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## Bio-epoxy resins with inherent flame retardancy: A mini-review

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## **Abstract**

Nowadays, roughly 90% of worldwide epoxy resin materials are made from diglycidyl ether of bisphenol A (DGEBA). This resin offers unique features such as outstanding mechanical properties, chemical resistance, and shape stability. By contrast, the growing awareness of environmental issues, global warming, and depletion of petroleum reservoir suggest search for alternative bio-epoxy resin from sustainable resources. Indeed, DGEBA is a petroleum-based monomer obtained from bisphenol A and epichlorohydrin, two potential harmful precursors. Moreover, the problem deepens when it comes to the high flammability of such materials, which restricts their use in many high-end applications. Although the introduction of flame retardant (FR) additives to epoxy matrices has been a major strategy to induce flame retardancy, negative impact on mechanical properties and migration of FR's to the materials' surface remain unresolved issues. A means to overcome such drawbacks is to chemically bond reactive flame retardants to epoxy resins. This impedes the migration of FR's as well as not affecting the resins' mechanical properties. With the rapid development of reactive bio-based FR's and epoxy resins, production of flame retardant bio-epoxy with high biomass content has become a promising strategy to address these issues. This mini-review encompasses the development of flame retardant bio-epoxy resins from different resources with inherent chemical structures of either epoxy monomers or embedded reactive flame retardant elements.

**Keywords:** Bio-based epoxy resin; Flame retardancy; Thermoset composites

## **1. Bio-epoxy versus conventional petroleum-based epoxy**

Epoxy resins offer versatile integrated features such as outstanding mechanical properties, chemical resistance, and shape integrity in harsh conditions. These functional properties are the result of a crosslinked 3D network obtained by the chemical reaction between an epoxy monomer and a curing agent [1, 2]. The use of epoxy thermosets has been surged over the last decade in a wide range of applications such as coatings, adhesives, solar cells, electronic apparatus, as well as in automotive and aerospace industries [3, 4]. Such applications are expected to receive more attention in the near future. Petroleum-based diglycidyl ether bisphenol A (DGEBA) accounts for ca. 90% of the epoxy resin worldwide usage. This monomer is produced from the reaction between bisphenol A (BPA) and epichlorohydrin (ECH) in sodium hydroxide media (NaOH) [5]. Although DGEBA displays fascinating properties such as chemical resistance, good adhesion, and superior mechanical properties, the use of this monomers encounters several barriers [6] summarized as follows:

- (I) It has been proved that DGEBA has severe effects on living organisms due to the toxicity of BPA [7]. Since BPA has been involved in the manufacture of many products, especially in epoxy resin thermosets, concerns about exposure to high dosages of BPA that might be harmful for human have consequently risen. Given this, legislation in many countries has banned use of BPA in infant-related products [8].
- (II) From an economic point of view, as DGEBA is derived from petroleum, it has experienced a rise in raw materials prices that have had a negative effect on the market.
- (III) Emitted CO<sub>2</sub> from fossil fuels is the major suspect for recent global warming, which has encouraged researchers to substitute petroleum-based products with

renewable green products. In addition, unreacted BPA might be released during products production and ageing, and hence be rejected to the environment. [9].

Thus, taking into consideration of the worldwide volume of DGEBA usage, a great deal of work has been devoted to explore bio-based epoxy resins from renewable resources such as plant oils [10, 11], lignin [12], rosin acids [13], tannins [14], cardanol [15], and itaconic acid [16] to replace traditional petroleum-based DGEBA. Rapid development in the synthesis of bio-epoxy resins and their outstanding characteristics nominate them as powerful building blocks to possibly overtake commercial DGEBA market [17, 18]. In terms of curing potential, substantial attempts have been made in our group to define, quantify, and explain mechanism of network formation in thermoset systems [19-21]. However, potential curability of bio-epoxy resins are lower than the commercial DGEBA, which needs to be studied because of the fact that almost the whole ultimate properties of thermosets strongly depend on the epoxy curing state [22, 23]. Analysis of mechanical properties revealed that bio-epoxy resins derived from rigid chemical structures such as diphenolic acid, rosin acid, and 2,5-furandicarboxylic acid (FDCA) show mechanical properties comparable to DGEBA [24, 25]. However, natural oil-based resins display inferior mechanical and thermal properties due to their long aliphatic chains, and because of their lower crosslinking density [25]. Furthermore, it was documented that the analysis of kinetics of epoxy curing provides a practical tool to compare the reactivity of bio-epoxy monomers with flame retardant additives [26]. *Flame Retardancy Index* was recently defined to quantitatively study flame retardancy potential of polymer composites, but revisiting must be applied for inherently bio-epoxy systems [27]. Incorporation of flame retardant additives impedes the curing reaction and consequently lower the matrices' mechanical properties. Such an influence can also be detected by another useful criterion, namely *Cure Index* [28].

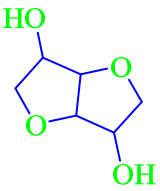
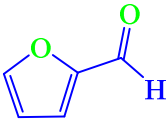
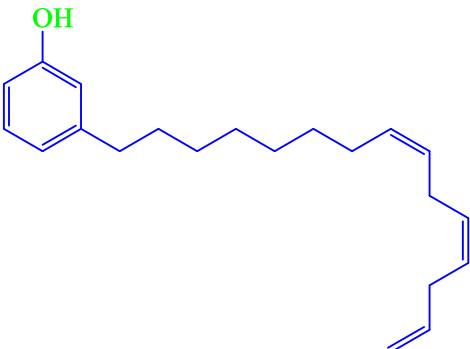
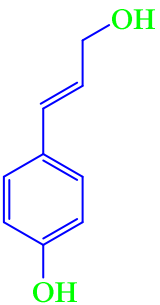
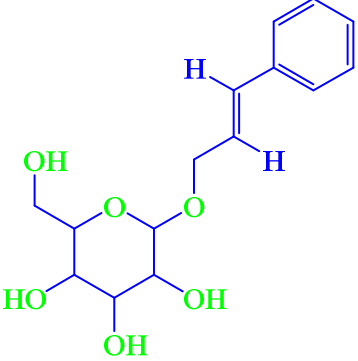
**Table 1** presents the main class of bio-based epoxy resins derived from sustainable resources. Overall, epoxy resins derived from renewable resources benefit from identical properties to those of commercial DGEBA, while eliminating the environmental and production drawbacks. However, like petroleum-based epoxies, bio-epoxy resins suffer from high flammability, which is a crucial prerequisite for many applications such as transportation, construction, and electronic appliances [29-33]. Overall, two strategies can be used to achieve an adequate level of flame retardancy performance.

- (I) The starting of using epoxy monomers with high char content and low combustion energy, which impart flame retardancy to the structure of epoxy building blocks [14].
- (II) The strategy of incorporation of flame retardant (FR) to the epoxy matrix is based on chemical bonding of FR's to epoxy monomers or physical blending with epoxy resins [34]. Even if the physical blending of FR's is still a cheaper method from an industrial point of view, it remains challenging due to the difference in chemical structures between the FR's and the epoxy matrix. This leads to poor miscibility and difficult handling of the epoxy filled with flame retardant formulations [35]. In addition, migration or leaching of FR's during life cycle, as well as a negative effect of additives on the epoxies crosslinking density [36] and consequently a loss of mechanical properties remain as unresolved issues. However, a means to overcome all these issues is to chemically bond FR's to epoxy monomers so as to obtain captive FR's in the polymer network.

In addition, two parallel fields of research, as regards the development of the bio-based epoxy resin and the bio-based flame retardant are at cutting edge. Thus, both approaches need to meet on a common ground to benefit the design of fully bio-epoxy resins with high biomass content [37-41]. However, to the best of our knowledge, only few works reported

the synthesis of fully bio-epoxy resins with flame retardancy properties. In this sense, this short mini-review aims to highlight the current development of flame retardant bio-based epoxy resins. Even though several review papers have been published to cover the bio-based epoxy resin [6, 42] and bio-based flame retardants [43], the area of inherently flame retardant epoxy resins from sustainable resources remains largely intact.

**Table 1.** Chemical structure and main sources of bio-epoxy resins [42].

Class	Chemical structure	Main sources
Isosorbide-based epoxy		Starch
Furan-based epoxy		Corn cobs, biomass wastes
Phenolic- and polyphenolic-based epoxy		Black Mimosa Bark, Quebracho Wood
Lignin-based epoxy derivatives		Wood
Rosin-based epoxy		Pine resin



## 2. Inherently flame retardant bio-epoxy resins

Synthesis of flame retardant bio-epoxy resins from renewable resources capable of giving adequate mechanical properties, comparable to that of DGEBA is of a prime importance in developing bio-based formulations.

Miao et al. [44] compared the flammability of bio-based bis(2-methoxy-4-(oxiran-2-ylmethyl)phenyl)furan-2,5-dicarboxylate (EUFU-EP) with the commercial DGEBA cured with methyl hexahydrophthalic anhydride (MHHPA) in terms of time to ignition (TTI), peak of heat release rate (pHRR) and total heat release (THR). Aside from identical TTI values for both systems, EUFU-EP had lower pHRR and THR values, which were indicative of higher flame retardancy performance for EUFU-EP. This was mainly explained by the presence of a packed aromatic structure in EUFU-EP resin, which reflected in higher char content and glass transition temperature ( $T_g$ ). Although the crosslinking density of EUFU-EP/MHHPA was lower than that of the EUFU-EP/MHHPA system, the mechanical properties of EUFU-EP/MHHPA were improved due to the presence of furan and aromatic structures in the EUFU-EP backbone.

Likewise, Dai et al. [45] revealed that bio-based diglycidyl ether of daidzein (DGED) cured with 4,4'-diaminodiphenylmethane (DDM) was more reactive than the petroleum-based DGEBA. Such a higher reactivity was attributed to the additional unsaturated double bonds in DGED structure involved in the course of curing reaction. Consequently, the viscosity of DGED increased faster than that of DGEBA and; thus, the thermo-mechanical properties of DGED/DDM stand over DGEBA/DDM systems. From the flammability point of view, DGED formed char at the surface during combustion, which protected the bottom layers from heat transfer leading to self-extinguish in just 3 s with a very smaller flame. Since no complementary flame tests such as cone calorimetry were conducted, it appears difficult to

understand the flame behaviour of the proposed system taking into account the resistance of material contributed from condensed phase.

Wan et al. [46] synthesized bio-epoxy resins by making linked two eugenol molecules together followed by epoxidation of terminal groups (DEU-EP), which resulted in a product with very high bio-based content of ca. 70 wt.%. This monomer was cured with DDM. The authors studied cure kinetics mechanism of bio-epoxy using model-free isoconversional approach and reported that addition of eugenol building blocks in the chain backbone as well as and their arrangement greatly affected cure behavior of DEU-EP/DDM systems. As a result, mechanical properties and high-temperature charring ability and flammability resistance were enhanced. It was also reported that DEU-EP/DDM resin left 38% char at 800 °C, which was almost twice the amount left by the DGEBA/DDM system. Moreover, pHRR (201 kW/m<sup>2</sup>) and THR (16.3 kJ/m<sup>2</sup>) for DEU-EP were much lower than the values obtained for DGEBA. Eventually, self-extinguishing DEU-EP was attained in 10 s, which proved an inherent flame retardancy behavior. However, the storage modulus of DEU-EP dropped suddenly at higher temperatures where glass transition temperature occurred at 114 °C due to an increase in free volume and molecular mobility of DEU-EP polymer chains. Later, this group [47] developed eugenol-based bifunctional epoxy resins (TPEU-EP) with improved flame retardancy thanks to the full aromatic ester backbone of TPEU-EP. Despite lower crosslinking density of TPEU-EP compared to commercial DGEBA, an enhanced mechanical property was observed, which again was attributed to the aromatic structure of TPEU-EP. Cone calorimetry and burning analysis of TPEU-EP provided concrete evidence for potential application of TPEU-EP as an alternative for DGEBA of the synthesis route of TPEU-EP was economic-friendly for large scale production. Literature survey suggests that synthesis of flame retardant bio-epoxy experiences an early stage flourishing period, while chemically embedded FR elements in bio-epoxy were alternatives for inherent flame retardant bio-epoxy.

### **3. FR elements chemically embedded in bio-epoxy backbone**

#### **3.1. Silicon-containing FR**

Silicon compounds improve flame retardancy of epoxy resins as a result of formation of residue in the condensed phase as well as the presence of radicals in vapour phase [48-50]. Li et al. [51] linked epoxidized eugenol bio-epoxy (EPEU) with silicon-containing bridges with different lengths and chemical structures. It was found that the flammability of the prepared silicon-containing bio-epoxy resin was significantly improved in comparison to the commercial DGEBA. The value of LOI reported for DGEBA was 22.8%, which was improved up to 31% for phenyl siloxane-containing bio-epoxy resins. This was explained by the carbonation of phenyl groups as well as the migration of Si-O to the surface, which formed an ablative layer that avoided the penetration of oxygen and fuel through the combustion layer. Moreover, the viscosity of the prepared silicon-containing bio-epoxy decreased when the length of siloxane linker increased, which eased epoxy curing reaction. The authors did not report on the mechanical and thermal properties of the prepared systems.

#### **3.2. Phosphorous-containing FR**

There are numerous works reporting the flame retardancy effect of phosphorous-containing compounds, which mainly benefit from char formation in the condensed phase [48, 52].

Menard et al. [38] embedded diglycidyl mono-phosphonated phloroglucinol reactive flame retardant derived from renewable resources of phloroglucinol in triglycidyl phloroglucinol (P3EP), and reported that the phosphorous flame retardant embedded in P3EP deteriorated thermal stability of epoxy resin; Such a behavior was explained by the plasticizing role of the flame retardant. However, the flammability of phosphorous flame retardants embedded in bio-epoxy was improved significantly, as confirmed by pyrolysis combustion flow calorimetry (PCFC) data together with char content measurements. Nevertheless, it should be

noticed that the complementary flammability tests were principally needed to be conducted for this system to fully comprehend the flame behaviour of system.

Elsewhere [53], a phosphorus-containing bio-epoxy resin (EADI) was prepared based on itaconic acid (IA) and 9,10-dihydro-9-oxa-10-phosphaphenanthrene 10-oxide (DOPO), then it was used as bio-based flame retardant in DGEBA system. Mechanical and thermal properties of DGEBA/EADI were found to be as good as those of DGEBA systems, with a significant improvement flame retardancy in of bio-based system in terms of LOI, char content and burning time.

In search for bio-epoxy resins, Lligadas et al. [35] synthesized two different epoxidized monomers including 10-undecenoyl triglyceride (UDTGE) and methyl 3,4,5-tris(10-undecenoyloxy) benzoate (UDBME) from fatty acids. To improve their flame retardancy properties, 10-[2',5'-bis(9-oxiranyl-nonayloxy)phenyl]-9,10-dihydro-9-oxa-10-phosphaphenanthrene-10 oxide (DOPO-III) and bis(m-aminophenyl) methylphosphine oxide (BAMPO) were added to the structure of epoxy resin as flame retardant and curing agent, respectively. It was found that the  $T_g$  of UDBME-based resin was higher than that of UDTGE due to the presence of aromatic groups in the chemical structure of UDBME. However,  $T_g$  decreased upon addition of phosphorous-containing FR due to a lower crosslinking density. From a flammability point of view, LOI values and charring residue were both improved upon addition of phosphorous-containing DOPO-III and BAMPO. However, more accurate and reliable tests were required to fully analyse the flame behavior performance of the proposed system.

#### 4. Concluding remarks and recommendations for future works

DGEBA is the most sought epoxy resin in industrial applications thanks to its remarkable features. However, high volume usage of this monomer in various applications has risen increasing environmental concerns. By contrast, bio-epoxy resins produced from sustainable resources promise a green alternative for DGEBA. Such resins possess comparable properties to commercial DGEBA in terms of mechanical and thermal properties. Yet, bio-based epoxy resins suffer from high flammability, which jeopardize their potential application in many technical fields. Flammability of bio-epoxy resins has been addressed mainly through the incorporation of flame retardant elements or synthesis of bio-epoxy monomers with high char yield.

Up to date, seldom investigations have highlighted the flammability of bio-epoxy resins, which are summarized in **Table 2**. For most cases, inadequate flame resistance of the proposed bio-epoxy systems has been highlighted by the investigators, which needs further investigations. On the other hand, flame retardancy of polyphenols derived from sustainable resources offer a great potential for fabrication of fully bio-epoxy resin, and this deserve to be considered for future works. For instance, Qi et al. [54] cured epoxidized soybean oil (ESO) with Tannic acid (TA) and histidine (His) as the curing agent and accelerator, respectively. The curing reaction between ESO and TA is relatively slow, but the addition of His improves the curing rate significantly, which was evident by nonisothermal analysis of curing kinetics. In addition, ESO/TA resins are thermally stable with an initial decomposition at 270 °C. However, the flame behaviour of this system has not been fully addressed yet. We believe that polyphenols with numerous hydroxyl groups provide a great substrate to link with the listed bio-epoxy resins observed in **Table 1**. Thus, this mini-review has aimed its focus on the importance of the study and development of fully bio-epoxy resins with fire retardancy properties by highlighting the importance of synthesis of flame resistant bio-epoxy resins.

Table 2: Flame behaviour of reported bio-based epoxy resins

Epoxy resin	Curing agent	FR	$T_g$ (°C)	LOI (%)	Residue (%)	Cone calorimetry			UI-94	Ref.
						TTI (s)	pHRR (kW.m <sup>-2</sup> )	THR (mJ.m <sup>-2</sup> )		
EUFU-EP	MHHPA	-	153	-	10.9	200	291.3	20	-	[44]
DGED	DDM	-	205	31.6	42.9	-	-	-	V0	[45]
DEU-EP	DDM	-	114	-	38	-	-	-	-	[46]
TPEU-EP	DDS	-	168	26.8	31.7	33	860	50.1	-	[47]
EPEU	DDS	Siloxane	-	28	14.9	28	662	73.9	-	[51]
P3EP	DIFFA	P2EP1P	124	-	43.5	-	-	-	-	[38]
DGEBA	MHHPA	EADI	109	31.4	5.55	-	-	-	V0	[53]
UDTGE, UDBME	BAMPO	DOPO-III	≈80	>28	>18	-	-	-	-	[35]
ESO	TA		57		8.7	-	-	-		[54]

## References

- [1] F.-L. Jin, X. Li, S.-J. Park, Synthesis and application of epoxy resins: A review, *Journal of Industrial and Engineering Chemistry*, 29 (2015) 1-11.
- [2] J.K. Fink, 3 - Epoxy Resins, in: J.K. Fink (Ed.) *Reactive Polymers: Fundamentals and Applications* (Third Edition), William Andrew Publishing, 2018, pp. 139-223.
- [3] M.H. Kothmann, R. Zeiler, A. Rios de Anda, A. Brückner, V. Altstädt, Fatigue crack propagation behaviour of epoxy resins modified with silica-nanoparticles, *Polymer*, 60 (2015) 157-163.
- [4] S. Kenig, *Processing of Polymer Nanocomposites*, Carl Hanser Verlag GmbH Co KG, 2019.
- [5] M. Shibata, T. Ohkita, Fully biobased epoxy resin systems composed of a vanillin-derived epoxy resin and renewable phenolic hardeners, *European Polymer Journal*, 92 (2017) 165-173.
- [6] S. Kumar, S. Krishnan, S. Mohanty, S.K. Nayak, Synthesis and characterization of petroleum and biobased epoxy resins: a review, *Polymer International*, 67 (2018) 815-839.
- [7] Y. Huang, C. Wong, J. Zheng, H. Bouwman, R. Barra, B. Wahlström, L. Neretin, M.H. Wong, Bisphenol A (BPA) in China: a review of sources, environmental levels, and potential human health impacts, *Environment international*, 42 (2012) 91-99.
- [8] R. Valentino, V. D'Esposito, F. Ariemma, I. Cimmino, F. Beguinot, P. Formisano, Bisphenol A environmental exposure and the detrimental effects on human metabolic health: is it necessary to revise the risk assessment in vulnerable population?, *Journal of endocrinological investigation*, 39 (2016) 259-263.
- [9] J. Corrales, L.A. Kristofco, W.B. Steele, B.S. Yates, C.S. Breed, E.S. Williams, B.W. Brooks, Global assessment of bisphenol A in the environment: review and analysis of its occurrence and bioaccumulation, *Dose-Response*, 13 (2015) 1559325815598308.
- [10] G. Das, N. Karak, Vegetable oil-based flame retardant epoxy/clay nanocomposites, *Polymer degradation and stability*, 94 (2009) 1948-1954.
- [11] F.L. Jin, S.J. Park, Thermomechanical behavior of epoxy resins modified with epoxidized vegetable oils, *Polymer International*, 57 (2008) 577-583.
- [12] T. Malutan, R. Nicu, V.I. Popa, Lignin modification by epoxidation, *BioResources*, 3 (2008) 1371-13767.
- [13] A.M. Atta, R. Mansour, M.I. Abdou, A.M. Sayed, Epoxy resins from rosin acids: synthesis and characterization, *Polymers for Advanced Technologies*, 15 (2004) 514-522.

- [14] S. Benyahya, C. Aouf, S. Caillol, B. Boutevin, J.P. Pascault, H. Fulcrand, Functionalized green tea tannins as phenolic prepolymers for bio-based epoxy resins, *Industrial Crops and Products*, 53 (2014) 296-307.
- [15] S. Kanehashi, K. Yokoyama, R. Masuda, T. Kidesaki, K. Nagai, T. Miyakoshi, Preparation and characterization of cardanol-based epoxy resin for coating at room temperature curing, *Journal of Applied Polymer Science*, 130 (2013) 2468-2478.
- [16] S. Ma, X. Liu, Y. Jiang, Z. Tang, C. Zhang, J. Zhu, Bio-based epoxy resin from itaconic acid and its thermosets cured with anhydride and comonomers, *Green Chemistry*, 15 (2013) 245-254.
- [17] M. Chrysanthos, J. Galy, J.-P. Pascault, Preparation and properties of bio-based epoxy networks derived from isosorbide diglycidyl ether, *Polymer*, 52 (2011) 3611-3620.
- [18] C. Aouf, H. Nouailhas, M. Fache, S. Caillol, B. Boutevin, H. Fulcrand, Multi-functionalization of gallic acid. Synthesis of a novel bio-based epoxy resin, *European Polymer Journal*, 49 (2013) 1185-1195.
- [19] M.R. Saeb, F. Najafi, E. Bakhshandeh, H.A. Khonakdar, M. Mostafaiyan, F. Simon, C. Scheffler, E. Mäder, Highly curable epoxy/MWCNTs nanocomposites: an effective approach to functionalization of carbon nanotubes, *Chemical engineering journal*, 259 (2015) 117-125.
- [20] M.R. Saeb, E. Bakhshandeh, H.A. Khonakdar, E. Mäder, C. Scheffler, G. Heinrich, Cure kinetics of epoxy nanocomposites affected by MWCNTs functionalization: a review, *The Scientific World Journal*, 2013 (2013).
- [21] D. Puglia, H. Rastin, M.R. Saeb, B. Shojaei, K. Formela, Cure kinetics of epoxy/MWCNTs nanocomposites: isothermal calorimetric and rheological analyses, *Progress in Organic Coatings*, 108 (2017) 75-83.
- [22] M.G. Sari, M.R. Saeb, M. Shabaniyan, M. Khaleghi, H. Vahabi, C. Vagner, P. Zarrintaj, R. Khalili, S.M.R. Paran, B. Ramezanzadeh, M. Mozafari, Epoxy/starch-modified nano-zinc oxide transparent nanocomposite coatings: A showcase of superior curing behavior, *Progress in Organic Coatings*, 115 (2018) 143-150.
- [23] H. Rastin, M.R. Saeb, M. Nonahal, M. Shabaniyan, H. Vahabi, K. Formela, X. Gabrion, F. Seidi, P. Zarrintaj, M.G. Sari, P. Laheurte, Transparent nanocomposite coatings based on epoxy and layered double hydroxide: Nonisothermal cure kinetics and viscoelastic behavior assessments, *Progress in Organic Coatings*, 113 (2017) 126-135.
- [24] J. Deng, X. Liu, C. Li, Y. Jiang, J. Zhu, Synthesis and properties of a bio-based epoxy resin from 2, 5-furandicarboxylic acid (FDCA), *Rsc Advances*, 5 (2015) 15930-15939.
- [25] X. Liu, W. Huang, Y. Jiang, J. Zhu, C. Zhang, Preparation of a bio-based epoxy with comparable properties to those of petroleum-based counterparts, *Express Polymer Letters*, 6 (2012).
- [26] G. Mashouf Roudsari, A.K. Mohanty, M. Misra, Study of the curing kinetics of epoxy resins with biobased hardener and epoxidized soybean oil, *ACS Sustainable Chemistry & Engineering*, 2 (2014) 2111-2116.
- [27] H. Vahabi, B.K. Kandola, M.R. Saeb, Flame Retardancy Index for Thermoplastic Composites, *Polymers*, 11 (2019) 407.
- [28] M. Jouyandeh, S.M.R. Paran, A. Jannesari, M.R. Saeb, 'Cure Index' for thermoset composites, *Progress in Organic Coatings*, 127 (2019) 429-434.
- [29] H. Vahabi, M.R. Saeb, K. Formela, J.-M.L. Cuesta, Flame retardant epoxy/halloysite nanotubes nanocomposite coatings: Exploring low-concentration threshold for flammability compared to expandable graphite as superior fire retardant, *Progress in Organic Coatings*, 119 (2018) 8-14.
- [30] H. Vahabi, M. Jouyandeh, M. Cochez, R. Khalili, C. Vagner, M. Ferriol, E. Movahedifar, B. Ramezanzadeh, M. Rostami, Z. Ranjbar, B.S. Hadavand, M.R. Saeb, Short-lasting fire in partially and completely cured epoxy coatings containing expandable graphite and halloysite nanotube additives, *Progress in Organic Coatings*, 123 (2018) 160-167.
- [31] M. Rakotomalala, S. Wagner, M. Döring, Recent developments in halogen free flame retardants for epoxy resins for electrical and electronic applications, *Materials*, 3 (2010) 4300-4327.

- [32] B. Perret, B. Schartel, K. Stöß, M. Ciesielski, J. Diederichs, M. Döring, J. Krämer, V. Altstädt, Novel DOPO-based flame retardants in high-performance carbon fibre epoxy composites for aviation, *European Polymer Journal*, 47 (2011) 1081-1089.
- [33] X. Wang, Y. Hu, L. Song, W. Xing, H. Lu, P. Lv, G. Jie, Flame retardancy and thermal degradation mechanism of epoxy resin composites based on a DOPO substituted organophosphorus oligomer, *Polymer*, 51 (2010) 2435-2445.
- [34] R. Ménard, C. Negrell, L. Ferry, R. Sonnier, G. David, Synthesis of biobased phosphorus-containing flame retardants for epoxy thermosets comparison of additive and reactive approaches, *Polymer Degradation and Stability*, 120 (2015) 300-312.
- [35] G. Lligadas, J. Ronda, M. Galià, V. Cádiz, Development of novel phosphorus-containing epoxy resins from renewable resources, *Journal of Polymer Science Part A: Polymer Chemistry*, 44 (2006) 6717-6727.
- [36] H. Vahabi, M. Jouyandeh, M. Cochez, R. Khalili, C. Vagner, M. Ferriol, E. Movahedifar, B. Ramezanzadeh, M. Rostami, Z. Ranjbar, Short-lasting fire in partially and completely cured epoxy coatings containing expandable graphite and halloysite nanotube additives, *Progress in Organic Coatings*, 123 (2018) 160-167.
- [37] L. Costes, F. Laoutid, S. Brohez, P. Dubois, Bio-based flame retardants: When nature meets fire protection, *Materials Science and Engineering: R: Reports*, 117 (2017) 1-25.
- [38] R. Ménard, C. Negrell, M. Fache, L. Ferry, R. Sonnier, G. David, From a bio-based phosphorus-containing epoxy monomer to fully bio-based flame-retardant thermosets, *RSC Advances*, 5 (2015) 70856-70867.
- [39] T.C. Mauldin, M. Zammarano, J.W. Gilman, J.R. Shields, D.J. Boday, Synthesis and characterization of isosorbide-based polyphosphonates as biobased flame-retardants, *Polymer Chemistry*, 5 (2014) 5139-5146.
- [40] G. Marosi, B. Szolnoki, K. Bocz, A. Toldy, Fire-retardant recyclable and biobased polymer composites, in: *Novel Fire Retardant Polymers and Composite Materials*, Elsevier, 2017, pp. 117-146.
- [41] S. Liang, N.M. Neisius, S. Gaan, Recent developments in flame retardant polymeric coatings, *Progress in Organic Coatings*, 76 (2013) 1642-1665.
- [42] E. Ramon, C. Sguazzo, P. Moreira, A Review of Recent Research on Bio-Based Epoxy Systems for Engineering Applications and Potentialities in the Aviation Sector, *Aerospace*, 5 (2018) 110.
- [43] C.E. Hobbs, Recent Advances in Bio-Based Flame Retardant Additives for Synthetic Polymeric Materials, *Polymers*, 11 (2019) 224.
- [44] J.-T. Miao, L. Yuan, Q. Guan, G. Liang, A. Gu, Biobased heat resistant epoxy resin with extremely high biomass content from 2, 5-furandicarboxylic acid and eugenol, *ACS Sustainable Chemistry & Engineering*, 5 (2017) 7003-7011.
- [45] J. Dai, Y. Peng, N. Teng, Y. Liu, C. Liu, X. Shen, S. Mahmud, J. Zhu, X. Liu, High-performing and fire-resistant biobased epoxy resin from renewable sources, *ACS Sustainable Chemistry & Engineering*, 6 (2018) 7589-7599.
- [46] J. Wan, B. Gan, C. Li, J. Molina-Aldareguia, E.N. Kalali, X. Wang, D.-Y. Wang, A sustainable, eugenol-derived epoxy resin with high biobased content, modulus, hardness and low flammability: synthesis, curing kinetics and structure–property relationship, *Chemical Engineering Journal*, 284 (2016) 1080-1093.
- [47] J. Wan, B. Gan, C. Li, J. Molina-Aldareguia, Z. Li, X. Wang, D.-Y. Wang, A novel biobased epoxy resin with high mechanical stiffness and low flammability: synthesis, characterization and properties, *Journal of Materials Chemistry A*, 3 (2015) 21907-21921.
- [48] A. Kausar, I. Rafique, Z. Anwar, B. Muhammad, Recent developments in different types of flame retardants and effect on fire retardancy of epoxy composite, *Polymer-Plastics Technology and Engineering*, 55 (2016) 1512-1535.
- [49] W. Wang, L. Perng, G. Hsiue, F. Chang, Characterization and properties of new silicone-containing epoxy resin, *Polymer*, 41 (2000) 6113-6122.



- [50] E. Franchini, J. Galy, J.-F. Gérard, D. Tabuani, A. Medici, Influence of POSS structure on the fire retardant properties of epoxy hybrid networks, *Polymer Degradation and Stability*, 94 (2009) 1728-1736.
- [51] C. Li, H. Fan, T. Aziz, C. Bittencourt, L. Wu, D.-Y. Wang, P. Dubois, Biobased epoxy resin with low electrical permittivity and flame retardancy: from environmental friendly high-throughput synthesis to properties, *ACS Sustainable Chemistry & Engineering*, 6 (2018) 8856-8867.
- [52] M.M. Velencoso, A. Battig, J.C. Markwart, B. Schartel, F.R. Wurm, Molecular firefighting—how modern phosphorus chemistry can help solve the challenge of flame retardancy, *Angewandte Chemie International Edition*, 57 (2018) 10450-10467.
- [53] S. Ma, X. Liu, Y. Jiang, L. Fan, J. Feng, J. Zhu, Synthesis and properties of phosphorus-containing bio-based epoxy resin from itaconic acid, *Science China Chemistry*, 57 (2014) 379-388.
- [54] M. Qi, Y.-J. Xu, W.-H. Rao, X. Luo, L. Chen, Y.-Z. Wang, Epoxidized soybean oil cured with tannic acid for fully bio-based epoxy resin, *RSC Advances*, 8 (2018) 26948-26958.