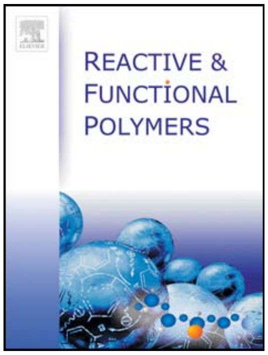

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Bio-based thermosetting resins composed of aliphatic polyol-derived polymaleimides and allyleugenol

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ABSTRACT

Bio-based bismaleimide (2MPD), trismaleimide (3MGC) and tetramaleimide (4MDG) were synthesized by reactions of 4-isocyanatophenylmaleimide with 1,3-propanediol, glycerol and α,α'-diglycerol, respectively. Although 2MPD did not melt until the temperature where thermal decomposition starts, 3MGC and 4MDG exhibited broad melting temperatures with onset points at 165 °C and 124 °C, respectively. 3MGC and 4MDG were homogeneously prepolymerized at 170 °C with 2,4-diallyl-6-methoxyphenol (rAEG) which was prepared by the Claisen rearrangement of allyl-etherified eugenol (AEG). The prepolymers were compression-molded at 250 °C to produce cured rAEG/3MGC (A3Mxy) and rAEG/4MDG (A4Mxy) with the allyl/maleimide ratio of x/y = 1/1, 1/2 or 1/3. The FT-IR analysis revealed that the ene reaction of allyl and maleimide groups and subsequent addition copolymerization occurred for the cured resins. The thermal and mechanical properties of the cured resins were compared with those of the cured rAEG/4,4'-bismaleimidodiphenylmethane (BMI) (ABMxy) with the same allyl/maleimide ratio. A3M13 and A4M13 showed no inflection point of thermal expansion due to glass transition until 300 °C, which is a little lower than the thermo-degradation temperature. Flexural strengths and flexural strains at break for A3Ms and A4Ms increased with the polymaleimide contents, and those of A3M13 and A4M13 were much higher than those of ABM13.

Keywords: glycerol; diglycerol; 1,3-propanediol; polymaleimide; thermosetting resins

1. Introduction

Development of bio-based polymers, i.e., polymers from renewable feedstock, has been driven by the growing concerns of long-term sustainability and negative impacts on the environment of petroleum-based polymer materials. So far, bio-based thermoplastic polymers such as polylactides, polyhydroxyalkanoates, polyamide 11 and cellulose esters have shown great potential to replace the petrochemical thermoplastics in many applications [1-4]. In recent years, effective utilization of renewable feedstock has increasingly penetrated thermosetting resins and their composites [5-8]. For example, soybean oil [9-11], glycerol [12,13], polyglycerol [14], sorbitol [15,16], isosorbide [17,18] and cardanol [19,20] etc. have been successfully utilized to the syntheses of epoxy resins. Vegetable oils [21-24], terpenes [25], fumaric acid and sebacic acid [26] etc. have been utilized to the syntheses of unsaturated polyester, vinylester and alkyd resins. However, these bio-based thermosetting resins mainly derived from aliphatic renewable feedstock were difficult to be used to the applications such as electronics and structural materials requiring excellent thermal and mechanical properties. Thermosetting resins based on allylphenolic-bismaleimide blend are an important class of high-performance thermosetting polymers [27]. Among them, a commercial high-performance thermosetting resin, Matrimid® 5292 (Huntsman Corp., former Ciba Specialty Chemicals Corp.), based on 2,2’-diallybisphenol A (DABA) / 4,4’-bismaleimidodiphenylmethane (BMI) is one of the leading matrix resins in carbon fiber composites for advanced aerospace application (Scheme 1) [28]. The flexural modulus (4.06 GPa) and 5% weight loss temperature (T_5: > 450 °C) of the cured DABA/BMI resin with the molar ratio of 1/1 are much higher than those (2.30 GPa and 284 °C) of the glycerol-based epoxy resin cured with diethyltoluenediamine

(DETDA) and those (2.12 GPa and 370°C) of the bisphenol-A-based epoxy resin cured with DETDA [13,28]. FT-IR analysis of cured DABA/BMI resin has shown its formation to proceed by an ene reaction followed by addition copolymerization [29,30]. Recently, we reported that BMI resins cured with eugenol (EG), bieugenol (BEG: 3,3'-dimethoxy-5,5'-diallyl-1,1'-biphenyl-2,2'-diol) or eugenol novolac (EGN) showed superior thermal and mechanical properties [31]. Furthermore, it was shown that BMI resins cured with allyl-etherified EG (AEG) or allyl-etherified BEG (ABEG) exhibited superior glass transition temperature (T_g) and T_5 that were higher than 350 °C and 450 °C, respectively [32]. When the bio-based allylphenolic compounds are combined with bio-based polymaleimides derived from industrially important renewable aliphatic polyols [33], it is expected that bio-based cured resins having much better thermal and mechanical properties than the already reported bio-based epoxy and unsaturated polyester resins are produced.

In this study, bismaleimide (2MPD), trismaleimide (3MGC) and tetramaleimide (4MDG) were synthesized by reactions of 4-isocyanatophenylmaleimide (ICPM) with 1,3-propanediol (PD), glycerol (GC) and α,α'-diglycerol (DG) as bio-based aliphatic polyols, respectively. The bio-based polymaleimides having aliphatic ether frameworks are expected to be more flexible than BMI, leading to the improvement of brittleness. In addition, especially for the tris- and tetra-maleimides, it is expected that the heat resistance is not so largely reduced because of the higher maleimide functionality than BMI. As a bio-based allylphenolic compound combining with the bio-based polymaleimides, Claisen-rearranged AEG (rAEG, 2,4-diallyl-6-methoxyphenol) was used in this study (Scheme 2). Regarding the ene reaction of allyl and maleimide groups, it is expected that rAEG has a higher reactivity than AEG, because it is known that *o*-allylphenol has a higher reactivity toward *N*-phenylmaleimide than allyl phenyl ether [34]. The present study describes the synthesis of 2MPD, 3MGC and 4MDG, and thermal and mechanical properties of cured rAEG/3MGC resins (A3Ms) and cured rAEG/4MDG resins (A4Ms) as compared with those of cured rAEG/BMI resins (ABMs) which have not been previously reported (Scheme 3).

2. Experimental

2.1. Materials

Eugenol (EG, purity > 98.0% by gas chromatography) and cyclopentyl methyl ether (CPME) were purchased from Wako Pure Chemical Industries, Ltd. (Osaka, Japan). α,α'-Diglycerol (DG) was supplied from Sakamoto Yakuhin Kogyo, Co. Ltd. (Osaka, Japan). 4,4'-Bismaleimidodiphenylmethane (BMI) and triphenylphosphine (TPP) were purchased from Tokyo Kasei Kogyo Co. Ltd. (Tokyo, Japan). 1,3-Propanediol (PD), glycerol (GC), *n*-hexanol, allyl bromide, sodium hydroxide, hydroquinone (HQ), 1,4-diazabicyclo[2.2.2]octane (DABCO) and dimethyl sulfoxide (DMSO) were purchased from Kanto Chemical Co., Inc. (Tokyo, Japan). All the commercially available reagents were used without further purification. *N*-[(4-azidocarbonyl)phenyl]maleimide (ACPM) was synthesized according to the procedures described earlier [35]. rAEG was also synthesized according to the procedures described earlier (Scheme 3) [32].

2.2. Synthesis of 1,3-bis[N-(p-maleimidophenyl)carbamoyloxy]propane (2MPD)

To a solution of ACPM (10.0 g, 44.0 mmol) in CPME (400 mL), HQ (100 mg) and DABCO (20 mg) were added under a nitrogen atmosphere. After the contaminated water was azeotropically removed by refluxing the solution at 120 °C for 30 min, a solution of PD (1.52 g, 20.0 mmol) in anhydrous DMF (100 mL) was added and stirred at 80 °C for 24 h. *n*-Hexanol (7 mL, 57 mmol) was added to the reaction mixture and stirred at 50 °C for 3 h in order to quench excess isocyanate which was produced from ACPM. After the reaction mixture was concentrated in vacuo, the viscous liquid was slowly added to diethyl ether (400 mL) under stirring. The formed precipitate was filtered and dried in vacuo at room temperature for 24 h to give 2MPD as a yellow powder (yield: 6.8 g, 67 %). MALDI-TOF-MS (*m*/*z*): calcd. for $C_{25}H_{20}N_4O_8$+Na 527.12, found 526.93.

2.3. Synthesis of 1,2,3-tris[N-(p-maleimidophenyl)carbamoyloxy]propane (3MGC)

To a solution of ACPM (7.53 g, 33.0 mmol) in CPME (400 mL), HQ (75 mg) and DABCO (20 mg) were added under a nitrogen atmosphere. After the contaminated water was azeotropically removed by refluxing the solution at 120 °C for 30 min, a solution of GC (0.921 g, 10 mmol) in anhydrous DMF (100 mL) was added and stirred at 80 °C for 24 h. *n*-Hexanol (5 mL, 41 mmol) was added to the reaction mixture and stirred at 50 °C for 3 h. After the reaction mixture was concentrated in vacuo, the viscous liquid was slowly added to diethyl ether (400 mL) under stirring. The formed precipitate was filtered and dried in vacuo at room temperature for 24 h to give 3MGC as a yellow powder (yield: 5.7 g, 77 %). MALDI-TOF-MS (*m*/*z*): calcd. for $C_{36}H_{26}N_6O_{12}$ + Na 757.15, found 757.63.

2.4. Synthesis of 1,2,6,7-tetra[N-(p-maleimidophenyl)carbamoyloxy]-4-oxaheptane (4MDG)

To a solution of ACPM (10.0 g, 44.0 mmol) in CPME (500 mL), HQ (100 mg) and DABCO (25 mg) were added under a nitrogen atmosphere. After the contaminated water was azeotropically removed by refluxing the solution at 120 °C for 30 min, a solution of DG (1.66 g, 10.0 mmol) in anhydrous DMF (125 mL) was added and stirred at 80 °C for 24 h. *n*-Hexanol (6 mL, 60 mmol) was added to the reaction mixture and stirred at 50 °C for 3 h. After the reaction mixture was concentrated in vacuo, the viscous liquid was slowly added to diethyl ether (500 mL) under stirring. The formed precipitate was filtered and dried in vacuo at room temperature for 24 h to give 4MDG as a yellow powder (yield: 9.0 g, 88 %). MALDI-TOF-MS (*m*/*z*): calcd. for $C_{50}H_{38}N_8O_{17}$ + Na 1045.23, found 1045.75.

2.5. Preparation of cured polymaleimide resins

A typical preparation method of the cured 3MGC (c3MGC) is as follow: A mixture of 3MGC (1.40 g, 1.90 mmol) and TPP (7 mg) was pulverized in a mortal. The pulverized mixture 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 Mini Test Press-10 (Toyo Seiki Co., Ltd, Tokyo, Japan) to produce c3MGC. The thickness of the molded plate was controlled using a stainless steel spacer (thickness: 1.0 mm) during the compression molding. The cured 4MGC (c4MGC) was prepared by a similar procedure. The curing conditions of c3MGC and c4MGC are summarized in Table 1.

2.6. Preparation of cured rAEG/polymaleimide resins

A typical preparation method of the cure rAEG/3MGC resin with the feed molar ratio of 1/1 (A3M11) is as follow: A mixture of rAEG (0.612 g, 3.00 mmol) and 3MGC (2.20 g, 3.00 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 to produce A3M11. Sample codes and curing conditions of all the cured rAEG/polymaleimide resins are also summarized in Table 1.

2.7. Measurements

Proton nuclear magnetic resonance (^{1}H-NMR) spectra were recorded on a Bruker AV-400 (400 MHz) (Madison, WI, USA) using DMSO-d_6 as a solvent. FT-IR spectra were measured on a FTIR 8100 spectrometer (Shimadzu Co. Ltd., Kyoto, Japan) by the KBr or attenuated total reflectance (ATR) methods. Matrix-assisted laser desorption/ ionization time-of-flight (MALDI-TOF) mass spectra were recorded with a SHIMADZU AXIMA Performance mass spectrometer with 2,5-dihydroxybenzoic acid (DHBA) as a matrix. The differential thermal analysis (DTA) of the sample (15-20 mg) was performed on a Shimadzu DTA-50 instrument at a heating rate of 10 °C min^{-1} in a nitrogen atmosphere. Thermomechanical analysis (TMA) of a square-shaped specimen (5 × 5 × 1 mm^3) was conducted on a TMA-60 (Shimadzu Co., Ltd.) at a heating rate of 10 °C min^{-1} in a nitrogen atmosphere. The T_g was determined from the intersect of tangents at the two points with a significant change in coefficient of thermal expansion (CTE). The T_5 of the sample (10-15 mg) was measured over the temperature range of room temperature to 500 °C on a Shimadzu TGA-50 thermogravimetric analyzer at a heating rate of 20°C min^{-1} in a nitrogen atmosphere. Flexural testing of the rectangular specimen (50 × 7 × 1 mm^3) was performed using an Autograph AG-1 (Shimadzu Co., Ltd.) based on 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 the mean value and standard deviation were calculated.

3. Results and discussion

3.1. Synthesis and characterization of 2MPD, 3MGC and 4MDG

First, we examined a direct esterification reaction of *p*-carboxyphenylmaleimide (CPMI) and PD or GC using dicyclohexylcarbodiimide as a condensation reagent, and two-step esterification via acid chloride of CPMI. However, we could not produce a pure esterified polymaleimide in a good yield. Therefore, the carboxy group of CPMI was converted to isocyanate group in order to enhance the reactivity toward hydroxy group. Synthesis routes of 2MPD, 3MGC and 4MDG are shown in Scheme 4. The synthetic procedure essentially involves addition reaction of a bio-based polyol and 4-(maleimido)phenyl isocyanate (MPIC). The MPIC was *in situ* generated by thermal Curtius rearrangement of ACPM, which was synthesized by the reaction of CPMI and diphenyl phosphoryl azide essentially according to the procedure described in the literature [34]. The carbon atom contents derived from renewable PG, GC and DGC for 2MPG, 3MGC and 4MDG were calculated to be 7.1, 4.9 and 7.1 wt%, respectively. Currently, several strategies are envisioned to produce bio-based maleic anhydride (MAH) from renewable resources such as bio-based succinic acid, crotonic acid and xylose [36-38]. If their processes are established, CPMI can be prepared from 4-aminobenzoic acid and the bio-based MAH. In such a case, the carbon atom contents derived from renewable resources (PD, GC, DG and MAH) for 2MPD, 3MGC and 4MDG are expected to be increased to 26.2, 24.5 and 25.8%, respectively.

Fig. 1 shows the ^{1}H-NMR spectra of 2MPD, 3MGC and 4MDG in DMSO-d_6. The ^{1}H signals at 9.82 (s, 1H), 7.59 (m, 2H), 7.25 (m, 2H) and 7.15 ppm (s, 2H) for 2MPD were assigned to H^d, H^b, H^c and H^a of the *N*-maleimidophenylcarbamoyloxy group, respectively. Also, the ^{1}H signals at 4.28 (m, 4H) and 2.05 ppm (m, 2H) were assigned to H^e and H^f of the 1,3-propanedioxy group, respectively. 3MGC and 4MDG displayed similar ^{1}H-signal pattern for the *N*-maleimidophenylcarbamoyloxy groups. The ^{1}H signals of H^f and H^e of the glycerol moiety of 3MGC were observed at 5.32 (m, 1H) and 4.52-4.05 (m, 4H), respectively. The ^{1}H signals of H^f, H^e and H^g of the diglycerol moiety of 4MDG were observed at 5.23 (m, 2H), 4.6-4.0 (m, 4H) and 4.0-3.4 ppm (m, 4H), respectively. The ^{1}H signal patterns of H^e and H^g became complex, because there are two sets of diastereomers (RS = SR and RR; RS = SR and SS) having different spectroscopic response for 4MDG due to the presence of two asymmetric carbons (C^f) and one symmetry plane.

Fig. 2 shows FT-IR spectra of 2MPD, 3MGC and 4MDG. The absorption band due to N-H stretching (ν) of formed urethane bond was observed at 3337 cm^{-1}. The urethane ν(C=O) band overlapped with maleimide ν(C=O) band at 1707 cm^{-1}. All the polymaleimides showed two absorption bands characteristic to maleimide group at 833 cm^{-1} and 689 cm^{-1}, which are attributed to out-of-plane bending (γ) of maleimide =C–H and deformation (δ) of maleimide ring [39]. These two bands characteristic to maleimide group were used for the check of progress of curing reaction of maleimide and allyl groups.

3.2. Thermal properties of 2MPD, 3MGC and 4MDG

Fig. 3 shows TG-DTA curves of 2MPD, 3MGC and 4MDG. The onset temperatures of thermal degradation for 2MPD, 3MGC and 4MDG were 220.3, 223.0 and 213.9 °C, respectively. 2MPD showed no endothermic peak due to melting until the onset degradation temperature. 3MGC and 4MDG started to melt at around 165 and 124 °C, respectively, which were lower than the onset degradation temperature. 3MGC displayed a melting peak-top temperature (T_m) at 214.3 °C and did not show an exothermic peak due to addition homopolymerization of maleimide group until the onset degradation temperature. 4MDG showed double melting peaks at 137.2 and 179.2 °C and an exothermic peak at 207.0 °C, which was close to the onset degradation temperature (213.9 °C). The fact that 4MDG showed double melting peaks may be related to the presence of diastereomers.

Fig. 4 shows DTA curves of 2MPD, 3MGC and 4MDG with 0.5 wt% TPP as a catalyst for anionic polymerization [40]. When 0.5 wt% TPP was added, an exothermic peak of 4MDG became 200.2 °C, which was lower than the onset degradation temperature, indicating that 4MDG with TPP can be thermally cured at around 200 °C. Although an exothermic peak of 3MGC with TPP was 228.5 °C which was still higher than the onset degradation temperature (223.0 °C), the onset exothermal temperature (200 °C) was lower than the onset degradation temperature, indicating that 3MGC with TPP can be cured at around 200-220 °C. Actually, 3MGC and 4MDG with 0.5 wt% TPP could be thermally cured at the curing process of 210 °C/1 h, 220 °C/2 h and 250°C/5 h to produce c3MGC and c4MDG as brown plates. Table 2 summarizes the TMA and TGA data of c3MGC and c4MDG. Both c3MGC and c4MDG showed no inflection points of TMA curves due to glass transition until 300 °C. T_5s of c3MGC and c4MDG were 359 °C and 372 °C, which were much higher than those (254.8 °C and 257.3°C) of 3MGC and 4MDG, respectively.

3.3. Curing reaction of rAEG and 3MGC or 4MDG

3MGC and 4MDG were prepolymerized with rAEG at the molar ratio of 1/1, 1/2 or 1/3 at 170-200 °C, and compression-molded at 210 °C/1 h, 220 °C/2 h and 250 °C/5 h to produce A3M11, 12 or 13 and A4M11, 12 or 13. Fig. 5 shows FT-IR spectra of A3Ms, A4Ms, c3MGC and c4MDG as compared with rAEG. In the spectrum of rAEG, the absorption bands due to the allyl ν(C=C) and γ(=C–H) were observed at 1637 cm^{-1} and 991, 908 cm^{-1}, respectively. The corresponding bands characteristic of allyl group were non-existent for A3Ms and A4Ms. The maleimide ring δ band at 689 cm^{-1} which was observed for 3MGC or 4MDG was almost non-existent for each cured resin. Although the maleimide γ(=C–H) band at 833 cm^{-1} of each cured resin was weaker than that of 3MGC or 4MDG, the band considerably remained even after curing. This result may be explained by the fact that the band at 833 cm^{-1} includes benzene ring γ(=C–H) band which does not change by curing in addition to maleimide γ(=C–H) band. If the ene reaction of eugenol and maleimide moiety occurs, succinimide-substituted isoeugenol moiety should be produced. The propenyl γ(=C–H) band of *trans*-isoeugenol is observed at 963 cm^{-1}. However, no clear absorption band related to the propenyl γ(=C–H) band at around 960-970 cm^{-1} was appeared for A3Ms or A4Ms, 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 [31,32]. It was revealed from the FT-IR analysis that most of the allyl and maleimide groups reacted for A3Ms or A4Ms. Similarly, it was confirmed that most of the allyl and maleimide groups reacted for ABMs, although their FT-IR spectra are not shown in Figure 5. Probable reaction scheme of rAEG with 3MGC, 4MDG or BMI is shown in Scheme 5. Thus, the ene reaction of the allyl and maleimide groups generates an ene adduct whose propenylidene moiety copolymerizes with maleimide group to produce a polymer network. Although we did not depict another probable reactions, the addition copolymerization of the original allyl and maleimide groups, and the Diels-Alder reaction of the ene adduct and maleimide group, and subsequent ene-reaction with the maleimide group are not excluded, as we had previously elucidated for the curing reaction of EG and BMI [31].

3.4. Properties of the cured resins

Fig. 6 shows TMA curves of all the cured resins. Coefficient of thermal expansion (CTE) between 100 and 200 °C and T_g measured from the TMA curve were also summarized in Table 2. Although A4M11, A4M12 and A3M11 displayed T_gs at 232, 266 and 277 °C, respectively, other cured resins with higher maleimide contents showed no inflection point in thermal expansion curve until 300 °C. The T_gs of the cured resins were much higher than the T_gs (86 and 65 °C) obtained from tan δ peak temperatures of dynamic mechanical curves of tetrafunctional pentaerythritol- and trifunctional glycerol-based epoxy resins cured with DETDA [13]. The CTEs of cured resins decreased with increasing maleimide content, and c4MDG and c3MGC had CTEs lower than 20 ppm.

Fig. 7 shows TGA curves of all the cured resins. It is obvious that c4MDG and c3MGC have much higher thermal degradation temperatures than A4Ms and A3Ms, respectively. Table 2 summarized T_5s measured by the TGA curves. The T_5s of A4Ms and A3Ms increased with increasing maleimide contents, and A4M13 and A3M13 showed the highest values (323 and 336 °C), which were higher than the previously reported T_5s (291 and 284 °C) of the pentaerythritol- and glycerol-based epoxy resins cured with DETDA [13]. When the cured resins with the same molar ratio were compared, although there were little difference in T_5s between A4Ms and A3Ms, A4Ms and A3Ms had much lower T_5s than ABMs did. This result is attributable that the former contain aliphatic and urethane linkages with a lower heat resistance than diphenyl methane moiety of the later.

Fig. 8 shows flexural properties of A4Ms and A3Ms as compared with those of ABMs. Although flexural moduli of ABMs slightly increased with increasing BMI contents, the flexural strengths and strains at break did not increase, indicating an increase of BMI content caused enhancement of brittle character. On the contrary, flexural strengths and flexural strains at break for A4Ms or A3Ms increased with 4MDG or 3MGC contents, respectively, indicating an increase of 4MDG or 3MGC content caused enhancement of toughness. The difference should be attributed to the fact that 4MDG and 3MGC have more flexible diglycerol and glycerol moieties than a diphenyl methane moiety of BMI. Consequently, A4M13 and A3M13 exhibited much higher flexural strengths (109.5 and 93.0 MPa) and flexural strains at break (2.06 and 2.30%) than ABM13 did (59.3 MPa and 1.34%). In addition, flexural moduli (3.01 and 3.48 GPa) of A4M13 and A3M13 were comparable to that of ABM13 (3.41 GPa). Also, flexural strengths and moduli of A4M13 and A3M13 were much higher than the previously reported flexural strengths (85.9 and 85.8 MPa) and moduli (2.50 and 2.30 GPa) of the pentaerythritol- and glycerol-based epoxy resins cured with DETDA, respectively [13].

4. Conclusions

2MPD, 3MGC and 4MDG were synthesized by reactions of MPIC with PD, GC and DG, respectively. Although 2MPD did not melt until the temperature where thermal decomposition starts, 3MGC and 4MDG exhibited broad T_ms with onset points at 165 °C and 124 °C, respectively. In this study, 3MGC and 4MDG except 2MPD were cured with rAEG at 250 °C, and the thermal and mechanical properties of A3Ms and A4Ms were compared with those of ABMs. The T_gs and T_5s of A3Ms and A4Ms increased with increasing polymaleimide contents, and these values were higher than those of the already reported cured materials of glycerol- and polyglycerol-based epoxy resins. However, T_5s of A3Ms and A4Ms were much lower than those of ABMs. Flexural strengths and flexural strains at break for A3Ms and A4Ms increased with polymaleimide contents, and those of A3M13 and A4M13 were much higher than those of ABM13. Consequently, the bio-based allylphenolic-polymaleimide resins derived from GC, DG and EG displayed much better thermal and mechanical properties than the aliphatic polyol-based epoxy resins. This bio-based resin system is suited for the applications which need a moderate heat resistance lower than 300 °C. In case of the uses which need much higher heat resistance, rAEG/BMI resin system is preferred.

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Table 1 Sample codes of cured resins, compostions of the feed monomers and catalyst, and the curing conditions.

Sample code	Feed monomers	Molar ratio	Curing catalyst (TPP)	Curing condition	
				Prepoly-merization	Compression molding
A4M11	rAEG/4MDG	1/1	-	170-200 °C/1 h	210°C/8 MPa/1 h, 220°C/8 MPa/2 h, 250 °C/8 MPa/5 h
A4M12	rAEG/4MDG	1/2	-		
A4M13	rAEG/4MDG	1/3	-		
c4MDG	4MDG	-	0.5 wt%	-	
A3M11	rAEG/3MGC	1/1	-	170-200 °C/1 h	210°C/8 MPa/1 h, 220°C/8 MPa/2 h, 250 °C/8 MPa/5 h
A3M12	rAEG/3MGC	1/2	-		
A3M13	rAEG/3MGC	1/3	-		
c3MGC	3MGC	-	0.5 wt%	-	
ABM11	rAEG/BMI	1/1	-	170-200 °C/1 h	210°C/8 MPa/1 h, 220°C/8 MPa/2 h, 250 °C/8 MPa/5 h
ABM12	rAEG/BMI	1/2	-		
ABM13	rAEG/BMI	1/3	-		

Table 2 T_gs and CTEs mesaured by TMA and T_5s measured by TGA for A4Ms, A3Ms and ABMs.

Sample code	T_g (°C)	CTE[*1] (ppm)	T_5 (°C)
A4M11	232	143.1	309
A4M12	266	74.4	315
A4M13	>300	52.2	323
c4MDG	>300	19.0	359
A3M11	277	79.9	308
A3M12	>300	48.0	316
A3M13	>300	37.8	336
c3MGC	>300	12.3	372
ABM11	>350	42.7	463.3
ABM12	>350	50.7	487.9
ABM13	>350	41.4	497.8

[*1] CTE (coefficient of thermal expansion) between 100 and 200 °C.

Figure and scheme captions

Scheme 1. Conventional allylphenolic-maleimide resin.

Scheme 2. Synthetic route of rAEG.

Scheme 3. Chemical structures of 2MPD, 3MGC and 4MDG, and abbreviations of the cured resins in this study. [*1] x/y is a molar ratio of allyl/maleimide (x/y = 1/1, 1/2 or 1/3).

Scheme 4. Synthetic routes of 2MPD, 3MGC and 4MDG.

Scheme 5. Probable reaction mechanism for rAEG and polymaleimides.

Fig. 1. ^{1}H-NMR spectra of 2MPD, 3MGC and 4MDG in DMSO-d_6.

Fig. 2. FT-IR spectra of 2MPD, 3MGC and 4MDG.

Fig. 3. TG-DTA curves of 2MPD, 3MGC and 4MDG.

Fig. 4. DTA curves of 2MPD, 3MGC and 4MDG with 0.5 wt% TPP.

Fig. 5. FT-IR spectra of rAEG, 4MDG, A4Ms, c4MDG, 3MGC, A3Ms and c3MGC.

Fig. 6. TMA curves of A4Ms, c4MDG, A3Ms and c3MGC.

Fig. 7. TGA curves of A4Ms, c4MDG, A3Ms and c3MGC.

Fig. 8. Flexural properties of A4Ms, A3Ms and ABMs.

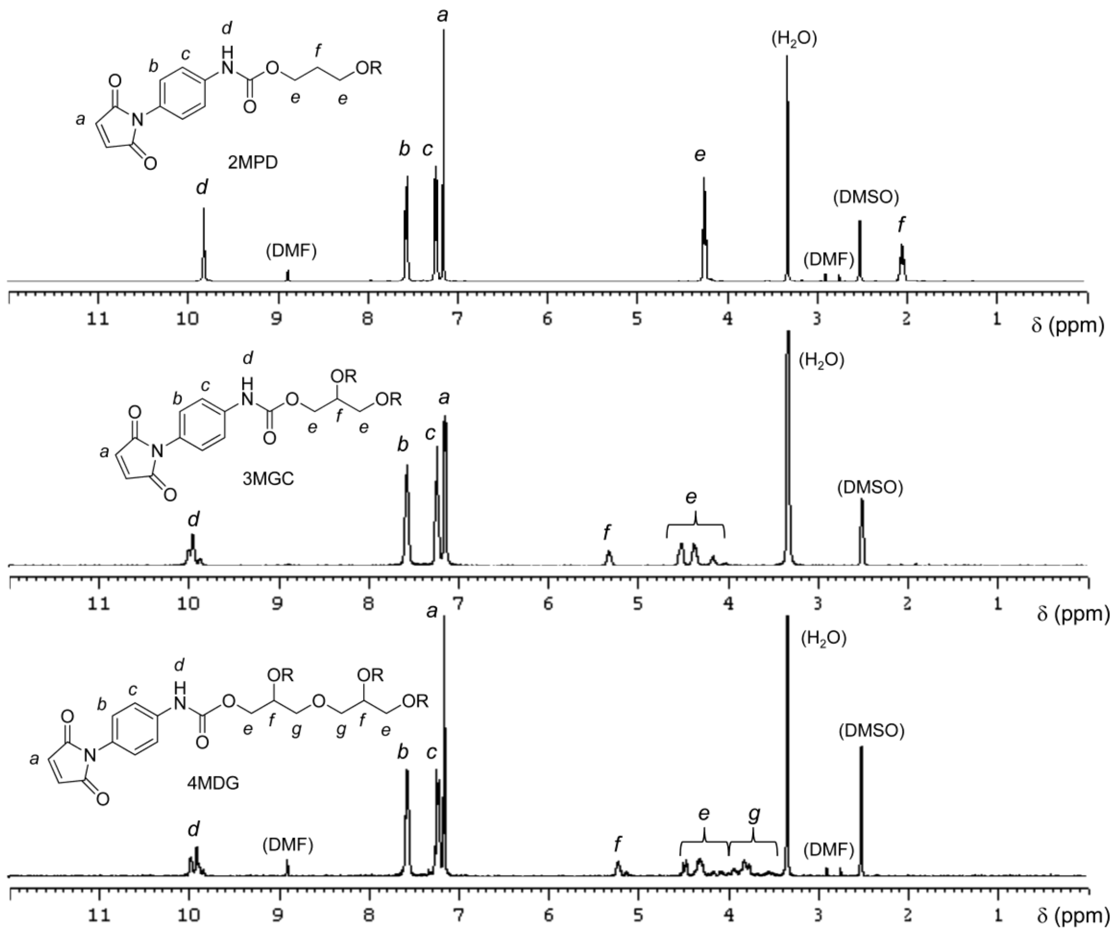


Fig. 1

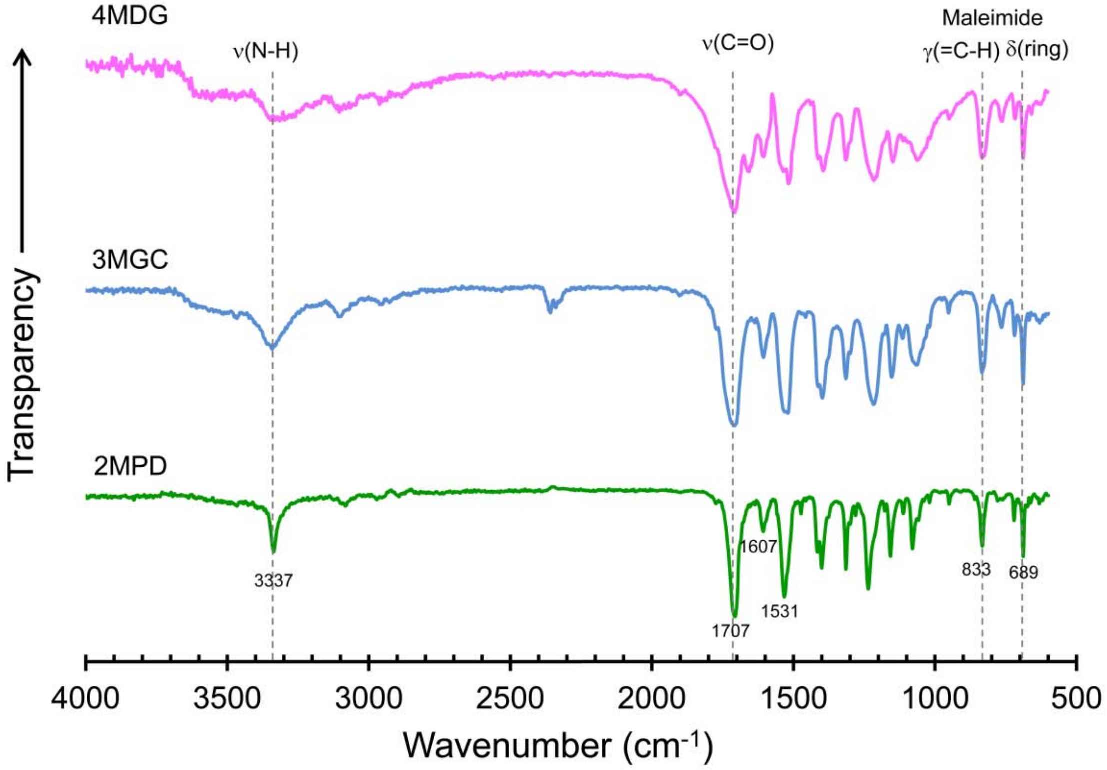

4MDG
3MGC
2MPD
ν(N-H)
ν(C=O)
Maleimide
γ(=C-H)
δ(ring)
3337
1607
1531
1707
833
689
Transparency
4000
3500
3000
2500
2000
1500
1000
500
Wavenumber (cm-1)

Fig. 2

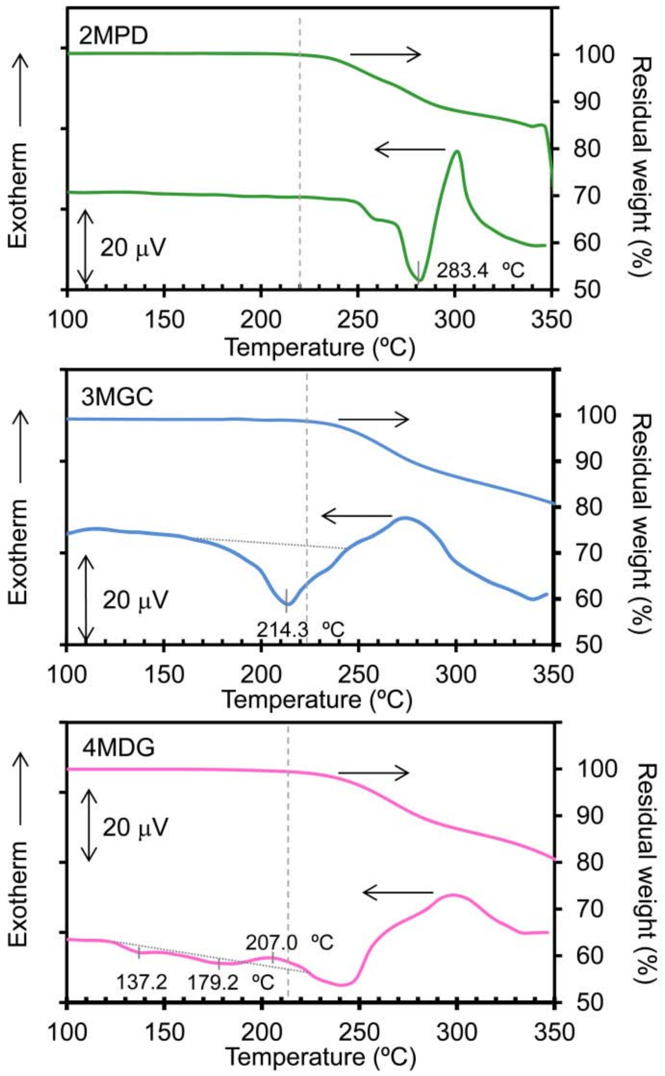

2MPD
Exotherm
20 μV
283.4 ºC
Residual weight (%)
100
90
80
70
60
50
100
150
200
250
300
350
Temperature (ºC)
3MGC
Exotherm
20 μV
214.3 ºC
Residual weight (%)
100
90
80
70
60
50
100
150
200
250
300
350
Temperature (ºC)
4MDG
Exotherm
20 μV
207.0 ºC
137.2
179.2 ºC
Residual weight (%)
100
90
80
70
60
50
100
150
200
250
300
350
Temperature (ºC)

Fig. 3

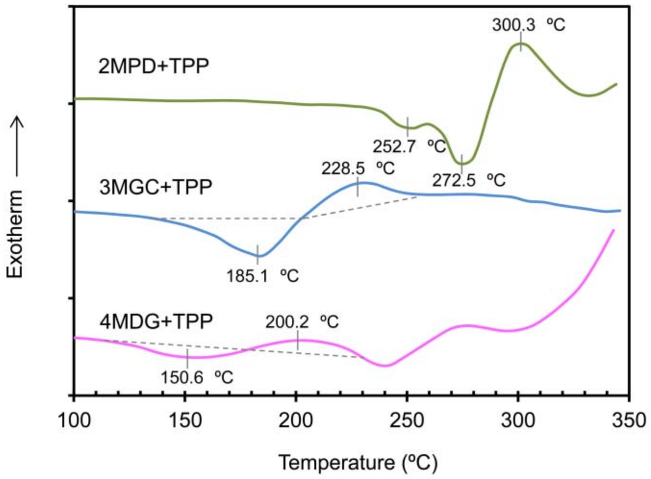

2MPD+TPP
300.3 ºC
252.7 ºC
272.5 ºC
3MGC+TPP
228.5 ºC
185.1 ºC
4MDG+TPP
200.2 ºC
150.6 ºC
Exotherm
100
150
200
250
300
350
Temperature (ºC)

Fig. 4

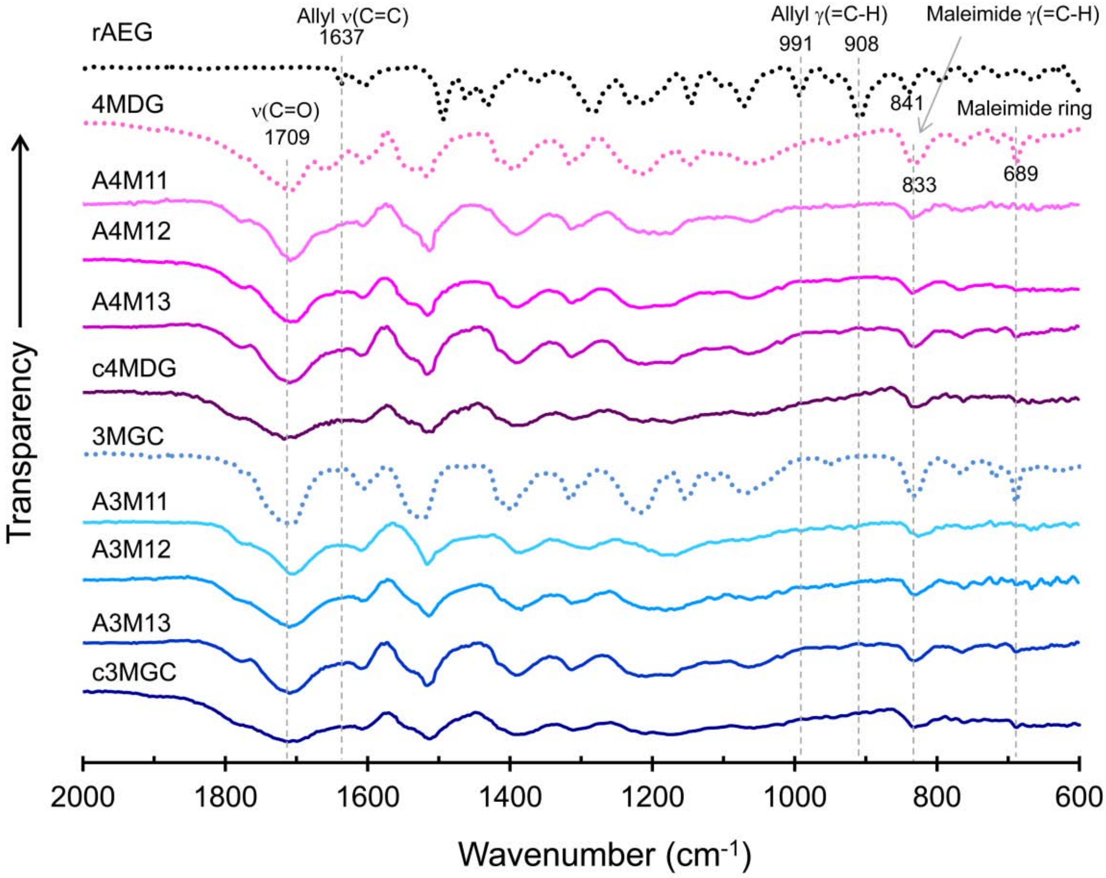

rAEG
4MDG
A4M11
A4M12
A4M13
c4MDG
3MGC
A3M11
A3M12
A3M13
c3MGC
Allyl ν(C=C)
1637
ν(C=O)
1709
Allyl γ(=C-H)
991
908
841
Maleimide γ(=C-H)
Maleimide ring
833
689
Transparency
2000
1800
1600
1400
1200
1000
800
600
Wavenumber (cm-1)

Fig. 5

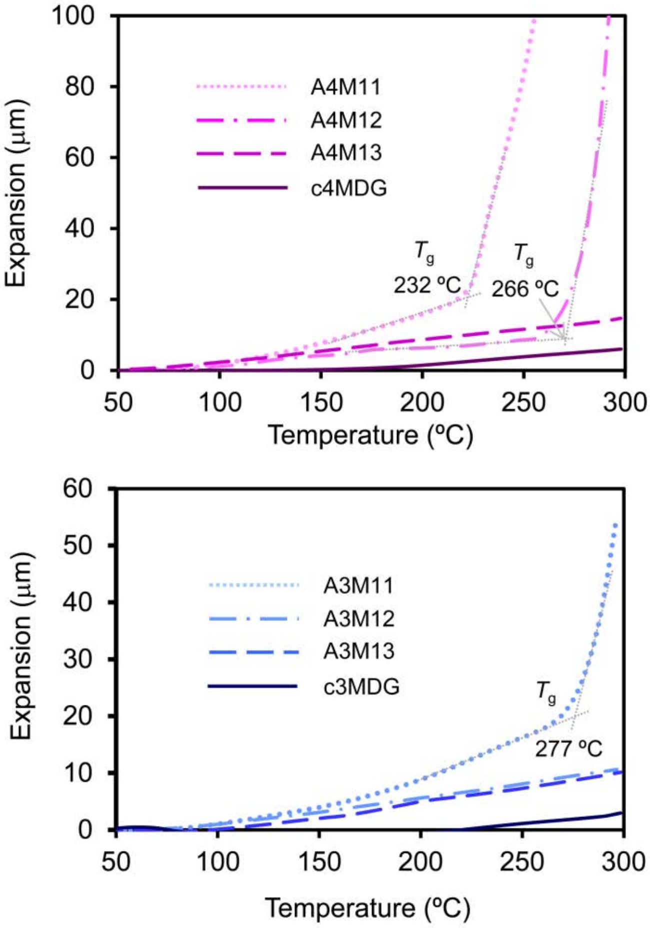

100
80
60
40
20
0
Expansion (μm)
A4M11
A4M12
A4M13
c4MDG
T_g
232 ºC
T_g
266 ºC
50
100
150
200
250
300
Temperature (ºC)
60
50
40
30
20
10
0
Expansion (μm)
A3M11
A3M12
A3M13
c3MDG
T_g
277 ºC
50
100
150
200
250
300
Temperature (ºC)

Fig. 6

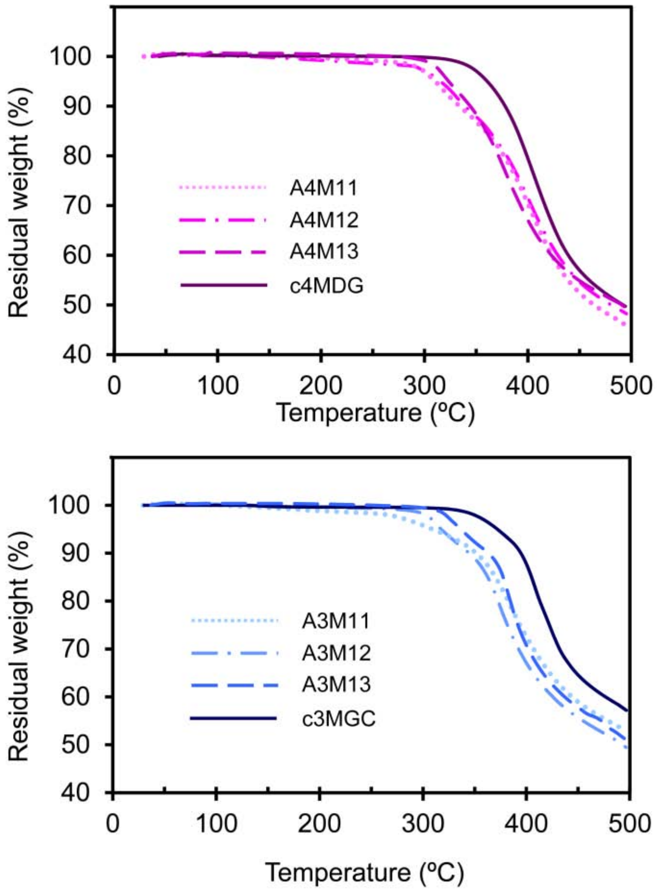

Residual weight (%)
100
90
80
70
60
50
40
0
100
200
300
400
500
Temperature (ºC)
A4M11
A4M12
A4M13
c4MDG
Residual weight (%)
100
90
80
70
60
50
40
0
100
200
300
400
500
Temperature (ºC)
A3M11
A3M12
A3M13
c3MGC

Fig. 7

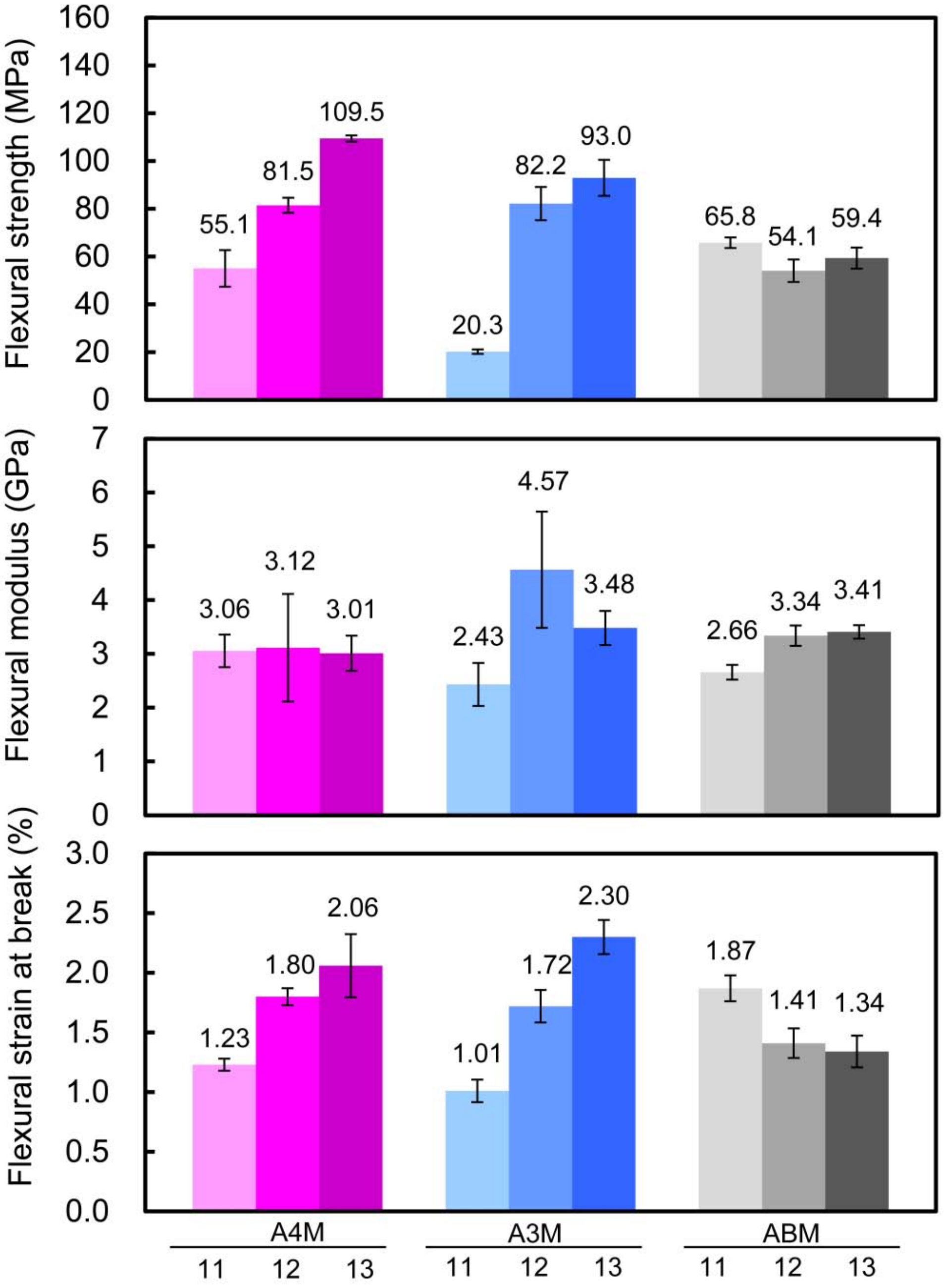
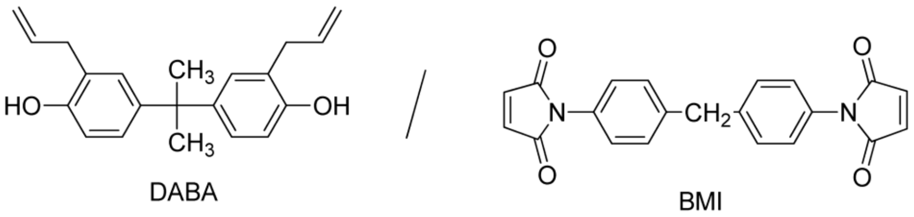
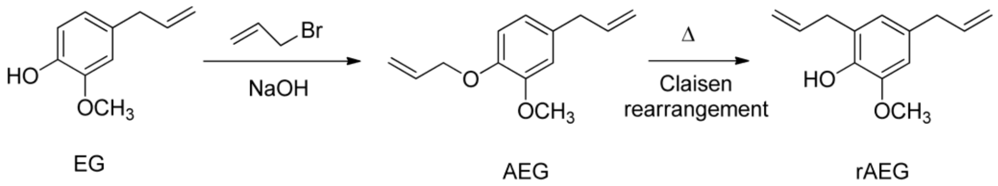

Flexural strength (MPa)
160
140
120
100
80
60
40
20
0
55.1
81.5
109.5
20.3
82.2
93.0
65.8
54.1
59.4
Flexural modulus (GPa)
7
6
5
4
3
2
1
0
3.06
3.12
3.01
2.43
4.57
3.48
2.66
3.34
3.41
Flexural strain at break (%)
3.0
2.5
2.0
1.5
1.0
0.5
0.0
1.23
1.80
2.06
1.01
1.72
2.30
1.87
1.41
1.34
A4M
11
12
13
A3M
11
12
13
ABM
11
12
13

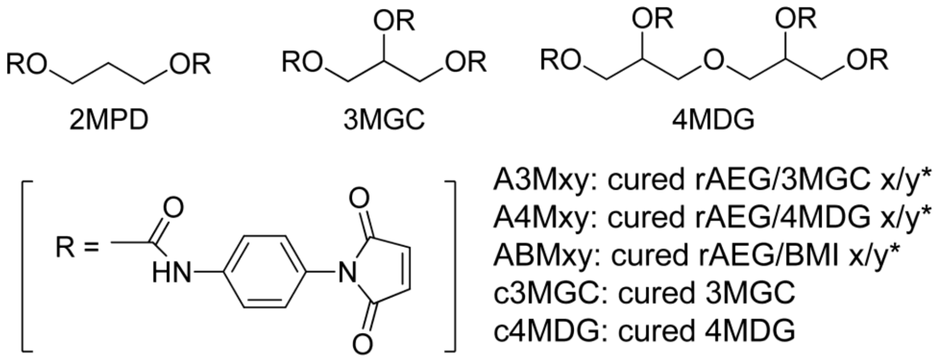
Fig. 8



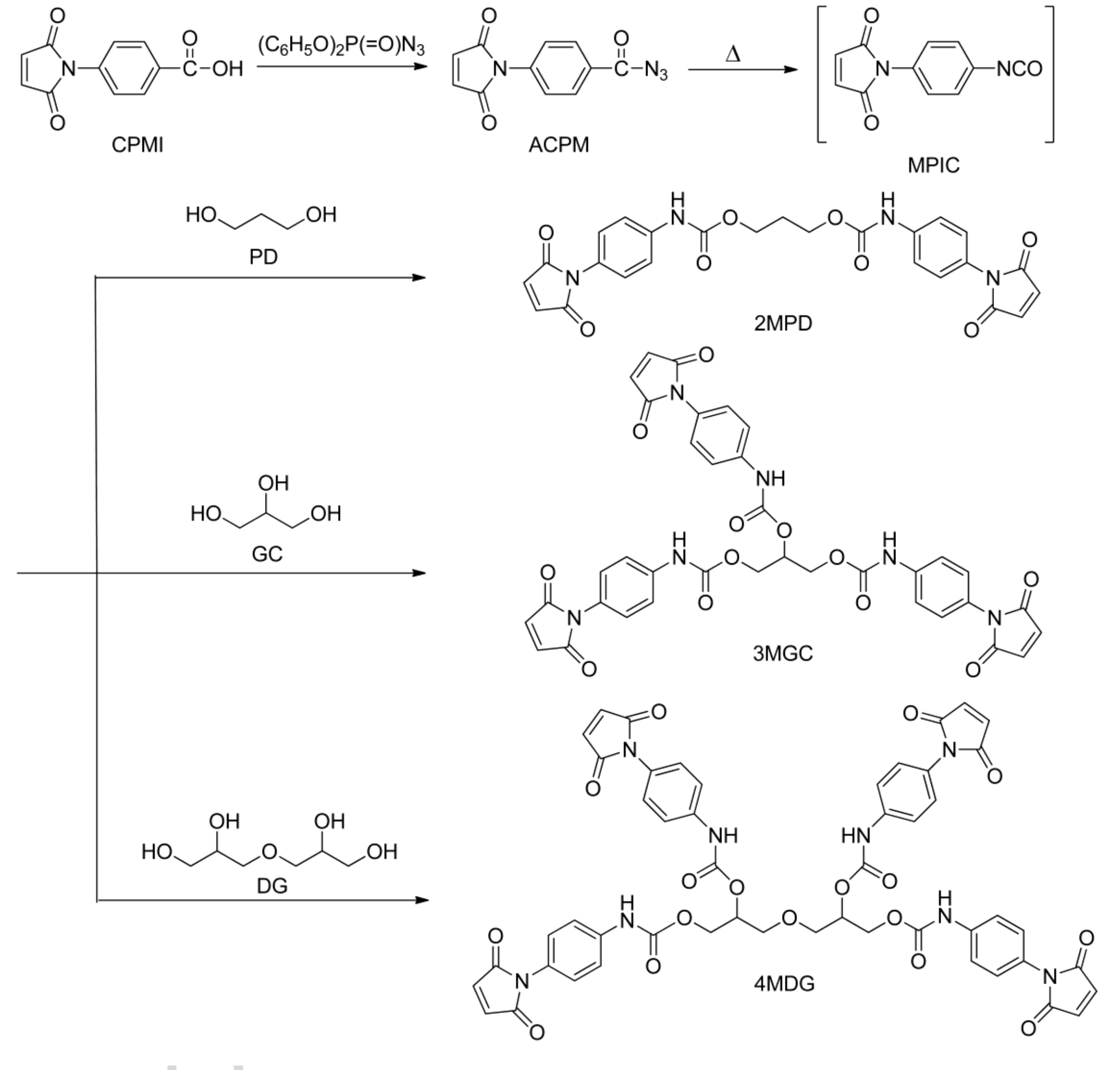
Scheme 1


HO
OCH3
EG
Br
NaOH
O
OCH3
AEG
Δ
Claisen
rearrangement
HO
OCH3
rAEG

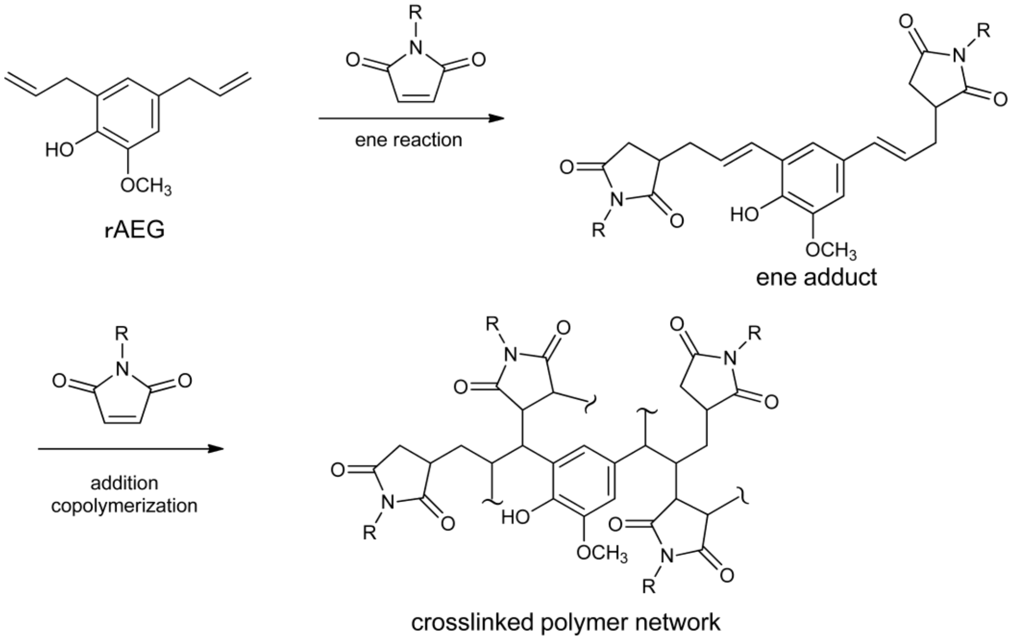
Scheme 2


RO
OR
2MPD
3MGC
4MDG
R =
O
HN
N
A3Mxy: cured rAEG/3MGC x/y*
A4Mxy: cured rAEG/4MDG x/y*
ABMxy: cured rAEG/BMI x/y*
c3MGC: cured 3MGC
c4MDG: cured 4MDG

Scheme 3



Scheme 4


rAEG
ene reaction
ene adduct
addition
copolymerization
crosslinked polymer network

Scheme 5