High Performance Bio-Based Thermosetting Resins Composed of Tung Oil and Bismaleimide

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ABSTRACT: The reaction of tung oil (TO) and 1,1'-(methylenedi-4,1-phenylene)bismaleimide (BMI) in 1,3-dimethyl-2-imidazolidinone (DMI) at 150°C for 4 h and subsequent precipitation gave TO/BMI prepolymer, which was cured at 200°C for 2 h gave crosslinked TO/BMI product with C=C ratio from 1/1 to 1/4. The FE-SEM analysis revealed that all the cured products are homogeneous and no phase separation was observed. The glass transition temperature and 5% weight loss temperature of the cured TO/BMI increased with increasing BMI content. The maximal tensile strength (38.1 MPa) and modulus (2.6 GPa) were obtained for the cured products with the C=C ratios of 1/2 and 1/3, respectively. To evaluate the reaction of TO and BMI, the model reaction products of TO and N-phenylmaleimide (PMI) in DMI were analyzed by ^{1}H-NMR spectroscopy. The NMR data of the reaction products of TO/PMI with the C=C ratio 2/1, 1/1, 1/2, 1/3, and 1/4 at 150°C for 24 h revealed that Diels-Alder reaction preferentially occurred at 2/1, and that ene reaction and other reactions such as radical homo and copolymerization gradually increased with decreasing C=C ratio of TO/PMI. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 119: 896–901, 2011

Key words: renewable resources; thermosets; Diels-Alder polymers; tung oil; bismaleimide

INTRODUCTION

Bio-based polymer products derived from annually renewable agricultural and biomass feedstock have become increasingly important as sustainable and eco-efficient products, which can replace the products based exclusively on petroleum feedstock.[1,2] Among the renewable natural resources, triglyceride plant oils represent a major class of such resources and are being used in an increasing number of industrial applications, in addition to being a food sources for human beings.[3,4] Tung oil (TO) is one of the oldest known drying oils and have been used extensively in the paint and coatings industries. It is a triglyceride extracted from the seeds of the tung tree (*Aleurites fordii*), in which approximately 80% of the fatty acid chains is α-eleostearic acid, that is, 9-*cis*,11,13-*trans*-octadecatrienoic acid, as is shown in Figure 1.[5,6] Minor fatty acid components of TO are oleic acid, linoleic acid, and saturated fatty acids *etc*. This highly unsaturated, conjugated system is largely responsible for the rapid polymerization and outstanding drying properties of the oil. Electrophilic substitution reactions of phenols with TO in the presence of acid catalyst give crosslinked and/or branched phenol resins.[7–10] Bio-based polyols prepared by chemical modification of TO can be used to the production of polyurethanes.[11,12] TO can be copolymerized with divinylbenzene and/or styrene by both free radical and cationic polymerizations.[13–16] Diels-Alder (DA) reaction of TO and 1,6-hexanediol diacrylate or 1,4-butanediol diacrylate and the properties of the obtained films are reported in the literature.[17] Also, highly regioselective DA reaction of methyl α-eleostearate and maleic anhydride is described in the literature.[18] We had already reported the bio-based thermosetting resins prepared by DA and ene reactions of dehydrated castor oil (DCO) and 1,1'-(methylenedi-4,1-phenylene)-bismaleimide (BMI).[19] Conjugated triene-based TO is expected to have a higher reactivity toward BMI than DCO with conjugated and/or isolated diene moieties.

In this study, bio-based high performance thermosetting resins were prepared by the reaction of TO and BMI and their mechanical and thermal properties were investigated as compared with those of the DCO/BMI cured products. As the partially crosslinked TO/BMI prepolymer was insoluble in general organic solvents, the soluble reaction products of TO and N-phenylmaleimide (PMI) were characterized by ^{1}H-NMR spectroscopy to evaluate the reaction of TO and BMI.
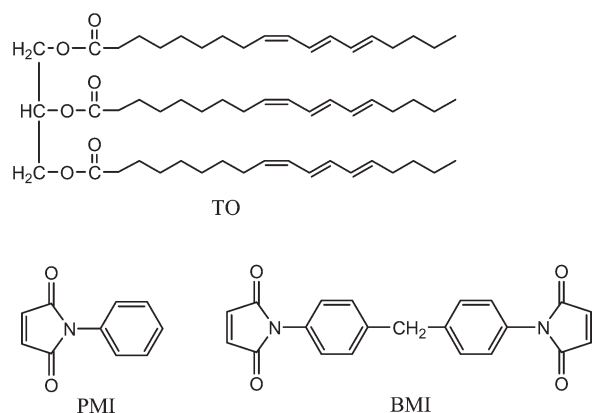
Figure 1 Structure of the main component of TO, PMI, and BMI.

EXPERIMENTAL

Materials

Tung oil (TO) was supplied from Sigma-Aldrich Japan (Tokyo, Japan). N-Phenylmaleimide (PMI), 1,1′-(methylenedi-4,1-phenylene)bismaleimide (BMI), hydroquinone (HQ), and 1,3-dimethyl-2-imidazolidinone (DMI) were purchased from Tokyo Kasei Kogyo Co. (Tokyo, Japan). Figure 1 shows the structure of TO, PMI, and BMI.

Model reaction of TO and PMI

A mixture of TO (1.26 g, C=C 11.0 mmol), PMI (3.81 g, 22.0 mmol), and HQ (0.254 g, 2.31 mmol) in 5 mL of DMI was stirred at 150°C for 24 h. After the reaction mixture was poured into excess water, the obtained precipitate was collected by filtration, washed with ion exchange water and dried at 65°C in a vacuum oven to give a TO/PMI reaction product (3.78 g) in a molar ratio of (C=C of TO)/(maleimide group of PMI) 1/2 as yellow powder. The obtained product was abbreviated to TO/PMI 1/2. The mole number of C=C groups for TO was calculated by use of the average number of C=C per triglyceride measured by ^{1}H-NMR (7.64) and the assumption that TO is a triglyceride of unsaturated carboxylic acids having 12 carbons. The mole number of maleimide group of PMI was calculated based on the structural formula. In a similar manner to TO/PMI 1/2, TO/PMI 2/1, 1/1, 1/3, and 1/4 were prepared.

Curing reaction of TO and BMI

A mixture of TO (5.85 g, C=C 51.0 mmol), BMI (9.13 g, 25.5 mmol), and HQ (0.749 g, 6.80 mmol) in 15 mL of DMI was stirred for 4 h at 150°C. After the reaction mixture was poured into excess water, the obtained precipitate was collected by filtration, washed with methanol and dried at 65°C in a vacuum oven to give a TO/BMI prepolymer (12.0 g) as

yellow powder. The prepolymer was compressed at 180°C and 5 MPa for 1 h, and subsequently postcured at 200°C for 2 h in an electric oven to give a TO/BMI cured product in a molar ratio of (C=C of TO)/(maleimide group of BMI) 1/1. The obtained cured product was abbreviated to TO/BMI 1/1. The mole number of maleimide group of BMI was calculated based on the structural formula. In a similar manner to TO/BMI 1/1, TO/BMI 1/2, 1/3, and 1/4 were prepared. Although we tried the preparation of TO/BMI 2/1, the DMI solution of TO and BMI became gelatinous material after 15 min at 150°C. Since the obtained hard gel did not become powder after mixing with water, we could not prepare the cured material.

Measurements

Proton nuclear magnetic resonance (^{1}H-NMR) spectra were recorded on a Bruker AV-400 (400 MHz) (Madison, WI) using CDCl$_3$ as a solvent. The morphology of the blends was observed by field emission-scanning electron microscopy (FE-SEM), using a Hitachi S-4700 machine (Hitachi High-Technologies Corporation, Tokyo, Japan). All samples were fractured after immersion in liquid nitrogen for about 30 min. The fracture surfaces were sputter coated with gold to provide enhanced conductivity. The 5% weight loss temperature was measured on a thermogravimetric analyzer TGA-50 (Shimadzu Co., Kyoto, Japan) in a nitrogen atmosphere at a heating rate of 20°C/min. Dynamic mechanical analysis (DMA) of the rectangular plates (length 40 mm, width 6 mm, thickness 1 mm) was performed on a Rheolograph Solid (Toyo Seiki Co., Tokyo, Japan) with a chuck distance of 20 mm, a frequency of 1 Hz and a heating rate of 2°C /min, based on ISO 6721-4:1994 (Plastics-Determination of dynamic mechanical properties, Part 4:Tensile vibration−Nonresonance method). Thermomechanical analysis (TMA) was conducted on a MAC Science TMA 4000S (Yokohama, Japan) at a heating rate of 10°C/min at a nitrogen atmosphere. Tensile tests of the rectangular plates (length 50 mm, width 7 mm, thickness 1 mm) were performed at 20°C using an Autograph AG-I (Shimadzu Co., Kyoto, Japan) based on the standard method for testing the tensile properties of plastics (JIS K7113-1995). Span length was 30 mm and the testing speed was 10 mm/min. Five composite specimens were tested for each set of samples, and the mean values and the standard deviation (σ) were calculated.

RESULTS AND DISCUSSION

Characterization of TO

Figure 2 shows the ^{1}H-NMR spectrum of the used TO in CDCl$_3$. The ^{1}H signals at 5.6–6.5 ppm are
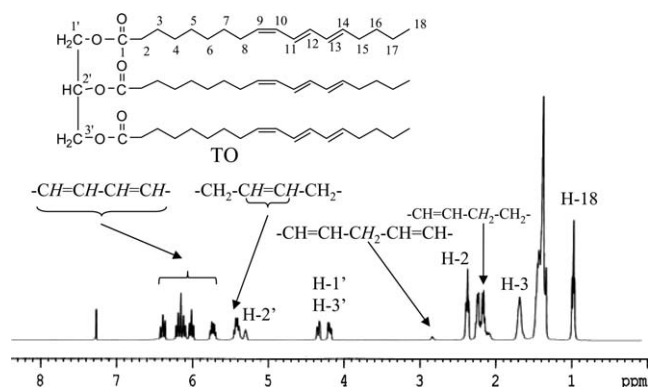
Figure 2 ^{1}H-NMR spectrum of TO in CDCl$_3$.

assigned to the conjugated olefinic protons of α-eleostearic acid moiety. The ^{1}H signals at 5.35–5.60 ppm are assigned to the nonconjugated olefinic protons of the moieties of oleic acid and linoleic acid etc., which are minor components of TO. The ^{1}H signals at 4.1–4.4 ppm are assigned to H-1′ and H-3′ of triglyceride moiety, whose integral area (IA) corresponds to four protons per triglyceride. The ^{1}H signals at 5.28 ppm are assigned to H-2′ of triglyceride moiety, whose IA corresponds to one proton per triglyceride. The IA of H-2′ was used for the calculation of average number of olefins (CH=CH) per triglyceride (A) of TO. The A value of TO was evaluated to be approximately 7.64 using the equation: $A = (\text{IA of } 5.35\text{–}6.50 \text{ ppm})/(\text{IA of } 5.25\text{–}5.35 \text{ ppm})$. The value by ^{1}H-NMR method (7.64) was in agreement with the value (7.5) of general tung oil reported in the literature.[4] The bisallylic methylene proton (CH=CH—CH$_2$—CH=CH) signals of linoleic acid moiety were observed at 2.85 ppm. The allylic methylene proton (CH=CH—CH$_2$—) signals of all the unsaturated fatty acid components were observed at 2.1–2.3 ppm. Terminal methyl proton signals of H-18 and methylene protons of H-2 adjacent to carbonyl group were observed at 0.95 and 1.68 ppm, respectively.

Characterization of the reaction products of TO and PMI

Probable reaction mechanism of TO and PMI is shown in Figure 3. DA reaction with maleimide group is possible for the conjugated diene moiety, whereas ene reaction with maleimide group is possible for allylic moiety. In addition to DA and ene reactions, homopolymerization of PMI, oxidative crosslinking reaction of TO, and radical copolymerization of TO and PMI are considered. It is known that the regio- and endo-stereoselective DA addition to C-11 and C-14 occurs in the reaction of methyl α-eleostearate and maleic anhydride at 150°C for 30 min.[18] Thus, the DA reaction occurs preferentially
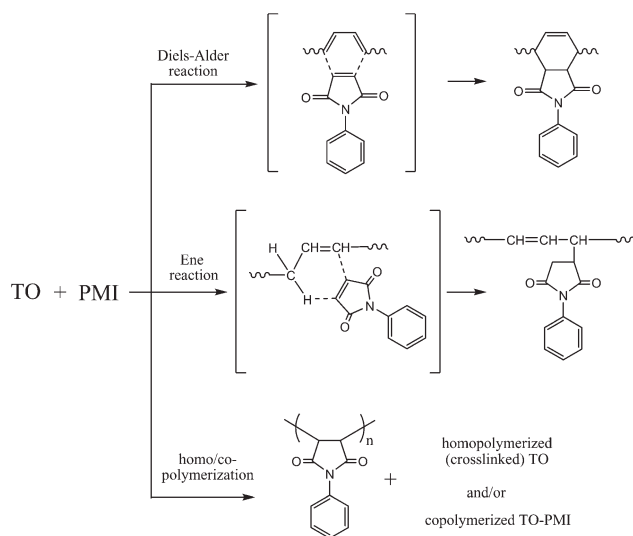
Figure 3 Probable reactions of TO and PMI.

at the 11,13-*trans* conjugated diene moiety, and ene adducts are not observed. If a similar reaction occurs in case of PMI and TO, the DA adduct as is shown in Figure 4 is expected to be formed.

The products obtained by the reactions of TO and PMI with C=C ratio 2/1, 1/1, 1/2, 1/3, and 1/4 in DMI at 150°C for 24 h were analyzed by ^{1}H-NMR spectroscopy. Figure 5 shows the typical NMR spectra of the products with C=C ratio 2/1 and 1/2. The ^{1}H-NMR spectrum of TO/PMI 2/1 suggested that the expected DA adduct at C-11 and C-14 is preferentially formed. Thus, H$_a$, H$_b$, and H-11 signals of the formed cyclohexene moiety are observed at 3.3 ppm. The olefinic protons of H-9,10,12,13 were observed at 6.03 (m, 1H), 5.83 (m, 2H), and 5.61 ppm (m, 1H). Although the spectrum of TO/PMI 1/2 is similar to that of TO/PMI 2/1, the olefinic proton signal of PMI at 6.85 ppm considerably remained, and methylene proton signals of succinimide moiety formed by ene reaction were observed at 3.11 ppm. Therefore, it is suggested that DA
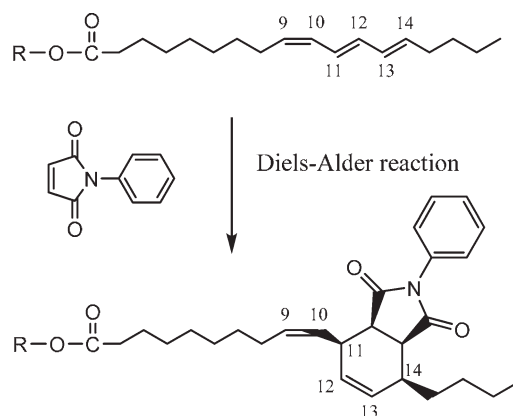

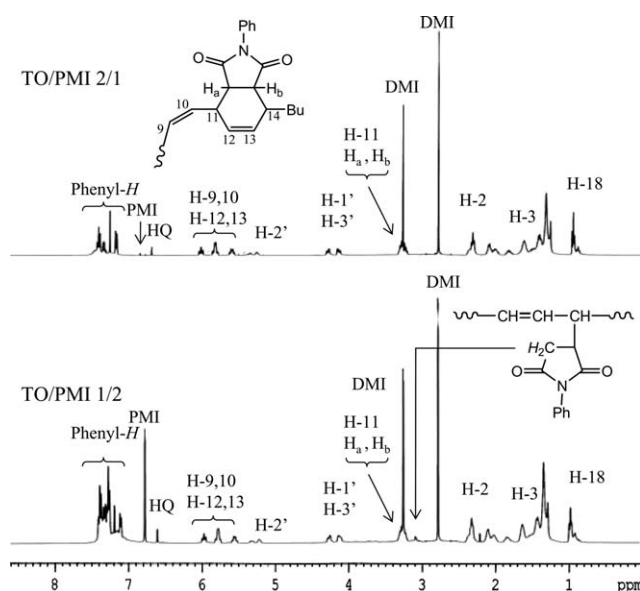**Figure 4** Partial structure of Diels-Alder adduct of TO and PMI.

Figure 5 ^{1}H-NMR spectra of TO/PMI 2/1 and TO/PMI 1/2 in CDCl$_3$.

reaction mainly occurs and some ene reaction simultaneously occurs for the reaction of TO and PMI at the C=C ratio of 1/2. Table I summarizes the number of various moieties per triglyceride classified into five categories determined from IA of various proton signals for all TO/PMI. The A value (7.64) is the number of olefins per triglyceride for TO. The B value is the number of residual olefins per triglyceride after the reaction of TO and PMI. The fact that the B value is lower than the A value indicates that the olefin-consuming reactions such as DA reaction and other radical polymerization occurred. The C value is the number of DA-reacted PMI per triglyceride, which is determined from IA of H-9,10,12,13 of DA adduct. The TO/PMI 1/1 exhibited the highest C value, and the C value gradually decreased with increasing PMI content. The D value is the number of ene-reacted PMI per triglyceride, which is determined from IA of the methylene protons of

succinimide moiety formed by ene reaction. The D value increased with increasing PMI content. The olefins consumed by other reactions than DA is evaluated by (A–C–B) value. The (A–C–B) value also increased with PMI content, suggesting the occurrence of oxidative crosslinking reaction of TO and radical copolymerization of TO and PMI *etc*. The E value means the number of unreacted PMI relative to one triglyceride molecule, which increased with PMI content, suggesting that homopolymerization of PMI does not occur so much at 150° in the presence of HQ in DMI.

Characterization and properties of the cured TO/BMI

The prepolymer prepared by the reaction of TO and BMI at 150°C for 4 h with the C=C ratio from 1/1 to 1/4 was cured at finally 200°C for 2 h to give a TO/BMI cured product. When the reaction time of the prepolymerization at 150°C was prolonged, the reaction mixture became a gelatinous material. Although TO and BMI are soluble in chloroform, dioxane, dimethyl sulfoxide, and DMI, all the cured TO/BMI products were insoluble to their solvents and other common organic solvents, indicating that the cured products have certainly crosslinked structure.

Figure 6 shows FE-SEM images of the cured TO/BMI 1/2 and 1/4. The large stripes are based on the patters of fractured surface, and no phase separation of TO and BMI components is observed for both the products. No phase separation was also observed for other TO/BMI 1/1, 1/2, and 1/3. This result is attributed to the occurrence of the reaction of TO and BMI such as DA and ene reactions in agreement with the results of model reaction of TO and PMI. It is a marked contrast with our previous result of the phase-separaed morphology of the cured product of DCO and BMI with C=C ratio of 1/2.[19] The difference is attributed to the higher reactivity of TO toward BMI than DCO. Although it is supposed that

TABLE I
Number of Various Moieties Per Triglyceride for the Reaction Product of TO and PMI Determined by ^{1}H-NMR[a]

Abbreviation	Residual olefins B	DA-reacted PMI C	Ene-reacted PMI D	Unreacted PMI E	Olefins consumed by other reactions[b] A−C−B
TO/PMI 2/1	4.66	2.09	0.09	0.05	0.85
TO/PMI 1/1	4.93	2.43	0.54	1.57	0.47
TO/PMI 1/2	4.51	2.39	1.01	3.92	1.05
TO/PMI 1/3	3.82	1.99	0.98	6.42	2.08
TO/PMI 1/4	3.39	1.76	1.19	7.85	2.71

[a] The B, C, D, and E values were calculated from the IA of specific proton signals in the ^{1}H-NMR spectra of TO/PMI reaction products using the following equations: B = (IA of 5.3–6.1 ppm)/(IA of 5.2–5.3 ppm); C = (IA of 5.9–6.1 ppm)/(IA of 5.2–5.3 ppm); D = (IA of 3.05–3.15 ppm)/2(IA of 5.2–5.3 ppm); E = (IA of 6.8–6.9 ppm)/2(IA of 5.2–5.3 ppm);
[b] The A value that is the number of olefins per triglyceride for TO is 7.64.
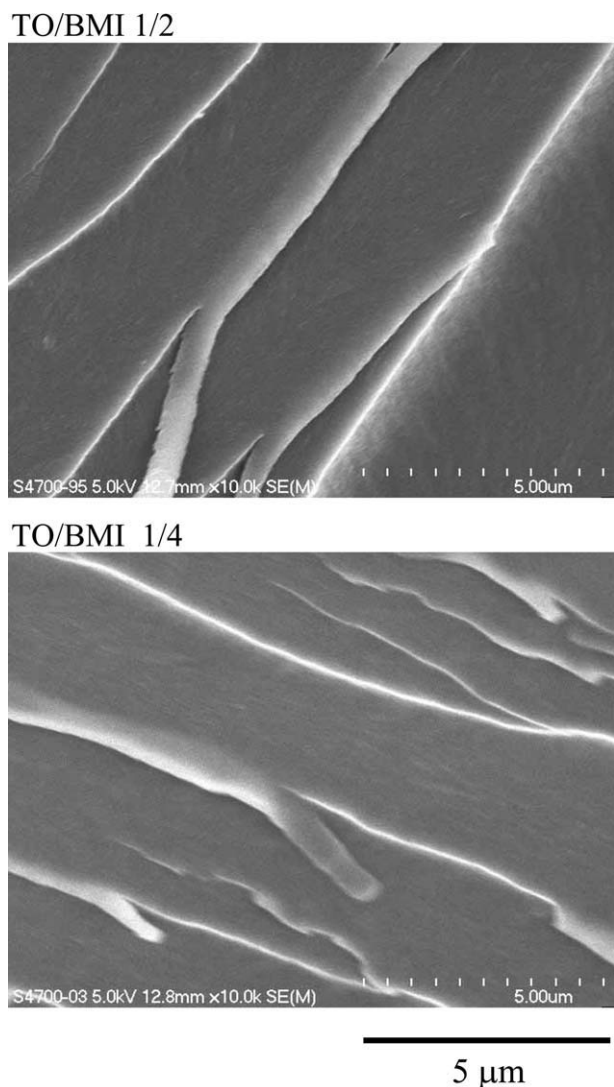
TO/BMI 1/2

TO/BMI 1/4

5 μm

Figure 6 FE-SEM images of the fractured surface of TO/PMI 1/2 and TO/PMI 1/4.

excess BMI remains in the prepolymer of TO and BMI in case of the reaction with a higher content of BMI, the BMI should homopolymerize at the final curing at 200°C for 2 h. The homogeneous morphology of TO/BMI 1/4 indicates that the homopolymerized BMI and the reaction products of TO and BMI are not phase-separated.

Figure 7 shows DMA curves of the cured TO/BMI products. The tan δ peak temperature corresponding to glass transition temperature (T_g) increased with increasing BMI content (Table II). The T_g of the BMI homopolymerized at 230°C in the presence of 5 phr triphenyl phosphine was 262°C as a comparison. The lowering of storage modulus (E') due to the transition from glassy to rubbery state also became smaller with increasing BMI content. An increase of E' over 200°C for TO-BMI 1/4 is probably due to the curing of the remained BMI on the DMA measurement. Table III summarizes the T_g and coefficient of
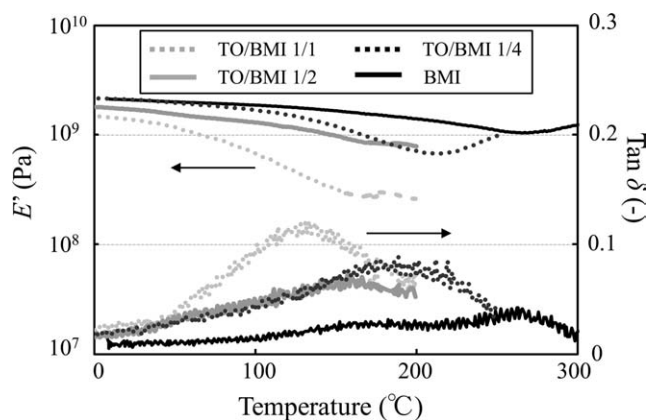
Figure 7 DMA charts of the TO/BMI cured products with the C=C ratio of 1/1, 1/2, and 1/4, and the BMI cured at 230°C.

thermal expansion (CTE) measured by TMA. The T_g measured by TMA also increased with increasing BMI content in agreement with the results of DMA. Both the CTE's (α_1 and α_2) lower T_g and higher T_g decreased with increasing BMI content for TO/BMI 1/1-1/3. The increases of T_g and E' and lowering of CTE's are related to what the intermolecular interaction is strengthened by the increase of the content of highly polar imide group and the crosslinking density increases by the crosslinking reaction of the maleimide groups. The fact that TO/BMI 1/4 had a higher CTE than TO/BMI 1/2 and 1/3 is probably attributed to the presence of unreacted BMI. Table III also summarizes the 5% weight loss temperature (T_d) measured by TGA. The homopolymerized BMI is an aromatic polyimide resin with a superior heat resistance, whose T_d is over 500°C. The T_d of TO/BMI increased with BMI content. The addition of bismaleimide compound to unsaturated plant oil is very effective on the improvement of the heat resistance.

Table II summarizes the tensile properties at 20°C for the cured TO/BMI. Tensile modulus increased and elongation at break decreased with increasing BMI content for TO/BMI 1/1-1/3. This result is related to the increases of intermolecular interaction between the highly polar imide groups and the

TABLE II
Tensile Properties of TO/BMI and DCO/BMI

Sample	Tensile modulus (GPa) [σ]	Tensile strength (MPa) [σ]	Elongation at break (%) [σ]
TO/BMI 1/1	1.67 [0.02]	37.2 [4.4]	2.92 [0.34]
TO/BMI 1/2	2.10 [0.11]	38.1 [5.1]	2.80 [0.61]
TO/BMI 1/3	2.58 [0.04]	35.0 [1.8]	1.67 [0.22]
TO/BMI 1/4	2.02 [0.17]	24.1 [2.6]	1.40 [0.21]
DCO/BMI 1/1[19]	0.56 [0.05]	18.0 [2.3]	5.77 [1.09]
DCO/BMI 1/2[19]	0.95 [0.15]	11.5 [1.8]	2.77 [0.49]

TABLE III
The T_g and CTE Measured by TMA and T_d Measured by TGA for TO/BMI and DCO/BMI

Sample	T_g (°C)	CTE ($10^{-6}\cdot K^{-1}$)		T_d (°C)[c]
		α_1[a]	α_2[b]	
TO/BMI 1/1	111	88.5	118	435
TO/BMI 1/2	120	71.0	88.0	446
TO/BMI 1/3	139	68.9	75.1	448
TO/BMI 1/4	150	75.8	95.1	468
DCO/BMI 1/1[19]	77.6	129	199	407
DCO/BMI 1/2[19]	87.3	119	174	441

[a] α_1 is CTE between $(T_g -35)$°C and $(T_g -10)$°C.
[b] α_2 is CTE between $(T_g +35)$°C and $(T_g +10)$°C.
[c] T_d means 5% weight loss temperature.

crosslinking density. The TO/BMI 1/1-1/3 had almost same tensile strength. The fact that TO/BMI 1/4 showed lower tensile strength, modulus, and elongation at break is also explained by the remaining of excess BMI. As is summarized in Tables II and III, the TO/BMI cured materials showed superior thermal and mechanical properties to the previously reported DCO/BMI cured materials.

CONCLUSIONS

As a model reaction of TO and BMI, the reaction of TO and PMI in DMI was analyzed by ^{1}H-NMR spectroscopy. As a result, it was revealed that the DA reaction occurs preferentially at the 11,13-*trans* conjugated diene moiety of TO for TO/PMI 2/1. The ene reaction and other reactions such as radical homo- and copolymerization gradually increased with decreasing TO/PMI ratio. The reaction of TO and BMI in DMI at 150°C for 3 h and subsequent precipitation gave TO/BMI prepolymer, which was cured at 200°C for 2 h gave the crosslinked TO/BMI product with C=C ratio from 1/1 to 1/4. The FE-SEM analysis revealed that all the cured products are homogeneous and no phase separation was

observed. The T_g and 5% weight loss temperature of the cured TO/BMI increased with increasing BMI content. The maximal tensile strength (38.1 MPa) and modulus (2.6 GPa) were obtained for TO/BMI 1/2 and 1/3, respectively. The curing of TO with BMI due to DA and ene reactions is expected to be applied for the method to improve the thermal and mechanical properties of various drying and semi-drying plant-based oils.

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