The Effect of Chemically Reactive Type Flame Retardant Additives on Flammability of PES Toughened Epoxy Resin and Carbon Fibre-Reinforced Composites

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The Effect of Chemically Reactive Type Flame Retardant Additives on Flammability of PES Toughened Epoxy Resin and Carbon Fibre-Reinforced Composites

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Abstract

The effect of different concentrations (4 and 8 wt-%) of chemically reactive type fire retardant (FR) chemicals on the thermal stability and flammability of an aerospace grade epoxy resin has been studied by thermal analysis, limiting oxygen index, UL-94 and cone calorimetry. Chemically reactive flame retardant term implies that they interact with the polymer during some part of the pyrolysis and fire chemistries. Flame retardant included (i) phosphorous- and nitrogen-containing, active in condensed phase, (ii) intumescent chemicals, active in condensed phase and also known as char promoters, (iii) organophosphates, active primarily in condensed phase, but in some polymers known to have also shown vapour phase activity, (iv) halogen-containing active in vapour phase. During curing process some of the flame retardants settled on the bottom of the resin plaque, affecting the flammability results. All FRs reduced the flammability of the resin, the extent of which depended upon the FR type, concentration of flame retardant elements in the formulation and the type of fire testing performed. With selective FRs, carbon fibre-reinforced composites have also been fabricated and tested for their fire and mechanical performance. FR chemicals decreased the flammability of composites up to 50% without affecting their mechanical properties.

Keywords : Epoxy resin; Fire retardants; Flammability; Thermal analysis; Cone calorimetry; Carbon fibre-reinforced composites.

1. Introduction

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The superior strength-to-weight ratio property of fibre-reinforced composite materials has a significant impact on their use as structural materials in various applications, including the aerospace sector. In recent years novel composite materials have replaced a range of old fashioned metallic parts and structures of aircrafts, rotorcrafts and modern helicopters. This substitution has reduced 25 – 45% of the weight of metallic parts [1] and hence, has raised the savings on fuel over the lifetime of the aircraft. Different types of fibre-reinforced composites are used in an aircraft, which are based upon the desirable properties of their application and type of the aircraft. Among different types of composites, carbon fibre-reinforced epoxy composites are most common and extensively used for structural parts of aircrafts [2]. Carbon fibres are preferred because of their higher rigidity and specific modulus, and lower density compared to glass fibres. Epoxy resins are chosen for structural aircraft parts because they are relatively tough, easy to process, and have moderate temperature processing capabilities. These properties of epoxy resins are mainly because of the existence of a three-membered (i.e. two carbon and an oxygen) cyclic bonded ring known as epoxide or oxirane group in their chemical structures. The capability of the epoxide group to react with a variety of substrates imparts versatility to the resins [3]. Therefore, epoxy resins can react with a variety of other moieties and hence, the polymer backbone can be tailored to provide specific resin processing and network properties.

The cured epoxy resins are very brittle, showing poor fracture toughness, poor resistance to crack propagation and low impact strength. The brittleness of epoxy resins is mainly due to the rapid cross-linking reactions leading to high cross-link density. The toughness of the resin can be improved by using additives, called ‘toughening agents’ or ‘tougheners’, which lower the rate of curing [4] and can also become cross-linked due to their reactive end groups [4,5] resulting in increase in molecular weight of the resin. The commercially available toughening agents include rubber, reactive diluents, siloxanes and engineering thermoplastics such as polyether sulphone (PES). Since the toughening agents used are reactive chemicals, they can affect other properties such as interfacial adhesion, chemical resistance and thermal stability [6] of the resin and hence, the composites.

The major drawback of composites is their flammability. The fire safety of aircraft composites is mandated by various regulatory bodies such as the Federal Aviation Authority (FAA) of USA [7], European Aviation Safety Agency (EASA) [8] and Australian Transport Safety Bureau (ATSB) [2]. In accordance with these legislations all composites have to meet certain regulated criteria for being

used in the aircraft, which mainly target to delay the combustion of materials by lowering the heat release rate from combustion so as to obtain higher evacuation time [9].

Out of many methods [10] to increase their thermal and fire stabilities, one commonly used method is the addition of inert fillers (such as quartz, talc etc.), flame retardant (FR) additives acting by physical means (such as alumina trihydrate, magnesium hydroxide, borax/boric acid combinations) or chemically reactive type FR additives (such as ammonium polyphosphate, melamine phosphate etc.) in the matrix. Filler and additives functioning by physical means are required at very high loading levels to be effective, which in turn can affect the mechanical performance of the laminate, hence are not suitable for composites used for structural applications [10]. Reactive type additives, however, can be effective at low concentrations [11,12]. These flame retardants function in condensed phase, vapour phase or both. This work explores the effect of different types of commercially available flame retardants on thermal stability and flammability of an aerospace grade epoxy resin containing 20 wt-% polyether sulphone (PES) toughening agent by partly replacing the latter (4 and 8 wt-%) by FR chemicals and hence, keeping the total additive content as 20 wt-%. The flame retardants were chosen based on their chemical composition and mode of action as : (i) phosphorous- and nitrogen-containing, active in condensed phase, (ii) intumescent chemicals, active in condensed phase and also known as char promoters, (iii) organophosphates, active primarily in condensed phase, but in some polymers known to have also shown vapour phase activity, (iv) halogen-containing, active in vapour phase. While some of these chemicals are commercially used for reduction of flammability of the fast curing epoxy resin used for other applications, their commercial use for aerospace grade toughened resin is limited due to the conception that they can affect the mechanical properties of the composites. Moreover, until recently the majority of the flame retardants used were halogen based, e.g. tetrabromobisphenol A (TBBPA) for electrical and electronic applications [13]. In Europe the current primary regulation for all chemical safety, including flame retardants, is achieved through REACH (Registration, Evaluation, Authorisation and Restriction of CHemicals) regulation (Regulation (EC) No 1907/2006) and RoHS (Restriction of Hazardous Substances Directive), which have identified some halogenated flame retardants as hazardous and banned their use in Europe. Due to this all halogenated chemicals are being questioned and hence alternative solutions are being sought. The purpose of this work is to study and compare the flame retardant effectiveness of different types of flame retardant chemicals at concentrations <10 wt-% in an aerospace grade epoxy resin containing polyether sulphone (PES) as a toughening agent and rank them based on their effectiveness in

different types of fire tests. In the first instance cast resin samples have been studied. Based on the observed performance of FRs in cast resins, selective FRs have been used to prepare carbon fibre-reinforced composites and their fire and mechanical performance studied.

2. Experimental

2.1 Materials

Resin : Epoxy resin, triglycidyl-p-aminophenol (TGAP), was supplied by Vantico Ltd, UK, while the curing agent 4,4'-diamino diphenyl sulphone (DDS) was provided by Acros Organics BVBA, Belgium. A thermoplastic toughener, polyether sulphone (PES) was sourced from Cytec, Netherlands.

Flame retardants (FR) : The following commercially available flame retardants were used without further purification :

Phosphorous and nitrogen based: Ammonium polyphosphate, APP (Antiblaze MC, Rhodia Specialities Ltd., UK); melamine phosphate, MP (Antiblaze NH, Rhodia Specialities Ltd., UK); melamine pyrophosphate, MPP (Antiblaze NJ, Rhodia Specialities Ltd., UK).

Intumescent chemicals: Phosphorylated pentaerythritol, Int 1 (NH 1197, Chemtura, UK); a mixture of phosphorylated pentaerythritol and melamine, Int 2 (NH 1511, Chemtura, UK)

Organophosphorus based (organophosphates): Resorcinol bis-(diphenyl phosphate), RDP (Chemtura, UK); bisphenol A bis-(diphenyl phosphate), BAPP (Chemtura, UK); triphenyl phosphate TPP (Rhodia Specialities Ltd., UK); tritolyl phosphate, TTP (Rhodia Specialities Ltd., UK)

Halogen based: Tris(tribromoneopentyl)phosphate, FR 372 (ICL, Israel); tris(tribromophenyl)cyanurate, FR 245 (ICL, Israel)

Reinforcing fibres for composites : Carbon Fabric (AP4 GB, 6K, supplied by Cytec Engineered Materials, UK), woven-roving, area density 377 g/m².

2.2. Sample Preparation

Cast resin plaques : Two sets of resin samples with fire retardant concentrations 4 and 8% (w/w), (Table 1) were prepared and tested for different flammability properties. Epoxy resin samples

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containing 100% epoxy resin (ER), 20% PES toughener (E, control sample), and different amounts of PES toughener and flame retardants (FRs) were formulated by a hot-melt method. The epoxy resin was heated to 120°C to melt it. In the molten resin required amounts of toughener and flame retardants were added slowly while stirring with a mechanical stirrer (IKA RW16 Overhead stirrer). The mixture was further stirred for 30 minutes. The temperature was lowered to 100°C, the curing agent DDS added and the mixture stirred at 100°C for 30 minutes in order to yield a homogeneous mixture. The mixture was then degassed at 85°C for two hours. Small quantities (~ 200 mg) of uncured samples were stored for thermal analytical tests and the rest poured in aluminium moulds of 5.5 cm diameter to cure for flammability testing. The resin in each mould was degassed again at 85 - 90°C for 15-20 minutes in a vacuum oven at 1 bar pressure to remove any trapped air in the resin during pouring. After all air bubbles were removal, the curing was carried out by heating at 120°C for 1 h and then at 180 °C for 3h. The sample compositions are given in Table 1. Percentage of flame retardant elements, i.e. phosphorus, nitrogen and halogen present in each sample is given in Table 2.

Composite laminates: Based on the flammability results of cast resin samples, composite laminates with two selected flame retardants, Int 2 (NH 1511) and FR372, using E-FR(8) formulations (Table 1) were prepared. Samples were prepared by impregnating 8 layers of woven roving (bi-directional) carbon fabric with resin, without/with flame retardants in a resin transfer moulder (Moore Max Mould Press, Cambridge, UK) connected to a vacuum pump. The mould was heated to 90°C during the resin impregnation process. The resin impregnated fabrics were vacuum bagged and cured at 180°C for 3 hours. The cured composites were cut into small specimens for fire and mechanical testing.

2.3. Thermogravimetric Analysis. Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) were performed on resin formulations (see Table 1), prior to curing using an SDT 2960 simultaneous DTA–TGA instrument from room temperature to 900°C using 10 ± 1 mg samples heated at constant heating rate of 10°C/min in air flowing at 100 ± 5 ml/min. The experiments were performed in triplicate and showed good reproducibility.

2.4 Flammability Testing : A Stanton Redcroft Limiting Oxygen Index Tester was used to carry out limiting oxygen test according to ISO 4589 [14] standard. The specimen size was 150 mm x 12 mm x ~ 2 cm. The UL-94 (in-house built according to UL-94 specifications) test was carried out according to ISO 1210 [15]. The sample size was 125 mm x 12 mm x ~ 2 mm of cast epoxy resin plaques. A

Fire Testing Technology cone calorimeter was used according to ISO 5660 / ASTM E1354 standard [16] to perform experiments on horizontally oriented samples. Round samples of diameter 5.5 cm were used. Due to exothermic nature of the reaction occurring during curing of resin, it was not easy to cast large amount of resins. Hence, this sample size was chosen to get three replicate specimens. A comparative study was undertaken by testing square shaped wood samples with standard dimensions (10 cm x 10 cm) and round shaped wood samples with 5.5 cm diameter and the results are tabulated in Table 3. The variation for **total heat release (THR)**, **peak heat release rate (PHRR)** and effective heat of combustion (H_c) was found as $\pm 5\%$ [17]. The variation in smoke was considerable. This is due to reason that the software used sample dimension for calculation of heat release, mass loss, etc., whereas the smoke analyser is independent and does not take this value into account. The smoke value of a sample depends upon specific extinction area. The area of round samples was about $\frac{1}{4}$ of square samples. To compensate for different samples sizes, values in the parentheses were normalised as per gram of the sample mass. The round samples of cast resins were used in this work. These results were used for relative study as to compare the effectiveness of different fire retardants. However for composite samples, 10 cm x 10 cm sample size is used.

2.5 Dynamic mechanical thermal analysis

A polymer laboratories dynamic mechanical thermal analyser was used in bending mode where samples of 46 ± 1 mm x 3 ± 0.5 mm x ~ 3 mm dimensions were clamped under dual cantilever loading using single point shaft. Frequency was maintained at 1 Hz and strain level at 64 micron. Dynamic heating was applied from room temperature to 340°C at $3^\circ\text{C}/\text{min}$.

2.6. Mechanical testing of composite laminates:

The composite samples were tested for mechanical performance by an Instron tensile tester 4303 for their flexural and tensile properties. For flexural performance, three point bending tests were carried out in a bending mode and four point bending tests in a compressive mode. The span length of samples was 100 mm. The applied load for 3 point and 4 point bending tests were 50 N and 90 N, respectively at 2 mm/min speed. These tests were carried out within the elastic range of the material.

For tensile tests the load up to 50 KN was applied at a cross head speed of 100 mm/min. The gauge length of each specimen was 100 mm and the polymeric tabs were bonded to their ends for improved gripping and to ensure failure within the gauge region.

3. Results and Discussion

3.1 Thermal analysis of resin formulations

Thermal analysis study of all resin formulations prior to curing has been used to study the effect of additives on the curing temperature and thermal stability of the resin. The effect of the PES toughener on the DTA and TGA behaviour of the epoxy resin has been discussed in detail in our previous publication [6], where it was observed that the toughener slightly increases the curing temperature (by up to 20°C) but has minimal effect on the decomposition temperature of the resin. The presence of PES however, enhances the thermal stability of epoxy resin in terms of reducing the mass loss at each temperature.

The DTA curve of the control epoxy resin containing PES (not shown here) showed three exotherms, the first representing curing (peak maximum at 237 °C); the second doubled peaked with maxima at 385 and 389 °C representing decomposition reaction and the third one (peak maximum at 566 °C) for the oxidation of the char produced in the second stage [6, 18]. The effect of different flame retardant chemicals on curing and decomposition peak maxima are plotted in Fig. 1, where it can be seen that all flame retardants affect the curing peak slightly. Except for MP and Int 2, all P-, N- containing and intumescent based flame retardants at 4 mass-% concentration increased the temperature of the curing peak maximum compared to that for the epoxy resin. For organophosphorus and halogenated FRs the increase was up to 25°C. The increase in concentration of the FRs from 4 to 8% had minimal further effect. The detailed discussion for selected samples is presented elsewhere [6]. This study shows that the curing of resin is only slightly affected by the inclusion of flame retardant chemicals.

All flame retardants shifted the onset and peak temperatures (see Fig. 1) of the decomposition exotherm of the resin to lower temperature compared to that of the control resin. The shift of the temperature however, depended upon the FR type. This can also be seen from TGA curves shown in Fig. 2, where all flame retarded samples start losing mass earlier than the control sample, hence

reducing the thermal stability of the resin up to about 420°C. This partly is due to the fact that these FR chemicals start decomposing earlier than the resin [6]. The decomposed products of FR chemicals react with the resin and help in increasing their thermal stability in terms of residual mass at temperatures above 420°C. However, even after compensating for the mass loss due to decomposition of the FR chemicals there is reduction in thermal stability of the resin as observed for these samples and other flame retarded resins [19], the reason for which is not completely understood. The trend however, is changed above 420°C where all FRs increased the thermal stability of the resin by increasing the residual mass, seen more clearly in Fig. 2(b) where the mass differences between flame retarded samples (8% FR) and the epoxy resin are plotted as a function of temperature. The extent of residual mass retention in this stage is very much dependent upon the mechanism of action of the FR in a particular sample.

In general all P- and N- containing FRs working in condensed phase [16, 17, 18] enhanced char formation of the resin (Fig. 2(b1)). The APP shows highest char formation at 700 °C, followed by melamine pyrophosphate and phosphate (Table 4). Both intumescent based FRs, in particular phosphorylated pentaerythritol enhanced char formation of the resin. The organophosphorus containing epoxy resins showed comparatively lower char formation than P- and N- containing FRs (Fig. 2(b)), which partly is due to lower phosphorus content in the former as shown in Table 2 and partly due to the possibility of them working in the gas phase as well. Organophosphates such as TTP, BAPP and RDP in some polymers are known to function also in gas phase. The halogenated flame retardants as expected showed minimal effect on char formation as seen from Fig. 2(b3) due to their gas phase mechanism of action. For detailed thermal analytical study of these samples relating to their mechanisms of action, reader is referred to our previous publications [6, 19, 19].

This study shows that P-and N- containing and intumescent based flame retardants are the most effective, followed by the organophosphate FRs (Table 4) in enhancing char formation. For samples with 8% FRs the effectiveness of P-N, intumescent and organophosphate flame retardants follow the trend as:

$$\text{APP} > \text{Int2} > \text{MPP} > \text{Int1} > \text{MP} \approx \text{RDP} > \text{TPP} > \text{TTP} > \text{BAPP}$$

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Since the char retained after burning a polymer is a measure of its flammability as suggested by the work of Krevelen [20] which correlated LOI with TGA-derived char levels in inert atmosphere and Zhang [21] in air atmosphere, the flammability of the above samples should also follow the same trend.

Halogenated FRs on the other hand work in gas phase, hence are least effective in char formation. Therefore, their flammability cannot be assessed by the char formation ability of the sample.

3.2 Physical and Flammability Properties of Cast Resins

3.2.1 Morphological and Physical Properties

All resin formulations discussed above were cured under conditions discussed in Section 2.2. Visual observation of cured samples indicated that all samples were well cured. Epocyc resin (ER) produced a transparent laminate and further addition of PES (sample E) did not cause any change in transparency, suggesting good miscibility of the thermoplastic toughening agent PES in the epoxy resin. Both ER and E samples were yellowish brown in colour, whereas all flame retarded samples were dark brown, some transparent and some opaque, with no obvious sign of bad dispersion. The cross-sections of all samples were studied by scanning electron microscopy (Cambridge Stereoscan 200) for flame retardant distribution through the thickness of the samples and selected results are presented in Fig.3. As can be seen from Fig. 3(a), the control sample is transparent.

It was observed during sample preparation that the addition of all P- and N- containing FRs or intumescent turned the liquid solution of epoxy resin blurry, due to immiscibility of FRs in the resin. These immiscible FRs seemed to be uniformly dispersed in the epoxy resin after mechanical stirring. However, the SEM images of cross-sections of the laminates indicated that the flame retardant particles settled down at the bottom of the cast resin, which was more noticeable for samples with higher level of FRs, as can be seen from SEM images in Fig. 3 for samples containing 8% melamine pyrophosphate (E-MPP (8)), (Fig. 3(b)) and phosphorylated pentaerythritol (E-Int 1 (8)), (Fig. 3(c)). This problem, not usually observed for fast curing resins such as low-temperature curing epoxies or unsaturated polyester [22], occurred due to stationary placement of the container during long curing time (see Section 2.2) and immiscible granules of flame retardants settled down at the bottom of the cast resin.

All organophosphates and halogenated FRs, however, mixed well with the epoxy resin and did not affect the transparency of the resin. The liquid organophosphates mixed homogeneously with the resin as shown in Fig. 3(d) for E-RDP (8) sample. Even the powder forms of organophosphates and halogenated FRs were miscible with resin and did not settle down on the bottom of the plaque indicating better dispersion. As an example SEM image of E-FR 245 (8) is shown in Fig. 3(e).

To observe whether FR containing samples are well cured or not, a few selected cured samples were subjected to thermal analysis again. The heat of reaction under the curing peak from DTA curves was calculated and the percentage of curing was obtained by measuring the percentage of reduction in heat of reaction of curing exotherm of cured samples. As shown in Table 4 all these samples are well cured, i.e. > 90%.

3.2.2 Flammability Properties

As discussed in Section 3.2.1, all samples containing P- and N- (APP, MP, MPP) and intumescent based FRs (Int 1 and Int 2) have poor dispersion of flame retardant chemicals, rendering resin rich surfaces. It is well known that for LOI and UL-94 tests, uniform test samples are required, otherwise depending upon where the flame is applied, misleading results are obtained. These samples however were tested for these tests as well as for cone calorimetry along with samples containing uniformly dispersed FRs (organophosphates and halogenated). The idea was to demonstrate that even with poor dispersion what positive/negative effects could be achieved and whether this concept can be used in design of the composites, where flame retardants are present in certain part of the structure, rather than uniformly distributed. Moreover when used for fibre-reinforced multi layered composite structures, the fibre layers will hold the FR particles and hence, FR chemicals will be present in different layers, although the surfaces will still be resin rich.

In context of this study, the discussion below is based on samples with poor and good dispersion. The LOI and UL-94 results for samples with poor dispersion are clearly marked in Table 4.

Limiting oxygen index (LOI) :

Both epoxy resin (ER) and the control epoxy sample (E) gave an LOI value of 24 vol-% (Table 4), indicating that the PES does not affect this value. All flame retardants at 4% concentration have been successful to raise the LOI of epoxy resin, E from 24 to more than 28 vol-%. Results for P- and N-

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and intumescent samples showed that all these FRs at 4% concentration raised the LOI of epoxy resin from 24 to more than 28 vol-%. Further addition of FR did not show any additional benefit, which is due to the non-uniformity of the samples. For samples with organophosphates and halogenated FRs, the LOI increased further at higher concentration of FR. The exact value of LOI however, depends upon the percentage of FR element, e.g. phosphorus, halogen etc. present in a particular formulation. To observe the effect of phosphorus concentration on the flame retardancy of the resin, the difference in LOI between the sample and the control epoxy resin (ΔLOI) of all organophosphorus FR containing epoxy samples are plotted against the phosphorus level in different samples in Fig. 4(a). It can be seen that ΔLOI for a sample increases as phosphorus content increases, which however also depends upon the fire retardant type, e.g. 4% RDP increased the ΔLOI value more than that by 8% TTP, although the phosphorus content in 4% RDP ($P = 0.43\%$) is less than that in 8% TTP ($P = 0.64\%$). This may be due to difference in condensed phase mechanisms of the two flame retardant types, as TTP is also known to be active in vapour phase in some cases.

The halogenated flame retardants FR 372 and FR 245 at 4% level increased the LOI of epoxy resin from 24 in control sample to 29.1 and 28.3 vol-%, respectively (Table 4). Further addition of these flame retardants increased the LOI by 2.8%. Slightly higher, but still within the experimental error range LOI value for FR 372 is due to higher percent of bromine (Table 2) and presence of additional phosphorus.

UL-94 :

All other samples were tested for UL-94 rating according to ISO 1210 standard [15], firstly for horizontal UL-94 rating and then the samples exhibiting better than UL-94 HB criteria were tested for vertical UL-94 test. In horizontal test, both epoxy resin samples without and with PES burnt slowly for 166 and 144 s, respectively with burnt lengths of 47 and 56 mm, hence failed the test. None of the flame retarded samples burnt, hence passed this test and all samples were subjected to vertical test. From vertical test, burnt length was noted and the results as percentage of original length (120 mm) and total burning time are given in Table 4. The control epoxy resin burnt completely within 39 s after single application of flame; melting, dripping and cotton ignition were observed, hence failed the test. Melt dripping in this sample was more than that for the epoxy resin ER sample due to presence of the thermoplastic PES in the control sample. The flame retarded samples showed remarkably different results compared to the control resin sample (Table 4). P- N- and intumescent flame retardants

containing samples despite non-uniform distribution of flame retardants, improved the fire performance of the resin. However, similar to LOI results, there was no further effect of increased FR concentration on the burning time or burnt length.

All other flame retardants reduced the burning time as well as the total burnt length without causing any melting, dripping and cotton ignition. This effect was greater for samples with higher level of flame retardants, Samples with 8% BAPP, TPP, TTP, FR 245 could achieve V1 and with FR372 VO rating. In terms of V0/V1 rating and the total burn time for samples with 4% FR, the effectiveness of different flame retardants can be ranked as:

$$\text{FR 372} \approx \text{BAPP} > \text{TPP} > \text{RDP} > \text{TTP} > \text{FR 245}$$

At 8% concentration of flame retardant, the trend is as :

$$\text{FR 372} > \text{BAPP} > \text{FR245} \approx \text{TPP} > \text{TTP} > \text{RDP}$$

This slight difference in trend at two different concentrations can be explained due to different P, N and halogen concentrations in the samples (Table 2), as a minimum concentration of a fire retardant element is required for it to be effective in reducing the flammability of a sample.

Cone calorimetry:

Flammability tests were also performed using cone calorimetry and fire performance parameters including time-to-ignition (TTI); the heat release rate, and in particular the peak value (PHRR); the total heat release (THR); the mass loss; and the amount of smoke produced during combustion were obtained. These data and some derived parameters such as the effective heat of combustion (Hc) and char yield are presented in Table 5. All results are average of three replicate runs and reproducible to $\pm 10\%$. Fig. 5 shows the HRR, mass loss and smoke release values as a function of time for the epoxy resin samples containing different FR additives. For sample with poor dispersion, resin-rich side was exposed to the heat flux.

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The time-to-ignition (TTI) of epoxy resin with PES (E) was 32 s as seen from Table 5, where the presence of PES has not shown any effect on TTI, compared to ER. Also both ER and E samples extinguished at 86 s with total burning time (BT) of 53 and 54 s, respectively. Although the duration of burning for ER and E samples was similar, but presence of PES affected other parameters as can be seen from Table 5. The inclusion of PES in sample E reduced the THR of ER from 44.4 to 38.5 MJ/m², PHRR from 1393 to 1086 kW/m², H_c from 19.7 to 17.3 MJ/kg, total smoke production from 2628 to 2401 (Table 5). Also in PES containing sample E, higher char formation 6.2 % compared to 2.3 % in ER at 240 s is observed. These cone calorimetric results indicate that PES containing sample is less flammable than resin only, which is contrary to UL-94 results, where PES presence indicated increase in the flame spread rate.

The inclusion of flame retardants had a little effect on time-to-ignition of the epoxy resin (Table 5). As seen from Fig. 5 (a) and Table 5, the peak heat release rate (PHRR) of epoxy resin (E) is reduced with the addition of fire retardants, which is further reduced with higher FR concentration, except for samples containing APP and BAPP. Apart from APP, all P- and N- containing flame retardants at 4% concentration lowered the PHRR of the epoxy resin (E) by at least 100 kW/m² (Fig. 5(a), Table 5), which is about 10% reduction compared to the epoxy resin (E) sample. This reduction was about 25% at 8% loading for P- and N- containing flame retardants. The poor performance of APP is due to its poor dispersion where the APP settled down at the bottom of the plaques and the top surface being resin rich, burnt easily, causing higher peak heat release rate. However, for other samples despite poor dispersion (see Fig.3), decrease in PHRR could be observed.

Amongst organophosphosphate flame retardants, BAPP and RDP were not effective in lowering the PHRR of the epoxy resin (Fig. 5(a)). TPP and TTP decreased the PHRR by about 250 kW/m². The halogenated samples reduced the PHRR significantly (Fig. 5(a)). FR 372 at 4% concentration reduced it by about 35% compared to the control epoxy resin, whereas increasing FR concentration to 8% had a little further effect. However, for FR 245, the reduction of PHRR was from 12 to 40% by increasing FR concentration from 4 to 8% (Table 5, Fig. 5(a)). Comparatively lower PHRR (Table 5) obtained for halogenated samples can be explained due to better dispersion of these FRs in the resin and the presence of halogen in required concentration to be effective in reducing flammability by acting in the vapour phase [23, 24]. FR 372 due to addition phosphorus presence, was more effective even at 4%, and further addition of flame retardant had no further effect. Amongst all flame retardants Int 1, FR

372 and FR 245 are most effective in reducing the PHRR as can be seen from Table 5, the overall trend of effectiveness of different FRs at 8% concentration in lowering PHRR of the resin can be summarised as:

Int 1> FR 245>FR 372>MP≈TTP≈ Int 2> TPP>MPP>RDP≈ BAPP>APP

All flame retardants were effective in reducing the total heat release of epoxy resin at 4% level and even more at 8% level (Table 5). For P- and N- containing FRs, the reduction was not significant (<15%) at 4% concentration. Except for E-APP (8), all other P- and N- containing flame retardants at 8% level reduced the THR of the resin by about 25%. Int 1 at 8% was most effective, which reduced the THR of the resin from 38.5 to 23.7 MJ/m² (Table 5). BAPP and TTP from organophosphorus flame retardants were less effective at 4% concentration, whereas other organophosphorus fire retardants, RDP and TPP reduced the THR by 5.9 and 5.1 MJ/m², respectively at 4% level and 7.8 and 10.7 MJ/m², respectively at 8% level (Table 5). Amongst halogenated samples, both FR 372 and FR 245 showed better efficiency in lowering down the total heat release rate of the resin by about 23% at 8% concentration. The overall trend can be summarised as:

Int 1>Int2>MP≈TPP>MPP>FR372≈FR245>RDP>APP>TTP>BAPP

These results indicate that in some samples, e.g. E-APP, E-MPP, where dispersion of flame retardants is not uniform and all flame retardants settled at the bottom of the sample, the PHRR was not reduced as expected, however reduction in THR could be observed. This can be explained on the basis that resin rich surfaces give higher PHRR, whereas once the flame retardant action of the chemicals is activated, the overall flammability is reduced.

The effective heat of combustion (H_c) over a given time is the quantity of heat produced by combustion of a unit quantity of a material. It is measured in the cone calorimeter throughout the burn period from the heat release and mass loss rates, and may thus be used to measure possible flame retarding effect of different flame retardants. All flame retardants decreased the effective heat of combustion of epoxy resin (E), except for BAPP (sample E - BAPP (4)) (Table 5). Int 1 from intumescent, TPP from organophosphorus fire retardants and both halogenated flame retardants were most effective in reducing the H_c of the resin as seen from Table 5.

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Since the char retained after burning a polymer is a measure of its flame retardancy [20], the mass loss curves give an insight into the flame retardant performance of the samples. Mass loss curves for all samples are given in Fig. 5 (b) and the char residue values recorded after 240 s of starting of the experiments are given in Table 5. It can be seen from Fig. 5 that all flame retardants, except FR 245 enhanced the stability of the resin, showing more residue at any particular time compared to the control resin sample (E). All flame retardants show significant char formation at 240 s in Table 5. All P- and N- containing samples had high char yields. Amongst organophosphorus flame retardants, TPP and TTP were less effective than RDP and BAPP. Amongst halogenated fire retardants, FR 245 was less effective compared to FR 372. Halogenated flame retardants usually function in vapour phase [233] and do not affect char formation. Better performance of FR 372 in terms of char yield can be explained due to additional presence of phosphorus in the flame retardant, which acts in condensed phase [23,25] and enhances char formation. The higher char formation of P- and N- containing samples in the cone calorimetric experiments (Table 5) is due to the formation of a thermally stable carbonaceous material resulting from condensed phase mechanism of these flame retardants [26]. As an example, chars formed by APP containing samples are shown in Fig. 6. The overall trend for effectiveness of different fire retardants at 8% concentration for char formation is:

$$\text{Int 1} > \text{MPP} > \text{Int 2} \approx \text{APP} > \text{RDP} > \text{MP} > \text{BAPP} > \text{FR 372} > \text{FR 245} > \text{TPP} > \text{TTP}$$

With regards to smoke production only P- and N- containing flame retardants decreased the total smoke production slightly, i.e. by about 10% compared to the epoxy resin, E (Table 5), whereas 4% organophosphorus FRs have minimal effect on smoke production (Fig 5(c)) . These flame retardants increased the total smoke compared to sample E, when present at 8% level. The halogenated flame retardants also increased the total smoke at both 4 and 8% levels (Table 5). The increase in smoke formation in flame retarded samples is due to incomplete combustion of the resin formulation [27, 28]. Flame retardants active in vapour phase enhance smoke production.

The FIGRA (Fire Growth Rate Index), which indicates the burning propensity of a material, has been calculated from the ratio of PHRR and time to PHRR for all samples in Table 5. Lower the FIGRA value, lower the fire growth in a material. Based on the data presented in Table 5, Int 1 was most

effective in reducing the fire growth compared to all other flame retardants used. The FIGRA value decreased with higher level of FR, except for samples containing RDP, BAPP and FR 372.

The overall fire performance from cone calorimetric tests of different samples containing 8% FR can be evaluated by plotting the THR versus the ratio of PHRR to TTI as shown in Fig. 7. The magnitude of THR represents the propensity for fire to burn over a prolonged time period while PHRR/TTI represents the rate of fire growth [29]. The proximity of the data points to the origin (0:0) for flame-retarded samples relative to the control suggests that the former have a better fire performance. The fire performance order beginning with the most fire safe sample in accordance with the above mentioned criterion follows the pattern:

Int 1>MP> Int 2>TPP>MPP>FR372>FR245> RDP>TTP >APP >BAPP

The flame-retarded samples have a lower propensity to cause fires of a long duration as seen from lower THR values when compared to the control, E. The propensity to cause a rapidly growing fire as measured by the PHRR/TTI (Fig. 7) also reveals retardation of fire growth following the addition of flame retardant additives to the resin.

Following the above observations it is observed that the P- and N- containing and intumescent based flame retardants despite their poor dispersion are effective in reducing the flammability of epoxy resin. Int 1 and Int 2 are most effective in this group. The cone calorimetric results for organophosphates show that they are less effective than P- and N- containing flame retardants despite their good dispersion, which can be explained due to low phosphorus content in these samples (Table 2). Halogenated flame retardants act in gas phase, hence, are effective in reducing PHRR but not in enhancing char formation. They also increase smoke production (Table 5) [277].

Based on above discussion it could be concluded that the flammability of the resin is influenced by the type of flame retardant present in the sample, whereas all flame retardants of one particular type were not equally effective in every type of fire testing. This is due to different conditions used for each type of fire test, such as LOI, UL-94 and cone calorimetry. Therefore, the flame retardants cannot be ranked generically for all types of tests.

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3.3 Physical, Mechanical and Flammability Properties of Carbon-Fibre Reinforced Composites

The aim of this part of the work was to evaluate whether the efficiency of the flame retardant chemicals observed in above section for the cast resin is maintained in carbon fibre-reinforced laminates as well and how do flame retardant additives affect the mechanical performance of the laminates. From a range of samples discussed above, only two chemicals, Int 2 and FR 372 based on their better dispersion in the resin, were selected to prepare carbon fibre-reinforced composites. The composition and physical properties of control and flame retarded laminates are given in Table 6.

3.3.1 Physical and Mechanical Properties

From dynamic mechanical thermal analysis (DMTA) glass transition temperature (T_g) was measured and the values are given in Table 6. The control composite laminate had T_g 205°C, which is lowered in presence of flame retardants. This may be due to plasticizing effect of FR additives in the resin [30]. The higher T_g values of the control C1 composite may also be due to slightly higher resin content (Table 6) and hence, higher number of sulphone groups which affect the toughening of the resin [31] compared to samples C2 and C3, where resin content is lowered due to additional FR chemicals presence.

Flexural and tensile results of all the samples are also given in Table 6. Since control and flame retarded samples have different fibre contents (represented by fibre volume fraction in Table 6), the modulus values for control sample was normalised to same as for flame retarded samples, i.e. 61.8%. The tensile modulus is associated with the low strain region (upto 0.15%) or design limit. As seen from Table 6 the presence of flame retardants has slightly increased both flexural and tensile moduli, and stress-at-failure values compared to the control sample, indicating that the presence of flame retardants has no adverse affect on the mechanical performance of the laminate.

3.3.2 Flammability Properties

The UL-94 results for three samples are given in Table 7. None of the composite samples ignited in the horizontal UL-94 test, therefore all the composites were subjected to the vertical UL-94 test. Out of three specimens tested, one specimen of control sample, C1 burnt completely, with the total

burning time of 52 s, hence the sample failed UL-94 rating criteria [15]. For cast resin sample also there was no UL-94 rating (Table 4). However, melting and dripping of resin observed for cast resin, was not noticed in the carbon fibre-reinforced composite laminates. The samples containing flame retardants C2 (Int 2) and C3 (FR 372), self-extinguished once the external flame was removed. None of the samples showed any melting or dripping or caused ignition to the underlying cotton. These results indicate that both fire retardants are effective in reducing flammability of the composite laminates and promoting UL-94 rating of epoxy composite from V1 to V0.

The cone calorimetric results in Table 7 show that although the FR additives lowered the time-to-ignition (TTI) of the fire retarded laminated compared to the control sample, they were effective in reducing the peak (PHRR) and total heat release (THR), effective heat of combustion (H_c) and smoke production. FR 372 is more effective than Int 2 in reducing these parameters as seen from Table 7. The inclusion of FR 372 decreases THR by about 45%, PHRR by 35% and H_c by 40% as compared to the control sample. Relatively lesser effectiveness of Int 2 in C2 sample can be explained due to lower phosphorus content (0.32%) in the sample (Table 6), whereas phosphorus content required to result in effective flame retardation is usually around 1% [32]. The bromine content of 1.47% in the composite laminates C3 (FR 372) is sufficient to be effective in rendering the composite flame retardant.

Comparing the cone calorimetric results of composite laminates discussed here with the cone calorimetric results of cast resin samples discussed in Section 3.2.2, it can be seen that composite laminates are less flammable than resin only samples. This is due to low resin content in the composite laminates and presence of carbon fabric, which acts as a filler reducing the flame spread. To compare effect of additives on flame retardant properties of cast resins and fibre-reinforced composites, percentage changes with respect to control E and C1, respectively are shown in Fig. 7. Due to the incombustibility of carbon fibre, flame retardant additives show less effect on the residual char weight of composites as compared to cast resin samples (see Fig. 7(c)). However, from Fig. 7 (a) it can be seen that effect of FR 372 on PHRR is similar in cast resin and fibre-reinforced composites, whereas it is more effective in reducing THR in composite as compared to the cast resin. Int 2 on the other hand is less effective in reducing both PHRR and THR in composite as compared to cast resin, which is due to low phosphorus content in the composite sample (see Table 6). Effective heat of

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combustion of fibre-reinforced composites are higher than respective cast laminates, which is due to the fact that carbon fibres oxidise on prolonged exposure to heat [33], hence releasing more heat.

4. Conclusions

The inclusion of all types (phosphorus- and nitrogen- containing, intumescent based, organophosphorus and halogentaed) of flame retardants in the resin enhanced the thermal stability in terms of residual mass and flame retardancy of the epoxy resin. On curing flame retarded formulations it was observed that all P- and N- containing and intumescent based FRs settled down on the bottom of the plaque. Visual inspection of these samples did not show signs of poor dispersion, which however was observed by scanning electron micrographs of the cross-section of these laminates. This problem however, does not occur in fast curing resins as seen previously in our work on unsaturated polyester [22]. These flame retardant chemicals can however be used fibre-reinforced composites, where fibre layers will hold the resin and additives or alternatively prepregs can be prepared with these formulations. Organophosphate and halogenated flame retardants were well dispersed in the resin.

In general for the high performance, aerospace grade epoxy resin used in this work, all flame retardants were effective in improving the UL-94 rating, LOI values and reducing total heat release rate of the resin. Intumescent based and P- and N- containing flame retardants were the most effective in enhancing char formation at higher temperatures, however their effectiveness for reducing peak and total heat release in cone experiments depended upon the phosphorus content in the cured resin sample. Halogenated fire retardants were very effective in reducing overall flammability of the resin.

The effect of the fire retardants was more pronounced in carbon fibre-reinforced, where halogenated FR 372 could reduce total heat release by nearly 45%. Int 2 was not as effective as FR 372, which was due to low percentage of phosphorus element in the laminate. The most important aspect was that there was no adverse effect of fire retardant chemicals on mechanical properties of the composite laminates. Therefore, this work suggests that the enhancement of thermal stability and fire retardancy of composites without any loss of mechanical characteristics can be achieved by using chemically reactive type flame retardants, which are effective at low concentrations, i.e., < 10 mass-% of the resin

mass.

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Captions for Figures

Fig. 1. Effect of different fire retardants on DTA peak maxima of (a) curing, (b) decomposition and (c) char oxidation stages of flame retarded epoxy resin, where suffix 1= P- and N- containing, 2 = organophosphorus containing and 3 = halogenated FRs.

Fig. 2. (a) TGA curves of epoxy resins containing 8% of flame retardants, and (b) their respective mass difference with respect to control epoxy sample, where suffix 1= P- and N- containing, 2 = organophosphorus containing and 3 = halogenated FRs.

Fig. 3. SEM images of cross-sections of control and 8% flame retardant containing cast resin plaques : (a) control E, epoxy resin, (b) E – MPP (8), (c) E – Int1 (8), (d) E – RDP (8) and (e) E – FR 245 (8).

Fig. 4. (a) Δ LOI of different FR epoxy samples from Table 4: (a) organophosphorus FR epoxy samples vs phosphorus content and (b) halogenated FR epoxy samples with respect to bromine content in different samples.

Fig. 5. (a) Heat release rate, (b) mass loss and (c) smoke release versus time curves for cast epoxy resin containing flame retardants, where suffix 1= P- and N- containing, 2 = organophosphorus containing and 3 = halogenated FRs.

Fig. 6. Digital images of cone burnt samples of epoxy resin with FR (APP) after 500 s of cone calorimetric test showing evidence of char formation: a) top view and b) side view.

Fig. 7. Fire performance evaluation of different samples in accordance to a plot of total heat release (fire duration) and PHRR/TTI (propensity to cause a rapidly growing fire) on exposure to a 50 kW/m² heat flux.

Fig. 8. Percentage change in a) PHRR, b)THR and c) residual char values from cone calorimetric data with respect to control resin and fibre-reinforced composite.

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Captions for Tables

Table 1. Composition of epoxy samples

Table 2. Phosphorous (P), nitrogen (N) and bromine (Br) contents in epoxy resin samples containing 4 and 8% fire retardants

Table 3. Comparison between cone calorimetric data of square and round wood samples at 50 kW/m² heat flux

Table 4. TGA of uncured epoxy resin, LOI and UL-94 results of cast epoxy resin with 4 and 8% fire retardants

Table 5. Cone calorimetric results of cast epoxy resin without/with 4 and 8% fire retardants at 50 kW/m² heat flux

Table 6. Physical and mechanical properties of carbon fibre-reinforced composite laminates

Table 7. Cone calorimetric results of carbon fibre-reinforced composite laminates at 50 kW/m² heat flux

P- and N- containing FRs

Organophosphorus FRs

Halogenated FRs

(a1)

(a2)

(a3)

(b1)

(b2)

(b3)

(c1)

(c2)

(c3)

Fig. 1. Effect of different flame retardants on DTA peak maxima of (a) curing, (b) decomposition and (c) char oxidation stages of flame retarded epoxy resin, where suffix 1= P- and N- containing, 2 = organophosphorus containing and 3 = halogenated FRs.

Fig. 2. (a) TGA curves of epoxy resins containing 8% of flame retardants, and (b) their respective mass difference with respect to control epoxy sample, where suffix 1= P- and N- containing, 2 = organophosphorus containing and 3 = halogenated FRs.

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Fig. 3. SEM images of cross-sections of control and 8% flame retardant containing cast resin plaques :
(a) control E, epoxy resin, (b) E – MPP (8), (c) E – Int1 (8), (d) E – RDP (8) and (e) E – FR 245 (8).

(a)

(b)

Fig. 4. (a) ΔLOI of different FR epoxy samples from Table 4: (a) organophosphorus vs phosphorus content and (b) halogenated vs bromine content in different samples.

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Fig. 5. (a) Heat release rate, (b) mass loss and (c) smoke release versus time curves for cast epoxy resin containing flame retardants, where suffix 1= P- and N- containing, 2 = organophosphorus containing and 3 = halogenated FRs.

Fig. 6. Digital images of cone burnt samples of epoxy resin with FR (APP) after 500 s of cone calorimetric test showing evidence of char formation: a) top view and b) side view.

Fig. 7. Fire performance evaluation of different samples in accordance to a plot of total heat release (fire duration) and PHRR/TTI (propensity to cause a rapidly growing fire) on exposure to a 50 kW/m² heat flux.

Fig. 8. Percentage change in a) PHRR, b)THR and c) residual char values from cone calorimetric data with respect to control resin and fibre-reinforced composite.

Table 1. Composition of epoxy samples.

Sample	Epoxy resin			FR (%)
	Resin (%)	Toughener (%)	Total resin formulation (%)	
ER	100	-	100	-
E (Control)	80	20	100	-
E-FR(4)	80	16	96	4
E-FR(8)	80	12	92	8

Note: FR = APP, MP, MPP, Int1, Int2, RDP, BAPP, TPP, TTP, FR372 and FR245

Table 2. Phosphorous (P), nitrogen (N) and bromine (Br) contents in epoxy resin samples containing 4 and 8% fire retardants

Samples	E- FR(4)			E-FR(8)		
	P (%)	N (%)	Br (%)	P (%)	N (%)	Br (%)
E-APP	1.20	0.64	-	2.40	1.27	-
E-MP	0.53	1.54	-	1.06	3.09	-
E-MPP	0.57	1.56	-	1.14	3.12	-
E-Int 1	0.68		-	1.36		-
E-Int 2	0.60		-	1.20		-
E-RDP	0.43		-	0.86		-
E-BAPP	0.35		-	0.70		-
E-TPP	0.38	-	-	0.76	-	-
E-TTP	0.32	-	-	0.64	-	-
E-FR372	0.12	-	2.80	0.24	-	5.60
E-FR245	-	0.16	2.68	-	0.31	5.36

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Table 3. Comparison between cone calorimetric data of square and round wood samples at 50 kW/m² heat flux

Sample geometry	THR (MJ/m ²)	PHRR (kW/m ²)	Hc (MJ/kg)	Total Smoke (l) / (l/g)*
Square	44.28	375.8	16.76	160.9 (16.0)
Round	42.15	352.1	16.14	840.3 (19.0)

* = Normalised with respect to sample mass

Table 4. TGA of uncured epoxy resin, LOI and UL-94 results of cast epoxy resin with 4 and 8% flame retardants

Samples	Degree of cure (%)	TGA mass at 700°C (%)		LOI (%)		UL-94 Burnt length (%)* / BT (s) / Rating	
		4	8	4	8	4	8
FR (%)	4	4	8	4	8	4	8
ER	96.7	0		24.0		100 / 71 / NR	
E (Control)	96.8	0		24.0		100 / 39 / NR	
E-APP	97.6	5.0	12.0	(28.3)	(29.0)	(34.6 / 39 / NR)	(18.6 / 11 / V1)
E-MP	-	2.0	2.0	(29.5)	(29.9)	(35.2 / 38 / NR)	(24.8 / 13 / V1)
E-MPP	95.8	1.0	6.0	(28.6)	(28.5)	(26.9 / 31 / NR)	(53.8 / 53 / NR)
E-Int 1	-	0	5.6	(30.0)	(29.8)	(21.1 / 17 / V1)	(52.5 / 36 / NR)
E-Int 2	-	2.0	7.0	(29.8)	(30.0)	(24.8 / 35 / NR)	(34.9 / 25 / V1)
E-RDP	97.9	0.3	2.0	31.1	34.5	31.4 / 38 / NR	27.1 / 37 / NR
E-BAPP	98.2	0.4	0	29.5	34.1	40.0 / 24 / V1	9.9 / 13 / V1
E-TTP	-	2.0	1.5	28.1	31.8	41.7 / 27 / V1	20.6 / 19 / V1
E-TTP	-	0	0.2	27.8	29.1	53.7 / 50 / NR	43.3 / 29 / V1
E-FR 372	-	0.8	0	29.1	31.9	39.8 / 23 / V1	22.0 / 4 / V0
E-FR 245	94.5	0.3	2.0	28.3	31.0	60.9 / 54 / NR	33.8 / 17 / V1

* = Sample length is 120 mm; BT = Burning time
The italicized values in the parenthesis are for samples with poor dispersion.

Table 5. Cone calorimetric results of cast epoxy resin without/with 4 and 8% fire retardants at 50 kW/m² heat flux

Samples	TTI (s)	PHRR (KW/m ²)	THR (MJ/m ²)	Hc (MJ/kg)	Smoke (l)	Char (%)	FIGRA (KW/m ² s)
FR (%)	4 8	4 8	4 8	4 8	4 8	4 8	4 8
ER	33	1393	44.4	19.7	2628	2.3	26.3
E (Control)	32	1086	38.5	17.3	2401	6.2	22.0
E-APP	38 40	1052 1090	33.1 33.6	16.9 17.1	2042 1838	19.7 20.0	21.6 21.3
E-MP	39 41	960 756	31.2 27.3	15.3 14.1	2061 2130	15.4 19.3	19.2 14.7
E-MPP	36 40	986 837	32.4 28.7	16.5 15.7	2080 2018	18.5 23.8	20.2 16.7
E-Int 1	39 40	715 611	26.6 23.7	14.4 13.4	2255 2347	22.2 26.4	14.3 12.2
E-Int 2	34 39	882 772	32.8 27.6	16.4 14.6	1882 2134	16.6 20.5	18.6 14.0
E-RDP	40 41	1023 879	32.6 30.7	14.7 16.0	2287 2330	8.0 19.8	18.3 24.4
E-BAPP	39 40	1096 1058	36.9 35.8	18.4 18.1	2401 2707	16.5 16.9	22.9 23.7
E-TPP	35 36	840 787	33.4 27.8	14.6 13.3	2356 2439	7.3 12.2	17.8 17.6
E-TTP	36 36	828 760	36.3 34.7	16.5 15.7	2246 2580	7.9 7.2	17.5 15.7
E-FR 372	29 28	731 711	36.4 29.6	17.6 15.1	2835 2895	17.8 15.8	15.2 19.0
E-FR 245	31 27	972 661	36.4 29.7	16.7 14.7	3172 3635	9.2 14.8	23.6 16.9

Note : The results presented are reproducible to within $\pm 10\%$

TTI = time-to-ignition; PHRR = peak heat release rate; THR = total heat release after 240s ; Hc = heat of combustion; Smoke = total smoke released after 240 s; Char = residual char yield after 240 s of exposure, FIGRA = Fire Growth Rate Index

Table 6. Physical and mechanical properties of carbon fibre-reinforced composite laminates

Sample	Composition (Mass %)			Fibre vol fraction	Thick- ness (mm)	T _g (from DMTA) (°C)	Mechanical properties			
	Carbo n fibre	Resin	FR				Flexural mod* (GPa)		Tensile	
							3 Pt- bending	4 Pt- bending	Mod* (GPa)	Stress-at- failure (MPa)
C1 (Control)	67.1	32.9	0	57.6	3.2	205	43.2	54.7	85.1	375
C2 (Int 2)	70.8	27.1	2.1 (0.32% P)	61.8	2.9	175	45.1	58.4	91.0	498
C3 (FR372)	70.8	27.1	2.1 (0.06% P; 1.47% Br)	61.8	2.9	186	43.1	58.8	87.3	440

*: Normalised to 61.8% fibre volume fraction. The results presented are reproducible to ± 10%

Table 7. UL-94 and cone calorimetric results of carbon fibre-reinforced composite laminates at 50 kW/m² heat flux

Sample	Cone calorimetric results						UL-94 rating
	TTI (s)	PHRR (kW/m ²)	THR (MJ/m ²)	H _c (MJ/kg)	Smoke (l)	Char (%)	
C1 (Control)	64	224	19.4	21.0	1404	74.2	NR
C2 (Int 2)	61	197	17.3	20.4	1399	77.9	V0
C3 (FR 372)	52	146	11.3	15.3	1312	80.6	V0

Note: The results presented are reproducible to ± 10%. THR, smoke and char yield values after 300 s of exposure