

Article

Green Regenerative Bamboo Lignin-Based Epoxy Resin: Preparation, Curing Behavior, and Performance Characterization

Jiayao Yang *, Jie Fei and Xingxing Wang

School of Biological and Chemical Engineering, Zhejiang University of Science and Technology, Hangzhou 310023, China; 222403857023@zust.edu.cn (J.F.); 212203817027@zust.edu.cn (X.W.)

* Correspondence: jiayao_yang@zust.edu.cn

Abstract

The dependence of conventional epoxy resins on fossil fuels and the environmental and health hazards associated with bisphenol A (BPA) demand the creation of sustainable alternatives. Because lignin is a natural resource and has an aromatic ring skeleton structure, it could be used as an alternative to fossil fuels. This study effectively resolved this challenge by utilizing a sustainable one-step epoxidation process to transform lignin into a bio-based epoxy resin. The results verified the successful synthesis of epoxidized bamboo lignin through systematic characterization employing Fourier transform infrared spectroscopy, hydrogen spectroscopy/two-dimensional heteronuclear single-quantum coherent nuclear magnetic resonance, quantitative phosphorus spectroscopy, and gel permeation chromatography. Lignin-based epoxy resins had an epoxy equivalent value of 350–400 g/mol and a weight-average molecular weight of 4853 g/mol. Studies on the curing kinetics revealed that polyetheramine (PEA-230) demonstrated the lowest apparent activation energy (46.2 kJ/mol), signifying its enhanced curing efficiency and potential for energy conservation. Mechanical testing indicated that the PEA-230 cured network demonstrated the maximum tensile strength (>25 MPa), whereas high-molecular-weight polyetheramine (PEA-2000) imparted enhanced elongation to the material. Lignin-based epoxy resins demonstrated superior heat stability. This study demonstrates the conversion of bamboo lignin into bio-based epoxy resins using a simple, environmentally friendly synthesis process, demonstrating the potential to reduce fossil resource use, efficiently use waste, develop sustainable thermosetting materials, and promote a circular bioeconomy.

Keywords: sustainability; bamboo lignin; bio-based epoxy resin; green chemistry; curing kinetics



Academic Editor: Francisco José Hernández Fernández

Received: 19 June 2025

Revised: 28 June 2025

Accepted: 4 July 2025

Published: 6 July 2025

Citation: Yang, J.; Fei, J.; Wang, X.

Green Regenerative Bamboo

Lignin-Based Epoxy Resin:

Preparation, Curing Behavior, and Performance Characterization.

Sustainability **2025**, *17*, 6201. <https://doi.org/10.3390/su17136201>

Copyright: © 2025 by the authors.

Licensee MDPI, Basel, Switzerland.

This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license

(<https://creativecommons.org/licenses/by/4.0/>).

1. Introduction

A significant obstacle to resource security and environmental sustainability is the widespread reliance on petroleum resources for the production of polymers [1–3]. Epoxy resins are used extensively in coatings, adhesives, composites, and electronics because of their superior mechanical qualities, strong adhesion, and resistance to chemicals [4,5]. However, all of the raw materials used to produce common commercial epoxy resins are non-renewable fossil fuels, endangering human health, in addition to causing major environmental issues. Specifically, BPA, a known endocrine disruptor, has had detrimental effects on ecosystems and newborn health [6,7]. Thus, a key approach to achieve the objective of sustainable development in the polymer industry is the creation of safer and more environmentally friendly alternatives based on renewable biomass resources.

Lignin, a natural polymer, ranks second to cellulose in global reserves and demonstrates significant potential as a sustainable raw material. As a significant by-product of the pulp and paper industry and developing biorefineries, it is frequently underutilized or incinerated for minimal energy value [8–11]. Lignin is a unique renewable natural polymer characterized by a complex aromatic structure and numerous reactive functional groups, presenting potential as a substitute for particular fossil resources [3,12]. Bamboo lignin, a distinct form of lignin, possesses several advantages. Bamboo, a renewable herbaceous plant characterized by rapid growth and significant carbon sequestration capacity, serves as a sustainable resource in Asia and Africa [8]. Bamboo lignin contains a higher concentration of p-hydroxyphenyl groups compared to herbaceous lignin, and its phenolic hydroxyl structure offers potential for lignin-based polymer synthesis [13,14]. The efficient utilization of bamboo lignin reduces environmental pollution and resource consumption while decreasing the reliance on finite fossil resources, aligning with the fundamental principles of sustainable development and the circular economy.

In recent years, studies have mainly explored two lignin-based epoxy resin strategies. The first is the conventional epoxidation of lignin after depolymerization to low-molecular-weight phenols. Although the resin properties obtained by this route are good, the depolymerization process usually requires harsh conditions and complex catalysts (difficult to recover and potentially polluting the environment) and suffers from high energy consumption, low yields, and poor economics [15–17], which is contrary to the fundamental goal of developing truly sustainable green lignin materials. The second is the direct epoxidation of partially depolymerized lignin fragments. This approach is simpler and more efficient and eliminates the need for deep depolymerization. Common organic solvent systems, such as acetone, are typically employed to facilitate dissolution and reaction environments, offering economic and sustainable advantages [18,19]. Therefore, the direct functionalization route is more compatible with sustainability goals, minimizing the processing steps, energy inputs, and environmental impacts. Bamboo lignin possesses remarkable renewability yet is generally regarded as industrial waste. The transformation of bamboo lignin into bio-based epoxy resin represents an efficient method for its high-value use. Nonetheless, the feasibility of synthesizing bamboo lignin into bio-based epoxy resin and the adequacy of its curing ability for practical applications require further investigation.

This study developed a green one-step process for the synthesis of epoxidized bamboo lignin (bamboo lignin-based epoxy). The method employs a water/acetone co-solvent system, thereby eliminating the requirement for benzene-based hazardous solvents and enhancing the environmental sustainability of the synthesis process. This study investigates the potential of bamboo lignin, a significant by-product of the bamboo pulp industry, as a substitute for conventional petroleum-based epoxy resins. It evaluates the curing behavior and performance characteristics of this bio-based epoxy resin sourced from underutilized bamboo lignin.

2. Materials and Methods

2.1. Chemicals and Reagents

Bamboo lignin (moso bamboo sulfate bamboo lignin, lignin content >95%, ash 0.18%) was purchased from Guangzhou Yingsheng Bioscience Co., Guangzhou, China. Acetone (analytically pure, ≥99.0%), acetonitrile (analytically pure, ≥99.0%), sodium hydroxide (analytically pure, ≥96.0%), N,N-dimethylformamide (analytically pure, ≥99.5%), pyridine (analytically pure, ≥99.5%), and epichlorohydrin (analytically pure, ≥99.5%) were purchased from Sinopharm Chemical Reagent Co., Shanghai, China. Deuterated chloroform (excellent purity, ≥99.8%), N-hydroxy-5-norbornene-2,3-dicarboximide (≥99.0%), methyl hexahydrophthalic anhydride (analytically pure), maleic anhydride (analytically

pure, $\geq 95\%$), 4,4-diaminodiphenylmethane (analytically pure, $\geq 99\%$), polyether amine 400 ($M_n \sim 400$), and polyether amine 2000 ($M_n \sim 2000$) were purchased from Shanghai Aladdin Biochemical Technology Co., Ltd., Shanghai, China. 2-Chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphosphorine (95%) was purchased from Sigma Aldrich (Shanghai) Trading Co., Ltd., Shanghai, China. Chromium acetylacetonate (III) ($\geq 98\%$) and polyether amine 230 ($M_n \sim 230$) were purchased from Shanghai Macklin Biochemical Technology Co., Ltd., Shanghai, China.

2.2. Purification of Bamboo Lignin

First, 50 g of raw bamboo lignin was incorporated into 500 mL of acetone and agitated at ambient temperature for 4 h. The insoluble substance was removed using filtration, and the filtrate was gathered to extract acetone under reduced pressure, resulting in purified bamboo lignin powder.

2.3. Epoxidation of Bamboo Lignin

First, 3 g of purified bamboo lignin was weighed and dissolved in 400 mL of a binary solvent composed of water and acetone (1:1, *v/v*). The mixture was heated to 55 °C while stirring for 30 min. Subsequently, 18.5 g of epichlorohydrin was added dropwise over 30 min, followed by the gradual addition of 12 mL of 10% NaOH solution dropwise over 30 min. The reaction was allowed to proceed for 4 h after the completion of the dropwise addition; then, it was terminated. Refer to Figure 1 for the reaction process. The reaction solution was cooled and transferred to 2 L of an acidic aqueous solution at a pH of 2–3 to induce precipitation. The product was promptly filtered post-precipitation, washed to neutrality with distilled water, and subsequently dried in a vacuum oven at 60 °C to yield epoxidized bamboo lignin powder (weight: approx. 2.8 g).

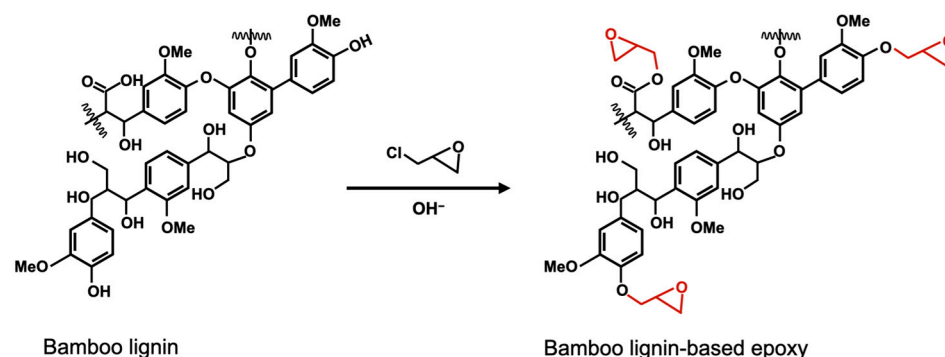


Figure 1. Epoxidized synthesis of bamboo lignin.

2.4. Preparation of Bamboo Lignin-Based Epoxy Curing System

Epoxidized lignin was combined with curing agents, including methyl hexahydrophthalic anhydride (MeHHPA), maleic anhydride (MA), 4,4-diaminodiphenylmethane (DDM), polyether amine 230 (PEA-230), polyether amine 400 (PEA-400), and polyether amine 2000 (PEA-2000), as detailed in Table 1, and the curing systems were positioned in metal molds. A quantity of 10–15 wt% of acetonitrile may be used as a co-solvent. The mixture was then subjected to a 50 °C oven for 30 min to evaporate the acetonitrile. Subsequently, it was placed in a metal mold for hot-press molding under curing conditions of 120 °C for 2 h and 140 °C for 2 h.

Table 1. Formulations of different curing systems.

Curing System	Bamboo Lignin-Based Epoxy/g	Curing Agent/g
MeHHPA	10	4.2
MA	10	2.5
DDM	10	1.5
PEA-230	10	1.7
PEA-400	10	3
PEA-2000	10	15

2.5. Fourier Transform Infrared Spectrometer (FTIR)

The infrared spectra of bamboo lignin and epoxidized bamboo lignin were determined by a Fourier infrared spectrometer, the Bruker Vetex-70 IR (Ettlingen, Germany), using the KBr press method with a scanning range of 4000–400 cm^{-1} .

2.6. Molecular Weight Determination

The molecular weights of bamboo lignin and epoxidized bamboo lignin were determined by gel permeation chromatography with a Waters 1525 (Milford, CT, USA) device, and the mobile phase was tetrahydrofuran.

2.7. Nuclear Magnetic Resonance Spectra (NMR)

The structures of acetylated bamboo lignin (see Supplementary Materials for preparation methods) and epoxidized bamboo lignin were determined by 1D and 2D NMR hydrogen spectroscopy, and the 1H and 2D HSQC were tested by a Bruker 400 M (Rheinstetten, Germany), in which the solvent was deuterated dimethylsulfoxide, and the reagent for the internal standard was p-nitrobenzaldehyde.

The hydroxyl content of bamboo lignin and epoxidized bamboo lignin was determined by quantitative phosphorus spectrometry, and ^{31}P NMR was tested by a Bruker 400 M (Rheinstetten, Germany). The sample preparation process was as follows: 15 mg of the sample was dissolved in 0.8 mL of a mixed solution (N,N-dimethylformamide–pyridine–deuterium chloroform = 0.4:0.6:1, $v/v/v$), which contained 1.63 μmol of the chiral agent chromium(III) acetylacetonate and 10 μmol of the internal standard reagent N-hydroxy-5-norbornene-2,3-dicarboximide. Finally, 0.15 mL of the phosphorylation reagent 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphosphorine was added for the phosphorylation of the cyclic ring for 20 min, and the sample was then tested.

2.8. Determination of Epoxy Value

The epoxide values and epoxy equivalents of the bamboo lignin-based epoxy were determined by quantitative NMR phosphorus spectroscopy and the dioxane hydrochloride method [20].

2.9. Thermogravimetric (TG) Analysis

The thermal stability of the cured products of bamboo lignin and bamboo lignin-based epoxy, as well as bamboo lignin-based epoxy, was determined by a thermogravimetric analyzer, the TG DTA 7200 (Tokyo, Japan), under a nitrogen atmosphere at test temperatures ranging from 30 to 600 $^{\circ}\text{C}$ with a temperature increase rate of 10 $^{\circ}\text{C}/\text{min}$.

2.10. Curing Thermal Behavior Test

The curing behavior of the reaction of bamboo lignin-based epoxy with the curing agent was tested by a differential scanning calorimeter (DSC), the TA-Q2000 (New Castle, DE, USA), with ramp rates of 5, 10, 15, and 20 $^{\circ}\text{C}/\text{min}$, at temperatures ranging from 30 to 300 $^{\circ}\text{C}$, under a nitrogen atmosphere with a nitrogen flow rate of 50 mL/min.

2.11. Mechanical Property Test

A universal mechanical testing machine CMT6104 (Shanghai, China) was used to test the mechanical properties of the products of cured bamboo lignin-based epoxy, following the tensile strength test method according to GB/T 1040.2-2006 [21]. The specimens were of the dumbbell type, the number of tests was no less than 6, and the test speed was 2 mm/min; it was performed at room temperature.

3. Results and Discussion

3.1. Infrared Spectral Analysis of Bamboo Lignin and Epoxidized Bamboo Lignin

This study utilized bamboo lignin as a raw material to synthesize lignin-based epoxy resin via a one-step procedure, investigated the structure and curing behavior of the resin, and found that bamboo lignin serves as an effective source of sustainable epoxy resin. This study performed the comprehensive characterization of the structure to demonstrate the successful preparation of lignin-based epoxy resin. Figure 2 illustrates the FTIR spectra of the bamboo lignin and epoxidized bamboo lignin. All bamboo lignin samples exhibited complete and typical characteristic features of bamboo lignin. Among these, the broad peak at 3440 cm^{-1} is the characteristic absorption peak of the hydroxyl group in lignin; the characteristic absorption peaks of the benzene ring of lignin are found at 1597, 1507, and 1420 cm^{-1} ; the vibrational absorption peak of the silymarinyl (S) C-H can be attributed to the absorption peaks at 1326 cm^{-1} and 1121 cm^{-1} ; the vibrational absorption peak of the guaiacyl (G) C=O stretching vibration is responsible for the absorption peak at 1267 cm^{-1} ; the absorption peak at 1121 cm^{-1} is primarily caused by the vibration of the C-C and C-O bonds of guaiacyl (G); and the CH vibrations of the 1,2,4,5-tetrasubstituted aromatic ring of p-hydroxyphenyl (H) are responsible for the absorption peaks at 835 cm^{-1} and 1033 cm^{-1} . As a result, it is discovered that bamboo lignin has the distinctive structure of a GSH-type lignin, which is typical of herbaceous lignin [22,23]. The natural features of the bamboo lignin structure have not been damaged, and the structural features of epoxidized lignin and the bamboo lignin structure are comparable. Among these, the hydroxyl group's absorption peak in epoxidized lignin was weaker at 3440 cm^{-1} , while the epoxy group's distinctive absorption peak emerged at 910 cm^{-1} . This suggests that some of the hydroxyl groups in bamboo lignin were changed to epoxy groups, which is consistent with the findings of Gioia's study [2].

3.2. Molecular Structure and Molecular Weight Analysis

The NMR technique is frequently employed for both the qualitative and quantitative structural analysis of substances. Figure 3 presents the ^1H NMR spectrum of acetylated bamboo lignin. The signal peaks at 10.15, 8.4, and 8.16 ppm correspond to p-nitrobenzaldehyde, utilized as the internal standard reagent. The broader signal peaks near 7 ppm primarily originate from the aryl ring region of bamboo lignin, while the methoxyl group signals are observed between 3 and 4 ppm. The peak at 2.5 ppm represents the solvent dimethyl sulfoxide (DMSO). Additionally, the signal at 2.23 ppm indicates the ester group derived from the phenolic hydroxyl group in bamboo lignin, and the peak at 1.99 ppm corresponds to the ester group from the aliphatic hydroxyl group in bamboo lignin. The ^1H NMR spectrum of epoxidized bamboo lignin resembles that of the original bamboo lignin; however, the signal peaks observed at 2.73 and 2.88 ppm are most likely derived from epoxy groups, consistent with the findings reported by Gioia [24,25].

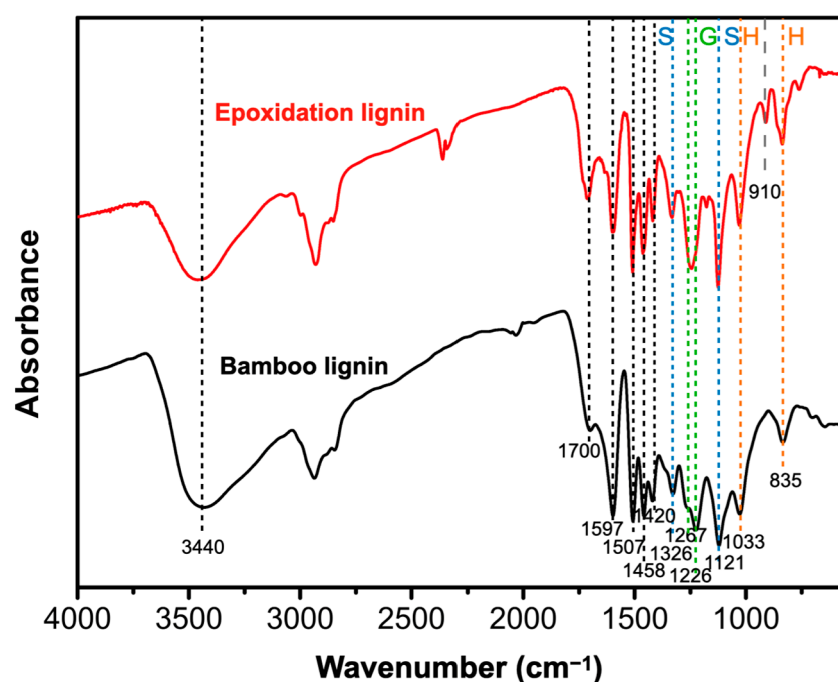


Figure 2. FTIR spectra of bamboo lignin and epoxidized bamboo lignin.

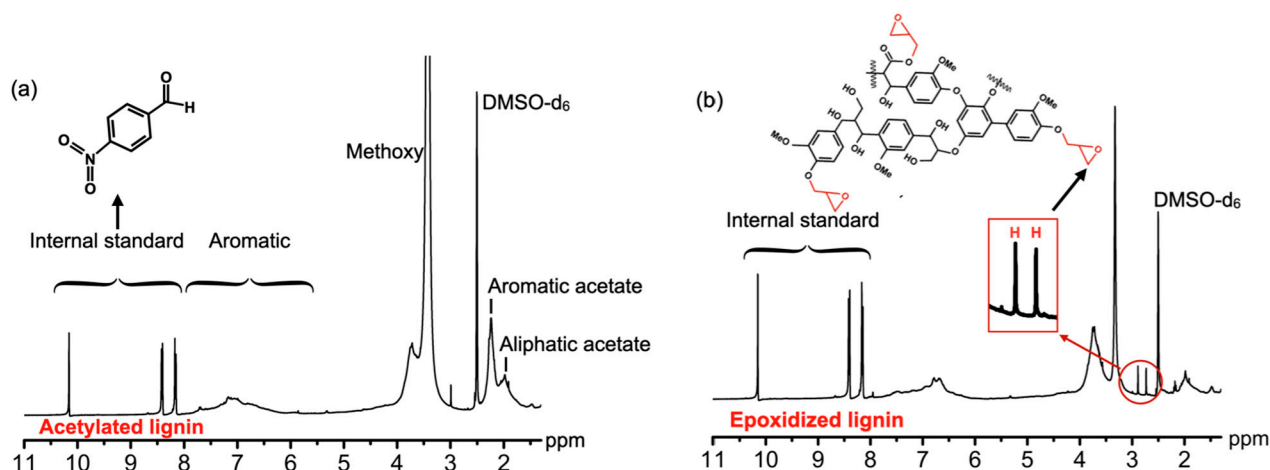


Figure 3. ^1H NMR of bamboo lignin (a) and epoxidized bamboo lignin (b).

To accurately assess the content of individual reactive hydroxyl functional groups in bamboo lignin, quantitative ^{31}P NMR spectroscopy was chosen as the most effective method. The ^{31}P NMR spectra for both bamboo lignin and epoxidized bamboo lignin are presented in Figure S1. In the ^{31}P NMR spectrum of bamboo lignin, the signal peak of the internal standard substance is observed at 152 ppm, while the aliphatic hydroxyl group exhibits signal peaks between 146 and 147 ppm. The phenolic hydroxyl group is indicated by signal peaks in the range of 138–143 ppm, and the carboxyl group shows a signal peak between 134 and 135 ppm. The ^{31}P NMR spectrum of epoxidized bamboo lignin indicated the disappearance of phenolic hydroxyl and carboxyl groups, alongside an increase in aliphatic hydroxyl content. This suggests that phenolic hydroxyl and carboxyl groups were transformed into epoxy groups, which were subsequently converted to aliphatic hydroxyls through reactions with phosphorylated reagents. The quantitative ^{31}P NMR spectrum provides data on the functional group content in bamboo lignin, as detailed in Table 2. Table 2 indicates that the epoxy equivalents of epoxidized bamboo lignin amounted to approximately 350–400 g/mol, with epoxy values ranging from 0.25 to 0.28. Comparable epoxy values were also determined through titration.

Table 2. Content of hydroxyl and carboxyl groups in bamboo lignin.

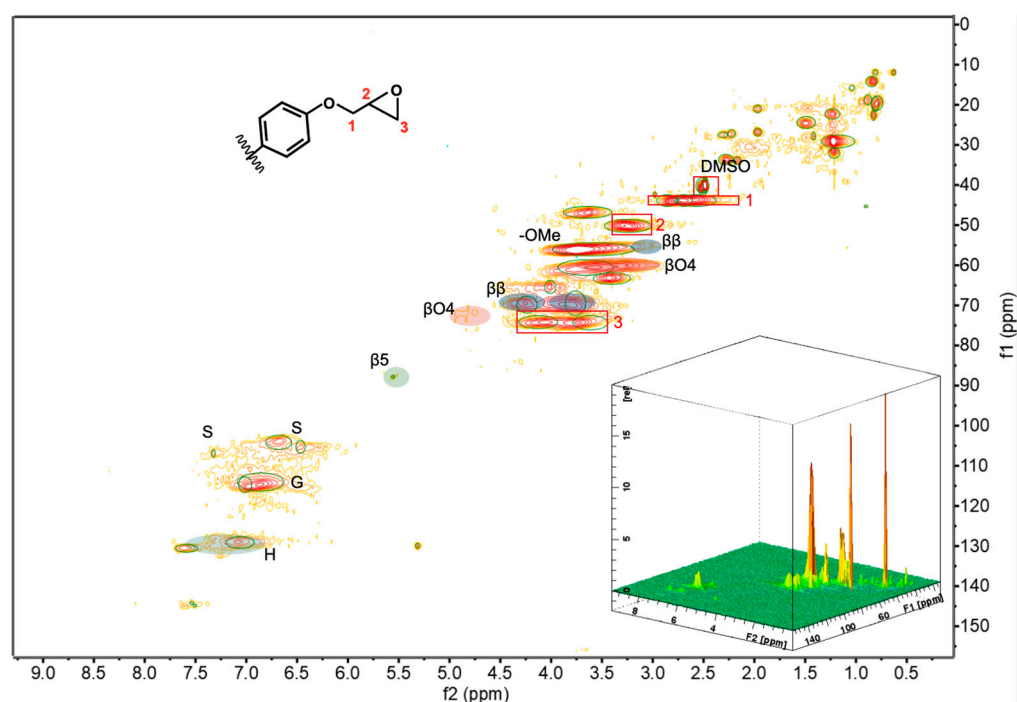
Sample	Hydroxyl Groups (mmol/g)		Carboxyl Groups (mmol/g)
	Aliphatic Hydroxyls	Phenolic Hydroxyls	
Bamboo lignin	2.01	2.89	0.31

The molecular weight distributions of bamboo lignin and epoxidized bamboo lignin, according to the GPC test, are shown in Figure S2, and their molecular weights are listed in Table 3. The weight-average molecular weight (Mw) of bamboo lignin was 4197 g/mol and the polydispersity index (PDI) was 3.68. The molecular weight distribution of bamboo lignin after epoxidation did not change significantly, and the number average molecular weight (Mn) of epoxidized bamboo lignin was 1231 g/mol, the weight-average molecular weight was 4853 g/mol, and the polydispersity index was 3.94.

Table 3. Molecular weights of bamboo lignin and epoxidized bamboo lignin.

Sample	Molecular Weight (g/mol)		PDI
	Mn	Mw	
Bamboo lignin	1138	4197	3.68
Epoxidized bamboo lignin	1231	4853	3.94

Two-dimensional NMR hydrogen spectroscopy (HSQC) revealed additional characteristics of the bamboo lignin's backbone structure, with the 2D NMR hydrogen spectrum of epoxidized bamboo lignin illustrated in Figure 4. Most signal areas in the figure correspond to the literature [23,24], where the side-chain region exhibits distinctive signals of epoxy groups at 2.68/44 ppm, 3.27/50 ppm, 3.73/74.17 ppm, and 4.06/74.17 ppm, respectively. The bond structure of bamboo lignin is illustrated in the side-chain region, encompassing aromatic ether β -O-4, aryl alkyl β -5 and β -1, and alkyl alkyl β - β linkage structures.

**Figure 4.** The 2D-HSQC spectrum of epoxidized bamboo lignin.

Furthermore, three structural units—guaiacyl (G), silymarinyl (S), and p-hydroxyphenyl (H)—are distinctly identifiable in the aryl ring region. Guaiacyl-related signals are found at 6.87/114 ppm and 6.98/115 ppm, silymarinyl-related signals at 6.68/104 ppm and 7.32/107 ppm, and p-hydroxyphenyl-related signals at 7.09/128 ppm, thereby further substantiating the structural characterization of bamboo lignin.

3.3. Thermal Stability Analysis of Bamboo Lignin

The thermal stability of bamboo lignin and bamboo lignin-based epoxy is shown in Figure 5. Bamboo lignin primarily comprises a benzene ring structure and does not exhibit melting, thereby demonstrating excellent thermal stability. Bamboo lignin degrades at temperatures over 200 °C, experiences accelerated breakdown between 300 and 400 °C, and retains around 45% char at 600 °C. The thermal weight curve resembles the weight loss curve of bamboo lignin post-epoxidation, exhibiting comparable thermal stability. The thermogravimetric curve of epoxidized bamboo lignin resembled that of untreated bamboo lignin, exhibiting comparable thermal stability characteristics. The thermal stability of the bamboo lignin-based epoxy exceeded that of bamboo lignin during the initial degradation phase, with a decomposition temperature increase of 14 °C at a 10% weight loss rate, and it also surpassed bamboo lignin in terms of the maximum weight loss rate. Nevertheless, the residual char yield at 600 °C was decreased for the bamboo lignin-based epoxy compared to bamboo lignin. The difference in the thermal stability of epoxidized lignin primarily arises from the incorporation of the epoxy ring, resulting in an initial enhancement in thermal stability during the early and intermediate phases of thermal decomposition [26,27]. However, as the decomposition escalates at elevated temperatures, the bamboo lignin-based epoxy, characterized by an increased number of side chains, exhibits a reduction in the final residual char yield. Despite a modest reduction in the residual char rate of the bamboo lignin-based epoxy, its overall thermal stability remains favorable.

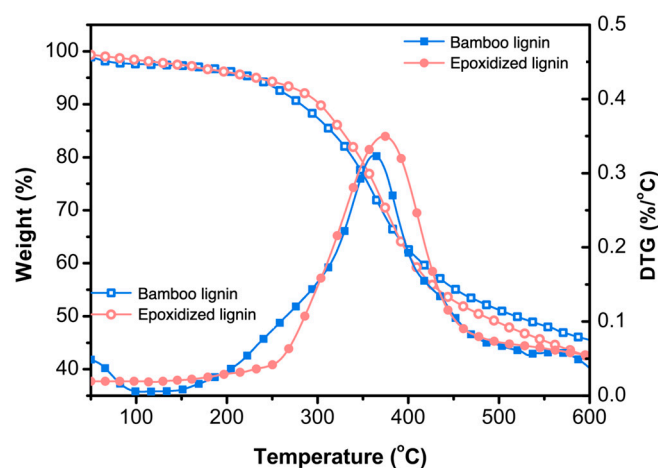


Figure 5. Thermal stability of bamboo and epoxy lignin.

3.4. Curing Kinetics of Bamboo Lignin-Based Epoxy

Epoxy resin monomers primarily interact with curing agents to produce thermosetting resins characterized by three-dimensional crosslinked networks. Therefore, the applicability of bamboo lignin-based epoxy as an epoxy resin is largely contingent upon the curing properties of the epoxidized lignin. This study selected six commonly used curing agents—maleic anhydride (MA), methylhexahydrophthalic anhydride (MeHHPA), the aromatic amine curing agent diaminodiphenylmethane (DDM), and aliphatic amine curing agents with varying molecular weights of polyether amines, namely PEA-230 (230), PEA-400 (400), and PEA-2000 (2000)—to investigate the epoxidized lignin. Figure 6 illustrates

the relationship between the curing degree and temperature for the six curing agents interacting with the epoxidized lignin. All curing agents could facilitate crosslinking reactions with the bamboo lignin-based epoxy, exhibiting varying curing behavior at different rates of temperature increase and with distinct curing agents. The curing temperature of epoxidized lignin increased with a higher rate of temperature elevation. The curing temperatures, at a rate of temperature increase of 10 °C/min and a curing degree of 0.5, were ranked as follows: MeHHPA exhibited the highest curing temperature, followed by PEA-2000, MA, PEA-400, DDM, and PEA-230, which had the lowest curing temperatures.

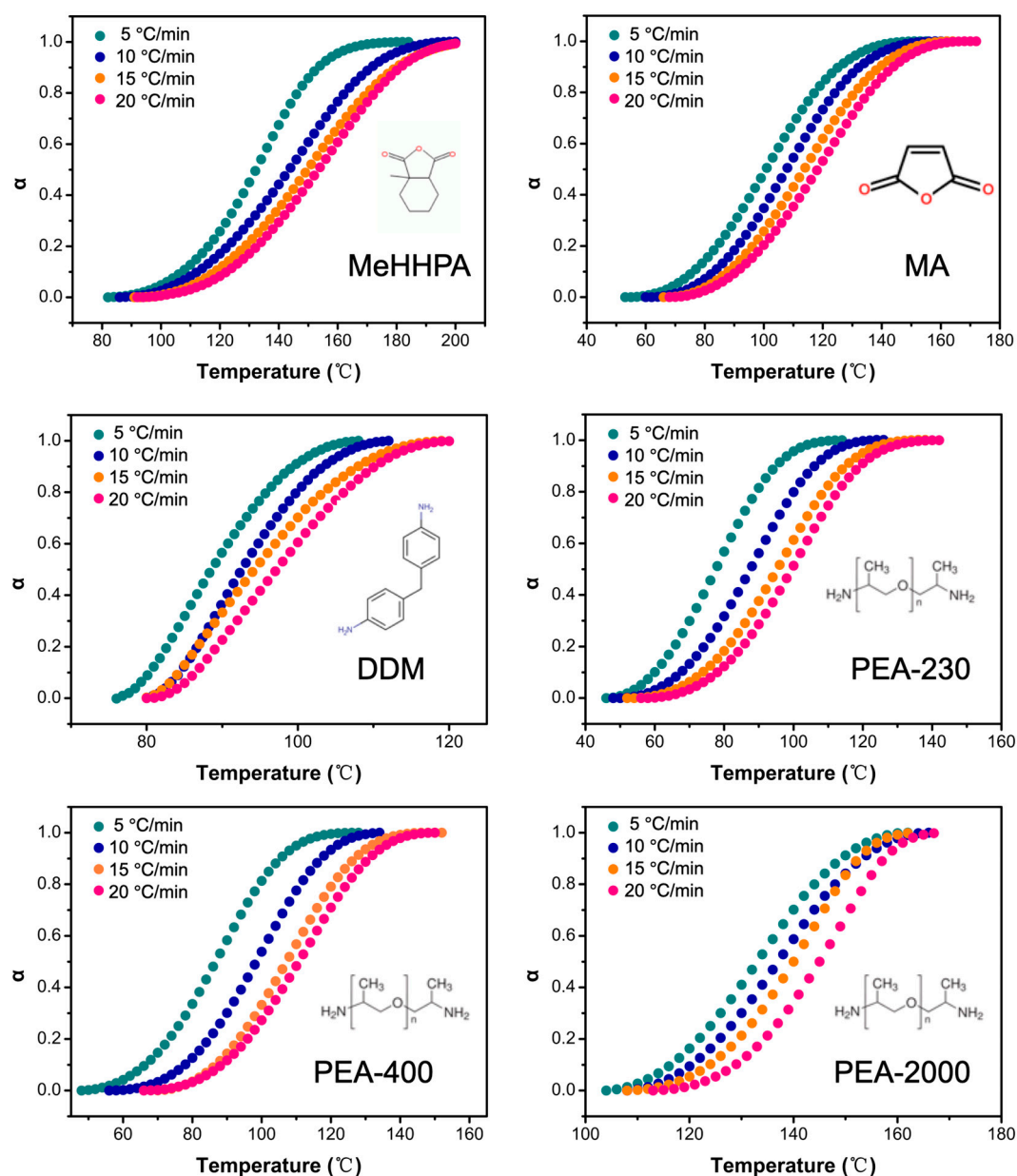


Figure 6. Relationship between epoxy of bamboo lignin, reaction curing degree, and temperature with different curing agents.

The Kissinger and Ozawa methods are frequently employed to assess the curing kinetic parameter known as the apparent activation energy (E_a), which is a critical energy parameter that dictates the feasibility of the curing reaction and is essential in comprehending the curing process [28–30]. According to Kissinger Equations (S1) and (S2) (all equations refer to the Supplementary Materials), as displayed in Figure 7a, the Kissinger

model can be simplified to Equation (S3), as $\ln(\beta/T^2)$ has a linear relationship with $1/T$ (Figure 7a), where the slope is $-E_a/R$. The E_a for the curing reaction can also be obtained using the Ozawa model (Equations (S4) and (S5)). Since $\ln\beta$ and $1/T$ can be fitted to a straight line, as shown in Figure 7b, with a slope of $-1.052 E_a/R$, the Ozawa equation can also be expressed as Equation (S6).

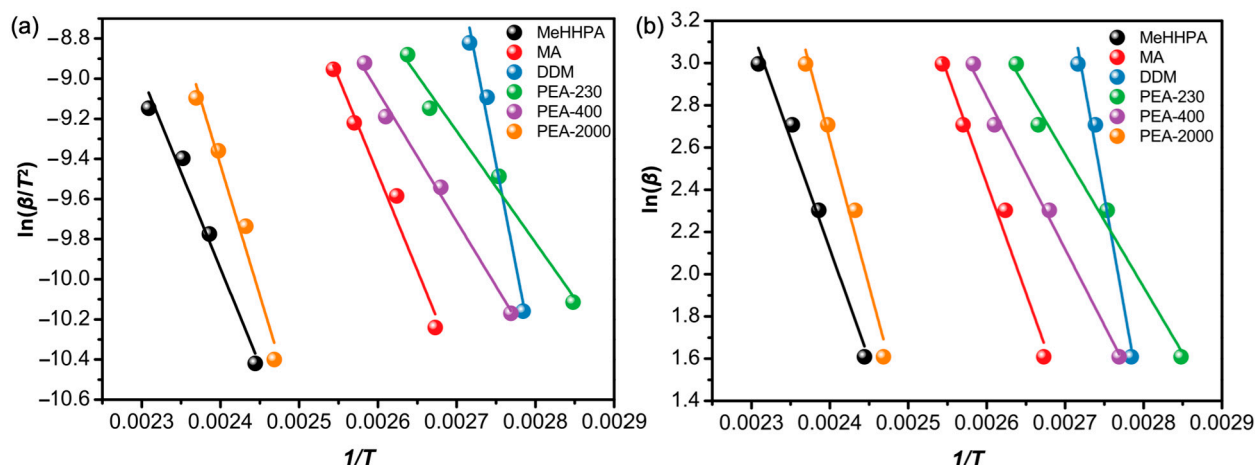


Figure 7. Linear fitting of Kissinger (a) and Ozawa (b) methods.

Figure 8 illustrates the apparent activation energies (E_a) for the reaction of the bamboo lignin-based epoxy with the six curing agents, as determined by the Kissinger and Ozawa methods. The Kissinger method is often used to describe n th-order reactions and is more sensitive to complex reaction mechanisms. The Ozawa method, in contrast, is mechanism-independent and is appropriate for characterizing autocatalytic reactions. Due to the ambiguity of the reaction mechanism in this investigation, both methodologies were employed for assessment. The activation energy (E_a) determined by the Ozawa approach differs from that derived via the Kissinger method; nonetheless, the values from both methodologies exhibit a consistent trend. The anhydride curing agents MeHHPA and MA exhibited comparable apparent activation energies, with E_a values of approximately 90 kJ/mol. The aromatic amine curing agent DDM exhibited the highest apparent activation energy, recorded at an E_a value of 167.5 kJ/mol. The observed activation energies of the fatty amine curing agents consisting of PEA show an increase corresponding to the molecular weight of the PEA. Specifically, PEA-230 exhibits the lowest apparent activation energy at 46.2 kJ/mol, while PEA-2000 presents the highest at 107.8 kJ/mol. The apparent activation energy associated with the curing reaction typically reflects the complexity of the process. A lower apparent activation energy suggests that the reaction is more straightforward to execute, while a higher value indicates a more challenging curing reaction [5,20,28]. Consequently, the polyether amine PEA-230 demonstrated significant reactivity with epoxidized lignin.

The curing reaction kinetics model could use a simplified rate equation (Equation (S7)) combined with the Arrhenius equations (Equations (S8)–(S10)) to formulate a novel curing kinetics equation (Equation (S11)) [21,28]. The reaction order n can ultimately be established using the Crane equation (Equation (S12)) [29]. The diverse curing kinetic parameters and kinetics are enumerated in Table 4. The table indicates that the reaction sequence of bamboo lignin-based epoxy resin with the six curing agents is of the first order. The curing rate of bamboo lignin-based epoxy resin is essentially contingent upon its epoxy equivalent, and its curing mechanism is very straightforward, facilitating a cost-effective and quick curing procedure.

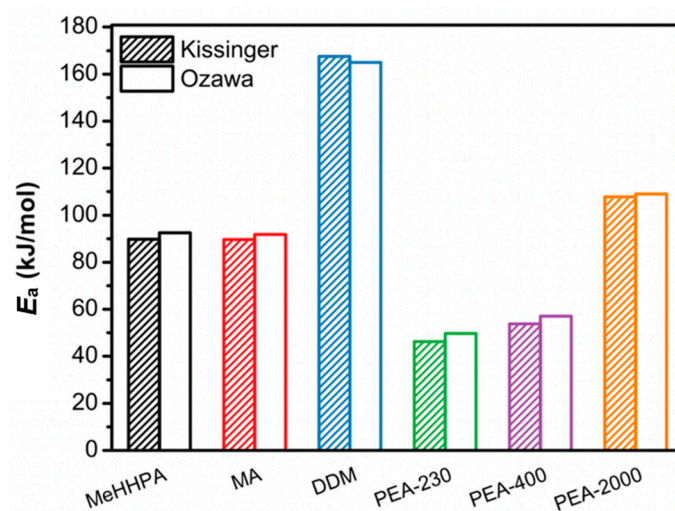


Figure 8. Activation energy of epoxidation bamboo lignin with different curing agents.

Table 4. Kinetic models of the curing reactions of epoxy composites.

Curing System	A	n	Dynamic Model
MeHHPA	4.83×10^9	0.99	$\frac{d\alpha}{dt} = 4.83 \times 10^9 (1 - \alpha)^{0.99} \exp\left(\frac{-89.8}{RT}\right)$
MA	5.59×10^{10}	0.99	$\frac{d\alpha}{dt} = 5.59 \times 10^{10} (1 - \alpha)^{0.99} \exp\left(\frac{-89.7}{RT}\right)$
DDM	1.92×10^{24}	0.99	$\frac{d\alpha}{dt} = 1.92 \times 10^{24} (1 - \alpha)^{0.99} \exp\left(\frac{-167.5}{RT}\right)$
PEA-230	1.89×10^6	0.99	$\frac{d\alpha}{dt} = 1.89 \times 10^6 (1 - \alpha)^{0.99} \exp\left(\frac{-46.2}{RT}\right)$
PEA-400	1.58×10^7	0.99	$\frac{d\alpha}{dt} = 1.58 \times 10^7 (1 - \alpha)^{0.99} \exp\left(\frac{-53.8}{RT}\right)$
PEA-2000	3.83×10^{13}	0.99	$\frac{d\alpha}{dt} = 3.83 \times 10^{13} (1 - \alpha)^{0.99} \exp\left(\frac{-107.7}{RT}\right)$

3.5. Mechanical Properties of Bamboo Lignin-Based Epoxy Curing Products

The excellent mechanical qualities of epoxy resins contribute significantly to their extensive utilization; hence, the physico-mechanical properties of epoxidized lignin cured with six distinct curing agents were assessed, and their tensile properties are illustrated in Figure 9. MeHHPA, MA, and DDM have comparable tensile strength and elongation at break, both of which are relatively low, indicating a lack of application potential. Polyether amine curing agents enhance the physical and mechanical properties of epoxidized lignin, with PEA-230 exhibiting superior tensile properties, achieving tensile strength exceeding 25 MPa. As the molecular weight of the polyether amine increases, the tensile strength of the cured product diminishes, while the elongation at break correspondingly increases. PEA-2000 can achieve an elongation at break of 15% or more, demonstrating commendable toughness [26].

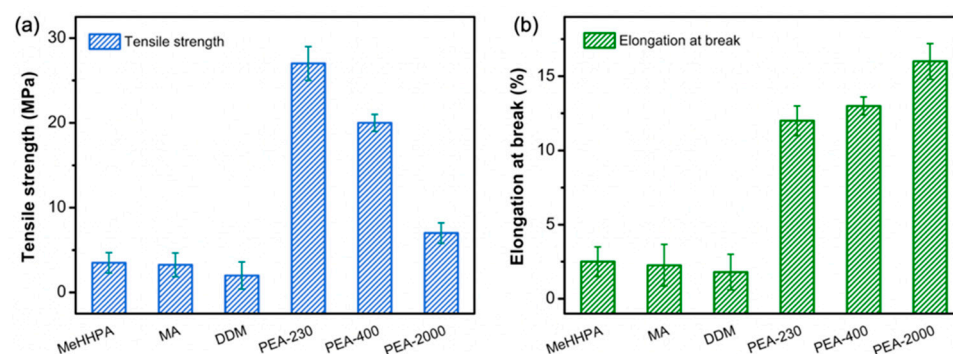


Figure 9. Tensile strength (a) and elongation at break (b) of epoxidation bamboo lignin cured products.

3.6. Thermal Stability of Bamboo Lignin-Based Epoxy Curing Products

The thermal stability of cured products derived from epoxidized lignin with various curing agents is illustrated in Figure 10. The cured products utilizing two anhydride curing agents exhibited poor thermal stability during the initial and intermediate stages. In contrast, the cured products with DDM demonstrated no significant deterioration in thermal stability during these stages and maintained a high residual char yield. Additionally, the cured products from polyether amines of varying molecular weights displayed distinct thermal stability. The thermal stability of PEA-230 and PEA-400 remained consistent during the initial and intermediate stages of thermal decomposition. In contrast, PEA-2000 exhibited a notable enhancement in thermal stability, achieving the highest temperature for the maximum thermal decomposition rate, albeit with a lower residual carbon rate. As the length of the polyether amine molecular chain increases, the degree of curing increases, resulting in the enhanced stability of the entire system and a reduced likelihood of decomposition [21]. Commercial bisphenol A epoxy resins generally have a maximum thermal degradation temperature of 400–420 °C, with residual char content of around 10% [26]. Under PEA-2000 curing, the peak thermal breakdown temperature of bamboo lignin-based epoxy resins approximates that of commercial epoxy resins; nevertheless, the residual char content is markedly greater than that of commercial epoxy resins. This is mainly due to lignin being a natural polymer present in plant cell walls, characterized by a substantial quantity of aromatic rings in its structure. These aromatic rings have significant chemical stability owing to their conjugated π electron systems. Aromatic rings are unlikely to fully volatilize during high-temperature decomposition; instead, they typically reorganize into stable carbon-based structures [1].

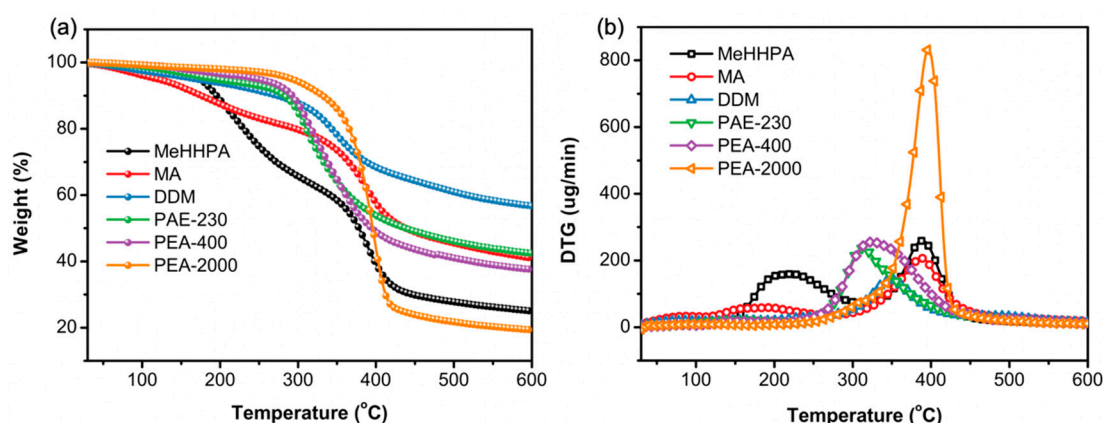


Figure 10. TG (a) and DTG (b) curves of the cured products of epoxidized bamboo lignin.

3.7. Potential Curing Mechanism of Bamboo Lignin-Based Epoxy Resin

This study indicates that bamboo lignin-based epoxy can interact with curing agents to regenerate a three-dimensional network structure, suggesting its potential as a bio-based epoxy resin. Bamboo lignin exhibits structural differences compared to conventional epoxy resin prepolymer monomers, resulting in variations in curing behavior and overall performance. The prevalent commercial bisphenol A-type epoxy resin prepolymer features a straight chain structure, with epoxy groups at both ends of the molecular chain. These groups can react with polyacids or polyamines, thereby extending the epoxy molecular chain. This curing reaction enhances both the length of the molecular chain and the degree of crosslinking between chains, ultimately resulting in the formation of an insoluble and non-fusible three-dimensional structure (Figure 11). The curing reaction of bisphenol A-type epoxy resin occurs through three stages: chain initiation, chain growth, and chain termination. The reaction progresses from a flow state to a gel state, ultimately transitioning

to a glassy state, resulting in the formation of a complete curing network [4,6]. The structure of bamboo lignin is marked by complexity, disorder, polydispersity, and high crosslinking density, which prevents it from undergoing the curing process typical of bisphenol A-type epoxy resin. The structure of lignin is complex and disordered, lacking a definitive chemical formula. It features a highly crosslinked three-dimensional architecture, with a disordered distribution of functional groups. Additionally, the presence of spatial resistance further complicates its reaction with curing agents. Bamboo lignin lacks a melting point, and its glassy effect on thermosetting resin curing is significant. Once the material enters the glassy region, it severely hinders the polymerization kinetics. Consequently, the immobility of lignin substantially decreases the migration rate of the entire curing system, thereby impeding the overall curing process [4]. The curing of bamboo lignin epoxy resin is characterized not by the gradual polymerization of small molecules into macromolecules but by the reconnection of lignin fragments through epoxy groups [9]. An analysis of the curing kinetics, physico-mechanical properties, and thermal stability revealed that, while conventional curing agents can interact with the epoxy groups in bamboo lignin-based epoxy resins, the resulting curing behaviors and material properties differ significantly. Notably, only polyether amine curing agents exhibited favorable curing behaviors and properties. This can be attributed to the structural characteristics of bamboo lignin-based epoxy resins, which provide flexibility due to their mobility and long molecular chains. The structural characteristics of bamboo lignin-based epoxy resins contribute to their enhanced affinity for medium- and low-temperature curing agents, which possess a degree of fluidity and flexibility in their long molecular chains.

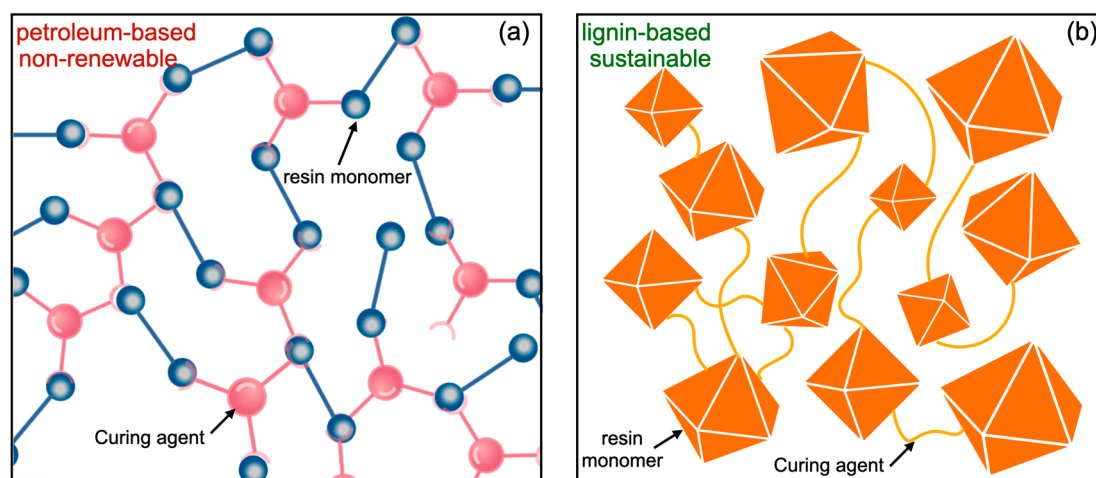


Figure 11. Curing network diagram of bisphenol A epoxy (a) and lignin-based epoxy (b).

4. Conclusions

This research effectively transformed bamboo lignin into a bio-based epoxy resin via a straightforward one-step epoxidation process that eliminates the need for highly hazardous benzene-based solvents or extreme temperature and pressure conditions. Thorough characterization validated the effective synthesis of epoxidized bamboo lignin, which possesses an epoxy equivalent value that is appropriate for thermosetting applications. Significantly, the curing kinetics analysis demonstrated that EBL cured with polyether amine PEA-230 displayed the lowest apparent activation energy (46.2 kJ/mol) among all evaluated curing agents, suggesting considerable potential for energy conservation in industrial processing—an essential benefit for sustainable manufacturing. The network treated with PEA-230 attained the highest tensile strength (>25 MPa), exhibiting competitive mechanical capabilities, whereas high-molecular-weight polyether amines offered

enhanced elongation. The distinctive curing characteristics resulting from lignin's inflexible structure underscore the optimal compatibility of lignin-based epoxy resins with pliable, low-temperature curing agents such as PEA-230. This study presents persuasive evidence for the transformation of lignin waste into a renewable bio-based epoxy resin substitute. This technique directly tackles significant environmental issues, such as decreasing the dependence on fossil resources, reducing the utilization of hazardous compounds, augmenting the value of industrial waste, and diminishing the carbon footprint linked to resin production and processing. This also signifies a crucial advancement in the development of sustainable thermosetting materials and the promotion of circular bioeconomy concepts.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/su17136201/s1>, Figure S1: Epoxidized bamboo lignin ³¹P NMR; Figure S2: The GPC of bamboo lignin (a) and epoxidized bamboo lignin (b); Figure S3: One-dimensional spectra and the 2D spectra spectrum of epoxidized bamboo lignin.

Author Contributions: J.Y.: writing—original draft preparation, data curation, methodology, formal analysis, project administration, funding acquisition. J.F.: conceptualization, writing—review and editing. X.W.: writing—review, formal analysis. All authors have read and agreed to the published version of the manuscript.

Funding: “Pioneer” and “Leading Goose” R&D Program of Zhejiang (2022C02023).

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Data are contained within the article and Supplementary Materials.

Conflicts of Interest: The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

References

1. Fache, M.; Boutevin, B.; Caillol, S. Epoxy thermosets from model mixtures of the lignin-to-vanillin process. *Green Chem.* **2016**, *18*, 712–725. [CrossRef]
2. Anidha, S.; Latha, N.; Muthukumar, M. Effect of polyaramid reinforced with sisal epoxy composites: Tensile, impact, flexural and morphological properties. *J. Mater. Res. Technol.* **2020**, *9*, 7947–7954. [CrossRef]
3. El-Gawad, W.M.A.; Zaher, K.S.A.; Nawwar, G.A.M. Exploring the utilities of rice straw black liquor (part XI): Enhancing the UV resistance, color, antimicrobial, and mechanical characteristics of epoxy coatings using lignin-based hybrid nano-pigments. *Prog. Org. Coat.* **2024**, *197*, 108866. [CrossRef]
4. Vidil, T.; Tournilhac, F.; Musso, S.; Robisson, A.; Leibler, L. Control of reactions and network structures of epoxy thermosets. *Prog. Polym. Sci.* **2016**, *62*, 126–179. [CrossRef]
5. Zou, T.; Sipponen, M.H.; Henn, A.; Osterberg, M. Solvent-resistant lignin-epoxy hybrid nanoparticles for covalent surface modification and high-strength particulate adhesives. *ACS Nano* **2021**, *15*, 4811–4823. [CrossRef] [PubMed]
6. Zhao, L.; Mao, Z.; Xu, H.; Wang, B.; Zhong, Y.; Ji, B.; Feng, X. Preparation of epoxy resin adhesives based on high phenolic nanomodified lignin particles. *Int. J. Biol. Macromol.* **2025**, *309*, 142886. [CrossRef]
7. Zhang, S.; Zheng, J.; Zheng, S.; Song, M. Phenolic Hydroxyl-Activated Lignin for Preparation of Extreme Environments Adaptive Adhesives. *J. Appl. Polym. Sci.* **2025**, *142*, 56728. [CrossRef]
8. Vasquez-Garay, F.; Carrillo-Varela, I.; Vidal, C.; Reyes-Contreras, P.; Faccini, M.; Teixeira Mendonca, R. A Review on the Lignin Biopolymer and Its Integration in the Elaboration of Sustainable Materials. *Sustainability* **2021**, *13*, 2697. [CrossRef]
9. Song, X.; Lv, H.-B.; Jiang, Z.; Zhao, B.; Hu, W.; Zhang, K.; Shao, Z.-B. Sustainable lignin-based high-efficiency flame-retardant epoxy resins with excellent mechanical properties. *Int. J. Biol. Macromol.* **2024**, *282*, 136742. [CrossRef]
10. Kaur, R.; Thakur, N.S.; Chandna, S.; Bhaumik, J. Sustainable Lignin-Based Coatings Doped with Titanium Dioxide Nanocomposites Exhibit Synergistic Microbicidal and UV-Blocking Performance toward Personal Protective Equipment. *ACS Sustain. Chem. Eng.* **2021**, *9*, 11223–11237. [CrossRef]
11. Goliszek, M.; Podkosić, B.; Rybinski, P.; Kłapiszewska, I.; Klepka, T.; Masek, A.; Kłapiszewski, L. Toward a green economy: Lignin-based hybrid materials as functional additives in flame-retardant polymer coatings. *J. Polym. Res.* **2024**, *31*, 316. [CrossRef]

12. Costa, D.d.S.; de Novais, L.M.R.; D'Oca, C.D.R.M.; Marques, J.F.; Ferreira, C.A.; Mazzetto, S.E.; Lomonaco, D.; Avelino, F. Towards phosphorylated lignin-based epoxy resins: An integrated technological route to obtain a macromonomer with enhanced thermal and potential flame-retardant properties. *Int. J. Biol. Macromol.* **2025**, *304*, 140821. [\[CrossRef\]](#)
13. Karunarathna, M.S.; Smith, R.C. Valorization of Lignin as a Sustainable Component of Structural Materials and Composites: Advances from 2011 to 2019. *Sustainability* **2020**, *12*, 734. [\[CrossRef\]](#)
14. Rajagopalan, N.; Winberg, I.; Fearon, O.; Cardellini, G.; Liitia, T.; Kalliola, A. Environmental Performance of Oxidized Kraft Lignin-Based Products. *Sustainability* **2022**, *14*, 10897. [\[CrossRef\]](#)
15. Adamczyk, J.; Beisl, S.; Friedl, A. High Temperature Lignin Separation for Improved Yields in Ethanol Organosolv Pre-Treatment. *Sustainability* **2023**, *15*, 3006. [\[CrossRef\]](#)
16. Chen, H.; Wang, A.; Yan, C.; Liu, S.; Li, L.; Wu, Q.; Liu, Y.; Nie, G.; Nie, S.; et al. Study on the Solubility of Industrial Lignin in Choline Chloride-Based Deep Eutectic Solvents. *Sustainability* **2023**, *15*, 7118. [\[CrossRef\]](#)
17. Ferdosian, F.; Yuan, Z.; Anderson, M.; Xu, C.C. Sustainable lignin-based epoxy resins cured with aromatic and aliphatic amine curing agents: Curing kinetics and thermal properties. *Thermochim. Acta* **2015**, *618*, 48–55. [\[CrossRef\]](#)
18. Gouveia, J.R.; Garcia, G.E.; Antonino, L.D.; Tavares, L.B.; Dos Santos, D.J. Epoxidation of kraft lignin as a tool for improving the mechanical properties of epoxy adhesive. *Molecules* **2020**, *25*, 2513. [\[CrossRef\]](#)
19. Guo, X.; Xin, J.; Huang, J.; Wolcott, M.P.; Zhang, J. Preparation and toughening of mechanochemically modified lignin-based epoxy. *Polymer* **2019**, *183*, 121859. [\[CrossRef\]](#)
20. Kong, X.; Xu, Z.; Guan, L.; Di, M. Study on polyblending epoxy resin adhesive with lignin I-curing temperature. *Int. J. Adhes. Adhes.* **2014**, *48*, 75–79. [\[CrossRef\]](#)
21. Yang, J.Y.; He, X.W.; Wang, H.X.; Liu, X.H.; Lin, P.; Yang, S.X.; Fu, S.Y. High-toughness, environment-friendly solid epoxy resins: Preparation, mechanical performance, curing behavior, and thermal properties. *J. Appl. Polym. Sci.* **2020**, *137*, 48596. [\[CrossRef\]](#)
22. Wu, Z.; Prakash, B.; Shi, Y. Synthesizing lignin-based gelators to prepare oleogels used as green and fossil-free greases. *Int. J. Biol. Macromol.* **2025**, *305*, 141074. [\[CrossRef\]](#) [\[PubMed\]](#)
23. Zhen, X.; Li, H.; Xu, Z.; Wang, Q.; Zhu, S.; Wang, Z.; Yuan, Z. Facile synthesis of lignin-based epoxy resins with excellent thermal-mechanical performance. *Int. J. Biol. Macromol.* **2021**, *182*, 276–285. [\[CrossRef\]](#)
24. Gioia, C.; Lo Re, G.; Lawoko, M.; Berglund, L. Tunable thermosetting epoxies based on fractionated and well-characterized lignins. *J. Am. Chem. Soc.* **2018**, *140*, 4054–4061. [\[CrossRef\]](#)
25. Gioia, C.; Colonna, M.; Tagami, A.; Medina, L.; Sevastyanova, O.; Berglund, L.A.; Lawoko, M. Lignin-Based Epoxy Resins: Unravelling the Relationship between Structure and Material Properties. *Biomacromolecules* **2020**, *21*, 1920–1928. [\[CrossRef\]](#)
26. Yang, J.; Wang, H.; Liu, X.; Fu, S.; Song, P. A nano-TiO₂/regenerated cellulose biohybrid enables simultaneously improved strength and toughness of solid epoxy resins. *Compos. Sci. Technol.* **2021**, *212*, 108884. [\[CrossRef\]](#)
27. Feghali, E.; van de Pas, D.J.; Parrott, A.J.; Torr, K.M. Biobased epoxy thermoset polymers from depolymerized native hardwood lignin. *ACS Macro Lett.* **2020**, *9*, 1155–1160. [\[CrossRef\]](#)
28. Thanki, J.D.; Parsania, P.H. Dynamic DSC curing kinetics and thermogravimetric study of epoxy resin of 9,9'-bis(4-hydroxyphenyl)anthrone-10. *J. Therm. Anal. Calorim.* **2017**, *130*, 2145–2156. [\[CrossRef\]](#)
29. Zhang, Z.; Li, J.; Zhang, Y.; Jin, Z. Kinetics of partially depolymerized lignin as co-curing agent for epoxy resin. *Int. J. Biol. Macromol.* **2020**, *150*, 786–792. [\[CrossRef\]](#)
30. Ferdosian, F.; Zhang, Y.; Yuan, Z.; Anderson, M.; Xu, C.C. Curing kinetics and mechanical properties of bio-based epoxy composites comprising lignin-based epoxy resins. *Eur. Polym. J.* **2016**, *82*, 153–165. [\[CrossRef\]](#)

Disclaimer/Publisher's Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.