Chapter 5 A Review of Non-halogen Flame Retardants in Epoxy-Based Composites and Nanocomposites: Flame Retardancy and Rheological Properties

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Abstract Since more environmental regulations restricted to the use of halogenbased flame retardants are issued the halogen-free flame retardants have been gradually increased in demand at electronics applications. Several DOPO derivatives and recently developed phosphorus containing flame retardants are introduced into the market as a counterpart of tetrabromobisphenol A (TBBA). This short review paper focuses on their flame retardancy and material properties in epoxy resins. The inclusions of inorgano-metallic compounds and nanoparticles are also briefly reviewed for their potential opportunities in the epoxy composites.

Keywords Non-halogen flame retardants **·** DOPO derivatives **·** Epoxy-based composites **·** Nanocomposites **·** Nanoparticles

5.1 Introduction

For several decades, polymeric materials are extensively used in a variety of applications, such as consumer appliances, construction and transportation applications, and electrical/electronic devices because they are sustainable, lightweight and cost-effective $[1, 2]$ $[1, 2]$ $[1, 2]$ $[1, 2]$. In particular, epoxy resins are one of well-known thermosetting polymers and used for coating and adhesive applications, which can also be reinforced with fibers or additives for obtaining high strengths and good chemical resistances [[1–](#page-13-0)[4\]](#page-13-2). It is reported that almost 65 % of glass-fiber reinforced composites have been consumed at the sectors of transport and construction [[3\]](#page-13-3). However, they are intrinsically combustible and needed flame retarded [\[3](#page-13-3), [4\]](#page-13-2).

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It generally is believed that a degree of the flammability of epoxy resins depends on epoxy monomers and curing agents, where the epoxides containing aromatic groups produce more char formation when it is exposed to a heat source [\[5](#page-13-4), [6\]](#page-13-5). Although the cured epoxy resins have some degree of flame retardancy itself, it is not enough to pass a stringent industrial standard flammable test, such as UL-94 V0. Thus, the addition of flame retardants is one of practical means to improve the flame retardancy of epoxy resins system.

The majority of flame retardants for epoxy resins are currently halogen-based flame retardants because their flame retardancy is very effective at gas phase and cost-effective at an industrial scale. Tetrabromobisphenol A (TBBA) is the leading halogenated flame retardant in epoxy resins system for electrical and electronic devices since it has good thermal stability and flammability as well as high Tg when it is formulated with curing agents [[3\]](#page-13-3). However, since environmental concerns using the halogenated flame retardant arose from the daily consumer products, the two major brominated flame retardants, pentabromodiphenyl ether (PBDE) and octabromodiphenyl ether (OBDE) have recently been phased out in North America and European markets, which could release toxic gases and may be even accumulated in a living organisms for a long period time [\[7](#page-13-6)].

Due to the environmental issues mentioned in the previous paragraph, TBBA would be also eliminated in epoxy and reinforced epoxy markets near future [\[3](#page-13-3), [6\]](#page-13-5). Thus, new approaches for the developments of non-halogenated flame retardants have been initialized and flourished at both academics and industries. In this short review, we first describe the mechanism of non-halogen flame retardants and then review current developments of phosphorus-containing flame retardants for epoxy resins. In particular, cured epoxy composites system with different epoxy resins and curing agents are extensively reviewed in terms of their flammability and rheological/mechanical properties. Later on, a current development using inorgano-metalic compounds and nanofillers is reviewed in epoxy composites containing non-halogen flame retardants.

5.2 The Mechanism of Flame Retardant Materials in Epoxy-Based Composites

The combustion of polymeric materials is a complex processes involved with a series of heat and mass transfer at the surfaces of polymer melts so that an intervention of the combustion processes can be achieved by the addition of flame retardants (FRs) which makes the polymers less combustible [\[3](#page-13-3)]. FRs materials generally react at either gas phase or condensed phase. It depends on what types of FRs materials. In case of halogen-based FRs, the hydrogen halides are formed from the FRs decomposition, which subsequently reacts with free-radical species from decomposed polymers at gas phases [[4–](#page-13-2)[6\]](#page-13-5). On the other hands, in case of non-halogen-based FRs, the thermal insulation processes mainly occurs at condensed phases. For example, phosphorus-based FRs release PO_2 or PO_3 at gas phase and then is oxidized to P_2O_5 . A formation of the phosphoric acids can result

Scheme 5.1 A series of flame retardant reactions with polymers occurs at condensed and gas phases

in intumescing chars formation at the polymer surfaces, which acts as thermally protective layers on polymer-melts against heat front. These charring processes eventually interrupt the combustion processes [[7,](#page-13-6) [8\]](#page-13-7). A mechanism of flame retardants in polymer composites is shown in Scheme [5.1.](#page-2-0)

Epoxy-based composites formulated with TBBA and DDS as curing agent are flame-retarded in the decomposition steps: the halogen halides from TBBA are first released at above 300 °C and then the nitrogen element from DDS exists in a form of cross-linked structures in its residues [[9\]](#page-13-8). In contrast, the epoxy resins containing phosphorus-based flame retardants mainly decomposes at the condense phase in which P-rich residues are found at the end of combustion. This result may be explained by the existence of element P, which can act as a catalyst for promoting chars formation [\[10](#page-13-9)].

5.3 Review of Reactive Phosphorus-Based Flame Retardant Epoxy Resins System

In epoxy resins formulation, phosphorus-containing flame retardants can be applied as an additive, which is relatively easy to manufacturing process. However, it has some technical drawbacks, such as particle dispersion and deterioration of the physical properties of epoxy laminates when its loading is too high [\[5](#page-13-4)]. Thus, molecularly reactive phosphorus-containing flame retardants have been used for advanced epoxy laminates, which can give better performance on flame retardancy and material properties. The common epoxy resins are either *o*-cresol formaldehyde novolac (CNE) or diglycidyl either of bisphenol-A (DGEBA), which are frequently pre-reacted with non-halogen flame retardants in order to improve flame retardancy of the cured epoxy resins.

The majority of non-halogen flame retardants that pre-reacted with the epoxy resins are based on 9,10-dihydro-9-oxa-10-phosphaphenanthren 10-oxide (DOPO, I), which is shown in Fig. [5.1](#page-3-0). Because of its intrinsically high reactive properties the addition of DOPO can impart good flame retardancy to epoxy laminates applications [\[5](#page-13-4), [11\]](#page-13-10). Moreover, a combination of the DOPO with curing agents often help reducing the amount of % P that required for UL94-V0, which may result in obtaining an improvement on the materials properties of cured epoxy systems, such as phase transition temperature, thermal stability and modulus. They can also improved by different curing agents systems, such as phenolic novolac (PN) and 4,4-diaminodiphenylsulfone (DDS).

Thus, a variety of phosphorus-based flame retardants have been developed and studied for their flammability as well as rheological and mechanical properties. Recently, the two review papers extensively focused on the flame retardancy of

Fig. 5.1 9,10-dihydro-9 oxa-10-phosphaphenanthren 10-oxide (DOPO), I

non-halogen flame retardants for epoxy resins system [[5,](#page-13-4) [6](#page-13-5)]. However, few review papers were found for the rheological and mechanical properties of epoxy resins with non-halogen flame retardants. In this section, we review not only the flame retardancy of several DOPO derivatives and phosphorus-containing flame retardants but also their rheological and mechanical properties in cured epoxy resins, where a correlation with curing agents and % P content may exist at each epoxy resins system.

5.3.1 DOPO-Derivatives Flame Retardants System

Since the P-H group is highly reactive, it is relatively easy for the DOPO to be synthesized with several functional groups. Wang and Shielh reported that 1,4 benzenediol was synthesized with the DOPO and then evaluated as a curing agent in a CNE epoxy (EEW:192). They showed that the cured CNE epoxy containing 25 % of DOPO derivative (II) and 75 % phenolic navolac (PN) was ranked as UL94-V0 in which the total phosphorus content was 1.1% [\[11](#page-13-10), [12\]](#page-13-11). However, 4.4 % P content was required to keep the UL94-V0 when the DOPO derivative was solely used as curing agent. Rwel et al. [[13\]](#page-14-0) also showed that a mixture of two curing agent (i.e. DOPO with the $1,4$ -naphthalenediol(III) and PN) could have the reduced phosphorus content for obtaining higher residues and thermal stability in N_2 . Thus, the required % P content for good flame retardancy can be reduced by the combination of DOPO derivatives with conventional curing agents. Introducing phenol groups into the DOPO can improve char formation in epoxy resins. Liu et al. synthesized an alkyl novolac (IV) from a reaction of DOPO with 1,4-benzenedicarboxaldehyde and phenols. The alkyl novolac was used as a co-curing agent with PN in a CNE epoxy resin (EEW:200). Only 3.8 % P content in the cured epoxy could lead to having 55.4 % residues and 32.5 in. LOI [\[14](#page-14-1)]. It was interesting that the amount of the residues was highest when the similar level of % P content was found in cured CNE epoxy resins in which different DOPO derivatives (II–IV) was included. This may result from the existence of the hydroxyphenyl groups in the flame retardant backbone.

On the other hand, DOPO derivatives are frequently pre-reacted with epoxy groups since it has reported that the incorporation of organophosphorus molecules into epoxy backbones could release less smoke and toxic gases [\[15](#page-14-2), [16\]](#page-14-3). Wang et al. showed that $2.0-2.8\%$ P in the pre-reacted DGEBA with the diol flame retardants (II) could give UL94-V0 to the cured epoxy, whereas the DOPO derivative reacted with epoxy groups needed more % P content in order to obtain the same level of UL94 grade [\[11](#page-13-10), [16,](#page-14-3) [17](#page-14-4)]. This discrepancy may be explained by the use of different curing agents and epoxy equivalent weights (EEW). Wang et al. showed that the DOPO derivative (II) epoxy resin was cured with the three different curing agents. Both PN and DDS needed ~4.7 %P content for UL94-V0. But, the cured epoxy resin needed to have 7.2 % P content in case of DICY curing agent [[15\]](#page-14-2). He also demonstrated that either DDS or PN could give 30 in LOI when the EEW of DGEBA epoxy resins containing the DOPO derivative (II) was above 300, where the % P content was 1.7 % [[17\]](#page-14-4). Thus, DOPO derivatives can be variable to be used as either co-curing agent or pre-reacted with epoxy resins. The summary of the DOPO derivatives and its flammability are presented in Table [5.1](#page-5-0).

DOPO derivatives/epoxy resin	Epoxy resins or curing agents	$\%$ P	UL94 V-0, $\rm LOI$
D O OH HO (II)	o -Cresol formaldehyde novolac (CNE, EEW:192)	4.4	$V-0$ [11]
$O=$	o -Cresol formaldehyde novolac (CNE, EEW:195)	4.1	31 [13]
OH HO (III)			
∩⊦ 'n (IV)	o -Cresol formaldehyde novolac (CNE, EEW:200)	3.8	32.5 [14]
	Phenolic novolac (PN)	4.8	34 and $V-0$ [15]
$O =$	4,4-diaminodi- phenylsulfone (DDS)	4.5	32 and $V-0$ [15]
	Dicyandiamide (DICY)	$7.2\,$	36 and $V-0$ [15]
[EEW:223-228]			

Table 5.1 Several DOPO derivatives and their advanced epoxy resins are presented with different curing agents and its flammability

(continued)

Table 5.1 (continued)

5.3.2 Phosphorus Containing Flame Retardants System

Several research groups have reported that organophosphates or organophosphine oxides can be chemically pre-reacted to epoxy resins, which also imparts good flame retardancy to the cured epoxy resins [\[18–](#page-14-5)[23\]](#page-14-6). Cheng et al. reported that di-epoxide containing phenyl phosphonate [V] could be cured with DDS having 29–31 in LOI. However, the cured epoxy resin had a lower thermal stability and higher % P content needed to obtain the better flame retardancy [[20](#page-14-7), [21](#page-14-8)]. Moreover, the high level of the $%$ phosphorus content may be caused to lower the glass transition temperature (Tg) of the cured epoxy resins. Thus, the $\%$ P content in a finial epoxy formulation has to be reduced while other materials properties remain as same. Ren et al. showed [\[18](#page-14-5)] that the phenyl phosphine oxide with bis-phenoxyl (VI) was synthesized with the epoxy resins and then cured with DDS in which 34 of LOI and good thermal stability (~357 °C at 5 % weight loss in N₂) were obtained. The % P content was also reduced to 7.8 from 9.5. The concentration of the P content may be still high enough to affect the material properties of the cured epoxy resins. Therefore, the epoxides groups have to be replaced by more thermally stable and cross-linked epoxy resins.

DEGBA is a good cross-linked and relatively produces higher residues because of the bisphenol groups in its backbone. It can be also synthesized with a variety of phosphorus-based flame retardants. Lin et al. reported that the amount of % P was reduced by replacing the bis-phenoxyl with bis-diphenoxyl group in the DEGBA epoxy resin, where only 1.5 % P could be contributed to achieving above 30 in LOI, high Tg (180 °C) and higher residues remained (26 % in N₂) [[19\]](#page-14-9). In the report, the advanced epoxy resins with the phosphorus-based flame retardant [VII] had the highest number of LOI obtained among the epoxy resins with other flame retardants, such as TBBA, DHBP (dihydroxybiphenyl) and PPA (phenyl phosphonic acid).

Organophosphate molecules are also used to increase thermal stability of the cured epoxy resins. Derouet et al. synthesized a series of alkyl or aryl phosphates [VIII] with a DEGBA epoxy resin to make advanced epoxy resins having good flame retardant properties along with a higher Tg [\[22](#page-14-10)]. He demonstrated that the DEGBA epoxy resin with diphenyl phosphate achieved the highest number of

Phosphorus-containing flame retardants	Curing agents	$\%$ P	$\rm LOI$
$(\mathbf V)$	DDS	9.5	29-31 [20]
C HO, HO. (VI)	DDS	$7.8\,$	34 [18]
óн Ġн I ┚┉ (VII)	DDS	$1.5\,$	30.5 [19]
OH OR- OR	DDS	1.1	32 [22]
R: Ph (VIII)			

Table 5.2 Chemical structures of the phosphorous-containing flame retardants and their flame retardancy are presented with % P content and LOI

LOI value and Tg, which was 32 and 190 °C, respectively. A surprised discovery at his study was that the phenomena of intumescing chars formation could be only observed in the cured systems, where the pre-reacted DEGBA with the aryl or alkyl phosphates was cured by DDS curing agent. However, in the same cured DEGBA epoxy resin with DDS, the additive phosphates did not produce good chars formation. The summary of the phosphorus-containing flame retardants and its flammability are presented in Table [5.2](#page-7-0).

5.4 Review of Rheological and Mechanical Properties of Advanced Epoxy Resins Containing DOPO-Derivatives

The mobility of an entangled polymer chain is frequently determined by a glass transition temperature, which is an indication of a relaxation statue of the entangled polymer chains. Unlike thermoplastic polymers, epoxy monomers can be

chemically cross-liked at elevated temperatures by either itself or the aid of curing agents [[1\]](#page-13-0). Thus, a Tg of a cured epoxy resins can depend on the type of epoxy resins, curing agents and curing temperatures as well as flame retardants. It is important for epoxy laminates to obtain higher Tg at a low level of $\%$ P content, which may be a key factor to prevent a failure of the PCT (pressure cooker test) or soldering bath at electronic applications $[1-4]$ $[1-4]$. As we mentioned at the above section, DOPO derivatives can be used as a co-curing agent. We here have the three DOPO derivatives (II–IV) to present their rheological properties in terms of Tg versus % P content. In Fig. [5.2](#page-8-0), from the figure we can see that the two DOPO derivatives (II and III) have increased Tg when % P increases in the cured epoxy resins. Moreover, in case of the DOPO derivative (III), the Tg of the cured epoxy resins are slightly higher than that of the epoxy containing the 1,4-naphthalenediol DOPO (III), which may result from the existence of the resonant structures. However, the Tg of the cured CNE containing the DOPO derivative (IV) decreases as % P increases in the case of the DOPO derivative (IV), which may be explained by a reduced cross-linking density because of the relatively high volume of the bulky DOPO groups [\[14\]](#page-14-1).

On the other hand, the mechanical strength of cured epoxy resins can be measured by a relationship between storage modules and loss modules at elevated temperatures. Since epoxy laminates are composed of several stacked pregregs it may be a critical point to review what factors can be influenced to the strength. Here is an example of the factors in Figs. [5.3](#page-9-0) and [5.4:](#page-9-1) A relationship between Tg and $\%$ P or modulus of pre-reacted DGEBA containing the DOPO derivative (II), which were cured by different curing agents. As we can see from the figures, the higher Tg of the cured epoxy resins is obtained in case of DDS. However, the moduli of DDS-cured epoxy resins are lower than that of PN-cured epoxy resins, which could result from the different reactivity of the two curing agents. Therefore, the evaluation of the rheological and mechanical properties of cured epoxy resins can be considered in explaining how cured epoxy resins are evolved at different curing systems even though it is at the same level of % P content. Eventually, this evaluation would be useful for epoxy laminates applications, where the bonding strength may be a first priority.

A relationship between rheological properties of epoxy pregregs and curing processes in laminated structures: The absorption of small oligomers on different geometries surfaces has been extensively studied its thermal and rheological properties since the surface properties are modified by the absorbed substances and the geometries itself. In particular, because of its size nanoparticles are of great interest in academics and industries [[7\]](#page-13-6). Rod-type or hollow-type inorganic particles are relatively in many demands at the field of reinforced composites $[1, 2]$ $[1, 2]$ $[1, 2]$ $[1, 2]$. Marney et al. showed that phenyl phosphoric acids treated into halloysite nanotubes had a potential for flame retardant and reinforcing fillers in nylon 6 [[24\]](#page-14-11). Lin et al. also demonstrated that the addition of the functionalized halloysites with sodium dodecyl sulfate could improve the thermal stability and mechanical properties of the polystyrene matrix [\[25](#page-14-12)]. Nanotubes is also an interesting geometry to be adsorbed with phosphors-containing molecules [\[26](#page-14-13)]. Due to the cost-effective aspects, most reinforced polymer composites are filled with rod-type glass or carbon fibers in an industrial scale. On the other hand, epoxy resins are reinforced in forms of pregreg-mats, where a series of the autoclave-curing processes on epoxy pregregs are involved at elevated temperatures. Thus, the rheological properties of epoxy resins

on the prepregs-mats is an important property to be used for achieving a good epoxy laminates at the end. Since the epoxy-vanished pregregs are cured with pressure at different temperature profiles the viscosity of the epoxy resins on the pregregs is changed at a different rate with temperature. Thus, obtaining optimized curing process is necessary to impart good physical and chemical properties to epoxy laminates. Dynamic mechanical analysis (DMA) is a typical instrument of measuring the rheological properties of composite materials such as complex viscosity, storage and loss modulus. The complex viscosity of two different single prepreg formulated with different curing agents and DOPO derivatives are presented in Fig. [5.5](#page-10-0). As we can see the viscosity graph in the figure, the trace of the complex viscosity from the two single pregregs is relatively same with temperature. However, the temperature at starting to increase the viscosity is different at each epoxy pregreg, where one has a higher temperature and the other has a lower temperature. Moreover, the rate of increasing the viscosity is also different at each case, which may indicate that each epoxy formulation would undergo different curing behaviors.

In the previous paragraph, it has been shown that the viscosity of each single pregreg is changed at a different rate with temperature, which may imply that the rheological properties of epoxy laminates can be changed in a different way. The storage modulus and tan delta of the epoxy laminates, which has the lower rate of the viscosity in the pregregs, are presented in Fig. [5.6](#page-11-0). As we can see from the graph, a higher Tg is obtained at the lower curing temperature, whereas a lower Tg is obtained at the higher curing temperature. However, in case of the higher rate of the viscosity in the epoxy pregregs, the trend for Tg is vice versa. In Fig. [5.7,](#page-11-1) the Tg of the epoxy laminates at 170 \degree C for 1 h curing time is lower than that of the laminates at 160 °C for the same curing time, which could result from a faster curing process at the high temperature. This difference may be related to the density of cross-linked epoxy resins and the interactions of the polymer chains and the glass-fibers. Thus, it is believed that an optimized temperature and time in the curing process may be significantly dependent upon the viscosity of each pregregs.

5.5 Review of Inorganic and Metallic-Based Flame Retardants in Epoxy Resins

Because of the high efficiency of charring process, which results from the reaction of phosphoric acids with decomposed polymers, a series of metal salts of phosphors containing flame retardants were invented and commercialized by Clariant under a trade name of Exolit for thermosetting polymers, where 10–30 parts based 100 part resin was used to obtain the stringent flammability test, such as UL94-V0 and DIN4102 B1 [[27,](#page-14-14) [28\]](#page-14-15). On the other hand, the use of metal oxides or metalbased compounds recently reveals their potential flammability on polymeric materials due to their versatility to be formed in stable compounds at high temperatures [\[29](#page-14-16)[–31](#page-14-17)].

Layered double hydroxides (LDH) with metal ions was first investigated in epoxy resins. Zammarano et al. reported a variety of organic modifiers could be incorporated to magnesium-aluminum(MG) LDH via the ionic exchange method and lead to an increase in d spacing of the MG LDH [\[30](#page-14-18)]. They showed that the d spacing of cured DGEBA epoxy resins varied in different organic modifiers, which could result in an occurrence of the self-extinguishing behavior in the UL94 HB test. Manzi-Nshuti et al. [\[31](#page-14-17)] investigated three different metal-based flame retardant, CoAl layered-double hydroxide (LDH), Co oxide and zinc acetate dehydrate (ZnAc) on their flammability in a cone calorimetry. They found that a significant reduction on peak heat release rate (PHRR) was obtained by the small amount of zinc acetate dehydrate (ZnAc) added the cured epoxy resins while the addition of either CoAl LDH or colt oxides did not help reducing its PHRR noticeably. Nshuti et al. [[31\]](#page-14-17) also demonstrated the flame retardancy of the three zinc-based compounds, where the cured epoxy resin with the zinc hydroxystannate had the two steps of the decomposition while both zinc borate and zinc stannate had one decomposition step as nest cured epoxy resin did. In particular, in the case of zinc hydroxystannate, the highest reduction of pHRR and lowest time to ignition were obtained when its loading was 30 wt% in the cured matrix. Moreover, these zinc-based flame retardants can catalyze the promotion of chars formation when they are combined with melamine phosphates or aluminum phosphinates and borates [\[32\]](#page-14-19).

Another approach for flame retarding epoxy resins is the use of nanoparticles. It already has been proved that an inclusion of nanoparticles can impart superior thermal and mechanical properties such as an improvement of heat distortion temperature and a significant improvement of modules and strength [[33–](#page-15-0)[37\]](#page-15-1). However, there is one of important technical concerns using nanoparticles: How nanoparticle are dispersed in a polymer matrix [[35\]](#page-15-2). Recently, Pack et al. demonstrated a combination of two nanoparticles with different surface energy and interaction at the interfaces could help improve their dispersion in the polymer blends [\[36](#page-15-3)] later they showed that a direct absorption of the phosphors-based flame retardant was successfully achieved onto the montmorillonite (MMT) clays, which could be really exfoliated in several thermoplastic polymers and improve the compatibility of the polymer blends [[37\]](#page-15-1).

In contrast to thermoplastic polymers, the structure of a cross-linked network is various in each of thermosetting polymers system. Although the curing process of an epoxy resin is governed by the type of epoxy groups and curing agents, it becomes more dependent upon a degree of the nanoparticles in cured epoxy resins. A comprehensive review paper for CNT-epoxy composites reported that the physical and chemical aspects of CNT to epoxy monomers and curing agents could alter its curing reactions [\[38](#page-15-4)]. Since the use of CNT had some disadvantages in polymers and polymer compounds, such as its color and the possibility of toxic gases released when it is burnt, more environmental friendly nanotubes has been in great demand, which could lead to the research developments of Halloysite nanotubes (HNTs). Several research groups already reported their possibility in nanocomposites [\[39](#page-15-5)[–41](#page-15-6)]. Deng et al. [[41\]](#page-15-6) showed that the different chemical treatments affected on HNTs dispersion in the cured epoxy matrix, where a combination of a phosphoric acid treated HNTs with the enhanced ball mill process could improve the degree of dispersion of HNTs in the matrix.

5.6 Conclusion

We first reviewed the flame retardancy of DOPO derivatives and DOPO-free derivatives in cured epoxy resins. Most works had focus on their possibility of being used as co-curing agent, which could result in reducing the amount of % P for obtaining good flame retardancy, such as UL94-V0 and above 30 in LOI, significantly. Moreover, better materials properties of cured epoxy resins could be achieved when they were pre-reacted with epoxy resins. We also investigated that the rheological/mechanical properties of cured epoxy resins was adjustable by the curing agents and the flame retardants, which would predict the physical properties of epoxy laminates. In the review of flame retardancy of the inorgano-metalic compounds, they were relatively easier to be applied in epoxy resins but still have not been enough studied for their flame retardancy in epoxy resins matrix. Finally, the possibility of using nanoparticles in epoxy-based nanocomposites was briefly reviewed. The improvement of the nanoparticles dispersion could be one of key elements to be overcome during the curing process.

References

- 1. Lubin, G.: Handbook of Composites. Van Nostrand Reinhold, New York (1982)
- 2. Ashbee, K.: Fundermental Principles of Fiber Reinforced Composites. Technomic Publishing Company Inc., Lancaster (1989)
- 3. Rakotomalala, M., Wanger, S., Döring, M.: Recent developments in halogen free flame retardants for epoxy resins for electrical and electronic applications. Materials **3**, 4300–4327 (2010)
- 4. Bourbigot, S., Duquesne, S.: Fire retardant polymers: recent development and opportunities. J. Mater. Chem. **17**, 2283–2300 (2007)
- 5. Jain, P., Choudhary, V., Varma, I.K.: Flame retarding epoxies with phosphorus. J. Macromol. Sci-Polym. Rev. **C42**(2), 139–183 (2002)
- 6. Levchik, S.V., Weil, E.: Thermal decomposition, combustion and flame-retardancy of epoxy resins-a review of the recent literature. Polym. Int. **53**, 1901–1929 (2004)
- 7. Pack, S., Lewin, M., Rafailovich, M.: A review of engineering biodegradable polymer blends: morphology, mechanical property, and flame retardancy. In: Morgan, A.B., Wilkie, C.A., Nelson, G.L. (eds.) Fire and Polymers VI: New Advances in Flame Retardant Chemistry and Science. ACS Symposium Series 1118, Chapter 27 (2012)
- 8. Levchik, S., Wilkie, C.A.: Char formation in fire retardancy of polymeric materials. In: Grand, A. F., Wilkie, C.W. (eds.) Fire Retardancy of Polymeric Materials. Marcel Dekker Inc., New York
- 9. Luda, M.P., Balabanovich, Al, Camino, G.: Thermal decomposition of fire retardant brominated epoxy resins. J. Anal. Appl. Pyrol. **65**, 25 (2002)
- 10. Hergenrother, P.M., Thomposon, C.M., Smith, J.G., Connell, J.W., Hinkley, J.A., Lyon, R.E., Moulton, R.: Fire retardant aircraft epoxy resins containing phosphorus. Polymer **46**, 5012 (2005)
- 11. Wang, C.S., Shieh, J.Y.: Synthesis and properties of epoxy resins containing 2-(6-oxide-6H dibenz<c, e><1,2>oxaphosphorin-6-yl)1,4-benzeneliol. Polymer **39**(23), 5819 (1998)
- 12. Wang, C.S., Lin, C.H.: Synthesis and properties of phosphorus-containing epoxy resins by novel method. J. Polym. Sci.: Part A: Polym. Chem. **37**, 3903–3909 (1999)
- 13. Rwel, S.P., Liu, A.Y., Liou, G.S., Cheng, K.C., Guo, W.: Curing and pyrolysis of cresol novolac epoxy resins containing [2-(6-oxide-6H-dibenz(c, e) (1,2)oxaphosphorin-6-yl)-1, 4-naphthalenediol]. Polym. Eng. Sci. **44**(2) (2004)
- 14. Liu, Y.L., Wu, C.S., Hsu, K.Y., Chang, T.C.: Flame retardant epoxy resins from *o*-cresol novolac epoxy cured with a phosphorus-containing aralkyl novolac. J. Polym. Sci., Part A: Polym. Chem. **40**, 2329–2339 (2002)
- 15. Wang, C.S., Shieh, J.Y.: Shieh Phosphorus-containing epoxy resin for an electronic application. J. Appl. Polym. Sci. **73**, 353–361 (1999)
- 16. Wang, C.S., Lee, M.-C.: Synthesis and properties of epoxy resins containing 2-(6-oxide-6H dibenz<c, e><1,2>oxaphosphorin-6-yl)1,4-benzeneliol(II). Polymer **41**, 3631–3638 (2000)
- 17. Wang, C.S., Lin, C.H.: Synthesis and properties of phosphorus containing advanced epoxy resins. J. Appl. Polym. Sci. **75**, 429–436 (2000)
- 18. Ren, H., Sun, J., Wu, B., Zhon, Q.: Synthesis and properties of a phosphorus-containing flame retardant epoxy resin based on bis-phenoxy (3-hydroxy) phenyl phosphine oxide. Polym. Degrad. Stab. **92**, 956–961 (2007)
- 19. Lin, Y., Sun, J., Zhao, Q., Zhou, Q.: Synthesis and properties of a novel flame-retardant epoxy resin containing biphenylyl/phenyl phosphonic moieties. Polym.-Plast. Technol. Eng. **51**, 896–903 (2012)
- 20. Cheng, K.C., Yu, S.Y., Chiu, W.Y.: Thermal properties of main-chain phosphorus-containing epoxide cured with amine. J. Appl. Polym. Sci. **83**, 2733–2740 (2002)
- 21. Cheng, K.C., Yu, S.Y., Chiu, W.Y.: Thermal properties of side-chain phosphorus-containing epoxide cured with amine. J. Appl. Polym. Sci. **83**, 2741–2748 (2002)
- 22. Derouet, D., Morvan, F., Brosse, J.C.: Chemical modification of epoxy resins by dialkyl(or aryl) phosphates: evaluation of fire behavior and thermal stability. J. Appl. Polym. Sci. **62**, 1855–1868 (1996)
- 23. Wang, T.S., Parng, J.R., Shau, M.D.: The synthesis and properties of new epoxy resin containing phosphorus and nitrogen groups for flame retardancy. J. Appl. Polym. Sci. **74**, 413– 421 (1999)
- 24. Marney, D.C.O., Yang, W., Russell, L.J., Shen, S.Z., Ngugyen, T., Yuan, Q., Varley, R., Li, S.: Phosphorus intercalation of halloystie nanotubes for enhanced fire properties of polyamide 6. Polym. Adv. Technol. **23**, 1564–1571 (2012)
- 25. Lin, Y., Ng, K.M., Chan, C., Sun, G., Wu, J.: High-impact polystyrene/halloysite nanocomposites by emulsion polymerization using sodium dodecyl sulfate as surfactant. J. Colloid Interface Sci. **358**, 423–429 (2011)
- 26. Zhang, T., Du, Z., Zou, W., Li, H., Zhang, C.: Hyroxyl-phosphazen-wrapped carbon nanotubes and its application in ethylene-vinyl acetate copolymer. J. Appl. Polym. Sci. **130**, 4245–4254 (2013)
- 27. Hörold, S.: Phosphorus flame retardants in thermoset resins. Polym. Degrad. Stab. **64**, 427–431 (1999)
- 28. Clariant: Flame-retarding thermosetting composites, US patent 6420459 B1
- 29. Morgen, A.B. A review of transition metal-based flame retardants; transition-metal oxide/ salts, and complexes. In: Morgan, A.B., Wilkie, C.A., Nelson, G.L. (eds.) Fire and Polymers VI: Materials and Concepts for fire retardancy. ACS Symposium Series 1013. Chapter 19 (2009)
- 30. Zammarano, M., Franceschi, M., Bellayer, S., Gilman, J.W., Meriani, S.: Preparation and flame resistance properties of revolutionary self-extinguishing epoxy nanocomposites based on layered double hydroxides. Polymer **46**, 9314–9328 (2005)
- 31. Nshuti, C.M., Wu, Y., Nazarenko, S.: A comparative study of the fire retardant effect of several metal-based compounds added to an Epoxy-amine thermosets. In: Morgan, A.B., Wilkie, C.A., Nelson, G.L. (eds.) Fire and Polymers VI: New Advances in Flame Retardant Chemistry and Science. ACS Symposium Series 1118. Chapter 6 (2012)
- 32. Braum, U., Schartel, B., Fichera, M.A., Jager, C.: Flame retardancy mechanisms of aluminum phosphate in combination with melamine polyphosphate and zinc borate in glassfiber reinforced polyamide 6,6. Polym. Degrad. Stab. **92**, 1528–1545 (2007)
- 33. Kojima, Y., Usuki, A., Kawasumi, M., Okada, A., Fukushima, Y., Kurauchi, T. Mechanical properies of nylon 6-clay hybrid. J. Mater. Res. **8**, 1185 (1993)
- 34. Usuki, A., Kawasumi, M., Okada, A., Fukushima, Y.: Synthesis of nylon 6-clay hybrid. J. Mater. Res. **8**, 1179 (1993)
- 35. Balazs, A.C., Emrick, T., Russell, T.P.: Nanoparticle-polymer composites: Where two small worlds meet. Science **314**, 1107–1110 (2006)
- 36. Pack, S., Kahiwagi, T., Stemp, D., Koo, J., Si, M., Sokolov, J.C., Rafailovich, M.H.: Segregation of carbon nanotubes/organoclays rendering polymer blends self-extinguishing. Macromolecules **42**, 6698–6709 (2009)
- 37. Pack, S., Kahiwagi, T., Cao, C., Korach, C.S., Rafailovich, M.: Role of surface interactions in the synergizing polymer/clay flame retardant properties. Macromolecules **43**, 5338–5351 (2010)
- 38. Cividances, L.S., Simonetti, E.A.N., Moraes, M.B., Fernandes, F.W., Thin, G.P.: Influence of carbon nanotubes on epoxy resin cur reaction using different techniques: a comprehensive reivew. Polym. Eng. Sci. (2013). doi[:10.1002/pen.23775](http://dx.doi.org/10.1002/pen.23775)
- 39. Pack, S., Bobo, E., Muir, N., Yang, K., Swaraj, S., Ade, H., Cao, C., Korach, C.S., Kashiwagi, T., Rafailovich, M.H.: Engineering biodegardable polymer blends containing flame retardant-coated starch/nanoparticles. Polymer **53**, 4787–4799 (2012)
- 40. Yah, W.O., Takahara, A., Lvov, Y.M.: Selective modification of halloysite lumen with octadecylphosphonic acid: new inorganic tubular micelle. J. Am. Chem. Soc. **134**, 1853–1859 (2012)
- 41. Deng, S., Zhang, J., Ye, L.: Halloysite-epoxy nanocomposites with improved particle dispersion through ball mill homogenisation and chemical treatments. Compos. Sci. Technol. **69**, 2497–2505 (2009)