Intrinsically flame-retardant bio-based epoxy thermosets: A review

Xin Wang, Wenwen Guo, Lei Song, Yuan Hu

PII: S1359-8368(19)32780-5
DOI: https://doi.org/10.1016/j.compositesb.2019.107487
Reference: JCOMB 107487

To appear in: *Composites Part B*

Received Date: 15 June 2019
Revised Date: 23 September 2019
Accepted Date: 27 September 2019

Please cite this article as: Wang X, Guo W, Song L, Hu Y, Intrinsically flame-retardant bio-based epoxy thermosets: A review, *Composites Part B* (2019), doi: https://doi.org/10.1016/j.compositesb.2019.107487.

Intrinsically flame-retardant bio-based epoxy thermosets: A review

Xin Wang, Wenwen Guo, Lei Song*, Yuan Hu*

State Key Laboratory of Fire Science, University of Science and Technology of China, 96 Jinzhai Road, Hefei, Anhui 230026, P. R. China.

**Corresponding authors Tel/Fax: +86-551-63601664; E-mail address: yuanhu@ustc.edu.cn (Y. Hu), leisong@ustc.edu.cn (L. Song).*

Abstract

At present most of epoxy thermosets is dependent on petroleum-based resources especially diglycidyl ether bisphenol A (DGEBA)-type epoxy monomers produced from epichlorohydrin (ECH) and bisphenol A (BPA). Owing to the limitation of the greenhouse gas emission, development of the bio-based epoxy thermosets is gaining increasing attention to substitute the petroleum-based ones. However, the bio-based epoxy thermosets possess similar high flammability to their petroleum-based counterparts. It is thereby necessary to endow them with flame retardancy. This review article aims to summarize the most relevant and up-to-date advances in intrinsically flame-retardant bio-based epoxy thermosets. First, the approaches to synthesis of bio-based intrinsically flame retardant epoxy monomers are introduced briefly. Subsequently, the review focuses in particular on partly bio-based intrinsically flame retardant epoxy thermosets from either bio-based epoxy monomers or bio-based curing agents in terms of their flame retardant property as well as mechanical property and thermal stability. Additionally, the fully bio-based intrinsically flame retardant epoxy thermosets are also reviewed. Finally, we will provide a brief comment on opportunities and challenges for future growth of bio-based intrinsically flame retardant epoxy thermosets.

Keywords: Bio-based epoxy; Intrinsically flame retardant; Mechanical properties; Thermal properties

1. Introduction

Epoxy thermosets, as one of the most important thermosets, possess many favorable performances including excellent mechanical properties, good chemical and electrical resistance, superior moisture resistivity, and high dimensional stability [1-5]. These favorable performances make epoxy thermosets suitable for various end-use applications such as Electrical & Electronics, paints and coatings, adhesives, fiber-reinforced advanced composites, etc [6-9]. According to the Business Communications Company (BCC) Research report, the global market for epoxy thermosets was valued at USD 7.0 billion in 2015 and is forecasted to reach USD 10.2 billion in 2021 at a compound annual growth rate of 6.3% between 2016 and 2021 [10]. Currently, 90% global demand of epoxy thermosets originate from petroleum-based diglycidyl ether bisphenol A (DGEBA)-type epoxy monomers, which are prepared from reaction between epichlorohydrin (ECH) and bisphenol A (BPA) in the presence of sodium hydroxide [11]. Despite of these favorable performances of DGEBA aforementioned, the production of DGEBA-type epoxy monomers is mainly dependent on fossil resources, which is unfavorable to limit greenhouse gas emission [12, 13].

In this context, a large amount of efforts has been made to develop bio-based epoxy thermosets from renewable resources such as plant oil, furan, lignin, rosin, vanillin, itaconic acid, *etc*, to substitute petroleum-based epoxy thermosets [14, 15]. These bio-based epoxy thermosets display comparable properties to their petroleum-based counterparts but eliminate the drawbacks of petroleum-based counterparts. However, like petroleum-based epoxy, bio-based epoxy thermosets suffer from high flammability, which hinder their applications in the fields of cars, trains and airplanes, construction, and electronic appliance. It is thereby imperative to impart flame retardant property to bio-based epoxy thermosets. Generally, flame retardant technology can be divided to two primary categories: additive-type and reactive-type. The former one involves the physical blending of flame retardant additives to polymers, which usually requires high loading of flame retardant additives resulting in migration and leaching of additives that could have harmful effect due to human exposure, as well as deterioration in mechanical strength and thermal stability [16]. The latter one, also known as intrinsically flame retardant technology, involves the incorporation of flame retardant monomers into polymer networks through covalent bonds, which overcomes the drawbacks of additive-type flame retardants. In this review, we are focusing on intrinsically flame retardant bio-based epoxy thermosets.

The objective of this review is hence to provide an overview of the field by highlighting and discussing the state-of-the art, as well as future perspectives of intrinsically flame retardant epoxy thermosets derived from renewable resources. The synthetic approaches are mentioned to optimize the design of intrinsically flame retardant bio-based epoxy thermosets. Special emphasis will be focused on partly bio-based intrinsically flame retardant epoxy thermosets from either bio-based epoxy monomers or bio-based curing agents in terms of their flame retardant property as well as mechanical property and thermal stability. Furthermore, the fully bio-based intrinsically flame retardant epoxy thermosets are also reviewed. Finally, we will provide a brief comment on opportunities and challenges for future growth of bio-based intrinsically flame retardant epoxy thermosets.

2. Approaches to synthesis of bio-based intrinsically flame retardant epoxy monomers

The synthetic routes of bio-based intrinsically flame retardant epoxy monomers are very similar to the traditional ones, which are summarized as follows.

2.1. From epichlorohydrin (ECH)

The production of epoxy monomers from ECH results from the condensation reaction between phenols and ECH using sodium hydroxide as catalyst, as diagrammatically shown in Scheme 1. According to the previous report [17], the condensation reaction between the phenate ion (ArO^-) and ECH has two competitive mechanisms: (i) nucleophilic substitution (mechanism S_N2) with removal of the sodium chloride; (ii) ring opening of ECH with phenate ion followed by intramolecular cyclization (S_Ni) of the corresponding alcoholate. In this approach, it is crucial to synthesize phenols with flame retardant elements such as phosphorus, silicon and nitrogen, followed by reaction with ECH. This approach is the most popular to design bio-based intrinsically flame retardant epoxy monomers.

2.2. From double bond oxidation

Another approach to the production of bio-based intrinsically flame retardant epoxy monomers is the peroxidation of a carbon−carbon double bond (Scheme 2). The reactivity of the carbon−carbon double bond differs from the chemical surroundings of the double bonds. The oxidation of the double bonds in the aliphatic chains just requires the use of hydrogen peroxide [18]. However, stronger oxidative reagents such as m-chloroperbenzoic acid (m-CPBA) are needed when the double bonds belong to glycidyl type [19]. Additionally, selective epoxidation method for internal and terminal carbon−carbon double bonds was also reported by Colladon et al. [20]. Hydrogen peroxide together with a Pt(II) complex showed high selectivity in epoxidation for terminal carbon−carbon double bonds, while m-CPBA only favors epoxidation for internal double bond. The production of the intrinsically flame retardant epoxy monomers derived from bio-mass with C-C double bonds are usually adopted by this method.

3. Partly bio-based intrinsically flame retardant epoxy thermosets

Epoxy thermosets are prepared through formation of three-dimensional cross-linking networks from chemical reaction between epoxy monomers and curing agents. In this review, if the resultant epoxy thermoset is obtained from bio-based epoxy monomer plus petroleum-based curing agent or petroleum-based epoxy monomer plus bio-based curing agent, we call it partly bio-based epoxy thermoset. The following section will review partly bio-based intrinsically flame retardant epoxy thermosets from either bio-based flame retardant epoxy monomers or bio-based flame retardant curing agents.

3.1 Bio-based flame retardant epoxy monomers for thermosets

This section will highlight and discuss the state-of-the-art of thermosetting epoxy monomers derived from a wide variety of renewable resources including fatty acid, eugenol, vanillin, daidzein, furan, itaconic acid, etc. According to the chemical structure, the bio-based flame retardant epoxy monomers are divided into three categories: Bio-based aromatic epoxy monomers, bio-based epoxy monomers derived from terpenes and bio-based aliphatic epoxy monomers.

3.1.1 Bio-based aromatic epoxy monomers

Daidzein-based epoxy monomers. Daidzein is a natural bisphenol compound that can be isolated from soybeans [21]. It has been regarded as a green product for wide applications in the food and pharmacy industry [22]. Very recently, Dai et al. synthesized a diglycidyl ether of daidzein (DGED) through glycidylation reaction between daidzein and ECH (Scheme 3) [23]. The DGED was subsequently cured by 4, 4’-diaminodiphenylmethane (DDM) to obtain a thermosetting epoxy, and DGEBA cured by DDM was prepared as a comparative sample. Without the incorporation of additional flame retardants, the DGED/DDM thermosets displayed a relatively high limiting oxygen index (LOI) of 31.6% and V-0 classification in UL-94 vertical burning test, whereas the DGEBA/DDM showed a LOI of 24.5% and no classification in UL-94 vertical burning test. The superior flame retardancy of the DGED/DDM thermosets could be attributed to the excellent char-forming ability of the DGED, as evidenced by the char yield of 43% at 800 °C under nitrogen. The notably enhanced T_g and mechanical properties were ascribed to the high cross-link density of the cured DGED resulted from the dimerization of benzopyrone ring. As far as the outstanding integrated properties are concerned, daidzein is considered to be an ideal candidate for synthesis of high-performance epoxy thermosets, but the only negative outcome is the lower initial thermal degradation temperature of the DGED/DDM thermosets than that of the DGEBA/DDM thermosets.

Eugenol-based epoxy monomers. Eugenol is a major component of clove oil, which is less toxic and relatively cost-effective [24]. The chemical structure of eugenol simultaneously contains reactive phenolic hydroxyl group and allyl group, which could be used to synthesize bio-based epoxy through either glycidylation reaction with ECH or oxidation of double bond. Due to its unique structure, eugenol has gained considerable attention in the field of preparation of bio-based epoxy thermosets [15, 25-30]. Among these studies, there are several eugenol-based epoxy thermosets with intrinsical flame retardancy [29-31]. A eugenol-based difunctional epoxy monomer named TPEU-EP was synthesized by Wan et al. through two steps (Scheme 4a), and then cured by 3, 3’-diaminodiphenyl sulfone (33DDS) [29]. The TPEU-EP/33DDS system revealed a higher LOI of 26.8% than the DGEBA/33DDS (23.5%). In the microscale combustion calorimeter (MCC) measurements, the peak heat release rate (PHRR) and the total heat release (THR) of the TPEU-EP/33DDS were decreased by 68% and 40%, respectively, compared to those of the DGEBA/33DDS. In the UL-94 vertical burning test, the TPEU-EP/33DDS could self-extinguish in 24 s, while the DGEBA/33DDS burned out finally (Fig. 1), indicating intrinsic flame retardancy of the TPEU-EP/33DDS. In Wan's next work [30], another eugenol-based difunctional epoxy monomer named DEU-EP was synthesized (Scheme 4a) and cured by DDM. The PHRR and THR of the DEU-EP/DDM were reduced by 55% and 38%, respectively, as compared to those of the DGEBA/DDM in the MCC measurements. As well, the DEU-EP/DDM could self-extinguish in 10 seconds, whereas the DGEBA/DDM could not in the horizontal burning test. However, in Wan's studies, there is still space to further improve the performances of eugenol-based epoxy thermosets, like failure in UL-94 V-0 classification as well as deterioration in thermal stability in terms of lower T_g and initial thermal degradation temperature.

In order to further improve the flame retardancy of the eugenol-based epoxy thermosets, flame retardant elements like phosphorus and silicon are considered to incorporate into eugenol-based epoxy monomers. Faye and co-workers synthesized an eugenol-based epoxy monomer, tri(epoxized-eugenyl)phosphate (TEEP) (Scheme 4b) [31]. The TEEP cured by meta-xylylenediamine (MXDA) and 2,2'-(Ethane-1,2-diylbis(oxy)) bis(ethan-1-amine) (EDR-148) displayed a T_g of 84 °C and 62 °C, respectively, whereas the DGEBA/MXDA and the DGEBA/EDR-148 exhibited a much higher T_g of 116 °C and 98 °C. The presence of the methoxy groups in the TEEP was believed to induce undesirable effect on the T_g.

Due to the presence of the phosphate esters structure, the TEEP/MXDA and the TEEP/EDR-148 also showed lower thermal stability than their DGEBA counterparts. But a much higher char yield at 600 ^{o}C was observed for the TEEP/MXDA (33%) and the TEEP/EDR-148 (36%) in TGA test. Such a high char yield is favorable for improving flame retardancy. In another work, Miao et al. also synthesized the TEEP thermosets cured by DDM [32]. The LOI increased to 31.4% and the UL-94 vertical burning behavior enhanced to V-0 classification for the TEEP/DDM system. In the MCC measurements, the PHRR and the THR of the TEEP/DDM were 63.1% and 57.4% lower than those of the DGEBA/DDM. Furthermore, the TEEP/DDM presented lower dielectric constant and dielectric loss than the DGEBA/DDM, which is suitable for electrical and electronic applications. Very recently, Li et al. reported three kinds of silicone-containing eugenol-based epoxy monomers (SIEEP2, SIEEP4, and SIEPEP) (Scheme 4c) [33]. The LOI of the DGEBA cured by 4, 4’-diamino diphenyl sulfone (DDS) was 22.8%, whereas that for the SIEEP2/DDS, SIEEP4/DDS and SIEPEP/DDS was 26.0%, 28.0% and 31.0%, respectively. Although the PHRR and the THR of the SIEEP2/DDS, the SIEEP4/DDS, and the SIEPEP/DDS measured by cone calorimeter decreased obviously compared to those of the DGEBA/DDS, the time to ignition (TTI) shifted to lower temperature which was undesirable for flame retardant materials. Moreover, these silicone-containing eugenol-based epoxy monomers also displayed a relatively lower viscosity (<2.5 Pa·s) than the DGEBA (10.7 Pa·s) which was attractive for composites and prepregs applications. Ecochard *et al.* synthesized three kinds of phosphorylated eugenol-based epoxy thermoset

(TEEP, DEEP and DEEP-Ph, Scheme 4b and 4d) cured by MXDA [34]. In the MCC measurements, although the PHRR and the THR of the TEEP, DEEP and DEEP-Ph thermosets were reduced significantly compare to those of the DGEBA, no significant difference was observed between the TEEP, DEEP and DEEP-Ph thermosets, suggesting phosphate and phosphonate groups contributed equally to promote char and reduce flammability.

Furan-based epoxy monomers. Owing to a lot of merits including high bio-safety, ready availability and desirable biodegradability, furan-based chemicals have been identified as the top value-added building blocks for technology development by the U.S. Department of Energy [35]. Furan-based chemicals have also been considered to potentially substitute petroleum-based phenyl building blocks in synthesis of thermosetting materials because of their aromatic structures. Over the past decades, furan-based chemicals have widely been used as starting materials for synthesis of bio-based epoxy thermosets [36, 37]. However, only a limited number of furan-based epoxy thermosets focus on the flame retardancy. Miao et al. synthesized a bis(2-methoxy-4-(oxiran-2-ylmethyl)phenyl) furan-2,5-dicarboxylate (EUFU-EP) (Scheme 5a) [38]. The MCC tests manifested that both the PHRR and the THR of the EUFU-EP cured by methyl hexahydrophthalic anhydride (MHHPA) were 19.0% lower than those of the DGEBA/MHHPA (Fig. 2), which was attributed to the higher char yield. The highly compact aromatic rings in EUFU-EP accounted for the higher char yield that induced condensed-phase flame-retardant mechanism. The dynamic mechanical analysis (DMA) measurements indicated that the cured

EUFU-EP/MHHPA thermoset had higher T_g (153 °C) than the DGEBA/MHHPA thermoset (144 °C), owing to the presence of the rigid rod-like aromatic ester and furan structures in EUFU-EP. Similar to other bio-based epoxy thermosets, however, the cured EUFU-EP/MHHPA thermoset exhibited lower initial degradation temperature than the DGEBA/MHHPA thermoset, which is unfavorable for applications that require high thermal resistance.

Another two furan-based epoxy monomers, 2,5-bis[(2-oxiranylmethoxy) methyl]furan (BOF) and bis-furan diepoxide (OmbFdE), were reported very recently, as illustrated in Scheme 5b [39]. The BOF and the OmbFdE were cured with three different curing agents: 2, 2’-oxybis(ethan-1-amine) (DEGA), 2, 2’-(ethane-1,2-diylbis(oxy))bis(ethan-1-amine) (TEGA), and 2, 2’-((oxybis(ethane-2,1-diyl))bis(oxy))bis(ethan-1-amine) (TGDE) (Scheme 5b). Comparison between the OmbFdE/amine and the BOF/amine were studied to evaluate the effect of both furan cores and the ether motifs on the thermal property and the flame retardancy of the thermosets. In the burning test, the BOF/DEGA and the BOF/TEGA burnt out, while the OmbFdE/TEGA can self-extinguish within 30 seconds (Fig. 3). DSC thermograms indicated that the OmbFdE/amine and the BOF/amine showed a relatively low T_g (7~25 ^{o}C), which may allow their potential application as thermo-responsive polymers between ambient and body temperatures.

Vanillin-based epoxy monomers. Vanillin is a non-toxic and renewable product which can be produced from depolymerization of lignin. It contains an aromatic ring structure with hydroxyl and aldehyde functional groups, which enables it to be served as a fascinating building block for preparation of bio-based epoxy thermosets [40-42]. Until now, vanillin-based epoxy with intrinsic flame retardancy has been rarely reported. Wang *et al.* synthesized two vanillin-based epoxy monomers (EP1 and EP2), as illustrated in Scheme 6 [42]. The cured EP1/DDM and EP2/DDM showed excellent flame retardancy compared to the cured DGEBA/DDM. Specifically, the LOI value for the EP1/DDM and the EP2/DDM was 31.4% and 32.8%, respectively, while that for the DGEBA/DDM was 24.6%; moreover, both the EP1/DDM and the EP2/DDM achieved UL-94 V-0 classification. The authors attributed the excellent flame retardancy to the intumescent and dense char formation ability of the EP1/DDM and the EP2/DDM (Fig. 4). Additionally, the EP1/DDM and the EP2/DDM possessed relatively high T_g value of 183 and 214 ^{o}C, much higher than the cured DGEBA/DDM with T_g of 166 °C. The properties of vanillin-based epoxy thermosets could be easily tailored by adjusting the chemical structures of diamines serving as coupling agent in the synthesis process.

Cardanol-based epoxy monomers. Cardanol is a cost-effective and available by-product of the cashew industry, which could be used as a versatile platform for bio-based polymers and additives [43]. Ecochard *et al.* reported a phosphorylated cardanol based epoxy thermoset (TECP, Scheme 7) cured by MXDA [34]. As observed by cone calorimeter test, the TECP/MXDA thermoset showed a PHRR of 708 kW/m^2, which was much lower than the DGEBA/MXDA (1486 kW/m^2), but its THR (20.4 kJ/g) was very close to the DGEBA/MXDA (22.1 kJ/g), which was assigned to the aliphatic chains of cardanol. Undoubtedly, these aliphatic chains consisted of a high amount of carbon and hydrogen, contributing to heat release. It was also found that the phosphorylated eugenol based epoxy exhibited superior flame retardancy over the phosphorylated cardanol based one.

3.1.2 Bio-based epoxy monomers derived from terpenes

Rosin-based epoxy monomers. As an abundant and natural product, rosin is produced by heating fresh tree resin to remove the volatile liquid terpenes [28]. The production of rosin is approximately 1.2 million tons every year [44]. It has rigid hydrogenated phenanthrene ring in the molecular structure which makes it suitable as an alternative to DGEBA. Although the use of rosin and its derivatives in preparation of bio-based epoxy thermosets has been extensively investigated [15, 45, 46], the flame retardant rosin-based epoxy thermosets has rarely reported up to now. One example is a rosin-based siloxane epoxy monomer (AESE) that was prepared by the reaction of ethylene glycol diglycidyl ether modified acrylpimaric acid (AP-EGDE) with polymethylphenylsiloxane (PMPS) (Scheme 8) [47]. Table 1 lists the LOI value of the samples. It can be seen that the incorporation of PMPS results in the improvement in the LOI value compared to the AP-EGDE/MHHPA thermosets. The highest LOI value of 30.2% is observed for the AESE30/MHHPA (the number represents the PMPS weight percentage in the AESE) among the samples. Note that the char yield for both the AESE40/MHHPA and the AESE50/MHHPA is much higher than that for the AESE30/MHHPA, but their LOI value is lower than that of the AESE30/MHHPA. The authors attributed this abnormal phenomenon to that the initial decomposition temperature for the AESE40 and the AESE50 was too high to form a protective layer. Moreover, the LOI value of AESE30/MHHPA (chemical bonding between AP-EGDE and PMPS) is higher than that of PAESE30/MHHPA (physical mixture of AP-EGDE and PMPS). Owing to the presence of the flexible chains of the PMPS, all the AESE/MHHPA thermosets display a relatively low tensile strength (< 15 MPa) but a much larger breaking elongation (> 50%), demonstrating good toughening effect of the PMPS in the AESE monomer. Thereby, it is suitable to be used as a modifier for petroleum-based epoxy monomers like DGEBA that need to improve toughness and flame retardancy simultaneously.

3.1.3 Bio-based aliphatic epoxy monomers

Fatty acid-based epoxy monomers. Fatty acids are the major components of the triglyceride oils, which possess C-C double bonds in their chemical structures [48]. These double bonds could be used as reactive sites for modifications. Epoxidation is one of the most important modifications of these double bonds leading to fatty acid-based epoxy monomers. Lligadas et al. reported a novel phosphorous-containing fatty acid-based epoxy monomer (DOPO-III) and subsequently cured with DDM and bis(*m*-aminophenyl) methylphosphine oxide (BAMPO) (Scheme 9) [49]. The LOI values of the DOPO-III/DDM and the DOPO-III/BAMPO thermosets were 31% and 32%, respectively, implying good flame-retardancy. In another study [48], Lligadas et al. synthesized two fatty acid derived epoxy monomers: epoxidized 10-undecenoyl triglyceride (UDTGE) and epoxidized methyl 3,4,5-tris(10-undecenoyloxy)benzoate (UDBME) (Scheme 9). The UDTGE or the UDBME was combined with the DOPO-III and cured by DDM or BAMPO. The LOI values of the cured thermosets are listed in Table 2. It can be seen that the addition of DOPO-III increased the LOI of the cured thermosets obviously. The improved flame retardancy is attributable to the formation of a protective phosphorous-rich char layer that inhibits the combustible volatiles from the degraded polymer to fuel the flame. Unfortunately, because of the flexibility of long chain of fatty acids, the T_g values of the DOPO-III/DDM and the DOPO-III/BAMPO thermosets are 108 and 95 ^oC [49], respectively, which are much lower than those of the DGEBA-based thermosets as reported previously. As a result, fatty acid-based epoxy monomers remain limited to non-structural applications like paints and coatings.

Itaconic acid-based epoxy monomers. Itaconic acid (ITA) is produced from the fermentation of carbohydrate (like glucose) in the presence of *Aspergillus terreus* [50]. It has two carboxyl groups as well as one C-C double bond in the molecular structure, which makes it greatly suitable as a versatile platform for preparation of polymeric materials. Thereby, ITA has been regarded as one of the top twelve potential bio-based platform chemicals by the US Department of Energy [51]. Ma and co-workers synthesized a phosphorus-containing ITA-based epoxy monomer (EADI) (Scheme 10) [50]. The EADI/MHHPA showed intrinsic flame retardancy with a V-0 classification in the UL-94 vertical burning test, whereas the DGEBA/MHHPA burned out finally. Undoubtedly, the improvement in flame retardancy is attributable to the presence of phosphorus-containing structure in EADI, but the thermal stability in terms of the initial degradation temperature is deteriorated as well.

Sebacic acid-based epoxy monomers. Sebacic acid (SA), also known as

1,10-decanedioic acid, is normally made from castor oil. Owing to the presence of two carboxyl groups in the molecular structure, SA has been widely used in production of engineering plastics like polyester [52] and nylon [53, 54]. A phosphorus-containing SA-derived epoxy monomer (PSAE) was recently synthesized (Scheme 11), and mixed with a petroleum-based epoxy monomer (CE) at different ratios [55]. These mixtures were subsequently cured by polyamide hardener. The LOI value increased gradually with the increase of the PSAE loading in the thermosetting system. The LOI value reached 27% for the PSAE80/CE20 formulation (the number represents weight percentage). In the UL-94 vertical burning test, the self-extinguishing phenomenon within a period of 5-10 seconds was observed for the formulations of PSAE40/CE60, PSAE60/CE40 and PSAE80/CE20. Moreover, no dripping phenomenon was observed, suggesting good structural stability of the residual char. However, the SA has long aliphatic chains similar to the fatty acid, which induces low T_g and strength. As a consequence, such phosphorus-containing SA-based epoxy monomers remain limited to flame retardant coating applications.

Based on these bio-based flame retardant epoxy monomers aforementioned in this section, several phosphorus-containing bio-based epoxy monomers are selected to compare their flame retardant efficiency, as summarized in Table 3. It can be seen that char yield is roughly proportional to phosphorus content if epoxy monomers and curing agents have similar structures. Generally, higher char yield results in better flame retardancy for polymers [56]. If taking the chemical structures into account, epoxy monomers and curing agents with more aromatic structures is favorable to higher char yield, while those with aliphatic structures seems to generate lower char yield. In addition, epoxy thermosets with more aromatic structures possess high rigidity and T_g which are suitable for heat resistant thermosets applications, whereas those with aliphatic structures exhibit excellent flexibility which could serve as toughening agents.

3.2 Bio-based flame retardant curing agents for epoxy thermosets

Generally, the curing agents for epoxy thermosets include amines, amides, anhydrides, phenols, and polyphenols [57]. These curing agents contain reactive functional groups such as amino, hydroxyl and carboxyl groups, which can react with epoxide group to form three-dimensional cross-linked networks. This section will review bio-based flame retardant curing agents. However, only a few studies have been reported for bio-based flame retardant curing agents.

Mao and co-workers reported a castor oil-based binary acid as flame-retardant epoxy curing agent (IDDRA) (Scheme 12) [58]. The IDDRA was combined with methyl nadic anhydride (MNA) as co-curing agent for DGEBA. The LOI, tensile property and T_g of the samples are listed in Table 4. Although the LOI value increased gradually with the increase of the IDDRA loading, both the tensile strength and the T_g dropped significantly. The elongation at break of the epoxy thermosets increased obviously as the IDDRA loading increased, indicating good toughening effect which originated from the long aliphatic chains of the castor oil species in the IDDRA. The low tensile strength and the low T_g restricted the application of the IDDRA in high performance epoxy thermosets.

Guo *et al.* synthesized a cardanol-based phosphorus-containing benzoxazine (CBz) as a curing agent for DGEBA, as depicted in Scheme 13 [59]. The incorporation of 15 wt% CBz into DGEBA exhibited a high LOI of 32% as well as UL-94 V-0 rating, but the reduction in the PHRR and the THR was limited, and the thermal stability was lowered. Thereby, CBz was combined with boron doped graphene (BG) nanosheets to improve the flame retardant efficiency and the thermal stability of the epoxy thermosets. With the addition of 13 wt% CBz and 2 wt% BG, the resulting DGEBA thermoset exhibited 48% and 12% lower PHRR and THR than the un-modified DGEBA thermoset, respectively. Furthermore, the impact strength of the DGEBA thermoset with 13 wt% CBz and 2 wt% BG increased by 22% relative to that of the un-modified DGEBA thermoset. The improved flame retardant efficiency could be attributed to that the presence of BG could improve the resistance to thermal oxidative degradation of the char layers, and the enhanced toughness was assigned to the flexible aliphatic chains of cardanol moieties.

Another two phosphorus-containing vanillin-based curing agents (TP and MP) (Scheme 14) were reported for flame retardant DGEBA thermosets very recently [60]. The TP and MP were used as co-flame retardants with ammonium polyphosphate (APP) in the DGEBA/DDM thermosets. With 10 phr of APP, the DGEBA/DDM thermoset showed no classification in UL-94 burning test. By contrast, when TP or MP was combined with APP, the resulting DGEBA/DDM system passed UL-94 V-0 classification and the LOI value was around 29%. The T_g of the epoxy thermosets with the co-addition of TP or MP with APP was comparable to or even higher than the control sample, while that for APP alone-modified epoxy thermoset compromised a lot. Thereby, these vanillin-based curing agents are suitable to be used in fabrication of high-performance epoxy thermosets.

Yang et al. reported two bio-based phosphorus-containing curing agents (MMDOPO and MAPDGR) (Scheme 14) [61]. Owing to the unique chemical structure, the DGEBA/MMDOPO was a brittle material, whereas the DGEBA/MAPDGR was very flexible, as shown in Fig. 5. Thereby, these two curing agents were mixed with different weight ratios to form the cured DGEBA thermosets with balanced properties. This work provides a solution to tailor comprehensive properties of the cured epoxy thermosets by combining different bio-based curing agents.

4. Fully bio-based flame retardant epoxy thermosets

Fully bio-based flame retardant epoxy thermosets are defined as bio-based epoxy monomers cured by bio-based curing agent in this review. Owing to the increasing concern on sustainable development, the biomass content in the materials is expected as high as possible. Given this, it is desirable to develop fully bio-based flame retardant epoxy thermosets. This section will discuss the fully bio-based epoxy thermosets with intrinsic flame retardancy.

Menard and co-workers prepared a fully bio-based flame retardant epoxy thermoset through phloroglucinol-based epoxy monomers (P3EP and P2EP1P) and furan-based curing agent (DIFFA) (Scheme 15) [62]. For comparison, DGEBA and petroleum-based curing agents (IPDA and DA10) (Scheme 15) were also used to fabricate the control samples. The MCC results demonstrated that the flammability of the epoxy thermosets was mainly dominated by the charring ability of the epoxy monomers and the curing agents (Fig. 6). Generally, the charring ability was affected by the aromaticity and the phosphorus content of materials. Thereby, the fully bio-based epoxy thermoset based on P3EP and DIFFA showed much lower PHRR (119 W/g) than partly bio-based epoxy thermoset (395 W/g for P3EP/IPDA and 185 W/g P3EP/DA10) and petroleum-based epoxy thermoset (664 W/g for DGEBA/IPDA). The co-addition of P3EP and P2EP1P further decreased the PHRR value of the epoxy thermoset. However, the incorporation of P2EP1P into the epoxy thermosets led to decreased T_g because of the decreased crosslink density. The introduction of P2EP1P also decreased the thermal stability of the epoxy thermoset, but increased the char yield that accounted for the enhanced flame retardancy.

5. Summary and perspective

With the increasing awareness about sustainable development and environmental protection, bio-based epoxy thermosets made from various renewable products including fatty acid, eugenol, vanillin, daidzein, furan, itaconic acid, rosin, lignin, tannin, vegetable oils, etc, have attracted extensive attention to substitute petroleum-based counterparts over the past decades. Like most of synthetic polymeric materials, bio-based epoxy thermosets encounter the serious drawback of high flammability. It is thereby imperial to endow them with high flame retardancy. Up to now, intrinsically flame-retardant bio-based epoxy thermosets have not widely reported, suggesting that the research on this field is just beginning. Generally, intrinsically flame-retardant bio-based epoxy thermosets can be designed by two approaches: (i) selecting bio-based chemicals with high charring ability and abundant aromatic structures; (ii) incorporating flame retardant elements such as phosphorus, silicon, boron, etc into the molecular structure of bio-based epoxy monomers or curing agents.

Currently, although very high flame retardancy has been achieved for several bio-based epoxy thermosets, the thermal stability, the glass transition temperature and the strength are found to be inferior to their DGEBA counterparts. Additionally, the relatively high cost of bio-based materials for synthesis of bio-based epoxy thermosets restricts the scalable production. Owing to these problems, there is still a long way for commercialization of bio-based epoxy thermosets in replacement of the DGEBA ones. Considering the development trend in this field, increasing functionality of bio-based epoxy monomers or curing agents, improving bio-mass content and bio-degradation ability are several key factors for developing high performance bio-based epoxy thermosets in the future.

References

[1] Jin FL, Li X, Park SJ. Synthesis and application of epoxy resins: A review. J Ind Eng Chem 2015;29:1-11.

[2] Mohan P. A Critical Review: The modification, properties, and applications of epoxy resins. Polym-Plast Technol 2013;52:107-25.

[3] Kumar S, Krishnan S, Mohanty S, Nayak SK. Synthesis and characterization of petroleum and biobased epoxy resins: a review. Polym Int 2018;67:815-39.

[4] Wang X, Hu Y, Song L, Xing WY, Lu HD, Lv P, Jie GX. Flame retardancy and thermal degradation mechanism of epoxy resin composites based on a DOPO substituted organophosphorus oligomer. Polymer 2010;51:2435-45.

[5] Wang X, Hu Y, Song L, Xing WY, Lu HD. Thermal degradation behaviors of epoxy resin/POSS hybrids and phosphorus-silicon synergism of flame retardancy. J Polym Sci Pol Phys 2010;48:693-705.

[6] Fu XL, Wang X, Xing WY, Zhang P, Song L, Hu Y. Two-dimensional cardanol-derived zirconium phosphate hybrid as flame retardant and smoke suppressant for epoxy resin. Polym Degrad Stabil 2018;151:172-80.

[7] Qiu SL, Wang X, Yu B, Feng X, Mu X, Yuen RKK, Hu Y. Flame-retardant-wrapped polyphosphazene nanotubes: A novel strategy for enhancing the flame retardancy and smoke toxicity suppression of epoxy resins. J Hazard Mater 2017;325:327-39.

[8] Qiu SL, Ma C, Wang X, Zhou X, Feng XM, Yuen RKK, Hu Y. Melamine-containing polyphosphazene wrapped ammonium polyphosphate: A novel multifunctional organic-inorganic hybrid flame retardant. J Hazard Mater 2018;344:839-48.

[9] Zhou JJ, Xu KJ, Xie MJ, Wu HF, Hua Z, Wang ZK. Two Strategies to precisely tune the mechanical properties of plant oil-derived epoxy resins. Compos Part B: Eng 2019;173:106885.

[10] Kumar A. Epoxy resins: applications and global markets. Report from BCC Inc. Pub., 2017, PLS077B.

[11] Shibata M, Ohkita T. Fully biobased epoxy resin systems composed of a vanillin-derived epoxy resin and renewable phenolic hardeners. Eur Polym J 2017;92:165-73.

[12] Moudood A, Rahman A, Khanlou HM, Hall W, Ochsner A, Francucci G. Environmental effects on the durability and the mechanical performance of flax fiber/bio-epoxy composites. Compos Part B: Eng 2019;171:284–293.

[13] Cicala G, Pergolizzi E, Piscopo F, Carbone D, Recca G. Hybrid composites manufactured by resin infusion with a fully recyclable bioepoxy resin. Compos Part B: Eng 2018;132: 69-76.

[14] Boccarusso L, Durante M, Langella A. Lightweight hemp/bio-epoxy grid structure manufactured by a new continuous process. Compos Part B: Eng 2018;146: 165–175.

[15] Kumar S, Samal SK, Mohanty S, Nayak SK. Recent Development of Biobased Epoxy Resins: A Review. Polym-Plast Technol 2018;57:133-155.

[16] Wang X, Kalali EN, Wan JT, Wang DY. Carbon-family materials for flame retardant polymeric materials. Prog Polym Sci 2017;69:22-46.

[17] Auvergne R, Caillol S, David G, Boutevin B, Pascault JP. Biobased thermosetting epoxy: Present and future. Chem Rev 2014;114:1082-1115.

[18] Hidalgoa P, Navia R, Hunter R, Gonzalez ME, Echeverría A. Development of novel bio-based epoxides from microalgae Nannochloropsis gaditana lipids. Compos Part B: Eng 2019;166: 653–662.

[19] Aouf C, Nouailhas H, Fache M, Caillol S, Boutevin B, Fulcrand H.

Multi-functionalization of gallic acid. Synthesis of a novel bio-based epoxy resin. Eur Polym J 2013;49:1185-1195.

[20] Colladon M, Scarso A, Sgarbossa P, Michelin RA, Strukul G. Regioselectivity and diasteroselectivity in Pt(II)-mediated “green” catalytic epoxidation of terminal alkenes with hydrogen peroxide: Mechanistic insight into a peculiar substrate selectivity. J Am Chem Soc 2007;129:7680-7689.

[21] Liggins J, Bluck LJC, Runswick S, Atkinson C, Coward WA, Bingham SA. Daidzein and genistein content of fruits and nuts. J Nutr Biochem 2000;11:326-331.

[22] Kris-Etherton PM, Hecker KD, Bonanome A, Coval SM, Binkoski AE, Hilpert KF, Griel AE, Etherton TD. Bioactive compounds in foods: their role in the prevention of cardiovascular disease and cancer. Am J Med 2002;113:71-88.

[23] Dai J, Peng Y, Teng N, Liu Y, Liu C, Shen X, Mahmud S, Zhu J, Liu X. High-performing and fire-resistant biobased epoxy resin from renewable sources. ACS Sustain Chem Eng 2018;6:7589-7599.

[24] Lochab B, Shukla S, Varma IK. Naturally occurring phenolic sources: Monomers and polymers. RSC Adv 2014;4:21712-21752.

[25] Qin J, Liu H, Zhang P, Wolcott M, Zhang J. Use of eugenol and rosin as feedstocks for biobased epoxy resins and study of curing and performance properties. Polym Int 2014;63:760-765.

[26] Chen B, Wang F, Li JY, Zhang JL, Zhang Y, Zhao HC. Synthesis of eugenol bio-based reactive epoxy diluent and study on the curing kinetics and properties of the epoxy resin system. Chinese J Polym Sci 2019;37:500-508.

[27] Liu T, Hao C, Wang L, Li Y, Liu W, Xin J, Zhang J. Eugenol-derived biobased epoxy: Shape memory, repairing, and recyclability. Macromolecules 2017;50:8588-8597.

[28] Ng F, Couture G, Philippe C, Boutevin B, Caillol S. Bio-based aromatic epoxy monomers for thermoset materials. Molecules 2017;22:149.

[29] Wan JT, Gan B, Li C, Molina-Aldareguia J, Li Z, Wang X, Wang DY. A novel biobased epoxy resin with high mechanical stiffness and low flammability: Synthesis, characterization and properties. J Mater Chem A 2015;3:21907-21921.

[30] Wan JT, Gan B, Li C, Molina-Aldareguia J, Kalali EN, Wang X, Wang DY. A sustainable, eugenol-derived epoxy resin with high biobased content, modulus, hardness and low flammability: Synthesis, curing kinetics and structure-property relationship. Chem Eng J 2016;284:1080-1093.

[31] Faye I, Decostanzi M, Ecochard Y, Caillol S. Eugenol bio-based epoxy thermosets: from cloves to applied materials. Green Chem 2017;19:5236-5242.

[32] Miao JT, Yuan L, Guan Q, Liang G, Gu A. Biobased epoxy resin derived from eugenol with excellent integrated performance and high renewable carbon content. Polym Int 2018;67:1194-1202.

[33] Li C, Fan H, Aziz T, Bittencourt C, Wu L, Wang DY, Dubois P. Biobased epoxy resin with low electrical permissivity and flame retardancy: From environmental friendly high-throughput synthesis to properties. ACS Sustain Chem Eng 2018;6:8856-8867.

[34] Ecochard Y, Decostanzi M, Negrell C, Sonnier R, Caillol S. Cardanol and

eugenol based flame retardant epoxy monomers for thermostable networks. Molecules 2019;24:1818.

[35] Bozell JJ, Petersen GR. Technology development for the production of biobased products from biorefinery carbohydrates—the US Department of Energy's "Top 10" revisited. Green Chem 2010;12:539-554.

[36] Hu F, La Scala JJ, Sadler JM, Palmese GR. Synthesis and characterization of thermosetting furan-based epoxy systems. Macromolecules 2014;47:3332-3342.

[37] Shen X, Liu X, Wang J, Dai J, Zhu J. Synthesis of an epoxy monomer from bio-based 2,5-furandimethanol and its toughening via Diels–Alder reaction. Ind Eng Chem Res 2017;56:8508-8516.

[38] Miao JT, Yuan L, Guan Q, Liang G, Gu A. Biobased heat resistant epoxy resin with extremely high biomass content from 2,5-furandicarboxylic acid and eugenol. ACS Sustain Chem Eng 2017;5:7003-7011.

[39] Meng J, Zeng Y, Zhu G, Zhang J, Chen P, Cheng Y, Fang Z, Guo K. Sustainable bio-based furan epoxy resin with flame retardancy. Polym Chem 2019;10:2370-2375.

[40] Hernandez ED, Bassett AW, Sadler JM, La Scala JJ, Stanzione JF. Synthesis and characterization of bio-based epoxy resins derived from vanillyl alcohol. ACS Sustain Chem Eng 2016;4:4328-4339.

[41] Savonnet E, Grau E, Grelier S, Defoort B, Cramail H. Divanillin-based epoxy precursors as DGEBA substitutes for biobased epoxy thermosets. ACS Sustain Chem Eng 2018;6:11008-11017.

[42] Wang S, Ma S, Xu C, Liu Y, Dai J, Wang Z, Liu X, Chen J, Shen X, Wei J, Zhu J.

Vanillin-derived high-performance flame retardant epoxy resins: Facile synthesis and properties. Macromolecules 2017;50:1892-1901.

[43] Caillol S. Cardanol: A promising building block for biobased polymers and additives. Curr Opin Green Sustain Chem 2018;14:26-32.

[44] Ma S, Li T, Liu X, Zhu J. Research progress on bio-based thermosetting resins. Polym Int 2016;65:164-173.

[45] Deng L, Ha C, Sun C, Zhou B, Yu J, Shen M, Mo J. Properties of bio-based epoxy resins from rosin with different flexible chains. Ind Eng Chem Res 2013;52:13233-13240.

[46] Atta AM, Mansour R, Abdou MI, Sayed AM. Epoxy resins from rosin acids: synthesis and characterization. Polym Advan Technol 2004;15:514-522.

[47] Deng L, Shen M, Yu J, Wu K, Ha C. Preparation, characterization, and flame retardancy of novel rosin-based siloxane epoxy resins. Ind Eng Chem Res 2012;51:8178-8184.

[48] Lligadas G, Ronda JC, Galià M, Cádiz V. Development of novel phosphorus-containing epoxy resins from renewable resources. J Polym Sci Part A: Polym Chem 2006;44:6717-6727.

[49] Lligadas G, Ronda JC, Galià M, Cádiz V. Synthesis and properties of thermosetting polymers from a phosphorous-containing fatty acid derivative. J Polym Sci Part A: Polym Chem 2006;44:5630-5644.

[50] Ma S, Liu X, Jiang Y, Fan L, Feng J, Zhu J. Synthesis and properties of phosphorus-containing bio-based epoxy resin from itaconic acid. Sci China Chem

2014;57:379-388.

[51] Werpy T, Petersen G, Top value added chemicals from biomass: volume I--results of screening for potential candidates from sugars and synthesis gas, in, National Renewable Energy Lab., Golden, CO (US), 2004.

[52] Zia KM, Noreen A, Zuber M, Tabasum S, Mujahid M. Recent developments and future prospects on bio-based polyesters derived from renewable resources: A review. Int J Biol Macromol 2016;82:1028-1040.

[53] Wang Z, Wei T, Xue X, He M, Xue J, Song M, Wu S, Kang H, Zhang L, Jia Q. Synthesis of fully bio-based polyamides with tunable properties by employing itaconic acid. Polymer 2014;55:4846-4856.

[54] He M, Wang Z, Wang R, Zhang L, Jia Q. Preparation of bio-based polyamide elastomer by using green plasticizers. Polymers 2016;8:257.

[55] Patil DM, Phalak GA, Mhaske ST. Novel phosphorus-containing epoxy resin from renewable resource for flame-retardant coating applications. J Coat Technol Res 2019;16:531-542.

[56] van Krevelen DW. Some basic aspects of flame resistance of polymeric materials. Polymer 1975;16:615-620.

[57] Baroncini EA, Kumar Yadav S, Palmese GR, Stanzione III JF. Recent advances in bio-based epoxy resins and bio-based epoxy curing agents. J Appl Polym Sci 2016;133:44103.

[58] Mao W, Li S, Yang X, Cao S, Li M, Huang K, Xia J. Preparation of a flame-retardant epoxy curing agent based on castor oil and study on the curing

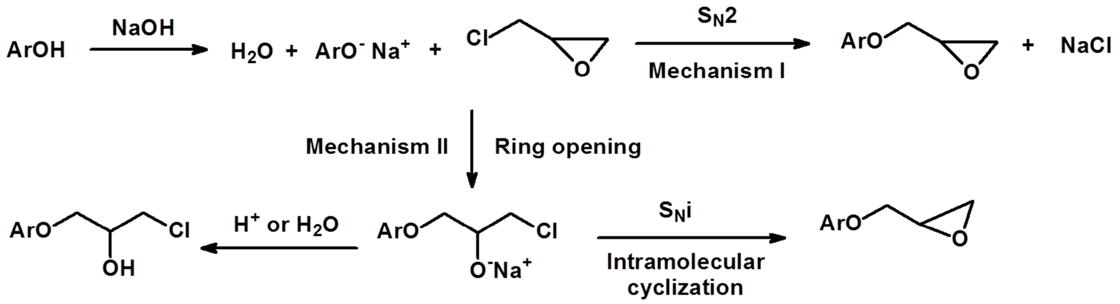
reaction kinetics. J Therm Anal Calorim 2017;130:2113-2121.

[59] Guo WW, Wang X, Gangireddy CSR, Wang JL, Pan Y, Xing WY, Song L, Hu Y. Cardanol derived benzoxazine in combination with boron-doped graphene toward simultaneously improved toughening and flame retardant epoxy composites. Compos Part A: Appl S 2019;116:13-23.

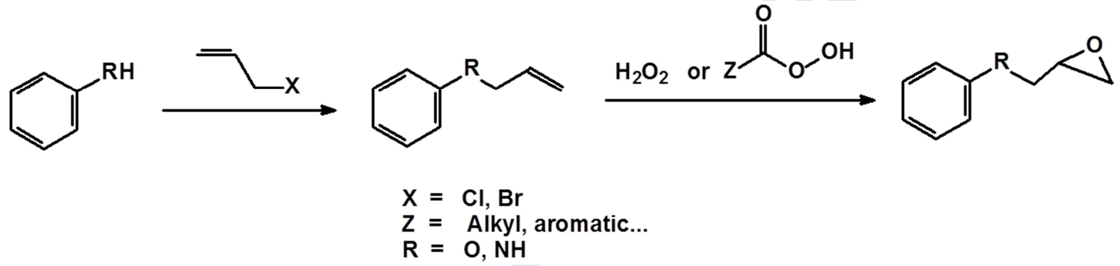
[60] Xu X, Wang S, Ma S, Yuan W, Li Q, Feng J, Zhu J. Vanillin-derived phosphorus-containing compounds and ammonium polyphosphate as green fire-resistant systems for epoxy resins with balanced properties. Polym Advan Technol 2019;30:264-278.

[61] Yang X, Wang C, Xia J, Mao W, Li S. Study on synthesis of novel phosphorus-containing flame retardant epoxy curing agents from renewable resources and the comprehensive properties of their combined cured products. Prog Org Coat 2017;110:195-203.

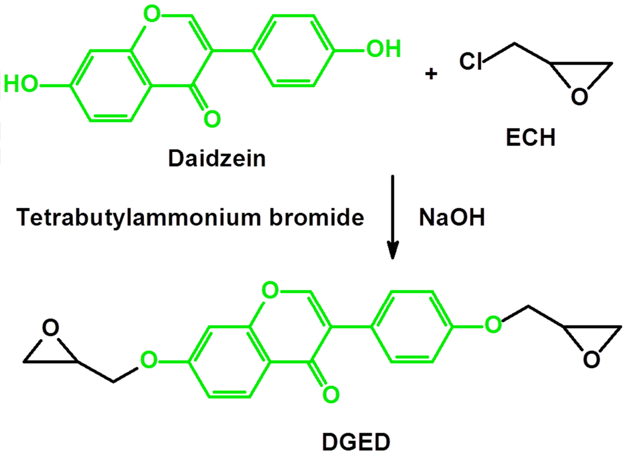
[62] Ménard R, Negrell C, Fache M, Ferry L, Sonnier R, David G. From a bio-based phosphorus-containing epoxy monomer to fully bio-based flame-retardant thermosets. RSC Adv 2015;5:70856-70867.



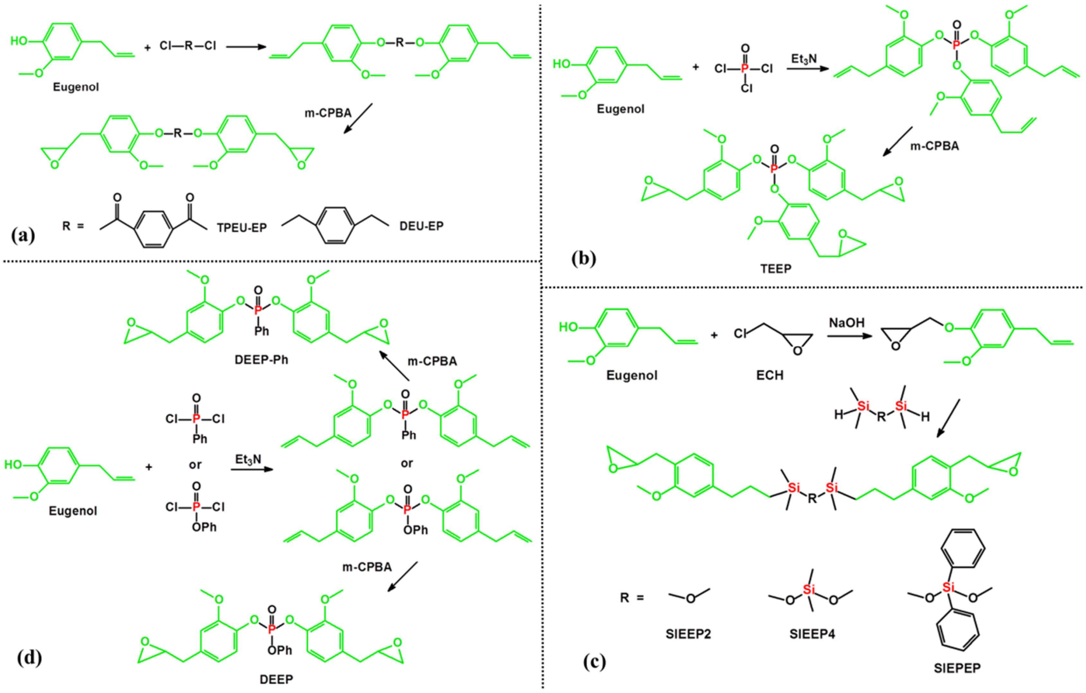
Scheme 1. Synthesis of epoxy resins from phenolic compounds via glycidylation reaction



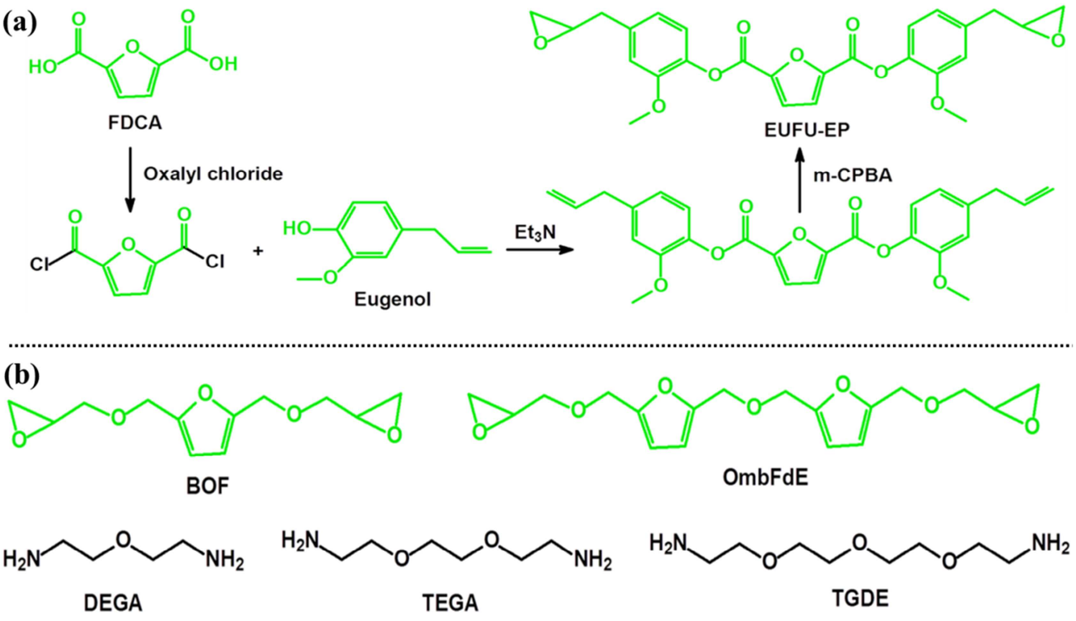
Scheme 2. Synthetic pathway to obtain epoxy resins from double bond oxidation



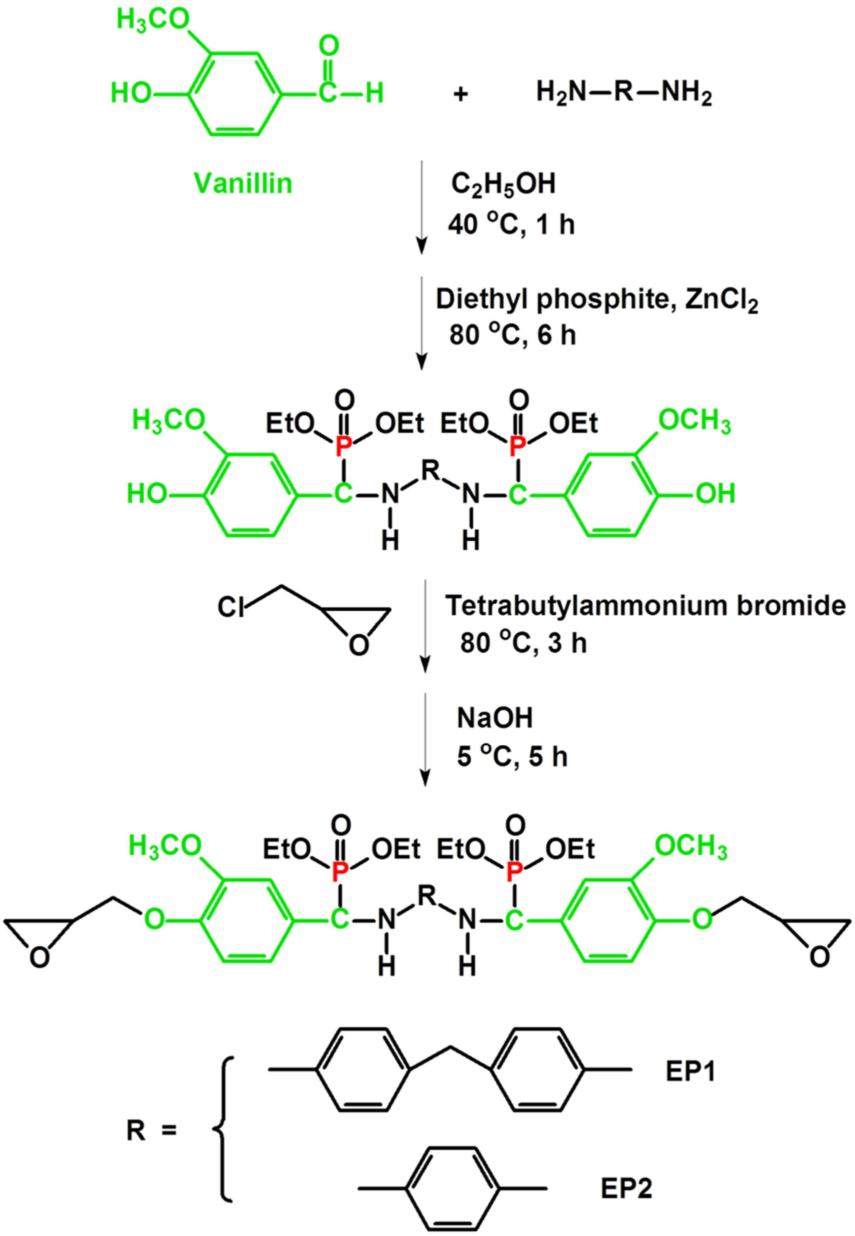
Scheme 3. Synthetic route to daidzein-based epoxy monomer (DGED)



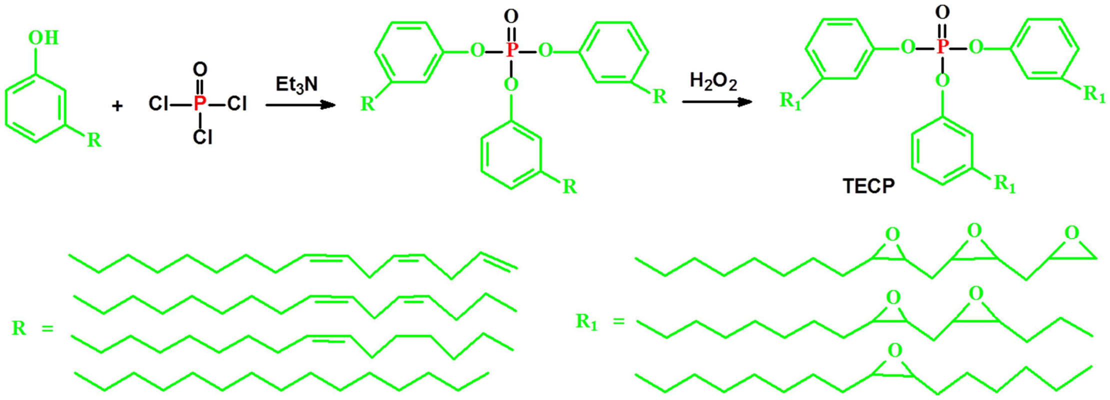
Scheme 4. Schematic for the synthesis route of various eugenol-based epoxy monomers



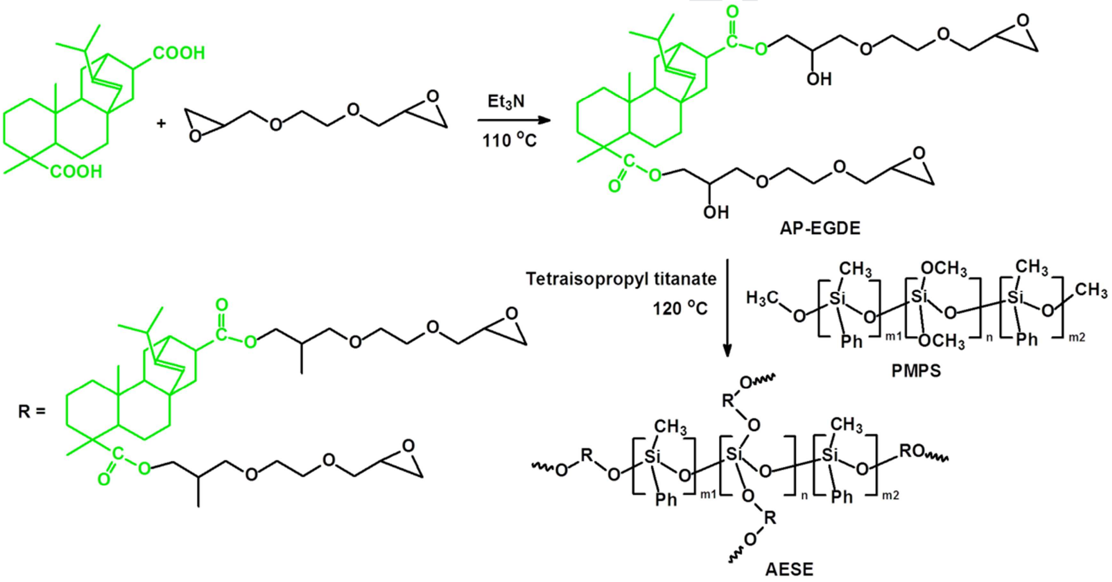
Scheme 5. (a) Synthesis of a difunctional furan-based epoxy monomer named EUFU-EP; (b) Chemical structures of furan-based epoxy monomers: BOF and OmbFdE, and different amines: DEGA, TEGA, and TGDE.



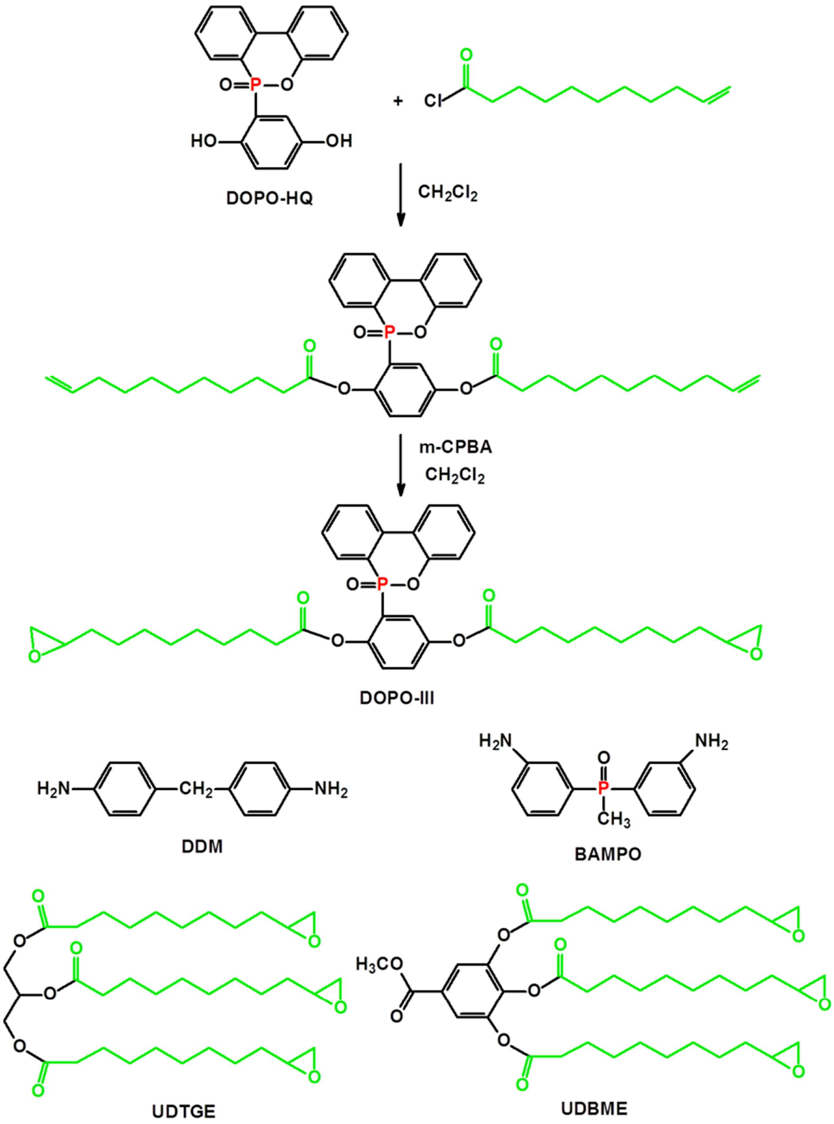
Scheme 6. Diagrammatical illustration showing the synthesis of two vanillin-based epoxy monomers called EP1 and EP2.



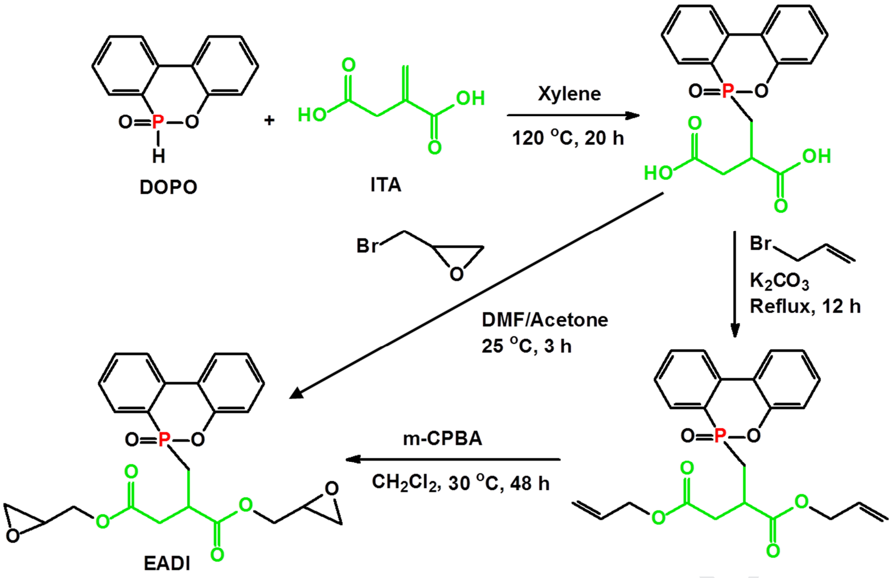
Scheme 7. Synthetic route to a cardanol-based epoxy monomer (TECP).



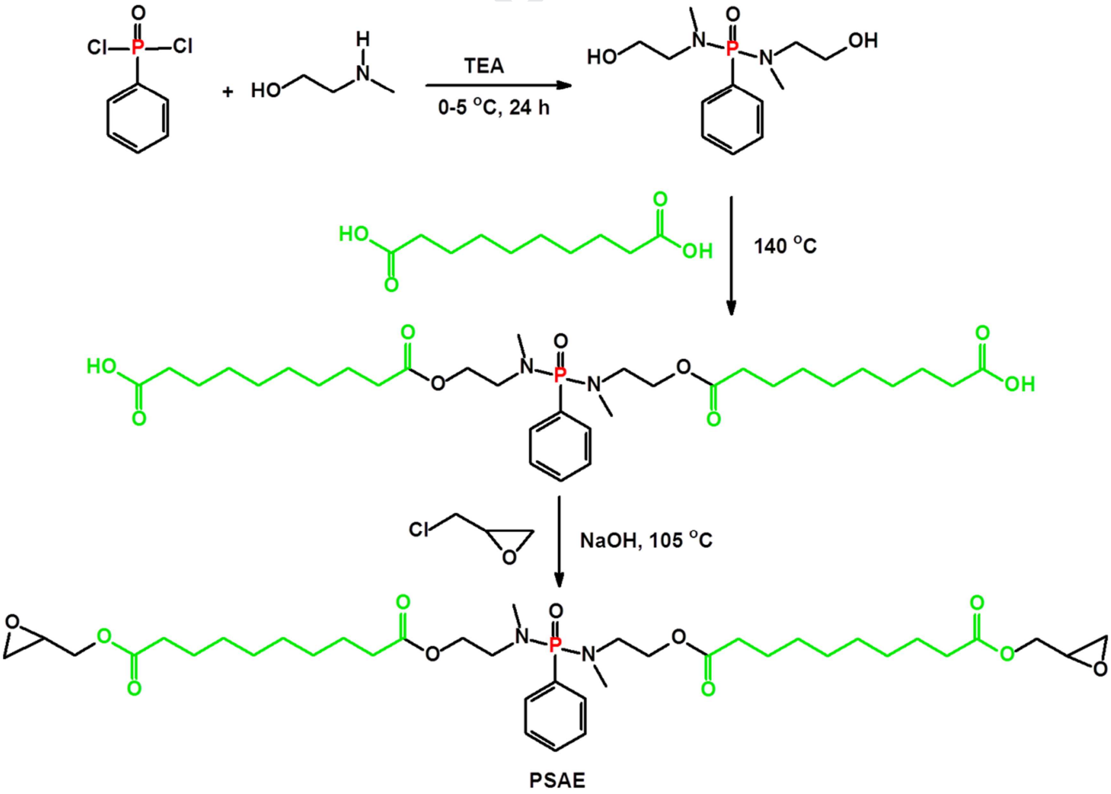
Scheme 8. Synthetic route to a rosin-based siloxane epoxy monomer (AESE).



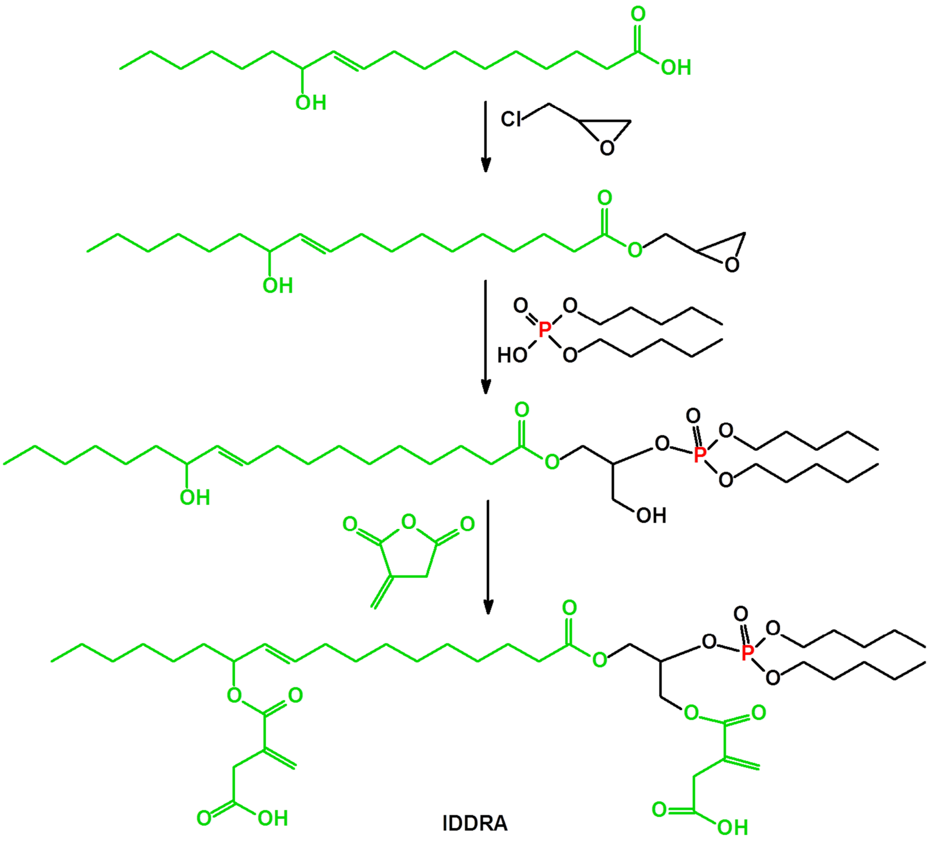
Scheme 9. Synthetic route to fatty acid-based epoxy monomer (DOPO-III) and chemical structures of UDTGE, UDBME, DDM and BAMPO.



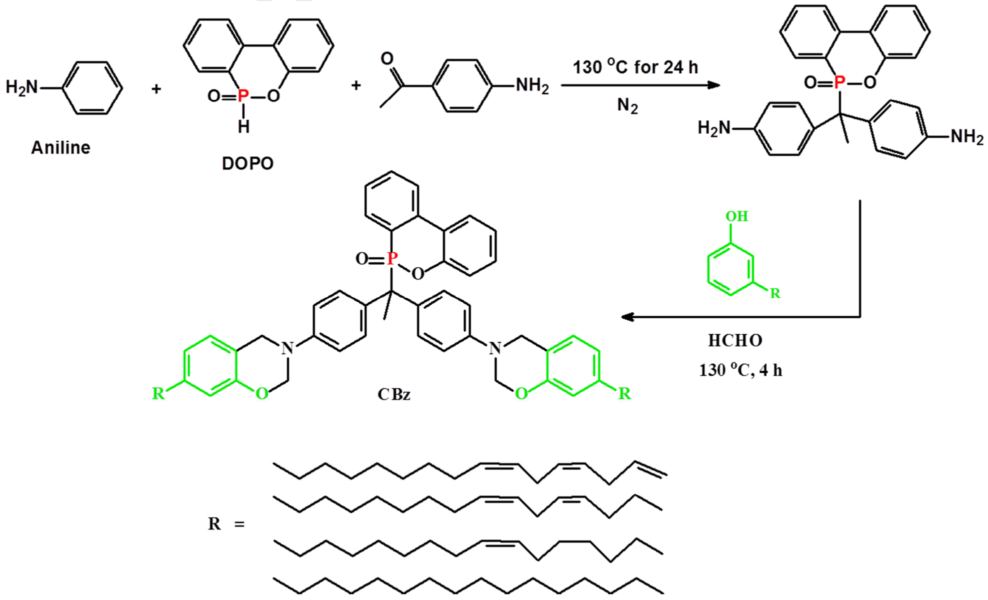
Scheme 10. Schematic representation of synthesis of a phosphorus-containing ITA-based epoxy resin (EADI).



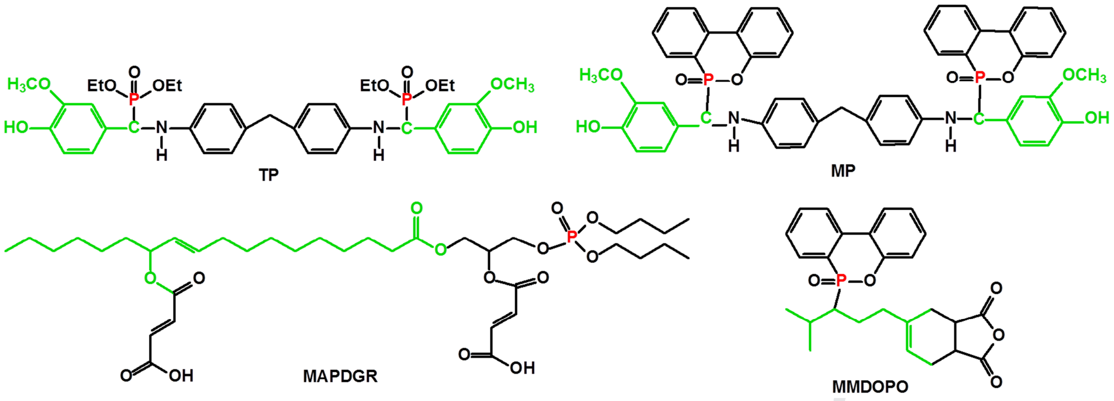
Scheme 11. Schematic representation of synthesis of a phosphorus-containing sebacic acid-derived epoxy monomer called PSAE.



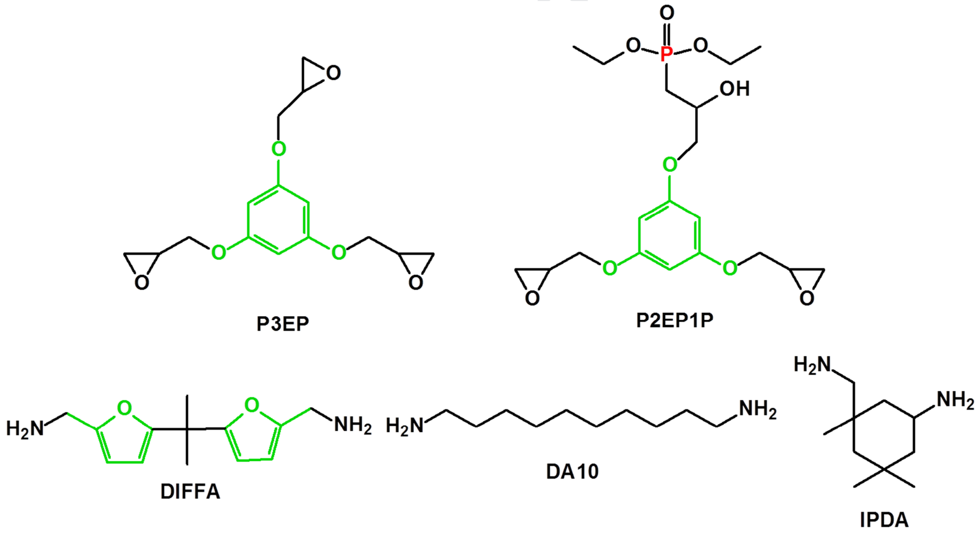
Scheme 12. Synthetic route to a castor oil-based curing agent named IDDRA.



Scheme 13. Diagrammatical illustration of synthesis of a cardanol-based phosphorus-containing benzoxazine (CBz).



Scheme 14. Chemical structures of TP, MP, MAPDGR and MMDOPO.



Scheme 15. Chemical structures of P3EP, P2EP1P, DIFFA, DA10 and IPDA.

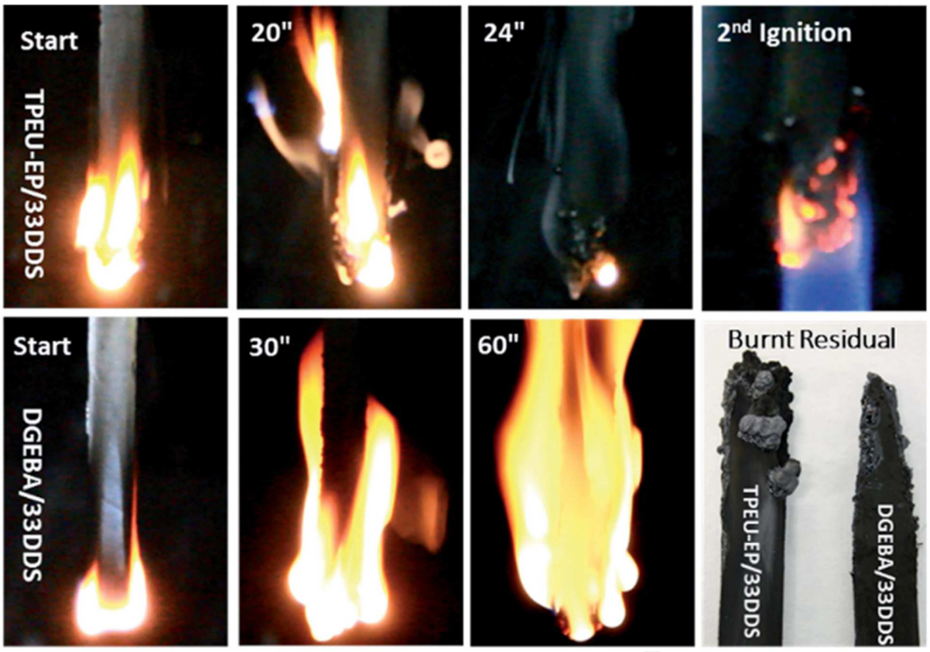
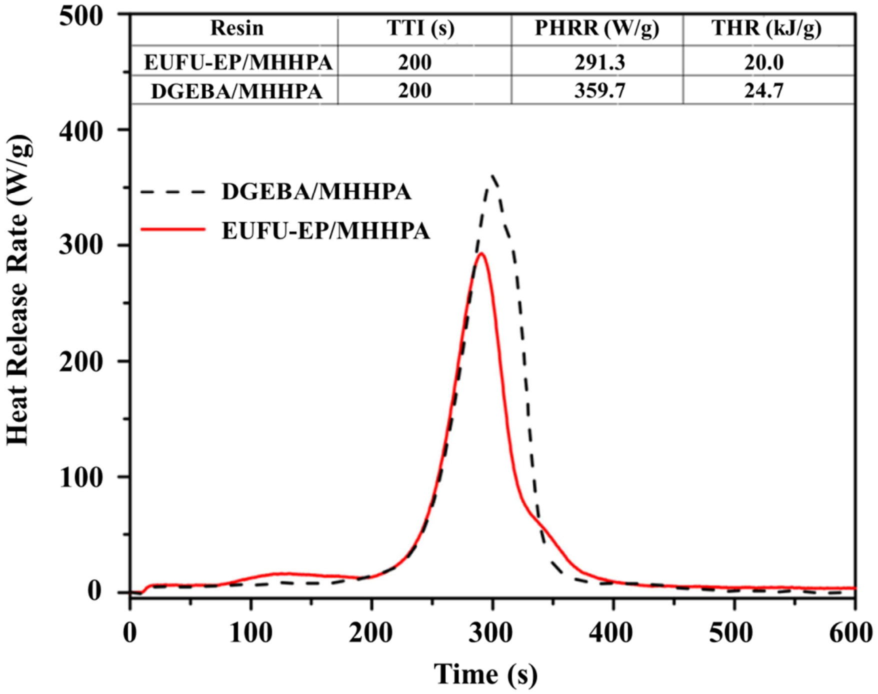


Fig. 1. Snapshots of the vertical burning test of DGEBA/33DDS and TPEU-EP/33DDS. The samples were ignited at the bottom by a Bunsen burner for 10 senconds. The burnt residues are compared in the bottom right image [24].



Resin	TTI (s)	PHRR (W/g)	THR (kJ/g)
EUFU-EP/MHHPA	200	291.3	20.0
DGEBA/MHHPA	200	359.7	24.7

Fig. 2. Heat release rate versus time plots from MCC tests for the cured EUFU-EP/MHHPA and DGEBA/MHHPA thermosets [33].

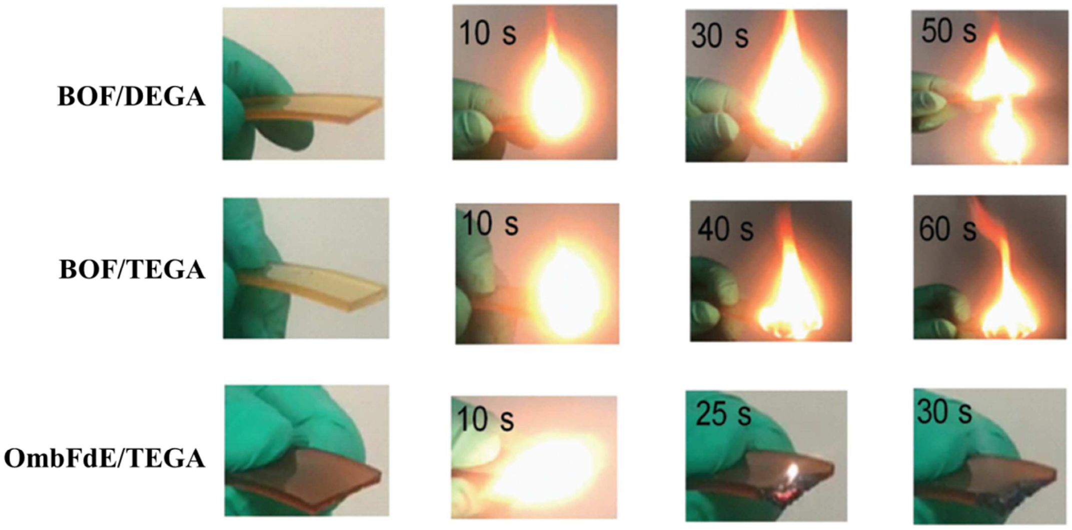


Fig. 3. Snapshots recorded for the burning test of the BOF/DEGA, the BOF/TEGA and the OmbFdE/TEGA [34].

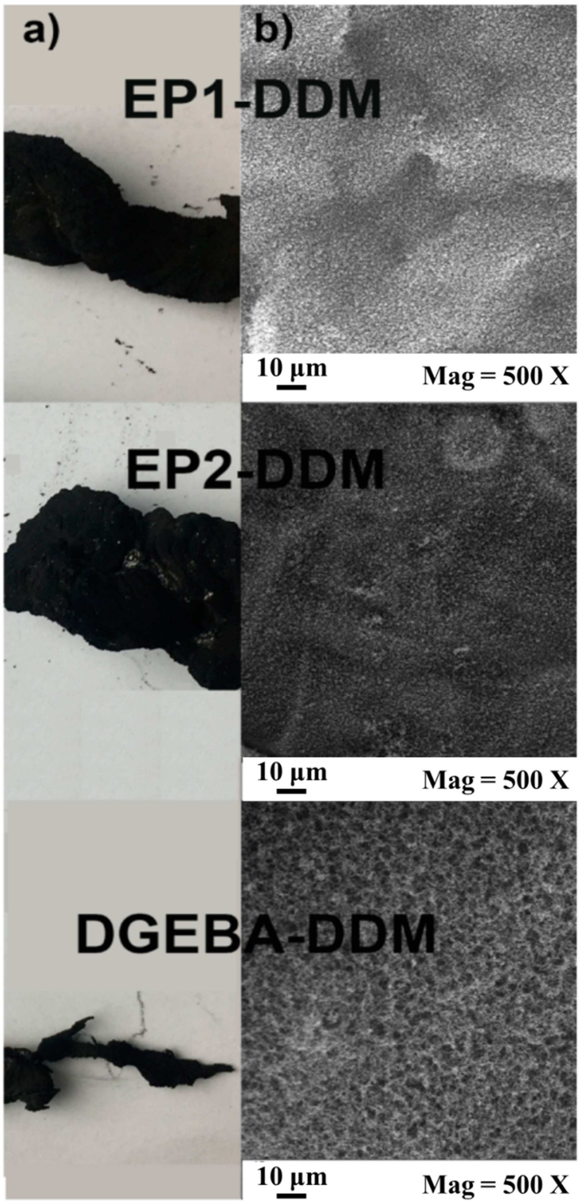


Fig. 4. (a) Digital photographs and (b) SEM microimages of the char residues after LOI test [37].

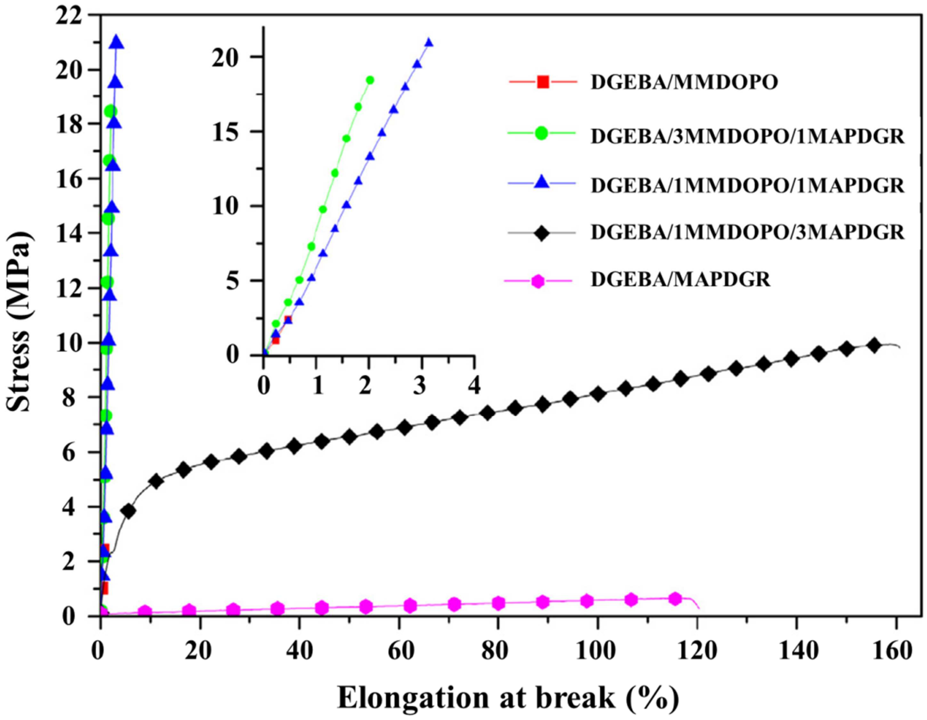


Fig. 5. The tensile strain-stress curves of cured DGEBA thermosets with different MMDOPO/MAPDGR weight ratios [56].

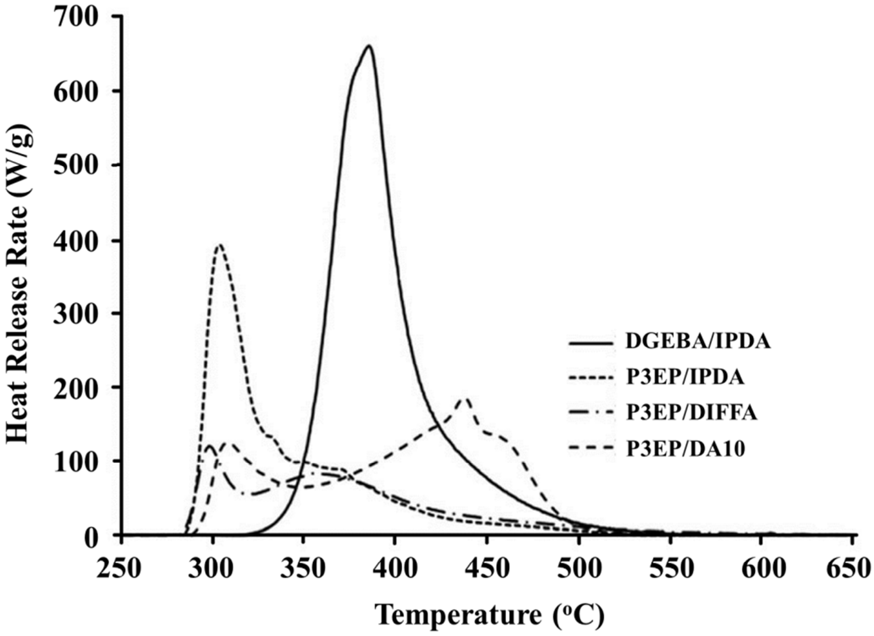


Fig. 6. Heat release rate versus time plots from MCC tests for the cured P3EP/IPDA, P3EP/DIFFA, P3EP/DA10 and DGEBA/IPDA thermosets [57].

Table 1. Effect of the AP-EGDE/PMPS ratio on the LOI and the residue of the cured samples [42].

Sample	AP-EGDE/PMPS ratio	LOI (%)	Residue at 700 °C (%)[a]
AP-EGDE/MHHPA	100/0	21.6	0
AESE20/MHHPA	80/20	30.0	8
AESE30/MHHPA	70/30	30.2	13
AESE40/MHHPA	60/40	28.6	19
AESE50/MHHPA	50/50	28.3	25
PAESE30/MHHPA[b]	70/30	25.3	16

a: determined by TGA, air atmosphere, 10 °C/min; b: PAESE means physical mixture of AP-EGDE and PMPS.

Table 2. Formulations and LOI values of the fatty acid-based epoxy thermosets [43, 44].

Sample	Molar ratio of epoxy monomers	Phosphorus content (%)	LOI (%)
UDTGE/DDM	/	0	21.9
UDTGE/DOPO-III/DDM	1/1[a]	1.8	27.7
UDBME/DDM	/	0	23.5
UDBME/DOPO-III/DDM	1/1[b]	1.9	28.5
UDBME/BAMPO	/	2.5	30.2
DOPO-III/DDM	/	3.9	31.0
DOPO-III/BAMPO	/	5.7	32.0

a: UDTGE/DOPO-III = 1/1; b: UDBME/DOPO-III = 1/1.

Table 3. Comparison of flame retardant property of several phosphorus-containing bio-based epoxy monomers

Epoxy monomers	Curing agents	P content (%)	Char yield (%)[a]	LOI (%)	UL-94	PHRR reduction (%)[b]	Reference
TECP	MXDA	2.4	12	/	/	52	[29]
TEEP	MXDA	4.5	43	/	/	56	[29]
DEEP	MXDA	5.8	41	/	/	60	[29]
DEEP-Ph	MXDA	5.8	35	/	/	55	[29]
EP1	DDM	6.5	53	31.4	V-0	/	[37]
EP2	DDM	7.2	58	32.8	V-0	/	[37]
DOPO-III	DDM	3.9	18	31	/	/	[44]
DOPO-III	BAMPO	5.7	16	32	/	/	[44]
EADI	MHHPA	4.4	5.3	22.8	V-0	/	[45]

a: Measured by TGA under nitrogen; b: Measured by cone calorimeter under 35 kW/m^2.

Table 4. The formulations, LOI and tensile property of the cured samples [53].

Sample	IDDRA/MNA ratio	LOI (%)	Tensile strength (MPa)	Elongation at break (%)
DGEBA/IDDRA/MNA-1	60/40	22.8	34.2	93.9
DGEBA/IDDRA/MNA-2	70/30	23.0	21.9	135.7
DGEBA/IDDRA/MNA-3	80/20	23.6	7.7	314.1
DGEBA/IDDRA/MNA-4	90/10	24.2	0.9	348.0
DGEBA/IDDRA	/	24.8	0.3	400.0

Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.