

Preparation and Characterization of Cardanol-Based Epoxy Resin for Coating at Room Temperature Curing

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ABSTRACT: Novel organic solvent-free bio-based epoxy resin for coating was prepared from cashew nut shell liquid which is one of renewable resources. The epoxy coating was fabricated by the reaction between amine compounds and epoxy cardanol prepolymer (ECP). The drying, physical, and thermal properties of the epoxy were investigated and compared with those of the commercial cashew coating. The ECP was synthesized by thermal polymerization under the various conditions. Based on the FT-IR analysis, hydroxyl and carbonyl groups were generated, and viscosity increased with increasing heating temperature and time. On the other hand, the NMR analysis showed decrease in the degree of unsaturation in the side group of cardanol. Based on these results, the polymerization of the ECP could be autoxidized in the unsaturated group in the side chains. The drying time until harden dry of the ECP coating took about 2.5 h at room temperature, which is faster than that of the commercial cashew coating. This is because that the curing of ECP coating was based on the prepolymer (i.e., high molecular weight) and crosslink reaction between epoxy and amine groups. The ECP coating was rubbery state due to the flexible side chains of cardanol. Furthermore, the ECP coating improved chemical stability compared with the commercial cashew. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 130: 2468–2478, 2013

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INTRODUCTION

Our daily life has become more comfortable and convenient based on the many functional polymer materials. However, most of these materials are derived from oil and require large amounts of energy to produce. Consequently, global warming, which is caused by the increase in greenhouse gases from the use of fossil fuels, has gradually become a serious worldwide environmental problem, along with the depletion of fossil fuels. Therefore, reduction in the emission of greenhouse gases and in the consumption of fossil fuels is necessary to prevent global warming. The use of bio-based polymer materials made from natural, environmentally-friendly, renewable resources, such as plant and non-food materials, is one way of addressing such environmental problems.

One of the important renewable resources for the chemical industry is plant oil. Among them, cashew nut shell liquid (CNSL) is a natural vegetable oil extracted from non-food cashew nut shells. CNSL contains chemicals such as linear unsaturated phenolic derivative, anacardic acid, cardanol, 2-methyl-cardol, and cardol.^{1,2} The composition of the phenolic derivative varies depending on the extraction method. For example, the cold-extraction method yields natural CNSL with 70% anacardic acid, whereas the hot-extraction

method yields technical CNSL with 90% cardanol but no anacardic acid.^{2,3} In the latter method, most of the anacardic acid is converted to cardanol by thermal decarbonation reaction. Therefore, this CNSL have been applied in phenolic chemical industries. In addition, CNSL has a considerable cost benefit.⁴ Recent interests using CNSL have been focused on the polymer resins including phenolic,^{5–7} epoxy,^{8,9} polyurethane,^{10,11} vinyl ester,^{12,13} and benzoxazine resins.^{14,15} However, these resins are fabricated using formaldehyde which is hazardous to human health (e.g., causes sick house syndrome). Therefore, alternative research for preparation of formaldehyde-free resin has been desirable. Previously, some researches for formaldehyde-free involving cardanol-furfural,¹⁶ acryl,¹⁷ crosslinked resins using enzyme,¹⁸ and oxidative polymerizations¹⁹ have been reported. However, these researches also used some catalysts such as polymerization initiator, enzyme, and heavy metal catalyst.

In this study, we attempt to develop the environmentally-friendly bio-based epoxy resins from CNSL by using the thermal technique without the use of formaldehyde and catalysts for the alternative of general commercial coatings which used organic solvent and formaldehyde. The resultant epoxy cardanol-based coating was investigated in terms of drying, physical, and



Figure 1. Chemical structure of cardanol used in this study.

thermal properties through the comparison of commercial cashew coating.

EXPERIMENTAL

Chemicals

Distilled CNSL and commercial cashew coating (No. 53, natural dry) were kindly supplied by Cashew Co., Ltd., Saitama, Japan, and these chemicals were used without further purification. The CNSL used in this study was analyzed by silica-gel column chromatography (FL60D, Fuji Silysia Chemical Ltd., Aichi, Japan) using a mixing solvent of *n*-hexane and ethyl acetate (99 : 1). The composition of CNSL was determined by thin-layer chromatography (Silica gel 60 F254, Merck Ltd., Tokyo, Japan) using a mixing solvent of *n*-hexane and ethyl acetate (3 : 1). Based on these results, this CNSL contained 89.50% cardanol, 2.35% 2-methylcardol, and 8.15% cardol. The structural analysis of cardanol was performed by gas chromatography/mass spectrometry (GC/MS, PY-2010D, Frontier Laboratories Ltd., Fukushima, Japan). The composition of cardanol was 2.7% saturate, 39.2% monoene, 23.0% diene, and 35.1% triene based on the GC/MS analysis. In addition, the chemical structure of cardanol used in this study was analyzed by nuclear magnetic resonance (NMR) measurement and confirmed the structure, as presented in Figure 1. Epichlorohydrin (>99% purity), potassium hydroxide (KOH, >85% purity), dimethylsulfoxide (DMSO, >98% purity), and ethylenediamine (EDA, >98% purity) were purchased from Nacalai Tesque, Inc, Kyoto, Japan. Diethylenetriamine (DETA, >98% purity) and tetraethylenepentaamine (TEPA, >95% purity) were purchased from the Tokyo Chemical Industry Co., Ltd., Tokyo, Japan. These chemicals were used without further purification.

Measurement

Structure Analysis. All characterization data were obtained using a minimum of three samples to confirm the reproducibility of the experimental results.

Proton and carbon NMR (1H - and ^{13}C -NMR) spectroscopies were conducted on a JNM-ECA500 spectrometer (JEOL Ltd.,

Tokyo, Japan). Samples were dissolved in deuterated chloroform solution with chemical shifts referenced from tetramethylsilane (TMS).

Fourier transform infrared (FT-IR) spectroscopy was performed on a FT/IR-4100 (JASCO Co., Tokyo, Japan) spectrometer using NaCl plate at $23^\circ C \pm 1^\circ C$. Each spectrum was averaged over 64 scans at a resolution of 2 cm^{-1} .

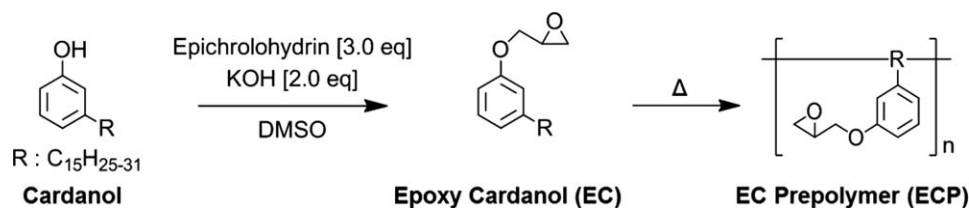
The molecular weight of ECP was determined at $40^\circ C$ by aqueous phase gel permeation chromatography (GPC; TSK-gel column α -3000, α -4000, and α -M, $\phi 7.8\text{ mm} \times 300\text{ mm} \times 3$, Tosoh Co. Ltd., Tokyo, Japan) using dimethylformamide (DMF) as an eluent with 0.01 mol LiBr on a high-performance liquid chromatography system with a refractive index detector RI-8012 with polystyrene standards. The elution rate was 0.8 mL/min.

The viscosities of ECP were determined at room temperature with a Brookfield programmable DV-II+ viscometer (Brookfield Engineering Laboratories Inc, MA). The spindle ware CPE-40 and CPE-51, the rotation speed was from 5 to 20 rpm, and the measurement sample was 0.5 mL.

Film Characterization. The drying process of the epoxy coatings at $23^\circ C \pm 1^\circ C$ can be divided into three stages: dust-free dry (DF), touch-free dry (TF), and harden dry (HD). Each stage was measured using an automatic drying time recorder (RC auto-recorder of painting drying time, TaiYu Co. Ltd., Osaka, Japan) at $23^\circ C \pm 1^\circ C$ and 60% relative humidity.

The hardness of pencil lead is determined using designations consisting of letters and numbers according to the current national standard of GB/T6739-1996. The meanings of H and B designate how hard or soft the tested coatings are, respectively. A higher number with H or B expresses the hardness or softness of the tested coatings, respectively. F and HB indicate medium hardness. However, F is a slightly harder coating than HB. In this study, pencil lead hardness was determined using a C-221 (Yoshimitsu Seiki, Tokyo, Japan) at $23^\circ C \pm 1^\circ C$.

The gel content of the epoxy coating was determined. Coatings were immersed in acetone at $23^\circ C \pm 1^\circ C$ for 24 h, and the non-soluble parts were filtered and dried in a Taiyo muffle furnace (Isuzu, Tokyo, Japan) for 1 h at $50^\circ C$, cooled, and subsequently examined at room temperature to remove residual solvent before weighing. The gel content was calculated using the following equation:



Scheme 1. Synthesis of epoxy-cardanol (EC) and EC prepolymer (ECP).

Table I. Effect of Heating Temperature on ECP Synthesis

Entry	Temperature (°C)	Atmosphere	Content ratio (%) ^a			Molecular weight			Unsaturation	Viscosity (mPa s)
			Monomer	Oligomer	Polymer	M_n	M_w	M_w/M_n		
1	r.t.	Air	100	0	0	390	420	1.07	1.64	39
2	100	Air	75.0	25.0	0	420	640	1.55	1.05	510
3	120	Air	62.9	37.1	0	470	910	1.97	0.83	2000
4	140	Air	51.3	47.9	0.8	470	1390	2.96	0.70	4600
5	160	Air	30.1	46.1	23.8	690	8500	12.4	0.27	7600
6	180	Air	N/A ^b	N/A	N/A	N/A	N/A	N/A	N/A	N/A

^aOligomer: dimer \leq molecular weight < 10,000 g/mol, polymer: molecular weight \geq 10,000 g/mol.

^bPolymer was gelation.

$$\text{Gel content (\%)} = \frac{M_1}{M_0} \times 100 \quad (1)$$

where M_1 and M_0 are the weight of the insoluble fraction and the original weight of the completely dried epoxy coating, respectively.

The film density was measured through floatation method at $23^\circ\text{C} \pm 1^\circ\text{C}$ using the calcium nitrate tetrahydrate (>98%, Junsei Chemical Co. Ltd., Tokyo, Japan).

The water uptake of films was determined by immersing them in water at $23^\circ\text{C} \pm 1^\circ\text{C}$ until equilibrium water sorption was attained. The water uptake was calculated as follows:

$$\text{Water uptake} = \frac{W_{\text{wet}} - W_{\text{dry}}}{W_{\text{dry}}} \times 100 \quad (2)$$

where W_{wet} and W_{dry} are the weights of a water-swollen film at equilibrium and dry states. The water contact angle was measured using an IMC-159D contact angle meter (Imoto Machinery Co., Ltd., Kyoto, Japan). Contact angle changes were recorded within 5 s at $23^\circ\text{C} \pm 1^\circ\text{C}$.

The chemical resistance test was performed by immersing the films in 3 w/v % sulfuric acid (H_2SO_4 , >95% purity, Nacalai Tesque, Inc, Kyoto, Japan.), 3 w/v % sodium hydroxide (NaOH, >97% purity, Nacalai Tesque, Inc, Kyoto, Japan.), and pure water solution at $23^\circ\text{C} \pm 1^\circ\text{C}$ for 7 days, during which, the changes in the coating color were observed. Coating color change was detected using a spectro-guide with D65/10° illuminant/observer and a $45^\circ/0^\circ$ geometry instrument (BYK Gardner GmbH, Germany).

Thermogravimetric analysis (TGA) was performed on a Pyris 1 TGA thermogravimetric analyzer (PerkinElmer, Inc, Shelton). The polymer sample (~1.0 mg) was heated in a platinum pan from 50°C to 600°C at a heating rate of $10^\circ\text{C}/\text{min}$ under a nitrogen atmosphere at a flow rate of 60 mL/min.

Differential scanning calorimetry (DSC) was determined using a Diamond DSC (PerkinElmer, Inc, Shelton). The sample pan-kit alum was made of aluminum. The scan was conducted from -100°C to 200°C at a heating rate of $10^\circ\text{C}/\text{min}$ under a nitrogen atmosphere. The glass transition temperature (T_g) was determined as the middle point of the endothermic transition in the second heating scan.

A rigid-body pendulum physical property-testing (RPT), RPT-3000W (A&D Ltd., Tokyo, Japan) was used to determine the viscoelasticity of epoxy resins. The T_g of the epoxy resin was also analyzed by RPT. The heat of the RPT oven was programmed to rise at a rate of $4.3^\circ\text{C}/\text{min}$ from -35°C to 200°C .

Synthesis

Epoxy-Cardanol (EC). Cardanol was isolated from CNSL using silica gel column chromatography. As shown in Scheme 1, 10.0 g (0.033 mol) isolated cardanol, 9.25 g (3.0 eq) epichlorohydrin, 4.40 g (2.0 eq) potassium hydroxide, and 30.0 mL DMSO solution were mixed in a 200 mL flask with stirring at room temperature for 24 h according to the literature for the epoxidation of cardanol.^{20,21} The solution was extracted with diethyl ether and washed with saturated sodium chloride solution. EC was obtained after dehydration with magnesium sulfate and vacuum drying to give transparent solution; 98 % yield; $^1\text{H-NMR}$ (CDCl_3): δ (ppm) 7.18 (*t*, 1H), 6.79(*d*, 1H), 6.72-6.75 (*m*, 2H), 5.82 (*m*, 1H), 5.31-5.46 (*m*, 2H), 5.05 (*dd*, 1H), 4.98 (*dd*, 1H), 4.19 (*dd*, 1H), 3.97 (*q*, 1H), 3.35 (*m*, 1H), 2.90 (*t*, 1H), 2.77-2.84 (*m*, 2H), 2.75 (*q*, 1H), 2.57 (*t*, 2H), 1.99-2.06 (*m*, 2H), 1.54-1.62 (*m*, 2H), 1.25-1.40 (*m*, 2H), 0.91 (*t*, 3H), 0.88 (*t*, 3H). $^{13}\text{C-NMR}$ (CDCl_3): δ (ppm) 158.47, 144.69, 136.81, 129.18, 126.80-130.38, 121.42, 114.93, 114.68, 111.46, 68.61, 50.16, 44.77, 35.96, 31.76, 31.50, 31.32, 28.97-29.73, 27.19, 25.63, 25.55, 22.78, 22.64, 14.09, 13.78 ppm. FT-IR (NaCl , cm^{-1}) 3007, 997, 911 (C=C stretch), 2926, 2854, 1450, 724 (C-C stretch, CH₂ bending), 3007, 911, 861 (epoxy), 1602, 1584, 1486 (benzene C=C stretch), 1261, 1046 (C-O-C stretch), 777, 695 (1,3-substituted benzene).

Epoxy-Cardanol Prepolymer (ECP). As shown in Scheme 1, 5.0 g (0.017 mol) EC was added into a 100 mL flask and subjected to an oil bath with stirring under the given synthesis conditions. We focused on certain synthesis conditions, such as heating temperature (100, 120, 140, 160, and 180°C), heating time (0, 12, 16, 20, 24, and 28 h), and heating atmosphere (air, nitrogen, and oxygen). Typical ECP synthesized at 160°C for 24 h in air was brown viscous solution. FT-IR (NaCl , cm^{-1}) 3470 (OH), 3001, 998, 910 (C=C stretch), 3001, 910, 861 (C=C stretch), 2927, 2855, 1450, 724 (C-C stretch, CH₂ bending), 1726 (C=O), 1602, 1584, 1486 (benzene C=C stretch), 1261, 1045 (C-O-C stretch), 778, 696 (1,3-substituted benzene).

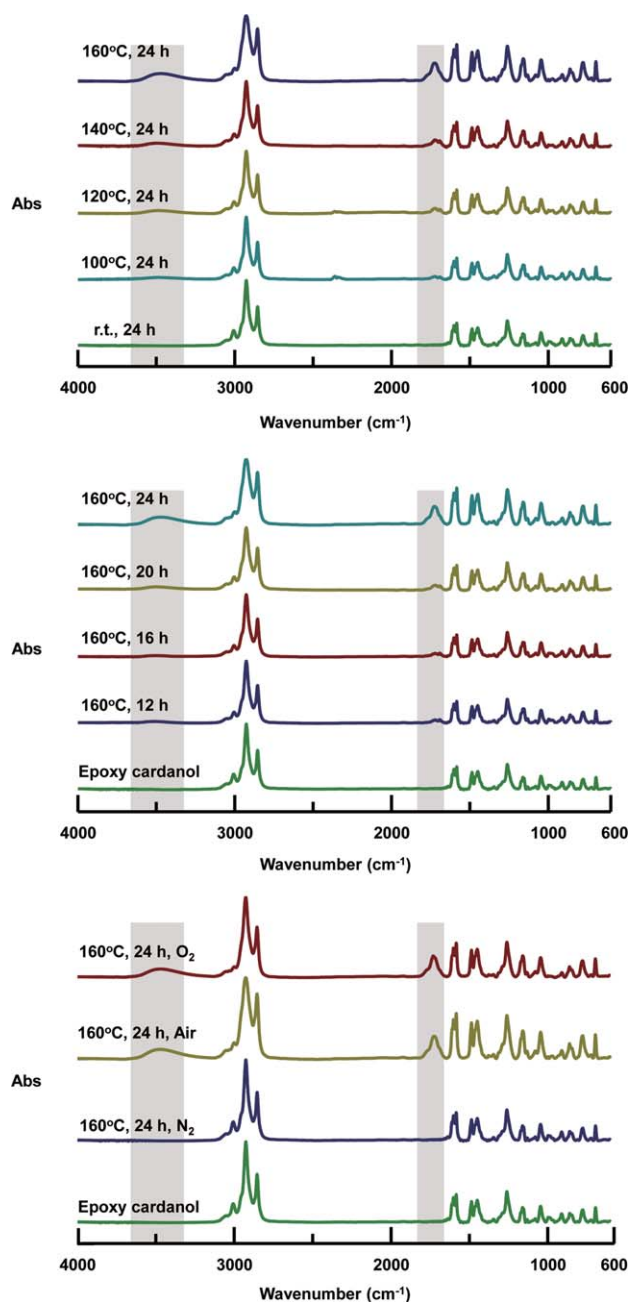


Figure 2. FT-IR spectra of ECP synthesized at various conditions. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Preparation of Epoxy Coating. The epoxy coating was prepared from ECP and amine compounds, EDA, DETA, and TEPA. Each amine compound was added and mixed with ECP for 5 min with a spatula. The resulting mixture was degassed with a vacuum pump to remove the dissolved air in the mixture. The optimum amount of amine compound was determined by examining 5, 10, and 15 wt % ECP. After degassing, the mixture was uniformly coated onto a 76 μm thick square glass plate (70 mm \times 70 mm \times 1.3 mm) at $23^\circ\text{C} \pm 1^\circ\text{C}$ using an applicator (Yoshimitsu Seiki, Tokyo, Japan). Each measurement of the

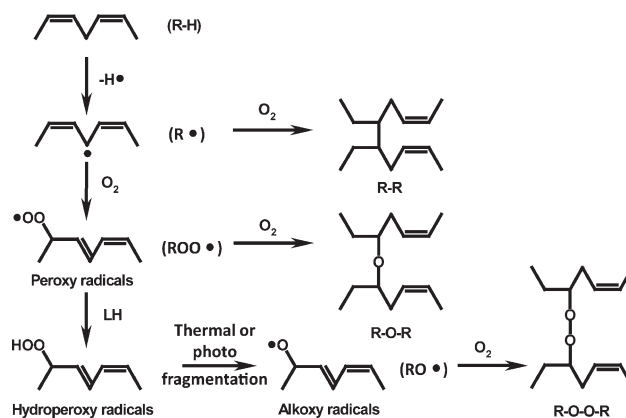


Figure 3. Mechanism of thermal polymerization of EC.

epoxy film was performed after immersion into methanol solution to remove the unreacted compounds.

RESULTS AND DISCUSSION

Synthesis of Epoxy-Cardanol

The conversion from the phenolic hydroxyl group to the epoxy group proceeded completely, considering the conversion from the hydroxyl group to the epoxy group in the cardanol was over 98%, based on the $^1\text{H-NMR}$ analysis. The yield of this reaction was 98%. The peaks at 3346 and 1265 cm^{-1} , which correspond to the phenolic hydroxyl group, disappeared, whereas the new peaks at 1261 and 1046 cm^{-1} , which correspond to ether, and at 861 cm^{-1} , which correspond to the epoxy group, were observed.

Synthesis of Epoxy-Cardanol Prepolymer

Heating Temperature. The molecular weight, degree of unsaturation, and viscosity of the ECP synthesized in air at the given temperatures (i.e., 100, 120, 140, 160, and 180°C) for 24 h are summarized in Table I. Gelation was observed at 180°C . The epoxy group was cleaved at 180°C . Therefore, this gelation could be based on the crosslink reaction between epoxy groups. On the other hand, no structural change occurred until 160°C in the epoxy and benzene groups according to the $^1\text{H-NMR}$ analysis. However, the degree of unsaturation decreased.

Figure 2 presents the FT-IR spectra of ECP. As the heating temperature increased, the peaks at 3500 cm^{-1} , corresponding to the hydroxyl group, and at 1720 cm^{-1} , corresponding to the carbonyl groups, appeared because the hydroxyl and carbonyl groups were formed during the autoxidation.^{22–24} The possible mechanism of autoxidation of cardanol was presented in Figure 3. Basically, 1,4-diene type structure is liable to occur during auto-oxidation because of the ease of hydrogen loss in the active methylene group. The formed radicals produce hydroxyl and carbonyl group under the presence of oxygen and hydroxyl radical during the thermal polymerization. In addition, the crosslink reaction also proceeded between formed radicals at oxygen atmosphere in parallel as presented Figure 3.

Figure 4 presents the content ratios of monomer, oligomer, and polymer determined by GPC. The monomer content decreased, whereas the oligomer content increased with the heating

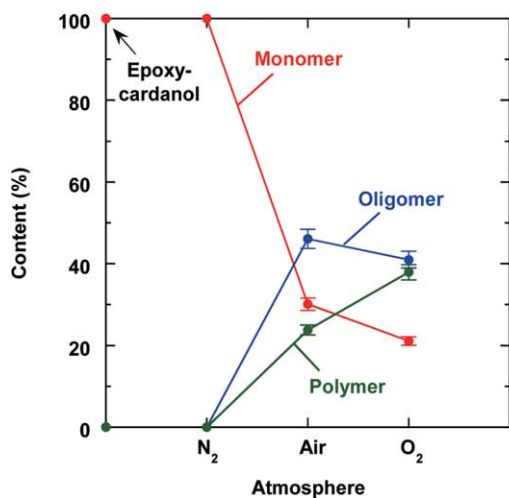
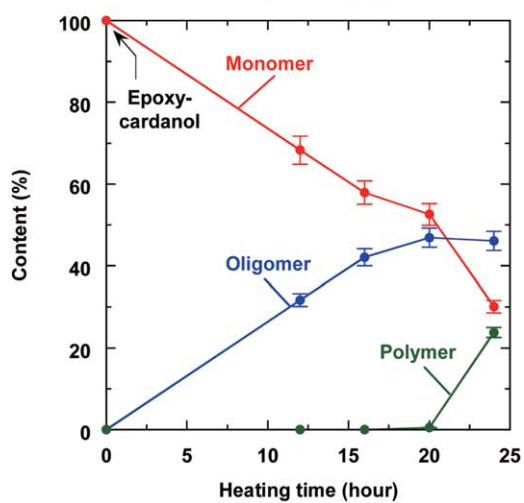
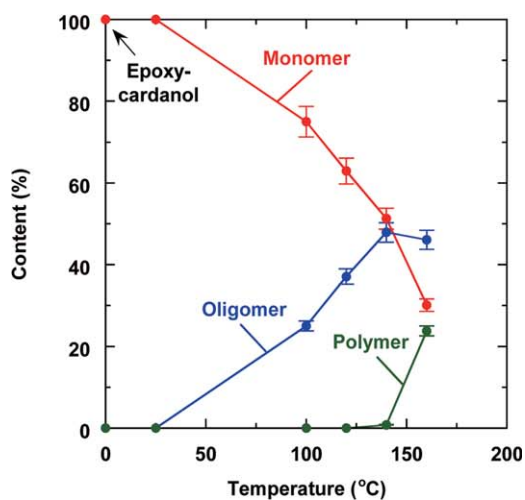


Figure 4. Changes in the composition of monomer, oligomer, and polymer of ECP. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

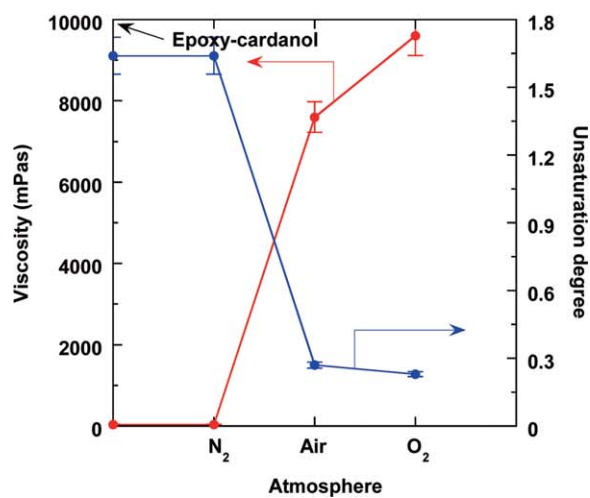
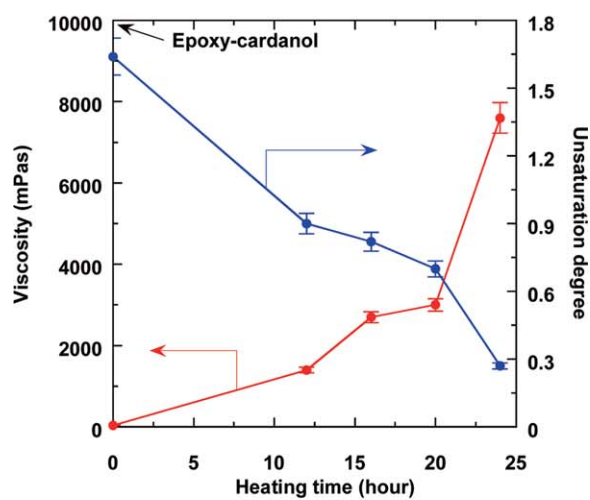
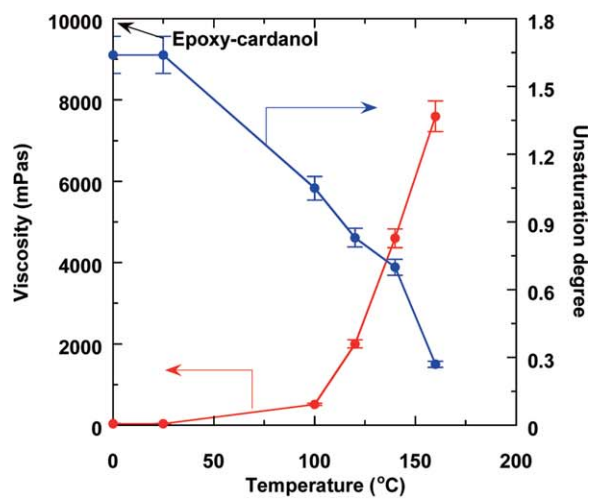


Figure 5. Changes in the viscosity associated with the decrease in the unsaturation degree of ECP. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table II. Effect of Heating Time on ECP Synthesis

Entry	Time (h)	Atmosphere	Content ratio (%) ^a			Molecular weight			Unsaturation	Viscosity (mPa s)
			Monomer	Oligomer	Polymer	M_n	M_w	M_w/M_n		
1	r.t.	Air	100	0	0	390	420	1.07	1.64	39
2	12	Air	68.3	31.7	0	500	820	1.64	0.90	1400
3	16	Air	57.9	42.1	0	500	1170	2.37	0.82	2700
4	20	Air	52.6	46.9	0.5	510	1330	2.62	0.70	3000
5	24	Air	30.1	46.1	23.8	690	8500	12.4	0.27	7600
6	28	Air	N/A ^b	N/A	N/A	N/A	N/A	N/A	N/A	N/A

^aOligomer: dimer \leq molecular weight < 10,000 g/mol, polymer: molecular weight \geq 10,000 g/mol.

^bPolymer was gelation.

temperature. In particular, the polymer content increased significantly at 160°C. Based on this result, the effective heating temperature of ECP synthesis is around 160°C to obtain the high polymer content before gelation.

Figure 5 shows the exponential increase in viscosity as the temperature increased over 100°C, whereas the degree of unsaturation decreased monotonously with increasing heating temperature. Thus, the polymerization of ECP under thermal treatment occurred by typical autoxidation at the side chain. Furthermore, the molecular weight distribution (i.e., polydispersity) increased exponentially with increasing heating temperature, indicating that the polymerization proceeded randomly at the side chain of cardanol.

Heating Time. The molecular weight, degree of unsaturation, and viscosity of the ECP synthesized at 160°C at the given heating times (i.e., 0, 12, 16, 20, 24, and 28 h) in air, are summarized in Table II. There is no structural change for up to 24 h in the epoxy and benzene groups according to the ¹H-NMR analysis, whereas the degree of unsaturation decreased with time. Thus, the reaction at the side chain of cardanol proceeded extensively. However, gelation was observed after 28 h, suggesting that the excess crosslink reaction at the side chain occurred. On the other hand, no structural change occurred in the epoxy and benzene groups according to the ¹H-NMR analysis, whereas the degree of unsaturation decreased. As the heating time increased, the peaks at 3500 cm⁻¹ and 1720 cm⁻¹ corresponding to the hydroxyl and carbonyl groups, respectively, appeared with autoxidation as presented in Figure 2. The

heating time increased, with decreasing monomer content, while the oligomer content increased as presented in Figure 4. Although the polymer was not produced until after 20 h, the content increased significantly after 24 h. Based on this result, the effective heating time of ECP synthesis is around 24 h at 160°C to obtain the high polymer content before gelation. The viscosity increased exponentially after 24 h, whereas the degree of unsaturation decreased linearly with increasing heating time, as presented in Figure 5. Furthermore, the molecular weight distribution increased exponentially with increasing heating time, indicating that the polymerization proceeded randomly at the side chain of cardanol.

Atmosphere. The molecular weight, degree of unsaturation, and viscosity of the ECP synthesized at 160°C for 24 h under various atmospheres (i.e., nitrogen, air, and oxygen) are summarized in Table III. Although the polymerization of ECP did not proceed in nitrogen as verified by the ¹H-NMR analysis, the polymerization proceeded at the side chain of the cardanol in both air and oxygen. The decrease in the degree of unsaturation in oxygen was larger than in air, suggesting that this polymerization is dependent on autoxidation. No difference in the FT-IR spectra of ECP was observed after polymerization in nitrogen as presented in Figure 2. On the other hand, the new peaks at 3500 and 1720 cm⁻¹ were observed after polymerization in air and oxygen. Only the monomer content was observed in nitrogen. However, it decreased in air and oxygen, whereas the oligomer and polymer contents increased. The decrease in the monomer content and the increase in the polymer content in

Table III. Effect of Atmosphere on ECP Synthesis

Entry	Temperature (°C)	Atmosphere	Content ratio (%) ^a			Molecular weight			Unsaturation	Viscosity (mPa s)
			Monomer	Oligomer	Polymer	M_n	M_w	M_w/M_n		
1	r.t.	Air	100	0	0	390	420	1.07	1.64	39
2	160	N ₂	100	0	0	390	420	1.07	1.64	39
3	160	Air	30.1	46.1	23.8	690	8500	12.4	0.27	7600
4	160	O ₂	21.1	41.0	37.9	1030	114,000	111	0.23	9600

^aOligomer: dimer \leq molecular weight < 10,000 g/mol, polymer: molecular weight \geq 10,000 g/mol.

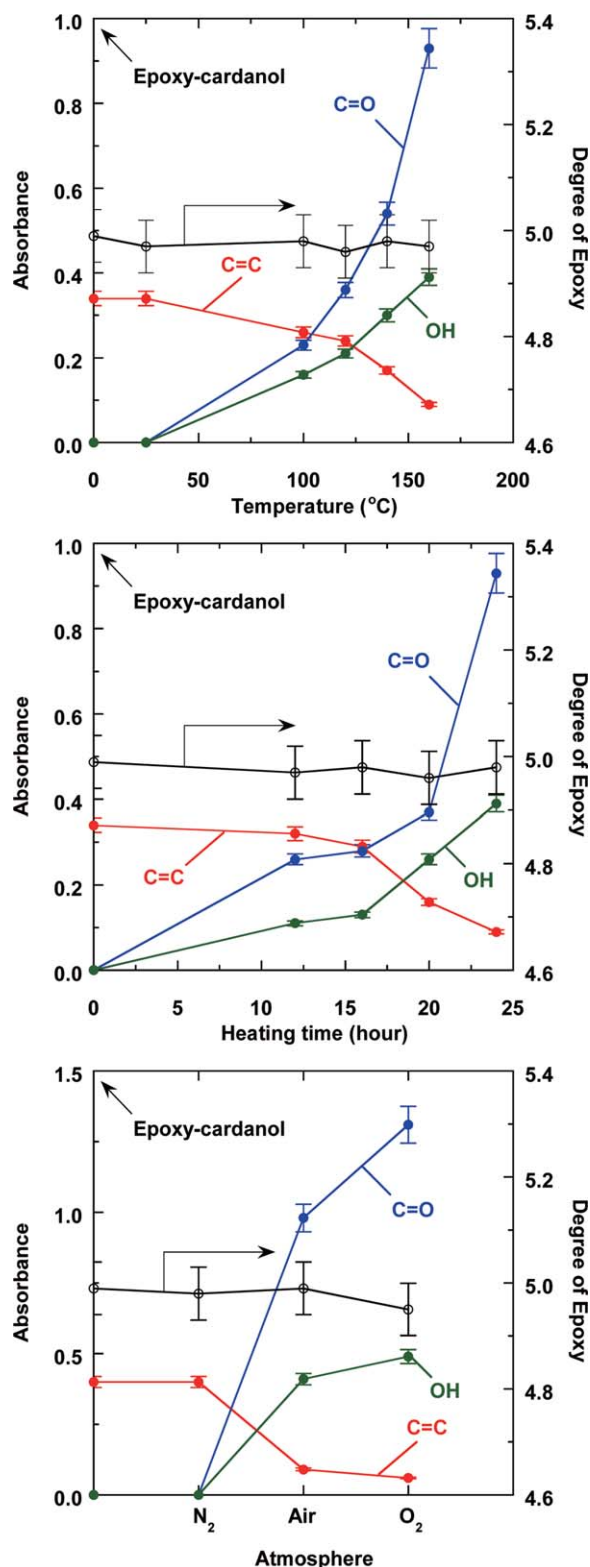


Figure 6. Relationship between the IR absorbance of C=C, C=O, and OH and the degree of epoxy group of ECP. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

oxygen were higher than those in air as presented in Figure 4. The viscosity was constant in nitrogen, whereas it increased significantly under air and oxygen. These behaviors are in good

agreement with those of the degree of unsaturation, as presented in Figure 5. The molecular weight distribution was widespread in oxygen, suggesting that the polymerization proceeded randomly at the side chain of cardanol, which required the presence of oxygen.

Based on these results, high temperature or prolonged heating time caused polymer gelation because of the excess reaction at the side chains in the cardanol. Each reaction showed high polydispersity, indicating that the prepolymer was considered a random structure. ECP polymerization proceeded at the side chain of cardanol based on the ¹H-NMR and FT-IR analyses. Furthermore, the polymerization mechanism of this prepolymer is dependent on the autoxidation reaction because of the increase in the formation of hydroxyl and carbonyl groups with increasing heat temperature in the presence of oxygen as presented in Figure 6. Based on these results, we employed further experiments using the prepolymer synthesized at 160°C for 24 h under air. The ECP coatings did not obtain from the other ECP because of the low molecular weight of the prepolymers.

Optimum of Amine Content. The effect of amine content was investigated in terms of the drying property, hardness, gel content, and glass transition temperature to determine the optimum preparation conditions for ECP coating. The properties of the ECP coatings prepared using the various amine compounds are summarized in Table IV. All ECP coatings required about 2.5 h to cure until HD, regardless of the amine content. However, when the amine content was over 15 wt %, the excess unreacted amine compound was breaded out from the epoxy coating, significantly reducing the drying property. The hardness of all the coatings was below 4B at 5 wt % epoxy content, whereas the hardness for 10 wt % epoxy content reached 2B after 2 days.

Figure 7 presents the gel contents, which reflect the degree of the crosslink reaction, for the various epoxy contents. The gel content for 5 wt % amine content was lower than that for 10 wt % and 15 wt %, indicating that 5 wt % amine content was not enough to react with the prepolymer. In addition, the soluble part of the epoxy coating prepared for 5 wt % was the unreacted prepolymer, whereas that for 10 wt % and 15 wt % showed the amine compound according to the ¹H-NMR analysis. The *T_g* of 5 wt % epoxy coating was lower than that of over 10 wt %. Given the *T_g* determined from RPT represents the degree of crosslink density, a density of over 10 wt % was higher than that of 5 wt %. Based on these results, we determined the optimum amine content was around 10 wt %. Further experiments were thus conducted using the ECP coating prepared with 10 wt % amine compound.

Film Characterization. Figure 8 presents the photographs of the ECP coatings. The ECP coatings exhibited a yellow color and self-standing property, regardless of the chemical structure of the amine compound. This yellow color could be based on the carbonyl group formed by a thermal autoxidation.

Figure 9 presents the FT-IR spectra of the ECP coating after 0 and 7 days curing at room temperature. The peaks initially observed at 3363 cm⁻¹ were attributed to the amine group and

Table IV. Drying Property and Hardness of ECP and Commercial Cashew Coatings

Amine component	Content (wt %)	Gel content ^a (wt %)	Drying property (h)			Hardness ^b				T_g (°C) ^c
			DF	TF	HD	1 day	2 days	7 days	10 days	
EDA	5	83.2	0.4	0.6	2.5	5B	4B	4B	4B	22.2 ± 0.8
	10	88.1	0.4	0.7	2.5	4B	2B	2B	2B	29.2 ± 1.5
	15	87.5	0.5	0.8	2.7	4B	2B	2B	2B	29.1 ± 1.6
DETA	5	82.3	0.4	0.6	2.2	>6B	>6B	6B	6B	12.8 ± 1.2
	10	88.6	0.2	0.5	2.5	4B	2B	2B	2B	29.1 ± 1.2
	15	87.0	0.3	0.6	2.4	5B	2B	2B	2B	28.4 ± 0.8
TEPA	5	77.7	0.4	0.6	2.5	>6B	>6B	>6B	>6B	10.7 ± 0.6
	10	86.0	0.3	0.6	2.5	4B	2B	2B	2B	29.0 ± 1.2
	15	87.1	0.4	0.6	3.1	4B	2B	2B	2B	28.1 ± 1.8
Cashew Coating	–	98.3	0.8	4.0	8.0	3B	2B	H	H	53.6 ± 1.6

^a After 7 days.^b Pencil hardness: HD << 6B < B < HB < F < H << 9H.^c Determined by rigid-body pendulum physical property-testing (RPT).

DF: dust free dry, TF: touch free dry, HD: harden dry (based on JIS-K-5400).

those at 3001, 910, and 860 cm^{-1} were attributed to the epoxy group. However, these peaks disappeared, and a new peak at 3400 to 3500 cm^{-1} attributed to the hydroxyl groups appeared after 7 days. Therefore, the epoxy group reacted with the amine compound during curing at room temperature. As presented in Table IV, all ECP coatings showed around 90 wt % of the gel content. The drying times of all the epoxy coatings were 2.5 h until HD, whereas the commercial cashew coating took 8 h. The drying property of the ECP coating was about three times quicker than that of the commercial one because the commercial cashew coating is cured by slow autoxidation reaction at room temperature. On the other hand, the ECP coatings are easy to cure because of the properties of the prepolymer (i.e., high molecular weight) and crosslink reaction between epoxy and amine groups. The hardness of all ECP coatings after 7 days were 2B, regardless of the amine components, suggesting that the amine reaction in the epoxy groups is more likely to produce primary amines than secondary ones. In addition, this result implies that the primary amines are liable to react with polymer of higher molecular weight, whereas the secondary amines may react with lower molecular weight (e.g., oligomer). Therefore, there is no crosslink effect in the reaction of secondary amine groups in this study. This result also suggests that the crosslinked structures of all the ECP coatings seem to be similar, regardless of the kinds of amine compound. On the other hand, the hardness of commercial cashew was 2D, which is higher than that of the ECP. The ECP coating was more flexible than the commercial one because the ECP has flexible alkyl chains, whereas the higher hardness of the commercial cashew using formaldehyde was due to the rigid linkage between benzene rings.

The physical properties of each coating are summarized in Table V. The order of the density of each coating was commercial cashew > EDA > DETA > TEPA. The order of water uptake

was TEPA > DETA > EDA > commercial cashew, which was opposite to that of the density. The ratio of secondary amine groups increased in the following order; TEPA > DETA > EDA. Basically, the amine compounds exhibit hydrophilic properties. Furthermore, the water contact angle of each ECP coating was about 69°, whereas that of the commercial cashew coating was 83°, suggesting that the epoxy surface was more hydrophobic than that of the commercial cashew coating. Therefore, this hydrophilic property of the epoxy could be due to the hydrophilic amine compounds, mainly secondary amine groups.

Figure 10 presents the photographs with the color indices of the chemical stability of each coating. The ECP coatings showed good chemical resistance because there is no difference in the color indices after the experiment. On the other hand, the color change was observed in the commercial cashew coating after immersion in base solution because the phenolic hydroxyl group in the cashew coating reacts with the base compound. Therefore, the ECP coatings showed higher chemical stability compared with the commercial one. Possible reason for this result could be related to the complicated crosslink structure in the side chains of the ECP coatings.

Figure 11 presents the TGA curves of each coating; the thermal properties of each coating are summarized in Table VI. The 5 wt % weight loss, T_5 , and 10 wt % weight loss, T_{10} , determined from TGA curves for the cardanol-based epoxy were higher than that of the commercial one. On the other hand, the thermal decomposition temperature of the ECP coating was about 100°C lower than that of the commercial coating because the cashew coating forms a rigid crosslink structure between the benzene rings using formaldehyde.²⁵ The ECP coating has a flexible structure due to the flexible side chain of the cardanol. As expected, based on the hardness property, no difference was

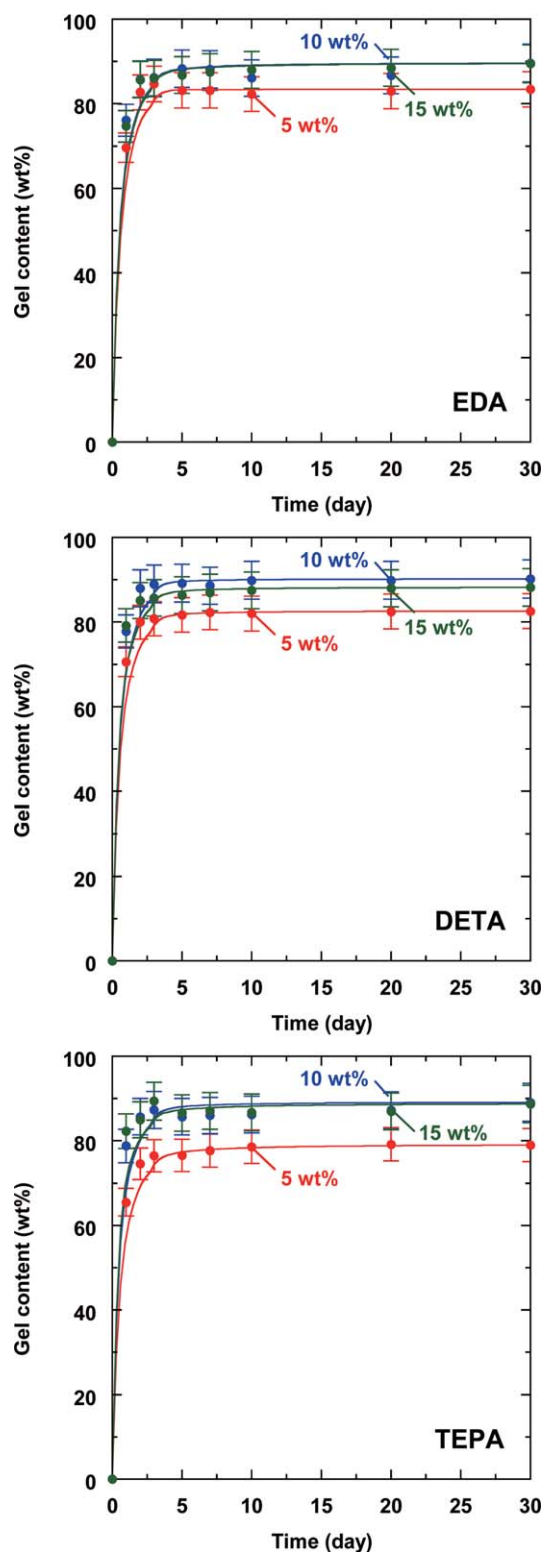


Figure 7. Time dependence of gel content in ECP coatings prepared with various amine contents. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

observed in the thermal property of the ECP coatings, regardless of the kinds of amine compounds, which may be because of the amine reaction that causes epoxy groups to proceed with the

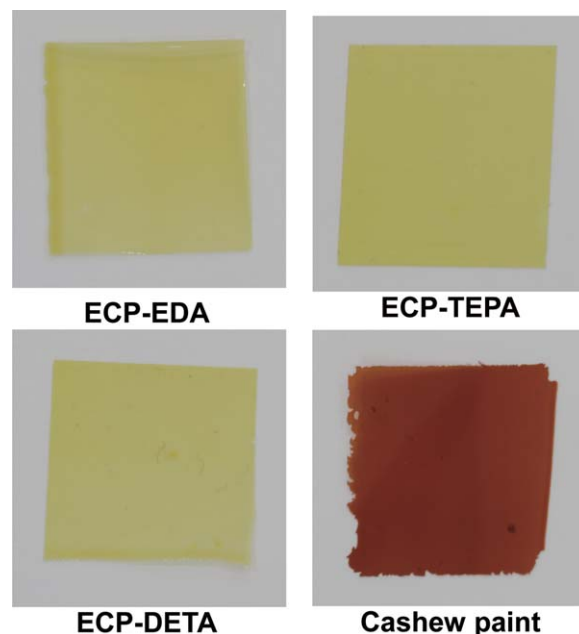


Figure 8. Photographs of ECP and commercial cashew coatings. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

primary amine than with the secondary one. The thermal decomposition behavior of these ECP coatings was similar with other epoxy resins.^{26–28} Consequently, the cured structures of all the ECP coatings were similar, regardless of the kinds of amine structure. Furthermore, the thermal decomposition of these ECP coatings possibly begins at the alkyl side chains of the cardanol. No differences were observed in the thermal decomposition behaviors of the ECP coatings. The T_g values of all ECP coatings determined by DSC analysis were around 25°C, indicating that the polymer is flexible rubbery state at room temperature. These results are in good agreement with the T_g determined by RPT measurement. On the other hand, the obvious transition peak in the DSC curve of the commercial cashew coating was not observed, and the T_g determined by

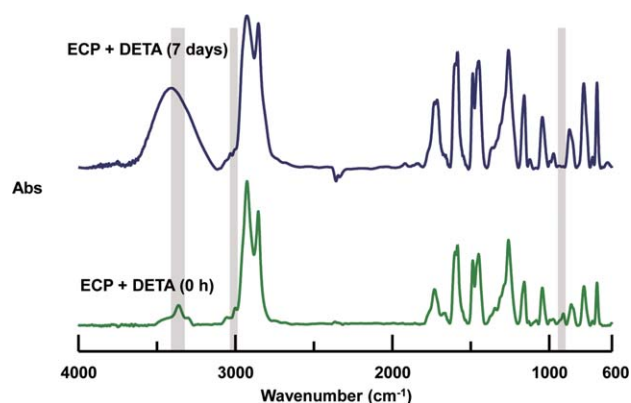


Figure 9. FT-IR spectra of ECP-DETA coating after 0 and 7 days. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table V. Physical Properties of ECP and Commercial Cashew Coatings

Amine component	Density (g/cm ³)	Water uptake (wt %)	Water contact angle (°)
EDA	1.020 ± 0.001	1.72 ± 0.08	69 ± 1
DETA	1.024 ± 0.001	1.82 ± 0.04	69 ± 1
TEPA	1.085 ± 0.001	1.95 ± 0.06	69 ± 1
Cashew coating	1.111 ± 0.001	1.56 ± 0.09	83 ± 1

RPT was about 54°C, which is higher than that of the ECP. The linkage between the benzene rings in the commercial cashew coating with formaldehyde enhances the polymer rigidity. Therefore, our ECP coatings can cure at room temperature without organic solvent and formaldehyde which were used in general commercial coatings. In addition, the drying property and chemical stability of ECP coatings were improved compared with the commercial cashew coating. Thus, the present ECP

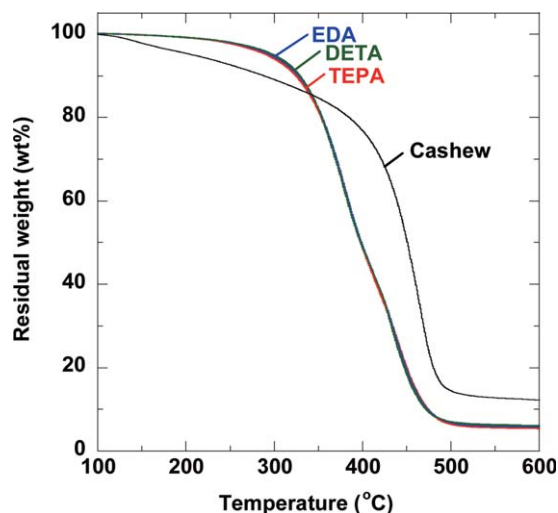


Figure 11. TGA curves of ECP and commercial cashew coatings. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

resin is expected to have large potential for use in epoxy resin applications as an environmentally-friendly bio-based polymer material.

CONCLUSIONS

Organic solvent-free bio-based epoxy resin was prepared from non-food CNSL which is one of renewable resources. The drying, physical, and thermal properties of the epoxy resins were investigated and compared with those of the commercial cashew coating. The cardanol-based epoxy coating was prepared from amine compounds and ECP synthesized by a thermal polymerization. FT-IR analysis showed that hydroxyl and carbonyl groups were produced, while the viscosity increased with increasing heating temperature and time. In addition, the degree of unsaturation in the side group of cardanol decreased based on the NMR analysis. The polymerization mechanism of ECP was autoxidation in the unsaturated group of the side chain because the polymerization did not proceed under a nitrogen atmosphere. The ECP coating showed yellow in color and self-standing property. The drying of the ECP coating required about 2.5 h to harden dry (HD), which is faster than that of the commercial cashew coating, because the curing of ECP coating was based on the prepolymer and crosslink reaction between epoxy and amine groups. Thermal analysis showed that the ECP coating was rubbery state at room temperature because of the flexible side chains of ECP. Furthermore, the ECP coating showed good chemical stability compared with the commercial cashew coating. These properties could be related to the complicated crosslink reaction based on the autoxidation of ECP. Therefore, the ECP coating synthesized in this study is expected to have a large potential for use in epoxy resin applications as environmentally-friendly bio-based polymer materials.

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Figure 10. Photographs of ECP and commercial cashew coatings after immersion in H₂SO₄ and NaOH solution at room temperature for 168 h. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table VI. Thermal Properties of ECP and Commercial Cashew Coatings

Amine component ^a	T_5 (°C)	T_{10} (°C)	T_d (°C)	W_R (600) (wt %)	T_g (°C) ^b	T_g (°C) ^c
EDA	292 ± 2	325 ± 2	335 ± 2	5 ± 1	22.7 ± 0.4	29.2 ± 1.5
DETA	296 ± 1	327 ± 1	332 ± 1	6 ± 1	22.8 ± 0.8	29.1 ± 1.2
TEPA	300 ± 1	330 ± 1	334 ± 1	6 ± 1	23.0 ± 0.8	29.0 ± 1.2
Cashew coating	208 ± 1	288 ± 3	432 ± 1	12 ± 1	N/A ^d	53.6 ± 1.6

^aAmine content was 10 wt %.

^bDetermined by differential scanning calorimetry (DSC).

^cDetermined by rigid-body pendulum physical property-testing (RPT).

^d T_g was not observed.

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REFERENCES

- Kumar, P. P.; Paramashivappa, R.; Vithayathil, P. J.; Subba Rao, P. V.; Srinivasa Rao, A. *J. Agric. Food Chem.* **2002**, *50*, 4705.
- Gedam, P. H.; Sampathkumaran, P. S. *Prog. Org. Coat.* **1986**, *14*, 115.
- Smith R. L., Jr.; Malaluan, R. M.; Setianto, W. B.; Inomata, H.; Arai, K. *Biores. Technol.* **2003**, *88*, 1.
- Lubi, M. C.; Thachil, E. T. *Design. Mon. Polym.* **2000**, *3*, 123.
- Campaner, P.; D'Amico, D.; Longo, L.; Stifani, C.; Tarzia, A. *J. Appl. Polym. Sci.* **2009**, *114*, 3585.
- Cardona, F.; Kin-Tak, A. L.; Fedrigo, J. *J. Appl. Polym. Sci.* **2012**, *123*, 2131.
- Barreto, A. C. H.; Rosa, D. S.; Fehine, P. B. A.; Mazzetto, S. E. *Compos. A* **2011**, *42*, 492.
- Kumar, R. P. *J. Coat. Technol. Res.* **2011**, *8*, 563.
- Yadav, R.; Awasthi, P.; Srivastava, D. *J. Appl. Polym. Sci.* **2009**, *114*, 1471.
- Gopalakrishnan, S.; Fernando, T. L. *Bull. Mater. Sci.* **2012**, *35*, 243.
- Mythili, C. V.; Retna, A. M.; Gopalakrishnan, S. *J. Appl. Polym. Sci.* **2005**, *98*, 284.
- Sultania, M.; Rai, J. S. P.; Srivastava, D. *Mater. Chem. Phys.* **2012**, *132*, 180.
- Sultania, M.; Rai, J. S. P.; Srivastava, D. *Eur. Polym. J.* **2010**, *46*, 2019.
- Lochab, B.; Varma, I. K.; Bijwe, J. *J. Therm. Anal. Calorim.* **2012**, *107*, 661.
- Rao, B. S.; Palanisamy, A. *Prog. Org. Coat.* **2012**, *74*, 427.
- Souza, F. G.; Orlando, M. T. D.; Michel, R. C.; Pinto, J. C.; Cosme, T.; Oliveira, G. E. *J. Appl. Polym. Sci.* **2011**, *119*, 2666.
- John, G.; Pillai, C. K. S. *J. Polym. Sci. Part A: Polym. Chem.* **1993**, *31*, 1069.
- Ikeda, R.; Tanaka, H.; Uyama, H.; Kobayashi, S. *Polym. J.* **2000**, *32*, 589.
- Ikeda, R.; Tanaka, H.; Uyama, H.; Kobayashi, S. *Polymer* **2002**, *43*, 3475.
- Patel, M. B.; Patel, R. G.; Patel, V. S. *Thermochim. Acta* **1988**, *129*, 277.
- Bhunja, H. P.; Nando, G. B.; Basak, A.; Lenka, S.; Nayak, P. L. *Eur. Polym. J.* **1999**, *35*, 1713.
- Lazzari, M.; Chiantore, O. *Polym. Degrad. Stab.* **1999**, *65*, 303.
- Kundu, P. P.; Larock, R. C. *Prog. Org. Coat.* **2009**, *65*, 10.
- Soucek, M. D.; Khattab, T.; Wu, J. *Prog. Org. Coat.* **2012**, *73*, 435.
- Campaner, P.; D'Amico, D.; Longo, L.; Stifani, C.; Tarzia, A. *J. Appl. Polym. Sci.* **2009**, *114*, 3585.
- Gianni, A. D.; Sangermano, M.; Malucelli, G.; Voit, B. *Macromol. Mater. Eng.* **2006**, *291*, 1004.
- Sangermano, M.; Cerrone, M.; Colucci, G.; Roppolo, I.; Ortiz, R. A. *Polym. Int.* **2010**, *59*, 1046.