

## Recent Developments in Fire Retardation and Fire Protection of Fibre-Reinforced Composites

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**Abstract:** Fibre-reinforced polymer composites are increasingly being used as structural materials, especially in areas in which light weight coupled with good mechanical properties are required. However, unlike traditional materials such as ceramics, glasses and metals, many polymer composites are highly flammable owing to the ease with which the organic polymer matrix, such as a crosslinked epoxy, unsaturated polyester or vinyl ester resin, thermally degrades giving volatile, flammable vapours. For this reason, many applications of such composites require the material to be fire-retarded in some way. This article reviews recent work carried out in the laboratories of the Fire Materials Group at the University of Bolton, covering all aspects of the strategies used to fire retard polymer composites, namely (1) addition of conventional fire retardants to the matrix resin, (2) addition of nanoparticles such as nanoclays, nanosilicas, polyhedral oligomeric silsesquioxanes (POSS), carbon nanotubes and graphene, (3) blending of the matrix resin with a char-forming resin, such as a phenolic, amino or furan resin, and (4) applying a fire-resistant particulate or chemical surface coating. The merits and challenges of each method are outlined using specific examples demonstrating their effects on the fire performances of unsaturated polyester, vinyl ester and epoxy resin composites reinforced with glass fibres.

**Key words:** fire retardant; polymer composite; glass fibre reinforced; fire-retardant additives and coatings

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## 阻燃及防火纤维增强复合物的研究进展

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**摘要:** 防火纤维增强聚合物复合材料越来越多地被应用于结构材料中, 尤其是在要求轻质且具有良好机械性能的领域。但是, 不同于传统的材料, 例如陶瓷材料、玻璃材料和金属材料, 许多聚合物复合材料由于多使用有机聚合物基体而具有较高的可燃性, 例如交联环氧树脂、不饱和聚酯或者乙烯基酯树脂, 在热降解过程中易产生挥发性物质和可燃性气体。基于此种原因, 此类复合材料在许多应用领域要求具有一定程度的防火性能。综述了英国博尔顿大学防火材料组实验室在防火聚合物复合材料方面所做的一系列研究工作及采取的措施, 包括: (1) 在树脂基体中添加传统的阻燃添加剂, (2) 添加纳米颗粒, 例如纳米黏土、纳米二氧化硅、多面体聚硅氧(POSS), 碳纳米管和石墨烯, (3) 在基体树脂中混合成炭树脂, 如酚醛树脂、氨基或呋喃树脂, (4) 使用防火微颗粒或者化学表面涂层。用具体实例介绍了以上措施对玻璃纤维增强的不饱和聚酯、乙烯基酯和环氧树脂基复合材料防火性能的影响, 并分析了各种方法的优点及存在的挑战。

**关键词:** 阻燃剂; 聚合物复合材料; 玻璃纤维增强; 阻燃添加剂和涂层

### 1 Introduction

Fibre-reinforced composite materials in which a polymer matrix, either a thermosetting polymer or a thermoplastic, is reinforced with random or woven fibres to improve flexural and tensile strength are finding increasing use as light-

weight, structural materials in applications ranging from domestic (e. g. baths, shower trays, cladding, and decorative panels) to transport (e. g. boat hulls, automobile panels, seat frames, train and truck cabs, aircraft wing surfaces, tail planes, and cabin components). Most of these applications require the materials to be fire retardant. Of the thermosetting matrix resins, unsaturated polyester, vinyl ester and epoxy are the most widely used owing to their acceptable mechanical properties, especially when reinforced, but all three suffer from being highly flammable. Flammability is also an issue with many thermoplastic matrix materials, e. g. polyolefins, aliphatic polyamides, saturated polyesters, and polycar-

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bonate. For some specialist applications, acceptable thermal stability and hence fire retardance can only be achieved through the use of more inherently fire retardant thermosets such as phenolic and furan resins, or more exotic, and therefore expensive, thermosets and thermoplastics, such as aromatic polyamides, polyimides, bismaleimides, benzoxazines, and polyetherketones. However, some of these materials, even when reinforced, are relatively brittle (e. g. phenolics), or present processing difficulties, such as a requirement for a lengthy high-temperature or multistage cure, or the application of pressure to prevent voids being formed when volatile products of cure are released, e. g. water and formaldehyde during the curing of phenolic resins<sup>[1-2]</sup>.

Improving the fire retardance of the less fire retardant matrix resins requires either resin modification with a fire-retardant additive or reactive species, and/or fire protection through the application of a fire-retardant coating. In addition, where the reinforcing fibre is a natural material (e. g. a cellulose-based fibre, such as flax, jute or hemp) some treatments of the fibre may also be required since otherwise this too will contribute to the fire load. These various approaches to improving the fire retardance of fibre-reinforced composite materials have all been explored in our laboratories, and reviews of these, and the work of other groups in the area, have recently been published<sup>[3-7]</sup>.

In this paper we review more recent work in our laboratories, which has concentrated on understanding and improving the fire resistance of composites based on unsaturated polyester, vinyl ester and epoxy resins, since it is these resins that are the most widely used commercially in composite structures but which suffer most from poor fire performance.

## 2 Fire retarding matrix resins

### 2.1 Conventional fire retardants

The established way of fire retarding a polymer is to add a conventional fire-retardant, either one that works by a gas-phase mechanism, such as a halogenated additive, or one that operates in the condensed phase, for example a phosphorus-containing species that may react with the polymer during pyrolysis and, in so-doing, catalyse the formation of a protective char. The relative effects of different concentrations (4 and 8 wt%) of a variety of fire retardants (FRs) on the thermal stability and flammability of cured samples of a polyethersulfone-toughened, aerospace grade, epoxy resin (E) have been explored recently by thermal analysis, limiting oxygen index, UL94 tests, and cone calorimetry<sup>[8]</sup>. The fire retardants included ammonium polyphosphate (APP), melamine phosphate (MP), melamine pyrophosphate (MPP), phosphorylated pentaerythritol (Int1), phosphorylated pentaerythritol plus melamine (Int2), resorcinol bis-(diphenyl phosphate) (RDP), bis phenol a bis (-diphenyl phosphate), (BAPP), triphenyl phosphate (TPP), tritoly phosphate (TTO), tris(tribromoneopentyl) phosphate (FR

372), and tris(tribromophenyl) cyanurate (FR 245). It was observed that during the curing process, all P- and N-containing FRs or intumescent (APP, MP, MPP, Int1 and Int2) settled on the bottom of the resin plaque, indicating the problem of dispersion in the resin. This problem is more acute in slow curing resins such as used in this case compared to fast curing bifunctional epoxy or unsaturated polyester resins<sup>[9]</sup>. All organophosphates and halogenated FRs, however, mixed well with the epoxy resin and did not settle down on the bottom of the plaque indicating better dispersion. All FRs affected the curing temperature of the resin slightly, but in each sample >90% curing was achieved. Despite poor dispersion, all FRs reduced the flammability of the resin, the extent of which depended upon the FR type, concentration of fire-retardant elements in the formulation, dispersion in the resin and the type of fire testing performed. Even at 4% levels, use of MPP, RDP, BAPP and FR372 gave rise to a V1 UL-94 rating (control sample failed) and at 8%, use of FR372 gave rise to a V0 rating. The cone results at 50 kW · m<sup>-2</sup> radiant heating are summarised in Figure 1 where the total heat release (THR) against the fire growth rate values, calculated by dividing peak heat release rate (PHRR) by time-to-ignition (TTI) is plotted. Fire safe materials should have low THR and fire growth rate value (PHRR/TTI), hence the samples with the high fire safety should fall close to the coordinates (0, 0) on the 2-D plot. From this it can be seen that it is the intumescent formulation, Int 1, that performs the best, with Int 2 not far behind, probably because they contain pentaerythritol, a char-forming component. Epoxy resins without an FR form relatively little char on burning, although char-formation in epoxy resins can be catalysed by melamine phosphates, hence the good fire retardance seen also with MP and MPP. Relatively low char yields were seen with E-TTP, E-TPP and FR 245, indicating that in these cases fire retardance probably proceeds mainly via a gas-phase mechanism.

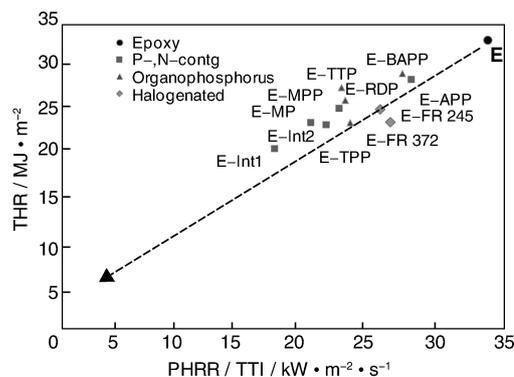


Fig. 1 Fire safety diagram, i. e. plot of total heat released (THR) vs. peak heat release rate (PHRR) divided by time to ignition (TTI), for epoxies (E) containing 8 wt% of various fire retardants (E-FR) based on cone calorimetric data recorded with 50 kW · m<sup>-2</sup> radiant heating [adapted from Ref<sup>[8]</sup>].

Although settling out of FR in cured resins affected flammability data in some cases, this was less of a problem in cured carbon fibre composite laminate samples made using selected resin/FR blends, in which the fibres helped to pre-

vent settling. For example, laminates made with C-Int2 and C-FR 372 showed good fire retardance with no significant change in physical and mechanical properties compared with a control laminate containing no FR(C) as shown in Table 1.

Table 1 Physical, fire and mechanical properties of carbon fibre-reinforced composite laminates containing FR additives [8].

Sample	Composition (Mass %)		Thick-ness /mm	$T_g$ (from DMTA) /°C	Mechanical properties		Fire properties				
	Carbon fibre	Resin/FR			Flexural mod /GPa	Tensile Mod /GPa	Cone results at 50 kW · m <sup>-2</sup>				UL-94 rating
							TTI /s	PHRR /kW · m <sup>-2</sup>	THR /MJ · m <sup>-2</sup>	Smoke /l	
C	67.1	32.9/0	3.2	61	43.2	85.1	64	224	19.4	1 404	NR
C-Int 2	70.8	27.1/2.1	2.9	52	45.1	91.0	61	197	17.3	1 399	V0
C-FR372	70.8	27.1/2.1	2.9	186	43.1	87.3	52	146	11.3	1 312	V0

In a similar work, the effect of the additives ammonium polyphosphate, alumina trihydrate, expandable graphite, talc and sepiolite clay on physical, thermal and mechanical properties of glass-reinforced unsaturated polyester composites has been studied [9]. Since the unsaturated polyester is mainly used in ships and hence, their durability to water absorption is important, the water durability properties were also observed by immersing laminates in water for 21 days prior to testing. Unsaturated polyester samples containing fire retardants absorbed more water than the control sample. The flammability behaviour of samples before and after they were immersed in water was assessed by cone calorimetry at 50 kW · m<sup>-2</sup> incident heat flux. Mixed, but insignificant changes in the TTI and the PHRR values were observed. Notable increments in the amount of smoke produced were observed for samples subjected to water treatment when compared to dry samples. However, the changes observed were similar for the control sample and the fire-retarded samples suggesting that there is no adverse effect on the physical properties of the polyester resin following the addition of fire retardants.

## 2.2 FR effects of nanoparticles

There have been many publications to date on the effects of nanoparticles such as nanoclays, carbon nanotubes, and nanosilicas on the fire retardance of polymers and polymer composites [6, 10].

For example, the addition of 10 wt% of either a mixture of polyhedral oligomeric silsesquioxane (POSS, a cage silicene) and triglycidylcyanurate or a functionalized POSS made by reaction of POSS with triglycidylcyanurate to an epoxy resin based predominantly on the diglycidyl ether of

butane-1, 4-diol (LY5052, Araldite), produces a significant improvement in fire retardance of amine-cured resin samples and of glass fibre-reinforced composite laminate samples based on them, when assessed by cone calorimetric experiments [11-12]. When the mixture of POSS and TGIC is used [12], PHRR, THR and CO production are all significantly reduced, albeit with some slight reduction in initial thermal stability, and consequently with shorter times-to-ignition. Nevertheless, thermal stability improves at higher temperatures leading to longer overall burn times. It is suggested that POSS reacts with the epoxy resin chains during later stages in the thermal degradation of the epoxy forming Si-O-C links, thus effectively crosslinking chains, aiding retention of material in the condensed phase, leading to longer burn times, and ultimately to greater char formation (ca. 8 wt% in resin plaques without POSS and 19 wt% with POSS). Similar differences in behaviour are seen also with the glass fibre-reinforced composite laminate samples, shown here in Table 2. However, the introduction of POSS reduces slightly both the flexural and the tensile moduli of the composite laminates, possibly owing to some reduction in fibre-resin bonding, although these mechanical properties are better retained in the POSS-containing laminates after exposure to radiant heat in the cone calorimeter. Interestingly, the introduction of the components of the functionalized POSS (POSS and triglycidyl isocyanurate) separately in the resin produces results little different from those obtained with POSS alone, from which it is concluded that there is no reaction between POSS and the isocyanurate in the resin, either during curing or during thermal degradation.

Table 2 Physical, fire and mechanical properties of glass fibre-reinforced composite laminates containing POSS, TGIC or POSS+TGIC [12].

Sample	Composition (Mass %)		Mechanical properties		Fire properties			
	Carbon fibre	Resin/POSS/TGIC	Flex mod /GPa	Tensile mod /GPa	TTI /s	PHRR /kW · m <sup>-2</sup>	THR /MJ · m <sup>-2</sup>	Residual wt%
FEP	50	50/0/0	13.9	7.5	125	857	50	54.5
FEP/POSS	50	45/5/0	10.7	6.1	121	420	32	61.5
FEP/TGIC	50	45/0/5	13.5	6.7	108	620	47	53.3
FEP/POSS/TGIC	50	45/2.5/2.5	13.9	5.8	114	385	32	58.1

The effects of layered silicate nanoclays, nanosilica and double-walled carbon nanotubes (DWNTs) on the thermal stability and fire reaction properties of cured LY5052 and of an advanced aerospace grade epoxy resin (MY721, Huntsman, a high temperature curing tetraglycidyl-4, 4'-diamino diphenyl methane) also have been investigated using thermal analysis, cone calorimetry, LOI and UL94 techniques<sup>[13]</sup>. The nanoclays included an alkyl quaternary ammonium modified montmorillonite (Cloisite<sup>®</sup> 30B, Rockwood Additives Ltd., UK), octadecyl ammonium ion-modified montmorillonite clay (I.30E, Nanocor Inc., China) and vinyl triphenyl phosphonium bromide clay (VTP), a result of organic-based quaternary ammonium salt modification of sodium montmorillonite clay (in-house preparation). Double walled carbon nanotubes (DWCNTs) were from Nanocyl, Belgium. The epoxy resin containing 30 wt% of nano-silica particles (EPR 486) was sourced from Bakelite AG. The morphology of the cured polymer/clay nanocomposites, determined by X-ray diffraction (Figure 2a) and transmission electron microscopy (Figure 2b), indicated intercalated structures, with evidence also for significant exfoliation in the case of the MY721 nanocomposites. The addition of 5 wt% nanoclay to both resins had a thermal destabilising effect (in terms of mass loss from TGA curves) at temperatures below 400 °C, akin to that seen with POSS, but led to higher char yields at higher temperatures, again similar to the behaviour observed with POSS. The inclusion of 30 wt% nanosilica significantly improved the thermal stabilities of the resins while DWNTs had an adverse

effect owing to their poor dispersion in the matrices. The overall stabilisation effect (OSE), calculated via integration of the areas under the  $\Delta$  mass % (mass of resin nanocomposite-mass of resin) versus temperature curves (for details see reference<sup>[14]</sup>) is presented in Figure 2c). A high positive OSE value indicates an improvement in the overall thermal stability of the polymer nanocomposite in the temperature range 30 ~ 800 °C while a negative value suggests that the overall thermal stability of the nanocomposite is inferior to that of the unmodified resin. DWNTs gave the most negative OSE value probably due to poor dispersion of the nano-additives in the resin matrices. 30B and VTP clays gave positive OSE values, while I.30E reduced the value. Nano-silica additives had the highest OSE value of all samples studied herein suggesting that this particular additive when used at 30 wt% has a remarkably significant effect on the thermal stability of epoxy resins.

DWNTs also produced only marginal improvements in the cone calorimetric experiments but performed better in UL94 and LOI tests, showing that different fire tests can produce different impressions of fire retardance. The nanoclays significantly increased the fire retardance of the tetrafunctional epoxy resin, the best improvement in fire retardance (lowest PHRR, see Figure 2d) was produced using a clay in which the interlayer sodium ions had been exchanged for vinyl triphenyl phosphonium ions via reaction with vinyl triphenyl phosphonium bromide (VTP); in this system it is likely that the phosphorus content of the clay also contributes to fire retardance.

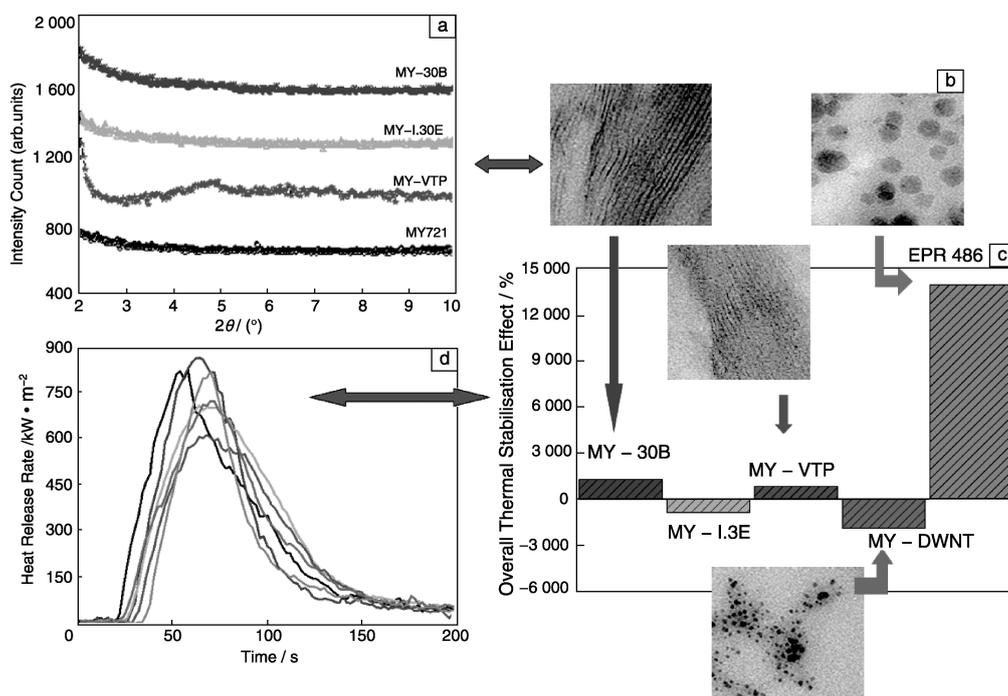


Fig. 2 Epoxy resin ( ( MY721) containing nanoclays ( 30B, I.3E and VTP ), nonosilica ( EPR 486) and nanotubes ( DWNT ) ): ( a) XRD patterns, ( b) TEM images, ( c) overall thermal stabilisation effect ( OSE) and ( d) HRR versus time curves at 50 kW · m<sup>-2</sup> heat flux.

### 2.3 Combinations of nanoparticles and FR additives

More recently, combinations of nanoparticles with other types of fire retardant additive, and of nanoparticles with other types of nanoparticle, have been added to epoxy resins and to epoxy resin composites in the hope of seeing synergistic effects on fire retardance. For example, the thermal stability of an aerospace grade epoxy resin containing a silicate-based nanoclay modified by an organophosphorus moiety ( VTP ), double-walled carbon nanotubes (DWCNTs) and/or conventional phosphorus-containing fire retardants (FRs) at weight fractions up to 20% have been investigated using thermogravimetric analysis (TGA) [14]. Fire retardants included ammonium polyphosphate, APP (Antiblaze MC, Rhodia, UK); resorcinol bis- (diphenyl phosphate), RDP (Chemtura, UK); and tris (tribromoneopentyl) phosphate, TBP (FR 370, DSBG, Israel). When FR additives (15 wt%) or VTP containing nanoclay (5 wt%) are used independently, the overall enhancement of thermal stability (residual mass at a particular temperature) of the epoxy resin follows the order: APP > nanoclay VTP > RDP > TBP. The addition of DWCNTs alone did not significantly alter the thermal stability of the epoxy resin matrix. The concomitant addition of VTP together with RDP, APP, and TBP at a cumulative weight fraction of 20% led to synergistic improvements in the thermal stability of the resin. Fire-retardant properties of glass fibre-reinforced laminates prepared from modified resin formulations were assessed by cone calorimetry under a heat flux of  $50 \text{ kW} \cdot \text{m}^{-2}$ . The addition of conventional FRs, with or without the nanoclay, significantly reduced the peak heat release rate and total heat released relative to the control sample. DWCNTs alone did not have a significant effect on the fire retardance of the epoxy resin composites. The burning behaviour of the fire-retarded samples as evaluated by cone calorimetry correlated well with TGA and differential thermal analysis (DTA) data. Depolymerization rates measured by DTA correlated well with HRR data from cone calorimetry, while times to ignition (TTI) correlated well with the onset of thermal degradation as determined by TGA. In a fire risk assessment based on cone calorimetry data (Figure 3), nanocomposites containing APP gave the highest fire safety rating.

The effect of these nanoparticles (silicate nanoclays and double walled carbon nanotubes) and microsized fire retardants (FRs) on the post heat/fire flexural performance of glass fibre-reinforced epoxy composites exposed to at varied incident heat fluxes ( $35 \sim 75 \text{ kW} \cdot \text{m}^{-2}$ ) have also been evaluated [15]. The flexural stiffness and modulus values of radiant heat-damaged GFR composites decreased rapidly with increasing incident heat flux. On the other hand, the post-fire flexural properties of these specimens exposed for  $30 \sim 90 \text{ s}$  post-ignition at  $50 \text{ kW} \cdot \text{m}^{-2}$  were 80% lower than the initial room temperature values. Despite significant improvements in the fire reaction properties, the post-fire flexural performance of the composites was least affected. This suggests that while these fire retardants are effective in promoting char formation, the resulting char networks are not consolidated enough to ef-

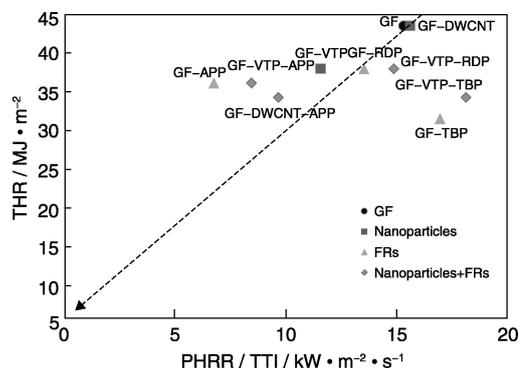


Fig. 3 Fire safety diagram, i. e. plot of total heat released (THR) vs. peak heat release rate (PHRR) divided by time to ignition (TTI), for glass fibre-reinforced epoxy composites containing nanoparticles, various fire retardants and combinations of both based on cone calorimetric data recorded with  $50 \text{ kW} \cdot \text{m}^{-2}$  radiant heating [adapted from Ref 14].

fectively constrain the fibre reinforcements.

In similar work, a commercial nanoclay (Cloisite 10A Southern Clay Products, USA) and vinyl triphenyl bromide (VTP) modified clay were used to prepare glass fibre-reinforced unsaturated polyester composite laminates with ammonium polyphosphate (APP, Antiblaze MCM, Rhodia Specialities), melamine phosphate (Antiblaze NH, Rhodia Specialities), dipentaerythritol / melamine phosphate intumescent mixture (Antiblaze NW, Rhodia Specialities) and alumina trihydrate [6]. The sample compositions, their mechanical properties, and the results of cone calorimetric experiments are shown in Table 3. The results generally show that the inclusion of functionalized nanoclays enhances the flexural performance of the resin owing to nano-level reinforcement, whereas the inclusion of fire retardants adversely affects the flexural moduli of the composite laminates. The presence of clay in Res/Clay/FR samples show small but not significant improvement compared to Res/FR samples. Cone calorimetric results for glass reinforced composites in general show a slight increase in TTI and time to flameout (FO) for samples with and without fire retardants, whilst PHRR and smoke production are reduced w. r. t. to the control sample. Despite the higher TTI values and longer FO times, all the Res/Clay/FR formulations have reduced THR suggesting reduced flammability. Composite laminate Res/Clay (i) /APP shows the highest reduction (43%) in PHRR as compared to the control sample, probably owing to the presence of phosphonium groups in the organic modifier used to functionalise the clay.

The effect of adding graphene to an epoxy containing either melamine phosphate (MP), an additive fire retardant, or 9, 10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO), a reactive fire retardant, on the thermal, mechanical and fire-retardant properties of glass fibre-reinforced epoxy composites has been investigated using thermal analysis; flexural, impact, and tensile tests; cone calorimetry and UL94 measurements [16]. The addition of 10

Table 3 Physical, flexural and flammability properties of glass reinforced unsaturated polyester-nanocomposite samples containing conventional fire retardants [6].

Samples	Composition (Mass%)		Thickness /mm	Flexural modulus /GPa	Cone data at 50 kW · m <sup>-2</sup>			
	Glass	Resin/Clay/FR			TTI/s	PHRR /kW · m <sup>-2</sup>	THR /MJ · m <sup>-2</sup>	Smoke /l
Res	67	33/0/0	2.42	14.91	36	401	31.0	359
Res/10A	62	36.1/1.9/0	2.43	16.35	41	370	35.3	357
Res/VTP	62	36.1/1.9/0	2.44	15.59	39	358	33.8	320
Res/APP	67	27.4/0/5.6	2.73	8.82	37	245	28.4	281
Res/ATH	63	30.7/0/6.3	2.79	8.32	40	260	33.8	423
Res/NH	64	29.9/0/6.1	2.67	9.94	42	340	30.1	422
Res/NW	64	29.9/0/6.1	-	-	39	239	22.5	389
Res/10A/APP	67	26.1/1.3/5.6	2.72	9.50	39	287	26.5	335
Res/VTP/APP	67	26.1/1.3/5.6	2.74	8.63	38	229	31.6	413
Res/10A/ATH	67	26.1/1.3/5.6	2.59	12.30	40	288	30.2	408
Res/10A/NH	67	26.1/1.3/5.6	2.72	7.99	40	291	30.8	409
Res/10A/NW	67	26.1/1.3/5.6	-	-	42	224	26.2	378

wt% MP or DOPO to the epoxy reduced PHRR, THR, and burning rate and produced an increased char yield. However, the inclusion of fire retardant slightly worsened the mechanical behaviour, which was attributed to the poor interfacial interactions in case of MP and to decreased crosslink density in case of DOPO fire-retarded resin. The addition of graphene improved flexural and impact properties, but slightly worsened tensile performance. Graphene also further decreased the PHRR, THR and burning rate owing to a barrier effect. The improved fire retardancy in all cases was at-

tributed mainly to the reduced release of combustible gaseous products.

The effects of graphene in combination with a POSS have been explored also. Simultaneous reduction and surface functionalization of graphene oxide (GO) was achieved by simple refluxing of GO with octa-aminophenyl polyhedral oligomeric silsesquioxanes (OapPOSS), without the use of any reducing agents, in order to render the surface of the graphene oxide more compatible with the epoxy resin [17]. The reaction between GO and the OapPOSS is shown schematically in Figure 4.

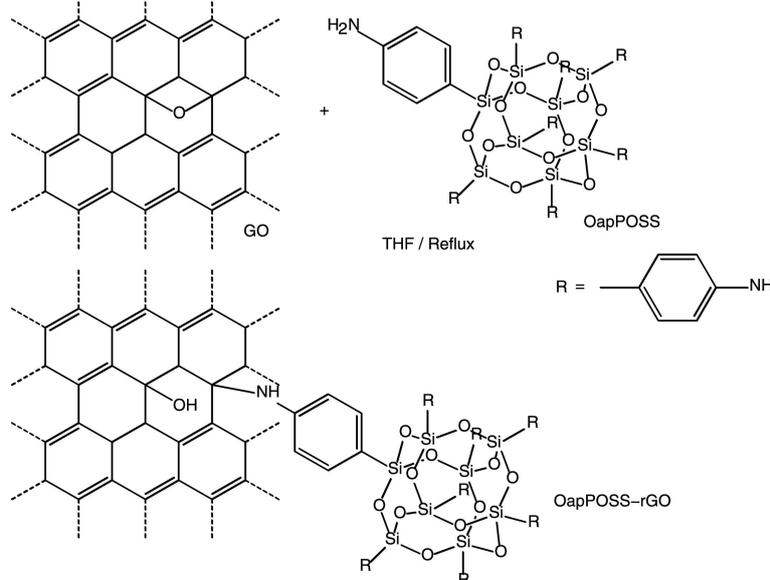


Fig. 4 Schematic representation of the reaction between GO and OapPOSS to give OapPOSS-rGO [adapted from ref 17]

As expected, the reaction with OapPOSS made the hydrophilic GO more hydrophobic, as shown by the good dispersion of the OapPOSS-reduced GO (OapPOSS-rGO) in tetrahydrofuran. The structure of OapPOSS-rGO was confirmed by XPS, FTIR and TEM. A morphological study showed

that, owing to the good interfacial interaction between the functionalized graphene and the epoxy (diglycidyl ether of bisphenol-A, Hefei Jiangfeng Chemical Industry), OapPOSS-rGO was dispersed well in the amine-cured matrix. With the incorporation of 2 wt% of OapPOSS-rGO, the onset tempera-

ture of thermal degradation of the epoxy nanocomposite was increased by 43 °C. Moreover, the PHRR, THR and rate of production of CO for OapPOSS-rGO/epoxy were reduced by 49%, 37% and 58%, respectively, compared to those of the neat cured epoxy. This dramatically reduced fire hazard was mainly attributed to a synergistic effect of OapPOSS-rGO in which the adsorption and barrier effect of the reduced graphene oxide inhibited heat transfer and gas release, thus promoting the formation of a graphitic char, while the OapPOSS improved the thermal oxidative resistance of this char.

## 2.4 Blending with char-forming resins

In the absence of added condensed-phase fire retardants, unsaturated polyester and vinyl ester resins form virtually no char when burnt, and epoxy resins produce only minor amounts. Thus, to achieve condensed-phase fire retardance in such resins, a char-forming substance must be added. For example, the addition of phenolic resoles to unsaturated polyester resins can satisfactorily fire retard such resins when used in amounts ranging from 20% to 50% by weight<sup>[18]</sup>. However, conventional resoles are neither chemically nor physically compatible with unsaturated polyesters since the former cure by a polycondensation reaction with the release of water and formaldehyde, whilst the latter are cured (usually after the addition of styrene as a crosslinking monomer) by a free-radical, chain-reaction mechanism. Also, conventional resoles are not miscible with unsaturated polyesters and phase separate during cure leading to poor physical and mechanical properties in the cured blend. However, we have shown that blends of unsaturated polyester with an allylically modified resole are not only physically compatible (miscible), but are also chemically compatible in that they co-cure to an extent via copolymerization of the allyl groups with styrene and maleate groups in the polyester to give a co-continuous, interpenetrating polymer network<sup>[19]</sup>.

In order to render phenolic resins more chemically compatible with unsaturated polyesters, they can be chemically functionalized with unsaturated groups capable of being free-radically copolymerized more readily than can allyl groups. For example, a novolac (a thermoplastic phenolic resin with no separately curable methylol groups) has been reacted with methacryloyl chloride to introduce methacrylate functional groups (Figure 5)<sup>[20]</sup>.

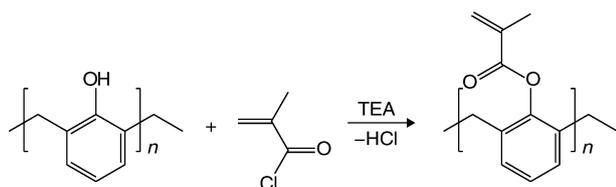


Fig. 5 Reaction of a phenolic novolac with methacryloyl chloride in the presence of triethylamine (TEA) to give a methacrylate-functional resin.

Homogeneous co-cured blends of this methacrylated novolac with unsaturated polyester and styrene have been pre-

pared under the relatively low temperature conditions used to cure unsaturated polyester/styrene mixtures. The methacrylated novolac may also be cured alone with styrene under the same low-temperature conditions, i. e. there is no need to employ the high temperatures and pressures that are required to cure conventional phenolic resins. The cured methacrylated novolac, and its blends with unsaturated polyester, are rigid materials with good mechanical strength, and have glass transition temperatures, thermal stabilities and fire retardancies superior to those of cured unsaturated polyester alone.

Other resins that may be blended with unsaturated polyesters to improve their char-forming potential include urea-formaldehyde, melamine-formaldehyde and furan resins<sup>[21]</sup>. However, such resins are neither physically nor chemically compatible with unsaturated polyesters unless chemically modified. Furan resins, for example those based on the acid catalysed chain extension and crosslinking of furfuryl alcohol, fail to cure fully in blends with unsaturated polyester leading to a phase-separated material with poor mechanical properties, albeit with good fire-retardance<sup>[22]</sup>. Fire-retardant and selected physical and mechanical properties of unsaturated polyester and 50/50 w/w blends with three char-forming resins are compared in Table 4.

It can be seen that for all UP blends, the fire retardant parameters, PHRR, THR and TSR, are better than those of UP itself and that there are significant char yields indicating that the mechanism of fire retardance in all three cases is principally a condensed-phase one. It is interesting to note also that for all three blends, single  $T_g$ s are observed, indicating complete miscibility of the components, and that for UP/AR and UP/MN, the storage moduli,  $E$ , are greater than those of the component resins consistent with co-curing to give a continuous bi-component network with significant reinforcement of one component by the other. However, for the UP/F blend,  $T_g$  is lower than that of either of the pure components as is  $E$  owing, as indicated above, to incomplete curing of the furan component leading to significant plasticization of the UP network.

As might be expected, the fire-retardance of blends of unsaturated polyester with char-forming resins may be further improved by the addition of conventional fire-retardants. For example, in cone calorimetric experiments, additions of 20 wt% resorcinol bis (diphenyl phosphate) (RDP, Chemtura UK), 20 wt% bisphenol-A bis (diphenyl phosphate) (BADP, Chemtura UK), and 10 wt% 9, 10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO, Tokyo Chemical Industry UK Ltd.) significantly reduce the PHRR and THR of blends of an unsaturated polyester with an allylic-functional phenolic resole (AR) and increase char yields,

Table 4 Limiting oxygen indices (LOI), times to ignition (TTI), peak heat release rates (PHRR), total heat released (THR), total smoke released (TSR), char yields, glass transition temperatures ( $T_g$ ) and storage moduli ( $E$ ) for unsaturated polyester (UP) and 50/50 w/w blends with three char-forming resins: an allyl phenolic resole (AR), a methacrylated phenolic novolac (MN) and a furan resin (F).

Resin system	LOI (%O <sub>2</sub> )	Cone results at 50 kW · m <sup>-2</sup>					DMTA results	
		TTI /s	PHRR /kW · m <sup>-2</sup>	THR /MJ · m <sup>-2</sup>	TSR /m <sup>2</sup> · m <sup>-2</sup> · s <sup>-1</sup>	Char /wt%	T <sub>g</sub> /°C	E /MPa
UP	17.9	38	1130	83	4 813	1.9	92	2 660
50/50 UP/AR	19.6	57	828	61	3 126	14	120	3 200
AR	2.2	72	804	48	2 209	27	285	3 120
50/50 UP/MN	19.7	39	840	64	3 623	12.4	126	2 590
MN	21.3	41	801	61	3 512	19.7	182	2 130
50/50 UP/F	19.0	16	911	57	2 520	13.6	61	500
F	22.7	19	854	32	95	38	144	1 400

albeit also with some increase in smoke output (TSR). The salient data for a 50/50 w/w blend of polyester and resole are given in Table 5. The fact that smoke output as well as char yields are increased with the addition of the fire retardants indicates that the fire retardants are active in both gas and condensed phases<sup>[23]</sup>.

Table 5 Effects of fire-retardant additives on fire retardance of a 50/50 UP/AR blend determined by cone calorimetry at 50 kW · m<sup>-2</sup>.

Resin System	PHRR /kW · m <sup>-2</sup>	THR /MJ · m <sup>-2</sup>	TSR /m <sup>2</sup> · m <sup>-2</sup> · s <sup>-1</sup>	Char /wt%
50/50 UP/AR	828	61	3 126	14
50/50 UP/AR + RDP (20%)	570	40	3 660	23
50/50 UP/AR + BADP (20%)	590	42	4 180	19
50/50 UP/AR + DOPO (10%)	530	44	4 220	18

### 3 Fire protection of composite surfaces

#### 3.1 Mineral and ceramic claddings

Use of mineral and ceramic claddings is quite popular in naval applications to fireproof conventional composite hull, deck and bulkhead structures. These barriers function as insulators providing 'passive fire protection' by decreasing heat transfer from the fire to the structure. Quite often these mats contain a chemical, such as expandable graphite, that helps in generating intumescent char. We have studied the effect of one such mat made of vitreous (silicate) fibres and containing expandable graphite (Tecnofire, UK) on glass-reinforced polyester composites<sup>[24]</sup>. These mats contained vitreous (silicate) fibres and expandable graphite. Composite laminates were prepared with seven layers of woven glass fibres plus top layers of intumescent mats of different thicknesses. The cone calorimetric results at 50 kW · m<sup>-2</sup> incident heat flux showed that with increasing thickness of the mat,

the PHRR decreased. However, the TTI was reduced and there was slow but prolonged burning, resulting in higher THR values for surface protected composites when compared to the control sample. While intumescent char-forming mats do provide thermal insulation to the core composite, they however need to be heated first and fast enough in order to allow time for char expansion before the temperature is high enough to initiate depolymerisation of the polymer resin in the underlying core composite. In a subsequent work, the use of insulative fabrics purely as surface barriers (no infused resin) gave better results<sup>[25]</sup>. Alternatively, the use of conventional fire retardant additives in the resin plus these surface mats is an effective way of fire protecting composites<sup>[25]</sup>. Thermal barrier effect of these intumescent mats was evaluated by measuring the temperatures on the reverse side of the samples using a thermocouple<sup>[24-25]</sup>. Despite improving the fire retardancy of the composites, the presence of fire-retardant additives alone does not improve retention of flexural modulus following exposure to a heat source. However, the introduction of a 'passive' fire proofing insulative fabric enhances fire performance while preserving the mechanical properties of composites exposed to high heat fluxes or fires. In our work, the control sample had no flexural strength after exposure to 50 kW · m<sup>-2</sup> in the cone calorimeter; with FR additives the flexural modulus was <10% of the initial value, whereas with FR additives and surface mat it was >80% and sometimes as much as 92% of the initial value<sup>[25]</sup>.

In a similar vein a thin glass-fibre veil impregnated with ammonium polyphosphate was bonded onto the flax/epoxy laminates and their corresponding balsa-core sandwich composites. The fire protection efficiency of this veil was evaluated by testing these samples in a cone calorimeter at an applied heat flux of 50 kW · m<sup>-2</sup><sup>[26]</sup>. Although there was no significant change in TTI with the introduction of the fire retardant glass fibre veil, the heat release rates, including peak values, for the fire-protected composites were significantly lower than those measured for their unprotected counterparts. Through-thickness temperature profiles across the sandwich composite revealed the effectiveness of the fire retardant veil in

minimizing thermal damage of underlying substrate composites.

### 3.2 Ceramic nano and micro particulate coatings

Organoclays, and other nanoscopic materials, can act as protective barriers when used as coatings on polymers and polymer composites, as well as when used as additives in the bulk. For example, the thermal barrier and fire retardant efficiencies of an organically modified clay (OC), when deposited on the surface of glass fibre reinforced epoxy (GRE) composites, have been found to be significant<sup>[27]</sup>. In this work, two approaches were undertaken: ① the OC was deposited on the surface of the GRE and then polymerized using an atmospheric argon plasma in the presence and absence of a silicon containing monomer and ② the OC was dispersed in a phenolic resin binder and applied as a surface coating. Fourier-transform infrared spectroscopy confirmed the polymerisation of the silicon containing monomer following the plasma treatment. The adhesion between the coating and the GRE was measured using the tape-pull method, which indicated that the OC was tightly embedded in the resin matrix after plasma treatment or with the resin binder. The surface morphologies of the coated surfaces were studied using scanning electron and digital microscopies. The thermal barrier effect of the OC-containing coatings was demonstrated by cone calorimeter at a heat flux of  $35 \text{ kW} \cdot \text{m}^{-2}$ , which showed an increase in TTI and time to peak heat release rate ( $T_{\text{PHRR}}$ ), and a decrease in PHRR for the coated samples compared to those of the control. The ceramic coating residue left after the cone calorimetric test is shown in Figure 6. However, for the coatings to be effective enough to be self extinguishing, the presence of an additional fire-retardant element in the coating, or on the surface layer of the GRE composite and beneath the clay layered coating, is required.

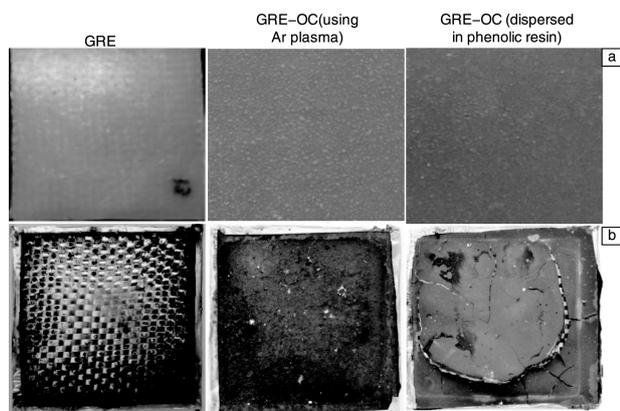


Fig. 6 Digital images of control (GRE), GRE coated with OC using atmospheric plasma and GRE coated with OC dispersed in phenolic resin binder; a) laminates and b) charred residues at the end of cone calorimetric experiment.

A number of commercially available ceramic particles have been used also as thermal barrier coatings on GRE composites<sup>[28]</sup>. The coatings were prepared by dispersing 70 wt% ceramic particle in 30 wt% fire-retarded epoxy resin. The ther-

mal barrier efficiency of the coatings on the composites was studied by measuring the temperature gradient through the thickness of the sample, using thermocouples beneath the coating and on the reverse side of the sample, while the surface was exposed to radiant heat of varying heat fluxes (20, 30, 40 and  $50 \text{ kW} \cdot \text{m}^{-2}$ ) in a cone calorimeter. Use of a cone calorimeter also allowed the flammabilities of the coated composites to be assessed. It was concluded that these ceramic-particle coatings containing the fire retarded epoxy resin binder act as an insulative thermal barrier and so reduce PHRR values and delay in the time to PHRR. However, the flammable, resin-rich, surface caused a decrease in TTI and an increase in THR of the laminates. Therefore, in the surface coating layer, fire-retardant additives/chemicals should be present also, so as to delay/stop ignition of the resin binder, as these ceramic particles act only as thermal insulators, not as fire retardants. In terms of heat penetration, at low heat fluxes all ceramic coatings gave rise to effective thermal barrier/insulative char layers, which helped to delay the heat transfer from surface to underlying layers, measured as a slower rise in temperature and increasing time to reach glass transition temperature ( $180 \text{ }^\circ\text{C}$ ) and pyrolysis temperature ( $250 \text{ }^\circ\text{C}$ ) on the reverse side of the laminate. Moreover, these ceramic coatings could have provided better thermal barrier performance if they had completely covered the surface and there were no holes on the surface through which heat could penetrate. To address this second point, in subsequent work an epoxy resin was used as a binder and, in some samples, extra ceramic particles were sprayed on the first coating while the resin was partially cured to enable the surface to be completely covered by ceramic particles, leaving no resin exposed<sup>[29]</sup>. Ceramic particles used in this work were yttria-doped zirconia (Zirconia (Zr), XZO1357, Mel Chemical, UK), a low melting silicate glass (Glass flake (Flek), Flekashield NGF Europe, UK), aluminium titanate (Recokit (Re), Ohcera. Co., Ltd., Japan), nanoclay (Cloisite 30B, Southern Clay Products) and nanosilica (Aerosol 200, Evonik Industries). All ceramic particles showed good performance as thermal barriers. On exposure to 35 and  $50 \text{ kW} \cdot \text{m}^{-2}$  heat fluxes, the coatings were very effective in increasing TTI of the composite, owing to the combination of ceramic particles and the inherently fire-retardant properties of the phenolic resin binder in the coating. The coatings could reduce PHRR and increase  $T_{\text{PHRR}}$ . At  $35 \text{ kW} \cdot \text{m}^{-2}$  some coatings prevented ignition (see Table 6). The additional ceramic particles amplified the thermal barrier effect of the ceramic coatings. The best performance was shown by Flekashield-containing coatings. All ceramic coatings delayed the rise in temperature at the back surface of the sample, increasing the times to reach  $180 \text{ }^\circ\text{C}$  and  $250 \text{ }^\circ\text{C}$  of the laminate. GRE-P/ReS gave the slowest rate of increase in temperature compared to the other coated samples, as it had the highest coating thickness. All ceramic coatings were durable to peeling and to the water soak test; however, they cracked/debonded when subjected to localised impact.

Table 6 Cone calorimetric data for a GRE control sample and for samples surface coated with ceramic particles at  $35 \text{ kW} \cdot \text{m}^{-2}$  heat flux without an ignition source

Sample	Coating thickness / $\mu\text{m}$	Cone results at $35 \text{ kW} \cdot \text{m}^{-2}$			Time required to reach the back surface temperature /s	
		TTI /s	PHRR / $\text{kW} \cdot \text{m}^{-2}$	THR / $\text{MJ} \cdot \text{m}^{-2}$	180 °C	250 °C
Control		104	526	36.8	40	72
GRE-P	200	108	490	46.4	44	73
GRE-P/30B	200	153	410	35.1	54	86
GRE-P/Si	190	–	–	9.1	54	82
GRE-P/Flek	310	–	–	7.2	48	75
GRE-P/Re	310	124	400	33.5	56	90
GRE-P/Zr	420	126	429	44.4	57	87
GRE-P/FlekS	330	–	–	6.6	51	80
GRE-P/ReS	660	157	443	36.4	89	135
GRE-P/ZrS	510	172	325	26.3	67	102

Note: GRE = Glass reinforced composite; P=Phenolic resin binder; 30B = nanoclay, Si = nanosilica; Flek = Flekashield (glass flakes), Re = Recoxit (aluminium titanate); Zr = zirconia. S denotes surface coated with extra ceramic particles

### 3.3 Chemical Coatings

An additional method of surface protection is to apply a fire-resistant chemical coating. Most common type of chemical coatings are intumescent coatings, which by the action of heat; melt, form bubbles and then expand rapidly to form a multi-cellular, carbonaceous or ceramic layer. The resultant carbonaceous or ceramic char layer acts as a thermal barrier thus effectively protecting the substrate against rapid increases in temperature<sup>[30]</sup>. Non-intumescent surface coatings containing char-forming or flame inhibiting additives can also be used. Generally, char-promoting agents such as phosphate derivatives are the active ingredients in these non-intumescent surface coatings. Gaseous-phase active halogenated additives such as chlorinated paraffin are the active ingredient in non-intumescent fire retardant surface coatings. Because of inherent differences in their fire retardation mechanisms, different types of fire resistant coatings demonstrate varying degrees of fire protection under the same principal test conditions.

In order to evaluate the fire retarding efficacy of different types of surface coatings under low, moderate and extreme thermal environments, in addition to a commercial intumescent surface coating (IC) from Leigh Paints UK, two non-intumescent surface coatings sourced from Bostik Findley Ltd were used; one that is active in the condensed phase (NIC) and which promotes surface char formation, and another that is active in the gaseous phase and which inhibits flaming combustion (NIH)<sup>[31-32]</sup>. NIC contains tricresyl phosphate in propan-2-ol. The NIH is a non-intumescent but halogenated co-polymer emulsion containing chlorinated paraffin (1~5%). The fire resistance of the surface-coated laminates was evaluated using a cone calorimeter at incident heat fluxes of 25, 50 and 65  $\text{kW} \cdot \text{m}^{-2}$ . For all test conditions, there was a significant improvement in the fire perform-

ance of surface-protected GRE laminates relative to their unprotected counterparts in terms of delay in TTI, time to peak heat release rate ( $T_{\text{PHRR}}$ ) and reduction in PHRR, as can be seen from Table 7. The  $T_{\text{PHRR}}$  and the magnitude of the THR were influenced by the quantity and morphology of the char formed by each type of surface coating in addition to the chemical nature of fire-retardant chemicals present in the coatings. The post-heat flexural performance of heat-damaged laminates was determined via three-point bending. There was a significant improvement in the post-heat flexural moduli retention in thermally protected glass/epoxy laminates (Table 7). This may be due to the fire retardation efficacy of the coatings and the ability of the charred structures to reduce the heat transfer into the substrate, thereby protecting the underlying composite and its mechanical integrity.

Also highly effective as a fire-retardant coating when applied by a UV polymerization technique to the surface of a glass-fibre reinforced epoxy (GRE) composite, is poly (vinyl phosphonic acid). On exposure to heat, such coatings intumesce and act as a thermal insulator, providing active fire protection to the composite structure<sup>[33]</sup>. The fire performance of coated GRE composite samples was studied by cone calorimetry at 35 and 50  $\text{kW} \cdot \text{m}^{-2}$  heat fluxes. While a sample with ca. 500  $\mu\text{m}$  thick coating did not ignite at either heat flux, one with the ca. 300  $\mu\text{m}$  thick coating ignited at 50  $\text{kW} \cdot \text{m}^{-2}$ ; however, the TTI was delayed from 60 s in the uncoated sample to 195 s and the PHRR reduced from 572  $\text{kW} \cdot \text{m}^{-2}$  to 86  $\text{kW} \cdot \text{m}^{-2}$ . The coatings do not peel off when subjected to a tape pull test and resist cracking and debonding during impact drop tests of up to 5 J energy. However, such coatings are hydrophilic, showing significant mass loss in water-soak tests and current research is aimed at improving this aspect.

Table 7 Cone calorimetric data and post-heat flexural modulus retention of glass/epoxy composite laminates with and without surface coatings under varied conditions of thermal damage.

Sample	Heat Flux /kW · m <sup>-2</sup>	Cone results at 35 kW · m <sup>-2</sup>				* Post heat flexural mod. retention /%
		TTI /s	PHRR /kW · m <sup>-2</sup>	T <sub>PHRR</sub> /s	THR /MJ · kg <sup>-1</sup>	
GRE	25	72	563	105	27	96.7
	50	52	733	95	38	58.8
	65	17	750	75	32	11.1
GRE-NIC	25	102[ +42]	494[ +12]	215	56[ -107]	96.4
	50	59[ +13]	584[ +20]	110	54[ -42]	86.1
	65	20[ +18]	631[ +16]	115	46[ -44]	19.0
GRE-NIH	25	171[ +138]	515[ +9]	255	54[ -100]	98.3
	50	70[ +35]	544[ +26]	125	50[ -32]	84.2
	65	27[ +59]	548[ +27]	100	42[ -31]	11.2
GRE-IC	25	204[ +183]	194[ +66]	400	28[ -4]	96.9
	50	81[ +56]	400[ +45]	195	55[ -45]	83.6
	65	32[ +88]	438[ +42]	140	48[ -50]	22.6

\* Post-heat flexural modulus retention following exposure to a particular heat flux for 60 s.

## 4 Conclusions

As we have demonstrated, the fire retardance of fibre-reinforced composite laminates may be significantly improved via a number of strategies, including obvious ones such as incorporating fire retardants in the matrix resin, both with and without the addition of a further char-forming component and/or char promoting additive. A more elegant solution, however, is provided by applying a fire-retardant surface coating to the composite or, better still, a surface fire-protective layer. This latter strategy requires no modification to the basic procedures by which the fibre-reinforced laminate is prepared and therefore may be more commercially acceptable. Such surface-coatings may retard ignition and slow down the subsequent burning of the sample, with reduced heat release, or may prevent ignition, and hence combustion, completely, depending upon composition. Surface coatings containing nano- and micro-particulates are particularly effective in this regard and protect underlying surface layers not only from fire but also from thermal degradation. Our researches in this important area are continuing.

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