

Biobased Thermosetting Resins Composed of L-Lysine Methyl Ester and Bismaleimide

Yuta Ozawa, Mitsuhiro Shibata

Department of Life and Environmental Sciences, Faculty of Engineering, Chiba Institute of Technology, 2-17-1, Tsudanuma, Narashino, Chiba 275-0016, Japan

Correspondence to: M. Shibata (E-mail: shibata@sky.it-chiba.ac.jp)

ABSTRACT: Lysine methyl ester (LME), which was generated *in situ* by the reaction of lysine methyl ester dihydrochloride and triethylamine in dimethyl sulfoxide (DMSO), was prepolymerized with 4,4'-bismaleimidodiphenylmethane (BMI) at 80°C for 2 h in DMSO. Then, the formed prepolymer was precipitated in water. The obtained LME/BMI prepolymers with molar ratios of 2:2, 2:3, and 2:4 were compression-molded at a final temperature of 230°C for 2 h to produce cured lysine methyl ester/4,4'-bismaleimidodiphenylmethane resins (cLBs; cLB22, cLB23, and cLB24, respectively). Fourier transform infrared (FTIR) analyses revealed that the Michael addition reaction of amino groups to the C=C bonds of the maleimide group occurred in addition to the homopolymerization of the maleimide group. The glass-transition temperature (T_g) and 5% weight loss temperature (T_5) of the cured resin increased with increasing BMI feed content, and cLB24 showed the highest T_g (343°C) and T_5 (389°C). The flexural strengths (131–150 MPa) and moduli (3.0–3.6 GPa) of the cLBs were comparable to those of the conventionally cured resins of BMI and 4,4'-diaminodiphenylmethane. Field emission scanning electron microscopy analysis revealed that there was no phase separation for all of the cured resins. Although cLB23 and cLB24 were not biodegradable, cLB22 had a biodegradability of 8.5% after 30 days in an aerobic aqueous medium containing activated sludge. © 2014 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2014**, *131*, 40379.

KEYWORDS: biodegradable; biopolymers and renewable polymers; crosslinking; polyimides; thermosets

Received 18 September 2013; accepted 30 December 2013

DOI: 10.1002/app.40379

INTRODUCTION

In recent years, renewable-resource-derived polymers (biobased polymers) have attracted a great deal of attention because of the advantages of these polymers, which include the conservation of limited petroleum resources, the control of carbon dioxide emissions that lead to global warming,^{1–4} and possible biodegradability. Most recently, much focus has been placed on biobased thermosetting resins, such as epoxy resins, phenol resins, unsaturated polyester resins, and their composites, because these materials are hard to recycle because of their infusible and insoluble properties.^{5–9} Petroleum-based thermosetting bismaleimide resins have been used as matrix resins for multilayer printed circuit boards and advanced composite materials in the aerospace industry.^{10–22} Although 4,4'-bismaleimidodiphenylmethane (BMI) is exclusively used as a bismaleimide component in thermosetting bismaleimide resins, homopolymerized BMI is a very brittle material because of its high crosslinking density. To improve its brittleness, BMI is copolymerized with other components with two or more functional groups that can react with the maleimide groups. The Kerimid^{10–15} and Compimide series^{16,17} are the most well-known thermosetting bismaleimide

resins; they were commercialized by Rhône-Poulenc and Technochemie (now available from Evonik Industries), respectively. The monomers that were copolymerized with BMI for Kerimid and Compimide were 4,4'-diaminodiphenylmethane (DDM) and 3-aminobenzoic hydrazide (ABH), respectively. The curing mechanism of both the resin systems is based on the Michael addition reaction of the amino groups of DDM or ABH to the unsaturated C=C bonds of the maleimide groups of BMI and the homopolymerization of the maleimide groups to some extent. The Kerimid resin has become the industrial standard for polyimide-based multilayered printed circuit boards. Recently, this resin has been taken off the market because of the high free DDM content in the product. DDM is a toxic aromatic diamine. Humans who have been accidentally or occupationally exposed to DDM have developed toxic hepatitis, jaundice, cholangitis, and skin rashes.²³ It was also reported that chronic exposure to DDM in rodents leads to increases in thyroid and hepatic carcinomas.²⁴ Because of the potential for human injury and the widespread use of DDM, in 1993 the Occupational Safety and Health Administration lowered the exposure level for DDM in the workplace to less than 10 ppb in an 8-h time-weighted average.²⁵ Although the carcinogenicity of

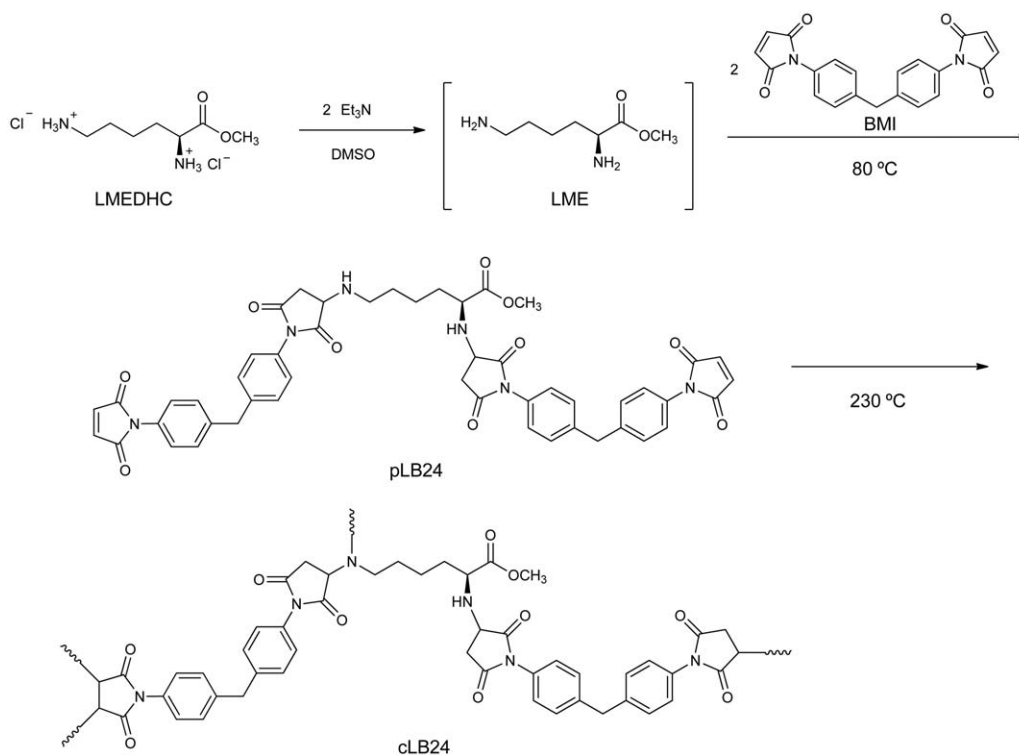


Figure 1. Reaction scheme for LME and BMI and probable chemical structures of pLB24 and cLB24.

ABH for Compimide resins has not been reported, it is also a harmful compound that irritates the skin, respiratory system, and eyes.²⁶

In this study, L-lysine methyl ester (LME) was used as a bio-based diamine and a substitute for DDM or ABH. L-Lysine is an α -amino acid with a pendant aminobutyl group and is industrially produced by a fermentation method with glucose and ammonium sulfate and so on as carbon and nitrogen sources, respectively. It has experienced increasing demand for farm animal foods, food additives, supplements, and pharmaceuticals, and the worldwide production was recently estimated to be above 1 million tons per year.²⁷ The lysine methyl ester/4,4'-bismaleimidodiphenylmethane prepolymer (pLB) prepared by the Michael reaction of LME to BMI in dimethyl sulfoxide (DMSO) was hot-pressed to produce a cured lysine methyl ester/4,4'-bismaleimidodiphenylmethane resin (cLB; Figure 1). The thermal, mechanical, and biodegradable properties of the cured resin were investigated.

EXPERIMENTAL

Materials

BMI and lysine methyl ester dihydrochloride (LMEDHC) were purchased from Tokyo Kasei Kogyo Co., Ltd. (Tokyo, Japan) and Wako Pure Chemical Industries, Ltd. (Osaka, Japan), respectively. Triethylamine and DMSO were purchased from Kanto Chemical Co., Inc. (Tokyo, Japan). All of the commercially available reagents were used without further purification.

Preparation of the pLB

To a solution of LMEDHC (5.32 g, 22.8 mmol) in DMSO (20 mL), we added triethylamine (4.62 g, 45.6 mmol) dropwise over

10 min, and then, the mixture was stirred for 30 min at room temperature. After the formed precipitate of triethylamine hydrochloride was filtered, BMI (16.3 g, 45.6 mmol) was added to the filtrate, and the solution was stirred at 80 °C for 2 h. The reaction mixture was precipitated in water, filtered, washed with water three times and then with methanol twice, and finally dried *in vacuo* at 40 °C for 24 h to give a pLB with a feed molar ratio of 2:4 (pLB24) as a pale yellow powder (17.7 g, 81.9%).

In a similar manner, pLBs with feed molar ratios of 2:3 and 2:2 (pLB23 and pLB22) were prepared at yields of 73.0 and 76.5%, respectively.

Preparation of the cLB

pLB24 was compression-molded at 150 °C and 5 MPa for 2 h and then at 230 °C and 5 MPa for 2 h with a Mini Test Press-10 (Toyo Seiki Co., Ltd., Tokyo, Japan) to produce a cLB with feed molar ratio of LME to BMI of 2:4 (cLB24) as a brown plate. In a manner similar, a cLB with feed molar ratios of 2:3 and 2:2 (cLB23 and cLB22, respectively) were prepared.

Measurements

FTIR spectra were obtained on an FTIR 8100 spectrometer (Shimadzu Co., Ltd., Kyoto, Japan) by the KBr or attenuated total reflectance method. ¹H-NMR spectra were recorded at room temperature on a Bruker AV-400 (400 MHz) with hexadeuterated dimethyl sulfoxide (DMSO-*d*₆) as a solvent and tetramethylsilane as an internal standard. Gel permeation chromatography (GPC) was carried out at 60 °C on a Shimadzu GPC analysis apparatus equipped with two OHpak SB-804 HQ GPC columns (Showa Denko) and a UV (wavelength = 280 nm) detector. DMSO was used as an eluent at a flow rate of 0.5 mL/min. Peptide standard

mixture with the molecular weight range from 132 to 66,000 was used for molecular weight calibrations. 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 in a nitrogen atmosphere. Thermomechanical analysis (TMA) was conducted on a TMA-60 (Shimadzu Co., Ltd.) at a heating rate of 10°C/min in a nitrogen atmosphere. The glass-transition temperature (T_g) was determined from the intersect of tangents at two points with a significant change in coefficient of thermal expansion (CTE). The 5% weight loss temperature (T_5) of the sample (10–15 mg) was measured over the temperature range from room temperature to 500°C on a Shimadzu TGA-50 thermogravimetric analyzer at a heating rate of 20°C/min in a nitrogen atmosphere. Dynamic mechanical analysis (DMA) of the rectangular plates (length = 30 mm, width = 5 mm, thickness = 0.5 mm) was performed on a Rheograph Solid instrument (Toyo Seiki Co., Ltd.) under an air atmosphere with a chuck distance of 20 mm, a frequency of 1 Hz, and a heating rate of 2°C/min on the basis of ISO 6721-4:1994 (“Plastics—Determination of Dynamic Mechanical Properties, Part 4: Tensile Vibration–Nonresonance Method”). Flexural testing of the rectangular specimen (50 × 10 × 2 mm³) was performed with an Autograph AG-1 (Shimadzu Co., Ltd.) on the basis of 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. Five specimens were tested for each set of samples, and the mean values were calculated. The morphology of the fractured surfaces of the cured resins after the flexural tests was observed by field emission scanning electron microscopy (FESEM) with a Hitachi S-4700 machine (Hitachi High-Technologies Corp., Tokyo, Japan). The fracture surfaces were sputter-coated with gold to provide enhanced conductivity. Biodegradability was determined according to JIS K6950-2000 (ISO 14851-1999) by the measurement of the biochemical oxygen demand (BOD) in an aerobic aqueous medium containing activated sludge. Phosphate buffer (pH 7.4, 200 mL) containing 0.25 mM CaCl₂, 0.09 mM MgSO₄, 0.09 mM NH₄Cl, and 0.9 μM FeCl₃ was mixed in a glass bottle. To the mixture, 4.35 mL of activated sludge, which was obtained from local sewerage facilities (Tsudanuma, Narashino, Japan) and contained 30 mg of insoluble parts, and a pulverized sample (20 mg) were added. The dispersion was steadily stirred with a magnetic stirring bar. BOD was measured at 25°C with a BOD tester 200F (Taitec Corp., Koshigaya, Saitama, Japan). Carbon dioxide was absorbed into 50% sodium hydroxide aqueous concentrate in a cup equipped within the glass bottle. The volume of the consumed oxygen was directly measured with a scaled cylinder.

RESULTS AND DISCUSSION

Preparation and Characterization of pLB and cLB

LMEDHC was soluble in DMSO, methanol, ethanol, and water, but it did not completely dissolve in amide-based polar aprotic solvents, such as *N,N*-dimethylformamide and 1-methyl-2-pyrrolidinone. We selected DMSO as a solvent that could dissolve both LMEDHC and BMI. A DMSO solution of LME was prepared by the deprotonation reaction of commercially available LMEDHC by triethylamine in DMSO, as shown in Figure 1. The *in situ* generated LME was prepolymerized with BMI at

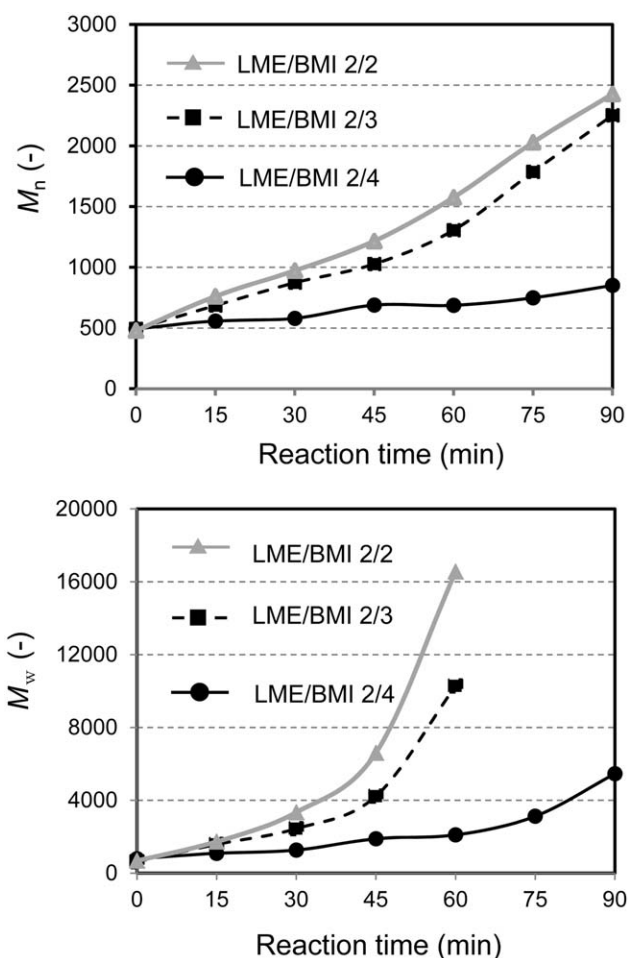


Figure 2. Changes in molecular weights of the LME/BMI reaction mixtures (2:2, 2:3, and 2:4) in DMSO at 80°C.

feed molar ratios of 2:2, 2:3, and 2:4 at 80°C in DMSO. Figure 2 shows the time course of the number-average molecular weight (M_n) and M_w of the reaction mixture measured by GPC. The M_n and M_w values of all of the reaction mixtures increased with the reaction time. When the samples with the same reaction times (≤ 60 min) were compared, the higher order of the molecular weight was LME/BMI = 2:2 > 2:3 > 2:4. This indicated that a linear polymerization by the Michael reaction of the primary amino group of LME and the maleimide group of BMI preferentially occurred rather than a branching reaction of the newly formed secondary amino group and excess maleimide groups. Although we do not show the M_n and M_w values of the LME/BMI 2:2 and 2:3 mixtures, which were reacted at 80°C for 75 min in the reactions shown in Figure 2, the values were very large (93,400 and 77,700, respectively). This suggested that some crosslinking reactions started to occur at times longer than 60 min for the LME/BMI 2:2 and 2:3 mixtures. After the DMSO solutions of LME/BMI at ratios of 2:2, 2:3, and 2:4 were stirred at 80°C for 2 h, the resulting viscous reaction mixtures were precipitated in water to eliminate DMSO and residual triethylamine hydrochloride to produce the isolated prepolymers (pLB22, pLB23, and pLB24). Prolonged stirring of the DMSO solution at 80°C resulted in the formation of a gelatinous

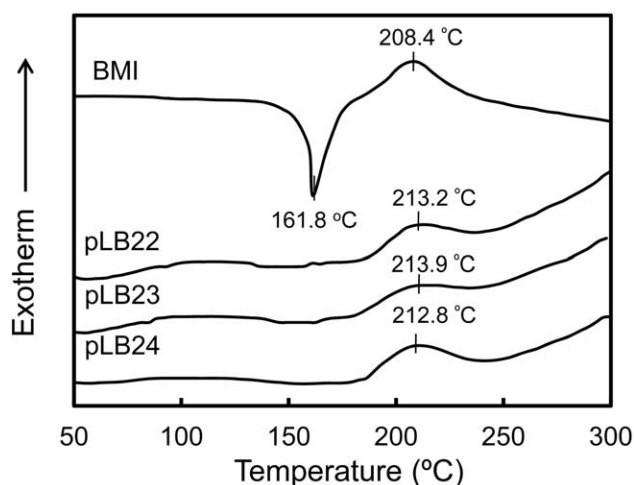


Figure 3. DTA curves of BMI, pLB22, pLB23, and pLB24.

material. The isolated pLBs were partially soluble in DMSO; this suggested that some crosslinking of the formed secondary amine and maleimide already occurred. The insoluble fractions of pLB22, pLB23, and pLB24 (1.00 g) in DMSO (50 mL) at room temperature were 0.85, 0.63, and 0.24 g, respectively. The LME/BMI compositional ratio for the DMSO-soluble part of pLB was estimated from the integral ratio of methoxy protons (3.65 ppm) for the LME component and aromatic protons (7.2–7.5 ppm) for the BMI component in the $^1\text{H-NMR}$ spectrum of the pLB soluble in $\text{DMSO-}d_6$. The LME/BMI compositional ratios for pLB22, pLB23, and pLB24 were 1.0:1.2, 1.0:2.0, and 1.0:5.2, respectively. This indicated that the soluble part with a lower crosslinked fraction was composed of a BMI-rich component. Although we attempted the precipitation of the prepolymer with water at a reaction time much shorter than 2 h to get a prepolymer with a lower insoluble fraction, the yield of the isolated prepolymer decreased considerably because of the preferential removal of the water-soluble LME-rich and low-molecular-weight component.

Figure 3 shows the DTA curves of the BMI and pLBs. The BMI showed a melting endothermic peak at 161.8°C and an exothermic peak at 208.4°C due to homopolymerization of BMI. All of the pLBs showed a broad and weak endothermic peak around $140\text{--}180^\circ\text{C}$ and an exothermic peak with a peak top temperature of $213\text{--}214^\circ\text{C}$ due to the Michael reaction of secondary amino groups to maleimide groups and/or the homopolymerization of the maleimide groups. On the basis of the DTA results, the compression molding and postcuring of the pLBs were carried out at 150°C and then 230°C . Actually, the brown translucent plates of cLB22, cLB23, and cLB24 were obtained by the hot pressing of pLB22, pLB23, and pLB24 at 150°C for 2 h and then at 230°C for 2 h.

Figure 4 shows the FTIR spectra of the LMEDHC, LME, BMI, pLBs, and cLBs. LMEDHC, which was a raw material, showed an absorption band of ester C=O stretching vibrations at 1736 cm^{-1} and those of N-H bending and stretching vibrations for ammonium groups at 1597 and $3000\text{--}2800\text{ cm}^{-1}$, respectively. As LME was generated *in situ* by the deprotonation reaction of LMEDHC with triethylamine, LME containing some amount of

triethylamine hydrochloride was isolated by the reaction of LMEDHC and triethylamine in methanol, evaporation, and subsequent extraction with dichloromethane. The isolated LME showed an absorption band due to ester C=O stretching vibrations at 1740 cm^{-1} , a band due to primary amine N-H bending vibrations at 1610 cm^{-1} , a broad band due to primary amine N-H stretching vibrations at 3404 cm^{-1} , and a broad band due to C-H stretching vibrations at 2937 cm^{-1} overlapped with the ammonium N-H vibration band of triethylamine hydrochloride. Although we tried the deprotonation of LMEDHC by sodium hydroxide to prepared LME without triethylamine chloride, it was unsuccessful because of the hydrolysis of the ester groups of LME, as was obvious from the considerable decrease of the ester C=O band at 1740 cm^{-1} . The BMI showed absorption bands due to imide C=O stretching, the benzene ring framework, C-N-C stretching, the in-plane bending of the maleimide ring, and the maleimide =C-H out-of-plane bending vibrations were observed at 1705 , 1510 , 1146 , 822 , and 689 cm^{-1} , respectively.²⁸ The absorption bands at 1146 , 822 , and 689 cm^{-1} , characteristic of maleimide groups, diminished with increasing LME content for the pLBs. The absorption bands characteristic to amine around 3400 and 1600 cm^{-1} were also diminished for all of the pLBs. Accompanied with the weakening of the absorption bands related to the reactants, all of the pLBs showed a new absorption band due to the C-N-C stretching vibrations of the succinimide ring and the C-N stretching vibrations of the aminosuccinimide moiety around 1175 cm^{-1} . These results indicate that the Michael addition reaction of the amino groups of LME to the maleimide groups of BMI proceeded during the prepolymerization process. Although the bands based on maleimide groups did not disappear for all of the pLBs, those bands almost completely disappeared for all of the cLBs. However, the bands based on amino groups around 1600 and 3400 cm^{-1} did not disappear for all of the cLBs. These results suggest that some amount of the secondary amino groups formed by the Michael reaction of the primary amino groups to maleimide groups remained, even after the postcuring at 230°C and that the residual maleimide groups for pLBs considerably homopolymerized during postcuring. The nucleophilic reactivity of the secondary amino groups formed by the reaction of the α -amino groups of LME and maleimide groups may have been low because of steric hindrance and an electron-accepting effect due to the adjacent carbomethoxyl groups. With the low reactivity of the secondary amino groups considered, a probable reaction scheme for prepolymerization and curing of LB24 is shown in Figure 1. If only the Michael reaction of amine to maleimide occurred for cLB24, the N-H and maleimide groups should have completely disappeared. However, the fact that the absorption band of N-H stretching vibrations for cLB24 remained suggested that the homopolymerization of maleimide groups was preferred to the formation of tertiary amines by the two-step Michael addition reactions.

Properties of the cLBs

Figure 5 shows the DMA curves of the cLBs. The $\tan \delta$ peak temperature related to T_g for the cured resin increased with increasing BMI content, and cLB24 had the highest $\tan \delta$ peak temperature (325°C) among the cured resins. However, the

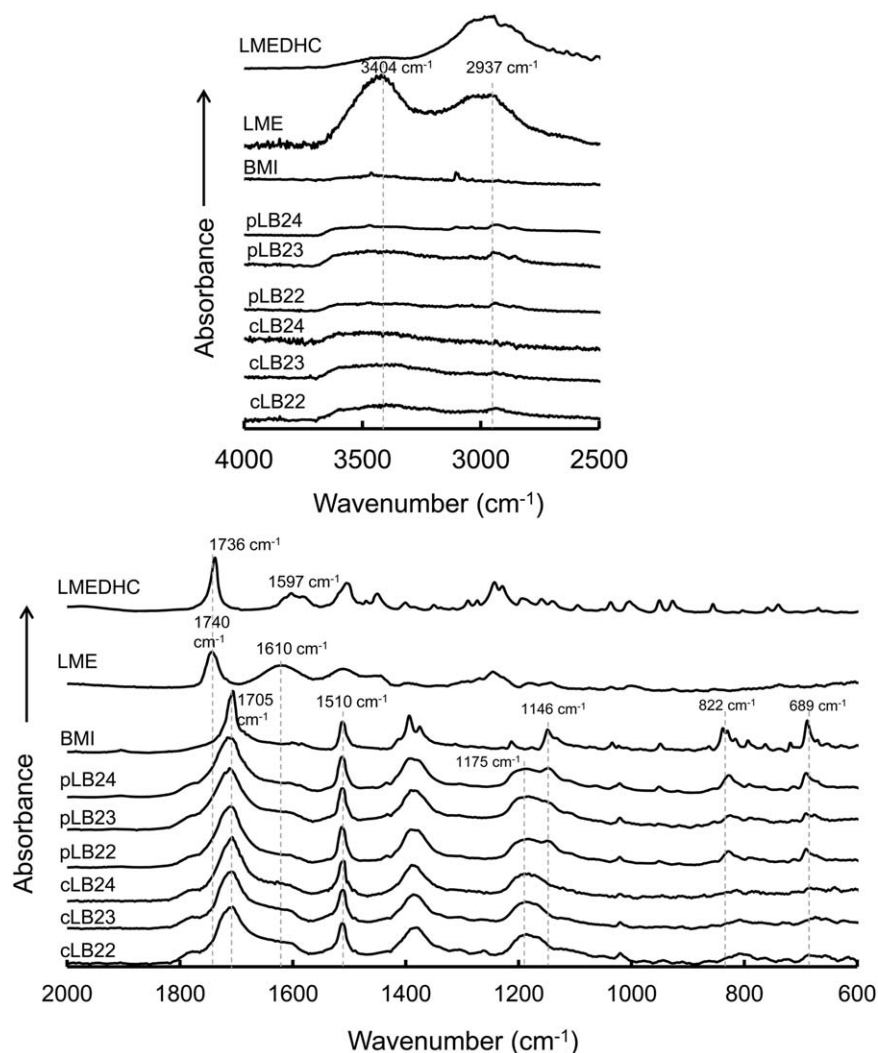


Figure 4. FTIR spectra of the LMEDHC, LME, BMI, pLBs, and cLBs.

storage modulus (E') around 0–100°C for cLB24 was rather lower than those of cLB23 and cLB22. If two maleimide groups reacted with one primary amino group to produce a highly crosslinked resin, cLB24 would have shown the highest E' . It was reported that the flexural modulus and $\tan \delta$ peak temperature of homopolymerized BMI were 1.45 GPa and greater than 350°C, respectively.²⁸ The possibility that the homopolymerized BMI content of cLB24 was larger than those of cLB23 and cLB22 may have been related to the inferior E' of cLB24.

Figure 6 shows the TMA curves of the cLBs. The T_g measured from an inflection point of CTE for the cured resin increased with increasing BMI content in accordance with the DMA result. Also, the average CTE between 200 and 250°C in a glassy state of cLB decreased with the BMI content (cLB22 CTE = $92.9 \times 10^{-6} \text{ K}^{-1}$, cLB23 CTE = $66.1 \times 10^{-6} \text{ K}^{-1}$, and cLB24 CTE = $42.3 \times 10^{-6} \text{ K}^{-1}$). The fact that CTE rose rapidly above the T_g s for cLB22 and cLB23 was related to a partial thermal decomposition, as was obvious from the thermogravimetric analysis (TGA) curves. Figure 7 shows the TGA curves of the

cLBs. The T_5 of cLB increased with the BMI content. The 10% weight loss temperature of homopolymerized BMI was reported to be 514°C.²⁸ The incorporation of amino acid units caused a decrease in the heat resistance. As the weight losses of cLB22 and cLB23 started around 280–300°C, their cured resins should have started to degrade around their T_g .

Figure 8 shows the flexural properties of the cLBs. As a whole, all of the cured resins showed flexural strengths (131–150 MPa) and moduli (3.0–3.6 GPa) that were comparable to the reported values (141 MPa and 3.8 GPa) of 1:2 DDM/BMI cured at 150°C for 1.5 h, at 200°C for 1.5 h, and finally, at 230°C for 1.5 h²⁹ and much higher than those of the cured materials of bio-based thermosetting resins of 2:2 myrcene/BMI (84 MPa and 2.0 GPa)²⁸ and 1:4 cardanol/BMI (78 MPa and 2.2 GPa).³⁰ When the flexural properties of cLB22, cLB23, and cLB24 were compared, cLB24 showed the lowest strength and modulus (131 MPa and 3.0 GPa). Although the homopolymerized BMI had a very high T_g , it was a brittle material whose flexural strength and modulus were 24.3 MPa and 1.45 GPa, respectively.²⁸ The inferior flexural properties of cLB24 may have been related to

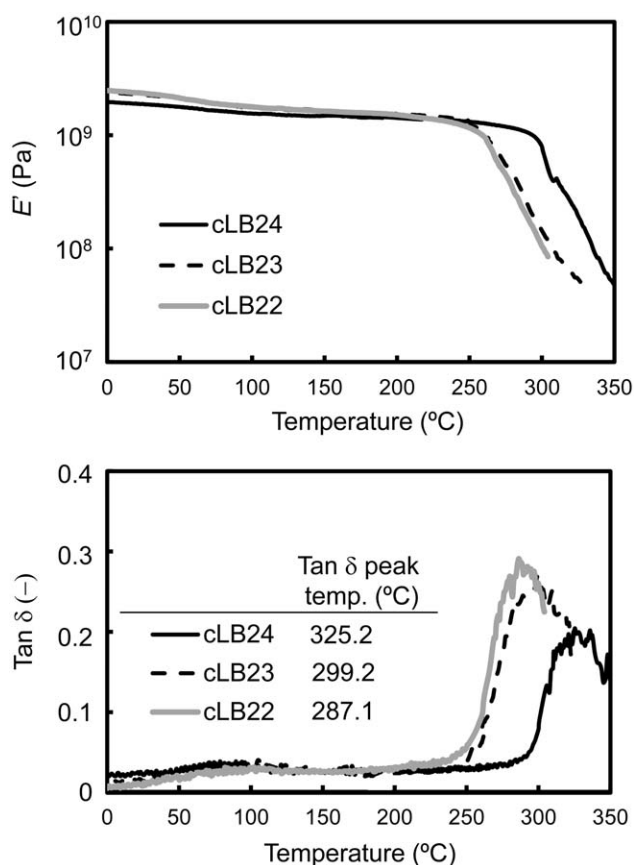


Figure 5. Temperature dependence of E' and $\tan \delta$ for cLBs.

its larger content of homopolymerized BMI compared to those of cLB23 and cLB22.

Figure 9 shows the FESEM images of the fracture surfaces of the cLBs. None of the cured resins showed any phase separation; this indicated that homogeneous materials were obtained by the compression molding finally at 230°C. Figure 10 shows the biodegradability of the cLBs in an aerobic aqueous medium containing activated sludge. Although cLB23 and cLB24 were not biodegradable, cLB22 had a biodegradability of 8.5% after 30 days and a biodegradability of 9.1% after 40 days. There was a tendency of the biodegradability of cLB24 to gradually level

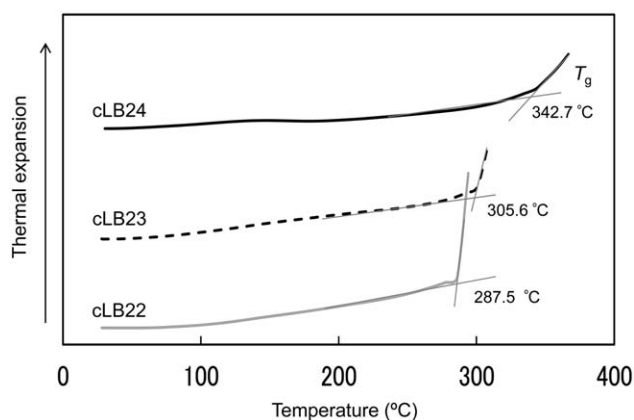


Figure 6. TMA curves of the cLBs.

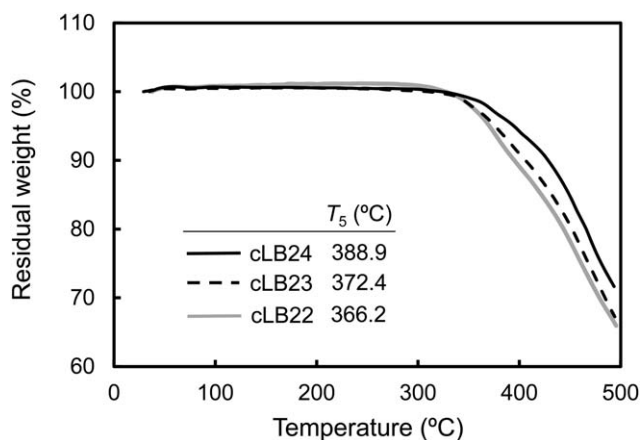


Figure 7. TGA curves of the cLBs.

off after 30 days. Those values were considerably lower than the content of the LME component for cLB24 (30.9 wt %). This suggested that the LME component incorporated into the cross-linked structure and possessing succinimide and diphenylmethane moieties was not easily biodegraded.

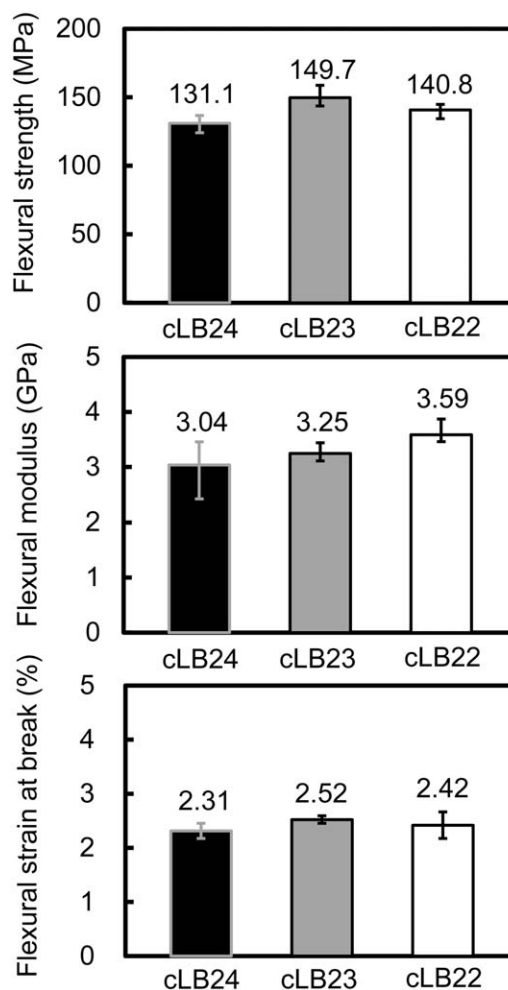


Figure 8. Flexural properties of the cLBs.

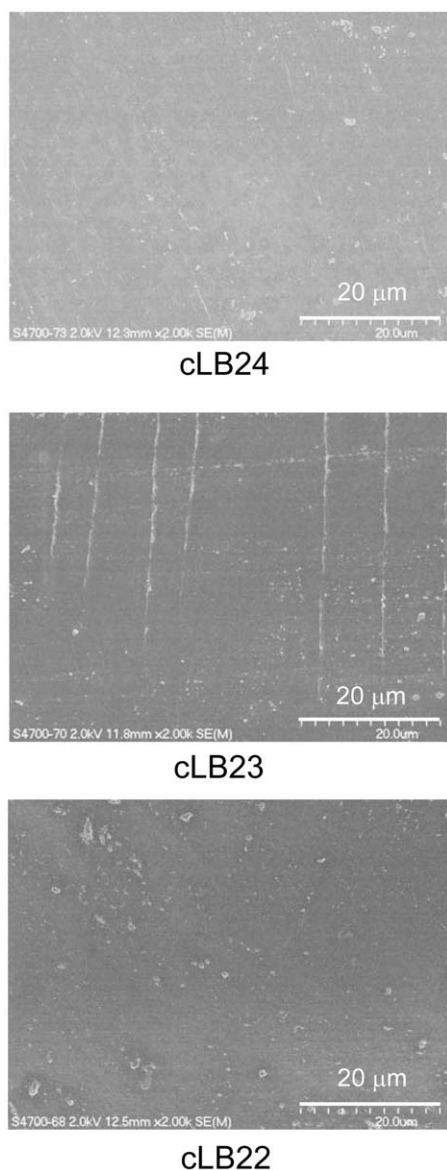


Figure 9. FESEM images of fracture surfaces of the cLBs.

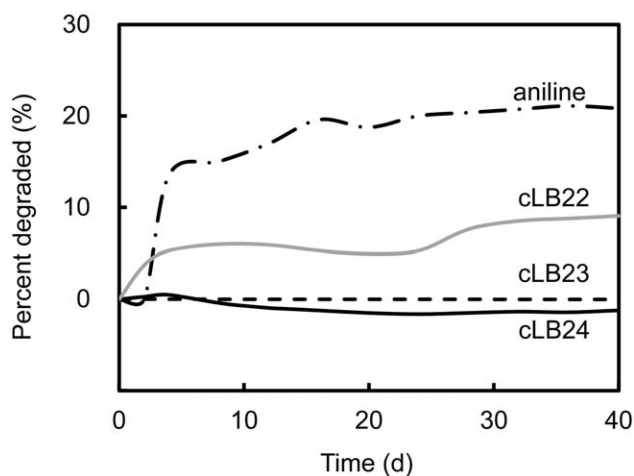


Figure 10. Aerobic biodegradability of the cLBs in aqueous media.

CONCLUSIONS

LME, which was generated *in situ* by the reaction of LMEDHC and triethylamine in DMSO, was prepolymerized with BMI at 80°C for 2 h in DMSO, and then, the formed prepolymer was precipitated in water. The obtained pLBs with molar ratios of 2:2, 2:3, and 2:4 were compression-molded at 150°C for 2 h and then at 230°C for 2 h to produce cLB22, cLB32, and cLB42. The FTIR analyses revealed that the Michael addition reaction of the amino groups to the C=C bonds of the maleimide groups occurred in addition to the homopolymerization of the maleimide groups. The T_g and T_5 values of the cured resin increased with increasing BMI feed content, and LB24 showed the highest T_g of 343°C and T_5 of 389°C. The flexural strengths (131–150 MPa) and moduli (3.0–3.6 GPa) of the cLBs were comparable to those of conventionally cured resins of BMI and DDM. The FESEM analysis revealed that there was no phase separation in any of the cured resins. Although cLB23 and cLB24 were not biodegradable, cLB22 had a biodegradability of 8.5% after 30 days in an aerobic aqueous medium containing activated sludge.

ACKNOWLEDGMENTS

The authors thank Naozumi Teramoto and Toshiaki Shimasaki (Department of Life and Environmental Sciences, Chiba Institute of Technology) for their helpful suggestions. They are also grateful to Ryusuke Osada (Material Analysis Center, Chiba Institute of Technology) for his assistance with the X-ray diffraction and FESEM measurements.

REFERENCES

- Sun, X. S. In *Biobased Polymers and Composites*; Wool, R. P., Sun, X. S., Eds.; Elsevier: Burlington, MA, **2005**; p 1.
- Kaplan, D. L. In *Biopolymers from Renewable Resources*; Kaplan, D. L., Ed.; Springer: Berlin, **1998**; p 1.
- Yu, L.; Petinakis, S.; Dean, K.; Bilyk, A.; Wu, D. *Macromol. Symp.* **2007**, *249*, 535.
- Yu, L.; Dean, K.; Li, L. *Prog. Polym. Sci.* **2006**, *31*, 576.
- Ronda, J. C.; Lligadas, G.; Galià, M.; Cádiz, V. *React. Funct. Polym.* **2013**, *73*, 381.
- Kim, J. R.; Sharma, S. *Ind. Crop Prod.* **2012**, *36*, 485.
- Raquez, J. M.; Deléglise, M.; Lacrampe, M. F.; Krawczak, P. *Prog. Polym. Sci.* **2010**, *35*, 487.
- Effendi, A.; Gerhauser, H.; Bridgwater, A. V. *Renewable Sustainable Energy Rev.* **2008**, *12*, 2092.
- Wool, R. P. In *Biobased Polymers and Composites*; Wool, R. P.; Sun, X. S., Eds.; Elsevier: Burlington, MA, **2005**; p 202.
- Stenzenberger, H. D. *High Performance Polymers; Advances in Polymer Science 117*; Springer: Berlin, **1994**; p 180.
- Fullerton, R.; Roylance, D. *Polym. Eng. Sci.* **1988**, *28*, 372.
- Donnellan, T. M.; Roylance, D. *Polym. Eng. Sci.* **1992**, *32*, 409.
- Hopewell, J. L.; George, G. A.; Hill, D. J. T. *Polymer* **2000**, *41*, 8221.

14. Regnier, N.; Fayos, M.; Lafontaine, E. *J. Appl. Polym. Sci.* **2000**, *78*, 2379.
15. Liu, F.; Wang, Z.; Lü, C.; Gao, L.; Ding, M. *Macromol. Mater. Eng.* **2005**, *290*, 726.
16. Stenzenberger, H. D. *Br. Polym. J.* **1988**, *20*, 383.
17. Canning, M. S.; Stenzenberger, H. *Mater. Des.* **1986**, *7*, 207.
18. Reghunadhan Nair, C. P. *Prog. Polym. Sci.* **2004**, *29*, 401.
19. Chaplin, A.; Hamerton, I.; Herman, H.; Mudhar, A. K.; Shaw, S. J. *Polymer* **2000**, *41*, 3945.
20. King, J. J.; Chaudhari, M.; Zahir, S. *SAMPE Symp.* **1984**, *29*, 392.
21. Morgan, R. J.; Shin, E. E.; Rosenberg, B.; Jurek, A. *Polymer* **1997**, *38*, 639.
22. Rozenberg, B. A.; Dzhavadyan, E. A.; Morgan, R.; Shin, E. *Polym. Adv. Technol.* **2002**, *13*, 837.
23. Chen, K.; Cole, R. B.; Cruz, V. S.; Blakeney, E. W.; Kanz, M. E.; Dugas, T. R. *Toxicol. Appl. Pharmacol.* **2008**, *232*, 190.
24. Lamb, J. C.; Huff, J. E.; Haseman, J. K.; Murthy, A. S. K.; Lilja, H. S. *J. Toxicol. Environ. Health* **1986**, *18*, 325.
25. Kanz, M. F.; Wang, A.; Campbell, G. A. *Toxicol. Lett.* **1995**, *78*, 165.
26. John Matthey Co. Hazard Statement of 3-Aminobenzhydrazide, 97% by Alfa Aesar. http://www.alfa.com/en/GP100_W.pgm?DSSTK=A11491 (accessed September 17, 2013).
27. Brautaset, T.; Ellingsen, T. E. In *Comprehensive Biotechnology*, 2nd ed.; Moo-Young, M., Ed.; Elsevier: Amsterdam, **2011**; Vol. 3, Section 3, p 541.
28. Shibata, M.; Asano, M. *J. Appl. Polym. Sci.* **2013**, *129*, 301.
29. Daiwakasei Industry Co. Properties of Cured Resins of BMI/DDM 2/1. <http://www.daiwakasei.jp/images/seihin/DKKJ.pdf> (accessed September 17, 2013).
30. Shibata, M.; Itakura, Y.; Watanabe, H. *Polym. J.* **2013**, *45*, 758.