

Article

Bio-Epoxy Composites Formulation Using Bio-Oils from Walnut and Almond Shell Pyrolysis: Influence of Temperature on Chemical Composition and Curing Behavior

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Abstract

In this study, we develop bio-epoxy composites incorporating bio-oils obtained from the pyrolysis of almond and walnut shells at 400 °C and 600 °C, with the aim of evaluating their potential as renewable precursors for epoxy resin modification. The influence of pyrolysis temperature on bio-oil yield and chemical composition is examined to identify phenolic-rich fractions relevant to epoxy curing. Bio-oil production increased with temperature, reaching 40.46% for walnut shells and 36.84% for almond shells at 600 °C. Chemical analysis revealed that aromatic compounds, particularly phenolics, were the major constituents associated with epoxy curing reactivity. For walnut hulls, the total aromatic fraction increased from 30.4% at 400 °C to 35.2% at 600 °C, while almond hulls showed an increase from 23.8% to 26.1% over the same temperature range. Incorporation of bio-oil into the epoxy matrix promoted three-dimensional network formation through reactions between epoxy groups and the functional moieties present in the bio-oil, resulting in a higher cross-linking degree, Young's modulus, and tensile strength. However, compared to neat epoxy, the bio-oil-modified systems exhibited reduced storage modulus (E') and glass transition temperature (T_g), attributed to the plasticizing effect of lighter oxygenated species. Overall, although bio-oil incorporation decreases T_g and cross-linking degree, it still provides a viable pathway toward partially bio-based epoxy resins with enhanced stiffness and competitive mechanical performance.

Keywords: bio-oil; pyrolysis; phenolic compounds; epoxy resin; bio-based thermosets; almond shells; walnut shells



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1. Introduction

Epoxy resins are polymeric materials with a range of valuable properties, highlighted by their excellent chemical and thermal resistance and high adhesiveness. These attributes link epoxy resins to diverse industrial sectors such as aerospace, construction, and automotive. However, as epoxy is a highly polluting material of petrochemical origin, it is proposed that polymers of natural origin with similar properties be developed. For example, lignin, an abundant aromatic biopolymer derived from plant biomass, is a promising candidate for

partial replacement of petrochemical epoxy components due to its rigid polyphenolic structure and wide availability as an industrial by-product. Incorporating such natural polymers could maintain mechanical strength and thermal stability comparable to commercial resins while improving sustainability.

Epoxy resins are amorphous, highly cross-linked polymers, and this structure results in these materials possessing various desirable properties, such as greater tensile strength and modulus, uncomplicated processing, fine thermal and chemical resistance, and dimensional stability [1]. However, higher costs and brittleness limit its application in industry [2]. Wood pyrolysis bio-oils have been used as additives, either physically blended with epoxy or reacted to form epoxy resins, to enhance properties. The results indicate that the hydroxyl groups in the bio-oil react with the epoxide groups, creating a cross-linked copolymer network and thereby altering the resin's properties.

Additionally, previous research has investigated chemically modified lignin (such as carboxymethylated lignin) as a renewable component in epoxy systems. Such modifications introduce reactive carboxyl and hydroxyl functionalities into lignin, allowing it to act as a co-curing agent that reinforces and toughens the epoxy network. Incorporating carboxylated lignin in epoxy formulations has been shown to enhance mechanical performance (e.g., increasing tensile and flexural strength) by leveraging lignin's rigid, highly branched aromatic structure. However, these strategies require additional chemical processing of lignin prior to use. In contrast, our approach directly utilizes lignin-derived phenolic compounds present in biomass pyrolysis bio-oil as epoxy modifiers, avoiding separate functionalization steps. This represents a novel pathway relative to existing literature by which agricultural waste biomass is thermochemically converted into a bio-oil rich in functional groups that can in situ participate in epoxy curing.

Pyrolysis bio-oils (liquid fractions) are produced from biomass pyrolysis conducted under anoxic (nonoxidizing) conditions at high temperatures (typically around 500 °C). Pyrolysis is the thermal decomposition of organic material, converting it into energy-dense products and chemical feedstocks. The process yields bio-oil, biochar, and non-condensable gas [3–7]. Bio-oil is a dark brown liquid containing alcohols, phenols, organic acids, and carbonyls as its principal organic compounds [8]. Bio-oil obtained from biomass pyrolysis can potentially be employed as a liquid fuel or as a source of biobased chemicals [9]. However, integrating raw bio-oil into existing fossil fuel infrastructure is hampered by its complex composition and poor properties, mainly due to high oxygen content [10]. Bio-oil has a slightly lower fuel value than diesel and other light fuel oils but a somewhat higher value than other oxygenated fuels like methanol and ethanol [11]. Thus, its use in chemical applications has great potential, for example, as an additive in polymer systems.

The pyrolysis of lignocellulosic biomass has become a valuable strategy for obtaining polymer precursors, thereby expanding biomass valorization opportunities. The influence of temperature on bio-oil yield has been widely analyzed, and for lignocellulosic biomass, the optimal pyrolysis temperature range is generally 400–600 °C [12–15]. However, few studies have examined how variations in bio-oil chemical composition at different pyrolysis temperatures affect the properties of structural polymers such as epoxy resin composites. Over the past decade, almond and walnut cultivation has increased significantly, driven by consumer demand for nutritious foods. The nuts are widely consumed for their health benefits, as they are rich in antioxidants, flavonoids, phenolic compounds, and fiber, which help prevent aging and support cardiovascular health. Chile has become a major producer and exporter of these nuts, with high yields due to abundant rainfall and favorable temperatures. This growth, however, has led to a surge in hull waste, which is typically discarded without valorization. Almond and walnut hulls are biodegradable agro-industrial by-products primarily composed of cellulose, hemicellulose, and lignin. These compo-

nents, removed during nut processing, account for 40–65% of the fruit's weight. These by-products can serve as sustainable, environmentally friendly, and low-cost alternatives for developing new biocomposites [16,17].

This manuscript investigates how pyrolysis temperature influences the yield and chemical composition of bio-oils derived from almond and walnut shells and evaluates their suitability as reactive precursors for the formulation of bio-based epoxy composites. The resulting bio-oils were incorporated into a petrochemical epoxy resin to produce cross-linked copolymer networks, whose cross-linking degree and thermal and mechanical properties were analyzed. Overall, this work provides an alternative valorization route for almond and walnut shells via pyrolysis and offers new insights into how the chemical composition of pyrolytic products affects the curing behavior and final performance of bio-based epoxy materials.

2. Materials and Methods

Almond and walnut hulls, residual biomass generated in southern Chile, were used for the production of bio-oil. The epoxy resin, bisphenol A diglycidyl ether (DGEBA, molecular weight 340.41 g/mol, CAS No. 1675-54-3), and tetraethylene pentamine (TEPA, molecular weight 189.3 g/mol, CAS No. 112-57-2) used as a curing agent were purchased from Sigma-Aldrich (Santiago, Chile). The solvents used in the treatment of bio-oil, chloroform (CHCl_3 , molecular weight 119.38 g/mol, CAS No. 67-66-3), ethyl acetate ($\text{C}_4\text{H}_8\text{O}_2$, molecular weight 88.11 g/mol, CAS No. 141-78-6), and hexane (C_6H_{14} , molecular weight 86.18 g/mol, CAS No. 110-54-3), were of analytical grade (Merck, Darmstadt, Germany).

2.1. Experimental Setup and Procedure

2.1.1. Pyrolysis of Biomass

The almond hull (AH) and walnut hull (WH) biomass feedstocks were ground and sieved to $<250\ \mu\text{m}$ particle size prior to pyrolysis. Slow pyrolysis was carried out in a fixed-bed cylindrical reactor (15 cm length $\times$ 1.5 cm diameter) under an inert nitrogen atmosphere. For each run, 10 g of biomass was pyrolyzed at either 400 °C or 600 °C, with a residence time of $\sim 3\ \text{h}$ at the target temperature to ensure complete conversion. The temperatures of 400 °C and 600 °C were selected based on literature showing strong temperature-dependent shifts in bio-oil yield and composition, with higher temperatures promoting secondary cracking and changes in oxygenated versus aromatic fractions [3,6,12–15]. Two temperatures were used to keep the experimental matrix tractable while providing a clear compositional contrast for subsequent epoxy modification. All pyrolysis tests were performed in triplicate. The heating rate was 10 °C/min, and nitrogen was flowed at 60 mL/min to maintain an oxygen-free environment. After pyrolysis, the condensable fraction (bio-oil) was collected and filtered through a paper filter with 11 μm pore size to remove char particles.

2.1.2. Preparation of Bio-Based Epoxy Blends

The bio-oil was mixed with DGEBA epoxy resin at weight ratios of 1:4 and 1:5 (bio-oil:DGEBA, w/w) to form bio-based epoxy blends (BEBs), as shown in Table 1. An acetone pretreatment was applied to all BEB samples following the method of Liu et al. (2017) as a conditioning step to partially remove volatile components of the bio-oil [18]. These fractions are not chemically stabilizing and may act as diluents and plasticizers if unreacted. The mass fraction removed during acetone pretreatment was not quantified; thus, the acetone step is reported as a conditioning procedure. In a glass flask with magnetic stirring and a reflux condenser, each BEB sample (10 g) was combined with acetone (10 g). The mixture was heated to 50 °C for 30 min, then to 85 °C for 2 h. Acetone was removed using a rotary vacuum evaporator at 60 °C, followed by additional drying in a convection oven

at 50 °C for 12 h to minimize residual acetone prior to curing. Subsequently, TEPA curing agent was added to the pretreated BEBs in a 1:0.1 weight ratio (BEBs: TEPA, *w/w*) and mixed for 10 min. The blends were poured into silicone molds, cured at 50 °C for 8 h, then post-cured at 65 °C for 12 h in an oven (Memmert UF-260). Finally, the cured samples were cooled and stored at room temperature before characterization.

Table 1. Composition of bio-based epoxy blends (BEBs).

BEBs	Bio-Oil/ DGEBA (<i>w/w</i>)	Formulation Description
Bio-based epoxy blends with almond hulls bio-oil		
AH 400 1:4	1:4	Bio-oil from Almond hulls pyrolyzed at 400 °C, mixed with DGEBA
AH 400 1:5	1:5	Bio-oil from Almond hulls pyrolyzed at 400 °C, mixed with DGEBA
AH 600 1:4	1:4	Bio-oil from Almond hulls pyrolyzed at 600 °C, mixed with DGEBA
AH 600 1:5	1:5	Bio-oil from Almond hulls pyrolyzed to 600 °C, mixed with DGEBA
Bio-based epoxy blends with walnut hulls bio-oil		
WH 400 1:4	1:4	Bio-oil from walnut hulls pyrolyzed at 400 °C, mixed with DGEBA
WH 400 1:5	1:5	Bio-oil from walnut hulls pyrolyzed at 400 °C, mixed with DGEBA
WH 600 1:4	1:4	Bio-oil from walnut hulls pyrolyzed at 600 °C, mixed with DGEBA
WH 600 1:5	1:5	Bio-oil from Walnut hulls pyrolyzed to 600 °C, mixed with DGEBA

2.2. Analytical Techniques

2.2.1. Elemental and Proximate Analysis

The elemental composition (C, H, N, S) of the almond and walnut hull biomass was measured using a CHNS analyzer (Thermo FlashSmart, Milan, Italy) according to UNE-EN 15104. Proximate analysis was conducted according to ASTM D3172 to determine moisture, volatile matter, fixed carbon, and ash content.

2.2.2. GC–MS Analysis

A wide variety of chemical species in the bio-oil samples were identified by gas chromatography–mass spectrometry (GC–MS). Before analysis, the crude bio-oil was diluted with ultrapure water (1:1 *v/v*), centrifuged, and the water-soluble supernatant was discarded. The resulting water-insoluble phase was subjected to silica gel column chromatography and fractionated sequentially with hexane, chloroform, and ethyl acetate, using a 1:3 (*v/v*) ratio of bio-oil to each solvent, following methods described in the literature [19–21]. Each collected fraction was subsequently analyzed by GC–MS. GC–MS analyses were performed using a Shimadzu QP2010-Plus system equipped with an HP-5MS fused-silica capillary column (30 m × 0.25 mm i.d., 0.25 µm film thickness). The oven temperature program was set as follows: initial temperature 35 °C (held 2 min), increased at 5 °C min^{−1} to 180 °C, then at 20 °C min^{−1} to 300 °C with a final hold of 5 min. The injector temperature was 250 °C with a split ratio of 25:1. Helium was used as carrier gas under constant-pressure mode (10 kPa), corresponding to a flow rate of 1 mL min^{−1}. The transfer line and ion source were maintained at 250 °C. Mass spectra were acquired in electron impact (EI) mode at 70 eV in full SCAN mode using a quadrupole detector. Chromatographic data were processed using GCMS-solution software (v2.53),

and compound identification was performed by comparison with NIST08 and NIST08s mass spectral libraries.

2.2.3. Thermogravimetric Analysis (TGA)

The thermal degradation of the cured epoxy samples was performed using a Shimadzu DTG-60H. Approximately 10 mg of each sample was heated from 20 to 800 °C at a rate of 10 °C min^{−1} under a nitrogen atmosphere. Mass loss was recorded to determine the onset degradation temperature (T_{onset}), endset temperature (T_{endset}), the temperatures at 5%, 10%, and 50% mass loss ($T_{5\%}$, $T_{10\%}$, and $T_{50\%}$), the temperature of maximum degradation rate (T_{max}), and the residual mass at 800 °C (R_{m800}).

2.2.4. Raman Spectroscopy

Raman spectroscopy was performed using an Unchained Labs Hound Raman spectrometer equipped with a 785 nm laser (adjustable up to 50 mW). The laser was coupled to a Horiba OEM mini-spectrometer and a 2048-pixel Sincerity CCD detector. Spectra were collected in backscattering configuration using an Olympus microscope with a 50× objective. The spectral range was 200–2000 cm^{−1} with a resolution of ~6 cm^{−1}. The intensity of the epoxide ring vibration band at 1275 cm^{−1}, normalized to the invariant phenyl ring band at 1160 cm^{−1}, was monitored over time to determine the cross-linking degree (α) [22]. The normalized epoxide band ratio, R_t , was defined as follows:

$$R_t = \frac{I_{1275,t}}{I_{1160,t}} \quad (1)$$

where $I_{1275,t}$ and $I_{1160,t}$ are the peak intensities at 1275 and 1160 cm^{−1} at time t , respectively. The cross-linking degree at time t was calculated as follows:

$$\alpha(t) = 100 \times \left(1 - \frac{R_t}{R_0}\right) \quad (2)$$

where R_0 is the normalized ratio at the beginning of curing and R_t is the normalized ratio at time t . A decrease in the 1275 cm^{−1} peak indicates consumption of epoxide groups during network formation.

2.2.5. Mechanical Testing

Mechanical properties, including tensile strength, elongation at break, and Young's modulus, were measured using an Instron 3369 universal testing machine (Norwood, MA, USA) following ASTM D638. Type I dog-bone specimens (standard ASTM dimensions) were tested at a crosshead speed of 5 mm/min at room temperature. Young's modulus was determined from the initial linear region of the stress–strain curve. Data acquisition and processing were performed using Instron Bluehill® Lite software (version 2.24).

2.2.6. Dynamic Mechanical Analysis (DMA)

Dynamic mechanical analysis was performed on a PerkinElmer DMA 7e using the single-cantilever mode. Rectangular specimens (approximately 19 mm × 19 mm × 3 mm) were tested from 25 °C to 250 °C at a heating rate of 10 °C/min under a nitrogen atmosphere (20 mL/min). A static force of 750 mN and a dynamic force of 700 mN were applied at a fixed frequency of 10 Hz. The storage modulus (E') and loss tangent ($\tan \delta$) were recorded as a function of temperature, and the glass transition temperature (T_g) was determined from the peak of the $\tan \delta$ curve.

3. Results and Discussion

3.1. Characterization of the Biomass of Almond Hulls (AH) and Walnut Hulls (WH)

The proximate and elemental analysis results for AH and WH are presented in Table 2. The two biomass types showed some differences: walnut hulls had slightly higher volatile matter and carbon content and lower ash content compared to almond hulls. Moisture contents were low (4–6%), which is favorable as lower moisture can lead to higher bio-oil yield and heating value [23,24]

Table 2. Proximate and elemental analysis of almond hull (AH) and walnut hull (WH) biomass.

	Fixed Carbon (%)	Volatile Matter (%)	Ash (%)	Moisture (%)	N (%)	C (%)	H (%)	O (%) *	S (%)
Almond hulls (AH)	30.23	49.33	14.91	5.53	0.32	40.69	5.59	53.40	-
Walnut hulls (WH)	31.22	56.12	8.71	3.95	0.00	44.81	5.39	49.80	-

* By difference ($O\% = 100 - C - H - N - \text{ash}$).

Ultimate analysis revealed carbon contents of ~41% (AH) and ~45% (WH), hydrogen ~5.5%, oxygen ~50%, and negligible nitrogen (<0.5%) in both. The high C and H content suggests the potential for a bio-oil with a relatively high calorific value [25], whereas the high oxygen content could result in oxygenated compounds that may reduce bio-oil stability [26]. The very low nitrogen in both hulls indicates minimal risk of NO_x emissions from combustion of the derived bio-oils. Lignocellulosic composition analysis (TAPPI T249 and T222) showed WH to contain ~35% lignin, 30% cellulose, and 25% hemicellulose, while AH contained ~29% lignin, 28% cellulose, and 32% hemicellulose. The higher lignin content in WH is expected to influence its pyrolysis behavior, potentially yielding more aromatic compounds.

3.2. Effect of Pyrolysis Temperature on Product Yields

The prepared biomass was subjected to pyrolysis at 400 °C and 600 °C temperatures. Figure 1 summarizes the yields of bio-oil, biochar, and non-condensable gases from AH and WH at 400 °C and 600 °C. According to the results obtained, the yields of bio-oil, biochar, and gas from WH varied between 39.59 and 40.46%, 27.58 and 32.43%, and 24.88 and 31.89%, respectively. Instead, the bio-oil, biochar, and gas yields from AH were between 35.99 and 36.84%, 29.60 and 34.63%, and 29.38 and 33.55%, respectively. In both feedstocks, a higher pyrolysis temperature resulted in a higher bio-oil yield and lower char yield. For instance, WH produced 39.59% bio-oil at 400 °C and 40.46% at 600 °C, while AH produced 35.99% at 400 °C and 36.84% at 600 °C. The char yield dropped from 32.43% to 27.58% for WH (temperature of 400 °C to 600 °C) and from 34.63% to 29.6% for AH. Gas production increased correspondingly at the higher temperature (e.g., WH gas yield from 24.88% to 31.89%). These trends are consistent with the literature, as higher temperatures promote further cracking of tar intermediates into volatiles (increasing bio-oil and gas) and reduce solid char [27–29]. The decomposition of lignin occurs between 250 and 500 °C, which constitutes the primary contribution to bio-oil formation during the pyrolysis process [13]. Shah et al. (2021) observed an increase in bio-oil yield from 28.8 to 44.7% by increasing the pyrolysis temperature from 300 to 550 °C, and a decrease to nearly 25% from 550 to 750 °C, using walnut shell [30]. He et al. (2018) also observed similar changes in bio-oil in five crop residues with increasing temperatures from 300 to 600 °C [31]. Higher pyrolysis temperatures enhance the degradation of lignin, cellulose, and hemicellulose, thereby increasing bio-oil production. As the temperature rises, biochar production decreases while the yield of synthesis gas rises. The increase in synthesis gas yield is attributed to secondary

cracking of vapors at elevated temperature, whereas the reduction in char is due to more complete decomposition of the biomass and char residues [32,33].

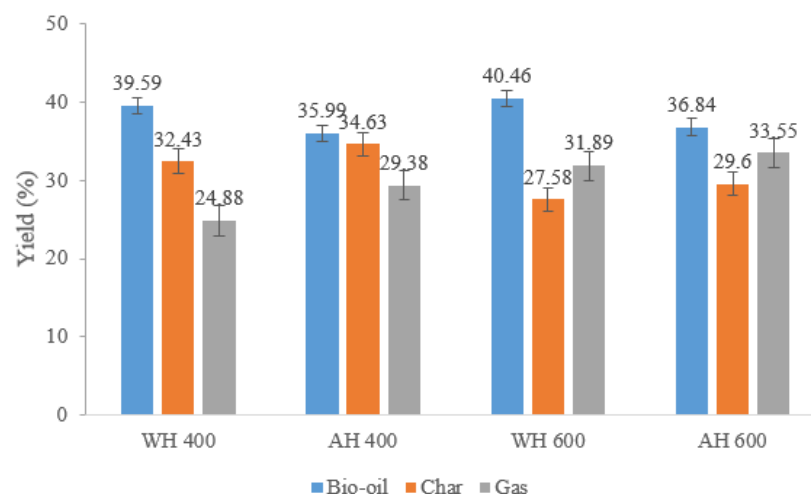


Figure 1. Yield distribution of pyrolysis products (bio-oil, char, and gas) for walnut hull (WH) and almond hull (AH) at 400 °C and 600 °C. WH 400: walnut hulls pyrolyzed to 400 °C; WH 600: walnut hulls pyrolyzed to 600 °C; AH 400: almond hulls pyrolyzed to 400 °C; AH 600: almond hulls pyrolyzed to 600 °C.

3.3. Characterization of the Bio-Oil

The bio-oil derived from the pyrolysis of WH and AH consisted of a complex mixture of aromatics (phenolic and furanoic compounds), hydrocarbons, alcohols, ketones, acids, amides, and ethers (Table 3). Figure 2 shows the composition of the bio-oils, expressed as the relative content of the major compound classes, while the GC–MS chromatogram (Figure 3) illustrates the elution profile of the individual constituents of WH and AH bio-oils at 400 °C and 600 °C. Early retention times are dominated by light acids, ketones, and furans, whereas phenolics and long-chain hydrocarbons elute at longer times, reflecting the typical thermochemical degradation pattern of lignocellulosic biomass. The predominant compounds identified were aromatic and hydrocarbon species, primarily arising from lignin decomposition during pyrolysis [34,35]. Lignin, a polyphenolic macromolecule, constitutes ~25–35% of lignocellulosic biomass [36] and tends to yield aromatic products upon thermal breakdown [37]. With increasing pyrolysis temperature, the total yield of aromatic compounds in the bio-oil increased from 23.8% at 400 °C to 26.1% at 600 °C for almond hulls (AH) and from 30.4% to 35.2% for walnut hulls (WH). Simultaneously, the hydrocarbon fraction increased from 32.2% to 46.8% for AH and from 45.9% to 49.9% for WH, indicating that temperature promotes the formation of aromatic and aliphatic hydrocarbon fragments through deoxygenation and cracking reactions. Thus, temperature is a key factor in producing aromatic and hydrocarbon-rich bio-oils.

At lower temperature (400 °C), the bio-oil retained a greater fraction of oxygenated compounds (notably alcohols, ketones, carboxylic acids, and ethers), derived from cellulose and hemicellulose decomposition. In contrast, the higher temperature of 600 °C favors the generation of aromatic phenolic species and long-chain hydrocarbons. This trend is evident for both WH and AH bio-oils, as reflected by the increase in aromatic and hydrocarbon contents. Consequently, the bio-oil produced at 600 °C contains a higher proportion of reactive functional groups (aromatic rings and –OH groups) that can participate in epoxy curing, whereas the bio-oil from 400 °C retains a greater proportion of oxygenated, non-aromatic components that are less effective in cross-linking the epoxy network.

Table 3. Main compound of bio-oil (relative content >1%) from pyrolysis of walnut hulls (WH) and almond hulls (AH) at 400 °C and 600 °C.

N°	Compounds	Formula	t _R (min)	Relative Content (%)			
				WH 400	WH 600	AH 400	AH 600
1	Acetic acid	C ₂ H ₄ O ₂	3.053	3.63	–	5.65	3.14
2	Propanoic acid	C ₃ H ₆ O ₂	4.102	–	–	7.16	–
3	1-Hydroxy-2-butanone	C ₄ H ₈ O ₂	4.219	3.75	–	–	–
4	Furfural	C ₅ H ₄ O ₂	5.203	–	–	8.27	–
5	2-Furanmethanol	C ₅ H ₆ O ₂	5.86	11.3	12.6	4.4	6.6
6	2-Hexene	C ₆ H ₁₂	7.436	–	–	1.1	–
7	Phenol	C ₆ H ₆ O	9.385	–	5.19	1.41	1.42
8	Furan, 2,5-diethoxytetrahydro	C ₈ H ₁₄ O ₃	10.073	–	–	5.2	13.3
9	1,2-Cyclopentanedione, 3-methyl-	C ₆ H ₈ O ₂	10.779	–	–	2.37	–
10	Phenol, 2-methoxy-	C ₇ H ₈ O ₂	12.622	–	–	3.17	–
11	Catechol	C ₆ H ₆ O ₂	16.131	18.41	13.86	–	11.93
12	Levogluconan	C ₆ H ₈ O ₄	16.554	–	–	8.95	–
13	5-Hydroxymethylfurfural	C ₉ H ₂₀	17.252	9.69	15.9	2.4	9.22
14	1,2-Benzenediol, 3-methoxy-	C ₇ H ₈ O ₃	17.865	2.31	2.13	–	3.56
15	3,5-Dihydroxytoluene	C ₇ H ₈ O ₂	18.938	–	–	2.68	–
16	Phenol, 2,6-dimethoxy-	C ₈ H ₁₀ O ₃	20.599	–	–	3.43	–
17	Vanillin	C ₈ H ₈ O ₃	22.007	–	–	1.29	–
18	1,2,4-Trimethoxybenzene	C ₉ H ₁₂ O ₃	23.096	–	–	1.13	–
19	Nonadecane	C ₁₉ H ₄₀	31.874	1.06	–	–	1.01
20	Eicosane	C ₂₀ H ₄₂	32.749	1.19	2.5	–	1.52
21	Heneicosane	C ₂₁ H ₄₄	33.475	2.14	4.3	–	–
22	Docosane	C ₂₂ H ₄₆	34.105	5.44	10.3	3.66	6.27
23	Tricosane	C ₂₃ H ₄₈	34.654	8.22	15.1	–	9.3
24	Tetracosane	C ₂₄ H ₅₀	35.157	9.02	10.1	27.4	8.9
25	Octadecanamide	C ₁₈ H ₃₇ NO	35.256	–	–	3.31	–
26	Pentacosane	C ₂₅ H ₅₂	35.668	11.67	–	–	7.99
27	Hexacosane	C ₂₆ H ₅₄	36.176	2.85	4.3	–	3.03
28	Heptacosane	C ₂₇ H ₅₆	36.732	–	–	–	2.53
29	Octacosane	C ₂₈ H ₅₈	37.352	2.55	3.3	–	2.93
30	Nonacosane	C ₂₉ H ₆₀	38.058	1.77	–	–	1.92
31	triacontane	C ₃₀ H ₆₂	38.883	–	–	–	1.42

WH 400: walnut hulls pyrolyzed to 400 °C; WH 600: walnut hulls pyrolyzed to 600 °C; AH 400: almond hulls pyrolyzed to 400 °C; AH 600: almond hulls pyrolyzed to 600 °C.

The identified aromatic compounds in the bio-oils include mainly methoxyphenols, benzenediols, alkyl phenols, and a variety of furanic compounds, all consistent with the known pyrolysis pathways of lignocellulosic biomass. The fraction of aliphatic oxygenated compounds, particularly carboxylic acids, decreased with increasing temperature, whereas aromatic phenolics increased. Among all functional groups present, aromatic –OH moieties constitute the most reactive sites toward epoxy curing [18], while aliphatic –OH groups may also contribute to a lesser extent. Although higher phenolic content can increase the acidity of the bio-oil and reduce its suitability as a fuel [38], the phenolic fraction plays a dominant role in epoxy reactivity and can be beneficially employed to form bio-based polymer networks [39,40]. Catechol is the most significant contributor to epoxy curing due to its high abundance (18.41% at 400 °C and 13.86% at 600 °C in WH, and 11.93% in AH 600) and its bifunctional structure, which enables efficient epoxide ring opening. Other phenolics, including guaiacol, 3,5-dihydroxytoluene, 2,6-dimethoxyphenol, phenol, vanillin, and methoxy-substituted dihydroxybenzenes, also provide nucleophilic aromatic hydroxyl groups capable of participating in the curing reaction. In contrast, compounds derived from hemicellulose and cellulose degradation (such as ketones, amides, and ethers),

consistent with prior studies [28,41–45], do not directly contribute to curing, but may influence viscosity, volatility, or processing behavior. Additionally, although furfural and 5-hydroxymethylfurfural possess aromatic ring structures, they are not functionally active toward epoxy reactivity and therefore do not participate in the curing reaction. Although furanic compounds are abundant in the bio-oils, they are expected to contribute mainly through physical effects (e.g., viscosity reduction and increased free volume) rather than direct participation in epoxy curing under the present conditions [8–11]. If retained as non-reactive species after curing, they may act as minor plasticizing components [18].

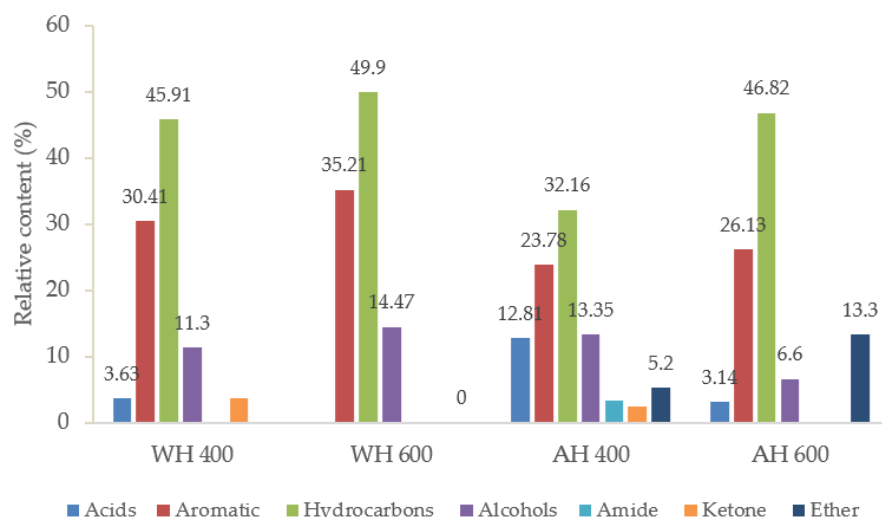


Figure 2. Composition of some compounds in bio-oil from pyrolysis of walnut hulls (WH) and almond hulls (AH) at 400 and 600 °C. WH 400: walnut hulls pyrolyzed to 400 °C; WH 600: walnut hulls pyrolyzed to 600 °C; AH 400: almond hulls pyrolyzed to 400 °C; AH 600: almond hulls pyrolyzed to 600 °C.

3.4. Cross-Linking Degree

The cross-linking degree in the bio-based epoxy blends is close to that of cured neat epoxy resin (72.16%), as shown in Table 4. The cross-linking degrees were higher using bio-oil pyrolyzed at 600 °C for both WH and AH biomass. The higher cross-linking degree was achieved with a 1:4 bio-oil/DGEBA weight ratio, due to higher concentrations of aromatic compounds, mainly phenolic compounds. This indicates that these compounds were incorporated into the epoxy resin.

Table 4. The cross-linking degree for cured neat epoxy resin (DGEBA) and bio-based epoxy blends.

Sample	Cross-Linking Degree (α)
DGEBA	72.16
Almond Hull (AH)	
AH 400 1:4	70.85
AH 400 1:5	64.30
AH 600 1:4	73.21
AH 600 1:5	70.90
Walnut hulls (WH)	
WH 400 1:4	72.80
WH 400 1:5	67.40
WH 600 1:4	76.99
WH 600 1:5	73.05

Figure 4 shows the Raman spectra of uncured DGEBA, cured DGEBA, and cured bio-based epoxy blends. The Raman band associated with the O–H stretching vibration

(3000–3500 cm^{-1}), originating from phenolic compounds and other hydroxyl-containing species in the bio-oils, disappears in the cured bio-based epoxy blends, indicating that these O–H groups participated in the epoxy resin curing reaction [46–50]. This confirmed the consumption of -OH groups upon reaction with uncured DGEBA to generate a chemical bond [18]. This behavior is attributed mainly to the phenolic constituents of the bio-oils, whose aromatic hydroxyl groups serve as the primary reactive sites for epoxide ring-opening, whereas non-phenolic oxygenated species (such as aldehydes, ketones, acids, and furans) do not significantly contribute to the curing reaction.

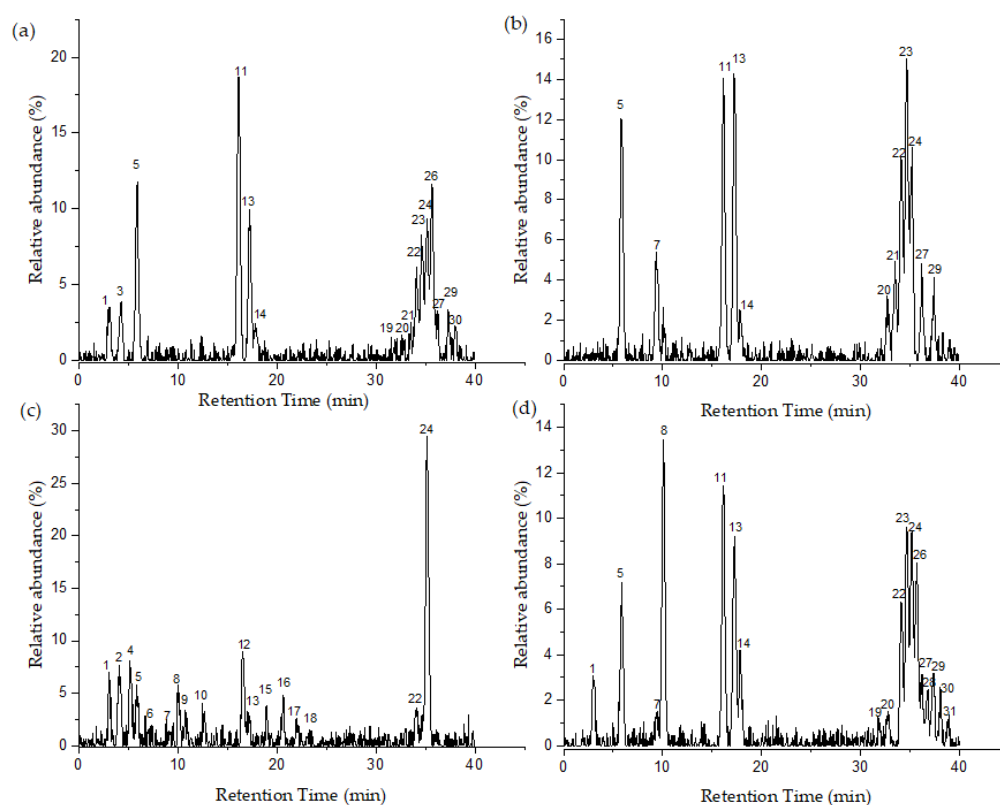


Figure 3. GC–MS chromatograms of bio-oil from pyrolysis of walnut hulls (WH) and almond hulls (AH) at 400 and 600 °C. (a) Walnut hulls pyrolyzed to 400 °C (WH 400). (b) Walnut hulls pyrolyzed to 600 °C (WH 600). (c) Almond hulls pyrolyzed to 400 °C (AH 400). (d) Almond hulls pyrolyzed to 600 °C (AH 600). Peaks were identified based on mass spectra and library matches (NIST08 and NIST08s).

In addition, after curing, the specimens of bio-based epoxy blends showed a significant reduction in the peak to 1275 cm^{-1} for epoxide vibration [51]. During chemical curing, the peak intensity decreases because the epoxide groups in the epoxy resin react with the hardener, forming a highly cross-linked three-dimensional network [22,52]. At this stage, the free epoxy groups are consumed during the vitrification process of the epoxy resin [53].

A band associated with the link formed between the hardener's amine group and the resin's epoxy group is found at 2835 cm^{-1} , corresponding to $-\text{CH}_2$ stretching [54]. This band is found in all cured specimens of the bio-based epoxy blends and DGEBA.

Other bands detected at 1112 cm^{-1} , 1186 cm^{-1} , and 1608 cm^{-1} are assigned to resin backbone vibrations that remain unchanged throughout the curing reaction, such as 1112 cm^{-1} and 1186 cm^{-1} corresponding to the C–C stretch, and 1608 cm^{-1} is assigned to the stretching of the phenyl ring [55].

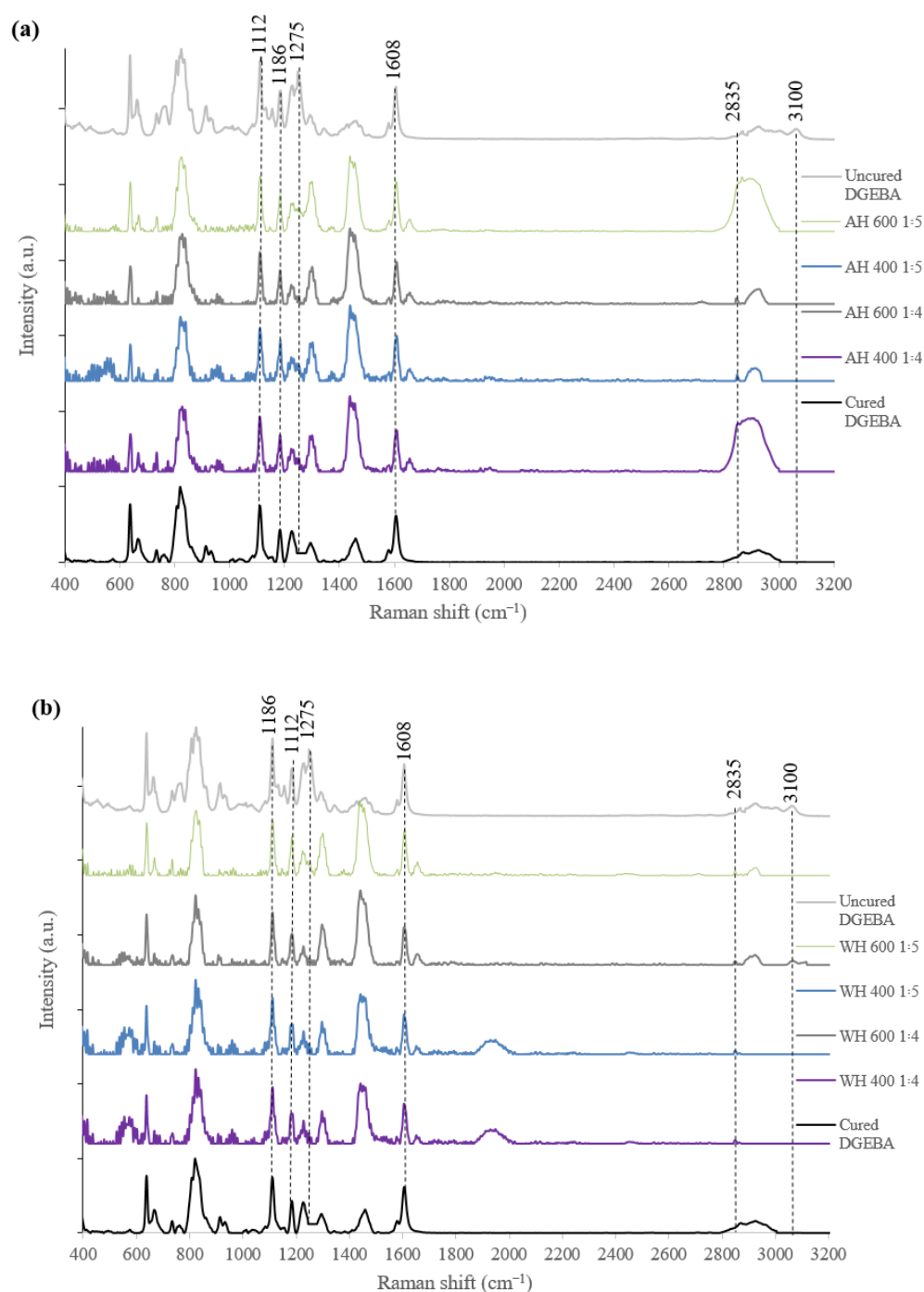


Figure 4. Raman spectra of (a) uncured DGEBA, cured DGEBA, and cured bio-based epoxy blends of AH (b) uncured DGEBA, cured DGEBA, and cured bio-based epoxy blends of WH.

3.5. Thermal Degradation Properties

Figure 5 shows TGA (weight loss) and DTG (derivative weight loss) curves for the cured neat epoxy resin and the cured bio-based epoxy blends of AH and WH. All samples exhibit a three-stage degradation process: an initial mass loss below 120 °C (attributable to moisture or volatile compounds) [56] a decomposition stage from 250 to 400 °C (degradation of the polymer network), and a final stage above 400 °C (breakdown of charred residues) [57,58].

When interpreting the thermal degradation behavior of BEBs, it is important to consider that the bio-oils contain a broad distribution of components, including low-molecular-weight oxygenates (such as furanic derivatives, light acids, ketones, and alcohol and ether

species) as well as higher-boiling aromatic and hydrocarbon fractions. The low-molecular-weight oxygenate fraction may contribute primarily through physical effects, such as volatilization, desorption, or plasticization, when not fully incorporated into the cured network, which can influence early-stage mass loss and onset-related thermal parameters (for example, $T_{5\%}$ and T_{onset}) relative to neat epoxy. In contrast, the higher-boiling aromatic and hydrocarbon fractions are expected to contribute more strongly to the composition of the cured network and to the higher-temperature decomposition profile, consistent with the main DTG events.

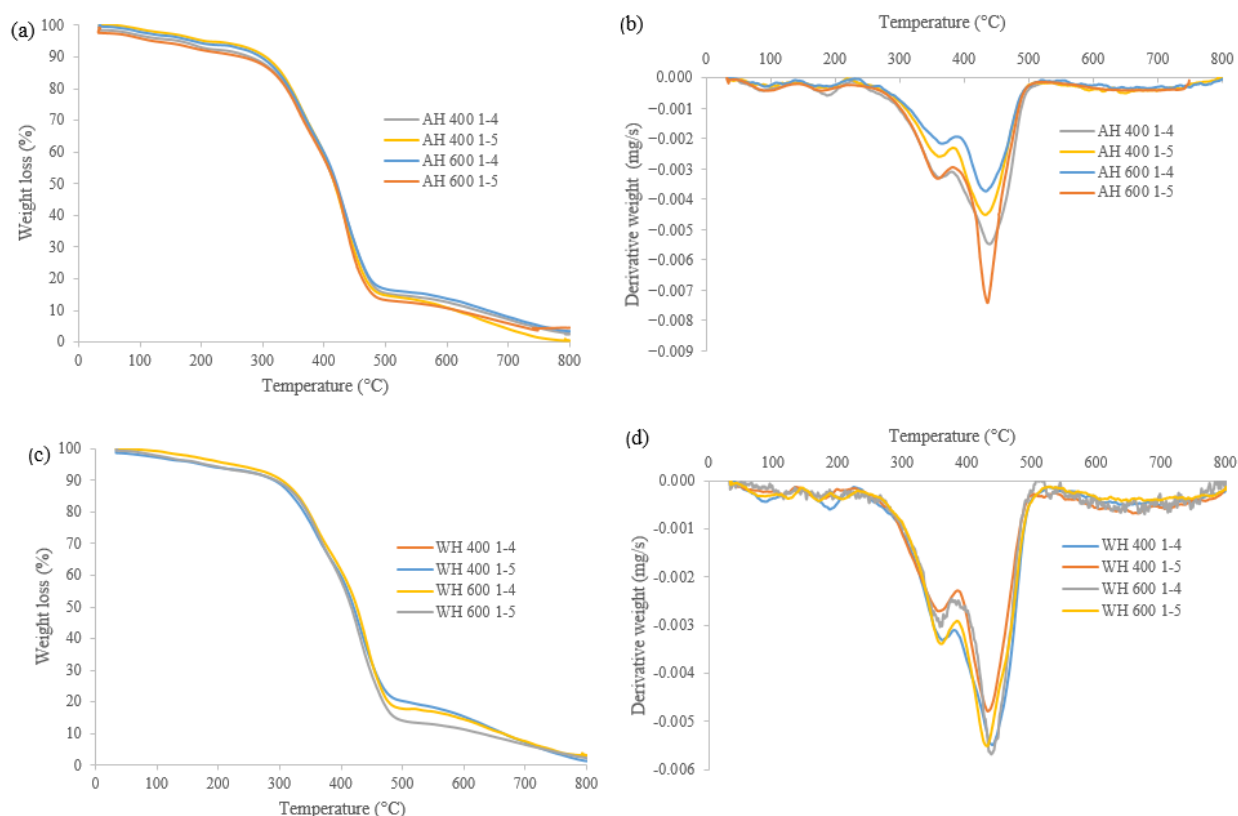


Figure 5. TGA (a) and derivative weight loss (DTGA) (b) curves for cured neat epoxy resin (DGEBA) and cured bio-based epoxy blends of AH. TGA (c) and derivative weight loss (DTGA) (d) curves for cured neat epoxy resin (DGEBA) and cured bio-based epoxy blends of WH.

The temperatures corresponding to mass loss are summarized in Table 5. It should be noted that T_{onset} and $T_{50\%}$ capture different aspects of thermal degradation: T_{onset} is sensitive to early-stage mass loss from more labile or volatile species, whereas $T_{50\%}$ reflects the thermal robustness of the bulk network at higher mass-loss conversion. The neat epoxy resin showed T_{onset} at 324.41 °C and T_{endset} at 507.51 °C, with 4.36% residual mass. In bio-based epoxy blends with bio-oil of WH and AH, both T_{onset} and T_{endset} were close values. For blends with bio-oil of AH, T_{onset} was between 295.83 and 297.54 °C, and T_{endset} was between 497.3 and 502.84 °C. For blends with bio-oil of WH, T_{onset} was between 293.40 and 296.41 °C, and T_{endset} were between 491.05 and 500.40 °C. The small reduction in T_{onset} for the bio-oil modified resins indicates a minor decrease in initial thermal stability, likely due to bio-oil components that start decomposing at relatively lower temperatures. The degradation of the bio-based epoxy blends begins several degrees earlier than that of neat epoxy, which can be attributed to the presence of thermally labile moieties derived from bio-oil. However, the bulk of degradation occurs in the same temperature range as the neat resin, suggesting that the primary epoxy network structure remains robust. Moreover, the residual char yields of the blends ranged from approximately 0.4% to 4.5%, in some cases

comparable to that of neat epoxy (4.36%). Nevertheless, certain formulations, particularly those cured bio-based epoxy blends of WH, exhibited minimal char formation upon thermal degradation. The lower char yield suggests more fuel gases were generated [59]. Overall, the thermal analysis indicates that introducing bio-oil into the epoxy matrix causes only a slight shift in thermal stability. Importantly, the major decomposition stage and the final char residue are comparable to the neat resin, implying that the fundamental network stability is largely preserved.

Table 5. Thermal degradation behaviors for cured neat epoxy resin (DGEBA) and bio-based epoxy blends.

Sample	T _{onset} (°C) ^a	T _{endset} (°C) ^b	T5% (°C) ^c	T10% (°C) ^d	T50% (°C) ^e	T _{max} (°C) ^f	Rm800 (%) ^g
DGEBA	320.41	507.51	328.53	350.53	415.75	450.62	4.36
Almond Hull (AH)							
AH 400 1:4	297.54	502.84	164.77	278.84	417.33	448.25	2.58
AH 400 1:5	295.83	498.7	206.33	304.78	416.80	434.23	0.43
AH 600 1:4	297.54	501.23	187.2	296.7	419.96	436.74	3.41
AH 600 1:5	295.83	497.3	122.57	265.71	417.48	437.22	4.51
Walnut hulls (WH)							
WH 400 1:4	294.3	491.05	211.28	303.69	421.41	437.29	3.12
WH 400 1:5	293.4	491.05	173.1	290.47	419.94	425.97	1.31
WH 600 1:4	296.41	494.34	223.04	302.92	425.22	437.29	3.15
WH 600 1:5	294.3	500.4	178.99	293.47	416.01	425.97	2.31

^a Initial degradation temperature (°C). ^b Final degradation temperature (°C). ^c 5% weight loss temperature (°C).

^d 10% weight loss temperature (°C). ^e 50% weight loss temperature (°C). ^f maximum mass loss rate, temperature (°C). ^g Residue (wt%) at 800 °C.

In cured bio-based epoxy blends, T5%, T10%, and T_{max} were lower than those of neat epoxy resin, indicating that degradation can begin at lower temperatures due to the presence of low-molecular-weight oxygenated species in the bio-oil. In contrast, T50% increased in all cured bio-based epoxy blends. The increase in T50% suggests that incorporating bio-oil into the epoxy resin can enhance the thermal robustness of the bulk matrix by increasing the fraction of thermally stable aromatic structures incorporated into the cured matrix. In particular, phenolic hydroxyl groups in the aromatic fraction can act as nucleophiles toward epoxy rings, promoting epoxy ring-opening and the formation of β-hydroxy ether linkages, which increase effective network connectivity and rigidity [57]. This can promote char formation and increase the thermal robustness of the bulk network, thereby increasing T50%. Conversely, T_{onset} can decrease because low-molecular-weight oxygenated species may volatilize or decompose at lower temperatures, contributing to early-stage mass loss. This interpretation is consistent with prior reports on phenolic hydroxyl-assisted epoxy ring-opening, leading to slightly more thermally robust networks [18,60–62].

The bio-oil obtained from WH pyrolysis at 600 °C contained a higher proportion of aromatic compounds compared with that produced at 400 °C. Similarly, AH bio-oils also exhibited an increase in aromatic content when the pyrolysis temperature was raised. The highest T50% value was achieved using a 1:4 bio-oil/DGEBA weight ratio, indicating that incorporation of bio-oil contributes to improved thermal stability in the cured epoxy networks.

Figure 6a,b shows the DMA results for the damping storage modulus (E′) and Tan δ versus temperature for AH 600 1:4 and WH 600 1:4, with a higher cross-linking degree (see Table 4). Table 6 presents the results for E′ and glass transition temperature (T_g), showing a decrease in both for cured bio-based epoxy blends compared to neat epoxy resin. In terms of thermo-mechanical behavior, the addition of bio-oil leads to a decrease in the

glass transition temperature (T_g) and storage modulus E' , which confirms a moderate plasticization effect attributed to the presence of flexible aliphatic hydrocarbon chains and the lower reactivity of bio-oil components [39]. The higher T_g of WH 600 1:4, compared to AH 600 1:4, could be attributed to the higher OH number of the bio-oil, an important parameter for epoxy curing. These groups can be generated due to the cleavage of ether and ester bonds during the pyrolysis process. Consequently, WH 600 1:4 likely contains fewer unreacted components than AH 600 1:4. This suggests that a greater number of components were incorporated into the epoxy matrix during cross-linking in WH 600 1:4. The bio-oil from walnut shells provided more reactive sites for cross-linking, mitigating the T_g depression to some extent by integrating more fully into the network.

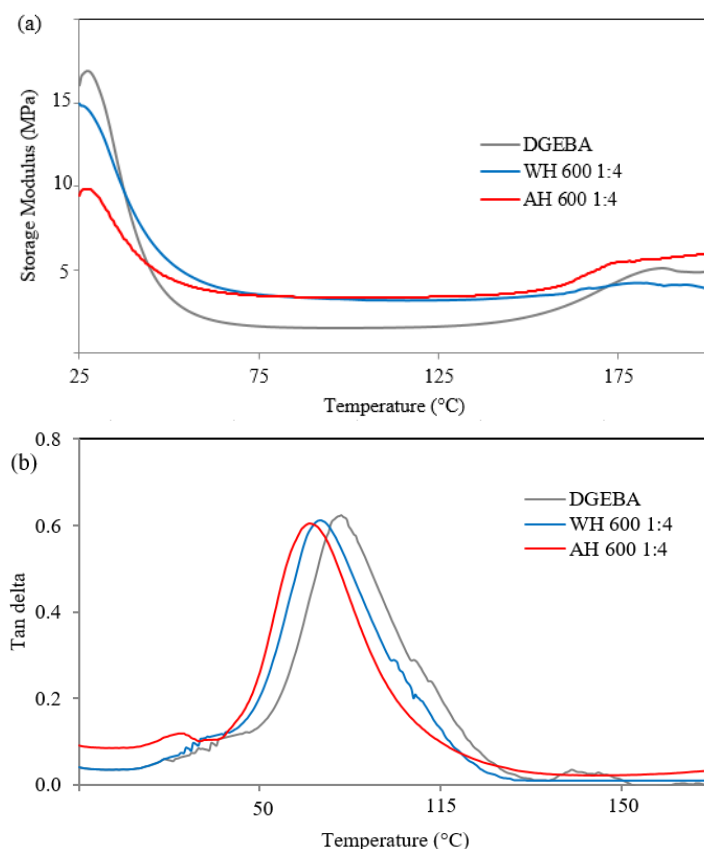


Figure 6. (a) Storage modulus and (b) loss tangent ($\tan \delta$) as a function of temperature of cured neat epoxy resin (DGEBA) and cured bio-based epoxy blends (AH 600 1:4 and WH 600 1:4). The peak of $\tan \delta$ defines the glass transition temperature (T_g) of each sample.

Table 6. DMA results for cured neat epoxy resin (DGEBA) and cured bio-based epoxy blends.

Sample	T_g (°C) ^a	E' at 30 °C (MPa) ^b
DGEBA	83.02	17.50
WH 600 1:4	76.01	14.70
AH 600 1:4	73.21	10.01

^a T_g taken as $\tan \delta$ peak temperature; ^b E' at 30 °C is in the glassy region.

3.6. Mechanical Properties

Figure 7 shows representative stress–strain curves for the cured neat epoxy resin and the cured bio-based epoxy blends, while Table 7 summarizes the corresponding tensile properties. Bio-based epoxy blends with bio-oil (especially from the 600 °C condition) show a significant increase in Young’s modulus and tensile strength of the epoxy. However, it

reduced the elongation at break, indicating a trade-off of higher stiffness and brittleness. For example, the neat epoxy resin had a tensile strength of 7.52 ± 1.09 MPa and a Young's modulus of ~ 1094 MPa, whereas the WH 600 1:4 blend reached 14.54 ± 4.30 MPa and ~ 3050 MPa, corresponding to an almost threefold increase in stiffness relative to the neat epoxy resin. AH 600 1:4 blend also showed improvements (12.78 ± 4.97 MPa strength, ~ 1951 MPa modulus) compared to neat epoxy resin. In both cases, the maximum strain at break of the blends (~ 0.5 – 0.6%) was lower than that of neat epoxy resin ($\sim 1.0\%$), reflecting increased brittleness due to the highly cross-linked network formed with bio-oil. Tensile strength and modulus were highest when bio-oil from WH pyrolyzed at 600°C was used. This trend is consistent with the higher aromatic content of the WH 600 bio-oil, which is associated with higher cure development and a more rigid, effectively connected network, leading to superior tensile properties in the cured polymer.

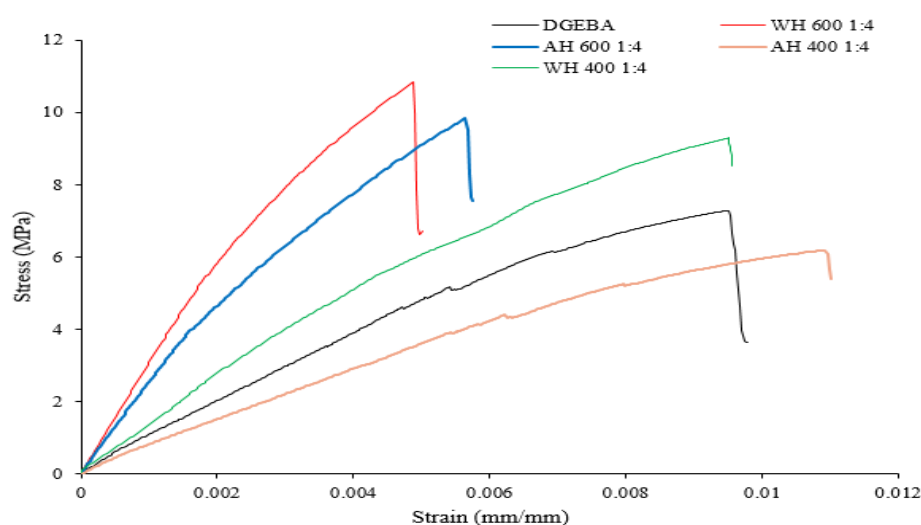


Figure 7. Representative stress-strain curves of cured neat epoxy resin (DGEBA) and cured bio-based epoxy blends.

Table 7. Tensile mechanical properties of cured neat epoxy resin (DGEBA) and bio-based epoxy blends.

Sample	Tensile Strength (MPa)	Strain at Break (mm/mm)	Young's Modulus (MPa)
DGEBA	7.52 ± 1.09	0.01	1093.69 ± 128.83
AH 400 1:4	6.45 ± 1.12	0.011	1300 ± 101.21
AH 600 1:4	12.78 ± 4.97	0.006	1950.90 ± 73.35
WH 400 1:4	9.25 ± 1.02	0.01	2000 ± 101.21
WH 600 1:4	14.54 ± 4.30	0.005	3050.02 ± 90.49

In contrast, the bio-oils produced at 400°C provide only limited mechanical improvement. In some blend compositions, stiffness and tensile strength remained comparable to, or slightly lower than, those of neat DGEBA. This behavior is consistent with a lower abundance of lignin-derived aromatic structures capable of contributing to epoxy ring-opening and network build-up, together with a relatively higher fraction of low-molecular-weight oxygenated compounds that can act as a plasticizing component. Consequently, the resulting thermoset may exhibit reduced effective network connectivity and lower load-bearing capability compared with bio-oils produced at 600°C .

This contrast highlights the influence of pyrolysis temperature on the functional composition of bio-oils. Bio-oils enriched in condensed aromatic moieties (e.g., those formed at

600 °C, particularly from walnut hulls) provide higher phenolic functionality that can more effectively contribute to epoxy network formation, yielding thermosets with improved tensile performance. Conversely, bio-oils generated at lower temperatures exhibit lower aromatic contribution and therefore lead to smaller improvements in mechanical performance.

While the observed mechanical trends are consistent with increased network rigidity associated with higher aromatic content, potential compatibility limitations between the bio-oil and the epoxy matrix should also be considered. Bio-oils comprise a broad distribution of polar oxygenated species and aromatic components that may exhibit incomplete miscibility with DGEBA, potentially leading to micro-heterogeneity or partial phase separation depending on composition and formulation. Such effects can influence stress transfer, local plasticization, and the effective mechanical response of the cured networks. Strategies commonly discussed to mitigate these limitations include fractionation to reduce low-molecular-weight species, optimization of formulation ratios, or the introduction of compatibilizing or reactive functionalities [63].

3.7. Semi-Quantitative Analysis of Aromatic Fraction of the Bio-Oil on Cure Development and Mechanical Performance

A semi-quantitative comparison indicates a positive association between the aromatic fraction of the bio-oil and both cure development (cross-linking degree, α) and tensile performance (Figure 8). As the aromatic fraction increases within each bio-oil samples when raising the pyrolysis temperature from 400 to 600 °C (23.8% to 26.1% for AH; 30.4% to 35.2% for WH), the cross-linking degree (α) for the 1:4 formulations also increases (70.85 to 73.21% for AH; 72.80 to 76.99% for WH), accompanied by improved tensile properties (e.g., Young's modulus increases from 1300 MPa for AH 400 (1:4) to 3050 MPa for WH 600 (1:4)). Overall, these results support a consistent composition–cure–property trend in which higher aromatic content is associated with more advanced network formation and an enhanced tensile response (higher Young's modulus and tensile strength). This behavior is plausibly linked to the phenolic –OH functionality and aromatic moieties present in the bio-oil, which may contribute to epoxy network build-up via a combination of (i) additional epoxy ring-opening reactions and (ii) an increased fraction of rigid aromatic linkages incorporated into the cured matrix.

Spearman's rank correlation analysis was applied to quantitative variables only (aromatic fraction, cross-linking degree (α), tensile strength, and Young's modulus). Strong positive monotonic correlations were observed between aromatic fraction and cross-linking degree ($\rho = 0.80$), tensile strength ($\rho = 0.80$), and Young's modulus ($\rho = 1.00$), supporting a consistent semi-quantitative relationship between aromatic content, effective cure development, and tensile performance. Given the limited number of formulations, this analysis is intended to highlight trends rather than establish predictive relationships.

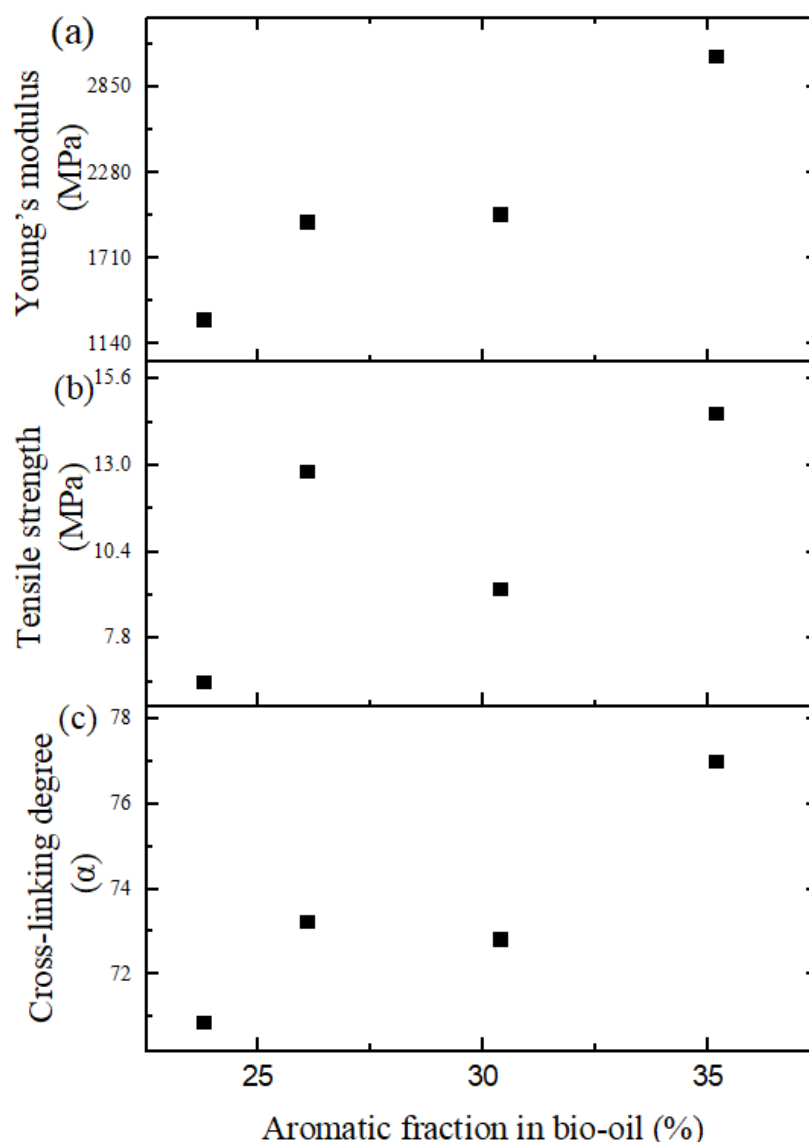


Figure 8. Semi-quantitative relationships between aromatic fraction in the bio-oil and (a) cross-linking degree (α), (b) tensile strength, and (c) Young's modulus for epoxy formulations at a 1:4 ratio. Symbols represent individual formulations, highlighting monotonic trends.

4. Conclusions

The yield and composition of bio-oils from AH and WH pyrolysis depend strongly on both the pyrolysis temperature and the intrinsic composition of the biomass. The highest bio-oil yield ($\approx 40.5\%$) was obtained at $600\text{ }^{\circ}\text{C}$ using WH, which contains a higher lignin content than AH. During pyrolysis, lignin decomposition was the primary contributor to bio-oil formation. The bio-oils from both feedstocks were characterized mainly by hydrocarbons and phenolic aromatic compounds, whose relative abundance varied with temperature. The total aromatic content increased with increasing pyrolysis temperature: for walnut hulls, aromatics rose from $\sim 30\text{ wt}\%$ at $400\text{ }^{\circ}\text{C}$ to $\sim 35\text{ wt}\%$ at $600\text{ }^{\circ}\text{C}$, while for almond hulls, they increased from $\sim 23\text{ wt}\%$ to $\sim 26\text{ wt}\%$. Moderate changes were observed in the oxygenated fraction with increasing temperature. While carboxylic acids and small oxygenated species tended to decrease or disappear, furanic compounds, particularly 2-furanmethanol and 5-hydroxymethylfurfural, showed a clear increase, especially in AH bio-oils. In WH bio-oils, a moderate increase in these furanic compounds was also observed, mainly associated with the rise in 2-furanmethanol and 5-hydroxymethylfurfural, whereas acids and other light oxygenates were no longer detected at $600\text{ }^{\circ}\text{C}$. Overall, higher pyrolysis

temperatures favored the formation of bio-oils richer in aromatic and hydroxyl-functional compounds, which constitute the main reactive species during epoxy resin curing.

When these bio-oils were incorporated into an epoxy resin, they engaged in cross-linking reactions to form a three-dimensional network, markedly altering the material's properties. Using bio-oil from 600 °C pyrolysis (especially from WH) led to an increase in cross-linking degree, Young's modulus, and tensile strength of the cured resin. However, the addition of bio-oil also reduced the composite's storage modulus (E') and glass transition temperature (T_g) compared to neat epoxy, particularly evident when the bio-oil had a high content of flexible, non-aromatic components. In contrast, incorporating bio-oil obtained at 400 °C generally resulted in lower cross-linking efficiency and less pronounced improvements in mechanical performance compared with bio-oil obtained at 600 °C. Notably, the AH 400 1:4 formulation can exhibit a higher Young's modulus than neat DGEBA, while tensile strength remains statistically comparable within experimental uncertainty, indicating increased stiffness without a significant change in ultimate strength. Biomass with a higher lignin content (such as WH) produced greater amounts of aromatic compounds at a given pyrolysis temperature, which contributed more effectively to the epoxy curing process and improved mechanical outcomes.

This work demonstrates a feasible route to develop partially bio-based epoxy resins by utilizing pyrolysis oils derived from agricultural waste. A critical finding is that the bio-oil's origin and production conditions (notably, a higher pyrolysis temperature yielding a lignin-rich, aromatic product) impact the resulting resin's performance. The bio-oil from walnut shells pyrolyzed at 600 °C acted as an effective cross-linking agent in the epoxy, significantly enhancing stiffness and strength, whereas bio-oils of lower aromatic content (e.g., from 400 °C or lower-lignin biomass) offered minimal benefit. These results highlight the importance of customizing bio-oil composition for polymer applications: selecting feedstocks with high lignin content and optimizing pyrolysis parameters can produce bio-oils well-suited for thermoset resin modification, providing a promising proof-of-concept for valorizing almond and walnut shell waste into high-value polymer materials, contributing to the circular economy and green material innovation in the polymer industry.

Limitations of the present study should be acknowledged. The bio-oils exhibit intrinsic compositional variability and were subjected only to limited conditioning before curing; therefore, the observed trends may be feedstock-dependent (e.g., WH vs. AH). These aspects warrant further investigation to strengthen the practical translation of bio-oil-modified epoxy systems. Future studies should further define robust formulation windows and performance consistency for targeted applications. Removal of hydrocarbon-rich fractions is feasible but was outside the scope of this screening study. A preliminary techno-economic assessment would be valuable to evaluate the cost and feasibility of scaling the pyrolysis and bio-oil conditioning steps for epoxy modification.

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