

10

Flame Retardancy of Bioepoxy Polymers, Their Blends, and Composites

Young-O Kim and Yong Chae Jung

Korea Institute of Science and Technology (KIST), Institute of Advanced Composite Materials, 92, Chudong-ro, Bongdong-eup, Wanju-gun, Jeonbuk 55324, Republic of Korea

10.1 Introduction

At present, over 90% of the world's epoxy resin materials are made of bisphenol-A-type diglycidyl ether (DGEBA) [1–3]. It is well established that the epoxy resins of bisphenol A type offer extraordinary physical properties including remarkable mechanical properties, chemical resistance, and form stability [1–5]. In general, epoxy resins cross-link into a rigid three-dimensional network structure by chemical reaction between monomers and hardeners [6]. These characteristics are employed in a wide range of applications such as coatings, adhesives, solar cells, automotive, and aerospace [7–9].

In recent years, problems associated with high combustibility, environmental issues, global warming, and oil depletion from the use of polymer materials as well as composite materials from epoxy have been observed. In addition, it has been recently demonstrated that the toxic effects of combustion severely affect humans as well as other living organisms [10–13]. Accordingly, significant research is being conducted on the development of renewable bio-based polymer materials from plants [14–17].

Technologies for developing bio-based polymer materials derived from plants or recycled materials can reduce the consumption of petrochemical products by petroleum-based engineering plastic producers [2, 14, 15, 17]. These technologies can also effectively reduce various environmental pollutants generated during production. Therefore, research on bio-based epoxy is both an important development direction in the field of polymer materials as well as an important means for saving energy, reducing pollutant emissions, and developing a low-carbon economy. In order to effectively solve these problems, in recent years, research has been performed on bio-based epoxy (i.e. from vegetable oil [18–20], lignin [21–24], rosin acid [25], tannin [26–28], and cardanol [29–33]) rather than on traditional petroleum-based epoxy. Significant attention has also been focused on the discovery of bio-based epoxy resins from renewable resources such as itaconic acid [34].

Because of the rapid advances in the synthesis of bioepoxy resins, these materials have been identified as potential candidates for replacing the commercial petroleum-based epoxy [14–34]. However, bio-based polymers are established to exhibit inferior mechanical and thermal properties owing to their long aliphatic chains and low cross-linking density [35]. In addition, the low curing behavior of resins results in the fatal degradation of bio-based epoxy resins.

Meanwhile, epoxy resins are vulnerable to heat. An increase in the temperature adversely affects the mechanical properties, and the combustion process generates smoke and hazardous substances. These are obstacles for the commercialization of composite materials. This problem highlights the need to improve the flame retardancy index of bioepoxy resins as well as petroleum-based epoxy resins [36–39]. Bioepoxy resins are also highly flammable. This problem must be resolved before these materials can be used in transportation, construction, and electronics. An effective strategy to improve the flame retardancy index of a resin is to add a flame retardant or to introduce a functional group capable of inducing flame retardancy to the matrix main chain or end group. However, the adverse effects of uniform dispersion or movement to the surface within the matrix still remain unresolved.

Bromine-based flame retardants are the most widely used flame retardants among the halogen-based flame retardants, accounting for 25% of the flame-retardant (FR) market in 2014 [40, 41]. These include Tetrabromobisphenol A (TBBPA), hexabromocyclododecane (HBCD), penta-BDE (bromodiphenyl ether), octa-BDE, and deca-BDE. However, halogen-based flame retardants are hazardous to humans as they cause cancers (octa-BDE and penta-BDE) or damage human lungs by generating toxic substances such as furan and dioxins or corrosive gases during combustion. They can also cause mechanical and electrical failures and severe problems such as accumulation in soil and air, which can destroy the ecosystem. In the early 2000s, international environmental regulations such as the Stockholm Convention banned the production and use of certain brominated flame retardants worldwide owing to the environmental debate. Accordingly, the development of eco-friendly bio-based epoxy resins and bio-based flame retardants with remarkable flame-retardant properties in the future can be considered to be an effective approach to solving the above problems [42–44].

Against this backdrop, we report on the present research into flame-retardant bio-based epoxy resins, in this chapter. Specifically, we describe the flame retardancy evaluation method, recent market trend, and flame retardancy of epoxy based on lignin and tannic acid (TA). Finally, the recent research trend of the flame retardancy of bioepoxy using nano- or micro-sized organic–inorganic additives is described.

10.2 Methods for Analyzing Flame-Retardant Properties

A flame-retardant material burns when it comes in contact with a flame. However, when the flame is removed, it prevents or suppresses combustion, i.e. the

material is not burned. It is a property that lowers or halts the propagation capability of fire. In general, flame-retardant materials have a limit of 25 or more. Combustion of plastics proceeds in the order of pyrolysis, and the combustion process can be classified into micro, macro, and mass, respectively. The macro, micro, and mass scales are with regard to the molecular behavior in plastics, the material behavior, and the behavior in real systems such as space or structure, respectively. Generally, flame-retardant combustion can be divided into five stages:

- (1) *Stage 1*: It is heating. The specific heat, thermal conductivity, latent heat, and phase transition (melting, sublimation, and evaporation) are the determining factors. Specific heat is the amount of heat required to increase the temperature of unit weight of material. The higher the specific heat, the more gradually the temperature increases. Furthermore, the higher the thermal conductivity is for a specified temperature variation and the material thickness, the more straightforward is the heat transfer.
- (2) *Stage 2*: It is the decomposition process. Here, combustible gas, noncombustible gas, liquid, solid, and smoke are generated. The main determinants are the initial decomposition temperature, light heat, and the decomposition behavior of polymer resins.
- (3) *Stage 3*: It is an ignition process, where combustible gases are inflamed in the presence of oxygen or an oxidant. The flash ignition temperature, self-ignition temperature, and limit oxygen concentration are the determining factors.
- (4) *Stages 4 and 5*: They are the processes of combustion and propagation. In the combustion stage, the combustion heat or the heat of emission emerges, and in the progress stage, the combustion is apparently diffused.

The flame-retardant test methods involve the measurement of the oxygen index, combustion rate, combustion time, and smoke generation. Countries use either their own standards or the universally accepted UL (Underwriters Laboratories) method. UL is an independent, not-for-profit organization that sets or tests standards for safety. This section introduces the most commonly used vertical test, 5V test, and oxygen index. The specifications of other countries are briefly described in Table 10.1.

Table 10.1 The oxygen index of representative plastics.

Plastic	LOI	Plastic	LOI
Polyoxymethylene (ACETAL)	14.9	polyethylene terephthalate (PET)	20.6
Poly methyl methacrylate (PMMA)	17.3	Poly(phenylene oxide) (PPO)/HIPS	24.3
Polyethylene (PE)	17.4	NYLON	24.3
Polypropylene (PP)	17.4	Polycarbonate (PC)	24.9
Polystyrene (PS)	17.8	Poly(vinyl chloride) (PVC)	45.0
High impact polystyrene (HIPS)	18.2	Amorphous silica (AS)	18.8
Styrene-acrylonitrile (SAN)	19.1		

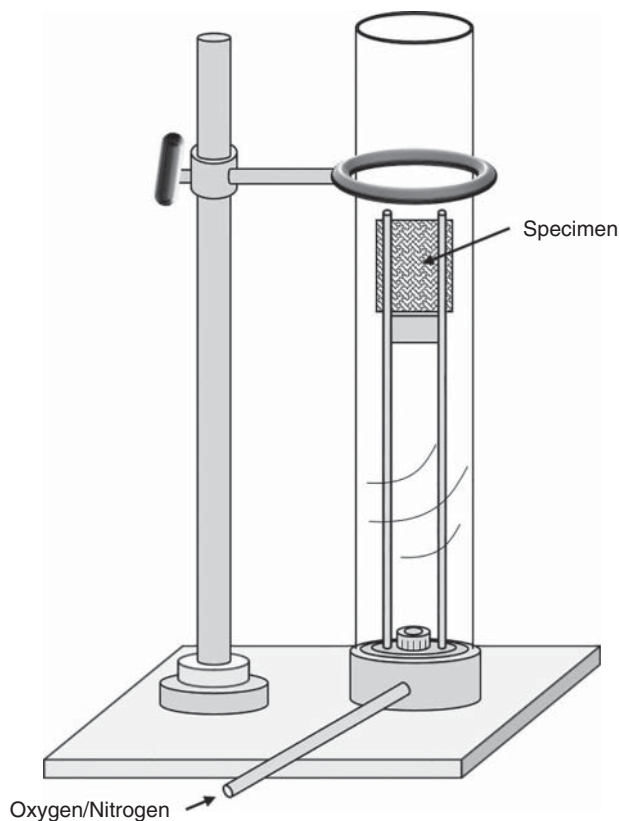


Figure 10.1 LOI test method.

10.2.1 LOI (Limiting Oxygen Index)

The limiting oxygen index (LOI) is a representative measurement method for evaluating the combustibility of a material as shown in Figure 10.1. It is the minimum oxygen concentration (of a nitrogen–oxygen mixture) required that supports the combustion of the material. In general, the higher the ignition resistance of a material is, the higher is the oxygen index [45].

The temperature of the gas mixture affects the oxygen index. The standard atmosphere at sea level has 21% oxygen. The LOI evaluation is performed after 24 hours of pretreatment in a constant temperature/humidity chamber at $23 \pm 2^\circ\text{C}$, $50 \pm 5\%$ RH, with specimens of 10 mm width and 120 mm length (according to ISO 4589, ASTM D 2863, and NFT 51-071) [46]. In the measuring method, the specimen is first fixed perpendicularly to the measuring equipment. Then, a certain amount of high-purity nitrogen and oxygen is introduced into the lower portion. At this time, the combustion source is ignited at the tip of the sample to assess the combustion behavior, and the likelihood that the combustion state can be maintained even after the heat source is removed. The limit oxygen index is defined as follows:

$$\text{LOI} = [\text{O}_2]/[(\text{O}_2) + (\text{N}_2)] \times 100 \quad (10.1)$$

where O_2 is the oxygen flow rate (l/min) and N_2 is the nitrogen flow rate (l/min). The limit oxygen index is defined as the minimum oxygen concentration of the oxygen–nitrogen mixture air required for a sample to ignite without burning for 90 seconds.

Consider the example of PET in Table 10.1. An LOI of 20.6% implies that if the oxygen concentration in the air is reduced below 20.6%, the combustion cannot be continued after the heat source is removed. In general, a material with an LOI of 20.9 or less burns well in the air; a material with an LOI between 20.9 and 27 burns gradually in air. If the LOI is 27 or more, the material can be considered as a self-extinguishing test piece that is difficult to burn in air.

The marginal oxygen index represents the burning characteristics of plastics. However, it differs slightly from the UL-94 flame retardant. This is discussed subsequently. The flame retardancy of various plastics exhibits a tendency to increase the LOI as the amount of flame retardant used increases. However, UL-94 flame retardancy is different in that the flame retardancy is realized only when a certain amount of flame retardant is present.

10.2.2 UL-94

Developed by the Underwriter's Laboratory (UL), a nonprofit organization founded by the American fire insurer in 1894, it is one of the most commonly used methods for evaluating the flame retardancy. The UL-94 test method is divided into the horizontal combustion test (HB) applied to noncombustible resins, vertical combustion test applied to flame-retardant resins, and flat combustion test. These are described in Figure 10.2 and are rated by combustion time, flame drop, and afterglowing extinguishing time.

10.2.2.1 Horizontal Testing (UL-94 HB)

UL-94 HB measurement provides the HB rating by measuring the flame propagation velocity for verifying the flame propagation pattern in the horizontal direction after providing the heat source to the specimen. The evaluation method comprises measuring the combustion time after the flame is applied to a 1 in. (25 mm) section after applying the flame for 30 seconds or until the mark is

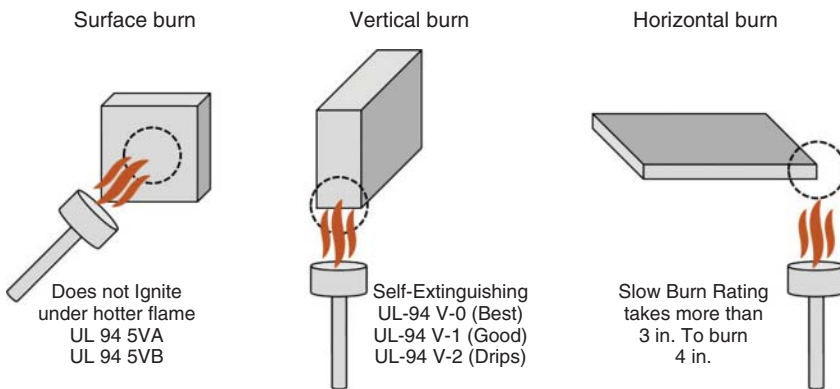


Figure 10.2 UL-94 method.

Table 10.2 UL-94 rating.

	V-0	V-1	V-2
Individual after-flame time, t_1 or t_2	≤ 10 s	≤ 30 s	≤ 30 s
Total after-flame time for any condition set, $t_1 + t_2$ for these five specimens	≤ 50 s	≤ 250 s	≤ 250 s
After-flame plus afterglow time for each individual specimen after the second flame application, $t_2 + t_3$	≤ 30 s	≤ 60 s	≤ 60 s
Burning up to the holding clamp (125 mm under line)	No		
Cotton ignition	No		Yes

reached. Moreover, it measures the combustion speed within the range up to 4 in. (100 mm). The HB rating is satisfied when specimens of thickness larger than 3.0 mm exhibit a burn rate of 40 mm/min or less and those of thickness less than 3.0 mm exhibit a burn rate below 75 mm/min.

10.2.2.2 Vertical Testing (UL-94 V)

It is a method of evaluating the combustion pattern of the product and the degree of flame propagation to the surroundings, upon the application of a flame to the test piece in the vertical direction. Install the specimen vertically and apply a flame under it for 10 seconds to measure the time until the fire on the specimen and the additional ignition caused by the falling drops are extinguished. If combustion stops within 30 seconds of applying the first flame, apply the flame again for another 10 seconds and measure the second combustion time. Grades are assigned based on this evaluation as illustrated in Table 10.2.

10.2.3 Cone Calorimeter

Cone calorimeter is a bench-scale test widely used for evaluating a material's fire hazard or flame retardancy. It measures the heat release rate (HRR) and the smoke and gas production as evaluation indices to quantitatively express the fire risk and hazard of new materials. In addition, because a combustion process initiated by thermal stimulation (generally called external heat flux) and spark during cone calorimeter analysis represents a typical fire-developing scenario, it is also effective for establishing the fire model occurring in materials by using a small specimen and reduced time and cost.

10.2.3.1 Configuration

A cone calorimeter for horizontal testing is generally used for analyzing the flame-retardant properties of samples and its structure is shown in Figure 10.3. The required sample is of size 100×100 mm and thickness between 2 and 50 mm. The edge of the sample is covered by a steel-framed holder, reducing the exposed area to 94×94 mm. The holder containing the sample is mounted on a load cell and is exposed to a conical heater, which controls the radiant heat flux. An electric spark is used to ignite the center of the specimens. The flames

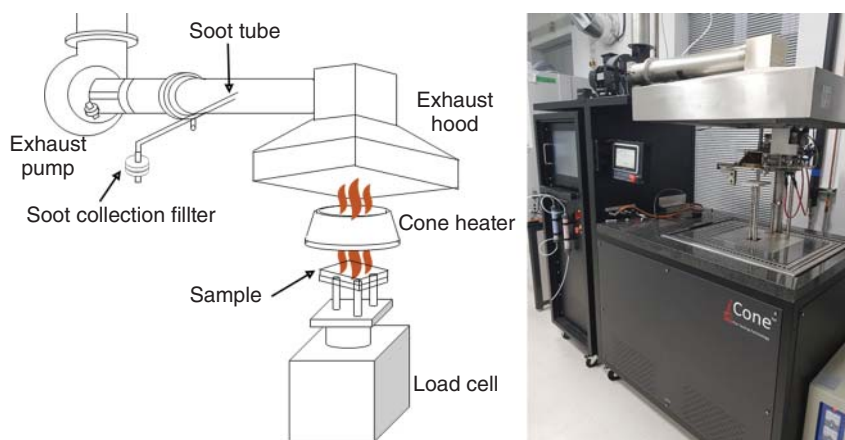


Figure 10.3 Cone calorimeter configuration.

and combustion products pass through the circular opening at the center of the heater and the exhaust hood. The oxygen depleted during the burning process of the sample is the basis for calculating the heat release. It is analyzed using a paramagnetic analyzer. In addition, CO and CO₂ are analyzed by a nondispersive infrared analyzer. Provided the effluent flow through the exhaust is effectively controlled, the heat release will be proportional to the oxygen depletion. Procedures for conducting cone calorimeter tests are described in ASTM E 1354 and ISO 5660.

10.2.3.2 Controlling Factors: Heat Flux, Thickness, and Distance Between Sample Surface and Cone Heater

Heat Flux Heat flux is the flow of energy per unit area per unit time. Therefore, different external heat fluxes can alter the fire behavior of samples. An increase in the external heat flux increases the time for attaining the ignition temperature, the expansion rate of decomposition, and fuel production rate. Ultimately, an increase in the external heat flux can increase the rate of release of heat from the burning samples. In general, as shown in Figure 10.4, with increasing external heat flux, the peak of the heat release rate (PHRR) appears at earlier time and increases linearly [47]. Meanwhile, the total heat release (THR), which is obtained by integration over time, is constant.

Thickness The thickness of the specimen on the cone calorimeter influences the flammability. Therefore, the thickness details must be discussed for analyzing the results of the cone calorimeter. The thickness-dependent flame retarding response of the specimen is illustrated in Figure 10.5 [48]. Thermally thin poly(methyl methacrylate) (PMMA) as a noncharring polymer exhibits a sharp HRR peak and short ignition time. As the thickness increases, the PHRR decreases, and the flaming time increases. In addition, an increase in the sample thickness increases the time to PHRR, owing to the increase in the time when the pyrolysis zone approaches the glass wool supporting the sample. This can

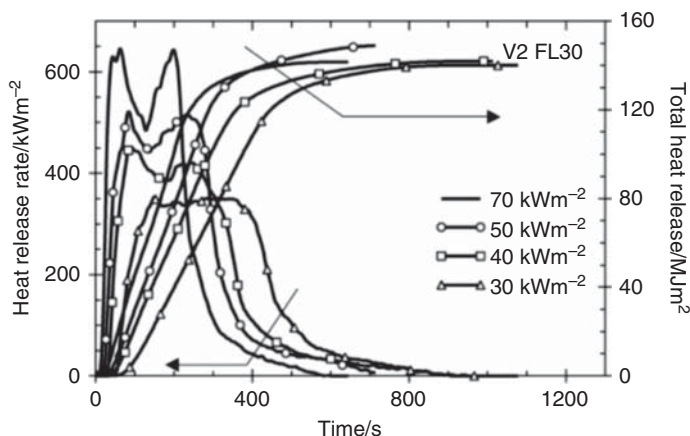


Figure 10.4 Heat flux-dependent HRR and THR for glass fiber-reinforced PA 66. Source: Reproduced from Schartel et al. [47]. © 2003, Elsevier.

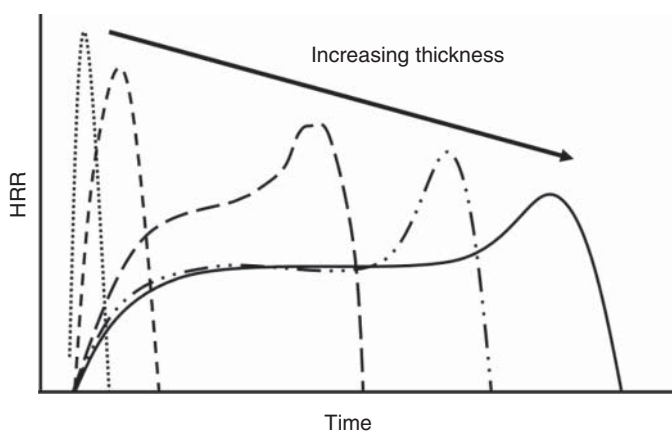


Figure 10.5 Sample thickness-dependent HRR for PMMA [48].

reduce the conductive heat flux. In contrast, for the char-forming material, the time to PHRR is constant, which is ascribed to the formation of PHRR by the ignition-initiated char formation. In general, a comparison of cone calorimeter results between new materials has been conducted with identical thickness of the samples. As shown in Figure 10.6, the characteristic response of the HRR vs. time can be determined by the type of the sample and thickness. This aids us in analyzing the flame retardancies of materials.

Distance Between Sample Surface and Cone Heater During the cone calorimeter analysis, a constant heat flux is applied to the sample such that its surface is gradually heated to temperatures above the decomposition temperature. The distance below the cone heater can affect the heat flux on the sample surface, i.e. the effective heat flux (Figure 10.7) [49]. The commercialized cone calorimeter

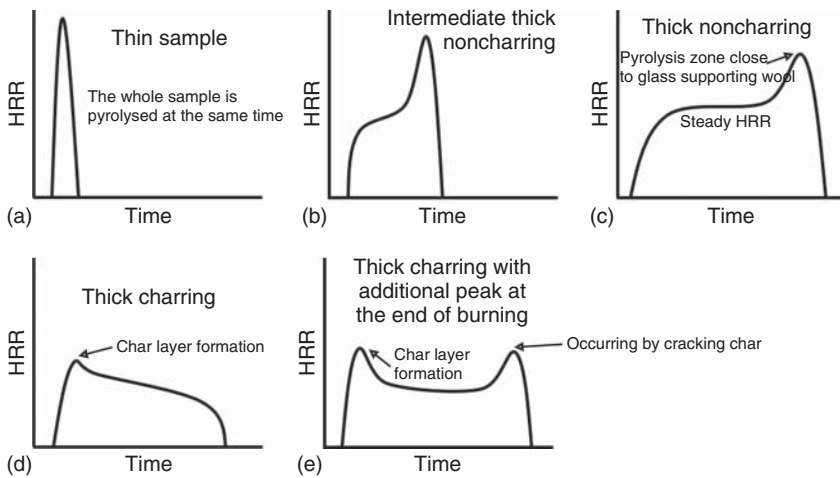


Figure 10.6 HRR curves for different types of samples. (a) Thin samples, (b) Intermediate thickness non-charring sample, (c) Thick non-charring sample, (d) Thick charring sample, and (e) Thick charring and non-charring sample.

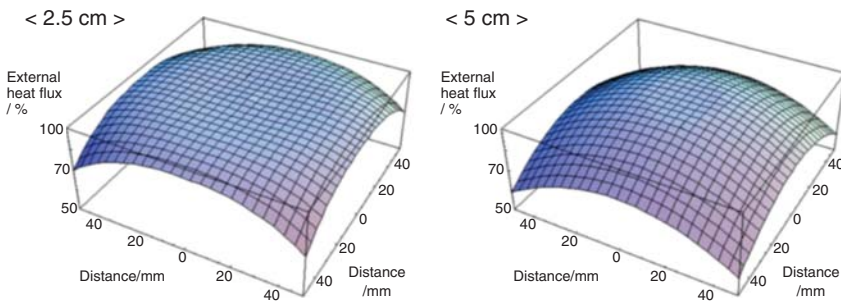


Figure 10.7 Effect of distance between a sample surface and the cone heater to external heat flux. Source: Reproduced from ScharTEL et al. [49]. © 2005, Elsevier.

is designed and optimized for a homogeneous heat flux on the whole sample surface. However, the distance between the sample surface and cone heater must be selected according to the purpose.

The distance between the sample surface and cone heater can also change based on the type of the sample. This change originates from the deformation of the sample during the combustion process. In thermoplastic materials, melting is generally induced before ignition, resulting in an increase in the distance. In most intumescent materials, whose flame-retarding mechanism arises from the expansion of the thermal insulating layer, the distance between the sample surface and cone heater decreases. Both cases can change the HRR pattern, leading to inaccurate data generation. Therefore, to improve the reproducibility and obtain accurate data, a protecting grid is used to reduce the deformation of the intumescent samples. In addition, if the combustion product is a liquid or a melt, which can cause material loss, an aluminum foil is used.

10.2.4 Microscale Combustion Calorimeter

The microscale combustion calorimeter (MCC) (pyrolysis combustion flow calorimetry (PCFC) was developed for the rapid and simple development of fire-resistant polymers by the U.S. Federal Aviation Administration (FAA). It is a miniature version of a cone calorimeter and requires only a milligram-size specimen. In addition, many factors considered for an accurate interpretation of the results can be excluded in this instrument. However, the obtained information is limited to that related to the HRR, such as the peak of the HRR, THR, and heat release capacity (HRC). The results obtained from the MCC are the HRR per mass unit of fuel volatiles (W/g) and specific HRR (Q) rather than the HRR per unit specimen area (W/m²). The HRC (J/g K) can be calculated by dividing the maximum Q by the heating rate (β , K/s).

Figure 10.8 shows the processes that a specimen undergoes in an MCC for gaining the flame-retardant properties. The specimen is subjected to an anaerobic (Method A) or aerobic (Method B) environment in a pyrolysis chamber. The sample is heated using linearly increasing temperature with a constant rate between 0.2 and 2 °C/s. This results in gaseous pyrolysis products and char formation. The gaseous pyrolysis products are completely oxidized at 900 °C, which is the temperature of the combustor. The gas stream exiting the combustor contains nitrogen, combustion products, and unreacted oxygen. This combustion gas stream cools and enters a Teflon tube tightly packed with anhydrous calcium sulfate (Drierite™) to remove moisture and acid gases from the sample stream, which can dilute the oxygen concentration measured by the oxygen analyzers.

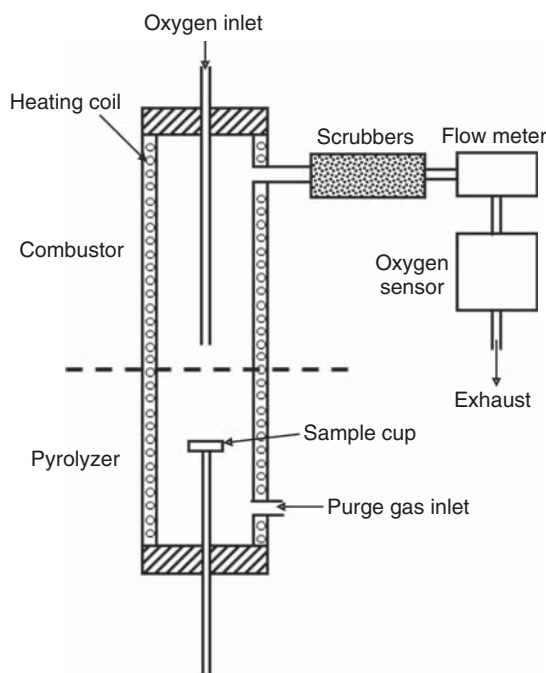


Figure 10.8 MCC configuration.

The transient HRR is calculated from the measured flow rate and oxygen concentration after correcting for flow dispersion. The HRR can be calculated from the depletion rate of oxygen required for completely oxidizing the pyrolysis gases using a polarographic or a zirconia oxygen analyzer. The heat of combustion of the volatile component and the net calorific value of the volatiles and solid residue during MCC are determined by Methods A and B, respectively.

10.3 Halogen-Free Flame-Retardant Market

The flame-retardant market was US\$8752.9 million and 2361.7 kilotons in 2015 [40, 41]. The market size is estimated at \$9385.7 million and 2489.5 kilotons in 2016 and is likely to attain \$12813.1 million and 3331.5 kilotons at a compound annual growth rate (CAGR) of 6.4% by 2021. In particular, in 2015, ATH (aluminum trihydrate) dominated the flame-retardant market, accounting for 35.6% of the total market. This is owing to its low cost, high efficiency, and minimal adverse impact on the environment compared to halogenated flame retardants. Among nonhalogenated flame retardants, phosphorus flame retardants are likely to have a maximum CAGR of 7.12% (volume) and 7.9% (value) between 2016 and 2021. Because the use of flame retardants for halogen compounds has been gradually reduced and banned since the 2000 Stockholm Convention, the development and use of flame retardants for nonhalogen compounds is likely to experience high demand in North America and the developed countries. Flame retardants are being and will be used in addition to various types of plastics and composites. Therefore, the demands for the use and development of flame retardants are increasing in developed and developing countries owing to stringent regulations to protect environmental safety and health.

Globally, China, Japan, and India in the Asia–Pacific region form a representative market (49.8% of the world market) that consumes flame retardants. Among these, China (which accounts for 38.2% of the total market in 2015) has a large ripple effect. The use of flame-retardant chemicals is increasing in the Asia–Pacific region owing to the presence of major developing countries such as China, India, and Korea. In all the countries in the Asia–Pacific region, regulations on fire safety and the demand for flame retardants are increasing.

10.4 Bioepoxy Polymers with Flame-Retardant Properties

Diglycidylether bisphenol A (DGEBA) constitutes 90% of the epoxy market. However, their inherently low flame retardancy induces the use of many flame retardants that are generally toxic halogen-containing materials. Therefore, to increase the intrinsic flame retardancy and decrease toxicity, greener halogen-free epoxy monomers have been considered, such as phosphorus- or aromatic structure-containing epoxy monomers. Phosphorus-containing

epoxy does not release toxic gases during the combustion process. Moreover, the phosphorus can spark the formation of the char layer as a gas and heat barrier. Aromatic structure-rich epoxy polymers are similar to the phosphorus-containing epoxy polymers with regard to the mechanism of improving the flame retardancy. With regard to char layer formation, an important information for designing epoxy polymers with flame retardancy is the char-forming tendency (CFT) [50]. It represents the degree of contribution to the amount of char residue depending on the molecular structures of polymers. According to Table 10.3, the aromatic structures exhibit a higher yield of combustion residue than the aliphatic structure. Moreover, they exert a higher flame-retardant effect in the solid phase.

There are abundant plant-based aromatic resources such as lignocellulosic and sugar biomass, furan, and tannins, with various functional groups. These have been chemically modified for producing bioepoxy polymers to be used as an epoxy monomer or a hardener. Hydroxyl, ethylene, and carboxylic acid groups are generally used to functionalize epoxy groups to bio-resources. In addition, phosphorus atoms are introduced into bio-resources for enhancing the flame-retardant properties of bioepoxy polymers by forming a char layer. In this section, we address the recently reported bio-resource-derived epoxy polymers without addition of flame retardant or other additives.









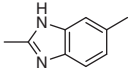

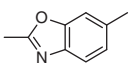
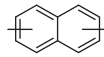
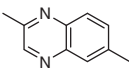
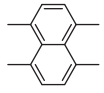
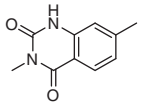
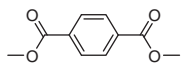
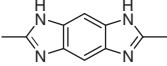
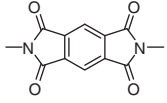
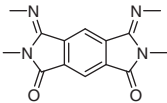
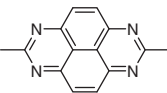
10.4.1 Lignocellulosic Biomass-Derived Epoxy Polymers

From lignocellulose, lignin, cellulose, and hemicellulose can be extracted. Lignin as the second most abundant natural organic material constitutes aromatic monomers. Monoaromatic compounds such as eugenol and vanillin having ethylene and aldehyde groups, respectively, in the *para*-position of 2-methoxyphenol (the so-called guaiacol) can be functionalized to a bioepoxy monomer form. Cellulose and hemicellulose are hydrolyzed and dehydrated, which can produce furan derivatives and can be modified for producing epoxy resins.

10.4.1.1 Eugenol

Eugenol-derived epoxy monomers for bioepoxy matrix with high flame retardancy can be conveniently obtained by oxidizing the double bond of an ethylene part using H_2O_2 /acetic acid or *meta*-chloroperoxybenzoic acid (mCPBA). Wang and co-workers [51] synthesized a eugenol-based epoxy monomer with full aromatic ester backbone (TPEU-EP [eugenol-based epoxy resin]) (Figure 10.9). They had it react with 3,3'-diaminodiphenylsulfone (33DDS) as a curing agent to produce a bio-based epoxy resin. Owing to its remarkable intumescent and high char yielding (31.7 wt%) capabilities, it exhibits a UL-94 V1 rating and has 1.14 times higher LOI than DGEBA/33DDS (26.8 vs. 23.5). The cone calorimetry data revealed that the PHRR, THR, total smoke release (TSR), and total smoke production (TSP) of TPEU-EP/33DDS decreased to 20%, 28%, 62%, and 61%, respectively, of those of DGEBA/33DDS. Resultantly, TPEU-EP/33DDS exhibits higher flame retardancy with low smoke production during combustion.

Table 10.3 CFT factors with variation of polymer molecular structures.

Structure	CFT	Structure	CFT
<i>Aliphatic</i>		<i>Heterocyclic</i>	
-CHOH-	1/3		1
Others	0		
<i>Aromatic</i>			
	1		3 × 1/2
	2		3 × 1/2
	3		3 × 1/2
	4		7
	6		7
	6		9
	10		11
	1 1/4		10
<i>Aromatic side chain</i>			12
>CH ₂ , >CH-CH ₂ -	-1		10
-CH ₃	-1 1/2		
>C(CH ₃) ₂	-3		
-CH(CH ₃) ₂	-1		15

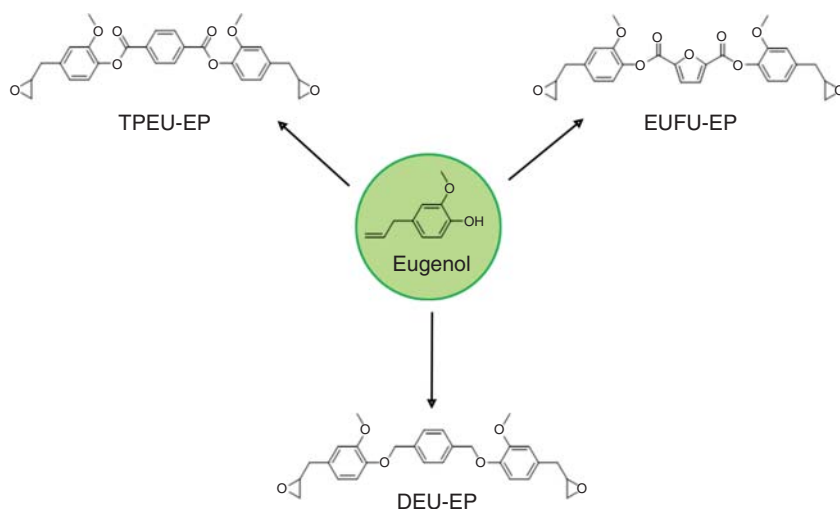


Figure 10.9 Eugenol-derived epoxy monomers.

The same group of authors developed a bio-based flame-retardant epoxy resin (DEU-EP) with a marginally different structure (Figure 10.9). It was synthesized from the start where two α,α' -dichloro-*p*-xylene molecules reacted with eugenol [52]. The net biomass content of the eugenol-based epoxy matrix from DEU-EP and 4,4'-diaminodiphenyl methane (DDM; curing agent) was 70.2%. It has a higher char yield (38 wt%) than the previously reported TPEU-EP/33DDS (31.7 wt%). Therefore, DEU-EP/DDM exhibits an improved inhibition of the flame propagation (self-extinguished at 10 seconds) compared to TPEU-EP/33DDS (24 seconds). From the microscale combustion calorimeter (MCC) data, the stark decreases (55% and 39%, respectively) in the PHRR and THR of DEU-EP/DDM compared to those of DGEBA/DDM are registered.

Gu and co-workers [53] used both 2,5-furfuran dicarboxylic acid (FDCA) and eugenol to increase the biomass content of a bio-based flame-retardant epoxy matrix. In this group, methyl hexahydrophthalic anhydride (MHHPA) as a curing agent is reacted with eugenol and furan-based epoxy resin (EUFU-EP). This produced EUFU-EP/MHHPA epoxy polymer with 93.3% of biomass content and 10.9 wt% of char yield. With regard to this material, only MCC is used as an instrument for the flame retardancy test. The PHRR and THR of DGEBA/MHHPA thermoset are 359.7 W/g and 24.7 kJ/g, respectively. However, when the epoxy resin was changed from DGEBA to EUFU-EP, the PHRR and THR decreased to 291.3 W/g and 20.0 kJ/g, respectively.

10.4.1.2 Vanillin

Zhu and co-workers [36] used Schiff-base structure formation and phosphorus-hydrogen addition to synthesize two vanillin-based epoxy monomers with flame retardancy (EP1 and EP2) (Figure 10.10). Each monomer was reacted with a DDM hardener, and their flame retardancy was compared to that of a DGEBA/DDM polymer. The char yields of EP1/DDM and EP2/DDM obtained

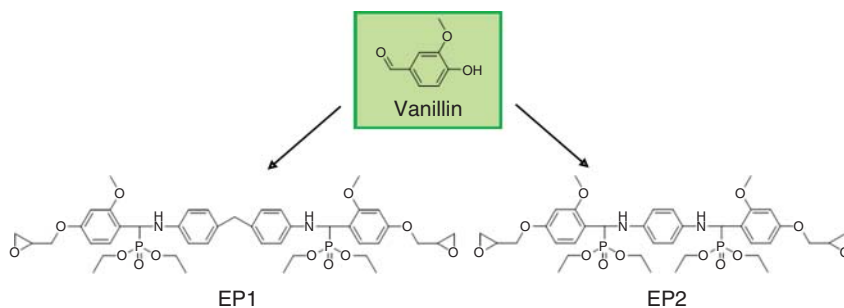


Figure 10.10 Vanillin-derived epoxy monomers.

from thermogravimetric analysis (TGA) under a nitrogen atmosphere are 53% and 58%, respectively. These values are significantly higher than those of nonphosphorous bio-based epoxy polymers. The phosphorus and nitrogen retention in their char residues is also high (EP1/DDM: 38.5%, EP2/DDM: 53.5%), resulting in remarkable flame retardancy with UL-94 V0 rating and LOI of 31.4% and 32.8%, respectively. Meanwhile, DGEBA/DDM has an LOI of 24.6% and no UL-94 rating.

10.4.2 Furan

We have introduced the EUFU-EP in Section 10.4.1.1. In the following context, only furan-based epoxy resins are described. In general, furan-based epoxy resins are synthesized from hydroxyethyl furfural (HMF) as starting materials (Figure 10.11). Guo and co-workers [54] produced 2,5-bis [(2-oxiranylmethoxy)methyl]furan (BOF) and difuranic diepoxide monomer (OmbFdE). They also compared the flame retardancies of epoxy polymers made

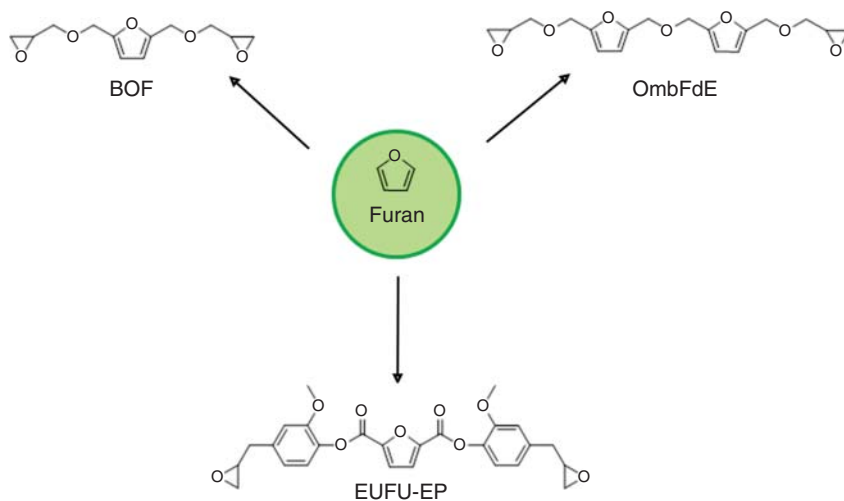


Figure 10.11 Furan-derived epoxy monomers.

from each furan-based monomer and the aliphatic diamine hardener (TEGA). From the TGA data obtained in an N_2 atmosphere, the char yields of BOF/TEGA and OmbFdE/TEGA are 19% and 19.8%, respectively. In addition, the MCC results represent the PHRR and HRR of BOF/TEGA and OmbFdE/TEGA. It is noteworthy that the OmbFdE/TEGA exhibited a higher PHRR value (174.7 [1st]/85.6 [2nd] vs. 71.2 [1st]/140.5 [2nd] W/g) and a lower THR value (13.7 vs. 15.6 kJ/g) than BOF/TEGA. This could be due to the degradation of the more numerous ether linkages in the matrix of OmbFdE accounted for the first PHRR. For the second PHRR, the contribution of more stable furan motifs should have caused the second peak heat release. Because the effect of the furan moieties is superior to that of the ether linkages, the THR of the OmbFdE/TEGA is lower than that of BOF/TEGA. However, because commercial epoxy resin such as DGEBA was not used as a control in this study, it is infeasible to objectively evaluate the flame retardancy of the furan-based epoxy monomers.

10.4.3 Tannins

Although tannins as polyphenolic compounds extracted from plants are considered as bio-based epoxy monomers with flame retardancy, there has not been any report on it. However, Jung and co-workers [55] used hydrolyzable tannin or tannic acid as a multifunctional epoxy hardener with flame retardancy. Using DGEBA as an epoxy resin, the flame retardancies of TA-based epoxy polymers were evaluated depending on the content of TA. A Jeffamine-type hardener (D230) was selected as a control. The char yield of the sample with a 1.2 TA molar ratio (TD 1.2; the maximum TA molar ratio in this study) is 21.9%. This is exceptionally higher than that of the control (4.1%). Based on the LOI and MCC instruments, TD1.2 exhibits 1.46 times higher LOI than the control, and 24.8% and 33.8% of decrease in the PHRR and THR as compared with DGEBA/D230. The flame suppression of the TD thermoset may be ascribed to the quenching effect of the phenoxy radicals formed during combustion and the formation of a char layer, which functions as a barrier obstructing heat flux and gas transport.

10.5 Use of Fillers for Improving Flame-Retardant Properties of Bioepoxy Polymers

Organic/inorganic nanocomposites are prepared by uniformly dispersing nano-sized organic and inorganic particles in a polymer matrix. The mechanical and thermal properties, impact resistance, chemical resistance, heat resistance, and flame retardancy can be improved over conventional single polymer materials. Nanomaterials (particles) have a small particle size and are well dispersed in the polymer matrix. Moreover, the specific surface area is large, so that the addition of even a small amount is likely to yield remarkable properties.

Conventionally, to increase the flame retardancy of a polymer and thus improve its physical properties, a flame retardant is incorporated as a filler or additive. However, as described above, the use of halogens and phosphorus-based

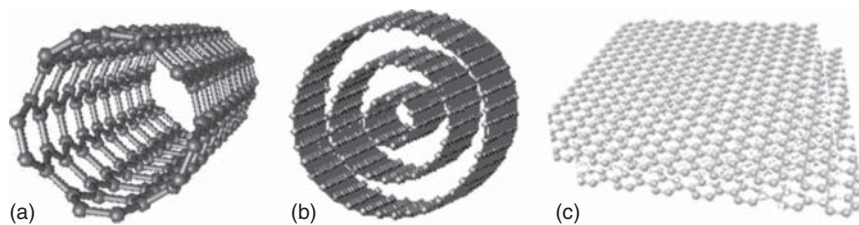
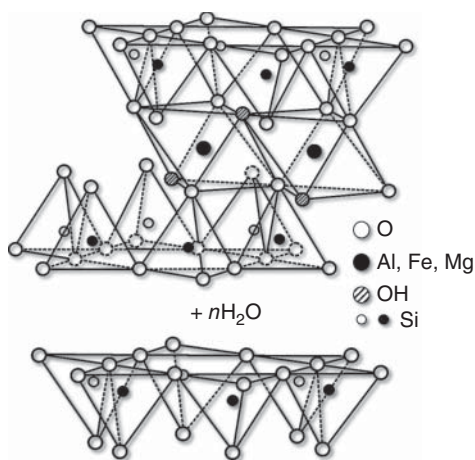


Figure 10.12 Conceptual diagram of (a) single-walled carbon nanotube (SWCNT), (b) multiwalled carbon nanotube (MWCNT) [58], and (c) graphene layer. Source: Reproduced from Geim and Novoselov [59]. © 2007, Springer Nature.

Figure 10.13 Structure of 2 : 1 layered silicate such as montmorillonite clay [56, 57].



substances gradually decreased owing to the emission of toxic gases in the fire and the unsafe lighting. Recently, studies on improving flame retardancy using various organic fillers have been reported. Clay [56, 57], carbon nanotubes [58], graphene [59], and expanded graphite are used as representative nanoadditives to improve flame retardancy (Figures 10.12 and 10.13).

Bioepoxy has also been reported to improve the flame retardancy index by using the aforementioned additives, and a few examples are provided. Lijun Qian's research group [60] coated phosphor–nitrogen flame retardant on carbon nanotubes (PDAP-CNT) and used it as a filler in epoxy (Figure 10.14). In summary, PDAP-CNT exhibited remarkable flame-retardant performance in flame-retardant EP composites (FR-EP). Moreover, the incorporation of 5.0 wt% PDAP-CNT improved the LOI of EP from 26.0% to 31.8%. Moreover, UL-94 exhibited a V-0 rating. This improvement can be considered as owing to the thermal stability of the carbon nanotubes and the synergistic effect of the phosphorus–nitrogen-containing coating layer coated on the surface. In addition, because of the flame retardant coated on the nanofiller, a continuous and compact char layer is formed in the condensation step. This suppresses the second- and third-order heat transfer.

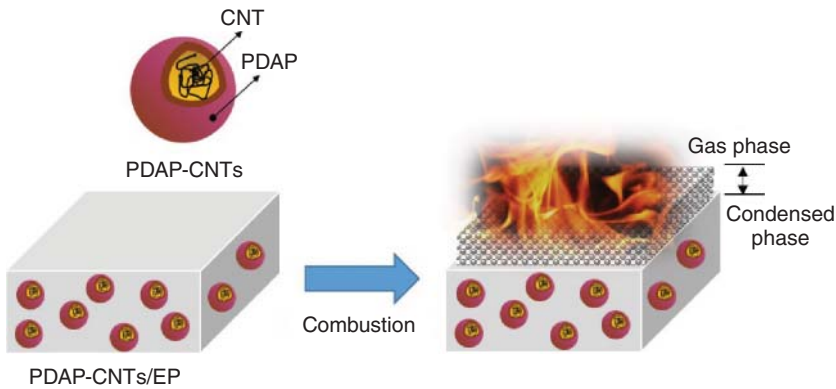


Figure 10.14 Carbon nanotubes coated with phosphorus–nitrogen flame retardant and its application in epoxy thermosets. Source: Reproduced from Fei et al. [60]. © 2019, Taylor & Francis.

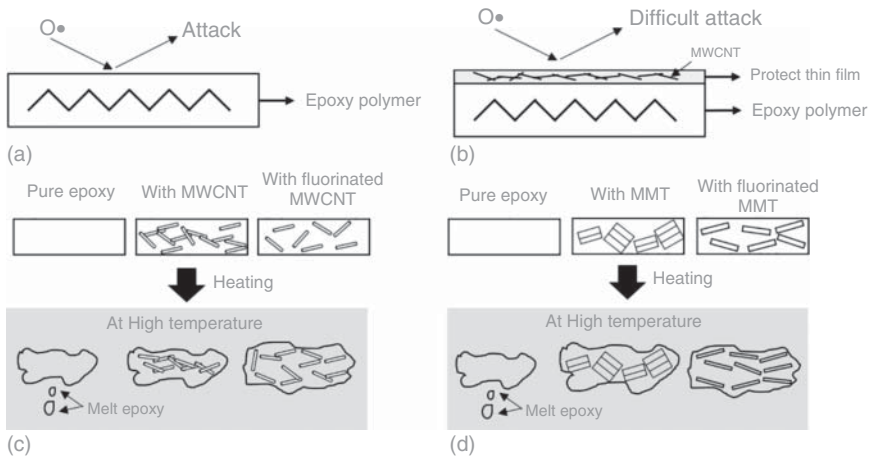


Figure 10.15 Postulated mechanism of flame-retardant additives. al. [61, 62].

Lee and co-workers [61, 62] reported the results of adding montmorillonite (MMT) and multiwalled carbon nanotubes as flame retardants to epoxy resins to improve the oxidation resistance and flame retardancy of the resins. MMT used as a flame-retardant additive functioned as an energy storage medium to prevent heat transfer in epoxy composites. Multiwalled carbon nanotubes were observed to be a medium for effectively reducing the decomposition rate of epoxy and increasing the yield of charcoal. Moreover, the combined use of these two additives increased the thermal activity energy of the epoxy resin, which contributed significantly to the improvement in the antioxidant and flame retardancy index. In addition, it has been verified that the addition of epoxy resin through the fluorination treatment to the existing MMT increased the heat activation energy to more than two times that of the value in the previous research results. The mechanism is described in Figure 10.15 [61, 62].

Meanwhile, there are a few examples of utilization of the structural properties of additives. As the use of wood-based building materials increases, flame-retardant treatment technology gains importance. This intumescent system is a nonhalogen flame-retardant system that combines the technology of polymer foaming and carbonization layer formation [63].

Intumescent–nanoclay (INC) composites [64–66] are highly advanced flame-retardant materials that combine foam, carbonization, and clay insulation technology in an integrated system. The use of INC composites has expanded in Europe since the late 2000s. INC composite materials exhibit a mechanism wherein a carbonization layer is formed simultaneously with initial foaming. A system is also implemented simultaneously to form an isolation layer that blocks external energy during rearrangement of the stacking of nanoclay that is spread on the surface. Therefore, the combustion process exhibits a delay and a combustion blocking effect simultaneously. Intumescent system is a technology that is directly applied to fire protection paints. It has a structure that maximizes performance by integrating with nanotechnology.

B. Szolnoki and co-workers [67] has developed a new flame-retardant carbon-fiber-reinforced composite using glucofuranoside-based flame-retardant bioepoxy resin trifunctional epoxy monomer (GFTE) and aromatic amine as a curing agent (Figure 10.16). The flame-retardant epoxy carbon-fiber-reinforced composite material was prepared by combining a liquid resorcinol bis(diphenyl phosphate) (RDP) and a solid ammonium polyphosphate (APP) to prepare

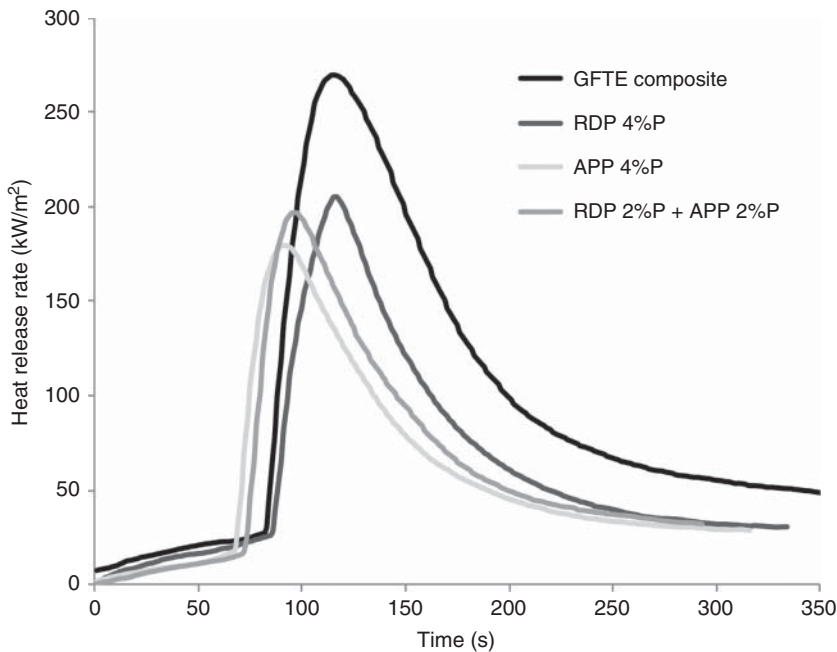


Figure 10.16 Heat release rate of reference and flame-retarded GFTE composite. Source: Reproduced from [67]. © 2017, Elsevier.

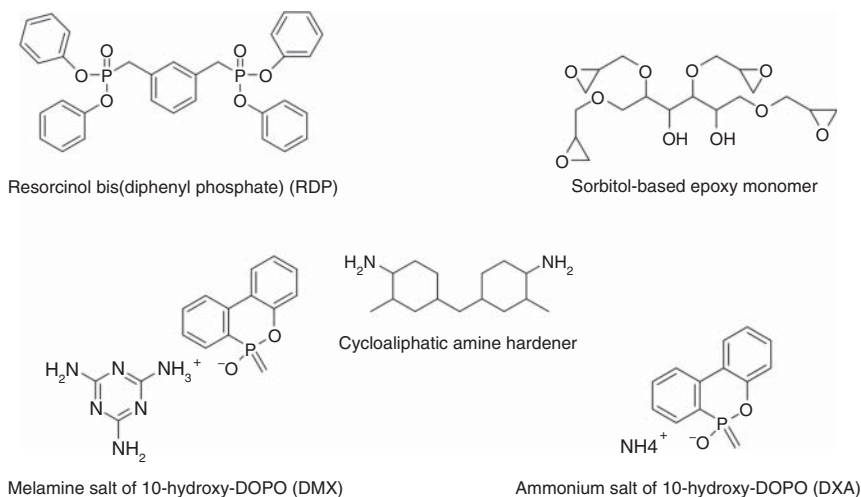


Figure 10.17 Chemical structure of the epoxy resin components and applied flame retardants.

a sample containing approximately 4% phosphorus. This combination could effectively compensate for the plasticization effect with the P-containing and improved thermal mechanical properties. UL-94 has a V-0 rating. In addition, when manufacturing a carbon-fiber-reinforced composite material using a conventional bioepoxy resin, the physical properties exhibited a tendency to weaken owing to the attenuated mechanical properties and decrease in plasticization temperature. However, this study can be said to be the result of solving the existing problems effectively.

György Maro and co-workers [68] prepared a bioepoxy using sorbitol monomer. Moreover, APP and RDP were added, resulting in the synthesis of flame-retardant bioepoxy. The synthesized bioepoxy exhibited a phosphorus content of approximately 3%. In particular, red phosphorus (RP) exhibit UL-94's V-0 grade, whereas melamine salt exhibits HB grade because of the lower phosphorus content in the sample. As the flame retardant was added to the matrix, the LOI of the sample increased significantly. However, the results revealed that the effects of different types of flame retardants varied (Figure 10.17).

10.6 Conclusion

Countries worldwide are deeply concerned about the severe pollution of the global environment. Under these circumstances, the substitution of halogen flame-retardant additives and petroleum-based epoxy materials, which have been causing severe environmental issues and human hazards, is a problem that must be solved to ensure a healthy future. In this context, the researchers' efforts to develop or replace eco-friendly epoxy-based or plant-based materials are highly commendable. This chapter describes recent research trends on bio-based epoxy development and bio-based retardants. In particular, bio-based flame

retardants were reported to improve the material properties and synergistic effects. Moreover, the flame-retardant mechanism for improving the flame retardancy index was discussed. At present, the newly developed materials are ineffective for replacing petroleum-based epoxy, which is being widely used now. However, the efforts of several researchers are likely to contribute to good results soon.

Acknowledgment

This work was supported by the KIST Institutional Program.

References

- 1 Hajime, K., Akihiro, M., Kiichi, H. et al. (1998). Epoxy resin cured by bisphenol a based benzoxazine. *J. Appl. Polym. Sci.* 68 (12): 1903–1910.
- 2 Elaheh, R.R., Henri, V., Agustin, R.A. et al. (2019). Bio-epoxy resins with inherent flame retardancy. *Prog. Org. Coat.* 135: 608–612.
- 3 Levchik, S., Piotrowskia, A., Weil, E., and Yao, Q. (2005). New developments in flame retardancy of epoxy resins. *Polym. Degrad. Stab.* 88 (1): 57–62.
- 4 Fregert, S. and Trulsson, L. (1978). Simple methods for demonstration of epoxy resins of bisphenol A type. *Contact Dermatitis* 4 (2): 69–72.
- 5 Ochi, M., Tsuyuno, N., Sakaga, K. et al. (1995). Effect of network structure on thermal and mechanical properties of biphenol-type epoxy resins cured with phenols. *J. Appl. Polym. Sci.* 56 (9): 1161–1167.
- 6 Anthony, R.P. and Richard, J.F. (1990). Evolution of residual stresses in three-dimensionally constrained epoxy resins. *Polymer* 31 (10): 1932–1936.
- 7 Fan-Long, J., Xiang, L., and Soo-Jin, P. (2015). Synthesis and application of epoxy resins: a review. *J. Ind. Eng. Chem.* 29: 1–11.
- 8 Chun-Shan, W. and Jeng-Yueh, S. (1999). Phosphorus-containing epoxy resin for an electronic application. *J. Appl. Polym. Sci.* 73 (3): 353–361.
- 9 Tsung-Han, H. and Chun-Shan, W. (2001). Modification of epoxy resin with siloxane containing phenol aralkyl epoxy resin for electronic encapsulation application. *Eur. Polym. J.* 37 (2): 267–274.
- 10 Clayton, M. (2018). *Epoxy Resins: Chemistry and Technology*. CRC Press.
- 11 Azar, N.G., Heidari, M., Bahrami, Z.S., and Shokri, F. (2000). In vitro cytotoxicity of a new epoxy resin root canal sealer. *J. Endodontic.* 26 (8): 462–465.
- 12 Gabriele, L., Jürgen, H., Georg, R. et al. (1999). Genotoxicity and cytotoxicity of the epoxy resin-based root canal sealer AH plus. *J. Endodontic.* 25 (2): 109–113.
- 13 Sushanta, K.S., Smita, M., and Sanjay, K.N. (2015). Synthesis and characterization of bio-based epoxy blends from renewable resource based epoxidized soybean oil as reactive diluent. *Chin. J. Polym. Sci.* 33 (1): 137–152.
- 14 Elyse, A.B., Santosh, K.Y., Giuseppe, R.P., and Joseph, F.S. III, (2016). Recent advances in bio-based epoxy resins and bio-based epoxy curing agents. *J. Appl. Polym. Sci.* 133: 45.

- 15 Saeid, N., Omid, Z., Susan, H. et al. (2017). A renewable bio-based epoxy resin with improved mechanical performance that can compete with DGEBA. *RSC Adv.* 7 (14): 8694–8701.
- 16 Jiang, Z., Chandrashekhara, K., Virgil, F., and Shubhender, K. (2004). Curing and mechanical characterization of a soy-based epoxy resin system. *J. Appl. Polym. Sci.* 91 (6): 3513–3518.
- 17 Jean-marie, R., Deléglise, M., Marie, F.L., and Patricia, K. (2010). Thermosetting (bio) materials derived from renewable resources: a critical review. *Prog. Polym. Sci.* 35 (4): 487–509.
- 18 Shida, M., Ping, W., Zhiguo, S., and Songping, Z. (2014). Vegetable-oil-based polymers as future polymeric biomaterials. *Acta Biomater.* 10 (4): 1692–1704.
- 19 Soo-Jin, P., Fan-Long, J., and Jae-Rock, L. (2004). Synthesis and thermal properties of epoxidized vegetable oil. *Macromol. Rapid. Commun.* 25 (6): 724–727.
- 20 Sylwia, D., Adrien, C., Dariusz, B. et al. (2015). Formulation of bio-based epoxy foams from epoxidized cardanol and vegetable oil amine. *Eur. J. Lipid. Sci. Technol.* 117 (11): 1893–1902.
- 21 Fatemeh, F., Yongsheng, Z., Zhongshun, Y. et al. (2016). Curing kinetics and mechanical properties of bio-based epoxy composites comprising lignin-based epoxy resins. *Eur. Polym. J.* 82: 153–165.
- 22 Fatemeh, F., Zhongshun, Y., and Mark, A. (2014). Synthesis of lignin-based epoxy resins: optimization of reaction parameters using response surface methodology. *RSC Adv.* 4 (60): 31745–31753.
- 23 Chahinez, A., Hélène, N., Maxence, F. et al. (2013). Multi-functionalization of gallic acid. Synthesis of a novel bio-based epoxy resin. *Eur. Polym. J.* 49 (6): 1185–1195.
- 24 Fatemeh, F., Zhongshun, Y., Mark, A., and Chunbao (Charles)X. (2015). Sustainable lignin-based epoxy resins cured with aromatic and aliphatic amine curing agents: curing kinetics and thermal properties. *Thermochim. Acta.* 618: 48–55.
- 25 Ayman, M.A., Mansour, R., Mahmoud, I.A., and Ashraf, M.S. (2004). Epoxy resins from rosin acids: synthesis and characterization. *Polym. Adv. Technol.* 15 (9): 514–522.
- 26 Rémi, A., Sylvain, C., Ghislain, D. et al. (2013). Biobased thermosetting epoxy: present and future. *Chem. Rev.* 114 (2): 1082–1115.
- 27 Wasiuddin, A.K., Zhiyuan, W., Mohammad, T.A. et al. (1988). Inhibition of the skin tumorigenicity of (\pm)-7 β , 8 α -dihydroxy-9 α , 10 α -epoxy-7, 8, 9, 10-tetrahydrobenzo [a] pyrene by tannic acid, green tea polyphenols and quercetin in Sencar mice. *Cancer Lett.* 42 (1-2): 7–12.
- 28 Mitsuhiro, S. and Nakai, K. (2010). Preparation and properties of biocomposites composed of bio-based epoxy resin, tannic acid, and microfibrillated cellulose. *J. Polym. Sci. Part B: Polym. Phys.* 48 (4): 425–433.
- 29 Fanny, J., Emilie, D., Amédée, R. et al. (2014). New biobased epoxy materials from cardanol. *Eur. J. Lipid. Sci. Technol.* 116 (1): 63–73.
- 30 Pietro, C., Daniele, D.A., Luigia, L. et al. (2009). Cardanol-based novolac resins as curing agents of epoxy resins. *J. Appl. Polym. Sci.* 114 (6): 3585–3591.

- 31 Aggarwal, L.K., Thapliyal, P.C., and Sukhdeo, K. (2007). Anticorrosive properties of the epoxy–cardanol resin based paints. *Prog. Org. Coat.* 59 (1): 76–80.
- 32 Xin, W., Ehsan, N.K., and De-Yi, W. (2015). Renewable cardanol-based surfactant modified layered double hydroxide as a flame retardant for epoxy resin. *ACS Sustain. Chem. Eng.* 3 (12): 3281–3290.
- 33 Emilie, D., Nelly, D., Bernard, B., and Sylvain, C. (2015). New cardanol/sucrose epoxy blends for biobased coatings. *Prog. Org. Coat.* 83: 47–54.
- 34 Songqi, M., Xiaoqing, L., Yanhua, J. et al. (2013). Bio-based epoxy resin from itaconic acid and its thermosets cured with anhydride and comonomers. *Green Chem.* 15 (1): 245–254.
- 35 Henri, V., Maryam, J., Marianne, C. et al. (2018). Short-lasting fire in partially and completely cured epoxy coatings containing expandable graphite and halloysite nanotube additives. *Prog. Org. Coat.* 123: 160–167.
- 36 Sheng, W., Songqi, M., Chenxiang, X. et al. (2017). Vanillin-derived high-performance flame retardant epoxy resins: facile synthesis and properties. *Macromolecules* 50 (5): 1892–1901.
- 37 Raphaël, M., Claire, N., Maxence, F. et al. (2015). From a bio-based phosphorus-containing epoxy monomer to fully bio-based flame-retardant thermosets. *RSC Adv.* 5 (87): 70856–70867.
- 38 Xin, W., Shun, Z., Wen-Wen, G. et al. (2017). Renewable cardanol-based phosphate as a flame retardant toughening agent for epoxy resins. *ACS Sustainable Chem. Eng.* 5 (4): 3409–3416.
- 39 Naheed, S., Mohammad, J., and Othman, Y.A. (2016). Recent advances in epoxy resin, natural fiber-reinforced epoxy composites and their applications. *J. Reinf. Plast. Compos.* 35 (6): 447–470.
- 40 Halogen-free flame retardants market, global forecasts to 2021, markets and markets. www.marketsandmarkets.com
- 41 Flame retardants market, global forecasts to 2021, markets and markets. www.marketsandmarkets.com
- 42 Kumar, K., Sukhila, K., Smita, M., and Sanjay, K.N. (2018). Synthesis and characterization of petroleum and biobased epoxy resins: a review. *Polym. Int.* 67 (7): 815–839.
- 43 Ramon, E., Carmen, S., and Pedro, M. (2018). A review of recent research on bio-based epoxy systems for engineering applications and potentialities in the aviation sector. *Aerospace* 5 (4): 110.
- 44 Christopher, E.H. (2019). Recent advances in bio-based flame retardant additives for synthetic polymeric materials. *Polymers* 11 (2): 224.
- 45 Norman, G.M., Buckley, C.P., Clive, B.B., and Bucknall, C.B. (1997). *Principles of Polymer Engineering*. USA: Oxford University Press, New York.
- 46 Maya, J.J. (2019). Green composite for automotive applications, chapter 2. In: *Flammability Performance of Biocomposites* (ed. J.J. Maya), 43–58. Woodhead Publishing.
- 47 Schartel, B., Braun, U., Schwarz, U., and Reinemann, S. (2003). Fire retardancy of polypropylene/flax blends. *Polymer* 44 (20): 6241–6250.
- 48 Babrauskas, V. (2002). Heat release rates. In: *The SFPE Handbook of Fire Protection Engineering*, 3e, (Chapter 3.1) (eds. D.N. PJ, D. Drysdale, C.L. Beyler, et al.), 3–8. National Fire Protection Association, Inc.

- 49 Schartel, B., Bartholmai, M., and Uta, K. (2005). Some comments on the use of cone calorimeter data. *Polym. Degrad. Stab.* 88 (3): 540–547.
- 50 (1975). Some basic aspects of flame resistance of polymeric materials. *Polymer* 16 (8): 615–620.
- 51 Jintao, W., Bin, G., Cheng, L. et al. (2015). A novel biobased epoxy resin with high mechanical stiffness and low flammability: synthesis, characterization and properties. *J. Mater. Chem. A* 3 (43): 21907–21921.
- 52 Jintao, W., Bin, G., Cheng, L. et al. (2016). 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.* 284: 1080–1093.
- 53 Jia-Tao, M., Li, Y., Qingbao, G. et al. (2017). Biobased heat resistant epoxy resin with extremely high biomass content from 2, 5-furandicarboxylic acid and eugenol. *ACS Sustainable Chem. Eng.* 5 (8): 7003–7011.
- 54 Jingjing, M., Yushun, Z., Guiqin, Z. et al. (2019). Sustainable bio-based furan epoxy resin with flame retardancy. *Polym. Chem.* 10 (19): 2370–2375.
- 55 Young-O, K., Jaehyun, C., Hyeonuk, Y. et al. (2019). Flame retardant epoxy derived from tannic acid as biobased hardener. *ACS Sustainable Chem. Eng.* 7 (4): 3858–3865.
- 56 Feng, Z., Yong, W., Shaoxiang, L., and Jun, Z. (2013). Influence of thermophysical properties on burning behavior of intumescent fire-retardant materials. *J. Therm. Anal. Calorim.* 113 (2): 803–810.
- 57 Anderson, J.R., Charles, E., Donald, E.K., and William, P.M. (1988). Thermal conductivity of intumescent chars. *J. Fire. Sci.* 6 (6): 390–410.
- 58 Peter, J.F.H. (2009). *Carbon Nanotube Science: Synthesis, Properties and Application*. USA: Cambridge University Press, New York.
- 59 Geim, A.K. and Novoselov, K.S. (2007). The rise of graphene. *Nat. Mater.* 6: 183–191.
- 60 Fei, X., Congcong, Z., Chao, G. et al. (2019). Carbon nanotubes coated with phosphorus-nitrogen flame retardant and its application in epoxy thermosets. *Polymer-Plast. Technol. Mater.* 58 (17): 1889–1899.
- 61 Lee, S.K. and Bai, B.C. (2010). Flame retardant epoxy complex produced by addition of montmorillonite and carbon nanotube. *J. Ind. Eng. Chem.* 16 (6): 891–895.
- 62 Im, J.S., Lee, S.K., In, S.J., and Lee, Y.-S. (2010). Improved flame retardant properties of epoxy resin by fluorinated MMT/MWCNT additives. *J. Anal. Appl. Pyrolysis.* 89 (2): 225–232.
- 63 Haiyun, M., Lifang, T., Zhongbin, X. et al. (2007). A novel intumescent flame retardant: synthesis and application in ABS copolymer. *Polym. Degrad. Stab.* 92 (4): 720–726.
- 64 Zhen-yu, W., En-hou, H., and Wei, K. (2007). Fire-resistant effect of nanoclay on intumescent nanocomposite coatings. *J. Appl. Polym. Sci.* 103 (3): 1681–1689.
- 65 Hao, W., Mourad, K., and Joseph, H.K. (2014). Flame retardant polyamide 6/nanoclay/intumescent nanocomposite fibers through electrospinning. *Text. Res. J.* 84 (10): 1106–1118.

- 66 Doğan, M. and Erdal, B. (2011). Synergistic effect of boron containing substances on flame retardancy and thermal stability of clay containing intumescent polypropylene nanoclay composites. *Polym. Adv. Technol.* 22 (12): 1628–1632.
- 67 Toldy, A., Péter, N., Zs, R., and Beáta, S. (2017). Flame retardancy of glucofuranoside based bioepoxy and carbon fibre reinforced composites made thereof. *Polym. Degrad. Stab.* 142: 62–68.
- 68 Beáta, S., Andrea, T., and György, M. (2019). Effect of phosphorus flame retardants on the flammability of sugar-based bioepoxy resin. *Phosphor. Sulfur Silicon Related Element.* 194 (4-6): 309–312.