

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

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ABSTRACT: The reaction of dehydrated castor oil (DCO) and 1,1'-(methylenedi-4,1-phenylene)bismaleimide (BMI) in 1,3-dimethyl-2-imidazolidinone (DMI) at 130°C for 6 h and subsequent precipitation gave DCO/BMI prepolymer, which was cured at 200°C for 2 h gave DCO/BMI cured product. The FE-SEM analysis revealed that the cured products with C=C ratio 2/1 and 1/1 are homogeneous, whereas phase separation occurs for the 1/2 product. The glass transition temperature, 5% weight loss temperature, and tensile modulus of the cured DCO/BMI increased with increasing BMI content. Regarding the tensile strength, the cured DCO/BMI 1/1 product showed the highest value. To evaluate the reaction of DCO and

BMI, the model reaction products of DCO and *N*-phenylmaleimide (PMI) in DMI were analyzed by ¹H NMR spectroscopy. The ¹H NMR data of DCO revealed that DCO has about 4.8 CH=CH bonds per triglyceride and that the ratio of conjugated and nonconjugated diene moieties is about 41/59. The NMR data of the reaction products of DCO/PMI with the C=C ratio 2/1 and 1/1 at 200°C for 24 h revealed that both Diels–Alder and ene reactions occurs in addition to radical polymerization. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 114: 1033–1039, 2009

Key words: renewable resources; thermosets; Diels–Alder polymers; dehydrated castor oil; bismaleimide

INTRODUCTION

The use of renewable resources as replacement materials for industrial products is attracting great interest with increasing emphasis on environmental issues, waste disposal, and depletion of earth's limited petroleum reserves.^{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} Castor oil is a relatively inexpensive plant oil obtained from the seed of *Ricinus communis*.⁵ It is a triglyceride in which approximately 90% of the fatty acid chains are ricinoleic acid, that is, (9*Z*, 12*R*)-12-hydroxyoctadec-9-enoic acid, as is shown in Figure 1. Because of its hydroxyl functionality, the oil is suitable for use in isocyanate reactions to synthesize cost-effective polyurethane elastomers.^{6–10} Castor oil has only one double bond in each fatty acid chain and, so, is classified as a nondrying oil. However, it can be dehydrated to give semidrying oil, which is used extensively in paints and varnishes. The dehydration process is performed about 250°C and in the presence of acid catalyst such as sulfuric acid and activated earth under an inert

atmosphere or vacuum.⁵ Under this condition of dehydration, the hydroxyl group and an adjacent hydrogen atom from the C-11 or C-13 position of the ricinoleic acid portion of the molecule is removed as water (Fig. 1). This process forms conjugated 9,11-diene and nonconjugated 9,12-diene moieties. The DCO is used in the preparation of alkyd resins¹¹ and styrenated-oil products^{12,13} that are used for paints, enamels, lacquers, and varnishes with high gloss, good adhesion, and wetting qualities. However, these DCO-based resins generally lack the rigidity and heat resistance required for structural and electronics materials.

In this study, bio-based high-performance thermosetting resins were prepared by the reaction of DCO and 1,1'-(methylenedi-4,1-phenylene)bismaleimide (BMI) and their mechanical and thermal properties were investigated. It is well known that maleimide group carries out Diels–Alder (DA) reaction and ene reaction with conjugated diene and allyl group, respectively.^{14–16} To evaluate the reaction of DCO and BMI, the model reaction of DCO and *N*-phenylmaleimide (PMI) was characterized by ¹H NMR spectroscopy.

EXPERIMENTAL

Materials

Dehydrated castor oil (DCO, iodine value 140.7 g-I₂/100 g) was supplied from Itoh Oil Chemicals Co.,

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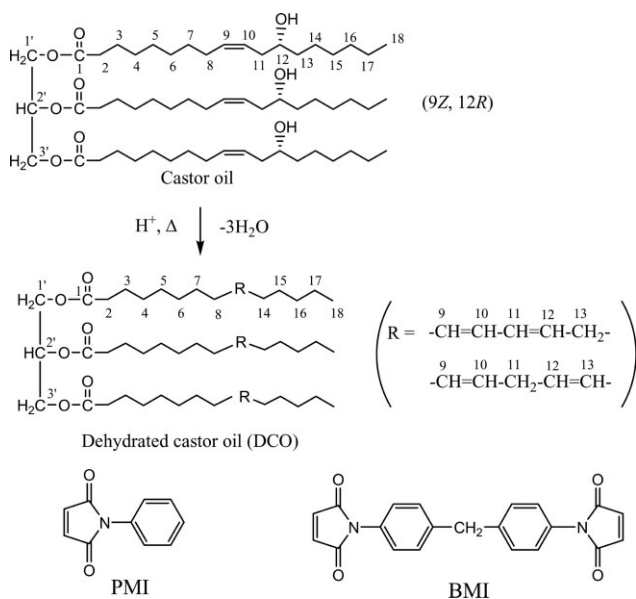


Figure 1 Structure of the main components of castor oil and DCO, PMI, and BMI.

Ltd. (Yokkaichi, 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. Ltd. (Tokyo, Japan).

Model reaction of DCO and PMI

A mixture of DCO (3.38 g, C=C 18.73 mmol), PMI (1.62 g, 9.35 mmol), and HQ (50 mg, 0.45 mmol) in 5 mL of DMI was stirred for 24 h at a prescribed temperature between 130 and 200°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 vacuo* to give a DCO-PMI reaction product in a molar ratio of (C=C of DCO)/(maleimide group of PMI) 2/1 as yellow powder. In a similar manner to the reaction of DCO/PMI (2/1), the reaction in the molar ratio of 1/1 was performed using DCO (2.55 g, C=C 14.1 mmol), PMI (2.45 g, 14.1 mmol).

Curing reaction of DCO and BMI

A mixture of DCO (10.02 g, C=C 55.51 mmol), BMI (4.98 g, 13.90 mmol), and HQ (0.150 g, 1.36 mmol) in 15 mL of DMI was stirred for 6 h at 130°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 vacuo* to give a DCO-BMI prepolymer as yellow powder. The prepolymer was pressure molded at 180°C and 3 MPa for 1 h, and subsequently postcured at 200°C for 2 h in an electric oven to give a DCO-BMI cured product in a molar ratio of (C=C of DCO)/(malei-

mid group of BMI) 2/1. In a similar manner to the reaction of DCO/BMI (2/1), the curing reaction in the molar ratio of 1/1 and 1/2 was performed using DCO (7.53 g, C=C 41.7 mmol), BMI (7.47 g, 20.9 mmol), and DCO (5.02 g, C=C 27.8 mmol), BMI (9.98 g, 27.8 mmol), respectively.

Characterization

Proton nuclear magnetic resonance (1H 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.

Solubility was tested after a mixture of sample (20 mg) and solvent (0.55 mL) was sonicated for 30 min. The 5% weight loss temperature was measured on a thermogravimetric analyzer TGA-50 (Shimadzu Co. Ltd., Kyoto, Japan) in a nitrogen atmosphere at a heating rate of 20°C/min. Dynamic mechanical analysis (DMA) of the rectangular plates (length 30 mm, width 5 mm, thickness 2 mm) was performed on a Rheograph Solid (Toyo Seiki Co., Ltd, Tokyo, Japan) with a chuck distance of 20 mm, a frequency of 10 Hz and a heating rate of 2°C/min. 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 80 mm, width 5 mm, thickness 2 mm) were performed at 20°C using an Autograph AG-I (Shimadzu Co. Ltd., 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

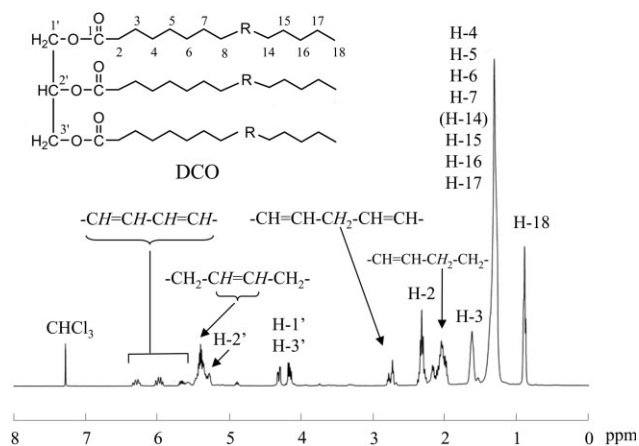


Figure 2 1H NMR spectrum of DCO in $CDCl_3$.

TABLE I
Assignment of ^1H Signals of DCO Measured in CDCl_3 (δ , ppm)

Isomer	H-1',3'	H-2'	H-2	H-3	H-4 ~ 7, H-15 ~ 17	H-8
Nonconjugated diene and Conjugated diene	4.16 (dd, $J = 11.8, 6.2$ Hz), 4.31 (dd, $J = 11.8, 3.8$ Hz)	5.26 (m)	2.33 (t, $J = 7.4$ Hz)	1.7 (m)	1.31 (bs)	1.9–2.2 (m)
Isomer	H-9,10	H-11	H-12	H-13	H-14	H-18
Nonconjugated diene	5.24–5.51 (m)	2.80 (t, $J = 6.2$ Hz), 2.75 (t, $J = 5.4$ Hz)	5.24–5.51 (m)		1.9–2.2 (m)	0.87 (m)
Conjugated diene	6.35–6.20 (m)	6.05–5.90 (m), 5.72–5.52 (m)		1.9–2.2 (m)	1.31 (bs)	

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 DCO

The main component of castor oil is a triglyceride of (9Z,12R)-12-hydroxyoctadec-9-enoic acid. DCO prepared by the dehydration reaction of castor oil contains octadeca-9,11-dienoic acid unit and octadeca-9,12-dienoic acid unit (Fig. 1). Although castor oil has 9Z-configuration, we did not confine the configuration of C-9,10 position of DCO because of the possibility of *cis-trans* isomerization from 9Z to 9E during the acidic dehydration reaction at about 250°C. Figure 2 shows the ^1H NMR spectrum of DCO in CDCl_3 . Table I summarizes the assignment of the ^1H signals of DCO. The peaks at 4.16 ppm (dd, $J = 11.8, 6.2$ Hz) and 4.31 ppm (dd, $J = 11.8, 3.8$ Hz) correspond to the four hydrogens (H-1' and H-3') of the methylene groups present in the glyceride moiety. The methyne proton signal of H-2' was

observed at 5.26 ppm, which was overlapped with the olefinic proton signals. Regarding the fatty acid units, the terminal methyl proton signals (H-18) were observed at 0.87 ppm (m), which is corresponding to 9H per triglyceride. The number of olefins ($\text{CH}=\text{CH}$) per triglyceride (A) was evaluated to be approximately 4.83 from the integral area (IA) of specific proton signals in the ^1H NMR spectrum of DCO using the equation: $A = [9(\text{IA of } 5.2\text{--}6.4 \text{ ppm}) - (\text{IA of } 0.7\text{--}1.0 \text{ ppm})]/[2(\text{IA of } 0.7\text{--}1.0 \text{ ppm})]$. The value by ^1H NMR method (4.83) was in agreement with the value (4.87) calculated from the iodide value of DCO (140.7 g - $\text{I}_2/100$ g). The olefinic proton signals of conjugated 9,11-diene moiety were observed at 6.35–5.52 ppm (m). We could not calculate the ratio of *cis,cis*; *cis,trans*; *trans,cis*; and *trans,trans*-conjugated isomers because of the complex coupling patterns. The bisallylic methylene proton ($\text{CH}=\text{CH}-\text{CH}_2-\text{CH}=\text{CH}$) signals of octadeca-9,12-dienoic acid unit were observed at 2.80 (t, $J = 6.2$ Hz) and 2.75 ppm (t, $J = 5.4$ Hz). Therefore, IA of olefinic proton signals of nonconjugated octadeca-9,12-dienoic acid unit should be double the IA of the bisallylic methylene proton signals. The ratio of

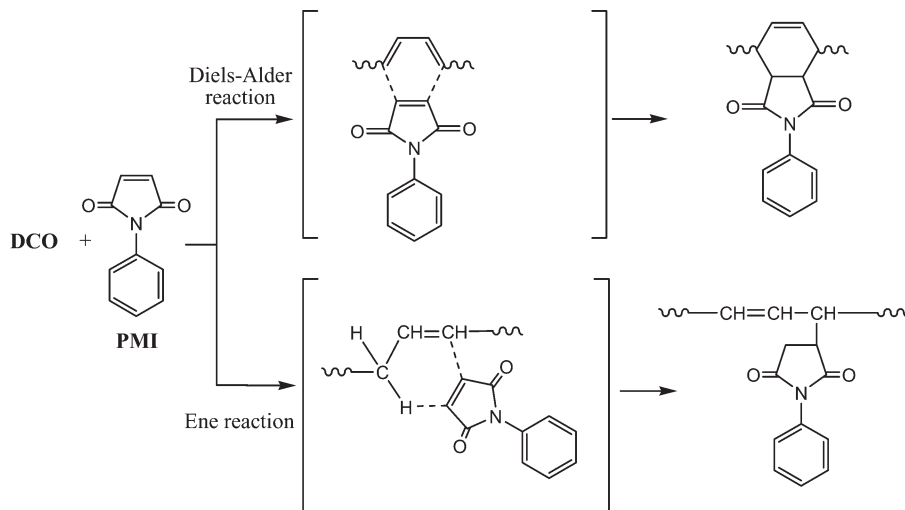


Figure 3 Diels–Alder and ene reactions of DCO and PMI.

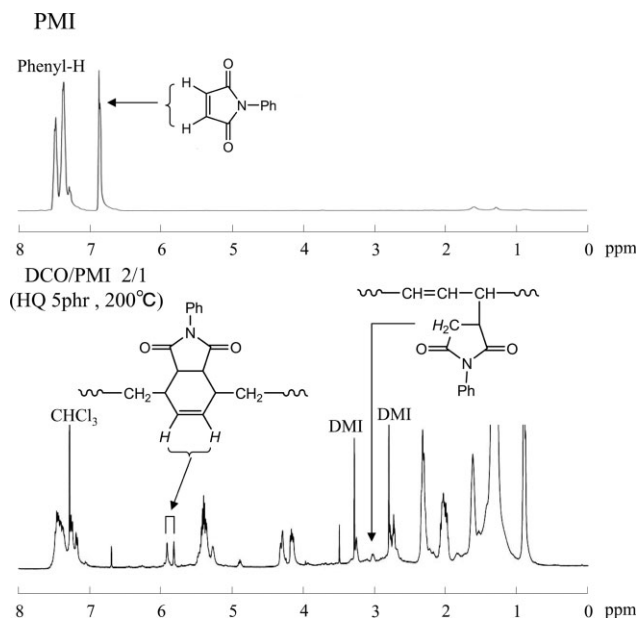


Figure 4 ^1H NMR spectra of PMI and the product obtained by the reaction of DCO and PMI with the C=C ratio 2/1 in the presence of HQ at 200°C for 24 h in CDCl_3 .

conjugated and nonconjugated diene moieties was evaluated to be 41/59, using the following equation: $(\text{IA of } 6.4\text{--}5.5 \text{ ppm})/[2(\text{IA of } 2.6\text{--}2.9 \text{ ppm})]$. Nonconjugated olefinic proton signals were observed at 5.24–5.51 ppm (m). The number of nonconjugated olefins other than bisallyl moiety per triglyceride was calculated to be about 1.2, using the following equation: $[9(\text{IA of } 5.2\text{--}5.5 \text{ ppm}) - (\text{IA of } 0.7\text{--}1.0 \text{ ppm})]$.

$-18(\text{IA of } 2.6\text{--}2.9 \text{ ppm})/[2(\text{IA of } 0.7\text{--}1.0 \text{ ppm})]$. This result is attributed to the fact that DCO contains a small amount of oleic acid unit and the ricinoleic acid unit, which was not dehydrated.

Characterization of the reaction products of DCO and PMI

Probable reaction mechanism of DCO and PMI is shown in Figure 3. DA reaction with maleimide group should be possible for the conjugated diene moiety, whereas ene reaction with maleimide group is possible for allylic moiety. The products obtained by the reactions of DCO and PMI with C=C ratio 2/1 and 1/1 with and without HQ in DMI at 130, 150, and 200°C for 24 h were analyzed by ^1H NMR spectroscopy. Figure 4 shows a typical NMR spectrum of the product with C=C ratio 2/1 with HQ at 200°C when compared with that of PMI. The olefinic proton signal of PMI at 6.86 ppm considerably diminished for the reaction product at 200°C, indicating that the addition reactions of PMI smoothly proceeded. Also, the H-9, 10, 11, 12 signals of 9,11-conjugated diene moiety observed at 6.35–5.52 ppm for DCO almost disappeared, suggesting that conjugated diene moiety almost completely reacted. The olefinic proton signals of DA adduct were observed at 5.92 and 5.82 ppm. Also, the methylene proton signals ($\text{CH}_2\text{--C=O}$) formed by ene reaction was observed at 3.03 ppm. Based on the fact that terminal methyl groups (H-18) of DCO do not change before and after reaction, number of the olefins per

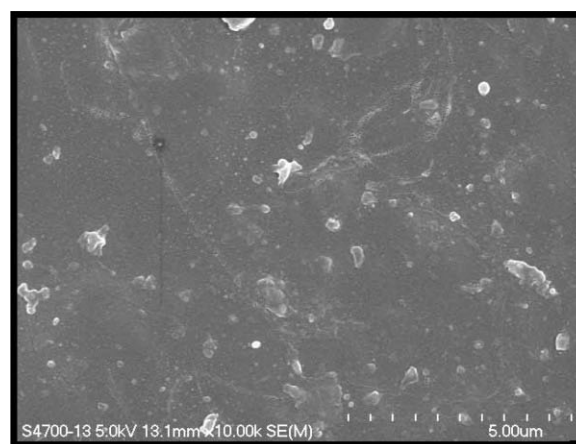
TABLE II
Number of Olefins per Triglyceride Determined by ^1H NMR Data for DCO and the Reaction Product of DCO and PMI^a

Abbreviation	HQ (phr)	Reaction temperature (°C)	Number of olefins per triglyceride				
			Reaction product	Product by DA reaction	Product by ene reaction	Unreacted or unknown	Consumed by other reaction ^b
			B	C	D	B–C–D	A–C–B
DCO/PMI 2/1	–	130	3.36	0.56	0.53	2.27	0.90
DCO/PMI 2/1	–	150	3.56	0.57	0.55	2.44	0.70
DCO/PMI 2/1	–	200	3.28	0.66	0.49	2.13	0.88
DCO/PMI 1/1	–	130	2.40	0.59	0.83	0.99	1.84
DCO/PMI 1/1	–	150	2.27	0.64	0.63	1.00	1.91
DCO/PMI 1/1	–	200	2.35	0.57	0.66	1.11	1.90
DCO/PMI 2/1	5	130	4.17	0.47	0.99	2.71	0.19
DCO/PMI 2/1	5	150	3.74	0.48	0.46	2.80	0.61
DCO/PMI 2/1	5	200	3.58	0.62	0.55	2.41	0.63
DCO/PMI 1/1	5	130	4.53	0.50	0.46	3.57	–0.20
DCO/PMI 1/1	5	150	3.54	0.54	0.80	2.20	0.74
DCO/PMI 1/1	5	200	3.49	0.80	0.72	1.97	0.54

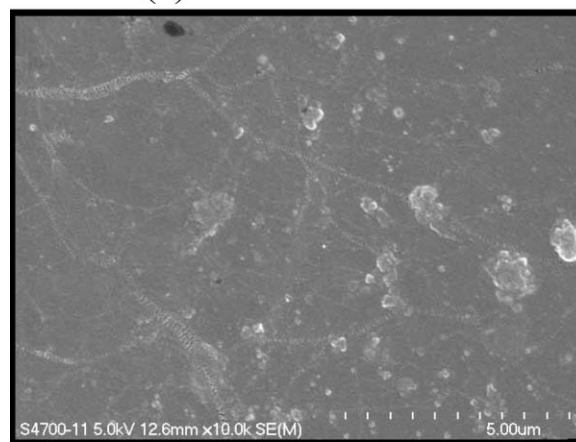
^a The B, C, and D values were calculated from the IA of specific proton signals in the ^1H NMR spectra of DCO/PMI reaction products using the following equations: $B = [9(\text{IA of } 5.2\text{--}6.4 \text{ ppm}) - (\text{IA of } 0.7\text{--}1.0 \text{ ppm})]/[2(\text{IA of } 0.7\text{--}1.0 \text{ ppm})]$; $C = 9(\text{IA of } 5.8\text{--}6.0 \text{ ppm})/[2(\text{IA of } 0.7\text{--}1.0 \text{ ppm})]$; $D = 9(\text{IA of } 2.9\text{--}3.1 \text{ ppm})/[2(\text{IA of } 0.7\text{--}1.0 \text{ ppm})]$.

^b The A value that is the number of olefins per triglyceride for DCO is 4.83.

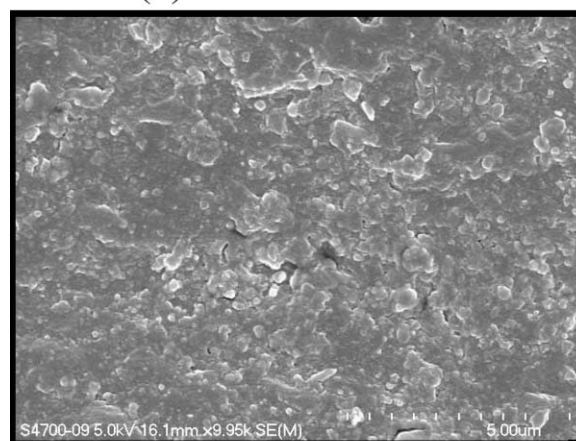
triglyceride classified into five categories was determined from IA of various proton signals of the reaction products of DCO and PMI (Table II). The number of olefins of reaction product (B) was lower than the number of olefins of original DCO (A) 4.83. When a radical polymerization inhibitor, HQ is not added, the B value was almost unchanged by the reaction temperature (130–200°C), and DCO/PMI 1/1 had a lower B value than DCO/PMI 2/1. The B value in the case of the addition of HQ was higher than that without HQ, indicating the radical polymerization of diene moieties is suppressed by the action of HQ. The B value in the case with HQ decreased with increasing reaction temperature. The number of olefins formed by DA reaction (C) is equal to the number of DA-reacted maleimide groups per triglyceride. The number of olefins formed by ene reaction (D) is also equal to the number of ene-reacted maleimide groups. It should be noted that the number of olefins per triglyceride does not change by ene reaction, whereas is reduced to one-half by DA reaction. In the case without HQ, the C value (0.56) was comparable with the D value (0.53) for DCO/PMI 2/1 at 130°C. When the reaction temperature was rose from 130 to 200°C, the C value increased and the D value decreased, suggesting DA reaction is promoted and ene reaction is suppressed. Also, DCO/PMI 1/1 had a higher D value than DCO/PMI 2/1, in agreement with that ene reaction is the reaction of the ratio of allyl/maleimide 1/1. The average number of conjugated diene per triglyceride for DCO is evaluated to be about 0.74 using the equation: $9(\text{IA of } 6.4\text{--}5.5 \text{ ppm})/[4(\text{IA of } 0.7\text{--}1.0 \text{ ppm})]$. The number of DA-reacted conjugated diene per triglyceride is equal to the C value. The reaction product of DCO/PMI 1/1 with HQ at 200°C had the largest C value (0.80), indicating that the conjugated diene moiety of DCO was completely consumed by DA reaction. Regarding the DA reaction of unsaturated fatty acid ester and maleic anhydride, it is known that *trans*, *trans*-conjugated diene moiety preferentially perform DA reaction relative to *cis*, *trans*-conjugated diene moiety.¹⁷ Although we could not determine the configuration of conjugated diene moieties, it is supposed that *trans*, *trans*-conjugated diene moieties, which was contained or isomerized from conjugated *cis,cis*- and *cis,trans*-diene moieties preferentially perform DA reaction. As another possibility, it is thought that *trans*, *trans*-conjugated diene moiety generates by the ene reaction of non-conjugated diene moiety with PMI, and then reacts with PMI. The number of unreacted olefins or unknown olefins per triglyceride is evaluated by $(B-C-D)$ value. The $(B-C-D)$ value of DCO/PMI 1/1 without HQ was lower than that of DCO/PMI 2/1 without HQ. The olefins consumed by other reactions than DA is evaluated by $(A-C-B)$ value. The



(a) DCO/BMI 2/1



(b) DCO/BMI 1/1



(c) DCO/BMI 1/2

Figure 5 FE-SEM images of DCO/BMI cured products with the C=C ratio of 2/1, 1/1, and 1/2.

$(A-C-B)$ value of the DCO/PMI 1/1 was higher than that of the DCO/PMI 2/1. These results indicate that radical polymerization of DCO-based olefins is promoted by the addition of PMI. On the other hand, the $(A-C-B)$ value in case with HQ became smaller than that without HQ, suggesting

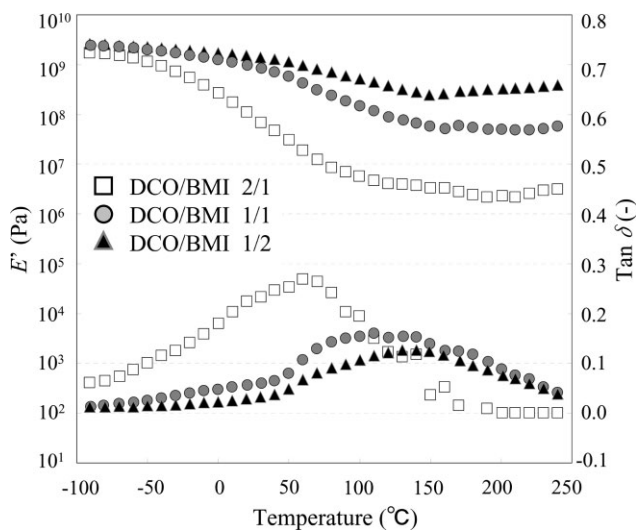


Figure 6 DMA charts of DCO/BMI cured products with the C=C ratio of 2/1, 1/1, and 1/2.

that the radical polymerization is suppressed by the action of HQ.

Characterization and properties of the cured DCO/BMI

Although DCO and BMI are soluble in chloroform, dioxane, dimethyl sulfoxide, and DMI, all the cured DCO/BMI products were insoluble to their solvents and other common organic solvents, indicating that the cured products have certainly crosslinked structure.

Figure 5 shows FE-SEM images of the cured DCO/BMI 2/1, 1/1, and 1/2. There is little phase separation for DCO/BMI 2/1 and 1/1, indicating that DCO reacted with BMI to give a homogeneous material. However, phase separation with the size less than several micrometers is observed for DCO/BMI 1/2, suggesting that excess BMI homopolymerized to form imide-rich particles. Although PMI used for the model reaction hardly homopolymerizes without catalyst at 200°C, BMI homopolymerizes at the same condition.^{18,19} Therefore, it is thought that the homopolymerization of BMI is in

TABLE III
The T_g and CTE for DCO/BMI 2/1, 1/1, and 1/2

Sample	T_g (°C)		CTE (ppm)		T_d (°C) ^c [TGA]
	[DMA]	[TMA]	α_1^a	α_2^b	
DCO/BMI 2/1	63.1	65.7	175	291	378.7
DCO/BMI 1/1	114.0	77.6	129	199	406.8
DCO/BMI 1/2	140.9	87.3	119	174	440.5

^a α_1 is CTE between T_g-35 and T_g-10 .

^b α_2 is CTE between T_g-35 and T_g-10 .

^c T_d means 5% weight loss temperature.

competition with the DA and ene reactions of BMI and DCO.

Figure 6 shows DMA curves of the cured DCO/BMI products. The $\tan \delta$ peak temperature corresponding to glass transition temperature (T_g) increased with increasing BMI content (Table III). The lowering of storage modulus (E') due to the transition from glassy to rubbery state also became

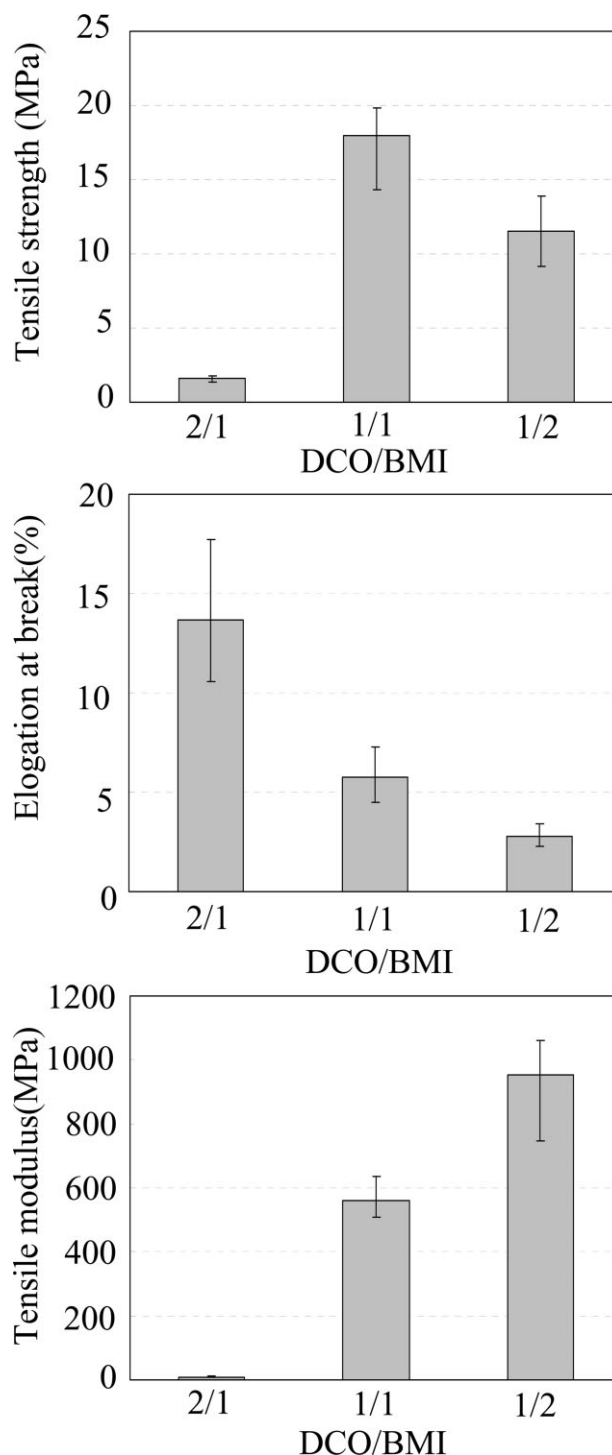


Figure 7 Tensile properties of DCO/BMI cured products with the C=C ratio of 2/1, 1/1, and 1/2.

smaller with increasing BMI content. Table III summarizes the T_g and coefficient of 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 CTEs (α_1 and α_2) lower T_g and higher T_g decreased with increasing BMI content. These increases of T_g and E' and lowering of CTEs are related to the facts that 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. 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 DCO/BMI increased with BMI content. The addition of bismaleimide compound to unsaturated plant oil is very effective on the improvement of the heat resistance.

Figure 7 shows the tensile properties at 20°C for the cured DCO/BMI. Tensile modulus increased and elongation at break decreased with increasing BMI content, in a similar reason mentioned earlier. The DCO/BMI 1/1 showed much higher tensile strength than DCO/BMI 2/1, whereas DCO/BMI 1/2 had a lower tensile strength than DCO/BMI 1/1. Because the phase separation was observed for DCO/BMI 1/2, the occurrence of the interfacial delamination should be a factor of the lowering of the strength for DCO/BMI 1/2.

CONCLUSIONS

The ^1H NMR analysis of DCO revealed that average number of olefins per triglyceride is about 4.8 and that the ratio of conjugated and nonconjugated diene moieties is 41/59. As a model reaction of DCO and BMI, the reaction of DCO and PMI in DMI was analyzed by ^1H NMR spectroscopy. As a result, it was revealed that conjugated diene moieties of DCO almost completely reacted and that DA and ene reactions occurred in addition to radical polymerization, and that the addition of HQ suppressed the

radical polymerization of the unsaturated fatty acid moieties. The reaction of DCO and BMI in DMI at 130°C for 6 h and subsequent precipitation gave DCO/BMI prepolymer, which was cured at 200°C for 2 h gave DCO/BMI cured product. The FE-SEM analysis revealed that the cured products with C=C ratio 2/1 and 1/1 are homogeneous, whereas phase separation occurs for the 1/2 product. The T_g , tensile modulus, and 5% weight loss temperature increased with increasing BMI content. Regarding the tensile strength, the DCO/BMI 1/1 cured product showed the highest value. The curing of DCO with BMI because of 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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