

特约专栏

# Efficiency of Different Classes of Flame Retardants for Epoxy Resins Designed for Coating Applications

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**Abstract:** The aim of this work is to study the efficiency of different classes of flame retardants for epoxy resins designed for coating applications. The thermal stability and fire retardant properties of the amine (JeffamineT403) cured epoxy resin, diglycidyl ether of bisphenol-A, have been studied using thermogravimetric analysis (TGA) under nitrogen atmosphere and cone calorimetry. In this study, an extensive series of flame retarded epoxy resins were prepared with commercially available flame retardant additives, including halogens, phosphorus, minerals, melamine derivative and intumescent additives. The range of flame retardant materials used in epoxy formulations of commercial interest was investigated. The amount of FR additives is maintained at 15 % (except mineral fillers 30 %, mass fraction) to avoid impairment of the mechanical properties of epoxy resin.

**Key words:** epoxy; flame retardant additives; curing agents; thermal properties; fire retardancy

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## 不同种类阻燃剂对涂层用环氧树脂的阻燃效率研究

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**摘要:** 主要研究了不同种类阻燃剂对涂层用环氧树脂的阻燃效率的影响。该环氧树脂由双酚 A 的二环氧丙醚胺类固化剂固化而得, 用氮气氛下的热重分析(TGA)和锥形量热研究了其热稳定性和阻燃性。本研究中, 所用的阻燃剂都是商业化应用的阻燃添加剂, 包括卤素、磷、无机物、三聚氰胺衍生物和膨胀型添加剂。研究所选用的阻燃环氧体系都具有较高的商业化应用价值。研究发现, 固化剂的种类对环氧树脂的阻燃性有较大影响, 在阻燃和抑烟方面, 溴系阻燃剂比氯系阻燃剂更有效。亚磷酸盐对于环氧树脂具有很好的阻燃作用。氢氧化镁、硼酸锌比氢氧化铝的阻燃效率高。三聚氰胺化合物能够赋予环氧树脂较好的阻燃和抑烟性, 此外膨胀型添加剂也是一种有效的阻燃剂。

**关键词:** 环氧树脂; 阻燃添加剂; 固化剂; 热性能; 阻燃剂

### 1 Introduction

Epoxy resins are unique among the thermosetting plastics due to the minimum pressure required for the fabrication of products, much lower cure shrinkage and hence lower residual stress in the cured product. A wide range of temperatures can be available by judicious selection of curing agents, which enables good control over the degree of cross-linking. Epoxy resins range from low viscosity liquids to tack-free solids, with high chemical and corrosion resistance, good mechanical and electrical properties, and also outstanding adhesion to a variety of substrates. Because of these unique char-

acteristics and useful properties, epoxy resins are widely used in surface coatings, binders for glass and carbon fiber reinforced composites, structural adhesives and laminates for electrical and electronics, construction, tooling, molding, casting, pipes, tanks, and sporting goods<sup>[1]</sup>. Approximately 50 % of the total amount of epoxy resins produced is used for protective surface coatings. The polyamine cured epoxy resins of the diglycidyl ether of bisphenol-A (DGEBA) have been used for surface coating applications. The major limitation of epoxy resin is their flammability, which has been addressed using either reactive or additive flame retardants<sup>[2-5]</sup>.

The most commonly used flame retardants for epoxy resins are aluminum trihydroxide, also known as alumina trihydrate(ATH), intumescent (IFR) additives and tetrabromobisphenol-A (TBBA) or brominated epoxy for coating as well as composites or/ electrical laminates. However, recently 9, 10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DO-

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PO) and modified DOPOs have been considered as alternatives for TBBA, due to the need for lead-free laminates and also to avoid environmental problems<sup>[6-7]</sup>. Some literature deals with FR epoxies based on commercially available FR additives, such as APP( Ammonium Polyphosphate ), melamine phosphate, DMMP ( Dimethyl Methyl Phosphonate ), RDP( Resorcinol Diphosphate ), ZB( Zinc Borate ), RP( Red Phosphorus ), MoO<sub>3</sub>, Sb<sub>2</sub>O<sub>3</sub>, melamine, calcium borate, Fyrol PMP( Poly( m-Phenylene Methyl Phosphonate ) ), ATH, TPP( Triphenyl Phosphate ), DOPO, EG( Expandable Graphite ) and intumescent additives<sup>[8-27]</sup>. The work in this paper focuses on the thermal and flame retardant properties of amine cured epoxy resin filled with different categories of commercially available flame retardants at the constant loading of 15 % ( mass fraction ). The main objective of this work is to

select the effective flame retardant ( greater reduction of peak HRR and smoke ) which could be employed for amine cured epoxy system suitable for coating applications.

2 Experimental

2.1 Materials

Diglycidyl ether of bisphenol-A ( Araldite GY6010, EEW 188 ) and polyether amine curing agents ( Jeffamine D-230, T-403, D-2000 and T-5000 ) were provided by Huntsman Advanced Materials. Diethylene toluene diamine ( DETDA, Ethacure 100 ) curing agent was obtained from Albemarle. Table 1 show the flame retardant additives ( chemical and trade name ) used in this study and their sources. All the chemicals were used as received.

Table 1 List of flame retardants used in this study

Flame retardants	Sources
Dechlorane plus 25 ( D-plus )	Laurel Industries
Decabromo diphenyl oxide ( Saytex 102E )	Albemarle
Ethane 1, 2-bis( pentabromophenyl ) ( Saytex 8010 )	Albemarle
Ethylene bis tetrabromo phthalimide ( Saytex BT93 )	Albemarle
Tetrabromo bisphenol-A ( Saytex CP2000 )	Albemarle
Dibromo neopentyl glycol ( FR522 )	Dead Sea Bromine group
Tribromo neopentyl alcohol ( FR513 )	Dead Sea Bromine group
Antimony trioxide	Laurel Industries
Triphenyl phosphate ( Reofos TPP )	Chemtura
Ethylene diamine phosphate ( Antiblaze NK )	Albemarle
Resorcinol diphosphate ( Reofos RDP )	Chemtura
Bisphenol A diphosphate ( Reofos BADP )	Chemtura
Red phosphorus ( Exolit RP6520 )	Clariant
Triphenyl phosphine oxide	Aldrich
Reofos NHP ( Structure proprietary )	Chemtura
Tris( dipropylene glycol ) phosphite ( Doverphos 72 )	Dover Chemicals
Triphenyl phosphite ( Doverphos10 )	Dover Chemicals
Alkyl ( C12-C15 ) bisphenol A phosphite ( Doverphos 613 )	Dover Chemicals
Bis( 2, 4-dicumylphenyl ) pentaerythritol diphosphite ( Doverphos S-9228 )	Dover Chemicals
Dimethyl methyl phosphonate ( Antiblaze DMMP )	Albemarle
Cyclic oligomeric phosphonate ( A-N )	Albemarle
Poly( m-phenylene methyl phosphonate ( Fyrol PMP )	Supresta
Aluminum salt of phosphinate ( Exolit OP1230, Exolit OP1314, Exolit OP1311 ( LV )	Clariant
9, 10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide	Krems Chemie
Ammonium polyphosphate ( Phoschek P/42 )	Astaris
Tris monochloroisopropyl phosphate ( A-80 )	Albemarle
Chloroalkyl phosphonate ( A-78 )	Albemarle
Aluminum hydroxide ( Martinal OL-107/LE )	Albemarle
Magnesium hydroxide ( Magnifin H7C ) ( MDH )	Albemarle
Zinc borate ( Firebrake ZB fine )	Rio Tinto
Melamine	Alfa Aesar
Melamine polyphosphate ( Melapur 200 – 70 )	Ciba Specialty Chemicals
Melamine cyanurate ( Budit 315 )	Budenheim
Expandable graphite ( EG220 – 80 )	GraftTech

## 2.2 Preparation of cured epoxy samples

The flame retarded epoxy samples were prepared by homogenous mixing of FR additives in the epoxy resin using a high speed mechanical stirrer. Then the stoichiometric amount of curing agent (31.9, 42, 273, 506 and 23.6 g of Jeffamine D230, T403, D2000, T5000 and DETDA based on 100 g of epoxy oligomer, respectively) was added and the resultant mixture was poured into a mold. The samples were cured at room temperature (RT) for 24 h, and then were kept in an oven at 80 °C for 2 h and 125 °C for 3 h for post curing (Jeffamine curing agents). The curing schedule for DETDA was 120 °C for 4 h and 200 °C for 2 h for direct curing (without RT curing).

## 2.3 Measurements

Thermogravimetric analysis (TGA) was conducted on the simultaneous TG and differential scanning calorimetry SDT Q600 (TA Instruments) at a heating rate of 20 °C/min. Samples were heated in the temperature range from 50 to 800 °C under nitrogen at a flow rate of 100 mL/min. Typical sample weights of 5 ~ 10 mg were employed. All samples were run at least in duplicate; temperature is reproducible to about  $\pm 2$  °C and mass to 0.2 %. A cone calorimeter (Atlas Cone 2) at 50 kW/m<sup>2</sup> of external heat flux was used to evaluate (as per ASTM E 1354) the flammability of cured epoxy samples having dimensions of 100mm  $\times$  100mm  $\times$  6 mm<sup>3</sup>. Three samples were tested per resin formulation. The results from cone calorimetry are reproducible to within about  $\pm 10$  %.

## 3 Results and discussion

This section demonstrates the influence of the different types of curing agents and curing conditions and different categories of flame retardant additives, halogens, phosphorus, mineral fillers, melamine compounds and intumescent additives on the thermal as well as fire retardant properties of amine cured epoxy resins.

### 3.1 Effect of curing agents and curing condition

The epoxy group is highly reactive towards a variety of nucleophilic and electrophilic reagents. Generally, there are two type of curing agents, either catalytic or reactive, used for the epoxy cross-linking reaction. The catalytic curing agent (tertiary amine, Lewis acids and bases, imidazole) functions as an initiator for epoxy resin homopolymerization, whereas the reactive curing agents (amines, amides, anhydrides, dicyandiamide, isocyanate, sulfides, mercaptans, alcohols, acids) acts as a comonomer in the polymerization or curing reaction. The selection of curing agent depends on the processing method, curing conditions (curing temperature and time), properties desired, toxicological and environmental limitations and cost<sup>[1]</sup>. In this study, the stoichiometric amount of two types of amine curing agents, polyamines (Jeffamine) with different 'n' values and aromatic diamine (Diethylene Toluene Diamine, DETDA) were used. A flexible structure with lengthy gelation time (> 30 days) was obtained with Jeffamine D-2000 and T-5000 as a curing agent, whereas Jeffamine D-230 and T-403 give glassy rigid structure having 8 h gelation time at room temperature. A highly cross-linked rigid structure with no gelation at room

temperature was obtained with DETDA as a curing agent.

Figure 1 shows the weight loss curve of epoxy cured with different amine curing agents. A rapid single step decomposition of epoxy takes place at around 400 °C regardless of type of curing agents and also Jeffamine D-2000 and T-5000 cured samples exhibited less residue at higher temperature compared to the other amines. This is probably due to the lower aromaticity present in the sample as evident from the initial stoichiometry of the composition. As expected, higher thermal stability was obtained with aromatic curing agent (DETDa) as compared to aliphatic curing agents (Jeffamines). Table 2 presents the onset ( $T_{10\%}$ ), maximum degradation temperature ( $T_{max}$ ) and residue of epoxy cured with different amine curing agents. There is not much change in onset temperature of Jeffamine cured samples, whereas  $T_{max}$  was slightly higher in case of Jeffamine D-2000 and T-5000 cured samples. Epoxy cured with Jeffamine T-5000 sample provides less residue compared to the other Jeffamines. Overall, epoxy cured with DETDA gives better thermal stability and higher residue compared to sample cured with the Jeffamines.

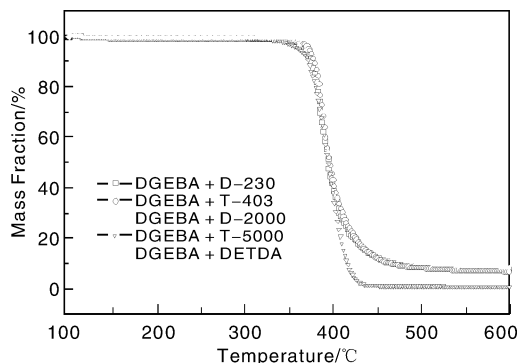


Fig. 1 TGA of epoxy cured with different curing agents

Table 2 Effect of curing agents on the thermal properties of epoxy resin

Sample	$T_{10\%}$ / °C	$T_{max}$ / °C	% residue at 700 °C
Epoxy + D-230	375	384	7.9
Epoxy + T-403	378	387	6.9
Epoxy + D-2000	375	398	5.2
Epoxy + T-5000	372	395	1.0
Epoxy + DETDA	393	402	8.2

Figure 2 displays the heat release rate of epoxy cured with different amine curing agents and the corresponding cone data are presented in Table 3. As expected, aromatic diamine cured samples show a higher time to ignition with lower peak HRR as compared to the aliphatic Jeffamine cured samples. Moreover, the aromatic diamine cured sample shows higher time to peak HRR than with the Jeffamines. A much lower time to ignition with lower peak HRR was observed from the flexible cured samples (Jeffamine D-2000 and T-5000) as compared to glassy samples, obtained from Jeffamine D-230 and T-403. During burning, aromatic diamine (DETDa) cured sample releases less heat (Total Heat Released, THR) with greater amount of smoke (Average Specific Extinction Area, ASE). Jeffamine D-2000 and T-5000 cured samples release much less smoke as compared to other

amine cured samples. There is not much change in mass loss rate of the cured epoxy samples regardless of the type of curing agents.

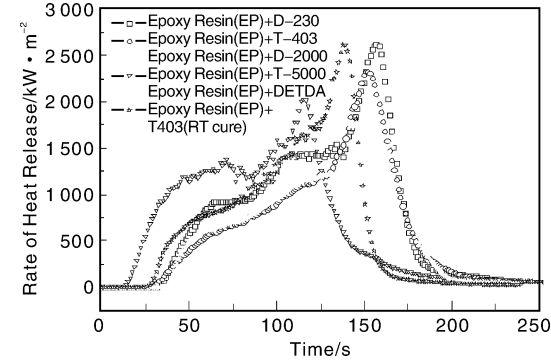


Fig. 2 Heat release curves of epoxy cured with different curing agents

Table 3 Cone calorimetric data for epoxy cured with different curing agents

Sample	$t_{\text{ign}}/\text{s}$	$P_{\text{HRR}}/\text{kW} \cdot \text{m}^{-2}$	THR/ $\text{MJ} \cdot \text{m}^{-2}$	AMLR/ $\text{g} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$	ASEA/ $\text{m}^2 \cdot \text{kg}^{-1}$
Epoxy + D-230	32 ± 1	2 572 ± 310	184 ± 2	51 ± 3	554 ± 11
Epoxy + T-403	29 ± 3	2 467 ± 150	164 ± 9	47 ± 2	753 ± 34
Epoxy + D-2000	15 ± 1	1 832 ± 95	173 ± 10	49 ± 2	239 ± 19
Epoxy + T-5000	13 ± 1	2 026 ± 16	178 ± 20	52 ± 5	132 ± 35
Epoxy + DETDA	37 ± 1	1 656 ± 36	139 ± 3	51 ± 3	919 ± 42
EP + T-403 (RT cure)	27 ± 1	2 656 ± 103	155 ± 1	58 ± 2	595 ± 37

Note:  $t_{\text{ign}}$  corresponding ignition time,  $P_{\text{HRR}}$  corresponding peak heat release rate, AMLR corresponding average mass loss rate.

The curing condition plays a major role in thermal stability as well as flammability of epoxy resin. Samples were cured with two different curing protocols, RT cured for 30 days and elevated temperature cured (80 °C/2 h and 125 °C/3 h). The room temperature (RT) cured sample shows inferior thermal stability (onset 365 °C) as well as flame retardant properties (shown in Figure 2 and Table 3) compared to the sample cured at elevated temperature. This indicates that incomplete curing takes place at room temperature (also confirmed through the curing kinetics of epoxy measured by DSC) and residual cross-linking takes place at elevated temperature. Overall, the thermal stability as well as flammability of epoxy resins depends on the extent of the cross-linking reaction.

In the remaining sections of this paper, the epoxy resin is cured with Jeffamine T403.

3.2 Effect of halogenated flame retardants

Antimony trioxide ( $\text{Sb}_2\text{O}_3$ ) improves the flame retardant action of a polymer matrix filled with halogenated compounds. In this study, six different brominated (three reactive and three additive) and one chlorinated additive were used in combination with  $\text{Sb}_2\text{O}_3$  at a constant ratio of 4:1 at loading of 15 % by weight. Figure 3 shows the thermal degradation of epoxy filled with different halogenated flame retardants and the corresponding data are shown in Table 4.

The thermal stability of epoxy decreases with the addition of halogenated FRs for both chlorine and bromine. The dechlorane plus filled sample shows greater thermal stability (except for the tribromo neopentyl alcohol filled sample) as well as a larger amount of residue retained at higher temperature than do the brominated samples. TBNPA (Tribromo Neopentyl Alcohol) has the lowest onset temperature (182 °C) of the materials studied and it also shows the highest onset temperature and  $T_{\text{max}}$  in epoxy resin as compared to the highly thermally stable FRs (>400 °C) filled samples such as Deca, EBPBP (Ethane 1, 2-Bis(pentabromophenyl) and EBTBPI (Ethylene Bis Tetrabromo Phthalimide). In all cases, the addition of a halogenated compound (and  $\text{Sb}_2\text{O}_3$ ) decreases the thermal stability of the epoxy resin, whether this is evaluated by the onset or the temperature of maximum degradation. The aliphatic reactive brominated (TBNPA and DBNPG (Dibromo Neopentyl Glycol)) filled samples showed greater  $T_{\text{max}}$  values compared to aromatic reactive (TBBA) and additive halogenated FR filled samples. Among the brominated compounds, the EBTBPI filled sample shows the highest char residue, which is attributed to the slow degradation of EBTBPI.

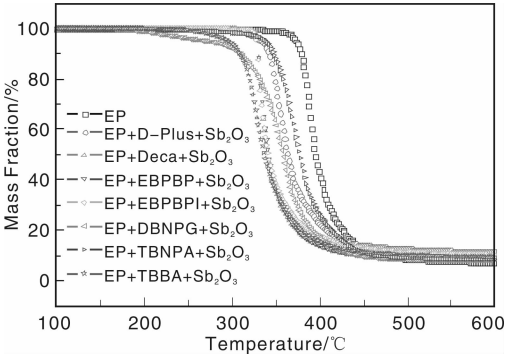


Fig. 3 TGA of epoxy filled with halogenated FRs with  $\text{Sb}_2\text{O}_3$  (4:1)

Table 4 Effect of halogenated FR additives on the thermal properties of epoxy

Sample	$T_{10} / ^\circ\text{C}$	$T_{\text{max}} / ^\circ\text{C}$	% residue at 700 °C
Epoxy	378	387	6.9
EP + 12 % D-plus + 3 % $\text{Sb}_2\text{O}_3$	342	355	11.2
EP + 12 % Deca + 3 % $\text{Sb}_2\text{O}_3$	330	332	7.9
EP + 12 % EBPBP + 3 % $\text{Sb}_2\text{O}_3$	330	333	7.8
EP + 12 % EBTBPI + 3 % $\text{Sb}_2\text{O}_3$	329	331	9.7
EP + 12 % DBNPG + 3 % $\text{Sb}_2\text{O}_3$	308	359	6.9
EP + 12 % TBNPA + 3 % $\text{Sb}_2\text{O}_3$	347	372	7.8
EP + 12 % TBBA + 3 % $\text{Sb}_2\text{O}_3$	309	328	8.8

The effect of halogenated flame retardants on the heat release rate of epoxy is shown in Figure 4 and the corresponding data are presented in Table 5. A significant reduction of heat release rate is observed upon the addition of halogenated compounds compared to the control sample. The brominated samples show lower heat release rates during combustion than the sample containing dechlorane plus at the same concentration. The TBBA filled sample shows an apparent two-step

burning process, but the total heat released is still much lower than in the pristine polymer. The ignition time for the filled epoxies slightly decreases upon the addition of halogenated flame retardants. Among the brominated FRs, the EBTBPI and TBNGA filled samples showed the greatest reductions of peak HRR ( $>70\%$ ). In all cases, there is a significant reduction of THR. For most systems, the mass loss rate is little changed, and in several cases it is higher, than in the pristine polymer, this is an indication that the mass loss rate is not important in the fire retardancy, probably because this is a vapor phase, radical trapping phenomenon. Dec plus, the chlorinated material exhibits a large smoke evolution as does TBBA; in general, the brominated fire retardants evolve less smoke than does the pristine epoxy.

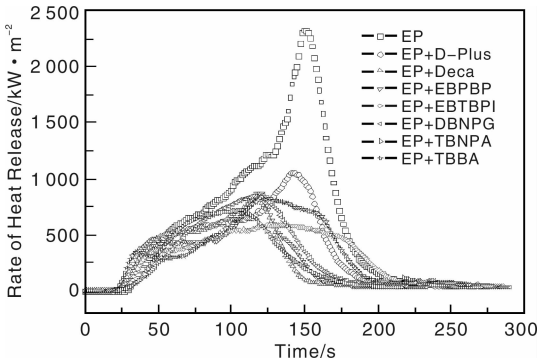


Fig. 4 Heat release curves of epoxy filled with halogenated FRs with  $\text{Sb}_2\text{O}_3$  (4:1)

Table 5 Cone calorimetric data for epoxy filled with halogenated additives

Sample	$t_{\text{ign}}/\text{s}$	$P_{\text{HRR}}/\text{kW} \cdot \text{m}^{-2}$ (% reduction)	THR / $\text{MJ} \cdot \text{m}^{-2}$	AMLR/ $\text{g} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$	ASEA/ $\text{m}^{-2} \cdot \text{kg}^{-1}$
Epoxy (EP)	29 ± 3	2467 ± 150	164 ± 9	47 ± 2	753 ± 34
EP + 12 % D-plus + 3 % $\text{Sb}_2\text{O}_3$	20 ± 2	1 052 ± 39 (57)	96 ± 2	42 ± 1	1 375 ± 228
EP + 12 % Deca + 3 % $\text{Sb}_2\text{O}_3$	23 ± 1	826 ± 160 (67)	64 ± 4	55 ± 3	750 ± 160
EP + 12 % EBPBP + 3 % $\text{Sb}_2\text{O}_3$	25 ± 1	846 ± 66 (66)	62 ± 1	55 ± 2	478 ± 88
EP + 12 % EBTBPI + 3 % $\text{Sb}_2\text{O}_3$	25 ± 1	556 ± 88 (77)	64 ± 16	48 ± 1	335 ± 32
EP + 12 % DBNPG + 3 % $\text{Sb}_2\text{O}_3$	25 ± 4	880 ± 155 (64)	75 ± 6	59 ± 2	381 ± 27
EP + 12 % TBNPA + 3 % $\text{Sb}_2\text{O}_3$	25 ± 2	718 ± 22 (71)	66 ± 3	60 ± 1	214 ± 18
EP + 12 % TBBA + 3 % $\text{Sb}_2\text{O}_3$	21 ± 1	798 ± 116 (68)	84 ± 4	39 ± 4	1670 ± 93

Note: Deca corresponding decabromo diphenyl oxide, DBNPG corresponding dibromo neopentyl glycol

Tetrabromobisphenol A (TBBA) is the most commonly used FR (Flame Retardant) for epoxy resins and, in this study, TBBA mixed with  $\text{Sb}_2\text{O}_3$  shows good fire retardancy in terms of reduction of peak HRR and THR, but a great deal of smoke is produced, which is undesirable in a fire. The following study is an attempt to decrease the smoke evolution at the same time preserving good flame retardancy. Figure 5 shows the heat release rates of epoxy filled with TBBA,  $\text{Sb}_2\text{O}_3$  and ZB and Table 6 collects the data together. As was hoped, the use of zinc borate rather than antimony oxide did not significantly impact the fire retardant properties in terms of  $P_{\text{HRR}}$  and THR and it did bring about a reduction in smoke.

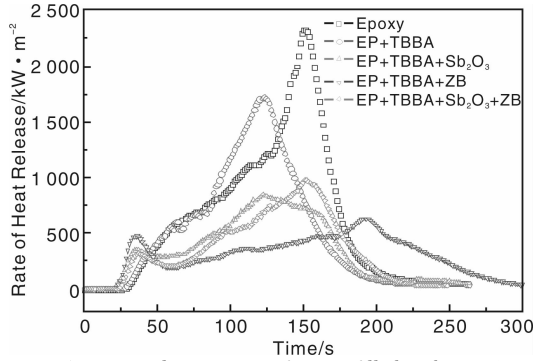


Fig. 5 Heat release curves of epoxy filled with TBBA,  $\text{Sb}_2\text{O}_3$  and ZB

Table 6 Cone calorimetric data for epoxy filled with TBBA,  $\text{Sb}_2\text{O}_3$  and ZB

Sample	$t_{\text{ign}}/\text{s}$	$P_{\text{HRR}}/\text{kW} \cdot \text{m}^{-2}$ (% reduction)	THR/ $\text{MJ} \cdot \text{m}^{-2}$	AMLR/ $\text{g} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$	ASEA/ $\text{m}^2 \cdot \text{kg}^{-1}$
Epoxy (EP)	29 ± 3	2 467 ± 150	164 ± 9	47 ± 2	753 ± 34
EP + 15 % TBBA	26 ± 1	1 549 ± 194 (37)	122 ± 5	46 ± 4	906 ± 46
EP + 12 % TBBA + 3 % $\text{Sb}_2\text{O}_3$	21 ± 1	798 ± 116 (68)	84 ± 4	39 ± 4	1 670 ± 93
EP + 12 % TBBA + 3 % ZB	20 ± 1	623 ± 22 (75)	91 ± 2	26 ± 2	1 258 ± 92
EP + 12 % TBBA + 1.5 % $\text{Sb}_2\text{O}_3$ + 1.5 % ZB	22 ± 1	970 ± 62 (61)	88 ± 2	38 ± 4	980 ± 58

3.3 Effect of phosphorus-based flame retardants

Inorganic and organic phosphorus compounds are used to achieve flame retardancy in epoxy resins and both additive and reactive phosphorus based flame retardants are commercially available. In this study, nearly all types of phosphorus

FRs are used at the constant loading of 15 % by weight. The effect of different phosphate FR additives on the thermal degradation of epoxy is shown in Figure 6 and Table 7. All phosphate filled samples decrease the thermal stability of epoxy, as expected. It is well known that phosphorus acids are re-

leased from the decomposition of phosphate FRs, which accelerate the decomposition of epoxy resin and the relatively easy thermal degradation of phosphate ester bonds. The sample filled with elemental (red) phosphorus, P<sub>4</sub>, shows the greatest thermal stability, while the poorest thermal stability is observed from the TPP filled sample. This may be attributed to the high and low thermal stability of RP (432 °C) and TPP (258 °C). The APP filled sample shows a large residue at higher temperature, while epoxy filled with TPPO showed very low residue.  $T_{max}$  was slightly increased with the addition of TPPO; similar observations have been reported in prior investigations<sup>[8-9,12-13,15,19]</sup>. Based on the amount of residue retained at higher temperature, the FR additives RDP, BADP (Bisphenol A Diphosphate), EDAP (Ethylene Diamine Phosphate) and APP are char forming additives and function by a condensed phase mechanism of flame retardation in epoxy resin. The other phosphates may follow a gas phase mechanism and/or completely volatilize at higher temperature. Xiao et al.<sup>[20]</sup> have shown that most of the TPP has been volatilized and a small amount of TPP decomposes in the condensed phase producing phosphorus acids in the epoxy system. The TPP filled sample retained little residue at higher temperature, in agreement with an earlier report<sup>[19]</sup>. Table 7 show the thermal properties of epoxy filled with different phosphorus FR additives. The onset temperature ( $T_{10\%}$ ) of epoxy decreases with the addition of phosphates.

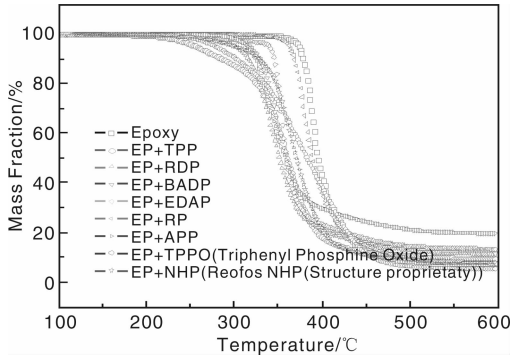


Fig.6 TGA of epoxy filled with organophosphate FR additives

Figure 7 shows the heat release rates of epoxy filled with different phosphate FR additives and the data are collected in Table 8. Upon the addition of phosphates, reduced heat release rates of epoxy are observed. Further, time to peak HRR also decreases with the addition of phosphates. Among the phosphates, the TPP and NHP filled samples release more heat in terms of peak HRR. Both the APP and EDAP filled samples show low heat releases with prolonged burning behavior and the formation of an intumescent char, while a two-step burning process is observed for epoxy filled with RDP and BADP. The time to ignition of epoxy is lower upon the addition of phosphates, except TPPO which is slightly higher. Katsoulis et al. also found a decrease in time to ignition of epoxy with the addition of RDP<sup>[13]</sup>. Epoxy filled with TPP, RP and APP shows the lowest ignition time, while the EDAP and APP filled samples show the greatest reduction of peak HRR, and TPP and NHP lead to the smallest reductions. This is probably due to the formation of an intumescent

char with EDAP and APP, which acts as a barrier to protect the underlying sample, with slow burning (lower AMLR), whereas TPP and NHP cause rapid degradation of sample (higher AMLR). The RDP filled sample shows better flame retardation than BADP and moreover, an almost comparable reduction is observed from RP and TPPO. A remarkable reduction of THR is observed in the presence of phosphates. The amount of smoke increases for all phosphates, except the NHP filled sample.

Table 7 Effect of different phosphorus compounds on the thermal properties of epoxy

Sample	$T_{10\%}/^{\circ}\text{C}$	$T_{max}/^{\circ}\text{C}$	% residue at 700 °C
Epoxy (EP)	378	387	6.9
EP + 15 % TPP	284	357	9.3
EP + 15 % RDP	315	337	12.1
EP + 15 % BADP	327	344	11.0
EP + 15 % EDAP	345	354	13.0
EP + 15 % RP	368	378	7.1
EP + 15 % APP	323	336	18.9
EP + 15 % TPPO	307	391	4.9
EP + 15 % NHP	328	360	7.6
EP + 15 % Doverphos 72	313	349	9.1
EP + 15 % Doverphos 10	297	341	16.8
EP + 15 % Doverphos 613	320	352	8.9
EP + 15 % Doverphos S9228	317	355	10.7
EP + 15 % DMMP	318	356	9.8
EP + 15 % A-N	320	346	8.7
EP + 15 % PMP	308	343	14.6
EP + 15 % OP1230	363	373	14.2
EP + 15 % OP1314	360	375	14.3
EP + 15 % OP1311 (LV)	349	375	10.9
EP + 15 % DOPO	335	367	7.0
EP + 15 % A-80 (TMCP)	296	353	8.9
EP + 15 % A-78	283	329	9.0

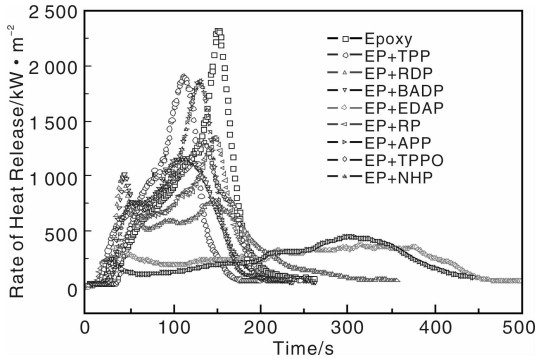


Fig.7 Heat release curves of epoxy filled with phosphates

Figure 8 shows the thermogravimetric analysis of epoxy filled with organophosphites, and the data are shown in Table 7. A considerable reduction of thermal stability (both onset and  $T_{max}$ ) of epoxy occurred in the presence of phosphites, probably due to the formation of phosphorus acids, caused by the low thermal stability (170 ~ 300 °C) of phosphites, which accelerates the de-

composition of epoxy. The Doverphos 10 (triphenyl phosphite) filled sample showed the lowest thermal stability. Although triphenylphosphite completely volatilized at around 300 °C, epoxy

filled with triphenyl phosphite shows greater char residue at higher temperature, probably due to some interaction between triphenyl phosphite and epoxy during pyrolysis.

Table 8 Cone calorimetric data for epoxy filled with different phosphorus compounds

Sample	$t_{\text{ign}}/\text{s}$	$P_{\text{HRR}}/\text{kW} \cdot \text{m}^{-2}$ (% reduction)	THR/ $\text{MJ} \cdot \text{m}^{-2}$	AMLR/ $\text{g} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$	ASEA/ $\text{m}^2 \cdot \text{kg}^{-1}$
Epoxy (EP)	29 ± 3	2 467 ± 150	164 ± 9	47 ± 2	753 ± 34
EP + 15 % TPP	12 ± 2	1 959 ± 101 (21)	128 ± 1	52 ± 1	971 ± 111
EP + 15 % RDP	21 ± 2	997 ± 24 (60)	121 ± 1	24 ± 3	1 284 ± 20
EP + 15 % BADP	24 ± 2	1 211 ± 136 (51)	126 ± 3	40 ± 1	995 ± 29
EP + 15 % EDAP	25 ± 1	359 ± 86 (85)	101 ± 9	15 ± 3	2 241 ± 416
EP + 15 % RP	11 ± 1	1 298 ± 155 (47)	118 ± 3	42 ± 1	1 019 ± 93
EP + 15 % APP	15 ± 3	403 ± 97 (84)	99 ± 3	12 ± 2	1 010 ± 62
EP + 15 % TPPPO	34 ± 1	1 310 ± 63 (47)	126 ± 2	40 ± 5	845 ± 85
EP + 15 % NHP	26 ± 1	1 915 ± 311 (20)	138 ± 1	49 ± 4	566 ± 73
EP + 15 % Doverphos 72	22 ± 1	835 ± 94 (66)	133 ± 4	28 ± 3	779 ± 70
EP + 15 % Doverphos 10	21 ± 1	504 ± 128 (80)	114 ± 5	18 ± 9	783 ± 163
EP + 15 % Doverphos 613	18 ± 5	1 114 ± 91 (55)	143 ± 27	38 ± 9	822 ± 47
EP + 15 % Doverphos S9228	18 ± 2	660 ± 16 (72)	127 ± 2	13 ± 2	852 ± 19
EP + 15 % DMMP	21 ± 1	962 ± 205 (61)	91 ± 2	44 ± 1	1 260 ± 297
EP + 15 % A-N	24 ± 1	1 429 ± 143 (42)	96 ± 2	51 ± 2	936 ± 38
EP + 15 % PMP	19 ± 3	545 ± 70 (78)	81 ± 3	28 ± 5	1 262 ± 43
EP + 15 % OP1230	21 ± 4	1 254 ± 103 (49)	115 ± 4	35 ± 1	1 082 ± 45
EP + 15 % OP1314	17 ± 2	860 ± 11 (65)	117 ± 5	31 ± 2	1 070 ± 30
EP + 15 % OP1311 (LV)	13 ± 1	1 050 ± 47 (57)	113 ± 2	38 ± 7	900 ± 73
EP + 15 % DOPO	24 ± 1	1 208 ± 160 (51)	84 ± 3.3	44 ± 4	514 ± 98
EP + 15 % A-80 (TMCP)	23 ± 1	660 ± 105 (73)	114 ± 3	20 ± 3	830 ± 23
EP + 15 % A-78	17 ± 1	1 264 ± 163 (57)	98 ± 8	41 ± 4	1 338 ± 341

Note: A80 is tris monochloroisopropyl phosphate, A-78 is chloroalkyl phosphonate

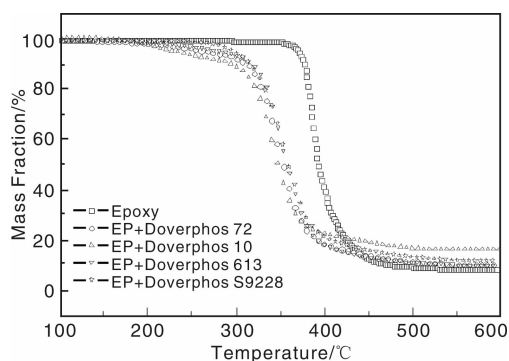


Fig. 8 TGA of epoxy filled with organophosphite additives

The effect of phosphites on the heat release rate of epoxy is shown in Figure 9 and the data are in Table 8. An early heat release rate is observed in the case of filled samples. Both the triphenylphosphite and S9228 filled sample show multiple peaks with large reductions in the HRR and longer burning times compared to other phosphites, likely due to the formation of a large amount of residue (intumescent) during burning. The ignition time of epoxy is decreased with the incorporation of phosphites, which may be

due to the low thermal stability of phosphites, which volatilize before epoxy does. The alkyl-aryl phosphite (Doverphos 613) filled sample shows the poorest flame retardant efficiency. All filled samples show low THR. And the smoke evolution is marginally higher in the case of phosphite filled samples; phosphite in epoxy releases less smoke than phosphate in epoxy.

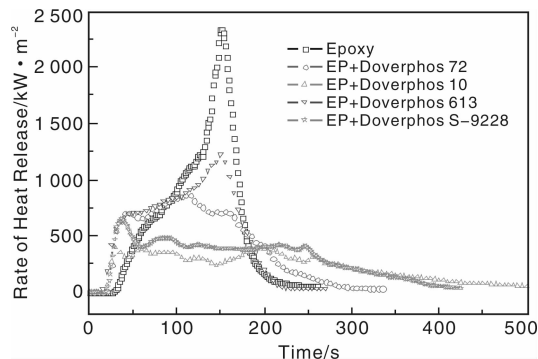


Fig. 9 Heat release curves of epoxy filled with phosphites

The effect of three different phosphonates (linear, cyclic and polymeric) on the thermal stability of cured epoxy resin is shown in Figure 10 and Table 7. The thermal stability of

epoxy decreases with the addition of phosphonates. Zerda and Lesser have also investigated the decrease in thermal stability of epoxy filled with DMMP<sup>[11]</sup>. DMMP almost completely volatilizes at temperature around 170 °C, but the DMMP filled sample shows better  $T_{\max}$  compared to other phosphonates. The Fyrol PMP filled sample shows the greatest residue at high temperature, which may be due to the polymeric form of Fyrol PMP leading to slow degradation as well as retaining greater amounts of residue at high temperature.

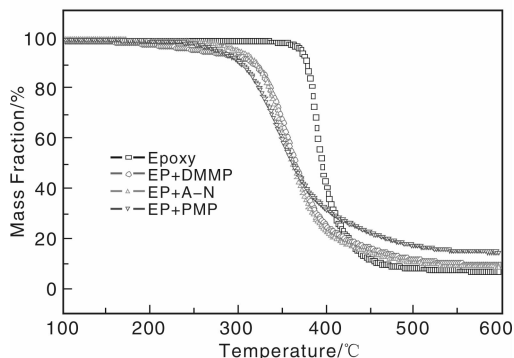


Fig. 10 TGA of epoxy filled with phosphonates

The effect of phosphonates on the heat release rate and the corresponding cone data are shown in Figure 11 and Table 8. The DMMP filled sample exhibits an early heat release behavior; all filled samples show lower time to peak HRR, while the time to ignition of filled samples is slightly lower. The Fyrol PMP filled sample shows the highest reduction of peak HRR and AMLR. There is a considerable reduction of THR of filled samples, but more smoke is released when phosphonates are added to the epoxy resin.

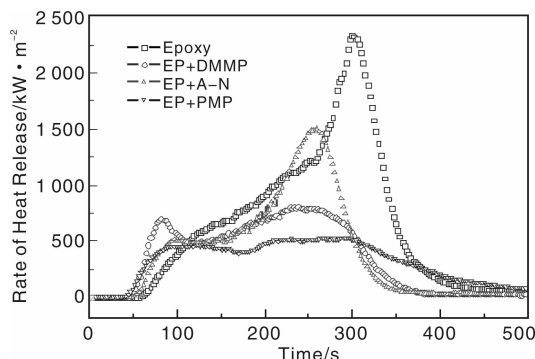


Fig. 11 Heat release curves of epoxy filled with phosphonates

There are two type of aluminum phosphinate additives used in this study, the pure form of aluminum diethylphosphinate (OP1230) and melamine phosphate blended phosphinate (OP1314 and OP 1311 (LV)). 9, 10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO) is a reactive phosphinate with a monofunctional reactive group, which can react with the epoxy oligomer during the curing process. Figure 12 displays the thermal degradation of epoxy filled with phosphinate flame retardants and the data are presented in Table 7. The thermal stability of epoxy decreases with the addition of phosphinates, moreover the DOPO filled sample shows the poor thermal stability as well as no char at higher temperature, compared to the aluminum phosphinates. This

may be due to low thermal stability of DOPO (onset 285 °C), which decomposes prior to epoxy and forms phosphorus acids, accelerating the decomposition of epoxy. Because DOPO acts as gas phase FR flame retardant, there is no residue at high temperature. Previous studies showed that the thermal stability of epoxy decreases in the presence of DOPO<sup>[22-23]</sup>. Further, it is observed that OP1230 and OP1314 filled samples show similar thermal stability and char residue at higher temperature, whereas the OP1311 (LV) filled sample shows slightly lower thermal stability and residue. Aluminum phosphinate filled samples show enhanced onset and  $T_{\max}$  temperatures and char yield compared to DOPO, probably due to the higher thermal stability (435 ~ 480 °C) and slow degradation of aluminum phosphinates and also due to the observation that aluminum phosphinates do not form phosphorus acids during thermal decomposition.

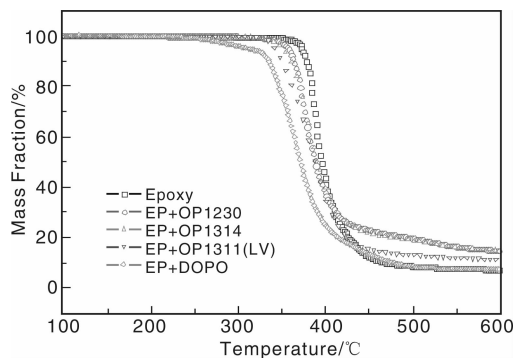


Fig. 12 TGA of epoxy filled with phosphinates

The heat release rate of epoxy filled with phosphinate flame retardants and the corresponding cone calorimetric data are shown in Figure 13 and Table 8. The time to ignition and peak HRR of epoxy decreases significantly upon the addition of phosphinates. The DOPO filled sample shows slightly higher ignition time and lower time to peak HRR compared to aluminum phosphinates. Hussain et al. have also shown that the ignition time of epoxy decreases with the addition of DOPO<sup>[22]</sup>. The OP1311 (LV) filled sample showed the lowest time to ignition. Epoxy filled with OP1314 shows the longest time to reach peak HRR, whereas the other aluminum phosphinate filled samples show nearly the same time to ignition. MP blended phosphinate filled samples show larger reductions in peak HRR than does the pure form of aluminum phosphinate, which is closely equivalent to the flammability reduction of DOPO at the same concentration. The DOPO filled sample shows lower THR and less evolution of smoke compared to aluminum phosphinate and the control sample. There is a report that the amount of smoke increases with the addition of DOPO to epoxy<sup>[22]</sup>. The DOPO filled sample decomposes completely, as evident from the AMLR, which closely matches the control sample. This further confirms the vapor phase flame retardation of DOPO in epoxy resin. Epoxy filled with the aluminum salt of phosphinates showed lower THR and AMLR with higher smoke evolution.

Figure 14 shows the thermal properties of epoxy filled with chloroalkyl phosphate (Antiblaze 80) and phosphonate (Antiblaze 78) and the data are shown in Table 7. Both materials contain the same amount of chlorine (33 %), but different amounts of phosphorus (A-80, 9.4 % and A-78,



12 %) and have different thermal stability, (A-80, 200 °C and A-78, 250 °C). The filled samples show poor thermal stability with little residue at high temperature. The chloroalkyl phosphate shows slightly higher onset and Tmax temperature than that of epoxy with the phosphonate (Table 7); there is no significant change in the residue at 700 °C for both.

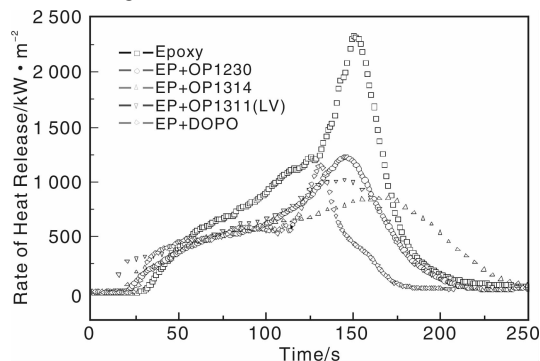


Fig. 13 Heat release curves of epoxy filled with phosphinates

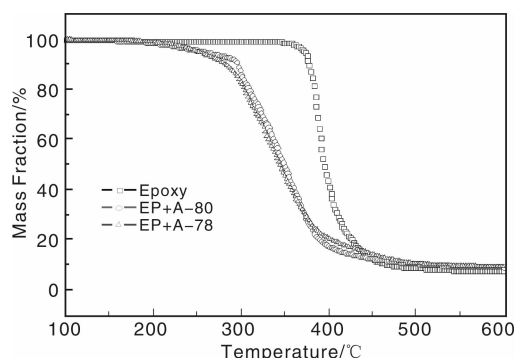


Fig. 14 TGA of epoxy filled with chloroalkyl phosphorus additives

The effect of chloroalkyl phosphate and phosphonate on the heat release rate of epoxy resin is shown in Figure 15 and the cone data are presented in Table 8. The time to ignition of the filled samples is lower than in epoxy. The chloroalkyl phosphate shows slightly higher ignition time and lower peak HRR with longer burning compared to the epoxy with the phosphonate. However, both samples show earlier heat release rate behavior with two HRR peaks compared to the control sample, which shows only a single HRR peak. Chloroalkyl phosphate shows greater reduction of peak HRR and AMLR and smoke evolution (Table 8) compared to epoxy with the chloroalkyl phosphonate.

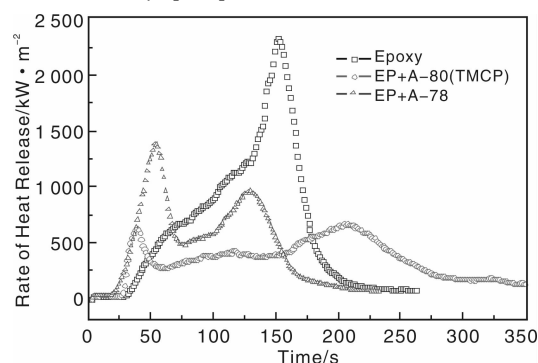


Fig. 15 Heat release curves of epoxy filled with chloroalkyl phosphorus additives

### 3.4 Effect of mineral fillers

In general, a high loading (>60 %, mass fraction) of mineral fillers is required to obtain effective flame retardancy of polymeric materials. At the same time, high loading leads to processing problems as a result of the increased viscosity and deteriorates the physico-mechanical properties of the polymer matrix. Due to the low cost of mineral fillers and the smoke reduction, these are quite commonly used. In this study, a constant loading of 30 % (mass fraction) of three different mineral fillers, alumina trihydrate (ATH), magnesium hydroxide (MDH) and zinc borate (ZB), is employed. The flame retardant effect of mineral fillers depends on a combination of the endothermic effect of dehydration of mineral fillers, the fuel dilution and flame retarding effect of the released water, the replacement of combustible polymer by noncombustible mineral, and the build-up of a non-combustible barrier and enhancement of char. Figure 16 displays the thermal degradation of epoxy filled with these three mineral fillers and the corresponding data are shown in Table 9. The samples all exhibit a decrease in thermal stability with a significant amount of char residue retained at high temperature. The ZB filled sample shows better thermal stability with a greater amount of char compared to ATH and MDH. This may be due to the higher thermal stability of ZB (425 °C) and also slow degradation with greater char residue (86 %) at high temperature compared to ATH (276 °C and 67 %) and MDH (373 °C and 71 %). It has been reported that on the addition of ATH, the thermal stability of epoxy decreased significantly<sup>[20]</sup>.

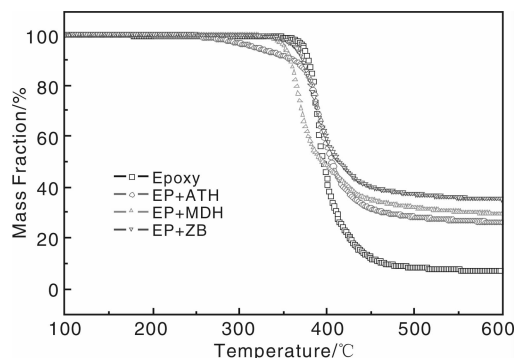


Fig. 16 TGA of epoxy filled with mineral fillers

Table 9 Effect of mineral fillers on the thermal properties of epoxy

Sample	$T_{10}$ /°C	$T_{max}$ /°C	% residue at 700 °C
Epoxy (EP)	378	387	6.9
EP + 30 % ATH	362	389	25.3
EP + 30 % MDH	358	366	28.7
EP + 30 % ZB	372	384	34.9

The effect of mineral fillers on the heat release rate of epoxy is shown in Figure 17 and the data are presented in Table 10. It is noteworthy that the filled samples showed higher ignition times compared to the control. De Fenzo *et al.* have investigated the ignition time of epoxy filled with ZB at higher loading ( $\geq 30$  %, mass fraction)<sup>[14]</sup>. The endothermic decomposition of mineral fillers removes heat from the sample,

thereby increasing the time to ignition. MDH and ZB filled samples show similar heat release rates with longer burning time as compared to the sample filled with ATH. In addition, the time to peak HRR of ZB is higher than that of the other fillers and the control. The ATH filled sample shows higher heat release rate with lower time to reach the peak HRR but it also shows lower THR and smoke evolution. This may be due to the early release of bound water (present in ATH), which removes some amount of heat from the sample and also dilutes the flammable gases during burning.

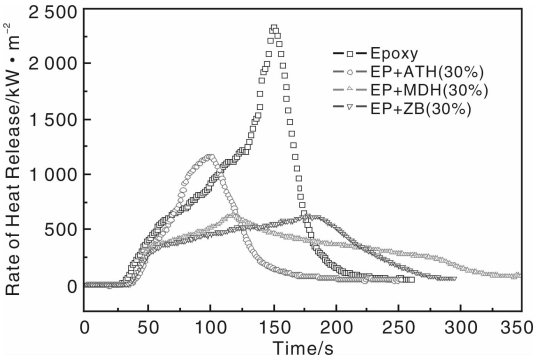


Fig. 17 Heat release curves of epoxy filled mineral additives

Table 10 Cone calorimetric data for epoxy filled with mineral fillers

Sample	$t_{\text{ign}}/\text{s}$	$P_{\text{HRR}}/\text{kW} \cdot \text{m}^{-2}$ (%reduction)	THR/ $\text{MJ} \cdot \text{m}^{-2}$	AMLR/ $\text{g} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$	ASEA/ $\text{m}^2 \cdot \text{kg}^{-1}$
Epoxy (EP)	$29 \pm 3$	$2\,467 \pm 150$	$164 \pm 9$	$47 \pm 2$	$753 \pm 34$
EP + 30 % ATH	$34 \pm 3$	$1\,233 \pm 169$ (50)	$75 \pm 1$	$51 \pm 2$	$306 \pm 40$
EP + 30 % MDH	$36 \pm 2$	$628 \pm 43$ (75)	$106 \pm 2$	$21 \pm 4$	$498 \pm 21$
EP + 30 % ZB	$34 \pm 2$	$648 \pm 26$ (74)	$98 \pm 3$	$22 \pm 1$	$691 \pm 14$

3.5 Effect of melamine and its derivatives

Considerable attention has been paid to the melamine based flame retardants because of the decreased amount of smoke released during combustion. In this study, melamine and its derivatives, melamine polyphosphate (MPP) and melamine cyanurate (MC), were used at the constant loading of 15 % (mass fraction).

Figure 18 shows the thermal degradation of epoxy filled with melamine, MPP and MC and the TGA data are collected

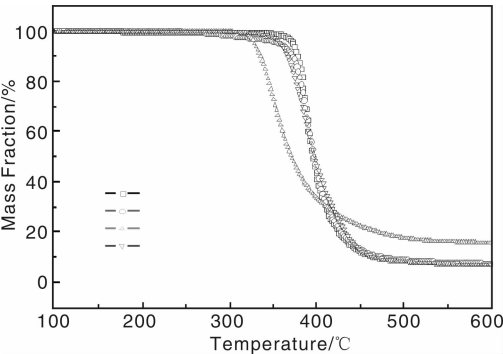


Fig. 18 TGA of epoxy filled with melamine compounds

in Table 11. The MPP filled sample shows a considerable decrease in thermal stability with a greater amount of residue at high temperature, whereas melamine and MC show a slight decrease in thermal stability with negligible amount of residue. Chen et al. also noticed a similar behavior with melamine phosphate as a flame retardant in epoxy<sup>[10]</sup>. It is known that phosphorus compounds accelerate the decomposition of the polymer matrix during pyrolysis while retaining residue at high temperature<sup>[28]</sup>. Destabilization of epoxy is observed on the addition of MPP while melamine and MC had slightly higher Tmax temperature than the control.

Table 11 Effect of melamine additives on the thermal properties of epoxy

Sample	$T_{10} \text{ } ^\circ\text{C}$	$T_{\text{max}} \text{ } ^\circ\text{C}$	% residue at 700 °C
Epoxy (EP)	378	387	6.9
EP + 15 % Melamine	372	388	7.4
EP + 15 % MPP	335	348	15.2
EP + 15 % MC	367	391	6.8

The effect of the melamine compounds on the heat release rate of epoxy is shown in Figure 19 and all of the cone data are collected in Table 12. The MPP filled sample shows a lower ignition time and a greater reduction in the PHRR, which is likely due to the endothermic decomposition of MPP releasing inert nitrogen-containing gases that dilute the oxygen and flammable gases in the flame. Often phosphoric acid is also formed as a decomposition product and promotes the formation of an insulating char (lower mass loss rate) on the surface of the sample. The heat release rate of epoxy decreases significantly upon addition of melamine and its derivatives; melamine derivatives show lower heat release rates compared to the sample filled with melamine. The MPP filled sample shows early heat release behavior as compared to the control, whereas the MC filled sample shows a slightly higher time to reach peak HRR; there is no change in time to reach peak HRR in case of melamine. The MPP filled sample shows a very low heat release rate with longer burning time than melamine and MC, indicating that MPP provides a good amount of residue during burning. The MPP filled sample shows a greater reduction of peak HRR compared to melamine and MC. The melamine derivatives showed lower THR compared to melamine filled sample. Melamine compounds, especially MC, release a lower amount of smoke during combustion. Polka also investigated melamine filled epoxy showed a slightly higher smoke value compared to the control<sup>[18]</sup>.

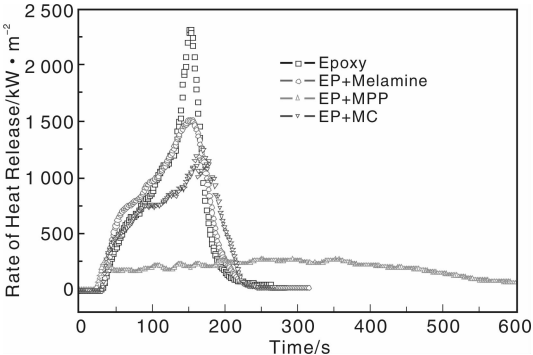


Fig. 19 Heat release curves of epoxy filled melamine compounds

Table 12 Cone calorimetric data for epoxy filled with melamine compounds

Sample	$t_{\text{ign}}/\text{s}$	$P_{\text{HRR}}/\text{kW} \cdot \text{m}^{-2}$ (% reduction)	THR/ $\text{MJ} \cdot \text{m}^{-2}$	AMLR/ $\text{g} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$	ASEA/ $\text{m}^2 \cdot \text{kg}^{-1}$
Epoxy (EP)	29 ± 3	2467 ± 150	164 ± 9	47 ± 2	753 ± 34
EP + 15 % Melamine	29 ± 2	1 548 ± 8 (37)	155 ± 6	40 ± 1	816 ± 69
EP + 15 % MPP	16 ± 2	296 ± 21 (88)	113 ± 2	9 ± 2	715 ± 9
EP + 15 % MC	28 ± 1	1 361 ± 140 (45)	139 ± 2	36 ± 2	524 ± 15

3. 6 Effect of intumescent additives

Generally, epoxy resins are used as the resin binder for intumescent (IFR) paints and mastics. The standard intumescent formulation contains ammonium polyphosphate as charring agent, pentaerythritol as the char former and melamine as the blowing agent; these three ingredients are typically in about 3:1:1 weight ratio<sup>[4]</sup>. In this study, two different IFRs were used; a classical IFR (APP:PER:Melamine) in the ratio of 3:1:1 and expandable graphite (EG) at 15 % (mass fraction). The effect of IFR on the thermal properties of cured epoxy resin is shown in Figure 20 and the data are shown in Table 13. Both IFR filled systems decrease in thermal stability compared to the control. The classic IFR filled sample shows, poor thermal stability with greater residue at high temperature compared to EG. Both onset and  $T_{\text{max}}$  temperature of epoxy decrease with addition of classical IFR, but a smaller decrease in onset with slightly higher  $T_{\text{max}}$  temperature is observed with EG. A significant amount of residue is retained at higher temperature in the case of IFR additives, in good agreement with earlier reports<sup>[24–25]</sup>.

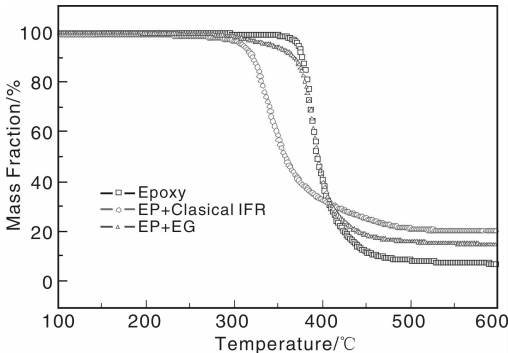


Fig. 20 TGA of epoxy filled with intumescent additives

Table 13 Effect of intumescent additives on the thermal properties of epoxy

Sample	$T_{10} / ^\circ\text{C}$	$T_{\text{max}} / ^\circ\text{C}$	% residue at 700 °C
Epoxy (EP)	378	387	6.9
EP + 15 % IFR	321	334	19.9
EP + 15 % EG	368	391	14.2

Figure 21 shows the heat release rate of epoxy filled with IFR additives and the data are shown in Table 14. The IFR filled samples show considerably lower peak HRR with longer burning time compared to the control. Moreover, the classical IFR shows lower ignition time with lower heat release and

prolonged burning time as compared to EG. There is no change in time to ignition of epoxy with the addition of EG. The classical IFR formulation shows greater reduction of peak HRR compared to the same loading of EG. Both IFR filled samples show considerable reduction of THR and AMLR, whereas the amount of smoke increases slightly as compared to the control.

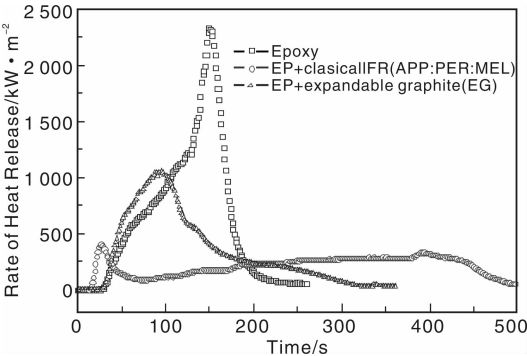


Fig. 21 Heat release curves of epoxy filled intumescent additives

Table 14 Cone calorimetric data for epoxy filled with intumescent compounds

Sample	$t_{\text{ign}}/\text{s}$	$P_{\text{HRR}}/\text{kW} \cdot \text{m}^{-2}$ (% reduction)	THR/ $\text{MJ} \cdot \text{m}^{-2}$	AMLR/ $\text{g} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$	ASEA/ $\text{m}^2 \cdot \text{kg}^{-1}$
Epoxy (EP)	29 ± 3	2 467 ± 150	164 ± 9	47 ± 2	753 ± 34
EP + 15 % IFR	11 ± 3	405 ± 35 (84)	107 ± 3	11 ± 1	922 ± 28
EP + 15 % EG	28 ± 1	1 091 ± 126 (56)	118 ± 2	13 ± 1	987 ± 153

4 Conclusion

In this study, representatives of every class of flame retardants have been studied with respect to both thermal stability and fire retardancy. In many cases, explanations have been offered for the observations that are made. It has been concluded that the flame retardancy of epoxy resin depends on the type of curing agents used. The brominated flame retardants are effective in flammability reduction of epoxy as well as smoke compared to the Dechlorane plus. Zinc borate can effectively replace the antimony trioxide in TBBA containing epoxy formulation in terms of both flame retardancy as well as smoke. Among the phosphorus compounds, phosphites give good flame retardancy. MDH and ZB can replace the ATH in flammability reduction of epoxy. Melamine compounds showed acceptable flame resistance and smoke retardation for epoxy resin and intumescent char forming additives are suitable candidate for epoxy flame retardant formation.

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