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Review

Bio-Oil-Based Epoxy Resins from Thermochemical Processing of Sustainable Resources: A Short Review

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Abstract: Epoxy is the most prevalent thermosetting resin in the field of polymer composite materials. There has been a growing interest in the development of bio-based epoxy resins as a sustainable alternative to conventional petrochemical epoxy resins. Advances in this field in recent years have included the use of various renewable resources, such as vegetable oils, lignin, and sugars, as direct precursors to produce bio-based epoxy resins. In the meantime, bio-oils have been produced via the decomposition of biomass through thermochemical conversion and mainly being used as renewable liquid fuels. It is noteworthy that bio-oils can be used as a sustainable resource to produce epoxy resins. This review addresses research progress in producing bio-oil-based epoxy resins from thermochemical processing techniques including organic solvent liquefaction, fast pyrolysis, and hydrothermal liquefaction. The production of bio-oil from thermochemical processing and its use to inject sustainability into epoxy resins are discussed. Herein, we intend to provide an overall picture of current attempts in the research area of bio-oil-based epoxy resins, reveal their potential for sustainable epoxy resins, and stimulate research interests in green/renewable materials.

Keywords: bio-oil; epoxy resin; thermochemical processing; sustainable material

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1. Introduction

Epoxy resins are a class of thermosetting pre-polymers and possess excellent physical properties, such as good processability, excellent mechanical strength, great chemical resistance, high adhesion strength, high thermal stability, and outstanding insulation capability after curing [1–4]. Epoxy resins are extensively used in a wide range of commercial products, including coatings, adhesives, and composite materials, for applications in industries such as transportation, construction, aerospace, electronics, etc.

Epoxy resins are generally derived from fossil fuels and produced through a series of chemical reactions. Diglycidyl ether of bisphenol A (DGEBA) is the most commonly used epoxy resin on the market, constituting about 75% of the overall epoxy resins [5]. DGEBA is produced by a condensation reaction between bisphenol A (BPA) and epichlorohydrin with a catalyst such as sodium hydroxide, as shown in Figure 1.

Epoxy resin must go through curing to solidify and achieve its final mechanical properties. In the curing process, a chemical compound (termed as+ curing agent or hardener) with two or more functional groups (e.g., amine functional groups, $-NH_2$) that can react with epoxide functional groups (a cyclic ether with a three-membered ring, also called oxirane) is added and reacts with epoxy resin, resulting in a crosslinked molecular network. The curing process can be accomplished through heat or light, e.g., heat curing or UV curing, and the final cured product is a thermoset polymer, which is stable and does not melt or dissolve.

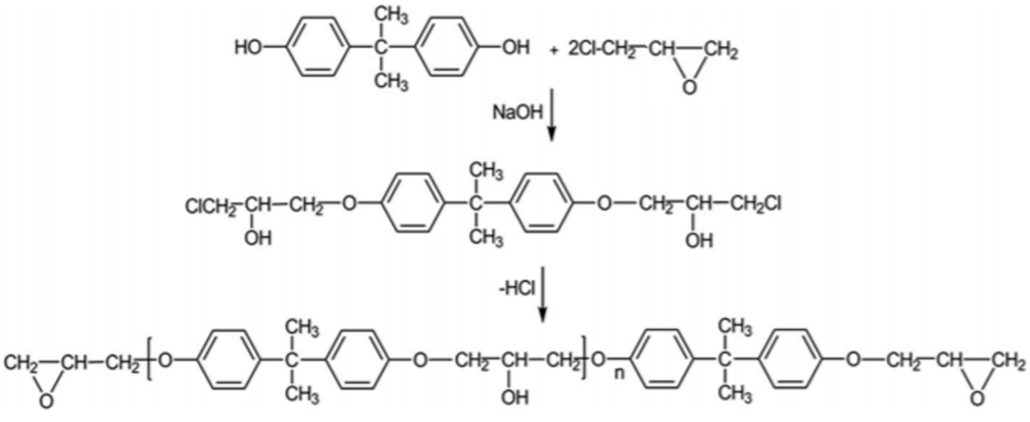


Figure 1. Synthesis of diglycidyl ether of bisphenol A (DGEBA) [6–8].

Although epoxy resins are widely used and offer many advantages, concerns have been raised about their negative impacts on our environment [9]. The production of epoxy resins requires large amounts of fossil fuels, which can contribute to greenhouse gas emission and climate change. The synthesis of epoxy precursors, e.g., epichlorohydrin and bisphenol A, can generate by-products such as chlorinated compounds, which negatively impact our environment. During the life cycle of epoxy-based composite materials, certain chemicals, like bisphenol A, are released, harming human health and ecosystems [10]. Furthermore, the disposal of end-of-life epoxy-based composite products can also be problematic. These products are not biodegradable, and they can stay in our environment for hundreds of years without experiencing significant degradation, posing a risk of contamination of the air, soil, and water. As a result, there has been a growing interest in the development of sustainable alternatives to traditional petrochemical-based epoxy resins [11,12].

In recent years, bio-based epoxy resins have gained increasing attention due to the inception of sustainable development and expansion of the bioeconomy [13]. Bio-based epoxy resins are produced by either partly or wholly substituting the conventional precursor materials for the synthesis of epoxy resin with natural/renewable resources such as vegetable oils, lignin, and sugars and have great potential to reduce environmental impact of epoxy-based products [14–16]. Vegetable oils like soybean oil and castor oil are the most common natural resources used to produce bio-based epoxy resins and are employed in a variety of products, such as plasticizers, lubricants, and surface coatings, as well as thermosets and composites [17,18]. These vegetable oils can be chemically modified through an epoxidation process to introduce epoxide (oxirane) functional groups. The epoxidation process typically involves the use of peroxy acid or peroxide to convert the carbon–carbon double bonds (C=C) present in the vegetable oils to epoxide functional groups by adding an oxygen bridge across the double bond, while other epoxidation methods are also available, such as metal-catalyzed epoxidation with hydrogen peroxide and chemoenzymatic epoxidation [17–19]. Epoxidized soybean oil now has a worldwide production of more than 200,000 tons per year [20]. Lignin, a complex phenolic polymer that occurs naturally in wood and other plant-based materials, can also be chemically modified to produce bio-based epoxy resins [21]. The presence of phenolic hydroxyl groups in lignin molecules allows them to substitute bisphenol A in epoxy resin synthesis as a bio-resource of phenol to react with epichlorohydrin [22–24]. Sugar is another starting material for bio-based epoxy resins through its reaction with epichlorohydrin or C=C double-bond oxidation [25,26]. Similar to conventional epoxy resins, bio-based epoxy resins are practiced in applications through heat curing, UV curing, or chemical curing. Making use of natural resources as a substitute to petroleum resources to synthesize bio-based epoxy resins will reduce the worldwide dependence on petroleum resources and eventually result in a sustainable future.

There are a few review papers that have been published on the topic of bio-based epoxy or green epoxy [26–31]. These published papers reviewed methods of making bio-based epoxy resins and curing agents through chemical reactions with various natural resources by agricultural and forestry practices as well as how to prepare, characterize, and improve bio-based epoxy formulations for composite purposes. However, these reviews did not include the research progress in producing bio-based epoxy resins from bio-oils via biorefinery processes. Bio-oils are produced by decomposition of biomass through thermochemical conversion [32] and are mainly utilized as renewable liquid fuels. It is noteworthy that bio-oils can also be used as a sustainable resource to produce chemicals [33]. Particularly the bio-oils contain a significant number of hydroxyl groups (−OH) that can be applied to synthesize bio-based epoxy resins [5,34,35]. Herein, we intend to complement previous published reviews by providing an overall picture of current research advances in bio-oil-based epoxy resins.

2. Thermochemical Approaches to Produce Bio-Oils for Epoxy Resins

Bio-oils are produced from biomass using three main processing techniques, namely (i) organic solvent liquefaction, which involves the utilization of organic solvents at relatively low temperatures to liquefy biomass [36]; (ii) fast pyrolysis, which involves the liquefaction of biomass at elevated temperatures in the absence of oxygen and a solvent [37]; and (iii) hydrothermal liquefaction, which breaks down biomass in water at elevated pressures and temperatures [38]. It is noteworthy that even though the products from the abovementioned three liquefaction processes are all called bio-oil, the properties of these bio-oils, such as hydroxyl number, chemical composition, and molecular weight, differ greatly. Therefore, the final physical properties of bio-oil-based epoxy resins depend on the processing conditions used for the corresponding bio-oils.

2.1. Organic Solvent Liquefaction

Organic solvent liquefaction is a thermochemical liquefaction process that makes use of functional groups from organic solvents and biomass to convert biomass into bio-oil. The generated bio-oil products can be utilized as precursor materials to synthesize epoxy resins as well as other polymers [39]. Organic solvent liquefaction usually takes place under high pressure in a relatively low-temperature ambience (<250 °C). In the course of organic solvent liquefaction process, biomass initially breaks down to smaller, reactive, and unstable molecules in appropriate solvent systems and undergoes re-polymerization and/or re-condensation to form a variety of bio-oil molecules with a various range of molecular weights [40–43]. Suitable solvents are selected to help reduce undesired reactions that lead to solid products and thus promote liquid-state bio-oil formation [42]. Different solvents can result in different liquefaction efficiencies, and a higher liquefaction yield has been observed with solvents that have a higher dielectric constant [44]. Some common solvents used in organic solvent liquefaction include dioxane, ethylene glycol, polyethylene glycol, ethylene carbonate, phenol, etc. [39,42]. One significant advantage of organic solvent liquefaction is that the feedstock does not need to be dried to proceed [42], while one big challenge in producing bio-oil via organic solvent liquefaction is that this processing technique requires more sophisticated and costly reactors [41].

2.2. Fast Pyrolysis

Fast pyrolysis (also called flash pyrolysis) is another biomass liquefaction process that takes place at elevated temperatures (400–600 °C) in the absence of oxygen and a solvent, in which fast cooling of vapors and aerosols in the processing generates bio-oil for the synthesis of epoxy resins. As a liquefaction process, fast pyrolysis can produce bio-oil with a yield as high as 70–80% depending on processing conditions such as temperature, residence time, etc. [33]. A typical fast pyrolysis system comprises a series of operations, beginning with a biomass feedstock such as wood, rice husk, or others (Figure 2) [45]. The essential conditions needed to obtain a high yield of bio-oil through fast pyrolysis include a fine particle size (<1 mm), moderately high pyrolysis temperature (450–500 °C), very high heating rate (>200 °C/s), short vapor residence time (<4 s), and rapid cooling of pyrolysis vapors.

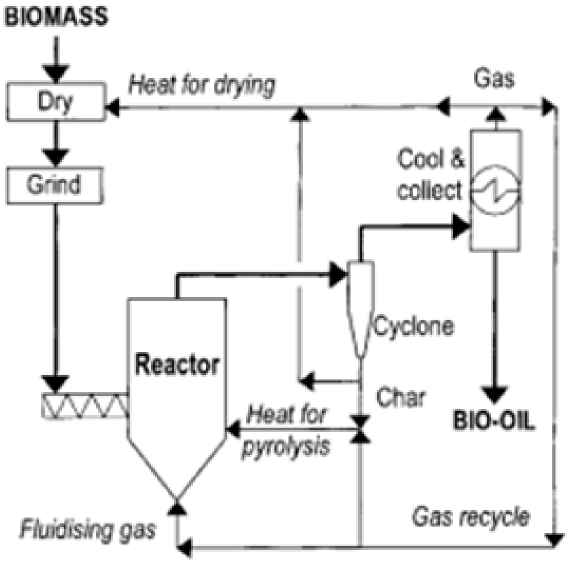
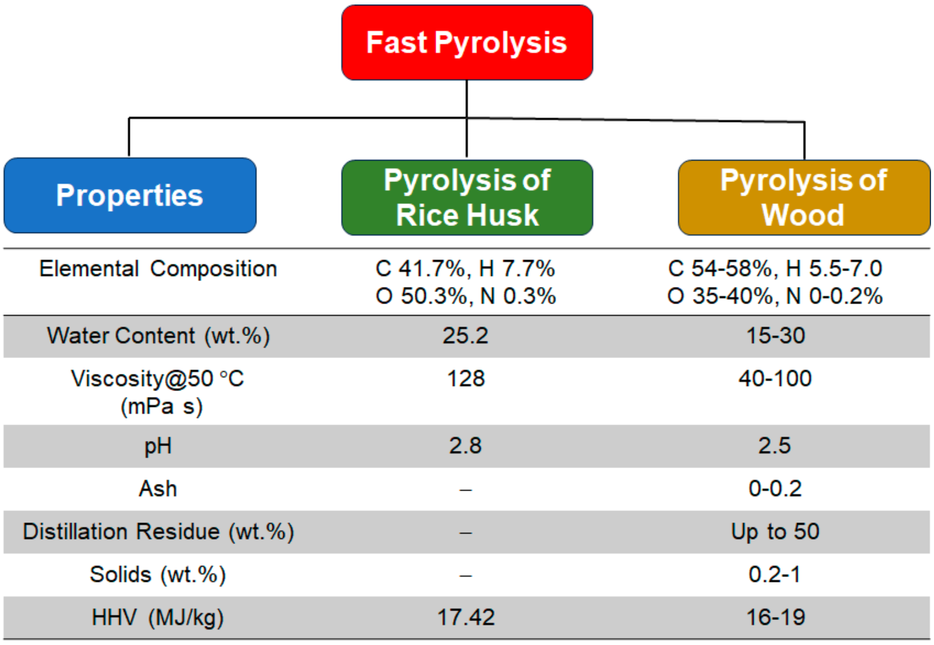


Figure 2. Schematic diagram of fast pyrolysis system [45].

The bio-oil produced from the fast pyrosis of lignocellulosic biomass is usually a free-flowing liquid that is dark brown in color with a hydrophilic phase and a hydrophobic phase [33,35,46]. The hydrophobic phase is rich in pyrolytic lignin and so has the potential to supplant bisphenol A to produce bio-oil-based epoxy resins. The yield and quality of bio-oil produced from fast pyrolysis depend on both the processing parameters and specific biomass being employed (Figure 3) [47]. For example, the bio-oil produced from pyrolysis of rice husk exhibited excess water content and a higher level of viscosity than the one produced from pyrolysis of wood.



Fast Pyrolysis

Properties	Pyrolysis of Rice Husk	Pyrolysis of Wood
Elemental Composition	C 41.7%, H 7.7% O 50.3%, N 0.3%	C 54-58%, H 5.5-7.0 O 35-40%, N 0-0.2%
Water Content (wt.%)	25.2	15-30
Viscosity@50 °C (mPa s)	128	40-100
pH	2.8	2.5
Ash	–	0-0.2
Distillation Residue (wt.%)	–	Up to 50
Solids (wt.%)	–	0.2-1
HHV (MJ/kg)	17.42	16-19

Figure 3. A comparison between bio-oils from fast pyrolysis of rice husk and wood in terms of properties [47].

2.3. Hydrothermal Liquefaction

Among the three biomass liquefaction processes, hydrothermal liquefaction is a favorable technique to synthesize bio-oil with a significant potency for commercial use due to having the most affordable cost [48]. The biomass that has been used in research so far as feedstock for hydrothermal liquefaction has had high lignin and cellulose contents. The research results over recent years, as shown in Table 1, indicate that hydrothermal liquefaction is a practicable technique for the transformation of biomass to bio-oil [49]. Unlike organic solvent liquefaction, hydrothermal liquefaction uses water as the liquefying solvent at sub- or super-critical conditions to convert lignocellulosic biomass into bio-oil [5]. Depending on the hydrothermal parameters that are employed in the processing, the hydrothermal liquefaction of lignocellulosic biomass can provide a bio-oil yield in the range of about 30–40 wt.% [50]. Moreover, the yield of hydrothermally liquified bio-oil can be increased to about 65 wt.% when ethanol is used as a co-liquefying solvent along with water [51]. Furthermore, Celikbag et al. [38] examined the effects of ethanol and temperature on the number of hydroxyl and carbonyl groups in a bio-oil product produced from hydrothermal liquefaction of loblolly pine. The results indicated that addition of ethanol as a co-solvent increased overall hydroxyl number of the generated bio-oil but decreased the number of phenolic-type hydroxyl groups in the bio-oil.

Table 1. Hydrothermal liquefaction of various biomasses to produce bio-oils as discussed in the literature.

Feedstock	Temperature (°C)	Pressure (MPa)	Time (s)	Yield of Oil (%)	Calorific Value (MJ/Kg)	Reference
Dairy Manure	250–380	10–34	–	50	–	[52]
Sewage Sludge	300	10	30–1200	48	37–39	[53]
Rubbish	250–340	6–8	360–7200	27.6	36	[54]
Sewage Sludge	150–300	8–20	0–10,800	44.5	35.7	[55]
Sewage Sludge	250–350	8–20	–	30.7	36.4	[49]
Municipal Solid Waste	260–340	13–24	–	32	46	[56]
Municipal Solid Waste	295–450	–	1200–5400	35–63.3	–	[57]
Sewage Sludge	300–360	10–18	5–20	–	30–35	[58]
Swine Manure	305	10.3	80	70	25–33	[59]

3. Injection of Sustainability into Epoxy Resin with Bio-Oils Produced from Thermochemical Processing

The environmental and economic concerns about petroleum-based epoxy resins as well as the unpredictability of limited petroleum resources have spurred considerable interest in the research and development of epoxy resins that are synthesized or modified with bio-oils via thermochemical processing.

3.1. Synthesis of Epoxy Resin with Bio-Oil

Research has been carried out to utilize bio-oils produced from organic solvent liquefaction (or simply "liquefaction" in the literature) as a polyol to substitute bisphenol A in epoxy synthesis [60–63]. Hydroxyl groups from the liquefied biomass could react with epichlorohydrin and confer epoxy functionality based upon the glycidyl etherification reaction. It is noteworthy that the properties of resultant epoxy resins could be adjusted by altering the number of hydroxyl groups of the liquefied biomass, which can be achieved by varying liquefaction processing parameters such as liquefaction time and temperature.

Kishi et al. [60] synthesized wood-based epoxy resins by first liquefying wood (Picea abies) in the presence of resorcinol and then carried out the reaction between the liquefied wood and epichlorohydrin. The epoxy index (defined as the number of moles of epoxy group per kilogram of epoxy resin with the unit eq./kg) of the synthesized resin was in the range of 2.5–4 eq./kg, as determined according to JIS K7236. The flexural strength and modulus of the cured wood-based epoxy resin at room temperature were slightly higher than those of a bisphenol A epoxy resin (used as a reference) (Figure 4A). Moreover, the wood-based epoxy resin also showed a better ability to adhere to plywood than the bisphenol A epoxy resin (Figure 4B). Furthermore, a natural plant-fiber-reinforced composite material consisting of flax fibers and the wood-based epoxy resin matrix was fabricated, and the wood-based epoxy resin exhibited better adhesion to the flax fibers than the bisphenol A epoxy resin according to the coverage of epoxy resin on surface of flax fibers determined via fracture surface morphology through SEM images. This result indicated a high potential of the bio-oils produced from organic solvent liquefaction to be used to prepare bio-based epoxy resins for green composite purpose.

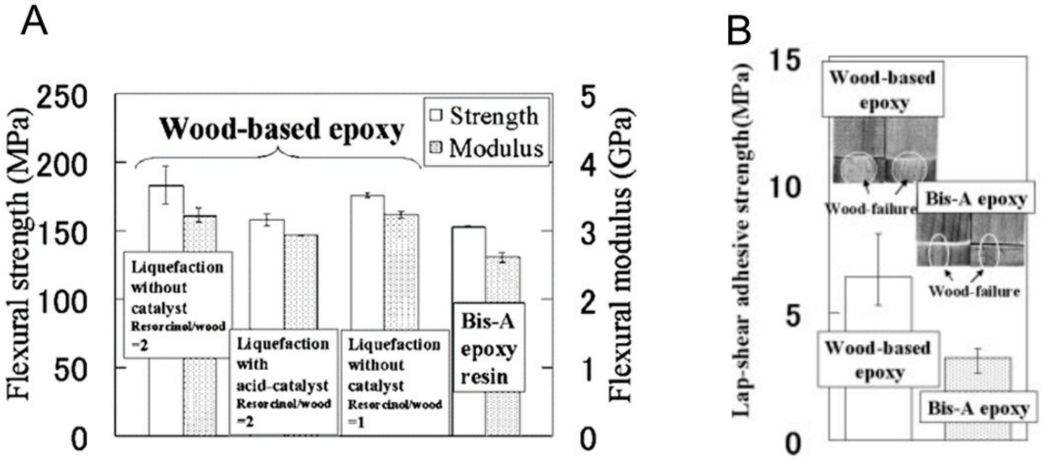


Figure 4. Flexural properties of wood-based epoxy resins (liquefaction time: 1.5 h) (**A**) and lap-shear adhesive strength of the wood-based epoxy resin (liquefaction time: 1.5 h, resorcinol-to-wood ratio (1:1)) to substrate of plywood (**B**). In both cases, bisphenol A epoxy resin was used as reference [60].

Later, Kishi et al. [34] liquefied the same wood (Picea abies) with polyethylene glycol (PEG) and glycerin through organic solvent liquefaction and subsequently synthesized new wood-based epoxy resins using the liquefied wood through a reaction with epichlorohydrin. The obtained epoxy resin possessed an epoxy equivalent weight (EEW, the weight of epoxy resin in grams that contains the equivalent of one mole of epoxy groups with the unit g/eq.) of 150 g/eq., as assessed using the titration method (JIS K7236), which is higher than the EEW of 245 g/eq. of the PEG/glycerin epoxy resin (i.e., the product from the reaction between PEG/glycerin and epichlorohydrin). Compared to the PEG/glycerin epoxy resin, the PEG/glycerin-liquefied wood-based epoxy resin, after curing, showed a higher glass transition temperature (T_g) due to its higher cross-linking density as well as relatively rigid chemical structure of the wood-derived bio-oil molecules. At the same time, the wood-based epoxy resin exhibited a much higher tensile strength (27.9 MPa), modulus (1.27 GPa), and lap-shear adhesive strength in adhering to steel plate (14.5 MPa) than those of PEG/glycerin epoxy resin, i.e., 1.4 MPa, 0.04 GPa, and 1.5 MPa, respectively. Moreover, the adhesive strength of the wood-based epoxy resin when adhering to a steel plate was similar to that of the petroleum-based bisphenol A-type epoxy resin (14.6 MPa). Zhang et al. [61] liquefied corn bran with phenol for different durations (5 min–180 min) and then prepared liquefied corn-bran-based epoxy resin (LCBER) by carrying out a reaction between the liquefied corn bran and epichlorohydrin. The LCBER showed an epoxy index of 1.5–3.5 eq./kg according to GB/T 1677-2008 and demonstrated good physical properties, including adhesive property with a tensile adhesive shear strength up to 5.5 MPa according to ISO 6238:1987; thermal stability with T_g up to 104.1 °C and the temperature of 5 wt.% weight loss up to 264.5 °C. Wu et al. [62,63] liquefied Dendrocalamus latiflorus (ma bamboo) in phenol and polyethylene glycol/glycerol, respectively, with H_2SO_4 as catalyst and synthesized copolymer epoxy resins by reacting the liquefied bamboo with bisphenol A and epichlorohydrin in the presence of NaOH. The neat bisphenol A epoxy resin held an EEW of 241.3 g/eq. and viscosity of 3480 c.p.s. The copolymer epoxy resins had EEW values in the range of 254.8 g/eq. to 1173.4 g/eq. and viscosities in the range of 2953 c.p.s. to 29,840 c.p.s., depending on the ratio of bisphenol A/liquefied bamboo. Both the viscosity and EEW of the prepared copolymer epoxy resins increased with the proportion of liquefied bamboo. The copolymer epoxy resins showed good reactivity and could be cured at room temperature. The copolymer epoxy resin, however, demonstrated a lower T_g than neat bisphenol A epoxy resin, and the greater amount of bisphenol A being substituted with the liquefied bamboo, the lower T_g.

Unlike the bio-oil produced from organic solvent liquefaction, the bio-oil produced from fast pyrolysis (also termed pyrolysis oil) usually exhibits a lower hydroxyl number due to the absence of solvent in the process of fast pyrolysis liquefaction [5]. Nevertheless, pyrolysis oil has also been used to synthesize epoxy resins. Barde et al. [64] used a pyrolysis oil from hardwood to synthesize epoxy resin following a two-step glycidylation method with epichlorohydrin in the presence of benzyltriethylammonium chloride ($BnEt_3NCl$) as a phase transfer catalyst and sodium hydroxide (Figure 5). The epoxy resin exhibited an EEW of 314 g/eq. through the titration method. After being cured with Jeffamine T-403, the epoxy resin showed a T_g of 92 °C and storage modulus of 1.88 GPa at room temperature according to dynamic mechanical analysis (DMA), which are higher values than those achieved with a commercial epoxy resin (Epon 828), i.e., 80 °C and 1.77 GPa, respectively. Sibaja et al. [65], from the same research group, synthesized a bio-oil-based epoxy resin via the fast pyrolysis of bio-oil from hardwood (Oak) using a similar procedure involving glycidylation with epichlorohydrin in alkaline conditions. The glycidylated bio-oil possessed an EEW of 333 g/eq. through the titration method, which is approximately half of that of a commercial epoxy resin, EPON 828 (185–192 g/eq). The bio-oil-based epoxy resin was cured with triglycidylated ether of α-resorcylic acid using 4-dimethylaminopyridine. A commercial bio-based epoxy, Entropy Super Sap 100 Epoxy resin, was chosen as a control to evaluate the thermo-mechanical behavior of the bio-oil-based epoxy resin. The comparison results indicated that the mechanical properties of the pyrolysis oil-based epoxy resin were better than those of the commercial counterpart, with dynamic storage moduli from DMA in the range of 1.5–3.4 GPa at room temperature and T_gs above 100 °C.

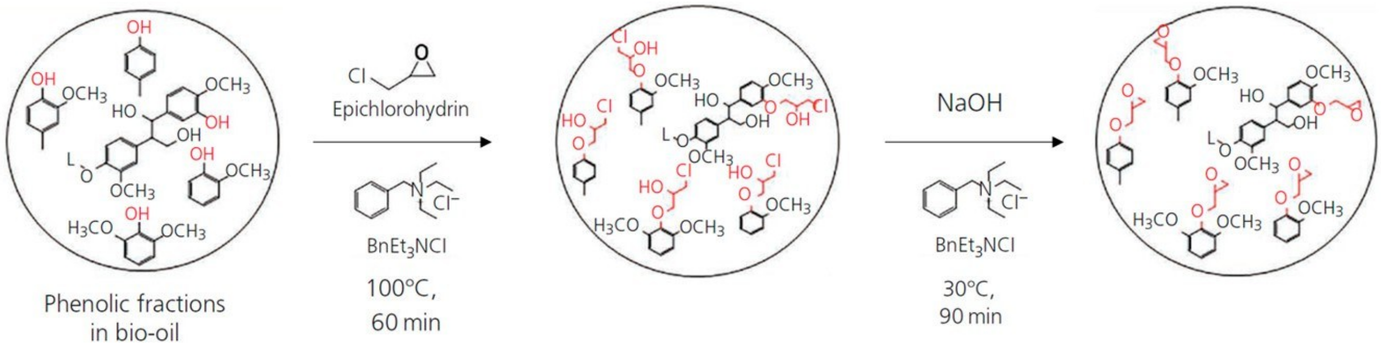


Figure 5. Synthesis of epoxy resin with fast pyrolysis bio-oil from hardwood [64]. The functional group evolution is marked in red.

In spite of the large numbers of hydroxyl groups in the bio-oils produced via hydrothermal liquefaction, there is very limited research on the utilization of the bio-oils produced from hydrothermal liquefaction as bio-polyols for epoxy resin synthesis. Celikbag et al., for the first time, synthesized epoxy resin with the bio-oil produced from hydrothermal liquefaction of loblolly pine [5]. They first produced bio-oil from hydrothermal liquefaction of loblolly pine wood chips in the media composed of water and water/ethanol at 350 °C and 300 °C, respectively, and then used the obtained bio-oils to synthesize epoxy resins. The individual epoxy resin was produced in two steps (Figure 6). The first step was carried out at 80 °C for 1 h, utilizing triethylbenzylammonium chloride as a catalyst in a mixture of bio-oil and epichlorohydrin at a weight ratio of 1:10 followed by the second step, which occurred at room temperature for 2 h, employing sodium hydroxide as a catalyst. The resultant mixture was filtered, and all the solvents were evaporated to obtain a final dark viscous liquid referred to as the bio-oil-based epoxy. The epoxy resins obtained from the bio-oil produced via hydrothermal liquefaction using water and the bio-oil produced via hydrothermal liquefaction using water/ethanol mixture showed EEW values of 230–420 g/eq. and 180–300 g/eq., respectively, according to ASTM D1652-11. The researchers also figured out the optimum amount of catalyst for the production of bio-oil-based epoxy resin and found it had a self-curing capability upon multi-step heating up to 160 °C. The addition of ethanol in the hydrothermal liquefaction processing could improve the thermomechanical property and thermal property of the cured bio-oil-based epoxy resin. The obtained epoxy resin exhibited a modulus of 845 MPa and a T_g of 96 °C along with a cross-linking density of 58.7 mol/m^3 after curing. These results indicated that the bio-oil produced from hydrothermal liquefaction can indeed be used as a substitute for bisphenol A in epoxy synthesis. A noteworthy fact is that the chemical reactivity, thermal property, and mechanical performance of the resultant epoxy resin, as well as the amount of catalyst in the synthesis, are dependent on the hydroxyl (OH) number of the bio-oil. This research demonstrated the potential to replace petroleum-based phenolic resources with bio-oil produced from hydrothermal liquefaction for epoxy resin synthesis. However, no mechanical property was directly evaluated. Furthermore, there is a lack of research outcome that correlates the hydrothermal liquefaction processing parameters with the number of hydroxyl groups in the resultant bio-oil. More research efforts should be devoted to this area in the near future.

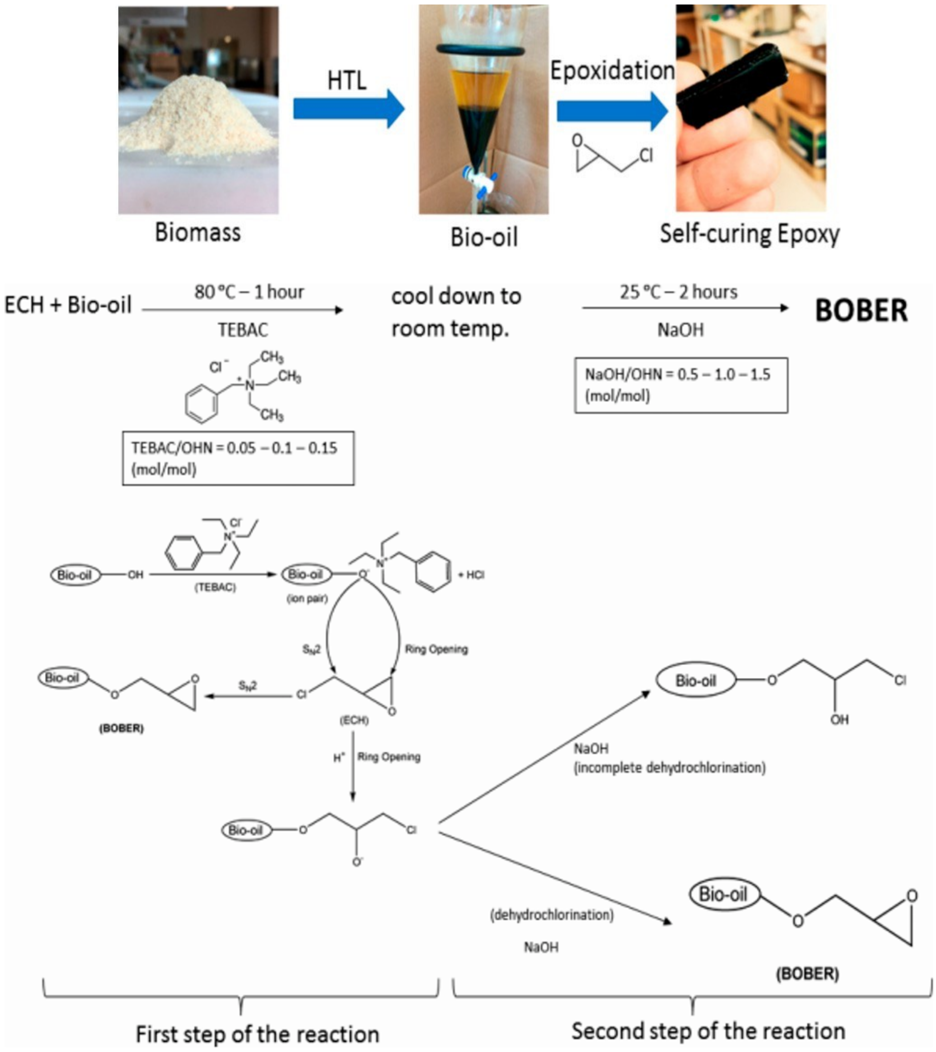


Figure 6. Production of bio-oil-based epoxy resin from the bio-oil acquired via hydrothermal liquefaction [5].

3.2. Blending Bio-Oil with Conventional Petrochemical Epoxy Resins

In addition to synthesizing epoxy resins by substituting bisphenol A with bio-oils produced from thermochemical processing, there has also been research aiming to modify conventional petrochemical epoxy resins by blending them with the bio-oils. Bio-oil is a complex mixture of organic compounds that contains various functional groups, including hydroxyl, carboxyl, carbonyl groups, etc., which can react with epoxide functional groups in epoxy resin to realize cross-linking or curing of epoxy resin. Thus, bio-oil can partially or wholly serve as a renewable and sustainable alternative to curing agents from the petrochemical industry, making it an eco-friendly option for epoxy resin manufacturing.

The bio-oil produced via organic solvent liquefaction has been used to modify petroleum-based epoxy resin. Wu et al. [66] liquefied Cryptomeria japonica (Japanese cedar) wood using polyethylene glycol (PEG-400 & PEG-600)/glycerol as solvent system and H_2SO_4 as the catalyst. They mixed the liquefied wood with a self-made bisphenol A epoxy resin at various weight ratios (100:20, 100:40, and 100:60) and cured it with triethylene tetramine as a hardener. The blended epoxy resins could be cured under room temperature and showed good dry bonding strength up to 12.2 MPa at room temperature according to a compression shear test according to CNS 5809 when being used to glue wood strips. The maximum bonding strength was realized by blending 20 parts of PEG-600-liquefied wood and 100 parts of bisphenol A epoxy, but most of their dry bonding strengths were slightly lower than that of neat epoxy resin (11.4 MPa). Wei et al. [67] liquified switchgrass with an environmentally friendly solvent, diethylene glycol, in the presence of H_2SO_4 at various temperatures in the range of 200–260 °C for 1–3 h and blended the obtained bio-oils with regular bisphenol A/epichlorohydrin epoxy resin (Epon 828) at different weight ratios of epoxy/bio-oil, from 1:1 to 1:4, with triphenylphosphine as a catalyst. The blended resin could be cured by a ramp heating of 30 min at 80 °C, 30 min at 105 °C, 2 h at 150 °C, 1 h at 180 °C, and 1 h at 200 °C. The optimal recipe for liquefaction was 250 °C for 2 h, and the blending ratio for the best mechanical (storage modulus) and thermal properties (degradation temperature from TGA) was 1:1 (wt.). It was concluded that the liquefaction processing parameters and the blending ratios of bisphenol A epoxy/bio-oil were effective in controlling the cross-linking density and thermal/mechanical properties of the resultant epoxy composite materials.

Celikbag et al. prepared a bio-oil from fast pyrolysis of loblolly pine (Pinus spp) in the temperature range of 425–500 °C for ~10 s and mixed the obtained pyrolysis oil with a conventional bisphenol A epoxy resin (Epon 828) to prepare bio-enhanced epoxy resins [35]. The pyrolysis bio-oil was mixed homogeneously with Epon 828 at weight ratios from 1:3 to 1:8 with the aid of tetrahydrofuran as a solvent. Using triphenylphosphine as a catalyst, the prepared bio-enhanced epoxy resin was cured under the conditions of 1 h at 80 °C, 2 h at 150 °C, and 2 h at 200 °C followed by cooling to room temperature. Their results demonstrated that the T_g and cross-linking density of the bio-enhanced epoxy resin after curing decreased with the proportion of pyrolysis oil. The cured bio-enhanced epoxy resins exhibited the highest T_gs of 113 °C and 120 °C, the largest cross-linking densities of 1651 mol/m^3 and 1891 mol/m^3, and the smallest mass loss after acetone extraction (~0.5%) at 1:7 and 1:8 pyrolysis oil/epoxy mixing ratios, respectively. It is noteworthy that the T_gs of the cured bio-enhanced epoxy resins were even comparable to that of the conventional Epon 828 resin cured with different curing agents (93–134 °C). The higher T_g of the epoxy resin prepared with pyrolysis oil could be attributed to the higher OH number of the pyrolysis oil as well as the solvent-free fast pyrolysis process, which prevented the plasticizer effect of small solvent molecules. The promising finding herein is that the pyrolysis oil could be utilized to cure bisphenol A epoxy resin without using any petroleum-based curing agent.

4. Perspectives

So far, bio-oil-based epoxy resins produced from thermochemical processing of sustainable resources have shown some characteristics of engineering thermosetting resin and demonstrated their potential to replace conventional epoxy resins from petrochemical industries. Along with their environmental friendliness and low cost, bio-oil-based epoxy resins also possess advantageous properties, such as their hydrophilic property, which could enhance natural-fiber-reinforced epoxy composite materials due to the good compatibility of the bio-oil-based epoxy resin with natural fibers.

It has to be pointed out that the practical use of bio-oil-based epoxy resins remains a challenge. The bio-oils produced from thermochemical processing have some drawbacks, such as low pH value, high viscosity, large oxygen, water, and solid contents, thermal and chemical instability, etc., which may be problematic for processing and storage. For instance, a low pH could result in corrosion of production and storage facilities. In the meantime, the resultant bio-oil-based epoxy composite materials may have higher water adsorption and less dimensional stability than conventional petroleum-based epoxy composite materials. Thus, the utilization of bio-oil produced from thermochemical processing to synthesize epoxy resins is restricted by those undesired properties [39,47,66].

Furthermore, current research mostly focuses on the synthesis, characterization, and curing of bio-oil-based epoxy resins. There is very limited information about the processability of these epoxy resins. For bio-oil-based epoxy resins alone, common composite processing techniques may be applicable. However, the viscosity of these bio-oil-based epoxy resins must be considered. It was repeatedly reported that bio-oil-based epoxy resins generally have a higher viscosity compared to that of conventional bis-phenol A-type epoxy resins [62,63], and this could influence the filling of the cavity during the resin infusion process of fiber-reinforced composite fabrication within the time limits set with the consideration of proper curing [68].

The most important and the biggest challenge of bio-oil-based epoxy resins is that they normally have a lower T_g, less thermal stability, and reduced mechanical property after curing compared to conventional bisphenol A-based epoxy resins. To the best of our knowledge, bio-oil-based epoxy resins with a T_g higher than 100 °C and modulus larger than 3 GPa have rarely been reported. These inferior properties could be the result of low-molecular-weight components in the bio-oils after thermochemical processing. It is noteworthy that thermochemical processing breaks down large biomass molecules and generates many smaller molecules. The resultant bio-oil is actually a mixture of many different types of molecules with a variety of molecular weights. Small molecules could act as a plasticizer in cured epoxy resins, and thus reduce T_g and lower mechanical strength of the cured composite materials [35,67]. For example, in Kish et al.'s work [34], a bio-oil-based epoxy resin produced from PEG/glycerin-liquefied wood powder (Picea abies) exhibited lower mechanical properties than a conventional petroleum-based counterpart even though the bio-oil-based epoxy resin outperformed the PEG/glycerin epoxy resin (Table 2). This could be a result of low-molecular-weight components as well as a significant amount of remaining high-boiling-point solvent molecules in the bio-oil, for example, ethylene glycol [36]. It is important to point out that the compositions of bio-oils can be completely different depending on the choice of biomass as well as the thermochemical processing technique and conditions being used. Therefore, it is difficult to implement universal quality control for the synthesis and curing of bio-oil-based epoxy resins.

Table 2. Comparison of mechanical properties of the cured epoxy resins produced from the alcohol-liquefied wood bio-oil with those of bisphenol A-type epoxy resin [34].

	PEG400/Glycerin-Liquefied Wood-Based Epoxy Resin	PEG400/Glycerin Epoxy Resin	PEG200 Epoxy Resin	Bisphenol A-Type Epoxy Resin
Tensile strength (MPa)	27.9	1.4	3.5	62.8
Yield stress (MPa)	31.6	-	-	-
Tensile modulus (GPa)	1.27	0.04	0.01	2.06
Lap-shear adhesive strength (MPa)	14.5	1.5	1.7	14.6

Recently, nanofiller materials such as silica nanoparticles, electrospun nanofibers, carbon nanotubes, and many more have demonstrated their outstanding capability to improve the mechanical properties of polymer matrix composite materials [69–71]. The advantage of nano-scaled fillers over traditional fillers in polymer composite materials is their outstanding specific surface area and consequently the remarkably large interfacial area between the polymer matrix and nanofillers, which tends to induce a significantly stronger interfacial bonding. This concept is already in practice to improve the mechanical properties of petroleum-based epoxy resins [72,73]. The same concept and knowledge of nanofillers can also be applied to increase the mechanical performance of bio-oil-based epoxy resins [4]. For example, a bio-based nanocomposite with petroleum-based unsaturated polyester resin, plant-oil-based bio-resin (epoxidized methyl linseedate), and nanoclay demonstrated excellent mechanical properties [74]. The integration of nanofiller materials with bio-oil-based epoxy resins not only improves the mechanical performance of the epoxy resins to a greater extent but also holds great potential to improve a multitude of physical properties, like flame resistance, uptake of solvent, thermal stability, and rate of biodegradability [75,76].

Finally, speaking of practical/commercial applications, large-scale production of bio-oil-based epoxy resins from thermochemical processing of sustainable resources needs to be addressed in the future. It is essential for us to develop the following: (1) facilities for biomass feedstock; (2) strategies to reduce small molecules or increase the number of molecules with a large molecular weight in current thermochemical manufacturing process; and (3) effective quality control to retrieve consistent bio-oil-based epoxy products.

5. Conclusions

Bio-oils from biomass that undergoes thermochemical processing methods including organic solvent liquefaction, fast pyrolysis, and hydrothermal liquefaction have been successfully employed to synthesize epoxy resins or modify conventional epoxy resins from the petrochemical industry. These environmentally friendly and sustainable bio-oil-based epoxy resins have shown promising characteristics similar to those of engineering thermosetting resins and demonstrated their potential to replace petrochemical epoxy resins. It is noteworthy that there are fewer reports on the synthesis/modification of epoxy resins with bio-oils produced from hydrothermal liquefaction, which deserves more attention due to its use of water as a liquefying solvent and relatively low cost. Despite continuous research attempts in this field, bio-oil-based epoxy resins are still in their infancy for practical use due to the biggest challenge so far of reaching a mechanical performance that is comparable to that of conventional bisphenol A-based epoxy resins after curing. Significant research efforts should be devoted to the reduction in small molecules in the process of thermochemical processing as well as the integration of bio-oil-based epoxy resin with nanoscale fillers to eventually acquire bio-oil-based epoxy resins with a similar mechanical performance to conventional petroleum-based epoxy resins after curing. All in all, bio-oil-based epoxy resins are young but promising sustainable materials and deserve much more attention and research efforts in the following years.

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