Applications of Bio-Epoxies in Composites

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Despite the reliability of traditional epoxy systems, the increasing demand for sustainability has driven researchers and industries to explore new bio-based alternatives. Additionally, natural fibers have the potential to serve as environmentally friendly substitutes for synthetic ones, contributing to the production of lightweight and biodegradable composites. Enhancing the mechanical properties of these bio-composites also involves improving the compatibility between the matrix and fibers. In this sense, the use of bio-epoxy resins facilitates better adhesion of natural composite constituents, addressing sustainability and environmental concerns.

bio-based thermosets | lignin | cardanol | vegetable oils | natural fibers

1. Introduction

By the name of ethoxyline resins, epoxy resins were patented by the German P. Schlack in 1934. Since then, they have gained growing significance across a wide range of applications. These polymers consist of two components: hardner and resin which exothermically react. The epoxy synthesis is made in two phases: the monomer formation and the polymerization. The latter phase includes the harderner use, commonly the epichlorohydrin (ECH), which reacts with the bisphenol A (BPA) producing the bisphenol A diglycidyl ether (DGEBA). Despite the most common type of epoxy resin is the DGEBA-based epoxy resin (**Figure 1**), Bisphenol F or brominated can be used instead of BPA. The resulting epoxy polymers are more chemically resistant and less viscous, since for the same weight they have more epoxy groups than BPA.

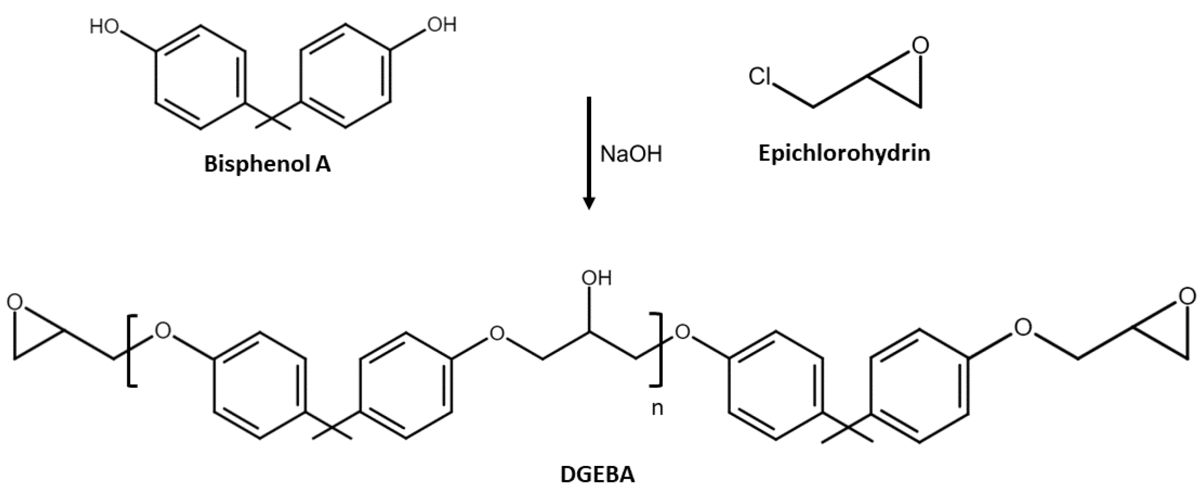

Figure 1. Synthesis of epoxy resin from BPA and ECH.

The epoxy content, quantified by the epoxide equivalent weight (EEW), representing the quantity of epoxy resin grams required to produce 1 mole of epoxy groups, serves as a pivotal parameter in assessing the mass of hardening or curing agents to optimize the polymerization process. The ultimate properties of thermosetting materials are contingent upon the specific combination of hardening agents and epoxy resins. For instance, the glass transition temperature of cured resins strictly depends on the molecular structure of the hardening agents. The hardening process, indeed, significantly augments the final properties of the resin, encompassing mechanical and thermal attributes. Notably, cure at lower temperatures, such as at room temperature, results in a progressive increase over time in both tensile strength and elastic modulus [1].

Nowadays epoxy resins constitute a preeminent class of thermosetting polymers extensively employed in different fields including engineering [2], electronics [3], civil construction [4], and biomedical industries [5]. This widespread adoption is attributable to their exceptional mechanical attributes, chemical and water resistance, long-term robustness, adaptability, and facile manufacture. In composite applications epoxy can be used either as filler (or modifiers) to enhance reinforcements of polymer composites or as thermoset matrix reinforced with (synthetic or natural) fibers [6].

Despite the great reliability guaranteed by epoxy thermosets also in high-performing applications (like in aerospace [7] and automotive fields [8]) their use presents some drawbacks. First of all, most of the epoxies come from fossil feedstocks. The majority is highly toxic, such as BPA and ECH, which are carcinogenic and mutagen endangering the human health [9][10]. Although chemical recycling of epoxies has also been investigated [11][12][13], it is proved still quite difficult. Once the hardening process is done, it is impossible to separate the components again, which hold together thanks to strong chemical bonds. Epoxy resins can be disposed of through pyrolysis, a high energy-consuming process, which however under high temperature degrade them into unrecoverable fuel. Alternatively, it is possible to modify the critical parts of such composites to make them recyclable, for instance transforming the hardener component. In this regard, it is worth mentioning Recyclamine™ (by Connora Technologies) as a new class of high-performance amine-based epoxy curing agent. Such hardeners, thanks to enabling cleavage points at crosslinking sites, allow the transformation of thermoset epoxy into a thermoplastic state [14].

2. Bio-Epoxy Resins

Based on the aforementioned observations, the recent surge in the demand for sustainability has prompted a heightened effort of researchers and industries towards utilizing bio-derived feedstocks as a substitute for DGEBA. Epoxy resins, indeed, can be synthesized from various types of bio-based materials. The chemistry of epoxy thermoset itself suggests the type of sources to select as feedstocks. Wood takes center stage due to its exceptional resistance to heat and its non-melting characteristics. Comprising primarily cellulose, lignin, and water, each with its distinct melting point, wood, when subjected to heat, undergoes a transformation, yielding diverse substances like charcoal, methanol, and carbon dioxide. Thus, *lignin* can be regarded as a viable environmentally friendly substitute for BPA, serving as a source of phenolic compounds. The content of these compounds is not easily predictable through different extraction processes, as reported in the review by Lu and Gu [15]. Lignin is readily accessible, ranking second only to cellulose as the most abundant organic material on Earth, and can be extracted from various sources such as wood, cotton, jute, hemp, and black liquor. Identifying the source and extraction method is crucial, as it inevitably influences the structure and properties of the final product, as discussed later. Hence, lignin, due to its abundance, sustainability, and inherent polyphenolic structure, has been regarded as a promising renewable raw material for bio-based epoxy resins [16][17][18][19][20][21][22][23]. In addition, lignin depolymerization offers a route to generate alternative bio-based thermosetting systems, as those derived from *vanillin* [24][25][26]. Cellulose or lignin can be utilized also to derive *resorcinol* [27][28][29], a phenolic compound from which ensuing polymers find applications as adhesives, coatings, plastic moldings, and in the formulation of rubber composites. Furthermore, various types of wood, including oak, cedar, walnut, and select mahoganies, naturally contain *tannic acid*, a water-soluble polyphenolic compound with a substantial molecular weight. This compound can be employed as a bio-curing agent or epoxy monomer in epoxy systems [30][31][32][33][34] as well as *rosin*, which is another important abundant natural product extracted from conifer trees [35][36].

One of the notable alternatives to BPA among bio-aromatic compounds is *cardanol*, a brown liquid extracted from cashew nut shell liquid (CNSL). Given the substantial scale of cashew nut production, particularly in Africa and Asia, such non-edible compounds constitute a notably abundant resource in nature. A cardanol-derived epoxy formulation can be synthesized through either the epoxidation of cardanol or its utilization as a curing agent [37][38][39][40][41][42]. Moreover, bio-content can be integrated into epoxy systems using natural polysaccharides, such as *D-glucose* [43]. Further, as food waste-based feedstock, *furan* should be mentioned, which presents a compelling potential as substitute for phenyl building blocks derived from petroleum in epoxy thermosets [44][45][46][47][48]. This organic aromatic compound, composed of four carbon atoms and one oxygen, can be derived from bagasse, the residual material from sugar cane processing, as well as from corn cobs or other biomass sources. Additionally, clove, cinnamon, pepper, and turmeric can be considered viable bio-sources for epoxy, especially in the extraction of *eugenol* [27][28][46][49][50]. This phenolic compound is found in the oils of these plants and has demonstrated efficacy as a curing agent, flame retardant, or as an integral component in epoxy monomers. Epoxidation reaction also offers a possible pathway for incorporating natural oils into bio-epoxy resin formulations. Among edible oils, options such as *soybean* [51][52][53][54][55], *linseed* [54][56][57][58] and *hemp* [55][59][60], stand out as potential sources for developing environmentally sustainable epoxy systems, as extensively analyzed in the comprehensive overview by Mustapha et al. [61]. From triglyceride vegetable oils, such as coconut, soybean or palm oil, it is possible to obtain the *glycerol*, which is also commercially used to produce commercial resins [62][63][64] and proposed in the literature for the synthesis of new epoxy systems [33][65][66]. Furthermore, exploration into the integration of non-edible oils such as *castor* [67][68], *karanja* [32], and *canola* [69].

3. Proposed Applications

The thermomechanical and adhesion properties, along with the low cost of bio-based epoxy resins, suggest extensive practical applications as coatings and adhesives. Furthermore, these applications demonstrate an enhancement in the corrosion resistance properties of conventional epoxy systems when using bio-based raw materials.

3.1. Neat Bio-Epoxies

Despite the efficiency of epoxy coatings, long exposure to environmental parameters might compromise their corrosion resistance. Due to the presence of phenolic compounds and functional groups, lignin, vanillin, and TA have the potential to inhibit oxidation. In [70], the durability of epoxy as a coating system for steel components was improved through the addition of acetylated lignin, leading to a significant enhancement compared to traditional coal tar epoxy, without compromising the adhesive properties. Chang et al. [71] investigated the synergic enhancing effect of TA, DA-LIM, and nano-ZrO2

on the corrosion resistance of epoxy as coating protection for rusted steel. The rust conversion action of TA and the enhancement of the adhesion properties with steel substrates were further fostered by the presence of DA-LIM, preventing the coating/substrate interface from being touched by corrosion agents and avoiding TA leakage. Protection from UV radiation and photodegradation can also be successfully achieved through epoxidized vegetable oils as attested by Ammar et al. [72], who discussed the benefits of ESO in reducing corrosion in steel coatings. Branciforti et al. [73] practically used ELO and ESO for stereolithography, ensuring UV absorption as alternatives to acrylate monomers. These latter are a source of toxicity, which was observed to persist even after UV light treatment following the curing of 3D objects. For this reason, epoxidized vegetable oils were used as ecological alternative solutions. Coating application for mild steel and aluminum substrates was proposed by Kathalewar and Sabnis [74] for a cardanol-based epoxy resin. Bio-content from 40 to 50% ensured improved corrosion resistance compared to a counterpart DGEBA-epoxy system.

3.2. Bio-Fillers and Epoxy Composites

Comprehensively addressing sustainability concerns and achieving a satisfactory level of mechanical performance is imperative to enable practical applications of composites. To satisfy these requirements, natural and biodegradable waste feedstock—such as eggshell [75], seashell [76], plant char [77], coffee grounds [78], or even chicken feathers [79]—can be used as fillers in the matrix. The above-mentioned literature reveals that the addition of these substances enhanced the mechanical and thermal properties together with the amount of renewable content.

Apart from fillers, some research has analyzed the possible bio-composites applications. An example is the work by Ghoushji et al. [80], which investigated the crashworthiness properties of ramie/bio-epoxy composite square tubes with different lengths, and assessed their suitability as potential energy absorbing components. From static axial compression tests, the best properties in terms of average load and specific energy absorption (SEA) were observed for short tubes, and a significant improvement in SEA was detected as the number of layers increased. Since the geometry of the tubular structure also affected the performance results, more geometries need to be investigated to obtain a more complete idea of the suitability of ramie/bio-epoxy tubes for crash applications.

Another field in which bio-epoxy resins and relevant composites can be applied is the aviation sector. In this context, Ramon et al. [81] provided an overview of different bio-based epoxy systems (derived from natural oil, furan, lignin, and rosin) and compared their mechanical and thermal performance results with the petroleum-based systems already used in this sector. The results highlighted that these innovative resin systems can be considered favorable candidates to replace conventional epoxy resins for aircraft interiors, although some work still needs to be conducted. Another attempt in this regard was made by Yi et al. [82], whose described their efforts to develop an interior side panel for an aircraft and the body of an electric racing car using honeycomb sandwich composites and a 30% bio-content rosin-based epoxy resin.

Interesting applications were identified in connection with the use of vegetable oils such as ESO and karanja oil. In the first case, Pansumdaeng et al. [51] demonstrated the potential of fully bio-based ESO epoxy thermosets for the production of energy harvesting devices. In the second case, Kadam et al. [32] proposed an alternative application for the karanja oil-based epoxy thermoset. In addition to the examination of mechanical properties and biodegradability, a larvicide effect against mosquitoes on paper coating was analyzed. Hence, the application of karanja oil-based bio-epoxy on a paper coating revealed a valid protection against mosquito larvae, presenting a compelling solution to control dengue fever transmission through these vectors.

Finally, also 3D printing involves bio-based materials: resorcinol epoxy acrylated (REA) resin combined with synthetic fibers—such as glass, nylon, and polyester fibers—was used to create objects usinf this technology. A complete characterization of these three composites was made by Desai and Jagtap [29], who declared that nylon- and polyester-reinforced composites exhibited the best properties to be applied in this field.

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