

Recyclable Curcumin-Based Bioepoxy Resin with On-Demand Chemical Cleavability

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Cite This: *ACS Omega* 2024, 9, 9585–9592

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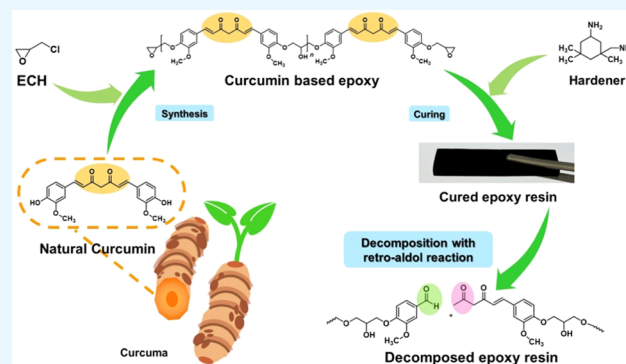


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Supporting Information

ABSTRACT: We synthesized a novel curcumin-based bioepoxy resin by introducing epichlorohydrin (ECH) into the hydroxyl groups of curcumin and analyzed it using Fourier transform infrared spectroscopy (FTIR) and nuclear magnetic resonance (NMR). The epoxy equivalent weight (EEW) was determined based on a reaction with sodium hydroxide (NaOH) through titration, and the actual curing process was conducted after exploring the optimal conditions using an amine-based curing agent through dynamic scanning in differential scanning calorimetry (DSC) and isotherm analysis. The cured epoxy resin had a tensile strength, Young's modulus, and glass transition temperature (T_g) of 33 MPa, 1.4 GPa, and 86 °C, respectively. Interestingly, the diunsaturated ketone contained in the epoxy resin showed on-demand chemical cleavability, in that it had been decomposed into an aldehyde and ketone only after having been converted to a hydroxyl ketone through an oxidation reaction. The results of this study can significantly contribute to improving the eco-friendliness and recyclability of epoxy resins used in fields requiring long-term stability and chemical resistance.



1. INTRODUCTION

Epoxy resins are thermosetting resins that are widely used because of their unique mechanical and electrical properties, excellent thermal and chemical stabilities, and high value in industrial applications.^{1–3} Disadvantageously, bisphenol A, which is present in diglycidyl ether of bisphenol A (DGEBA), a common epoxy resin, is associated with environmental and health risks.⁴ To address these challenges and meet the growing demand for environmentally friendly alternatives to DGEBA, many studies are actively undertaking efforts to use biomaterials.⁵ Incorporating biomaterials such as lignin,^{6–8} sugar,⁹ starch,¹⁰ and vanillin^{11,12} into thermosetting epoxy resin matrices exhibits promising potential in enhancing the performance of coatings and adhesives while minimizing negative environmental impacts.¹³ Moreover, the recycling issue of thermosetting epoxy is emerging as one of the key challenges in ensuring sustainability and environmental protection of modern industries. The limited recyclability of conventional thermosetting epoxies presents difficulties in waste disposal, resulting in a potential resource wastage. To solve this problem, studies have proposed methods employing heat, superheated steam, supercritical fluids, and chemical oxidation to break the chemical bonds of epoxy resins.^{14–18} Implementing these methods can be cumbersome and energy-intensive. Recent research in the design of epoxy resins has made active efforts to introduce chemical groups that can be easily decomposed using biomaterials and thereby simultaneously solve issues related to both environmental friendliness and recyclability. However, this

method has a disadvantage in that it must be accompanied by a chemical reaction to create a chemically decomposable group. Designing a natural product that inherently contains a group that can be easily decomposed chemically would be an effective approach to resolving the aforementioned issues. In our previous study, we reported that an unsaturated ketone group prepared using vanillin and raspberry ketones had been converted into a hydroxyl ketone through a retro-aldol reaction and that ultimately, it had rapidly decomposed into aldehydes and ketones. Additionally, this two-step decomposition reaction was carried out selectively, providing on-demand recyclability.¹⁹

In this study, we examined the possibility of creating an eco-friendly epoxy resin using curcumin, which has an inherently diunsaturated ketone group. The results revealed that it exhibited fast and on-demand recyclability through the retro-aldol reaction of unsaturated ketones. Notably, the proposed eco-friendly epoxy resin can effectively replace DGEBA and significantly contribute to the development of recyclable materials.

Received: November 27, 2023

Revised: January 30, 2024

Accepted: February 5, 2024

Published: February 17, 2024



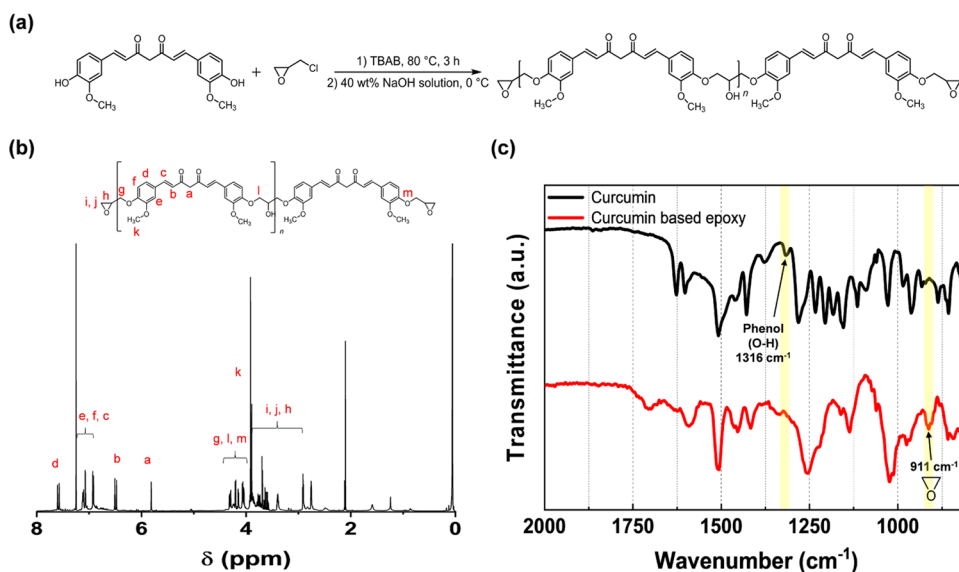


Figure 1. (a) Conditions for the synthesis of curcumin-based epoxy resin and the (b) NMR and (c) FTIR spectra of the curcumin (solid black line) and curcumin-based epoxy resin (solid red line).

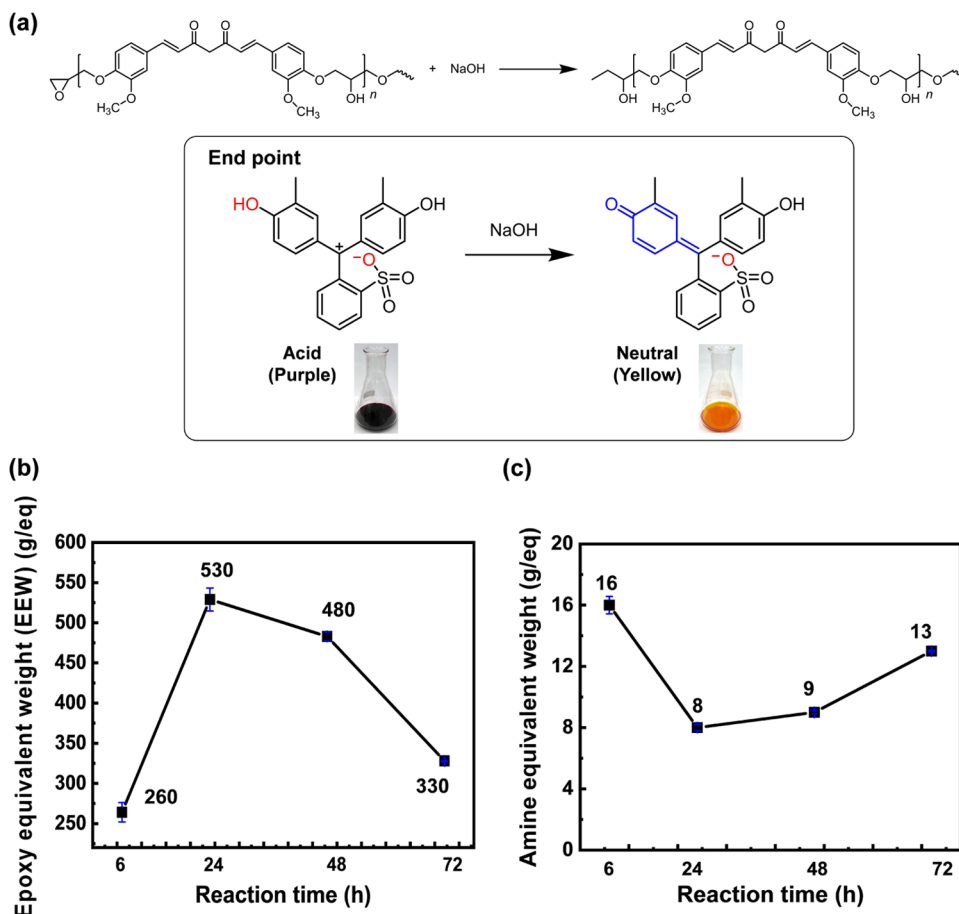


Figure 2. (a) Mechanism for appropriately determining the EEW, (b) the EEW over time, and (c) the equivalent weight of the amine over time.

2. RESULTS AND DISCUSSION

2.1. Characterization of the Curcumin-Based Epoxy. A curcumin-based epoxy product was synthesized, as shown in Figure 1a. Its chemical structure was confirmed using ¹H nuclear magnetic resonance (NMR) (Figure 1b) and Fourier transform infrared (FTIR) spectroscopy (Figure 1c). Clearly, NMR had an

aromatic structure at 6–8 ppm (d–f), and the epoxy structure peak was synthesized at 3–4 ppm (i, j, and h).²⁰ The FTIR results, which showed that the oxirane peak (911 cm⁻¹) had appeared in the curcumin-based epoxy material and that the phenol structure peak (1316 cm⁻¹) had disappeared, confirmed the successful synthesis of the epoxy resin.

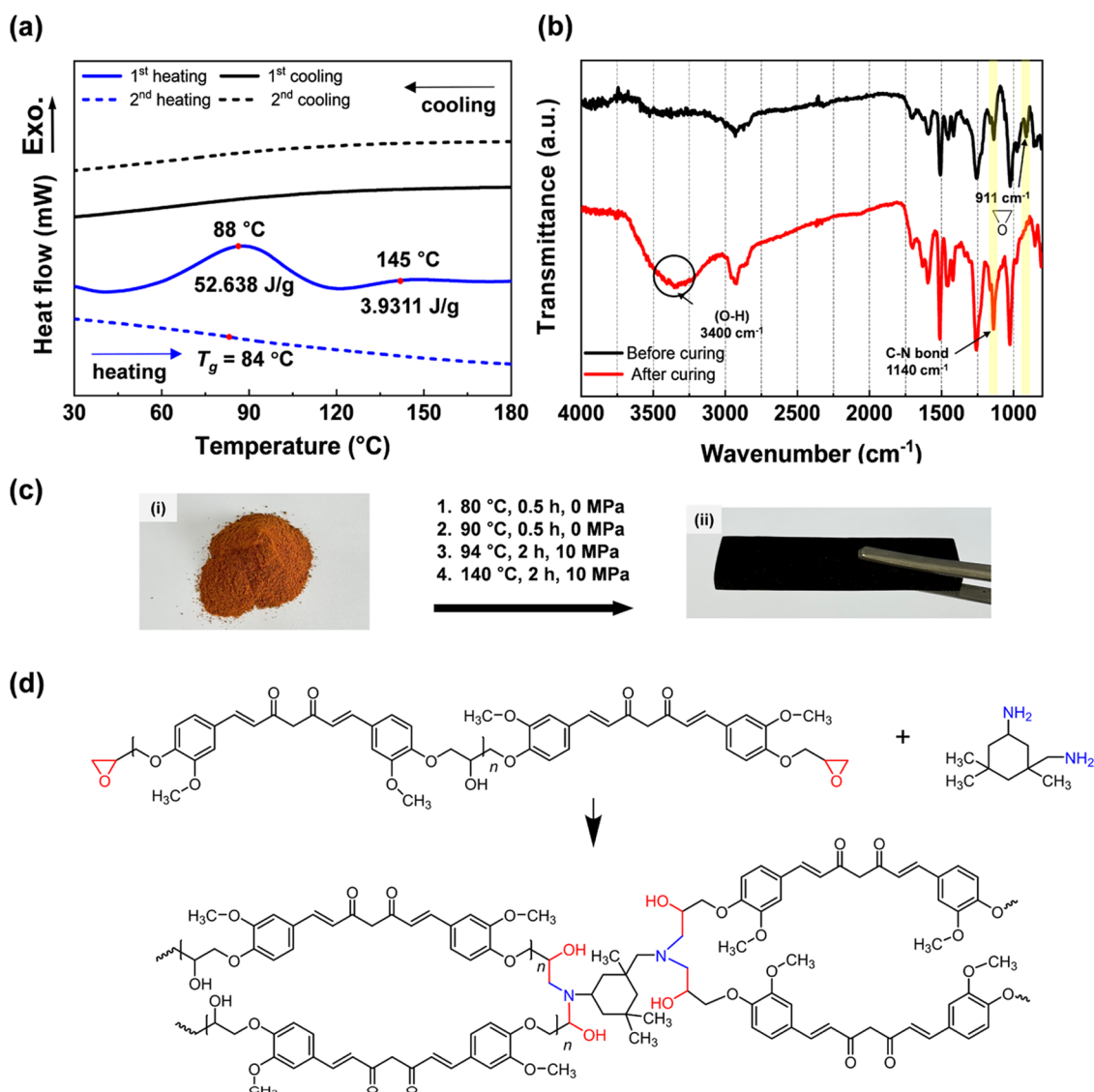


Figure 3. (a) DSC data of the curcumin epoxy and IPDA after the 48 h NaOH reaction, (b) FTIR data before and after curing, (c) curing times of the curcumin epoxy and IPDA, and (d) curing mechanism of the curcumin epoxy and IPDA.

NaOH was used in the synthesis of the resin,^{21–23} and the epoxy equivalent weight (EEW) was measured using Section 4.3. After the ring of the curcumin epoxy was opened using hydrochloric acid, NaOH was slowly added to change the C–Cl bond to C–OH. The end of the reaction was determined by the color change of the indicator from purple to yellow. A curing reaction was performed for the curing system by combining the epoxy and NH based on the average molecular weight per epoxy. The EEW was measured differently by adding NaOH and calculating the equivalent weight of the amine according to the following equation:

$$\text{equivalent weight of amine (g/eq.)} = \frac{\text{amine molecular weight}}{\text{number of active hydrogen atoms in amine}}$$

To evaluate the error range of the EEW, titration was conducted three times. The obtained values were then substituted into the equation in Section 4.3 for calculation. It was confirmed that the error of the EEW ranged from a minimum of 1 to a maximum of 15. Additionally, it can be

inferred that the amine equivalent ratio for each calculation remains constant with minimal deviation in the error range. After accurate identification based on the EEW and amine equivalent weight, we examined the curing method using DSC and proceeded with the curing system (Figure 2).

2.2. Thermal Mechanical Properties of the Curcumin Epoxy Resin. The DSC results confirmed that the T_m of the curcumin-based epoxy was 54 °C. Based on this T_m , isophorone diamine (IPDA) was selected as the curing agent. Then, the curing temperature was determined by conducting a thermal analysis of NH and epoxy in a 1:1 ratio based on the EEW and equivalent weight of the amine.^{24,25} The results in Figure 3b were confirmed by using FTIR to determine whether hardening had occurred. Prior to curing, the oxirane group at 911 cm^{-1} was shown; after curing, the oxirane group disappeared, and it was confirmed that the tertiary amine C–N bond at 1140 cm^{-1} had been cured. The DSC plot of the curcumin epoxy resin with various NaOH reaction times was investigated. An exothermic peak was observed within the curing temperature range of 80 to 145 °C.

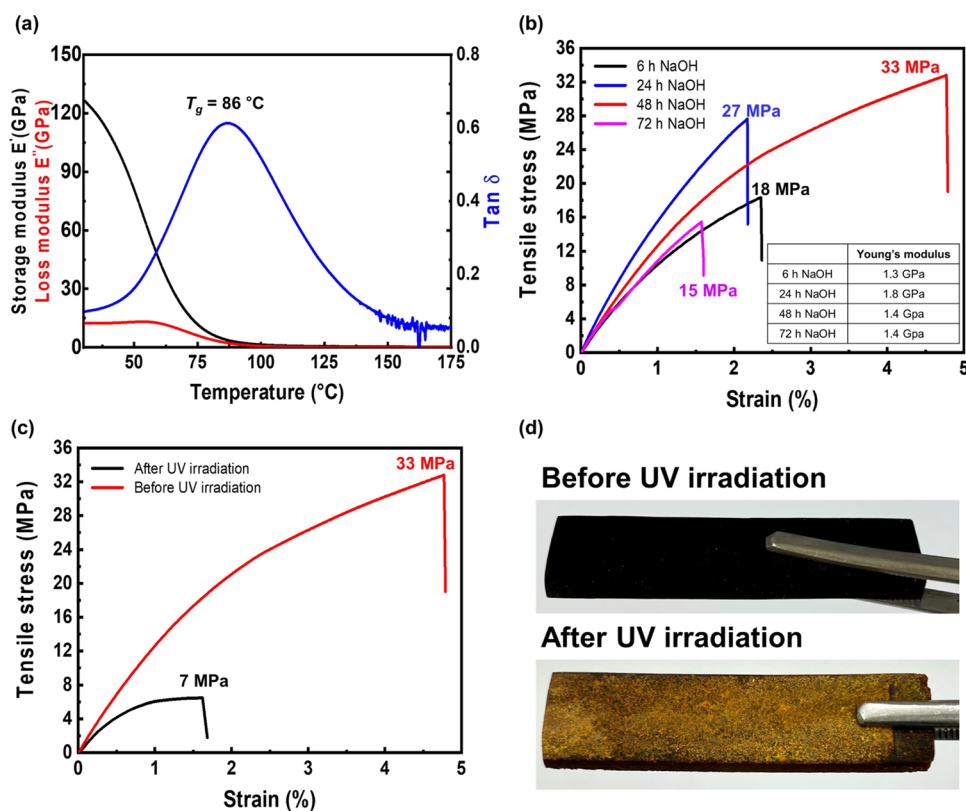


Figure 4. (a) Dynamic mechanical analysis data of the curcumin epoxy resin after the 48 h NaOH reaction and (b) tensile strength of the curcumin epoxy resin according to the NaOH reaction time. (c) Measuring the tensile strength of specimens before and after application of curcumin epoxy resin for UV irradiation. (d) Photographs of the curcumin epoxy resin before (top) and after (bottom) the UV irradiation.

The curing process was carried out by initial pre-curing at 80°C for 0.5 h under 0 MPa conditions, pre-curing at 90°C for 0.5 h under 0 MPa conditions, and then pre-curing for 0.5 h under 0 MPa conditions. Then, curing was carried out at 94°C for 2 h under 10 MPa conditions and was completed when it was performed at 140°C for 2 h under 10 MPa conditions (Figure 3c). Figure 3d shows the mechanism of the curing performed using the curing system shown in Figure 3c; it indicated that the NH and an epoxy group had been cured. The tensile strength and Young's modulus were measured, as shown in Figure 4b. As the NaOH reaction time increased from 6 to 48 h, the tensile strength tended to increase but decreased after 72 h. Additionally, the strength tended to increase as the EEW increased. However, the curcumin-based epoxy resin that had undergone a 24 h reaction with NaOH combined the NH with an epoxy group. This resulted in the amount of amine decreasing and hydrogen bonds forming during the bonding with the epoxy group, ultimately interfering with the bonding process.^{26,27} Thermogravimetric analysis (TGA) measurement was performed to evaluate the thermal stability of curcumin epoxy resin and DGBEA. During the heating process, the DGBEA resin displayed three distinct peaks within the temperature ranges of 100 – 200 , 200 – 500 , and 500 – 700°C . The initial weight loss (approximately 2 wt %) between 25 and 200°C was attributed to the vaporization of residual moisture in the sample. The subsequent weight loss (around 73 wt %) at 200 – 500°C was linked to the decomposition of hydroxyl and aliphatic functional groups. Lastly, an 8 wt % loss at 500 – 700°C was primarily due to the removal of ether groups and protons in the DGBEA resin. Consequently, the DGBEA resin exhibited a 4 wt % char yield at 700°C . In comparison, the TGA result for the curcumin epoxy

resin displayed a relatively large single peak around 200 – 550°C . Similar to DGBEA resin, a weight loss of approximately 5 wt % due to moisture was observed between 100 – 200°C , followed by a loss of about 58 wt % attributed to hydroxyl and aliphatic functional groups between 200 – 550°C . Notably, the TGA of curcumin epoxy resin demonstrated a high char yield of approximately 31 wt % at 700°C .²⁸ The curcumin-based epoxy resin exhibited a tensile strength of 15–33 MPa and a Young's modulus of 1.3 to 1.8 GPa. After the curcumin epoxy resin was reacted with NaOH for an additional 48 h, its T_g was 84 and 86°C , as determined using DSC and DMA, respectively (Figures 3a and 4a). In the previous study of epoxy resins using the aldol reaction performed by our group,¹⁹ a tensile strength of 58 MPa was achieved; however, the tensile strength did not reach such high levels in this study. This is thought to be because the purity was lower than that of substances synthesized using natural product-based curcumin, and oligomer molecules are included in the process of attaching ECH. To assess ultraviolet (UV) stability, the cured curcumin epoxy resin underwent evaluation for color change and tensile strength alteration after 3 days of UV exposure, as illustrated in Figure 4c. Samples subjected to UV light exhibited a shift in color from dark brown to partially yellow. Furthermore, the strength decreased from 33 to 7 MPa after UV irradiation. The FTIR results, shown in Figure S4, indicated that the 1140 cm^{-1} C–N bond decreased after the experiment compared to before the UV stability experiment. This outcome implies that UV-induced oxidation of curcumin epoxy occurred, resulting in a substantial reduction in the tensile strength.

2.3. Chemical Decomposition of the Curcumin Epoxy Resin Cured by the IPDA. Figure 5a shows the chemical

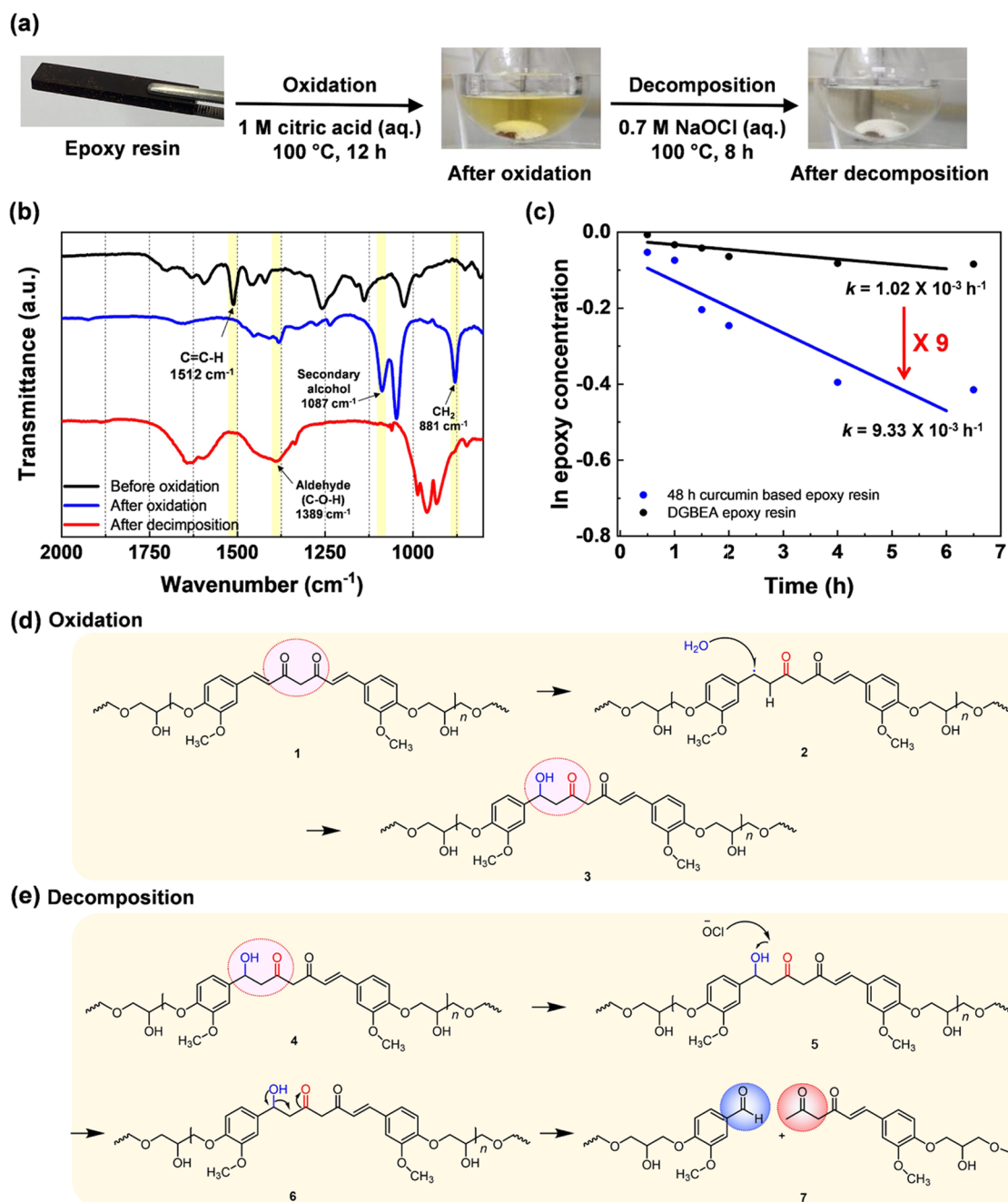


Figure 5. (a) Experimental process of decomposition of the curcumin epoxy resin. (b) FTIR spectra of the curcumin epoxy resin before oxidation, after oxidation, and after decomposition. The spectral line in the wavenumber range from 2000 to 800 cm⁻¹ is magnified. (c) Reaction kinetics of the DGBEA epoxy resin and curcumin epoxy resin. (d) Oxidation reaction mechanism of the curcumin epoxy resin. (e) Decomposition mechanism of the curcumin epoxy resin after oxidation.

decomposition process. An unsaturated alkene was attacked by a proton (H⁺) at the α site, as shown in Figure 5d, leading to the formation of cations and the release of H⁺, resulting in the formation of secondary alcohols. The OCl⁻ ions present in the NaOCl solution removed the protons from the secondary alcohol, and the reaction proceeded upon heating. Accordingly, the chemical decomposition of the curcumin epoxy resin structure led to the formation of aldehydes and carbonyls (Figure 5e). The FTIR analysis results showed that the C=C-H bond had been oxidized by the C-OH bond, and a peak was observed at 1087 cm⁻¹, indicating the formation of secondary alcohols. Additionally, it was confirmed that the C=C-H

had decreased at 1512 cm⁻¹ and that the C-OH aldehyde peak appeared and decomposed at 1389 cm⁻¹ (Figure 5b). To compare the chemical decomposition of the DGBEA and curcumin epoxy resins, decomposition was carried out at 2 h intervals. Based on the obtained results, the decomposition for each interval was calculated, and the decomposition rate constant was determined.¹⁷

$$\frac{d[\text{epoxy}]}{dt} = -k[\text{epoxy}][\text{NaOCl}]^n[\text{H}_2\text{O}]^m \quad (1)$$

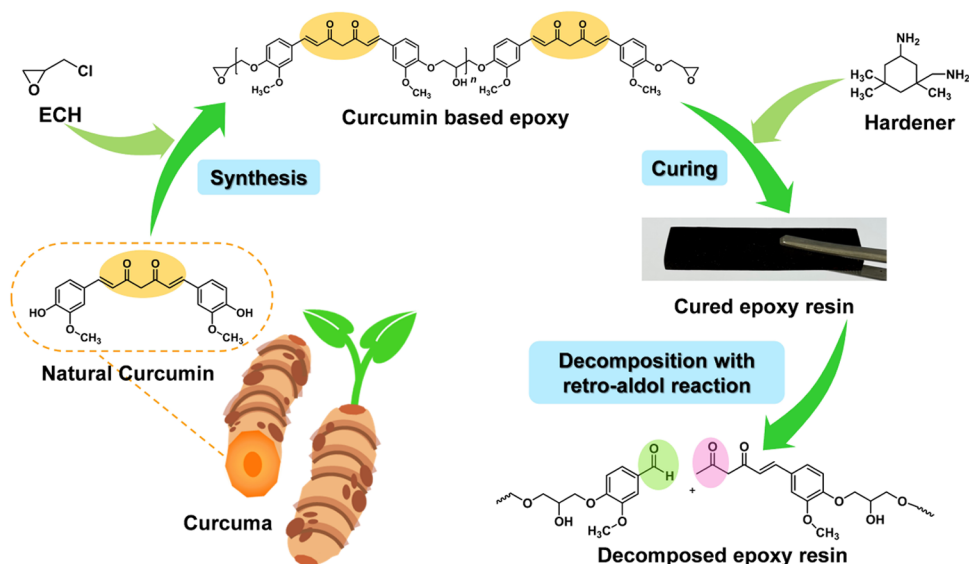


Figure 6. Synthesis of curcumin with ECH to obtain a biobased epoxy. Thermosetting plastics are prepared by mixing curcumin-based epoxy resin and IPDA and undergo decomposition through oxidation.

where $[\text{NaOCl}]$ and $[\text{H}_2\text{O}]$ represent the constant concentrations of H_2O and NaOCl , respectively, which are used in excess during decomposition.

$$\frac{d[\text{epoxy}]}{dt} = -k'[\text{epoxy}] \quad (2)$$

$$\ln \frac{d[\text{epoxy}]}{dt} = -k't \quad (3)$$

Equation 3 is derived by substituting the weight (g) of the epoxy specimen instead of the concentration, which is denoted as $[\text{epoxy}]$ because the epoxy specimen is solid. Figure 5c plots the reaction rate constant (k) for the DGBEA and curcumin epoxy resins over time; they had k values of 1.02×10^{-3} and $9.33 \times 10^{-3} \text{ h}^{-1}$, respectively. Based on the residual epoxy concentration, the decomposition reactions of both samples followed first-order kinetics. Moreover, the reaction rate constant of the curcumin-based epoxy resin was approximately nine times higher than that of the DGBEA epoxy resin. Figure 6 illustrates the entire synthesis process. Curcumin and epichlorohydrin (ECH), which are suitable biobased materials, were used for epoxy synthesis. After the epoxy resin was prepared by mixing a curcumin-based epoxy and IPDA, it was subjected to an oxidation reaction and underwent decomposition.

3. CONCLUSIONS

In this study, an eco-friendly thermosetting epoxy resin was synthesized using curcumin as a biomaterial. Through NMR and FTIR analyses, the presence of epoxy groups was confirmed at 3–4 ppm and 911 cm^{-1} , respectively. The EEW was determined by implementing the appropriate processes based on the NaOH reaction time, and the equivalent weight of the amine was determined. Based on the obtained data, IPDA was selected as the optimal curing agent and used to cure the epoxy resin. The curing process was confirmed through FTIR analysis, which showed a reduction in the peak at 911 cm^{-1} . The mechanical strength of the cured resin was evaluated by measuring the tensile strength and Young's modulus. The curcumin epoxy resin that had reacted with NaOH for 48 h exhibited the highest tensile strength. The T_g of the resin was determined by DSC and

dynamic mechanical analysis to be 84 and $86 \text{ }^\circ\text{C}$, respectively. The depolymerization reaction rate constant was found to be $9.33 \times 10^{-3} \text{ h}^{-1}$, which was nine times higher than that of the DGBEA epoxy resin. Overall, the results of the study highlighted that eco-friendly thermosetting epoxy resins could be chemically synthesized and decomposed using natural curcumin.

4. EXPERIMENTAL SECTION

4.1. Materials and Characterization. Curcumin, epichlorohydrin (ECH), and tetrabutylammonium bromide (TBAB) were purchased from Tokyo Chemical Industry Co., (Tokyo, Japan). Sodium hydroxide (NaOH), ethyl acetate (EA), and sodium sulfate anhydrous (Na_2SO_4) were purchased from Duksun Chemical Co., Ltd. (Seoul, Korea). Citric acid anhydrous (99.5%) and sodium hypochlorite solution (NaOCl solution) was purchased from Daejung Chemical Co., (Korea). Isophorone diamine (IPDA) was purchased from Kukdo Chemical Co., (South Korea). Fourier transform infrared spectroscopy (FTIR): Fourier transform infrared (FTIR) spectra were measured by using a JASCO FTIR spectroscope (FTIR 4100; Japan). Curcumin and curcumin-based epoxy before and after oxidation and decomposition were measured in solid powder form, and the spectra were recorded with a resolution of 4 cm^{-1} and 32 scans per sample across a range of $4000\text{--}800 \text{ cm}^{-1}$ Proton nuclear magnetic resonance (^1H NMR) spectroscopy: Proton nuclear magnetic resonance (NMR) analyses of curcumin-based epoxy was performed at 500 MHz on a JEOL 500 spectrometer (Japan) with the CDCl_3 solvent. The pulse width was $1 \mu\text{s}$, and the delay time was 2 s. The number of scans was 16 on ca. 0.1 mg of curcumin-based epoxy dissolved in CDCl_3 and packed into a glass sample tube. Differential scanning calorimetry (DSC): The Discovery DSC 25 was used to perform DSC under a nitrogen atmosphere. 3–4 mg of curcumin-based epoxy, a mixture of curcumin-based epoxy and IPDA, and curcumin-based epoxy/IPDA were encapsulated in an aluminum crucible and placed in the machine before the measurements. Each material was measured at a heating and cooling rate of $10 \text{ }^\circ\text{C min}^{-1}$. Dynamic mechanical analysis: DMA850 dynamic mechanical analyzer (TA Instruments, Newcastle, DE) was used to measure the

dynamic mechanical properties of the curcumin epoxy resin (having dimensions of 35 mm × 13 mm × 3 mm). The curcumin epoxy resin was scanned under heating from 30 to 175 °C at a heating rate of 3 °C/min, an amplitude of 10 μm, and a frequency of 1 Hz in the double-cantilever mode. Universal testing machine: Tensile tests (INSTRON-3369) were performed with a stretch rate of 5 mm/min at 25 °C. The curcumin epoxy resin measured 50 mm × 15 mm × 3 mm in size. Ultraviolet (UV) Stability test: UV stability test was assessed using a UVA-340 lamp with a typical irradiance of 0.89 W/(m² × nm) at 340 nm. The samples underwent an 8 h UV exposure with an uninsulated black panel temperature controlled at 60 °C. Following this, a 4 h condensation phase followed, maintaining the uninsulated black panel temperature at 50 °C.

4.2. Synthesis of Curcumin-Based Epoxy. In a 500 mL, round-bottom flask, curcumin (20 g, 54.29 mmol) was added to ECH (184.92 g, 1085.84 mmol) at 80 °C for 1 h. After curcumin was completely dissolved in ECH, TBAB catalyst (5.25 g, 16.29 mmol) was added to the mixture. Then, the mixture was stirred at 80 °C for 2 h. After the completion of the reaction, the mixture was cooled in an ice bath. Thereafter, 40 wt % NaOH solution (9 mL) was added dropwise over 10 min, and then the mixture was reacted for 6 h in the ice bath. After the completion of the reaction, the mixture was extracted by EA (100 mL × 3). The organic layer was collected and washed twice with brine, followed by drying with anhydrous Na₂SO₄. After filtration, the filtrate was concentrated under a reduced pressure. The compound was obtained as a brown solid after removal of the solvent.

4.3. Determination of the Epoxy Equivalent Weight (EEW). Erlenmeyer flask, 1.0 g of sample was precisely weighed and mixed with 20 mL of 0.2 N HCl in dioxane. After stirring the mixture for 30 min at 25 °C, the amount of unreacted acid was estimated by back-titration with 0.1 N NaOH (in methanol) using cresol red as an indicator. A blank was also performed under the same reaction condition.²⁹ The epoxy equivalent weight (EEW) value was calculated according to the following equation

$$\begin{aligned} \text{epoxy equivalent weight (EEW) (g/eq.)} \\ = \frac{10 \times \text{sample weight (g)}}{(B - A) \times F} \end{aligned}$$

where *A* is the NaOH solution consumed in the sample titration experiment, *B* is the NaOH solution consumed in the blank sample, and *F* is the factor of the NaOH solution.

4.4. Manufacturing of Curcumin Epoxy Resin (Curcumin-Based Epoxy/IPDA). Curcumin-based epoxy/IPDA: 4 g of curcumin-based epoxy and 0.60 g of IPDA (the molar ratio of the epoxy group to N–H was 1:1) were placed in a stainless steel cup and mixed. Afterward, the mixture was poured into a hot-press mold in which thickness was set to 3 to 4 mm. After precuring at 80 and 90 °C for 0.5 h, postcuring was done on hot-press at 94 and 140 °C for 2 h at 10 MPa pressure. Finally, the curcumin epoxy resin (curcumin-based epoxy/IPDA) was obtained after natural cooling.

4.5. Decomposition Process of the Curcumin Epoxy Resin. The decomposition of the curcumin epoxy resin is conducted through two distinct steps. First, a pretreatment reaction is performed by introducing the curcumin epoxy resin into a 1 M citric acid solution and maintaining it at 100 °C for 12 h. Subsequently, the pretreated sample undergoes washing with an aqueous solution, filtration, and drying in an oven set at 100

°C for 24 h. In the second stage, the pretreated sample is added to a 0.7 M NaOCl solution and subjected to filtration treatment at 100 °C for 8 h. Following the primary treatment, a similar process of washing and filtration is carried out using an aqueous solution, followed by drying at 100 °C for 24 h.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsomega.3c09464>.

DSC analysis of curcumin epoxy; DSC analysis of curcumin epoxy resin; TGA analysis of curcumin resin and DBGEA resin, and FTIR results before and after UV stabilization (PDF)

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Author Contributions

J.J.: investigation, methodology, validation, and writing—original draft. Y.J. performed experiments, took photos, and analyzed data. Y.H. analyzed data. D.O. performed experiments. M.G.: conceptualization, methodology, writing—review and editing, supervision, and funding acquisition.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This research was supported by the Alchemist Project (no. 20025647) funded by the Ministry of Trade, Industry & Energy (MOTIE, Korea) and by the National Research Foundation of Korea (NRF) grant funded by the Korea government (MSIT) (no. 2023R1A2C1003435). This work was also supported in part by Human Resources Development Program of the Korea Institute of Energy Technology Evaluation and Planning (KETEP) grant funded by the Ministry of Trade, Industry and Energy, Republic of Korea (no. RS-2023-00237035).

■ ABBREVIATIONS

DGEBAs, diglycidyl ether of bisphenol A; ECH, epichlorohydrin; TBAB, tetrabutylammonium bromide; NaOH, sodium hydroxide; EA, ethyl acetate; Na₂SO₄, sodium sulfate anhydrous; NaOCl solution, sodium hypochlorite solution; IPDA, isophorone diamine; FTIR, Fourier transform infrared; NMR, nuclear magnetic resonance; DSC, differential scanning calorimetry;

EEW, epoxy equivalent weight; DMA, dynamic mechanical analysis; T_g , glass transition temperature; UV, ultraviolet

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