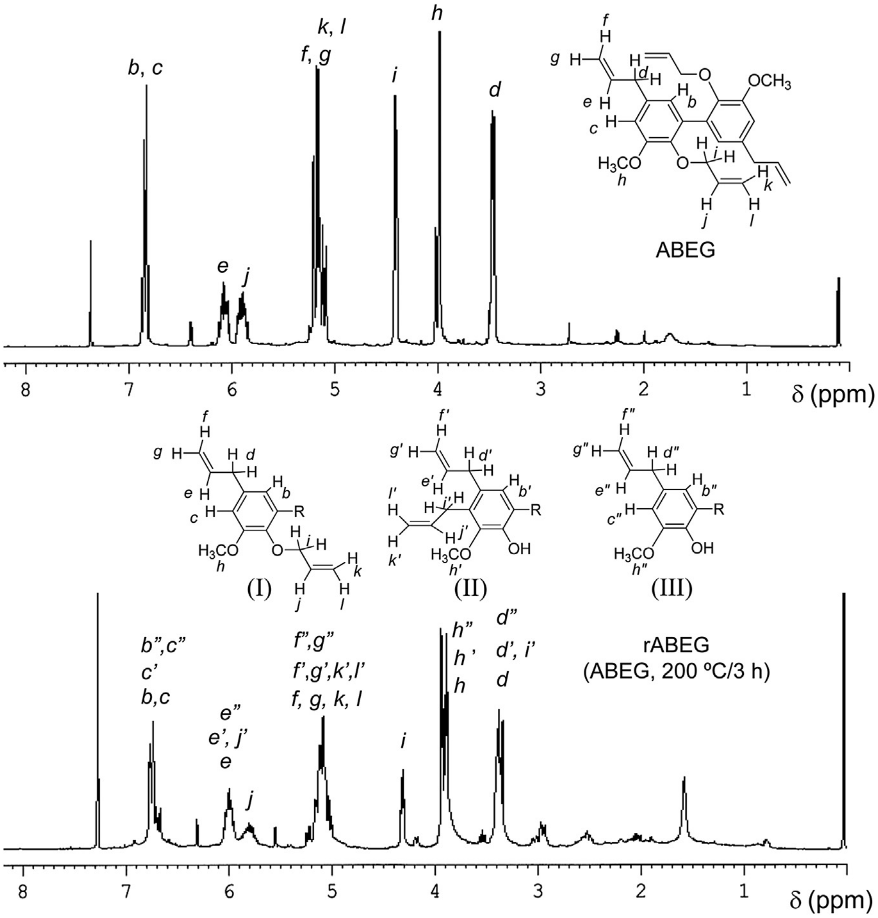

Fig. 3. ^1H NMR spectra of ABEG and rABEG in $CDCl_3$.

spectrometer (Shimadzu Co. Ltd., Kyoto, Japan) by KBr or attenuated total reflectance (ATR) methods. The temperature at which 5% weight loss occurred (T_5) was measured on a TGA7 thermogravimetric analyzer (PerkinElmer Japan Co. Ltd., Yokohama, Japan) in a nitrogen atmosphere at a heating rate of 20 °C min^{-1}. Dynamic mechanical analysis (DMA) of the rectangular plates (length 30 mm, width 5 mm, thickness 0.5 mm) was performed on a Rheolograph Solid instrument (Toyo Seiki Co., Ltd, Tokyo, Japan) under an atmosphere of air with a chuck distance of 20 mm, a frequency of 1 Hz and a heating rate of 2 °C min^{-1}, based on ISO 6721-4:1994 (Plastics — Determination of dynamic mechanical properties, Part 4: Tensile vibration — Non-resonance method). The glass transition temperature (T_g) was determined from the tan δ peak temperature. Flexural testing of the rectangular specimens (50 × 10 × 2 mm^3) was performed using an Autograph AG-1 (Shimadzu Co., Ltd.) using the standard method for testing the flexural properties of plastics (JIS K7171:2008 (ISO 178:2001)). The span length was 30 mm, and the testing speed was 10 mm min^{-1}. Five specimens were tested for each set of samples, and mean values were calculated for each set.

3. Results and discussion

3.1. Synthesis and characterization of AEG and ABEG

AEG and ABEG were synthesized by the reactions of allyl bromide with EG and BEG in the presence of sodium hydroxide in DMSO, respectively (Fig. 1). The use of excess sodium hydroxide and a prolonged reaction time at 70 °C resulted in the transformation of the formed allyl (2-propenyl) ether to 1-propenyl ether. Similar rearrangement under basic conditions has been reported in the past [36]. Therefore, we found the use of a small excess of sodium hydroxide and the termination of the reaction at 70 °C within an hour to be important for achieving a high-purity allyl ether. Figs. 2

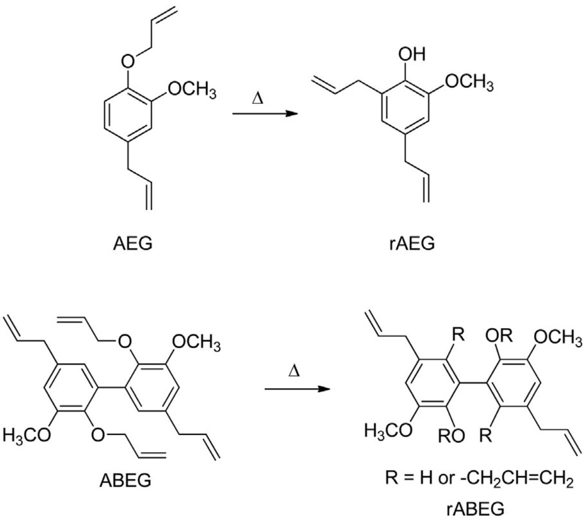

Fig. 4. Pyrolysis reactions of AEG and ABEG.

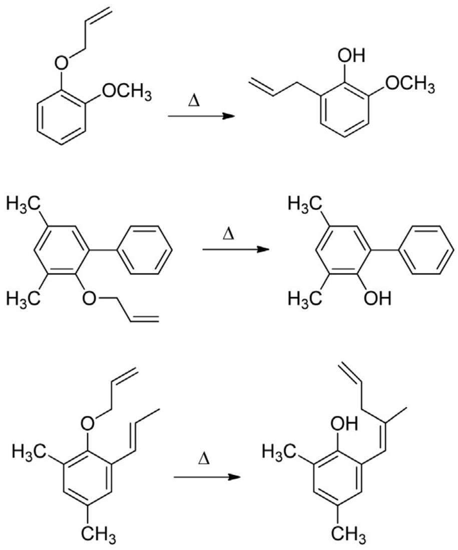

Fig. 5. Examples of Claisen and out-of-ring Claisen rearrangements reported in previous studies.

and 3 show the ^{1}H NMR spectra of AEG and ABEG in $CDCl_3$, respectively. The ^{1}H signals at 6.02 (m, 1H), 5.14 (m, 2H) and 3.42 ppm (m, 2H) for AEG are assigned to the protons H-*e*, H-*f*, *g* and H-*d* of the allyl group to which the benzene ring is attached, based on the corresponding ^{1}H signals of EG. The ^{1}H signals at 6.17 (m, 1H), 5.45 (m, 1H), 5.30 (m, 1H) and 4.60 ppm (m, 2H) for AEG are assigned to the H-*j*, H-*k*, H-*l* and H-*i* protons of the allyloxy group. The ^{1}H signals of the allyloxy group of ABEG, on the other hand, were observed at a slightly higher magnetic field region than those of AEG. The protons of the allyloxy groups, which are located on the benzene ring of ABEG, may have signals that are shifted due to interaction with the aromatic ring current. IR analysis of the compounds before and after allylation revealed an absorption band at 3400–3500 cm^{-1} on the spectrum of EG due to the stretching vibration of phenolic O–H. The corresponding bands on the spectra of AEG and ABEG almost completely disappeared (see Figs. 6 and 7), indicating that the allyl-etherification reaction in both cases proceeded quantitatively.

AEG and ABEG were pyrolyzed at 200 °C to clarify whether Claisen rearrangement occurs during the thermal curing with BMI. In the case of AEG, the pyrolysis was performed at 200 °C for 3 h in a sealed tube because no reaction occurred at 150 °C for 5 h in the atmosphere and the weight loss by vaporization of AEG started to occur at approximately 170 °C. The ^{1}H-signals of H-*a* on the benzene ring and H-*i* on the allyloxy group observed for AEG completely disappeared, and the olefinic ^{1}H-signals of two allyl group were conjointly observed at 6.02 ppm (m, 2H, H-*e*, *j*) and 5.09 ppm (m, 4H, H-*f*, *g*, *k*, *l*) in the ^{1}H NMR spectrum of the rAEG in $CDCl_3$ (Fig. 2). The ^{1}H-signal at 5.60 ppm was assigned to the generated hydroxy proton, as this signal disappeared in the ^{1}H NMR spectrum in CD_3OD. The absorption band due to the O–H stretching vibration was observed at 3514 cm^{-1} on the FT-IR spectrum of the pyrolyzed sample. These observations indicate that AEG was converted to 2,4-diallyl-6-methoxyphenol by Claisen rearrangement of the phenol moiety to the *ortho*-position (Fig. 4). Similarly, 1-allyloxy-2-methoxybenzene thermally rearranges to give 2-allyl-6-methoxyphenol in an 80–90% yield, as shown in Fig. 5 [37]. When ABEG was heated at 200 °C in the atmosphere, the viscosity of the sample gradually increased. Although the ^{1}H NMR spectrum of the sample after 0.5 h was only slightly changed compared with that of ABEG, a considerable decrease in the intensities of the ^{1}H signals of H-*b*, *c* of the benzene ring and H-*j*, *i* of the allyloxy group was observed, in addition to the appearance of some weak unidentified ^{1}H signals in the spectrum of rABEG (Fig. 3). Additionally,

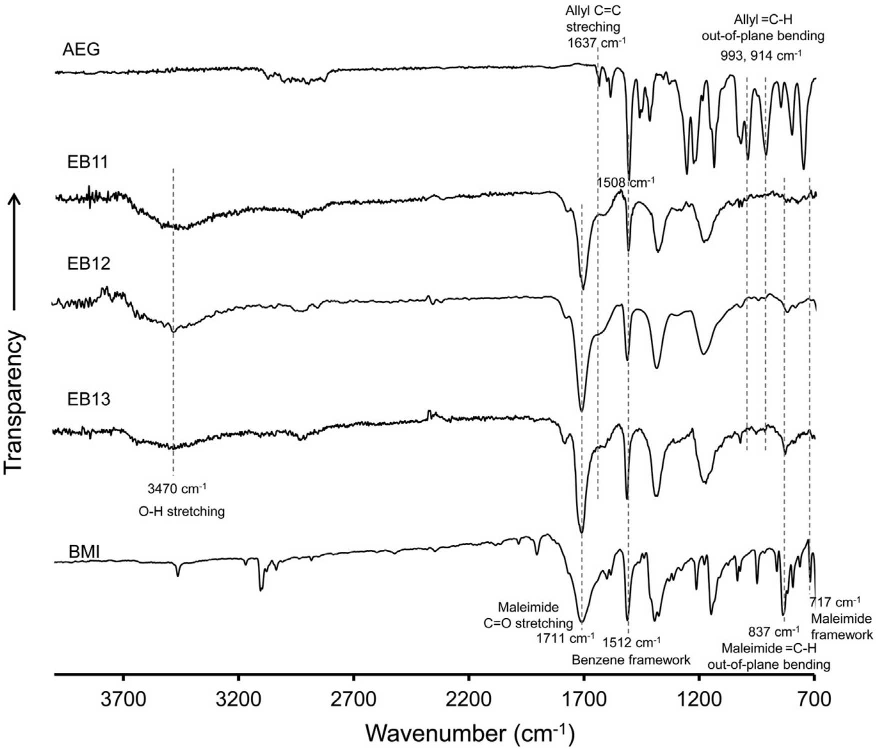

Fig. 6. FT-IR spectra of AEG, EB11, EB12, EB13 and BMI.

in the FT-IR analysis of rABEG, a new absorption band of O–H stretching vibration was observed. When the pyrolysis of ABEG at 200 °C was carried out for longer than 3 h, it resulted in the formation of polymerized solid product. For *ortho*- and *para*-blocked allyl aryl ethers, the following reactions have been reported in the past: pyrolysis of 2-allyloxy-3,5-dimethylbiphenyl at 220 °C for 5 h gave the parent phenol (2-hydroxy-3,5-dimethylbiphenyl) in 76–77% yield, and pyrolysis of 1-allyloxy-2,4-dimethyl-6-(1-propenyl)benzene gave a compound whose allyl group migrated to β-position of the propenyl group (an out-of-ring Claisen rearrangement); both reaction schemes are shown in Fig. 5 [38]. From these previous observations and our ^{1}H and FT-IR analyses for rABEG, the presence of 3-allyl-6-allyloxy-5-methoxyphenyl (I), 3,4-diallyl-6-hydroxy-5-methoxyphenyl (II), and 3-allyl-6-hydroxy-5-methoxyphenyl (III) moieties have all been identified in the structure of rABEG (Fig. 3). From the integral ratio of the ^{1}H-signals, the ratio of (I):(II):(III) present after pyrolysis was estimated to be 35:18:47. The (III) moiety is likely generated by allyl rearrangement to the *ortho*-position of the adjacent phenyl group, considering the out-of-ring Claisen rearrangement mentioned above. It is interesting to note that the (III) moiety is also the structure formed when Claisen rearrangement formally occurs at the *meta*-position of the allyloxyphenyl moiety.

3.2. Curing reactions of AEG/BMI and ABEG/BMI

AEG was prepolymerized with BMI at 160 °C for 1 h, 180 °C for 1 h and 200 °C for 1 h to give a gelatinous material. If the mixture is rapidly heated to 200 °C, a considerable amount of AEG vaporizes. In the case of ABEG/BMI, the mixture was melt-mixed at 170 °C and then gradually heated to 200 °C over 1 h to produce a gelatinous material. The obtained prepolymers of AEG/BMI and ABEG/BMI with allyl/maleimide ratios of 1/1, 1/2 and 1/3 were hot-pressed 210 °C for 1 h, 220 °C for 2 h and finally at 250 °C for 8 h to form cured AEG/BMI and ABEG/BMI resins. Figs. 6 and 7 show the FT-IR spectra of the EB11, 12, 13 and BB11, 12, 13 resins, respectively. In the spectra of AEG and ABEG, the absorption bands due to allyl C═C stretching and ═CH out-of-plane bending vibrations were observed at 1637 cm^{-1} and 993–989, 914 cm^{-1}. In the spectra of BMI, absorption bands due to ═CH out-of-plane bending of the maleimide group and maleimide framework vibration were observed at 837 cm^{-1} and 717 cm^{-1}. The bands related to allyl and maleimide groups almost disappeared for all of the cured resins, although small bands characteristic of maleimide were present for EB13 and BB13. If the ene reaction of allyl (2-propenyl) and maleimide groups occurs, a 1-propenyl group substituted by succinimide at the 3-position should be produced. The absorption band of a 1-propenyl ═CH out-of-plane bending vibration of *trans*-isoeugenol is observed at 963 cm^{-1}. However, no clear absorption band related to the 1-propenyl ═CH out-of-plane bending vibration at approximately 960–970 cm^{-1} appeared on the spectra of the EBs and BBs, suggesting that the propenyl group formed by the ene reaction of allyl group and maleimide group further reacted with maleimide group after curing at 250 °C. All of the cured EB and BB resins exhibited a broad absorption band at approximately 3470 cm^{-1} due to an O–H stretching vibration, suggesting that, to some extent, Claisen rearrangement of AEG and out-of-ring Claisen rearrangement of ABEG occurred. Consequently, the curing reactions of AEG/BMI and ABEG/BMI are thought to proceed as follows: for AEG/BMI, a fraction of AEG is converted to rAEG, and the rAEG as well as the residual AEG react with BMI through a sequential ene reaction, Diels–Alder reaction and addition copolymerization process. In the case of ABEG/BMI, a portion of ABEG is converted to rABEG, which reacts along with the residual ABEG with BMI by a combination of an ene reaction and addition copolymerization to form the cured resin. Both mechanisms presented here are similar to the analogous curing reactions of EG and BEG with BMI, reported previously [22].

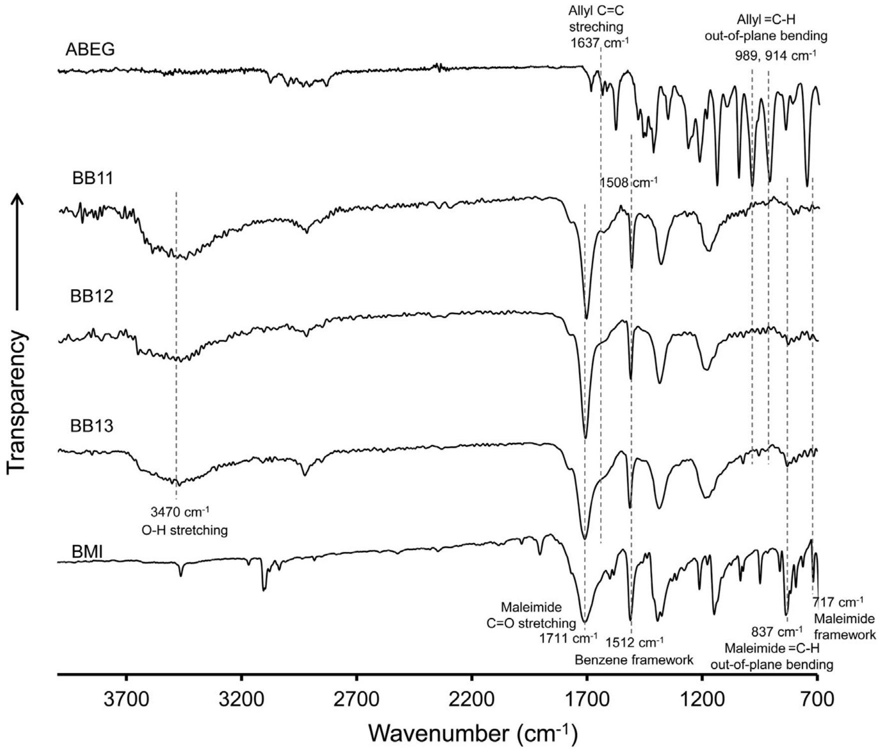

Fig. 7. FT-IR spectra of ABEG, BB11, BB12, BB13 and BMI.

3.3. Properties of the cured AEG/BMI and ABEG/BMI resins

Figs. 8 and 9 show the DMA curves of the EBs and BBs, respectively. The T_g's measured from the tan δ peak temperature for all of the cured resins increased with increasing BMI content, and those of EB13 and BB13 were over 400 °C (Table 1). The T_g's of the EBs and BBs were higher than those of the cured EG/BMI (1/1: 256.4 °C, 1/2: 345.8 °C and 1/3: 377.0 °C) and BEG/BMI (1/1: 201.2 °C, 1/2: 285.8 °C and 1/3: 336.1 °C) resins with the same allyl/maleimide ratios [22], respectively. Although the temperatures where the storage modulus (E') starts to decline for all of the cured resins were also over 300 °C, that of BB11 (310 °C) was the lowest among the cured resins. This result may be attributed to the fact that the actual allyl/maleimide ratio was lower than 1/1 due to the elimination of the allyl group in BB11.

Fig. 10 shows the TGA curves of the EB and BB resins. The T_5 values for all of the cured resins increased with increasing BMI content. All of the cured resins displayed excellent T_5 values that were higher than 450 °C (Table 1). The BB resins consistently possessed lower T_5 values than the EB resins containing the same allyl/maleimide ratio. This result is also attributable to the elimination of the allyl group for the BBs.

Fig. 11 shows the flexural properties of the EBs and BBs. The flexural strength of the EBs and BBs decreased with increasing BMI content. Conversely, the flexural moduli were found to increase with increasing BMI content for all of the cured resins except for EB13. These results are related to the brittle character of the cured bismaleimides. The fact that the flexural modulus of EB13 was lower than those of EB11 and EB12 may be attributed to the quantity of unreacted maleimide group remaining in the resin, as observed in the FT-IR spectrum (Fig. 6). The highest flexural moduli (observed for EB12 at 3.11 GPa and BB13 at 3.10 GPa) amongst the EBs and BBs were higher than the already reported highest values (cured EG/BMI13: 2.80 GPa and BEG/BMI: 2.70 GPa) among the cured EG/BMI and BEG/BMI resins, respectively [22]. Similarly, the highest flexural strength among the BBs (BB11: 68.2 MPa) was higher than the highest value (cured BEG/BMI 1/2: 55.9 MPa) among the cured BEG/BMI resins. However, the highest flexural strength (EB11: 59.1 MPa) among the EB resins was lower than those of cured EG/BMI 1/1, 1/2 and 1/3 resins (73.2, 84.5 and 71.0 MPa). In general, an increase in allyl functionality fostered by allyl etherification of the phenolic hydroxy groups of EG and BEG formed cured resins with a higher crosslink density and resulted in the improvement of the heat resistances (T_g and T_5) and flexural moduli of EBs and BBs than cured resins formed without an allyl etherification step.

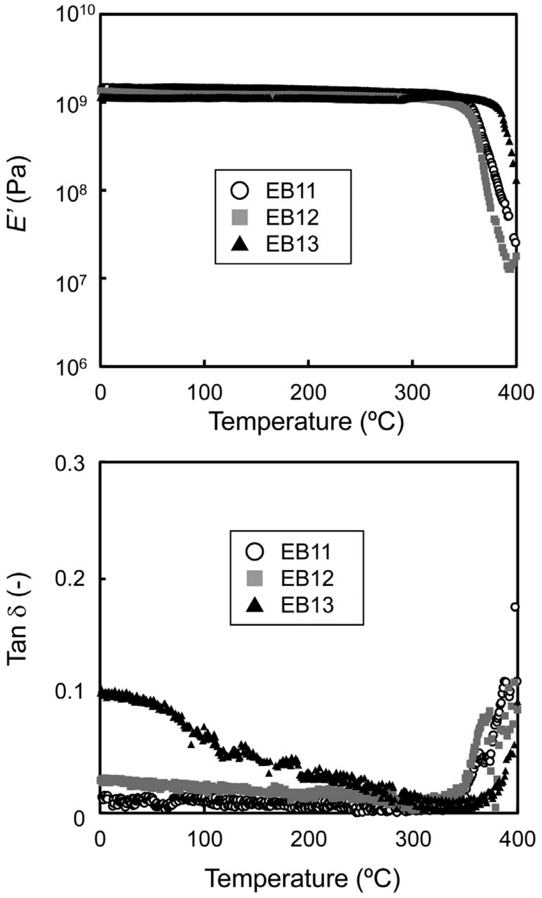

Fig. 8. DMA curves of EBs.

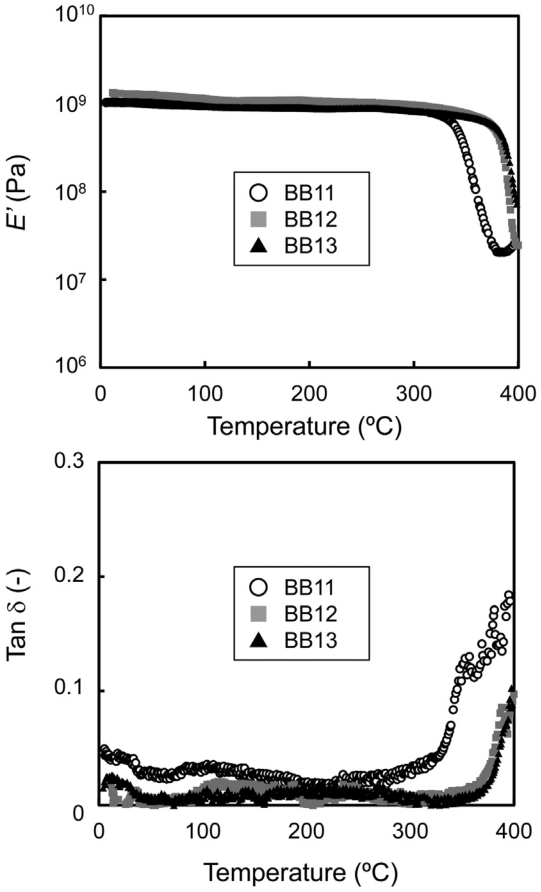

Fig. 9. DMA curves of BBs.

Table 1
T_g's measured by DMA and T_5's measured by TGA for EBs and BBs.

Sample	T_g (°C)	T_5 (°C)
EB11	357.6	475.9
EB12	373.1	486.3
EB13	>400	494.7
BB11	352.8	453.2
BB12	387.9	475.4
BB13	>400	481.4

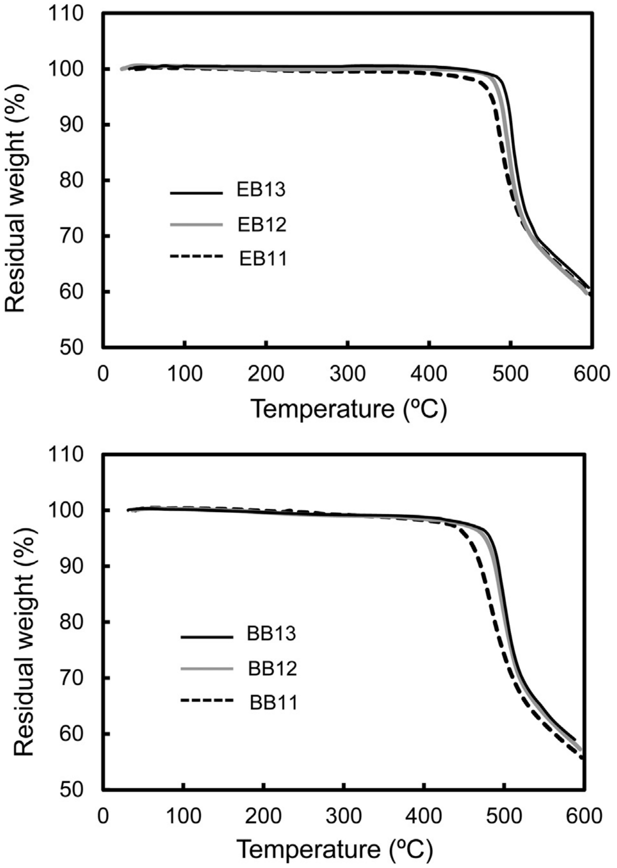

Fig. 10. TGA curves of EBs and BBs.

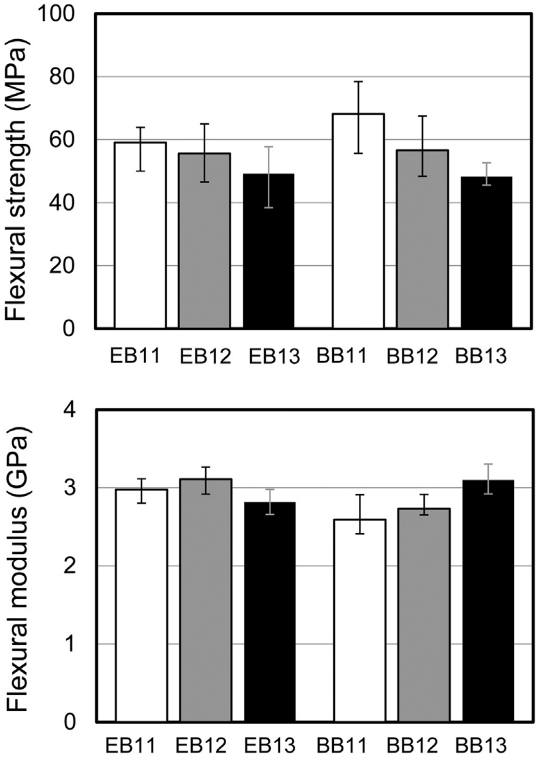

Fig. 11. Flexural properties of EBs and BBs.

4. Conclusions

AEG and ABEG were synthesized by reacting EG and BEG with allyl bromide in the presence of sodium hydroxide. The pyrolysis of AEG at 200 °C produced 2,4-diallyl-6-methoxyphenol by a Claisen rearrangement. In the case of the pyrolysis of ABEG, the allyl group of the allyloxy moiety was either eliminated or rearranged to the *ortho*-position of the adjacent phenyl group by an out-of-ring Claisen rearrangement. The AEG and ABEG were prepolymerized with BMI at 160–200 °C and then compression-molded at 250 °C for 5 h to produce EBs and BBs with allyl/maleimide unit ratios of 1/1, 1/2 and 1/3, respectively. FT-IR analysis of the cured resins showed that the original allyl and maleimide groups were almost entirely consumed and that the hydroxy group was newly formed by the pyrolysis of AEG and ABEG. In every case, the T_g and T_5 values of the EB and BB resins increased with increasing BMI content. All of the cured resins exhibited superior T_g and T_5 values that were higher than 350 °C and 450 °C, respectively, and were much higher than those of the already reported EG/BMI and BEG/BMI 1/1–1/3 cured resins. Furthermore, the flexural moduli (2.6–3.1 GPa) of the cured resins were also higher than those of the EG/BMI and BEG/BMI resins (0.78–2.8 GPa). In conclusion, the EB and BB resins described in this study hold promise as bio-based thermosetting resins with superior thermal stability and mechanical properties.

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