

Thermosetting bismaleimide resins generating covalent and multiple hydrogen bonds

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ABSTRACT: Prepolymerizations of 4,4'-bismaleimidodiphenylmethane (BMI), diallyl isocyanurate (DAIC), and melamine (ML) at 160–170°C and subsequent compression molding at 200–280°C yielded cured BMI/DAIC/ML resins with feed molar ratios of 4/1/1, 3/1/1, and 2/1/1 (BMI-DAIC-ML411, 311, and 211). Similarly, cured BMI/DAIC 1/1 and BMI/ML 3/1 resins (BMI-DAIC11 and BMI-ML31) were prepared. The FT-IR analysis revealed that the maleimide and allyl groups were almost consumed for all the cured resins, and the hydrogen bonding interaction became stronger with decreasing BMI contents for BMI-DAIC-MLs. Based on the cured structures elucidated from the FT-IR result, the numbers of multiple hydrogen bonds and cross-linking covalent bonds (N_{MHB} and N_{CB}), and total cross-linking bond energy (E_{TB}) were evaluated to be 0, 7.92, and 618 for BMI-DAIC-ML411, 0.71, 7.81, and 627 for BMI-DAIC-ML311, and 0.95 mol kg⁻¹, 7.61 mol kg⁻¹, and 617 kcal kg⁻¹ for BMI-DAIC-ML211, respectively. A higher order of glass transition and 5% weight loss temperatures for BMI-DAIC-MLs was 411 > 311 > 211 in accordance with a higher order of N_{CB} . BMI-DAIC-MLs displayed a weak $\tan \delta$ peak at 70–150°C due to dissociation of the hydrogen bonds. The flexural strength and modulus of BMI-DAIC-ML311 were higher than those of BMI-DAIC-ML411 in accordance with the difference of E_{TB} . © 2015 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2016**, *133*, 43121.

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INTRODUCTION

Covalently linked polymer networks produced by curing reactions of conventional thermosetting resins such as urea, melamine (ML), epoxy, phenol, and bismaleimide resins have been widely used for industrial materials due to the superior processability of the uncured resins with relatively low molecular weight, insoluble, and infusible properties of the cured resins, and controllable thermal and mechanical properties by changing the building block, functional group, and its functionality.^{1,2} The networks are formed almost exclusively by covalent bonds and are generally irreversible. Recently, considerable progress has been achieved on design of supramolecular polymer networks (SPNs) formed by multiple hydrogen bonding (MHB) between various components such as ureidopyrimidinone (UPy) dimer,^{3–6} Hamilton wedge/cyanuric acid,⁷ melamine (ML)/cyanuric acid (CA),^{7–9} and ML/thymine analogs,¹⁰ which are applicable to self-healing^{11,12} and shape memory materials,¹³ stimuli-responsive gels,^{14,15} drug delivery system,^{16,17} and so on. However, there are a few studies on polymer networks having both covalent and MHB cross-linkages.^{18,19} Wietor *et al.* partially replaced covalent urethane cross-linkages formed by the reaction

of a trihydroxy-terminated three-armed flexible aliphatic polyester and diisocyanate to UPy-based multiple hydrogen bonds. They found that the incorporation of the UPy units improves the mechanical strength.¹⁸ However, it is not explored whether this strategy is applicable to high-performance thermosetting resins.

Thermosetting bismaleimide resins are an important class of high-performance polymers that are used as matrices for advanced composites in aerospace and electronics industries. The most popular thermosetting bismaleimide resin systems are combination of 4,4'-bismaleimidodiphenylmethane (BMI) and 2,2'-diallylbisphenol A^{20,21} or 4,4'-diaminodiphenylmethane (DDM).^{22,23} As a convenient method introducing MHB interaction to the BMI-curing system, the utilization of ML and diallyl isocyanurate (DAIC) is considered (Figure 1). ML and DAIC can undergo MHB as is shown in Figure 2, in a similar manner to melamine cyanurate analogs.^{24–27} Amino groups of ML are possible to undergo Michael addition with maleimide groups of BMI in a similar manner to the curing reaction of BMI and DDM.^{28,29} Leu reported that addition copolymerization of triallyl isocyanurate and BMI occurs when triphenylphosphine

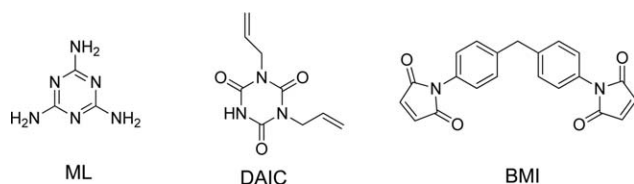


Figure 1. Chemical structure of ML, DAIC, and BMI.

(TPP) was used as a catalyst.³⁰ Therefore, it is expected that DAIC and BMI similarly react and the allyl-unsaturated imide group (C=ONHC=O) can form MHB with the diaminotriazine moiety which remains by nonstoichiometric reaction of BMI and ML. In this study, the influence of introduction of MHB into the BMI/DAIC/ML curing system on the thermal and mechanical properties was investigated by changing the feed molar ratio. In addition, their properties were compared with those of cured BMI/ML and BMI/DAIC resins.

EXPERIMENTAL

Materials

ML (mp > 300°C) was purchased from Junsei Chemical Co., Ltd. (Tokyo, Japan). DAIC (mp 148°C), BMI (mp 159°C), and triphenylphosphine (TPP) were purchased from Tokyo Kasei Kogyo Co. Ltd. (Tokyo, Japan). Chemical structures of BMI, DAIC, and ML are shown in Figure 1. All the reagents were used without further purification.

Preparation of Cured Resins

A mixture of BMI (5.16 g, 14.4 mmol), DAIC (0.753 g, 3.60 mmol), and TPP (12 mg, 0.046 mmol) was heated on a hot plate which was set at 160°C for 40 min, and then ML (0.454 g, 3.60 mmol) was added to the mixture. The reaction mixture was further heated on the same hot plate which was set at 170°C until the mixture becomes a gelatinous material (*ca* 30 min). The prepolymer which was obtained was compression-molded at 200°C for 2 h, 250°C for 3 h, and then 280°C for 1 h at a pressure of 5 MPa using Mini Test Press-10 (Toyo Seiki Co., Ltd, Tokyo, Japan) to produce a cured BMI/DAIC/ML resin with the feed molar ratio of 4/1/1 (BMI-DAIC-ML411) as a brown plate. Similarly, cured BMI/DAIC/ML resins with the feed molar ratio of 3/1/1 and 2/1/1 (BMI-DAIC-ML311 and 211) and cured BMI/DAIC resin with the feed molar ratio of 1/1 (BMI-DAIC11) were prepared. Also, cured BMI/ML resin with the feed molar ratio of 3/1 (BMI-ML31) was prepared by the prepolymerization of a mixture of BMI (6.00 g, 16.7 mmol) and ML (0.70 g, 5.56 mmol) at 170°C for 30 min and subsequent compression molding at the same condition as BMI-DAIC-ML411. Completion of the curing reactions for all the cured resins was confirmed by the fact that their specimens did not exhibit any exothermal peaks until 300°C on the differential scanning calorimetric analysis.

Measurements

Fourier-transform infrared (FT-IR) spectra were recorded at room temperature in the range from 4000 to 500 cm⁻¹ on an FT-IR 8400s (Shimadzu Co. Ltd., Kyoto, Japan) by the KBr pellet method using finely pulverized samples. The IR spectra were acquired using 50 scans at a resolution of 4 cm⁻¹. The 5% weight loss temperature (*T*₅) was measured on a thermogravi-

metric analyzer TGA-50 (Shimadzu Co. Ltd.) in a nitrogen atmosphere at a heating rate of 20°C min⁻¹. Dynamic mechanical analysis (DMA) measurements of rectangular plates (length 40 mm, width 9 mm, and thickness 1 mm) were performed on a Rheograph Solid (Toyo Seiki Co., Ltd, Tokyo, Japan) 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-Nonresonance method). Flexural testing of rectangular specimens (50 × 7 × 1 mm³) 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 composite specimens were tested for each set of samples, and the mean values and the standard deviation were calculated.

RESULTS AND DISCUSSION

Curing Reactions of BMI/ML, BMI/DAIC, and BMI/DAIC/ML

In the reactions of BMI, ML, and DAIC, it is theoretically expected that one amino (-NH₂) group of ML can react with two maleimide groups of BMI by the Michael addition reaction, and one allyl group of DAIC can undergo addition copolymerization with one maleimide group of BMI. The feed molar ratios of 3:1, 1:1, and 4:1:1 for BMI/ML, BMI/DAIC, and BMI/DAIC/ML, respectively, are based on the assumption that all the maleimide groups of BMI stoichiometrically react with amino groups of ML and/or allyl groups of DAIC as is shown in Figure 3. When the molar fraction of BMI is lower than BMI/DAIC/ML 4/1/1, the *N,N'*-disubstituted diaminotriazine moiety which remains by the nonstoichiometric reaction can form MHB with the imide group (C=ONHC=O) of the *N,N'*-disubstituted isocyanuric acid moiety as is shown in Figure 4. The number of multiple hydrogen bonds (*N*_{MHB}) per 1 kg of elemental cured structure for BMI-DAIC-ML211 [1000/(2 × 358 + 209 + 126) = 0.95 mol kg⁻¹] is higher than that for BMI-DAIC-ML311 [1000/(3 × 358 + 209 + 126) = 0.71 mol kg⁻¹], when *N*_{MHB}s were calculated based on the each elemental cured structure shown in Figure 4. Therefore, the reaction product of BMI/

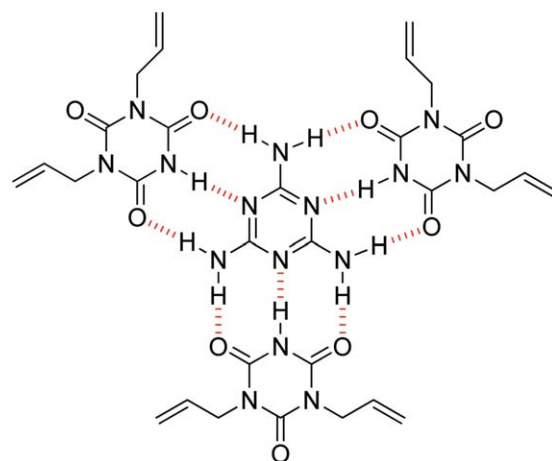


Figure 2. MHB interaction between ML and DAIC. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

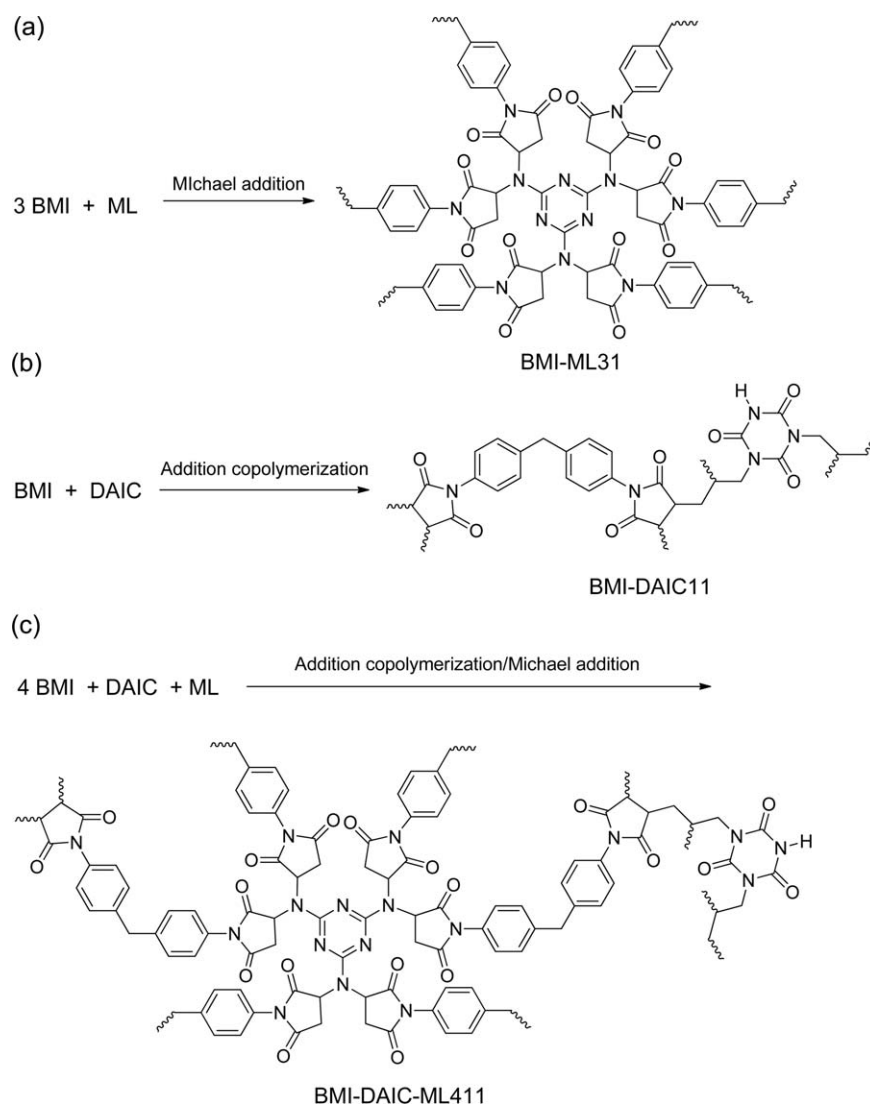


Figure 3. Theoretical cured structures for 3BMI/ML, BMI/DAIC, and 4BMI/DAIC/ML.

DAIC/ML 2/1/1 is considered to generate more MHB fraction than that of BMI/DAIC/ML 3/1/1.

Figures 5 and 6 show the FT-IR spectra of DAIC, ML, BMI, and a hydrogen-bonded complex of DAIC and ML (DAIC-ML) and those of BMI-DAIC11, BMI-ML31, and BMI-DAIC-MLs, respectively. In the spectrum of DAIC, absorption bands related to allyl $=\text{C}-\text{H}$ out-of-plane bending vibration ($\delta_{\text{C}-\text{H}}$) were observed at 989 and 939 cm^{-1} . Also, bands related to hydrogen-bonded N-H stretching vibration ($\nu_{\text{N}-\text{H}}$) and amide $\text{C}=\text{O}$ stretching vibration ($\nu_{\text{C}=\text{O}}$) were observed at 3236, 1720, and 1676 cm^{-1} , respectively. In the spectrum of ML, the $\nu_{\text{N}-\text{H}}$ bands were observed at 3470, 3420, and 3335 cm^{-1} , and the bands due to N-H bending vibration ($\delta_{\text{N}-\text{H}}$) and $\text{C}=\text{N}$ stretching vibration ($\nu_{\text{C}=\text{N}}$) were at 1649 and 1549 cm^{-1} , respectively.³¹ The DAIC-ML was prepared by evaporating an aqueous solution of DAIC/ML 1/1. The DAIC-ML displayed a very broad hydrogen-bonding $\nu_{\text{N}-\text{H}}$ band at approximately 3380 cm^{-1} , which was not appeared in the spectra of DAIC and ML. It is

known that hydrogen-bonding $\nu_{\text{N}-\text{H}}$ bands are observed at approximately 3400, 3200, and 3040 cm^{-1} in the FT-IR spectrum of melamine cyanate.³² In the case of DAIC-ML, the corresponding bands were observed as a very broad peak in the region of 3100–3600 cm^{-1} . The BMI showed the absorption bands characteristic of maleimide group at 1148, 837, and 689 cm^{-1} , in addition to an imide $\nu_{\text{C}=\text{O}}$ band at 1707 cm^{-1} and a band related to benzene ring at 1512 cm^{-1} .^{29,33} In the FT-IR spectrum of BMI-DAIC11, the bands characteristic to maleimide group around at 1148, 837, and 689 cm^{-1} and those characteristic to allyl group around at 989 and 939 cm^{-1} were almost nonexistent, and the band characteristic of succinimide moiety was observed at around 1186 cm^{-1} . These results suggest that addition copolymerization of maleimide and allyl groups certainly occurred in agreement with the cured structure of BMI-DAIC11 shown in Figure 3(b). In the FT-IR spectrum of BMI-ML31, although the bands characteristic to maleimide group were also nonexistent, weak $\nu_{\text{N}-\text{H}}$ and $\delta_{\text{N}-\text{H}}$ bands at 3468, 3418, and 1649 cm^{-1} , which resemble to those of primary

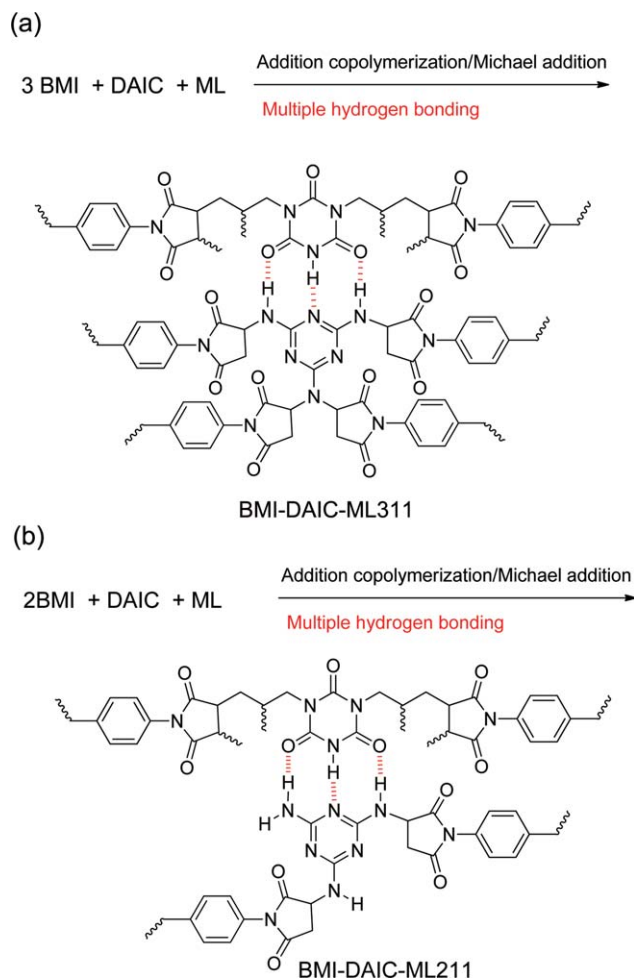


Figure 4. Theoretical cured structures for 3BMI/DAIC/ML and 2BMI/DAIC/ML. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

amino groups of ML were observed, suggesting that an ideal cured structure shown in Figure 3(a) is not completely formed and some amount of primary amino group is remaining. This result may be attributed to the following factors: ML has a poor solubility in melted BMI at 170°C; amino groups of ML have a weaker nucleophilicity than a general aromatic amine such as aniline and DDM; the anionic homopolymerization of BMI is promoted by the action of ML as a basic catalyst. Therefore, the chemical structure containing primary, secondary, and tertiary amino groups formed by Michael addition reactions between amino and maleimide groups, and homopolymerized maleimide moiety is inferred as a cured structure of BMI-ML31 (Figure 7). In the FT-IR spectrum of BMI-DAIC-ML411, the bands characteristic to maleimide and allyl groups were almost nonexistent, indicating that the addition copolymerization of maleimide and allyl groups, and the Michael addition between maleimide and amino groups certainly occurred. Additionally, although a weak and broad hydrogen-bonding band at 3200–3600 cm^{-1} was observed, the $\nu_{\text{N-H}}$ and $\delta_{\text{N-H}}$ bands related to primary or secondary amino group were much weaker than those of BMI-ML31. This result may be caused by a following possibility: ML has a better solubility in melted mixture of BMI/DAIC; the

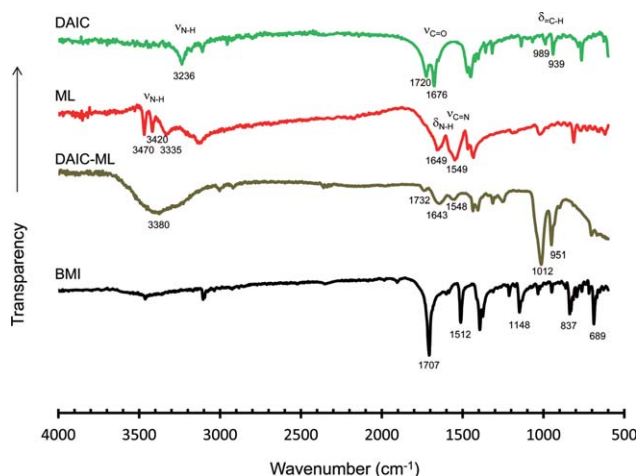


Figure 5. FT-IR spectra of DAIC, ML, DAIC-ML, and BMI. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

solubilized ML more easily performs the Michael reaction with BMI; and the N–H groups which remained by incomplete Michael reaction formed hydrogen bonding with the imide group ($\text{C}=\text{ONHC}=\text{O}$) of the *N,N'*-disubstituted isocyanuric acid moiety which was arisen from the copolymerized DAIC [Figure 3(c)]. In the FT-IR spectra of BMI-DAIC-ML311 and BMI-DAIC-ML211, although the bands characteristic to maleimide and allyl groups were similarly almost nonexistent, a broad $\nu_{\text{N-H}}$ band at around 3380 cm^{-1} characteristic of a hydrogen-bonded complex and the $\delta_{\text{N-H}}$ band at 1612 cm^{-1} were stronger than those of BMI-DAIC-ML411. Intensity of the $\nu_{\text{N-H}}$ and $\delta_{\text{N-H}}$ bands was stronger for BMI-DAIC-ML211 than for BMI-DAIC-ML311. These results indicate that MHB is certainly formed for BMI-DAIC-ML311 and BMI-DAIC-ML211, and BMI-DAIC-ML211 contains a higher fraction of hydrogen bonds than BMI-DAIC-ML311 does in agreement with the

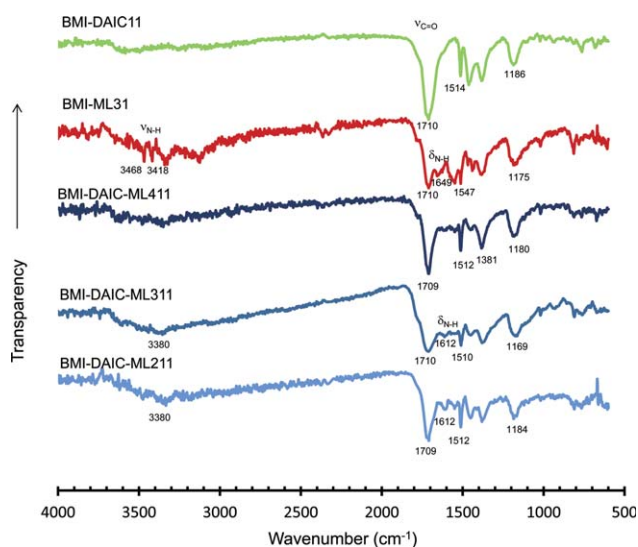


Figure 6. FT-IR spectra of BMI-DAIC11, BMI-ML31, and BMI-DAIC-MLs. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

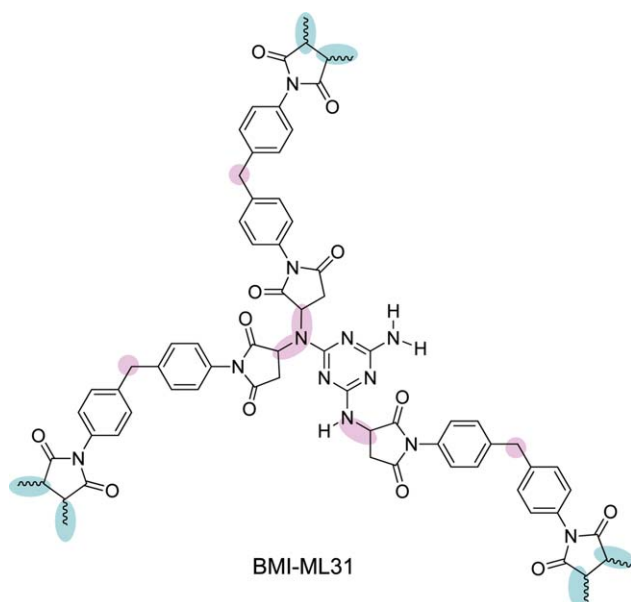


Figure 7. Probable cured structure of BMI-ML31. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

probable elemental cured structures which were shown in Figure 4.

Thermal and Mechanical Properties of Cured Resins

Figure 8 shows the DMA curves of all the cured resins. A higher order of the onset temperature of a drop in storage modulus (E') corresponding to glass transition temperature (T_g) was BMI-DAIC11 (316.3°C) > BMI-ML31 (275.9°C) \approx BMI-DAIC-ML411 (275.2°C) > BMI-DAIC-ML311 (255.2°C) > BMI-DAIC-ML211 (201.2°C). To evaluate cross-linking densities of cured resins, the number of covalent bonds (N_{CB}) which connect original phenyl maleimide, DAIC, and ML moieties per 1 kg of elemental cured structure was calculated based on each elemental cured structure as was shown in Figures 3(b,c), 4, or 7. For example, N_{CB} of BMI-ML31 is calculated to be $1000 \times [6 + (6/2)] / (3 \times 358 + 126) = 7.50 \text{ mol kg}^{-1}$, as the elemental cured structure shown in Figure 7 has 6 linkages between two moieties (red marks) and 6 half-linkages attached *N*-phenylsuccinimide moieties (blue marks) per 3BMI (MW:358) and one ML (MW:126). In a similar manner, N_{CB} s of BMI-DAIC11, BMI-DAIC-ML411, BMI-DAIC-ML311, and BMI-DAIC-ML211 became 8.82, 7.92, 7.81, and 7.61 mol kg^{-1} , respectively. The decreasing order of N_{CB} was in accordance with the decreasing order of T_g except for BMI-ML31. The fact that BMI-ML31 exhibited a higher T_g than the value expected from the N_{CB} is attributed to a more rigid structure of ML than DAIC. Although BMI-DAIC-ML211 exhibited $\tan \delta$ peak temperature at 315.6°C, other samples did not present $\tan \delta$ peaks because the DMA experiments stopped when the specimens broke due to the brittleness. A rubbery plateau region of E' which reflects the cross-linking density was observed only for BMI-DAIC-ML211 due to the same reason. Although a clear rubbery plateau region of E' was not observed for BMI-DAIC-ML311, it is considered that the sample broke at the beginning of the rubbery plateau and then the E' decreased steeply. The E' (ca 170

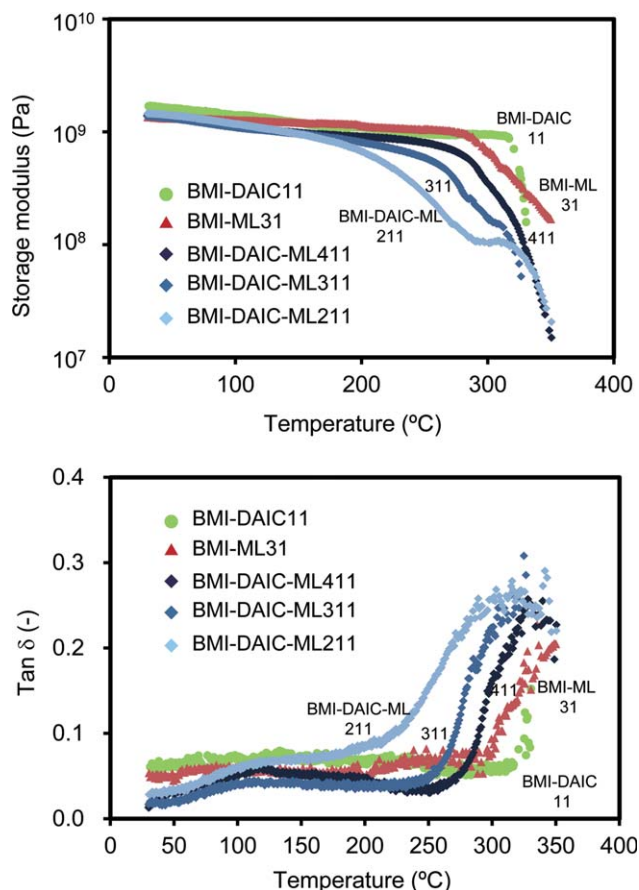


Figure 8. DMA curves of BMI-DAIC11, BMI-ML31, and BMI-DAIC-MLs. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

MPa) at the beginning of rubbery plateau for BMI-DAIC-ML311 was higher than that (105 MPa) for BMI-DAIC-ML211, in agreement with the fact that BMI-DAIC-ML311 has a higher cross-linking density than BMI-DAIC-ML211 does. The ternary

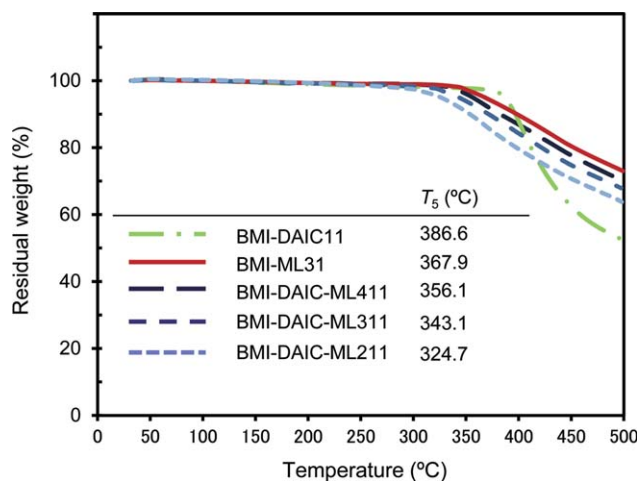


Figure 9. TGA curves of BMI-DAIC11, BMI-ML31, and BMI-DAIC-MLs. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

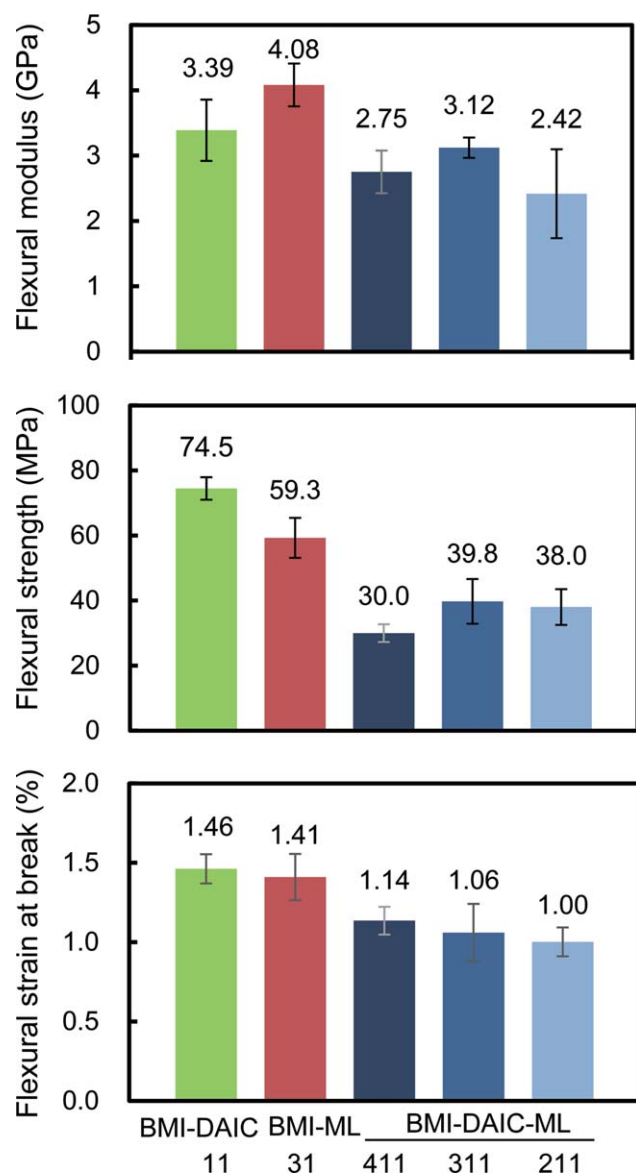


Figure 10. Flexural properties of BMI-DAIC11, BMI-ML31, and BMI-DAIC-MLs. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

cured resins BMI-DAIC-ML411, BMI-DAIC-ML311, and BMI-DAIC-ML211 exhibited one broad secondary dispersion peak of $\tan \delta$ at approximately 70–150°C, which is attributable to dissociation of MHB, considering that the MHB between a bismelamine compound and *N*-dodecylisocyanuric acid in cyclohexane-*d*₁₂ dissociates at approximately 75°C.²⁷

Figure 9 shows the TGA curves of all the cured resins. A higher order of T_5 was in accordance with the higher order of the T_g . As multiple hydrogen bonds completely dissociate at a temperature higher than 300°C where the covalent bonds starts to degrade, the thermal degradation temperature relates to the cross-linking density by covalent bonds.

Figure 10 shows the flexural properties of all the cured resins. BMI-ML31 and BMI-DAIC11 displayed the highest flexural

modulus (4.08 GPa) and strength (74.5 MPa) among all the cured resins, respectively. The fact that BMI-ML31 with the lowest N_{CB} value displayed the highest flexural modulus is attributable to the factors that BMI-ML31 has the highest BMI weight fraction (89.5 wt %) which leads to a rigid material, and that ML framework is more rigid than DAIC framework. These flexural modulus and strength was much higher than those of the cured resins of BMI/allyl etherified eugenol with the feed molar ratio of 1/1 (2.98 GPa and 59.1 MPa) which were previously reported.³³ Although BMI-DAIC-MLs possessed lower flexural moduli and strengths than BMI-ML31 and BMI-DAIC11 did, it is noteworthy that flexural modulus and strength of BMI-DAIC-ML311 are considerably higher than those of BMI-DAIC-ML411 in spite of the fact that the latter has a higher number of cross-linking covalent bonds than the former, as is obvious from the trends of the T_g and T_5 . This result is probably caused by strong multiple hydrogen bonds which are effectively exerted at the temperature of flexural testing at around 20°C for BMI-DAIC-ML311. However, BMI-DAIC-ML211 which has a larger N_{MHB} than BMI-DAIC-ML311 displayed a lower flexural strength and modulus than BMI-DAIC-ML311 did. These results are attributable to the following facts: (1) Bond energies (83 and 73 kcal mol⁻¹)³⁴ of C–C and C–N covalent bonds are much higher than that (25.5 kcal mol⁻¹)³⁵ of triple hydrogen bond of melamine cyanurate. (2) When the total cross-linking bond energy per essential cured structure per 1 kg (E_{TB}) are calculated using an average value (78 kcal mol⁻¹) of C–C and C–N bond energies and above bond energy of triple hydrogen bond, E_{TB} (627 kcal kg⁻¹) for BMI-DAIC-ML311 ($N_{CB} = 7.81$ mol kg⁻¹, $N_{MHB} = 0.71$ mol kg⁻¹) is higher than that (618 kcal kg⁻¹) for BMI-DAIC-ML411 ($N_{CB} = 7.92$ mol kg⁻¹, $N_{MHB} = 0$ mol kg⁻¹). (3) E_{TB} (617 kcal kg⁻¹) for BMI-DAIC-ML211 ($N_{CB} = 7.61$ mol kg⁻¹, $N_{MHB} = 0.95$ mol kg⁻¹) is lower than that (627 kcal kg⁻¹) for BMI-DAIC-ML311 ($N_{CB} = 7.81$ mol kg⁻¹, $N_{MHB} = 0.71$ mol kg⁻¹). Although there was a little difference in flexural strains at break among BMI-DAIC-MLs, the flexural strains at break slightly decreased with increasing N_{MHB} value, indicating that the MHB interaction is not effective to enhance the flexibility at least.

CONCLUSIONS

Prepolymerizations of BMI, DAIC, and ML at 160–170°C and subsequent compression molding at 200–280°C produced BMI-DAIC-ML411, BMI-DAIC-ML311, and BMI-DAIC-ML211. Also, BMI-DAIC11 and BMI-ML31 were prepared by a similar method. The FT-IR analysis revealed that the maleimide and allyl groups were almost consumed for all the cured resins, and hydrogen bonding interaction became stronger with decreasing BMI contents for BMI-DAIC-MLs. The DMA analysis revealed that a higher order of T_g was BMI-DAIC11 > BMI-ML31 ≈ BMI-DAIC-ML411 > BMI-DAIC-ML311 > BMI-DAIC-ML211, and BMI-DAIC-MLs displayed a weak $\tan \delta$ peak at 70–150°C due to dissociation of the hydrogen bonds. The flexural tests revealed that BMI-ML31 and BMI-DAIC11 displayed the highest flexural modulus and strength among all the cured resins, respectively, and the flexural strength and modulus of BMI-DAIC-ML311 were higher than those of BMI-DAIC-ML411.

There was a good correlation between the flexural properties and E_{TB} for BMI-DAIC-MLs. Consequently, it was revealed that introduction of MHB interaction into the polymer networks derived from thermosetting bismaleimide resins contributed to the improvement of mechanical properties, whereas it was not effective to improve the relatively high T_g s and T_5 s.

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