New Developments in Flame Retardancy of Glass-Reinforced Epoxy Composites

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ABSTRACT: This work involves the development of novel glass fiber–reinforced composite materials containing a commercially available epoxy resin, a phosphate-based intumescent, and inherently flame-retardant cellulosic (Visil, Sateri) and phenol–formaldehyde (Kynol) fibers. The intumescent and flame-retardant fiber components were added both as additives in pulverized form and fiber interdispersed with the intumescent as a fabric scrim for partial replacement of glass fiber. Thermal stability, char formation, and flammability properties of these novel structures were studied by thermal analysis, limiting oxygen index, and cone calorimetry. The results are discussed in terms of effect of individual additive component on thermal degradation/burning behavior of neat resin. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 88: 2511–2521, 2003

Key words: epoxy; composites; flame retardancy; intumescents; heat release

INTRODUCTION

Epoxy resins constitute the organic matrix for high performance composite materials used in the fabrication of light structural panels for aircraft and other transport vehicles. The major advantages of these composite structures over traditional metallic materials like steel and aluminum are their favorable mechanical and physicochemical properties, and high strength- to-weight ratio. To increase the market penetration and because of current stringent aviation and other legislation to increase safety, improvements in flame retardancy have been given significant priority. Because these resins crosslink on curing, their char-forming tendency and hence thermal stabilities can be increased by adding suitable additives. The ability to tailor the properties of composites makes it feasible to do this and examples are described in this study.

Intumescents are widely used as surface coatings for effective flame-retardant treatments.[1,2] However, they can be used as additives for thermoplastic and thermoset polymers[3–5] as char promoters. In our previous work,[6,7] we observed that phosphate-based intumescents interact with flame-retardant (FR) cellulosic fibers during the application of heat and form a complex "char-bonded" structure. The char formed is greater in mass, resistant to oxidation, and has better

thermal barrier properties and higher mechanical strength compared to those of the individual components. We then extended this research to enhance char formation of thermoset (epoxy, phenolic, and polyester) resins used in glass-reinforced rigid composites.[8] When studied by thermal analytical techniques, it has been observed that the introduction of an intumescent/flame-retardant cellulosic fiber (Visil, Sateri) to these resins results in physical and chemical interactions of three components leading to enhanced char formation.[9,10] The results indicated that laminates produced from these components should have superior flame-retardant properties. The intumescent/FR fiber combinations may be introduced either as a pulverized additive to the resin or as an additional textile fabric layer to the composite structure.[8] In our previous work we prepared such structures with polyester resins and studied their flammability, mechanical properties, and the effects of different variables on these properties.[11] In general it was observed that inclusion of intumescent and flame-retardant cellulosic fiber to polyester resin slows their burning process measured in terms of heat release rates.

In the present work similar structured epoxy composite laminates were prepared and studied for their flammability properties. Some of the structures contained another flame-retardant and high performance fiber, Kynol (Kynol, Japan), and their properties were compared with samples containing Visil fiber. The compatibility of the Kynol fiber and resin with and without intumescent was studied by thermal analysis.

TABLE I
Physical and Flammability (LOI)[a] Properties of Composite Laminate Samples (i)–(ix)

Sample	Weight fraction (%) in composite				Thickness (mm)	LOI (%)
	Glass	Resin	FR fiber	Int[b]		
(i) Ep	55.0	45.0	—	—	1.9	27.5
(ii) Ep + NH	53.0	42.3	—	4.7	2.0	35.2
(iii) Ep + Vis	53.0	42.3	4.7	—	2.1	28.1
(iv) Ep + Vis + NH	50.0	40.0	5.0	5.0	2.3	36.2
(v) Ep + Ky	53.0	42.3	4.7	—	2.4	27.7
(vi) Ep + Ky + NH	50.0	40.0	5.0	5.0	2.7	30.2
(vii) 4Gl–3Vis–NH	33.3	46.7	20.0*		2.1	38.4
(viii) 4Vis–NH–3Gl	25.4	47.5	27.1*		2.4	34.2
(ix) 5Gl–4Ky	38.8	52.9	8.3	—	2.4	27.8

[a] LOI, limiting oxygen index.
[b] Int, intumescent.
* Vis-Int fabric.

EXPERIMENTAL

Samples (i)–(vi)

Materials

Resin. B3B: a multifunctional epoxy resin (Hexcel Composites Ltd., UK).
Glass. E-glass in the form of woven roving (300 g^{-2}) (supplied by Glassplies, Southport, UK).
Flame-retardant (FR) fiber. Visil (Sateri Fibers, Finland): a cellulosic fiber containing polysilicic acid, in pulverized form (from original fiber length 40 mm, 3.5 dtex, and diameter 17 μm). Kynol, KF–10 BT: in powder form (average fiber length, 0.33 mm; diameter, 33 μm).
Intumescent. Antiblaze NH (Rhodia Specialities Ltd., UK): contains melamine phosphate.

Samples

(i). Ep: Eight layers of woven glass//resin
(ii). Ep + NH: Eight layers of woven glass//resin + NH
(iii). Ep + Vis: Eight layers of woven glass//resin + Visil
(iv). Ep + Vis + NH: Eight layers of woven glass//resin + Visil + NH
(v). Ep + Ky: Eight layers of woven glass//resin + Kynol
(vi). Ep + Ky + NH: Eight layers of woven glass//resin + Kynol + NH

Composite laminate preparation

Samples were prepared by impregnating glass fabric with resin and/or additive(s). Individual fabric layers impregnated with resin were dried in an oven at 40°C for 10 min. All the layers were stacked, laid up in vacuum bags, and cured at 135°C for 1 h in an autoclave.

The performance of composites is dependent on the properties of the materials constituting the composite and the process by which they are combined. It also very much depends on the type and amount of resin used. Hence for comparison reasons, the conditions and amounts of different components were kept constant. To keep the resin weight the same in all samples, sample (iv) was impregnated first. It contains 50% (w/w) glass and 50% (w/w) resin + additives. For other samples the resin content was kept the same and all additives were additional. The intumescent in sample (i) was 10% (w/w) with respect to resin. FR fiber in samples (iii) and (v) was also 10% (w/w) with respect to resin. In samples (iv) and (vi) FR fiber + NH was 20% (w/w) with respect to resin. However, the amounts of the components present in final laminates, as given in Table I, were different because these were the percentages within the respective final products.
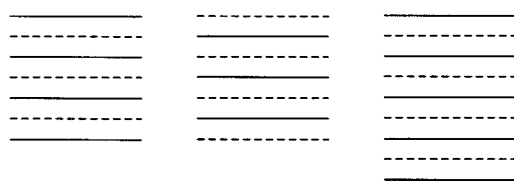
Samples (vii)–(ix)

Materials

Resin. A film of multifunctional epoxy resin (120 g^{-2} area density) was prepared commercially by Hexcel Composites Ltd.
Glass. E-glass in the form of woven roving (300 g^{-2}).
FR fiber. Visil–NH (240 g^{-2}). Prepared by padding on a nonwoven web of Visil (120 g^{-2}) with intumescent (100% w.r.t. fiber wt) and Vinamul 3303 resin (15% w.r.t. intumscent). Kynol (80 g^{-2}) in the form of nonwoven mat.
Intumescent. Antiblaze NH.

Samples

(vii). 4Gl–3Vis–NH: Four layers of glass and three layers of Visil–NH sandwiched between resin films.
(viii). 4Vis–NH–3Gl: Four layers of Visil–NH and three layers of glass sandwiched between resin films.
(ix). 5Gl–4Ky: Five layers of glass and four layers of Kynol sandwiched between resin films.

Sample (vii)   Sample (viii)   Sample (ix)

(solid line is glass and broken line is Visil-NH/Kynol fabric)

Scheme 1 Schematic representation of structures of samples (vii)–(ix).

The structures of these samples can be represented schematically as shown in **Scheme 1**:

Composite laminate preparation

Samples were prepared by using resin film (prepared and supplied by Hexcel). Each layer of glass and Visil was sandwiched between two resin films, ironed on, with the release paper peeled off. All subsequent layers were stacked and then processed like samples (i) to (vi).

Testing equipment

Thermal analysis

For simultaneous DTA/TGA analysis a TA Instruments SDT 2960 (TA Instruments, New Castle, DE) was used under flowing air (100 mL/min) and at a heating rate of 10 K min^{-1}. About 10.0 mg of sample was used in each case. The pulverized fibers were used in this study.

The following combinations were studied by simultaneous DTA/TGA to observe the compatibility of different components.

- Resin, intumescent, and fiber: individually
- Resin/intumescent: 1 : 1 mass ratio
- FR fiber/intumescent: 1 : 1 mass ratio
- Resin/FR fiber/intumescent: 1 : 0.5 : 0.5 mass ratio

Limiting oxygen index (LOI)

A Stanton-Redcroft LOI FTA analyzer was used to determine LOI values according to the standard procedure.[12]

Cone calorimetry

A cone calorimeter (Fire Testing Technology Ltd., UK) was used at an incident heat flux of 50 kW m^{-2} in an air atmosphere under free convective air flow condi-

tions according to ISO 5660.[13] Composite samples (100 × 100 mm) were wrapped in aluminum foil and placed in a specimen holder over a ceramic blanket at least 13 mm thick. A spacing of 25 mm was maintained between the bottom of the cone and top of the specimen. All the tests were performed with the retainer frame in place as recommended in ISO 5660-1, which helped in reducing edge effects and composite delamination. Because these samples do not intumesce in a conventional way and the intumescent chemicals react with the FR fiber (Visil) and resin to form a char-bonded structure,[9,10] no extra surface grid to stabilize the samples was required.

RESULTS AND DISCUSSION

Thermal analysis of component mixtures

Thermal analytical results and thermal degradation mechanisms of epoxy resin, Visil, intumescent Antiblaze NH (melamine phosphate) used in the present study, and their different combinations are discussed in detail in our previous communications.[9,10] As for the present work, in some samples [(v), (vi), and (ix)] Visil fiber was replaced by another high performance Kynol fiber. Thermal analytical studies of all the combinations with Kynol were carried out and here results are compared with the combinations containing Visil fiber.

In Figure 1(a) char yield differences between expected and calculated average values from TGA curves of individual components of fiber–intumescent and resin–fiber mixtures are plotted as functions of temperature. The details of interaction of both Visil and Kynol with melamine phosphate are discussed elsewhere.[9,10,14,16] As can be seen from Figure 1(a), the Kynol and melamine phosphate mixture shows evidence of greater interaction than Visil–melamine phosphate in the 470–680°C temperature range. However, above 700°C, the Visil–intumescent system is more stable than Kynol–intumescent. The TGA response showed that the former has 17% residual char remaining, whereas Kynol–intumescent char is totally oxidized and corroborates this observation. This indicates the Visil fiber and melamine phosphate are interacting to produce a "char-bonded" structure, which is comparable (and better at high temperatures) in performance to the one involving high performance (Kynol) fiber.

When the compatibility of each fiber with epoxy resin was studied, although the resin–Visil mixture shows more than the expected char formation in the temperature range 300–500°C [Fig. 1(a)], the original DTA curves indicated no significant interaction.[9,10] This greater char formation may be a physical effect, in that both Visil and resin exert an initial "filler effect" on each other, producing slightly more char than ex-
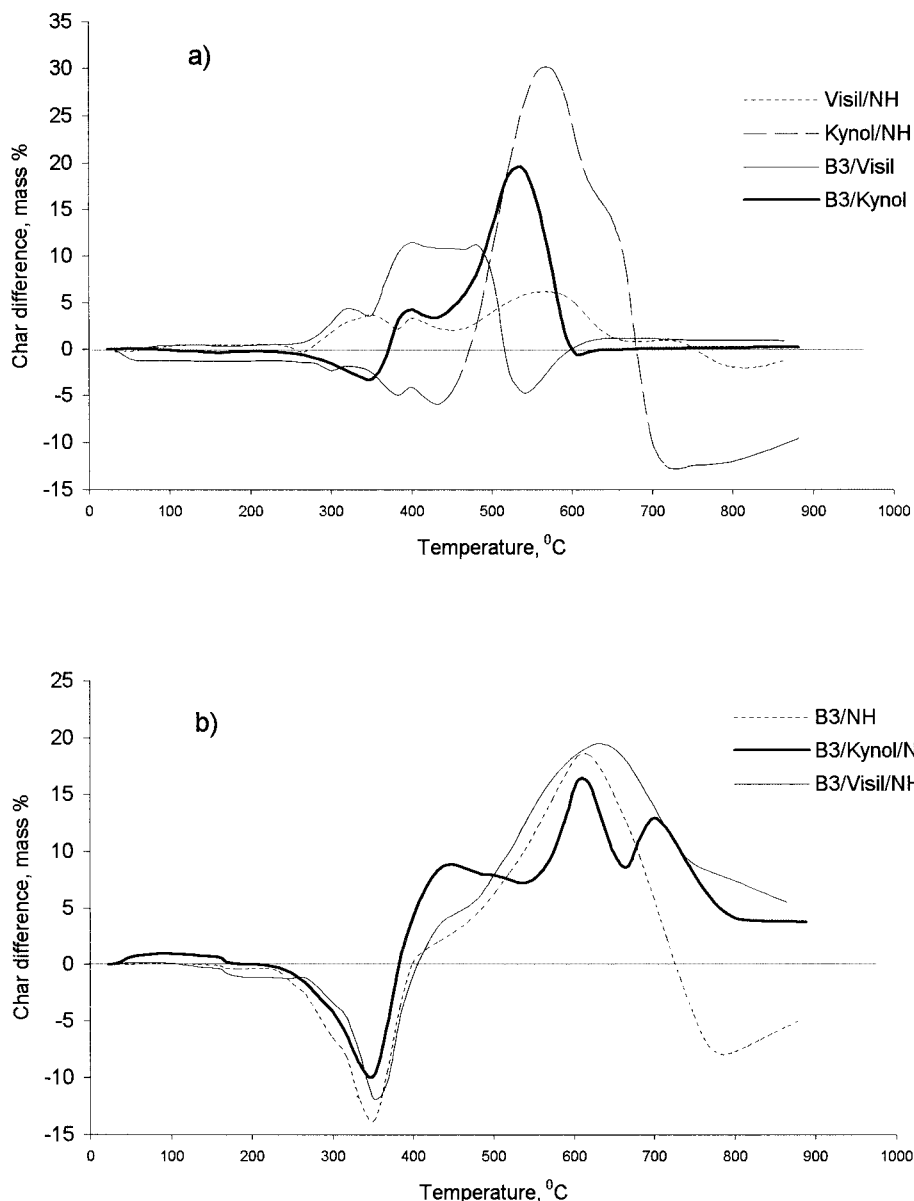
Figure 1 Percentage residual mass difference (actual − averaged) as a function of temperature for (a) Visil/NH (· · ·), Kynol/NH (– – –), B3/Visil (—), and B3/Kynol (—); (b) B3/NH (· · ·), B3/Visil/NH (—), and B3/Kynol/NH (—).

pected, which then oxidizes. Kynol, on the other hand, promotes char formation in the temperature range 370–600°C, which indicates some interaction between the crosslinking resin and the phenol–formaldehyde structure in the fibers.

The DTA and TGA results of resin/intumescent and resin/Visil/intumescent combinations showed that the behavior of mixtures is quite different from that of individual components and their calculated averages, thus indicating some kind of interaction.[9,10] The char yield differences between the expected and calculated values from TGA curves in Figure 1(b) show that melamine phosphate increases the char-forming ability of epoxy resin up to about 730°C. However, when either fiber is present, the system becomes stable up to

900°C and about 5% more than the expected char residue remains. Detailed modes of possible interaction are discussed elsewhere,[9,10] and this chemical interaction between these components indicates that composite laminates produced from these components should have superior flame-retardant properties.

Flammability of composites

Limiting oxygen index

LOI is considered to be a measure of flammability of a sample in terms of threshold oxygen concentration for sustained burning. LOI results for composite samples
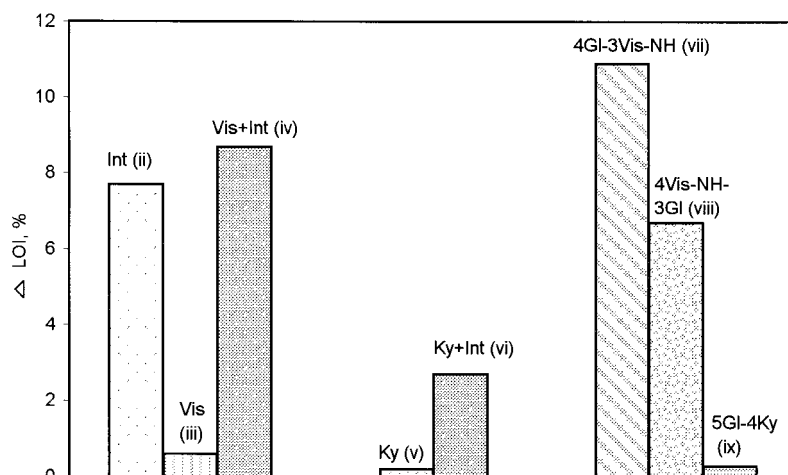
Figure 2 Change in limiting oxygen index (ΔLOI, %) of samples (ii)–(ix) compared to control sample (i).

are given in Table I. The value for the control sample (i) is 27.5%. The changes in LOI (ΔLOI) for other samples with respect to the LOI of the control sample (i) are shown in Figure 2. The presence of an intumescent [sample (ii)] increases LOI to 35.2, whereas Visil [sample (iii)] addition does not have much effect. The presence of both Visil and intumescent, however, increases the value to 36.2%. In samples (i)–(iv) the same amount of glass fabric is present; hence, ΔLOI for these reflects the effect of additives only. However, when Visil–NH is in fabric form [samples (vii) and (viii)], there is a greater increase in LOI values (38.4 and 34.2, respectively), probably because of a greater amount of Visil–Int compared to that of sample (iv) (see Table I) and the complex layered structures present.

Kynol in both fiber [sample (v)] and fabric [sample (ix)] form has little effect on LOI. Even when present with an intumescent [sample (vi), LOI = 30.2], it is not as effective as the resin, Visil, and intumescent combination [sample (iv), LOI = 36.2].

Cone calorimetry

Cone calorimetry enabled various parameters to be determined (see Table II). Selected results are also shown in Figures 3–5. The results presented here are averages of three runs for each sample.

Time to ignition (TTI). Time to ignition may be defined as the ease of ignition. For the control epoxy sample TTI is 42 s. The addition of intumescent, Visil fiber, and a mixture of both have little effect on TTI, as can be seen from Table II. The flameout times as given in Table II indicate that these samples are burning for similar times. However, Kynol with and without intumescent slightly increases TTI and burn time. The TTI values for layered composite structures are quite similar, whether it is Visil–NH fabric or Kynol fabric, but the burning times are different, depending on their resin contents.

Heat release rate (HRR). The heat release rate is the heat generated per unit time by the burning sample divided by the surface area of the sample. Hence, it is a

TABLE II
Cone Calorimetric Results for Composite Samples (i)–(ix) at 50 kW/m²

| Sample[a]	TTI (s)	Flameout (s)	Peak HRR (kW/m²)	TTP (s)	THR (MJ/m²)	Average values from ignition to 5 min				Smoke at 300 s (m²/m²)
						HRR (kW/m²)	H_c (MJ/kg)	CO yield (kg/kg)	CO$_2$ yield (kg/kg)	
(i)	42	220	385	60	21.8	84	19.8	0.089	1.44	908
(ii)	35	225	278	48	18.3	61	18.8	0.074	1.11	648
(iii)	41	219	329	61	19.4	65	16.6	0.089	1.21	614
(iv)	38	220	262	47	17.9	59	17.3	0.065	0.96	495
(v)	51	291	367	79	28.8	96	19.0	0.077	1.33	817
(vi)	55	273	354	79	23.2	77	16.8	0.085	1.09	748
(vii)	46	218	366	66	24.2	80	17.1	0.058	0.96	898
(viii)	47	300	348	85	28.3	94	17.3	0.054	0.92	870
(ix)	44	287	445	74	28.4	94	19.8	0.092	1.29	807

[a] As in Table I.
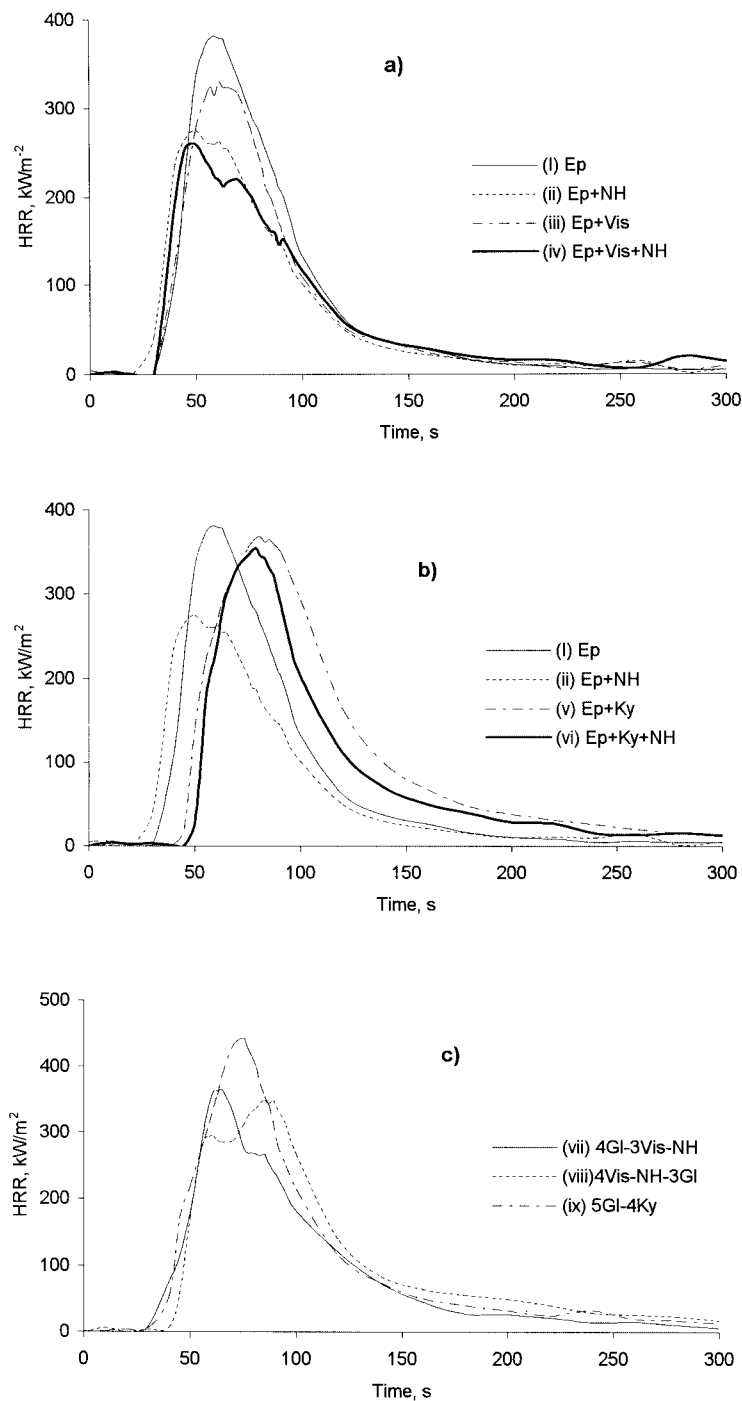
Figure 3 Heat release rate (HRR) versus time curves of samples (i)–(ix) at 50 kW/m² heat flux.

measure of the heat release rate to the surroundings per unit surface area of the burning material. The important parameters for assessing the fire performance of a material are the maximum or peak heat release (PHRR), average heat release (AvHRR), and total heat release rates (THR). HRR curves as a function of time for samples (i)–(ix) are given in Figure 3(a)–(c). As can be seen from Figure 3(a) and Table II, the presence of an intumescent reduces the PHRR from 385 to 278 kW/m², indicating a reduction in

volatile fuel formation. When both intumescent and Visil are present, the peak is further reduced to 262 kW/m². The presence of Visil alone [sample (iii)] also reduces the PHRR value and, as can be seen from the HRR curve in Figure 3(a), there are two peaks, representing reduction of resin volatilization and that derived from condensed phase activity of Visil. When both Visil and intumescent are present [sample (iv)], this effect becomes more pronounced [see Fig. 3(a)]. Kynol without and with intumescent has no such ef-
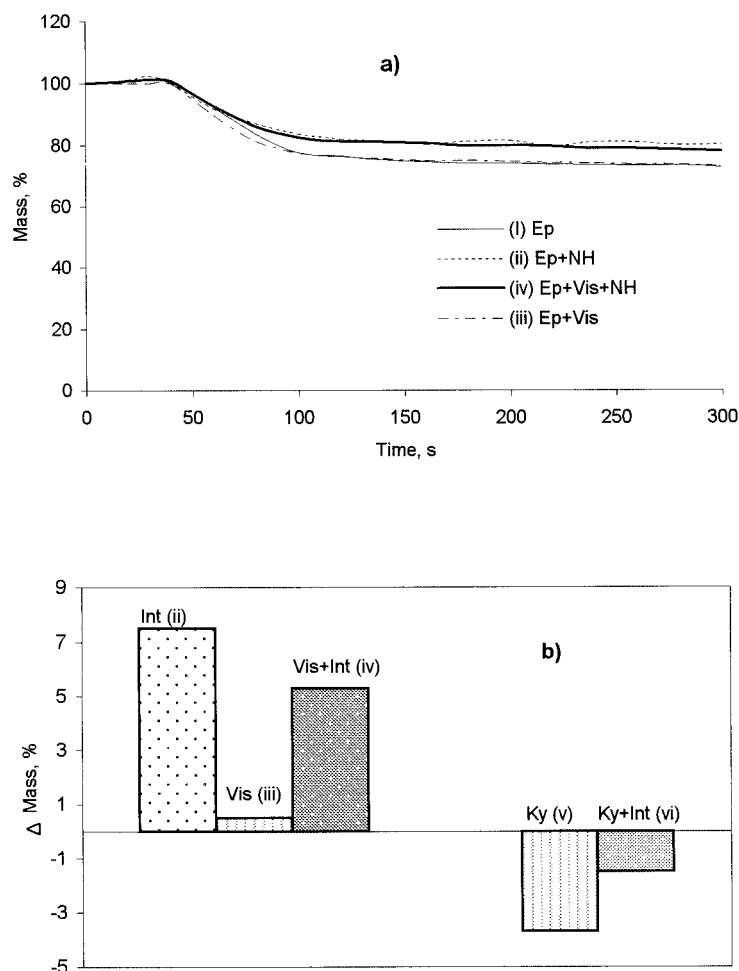
Figure 4 (a) Mass loss curves of samples (i)–(iv) at 50 kW/m² heat flux and (b) change in residual mass (Δmass, %) of samples (ii)–(vi) compared to control sample (i).

fect, with the values being 367 and 354 kW/m², respectively. However, as can be seen from Figure 3(b), and respective TTI and TTP (time to peak) values in Table II, the HRR curves are shifted toward longer times, indicating that they ignite slowly and burn for longer times. This indicates that the potentially crosslinking phenol–formaldehyde Kynol may interfere with the crosslinking epoxy resin and delay its degradation and volatilization without influencing its ultimate heat release.

When Visil–NH or Kynol fabric is used, the PHRR values are higher than that of control samples (see Table II), although there is no direct comparison, given that resin contents for these samples are different.

THR and AvHRR values also show similar trends, with the lowest value being for sample (iv) containing Visil and intumescent, which are even lower than that for sample (vi) containing Kynol and intumescent.

Effective heat of combustion (H_c). The effective heat of combustion over a given time frame (5 min in Table II) 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 HRR and mass loss and may thus be used to measure the possible flame-retarding effects of components present. Visil powder reduces the heat of combustion (19.8 MJ/kg for the control sample) in sample (iv) (16.6 MJ/kg), whereas Kynol has little effect [19.0 MJ/kg for sample (vi)], even when present in fabric form (19.8 MJ/kg). When both Visil and intumescent are present, the value is 17.3 MJ/kg and for the Kynol/intumescent mixture it is even lower (16.8 MJ/kg). This reflects the combined effect of intumescent and FR fiber components on volatile fuel formation and thus burning of the samples.

Mass loss. Because the char retained after burning a polymer is also a measure of its flammability, the mass loss curves give insight into the fire performance of the samples. Typical mass loss curves for selected samples and the effect of additives on their residual char retained after 5 min are given in Figure 4(a) and (b), respectively. The presence of intumescent alone and with Visil fiber increases the residual mass at any
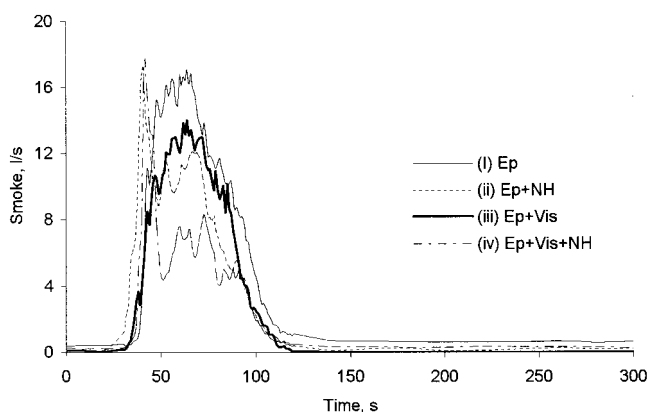
Figure 5 Smoke production curves of samples (i)–(iv) at 50 kW/m² heat flux.

time. This supports thermal analytical results that these components promote char formation of the resin. Kynol fiber when present with or without intumescent does not increase residual char of the resin. Again, for samples (viii) and (ix) there is no direct comparison, given that resin contents are different.

Smoke. The results of smoke generation can be expressed in different forms. Here smoke formed is expressed as a function of time for some typical curves as shown in Figure 5 and total smoke formed in 5 min is given in Table II. Both intumescent [sample (ii)] and Visil [sample (iii)] when present alone, reduce amounts of smoke compared to the control sample [sample (i)]. When both Visil and intumescent are present there is considerable reduction in smoke [sample (iv)]. However, when the Visil–intumescent combination is present in fabric form, the values are higher, although the resin and glass contents in these samples are also different from that in other samples. Kynol with and without intumescent is not as effective as Visil in reducing smoke but it is less effective than the control sample.

Carbon monoxide and carbon dioxide. Average CO and CO_2 productions in 5 min are given in Table II. Visil

and Kynol fibers on their own do not seem to affect CO and CO_2 values. The intumescent additive, with and without fiber, reduces these values. For samples (vii)–(ix), the values are still less than or close to those for the control sample.

Derived cone parameters

The fire growth rate (FIGRA) index

The fire growth rate, described by Sundstrom,[17] is helpful in ranking the materials in terms of potential fire safety because it combines peak fire size (PHRR) and time to achieve this (time to peak, TTP). Thus

$$\text{FIGRA index} = \text{PHRR}/\text{TTP (kW/s)}$$

The FIGRA index[17] values calculated for all samples are given in Table III. As the results show, the presence of Visil fiber only [sample (iii)] reduces this index value. The presence of intumescent without [sample (ii)] and with Visil [sample (iv)] reduces the value compared to that of the control sample, although this system is not as effective as Kynol without [sample (v)] and with intumescent [sample (vi)].

Unitized HRR values

From Table I it can be seen that all these samples have different mass fractions of resin. Thus from the cone results given in Table II, for sample (i), the following equation for PHRR can be written, assuming that the 0.55 mass fraction of glass has a zero fuel level:

$$0.45\text{Ep} = 385 \text{ kW/m}^2 \qquad (1)$$

to yield Ep = 855.6 kW/m² per unit mass fraction.

In a similar manner, the following equations (each expressed as kW/m²) hold for samples (ii)–(iv):

TABLE III
Derived Cone Parameters for Composite Samples (i)–(ix)[a]

Sample[b]	FIGRA (kW/s)	PHRR (kW/m²)	THR (MJ/m²)	H_c (MJ/kg)	Residual mass (%)	Smoke (m²/m²)
(i)	6.4					
(ii)	5.8					
(iii)	5.4					
(iv)	5.6	231 (31)	16.5 (1.4)	16.0 (1.3)	30.1 (−2.1)	373 (122)
(v)	4.6					
(vi)	4.5	269 (85)	25.9 (−2.7)	18.4 (−1.6)	25.9 (−4.7)	576 (172)
(vii)	5.5	180 (186)	16.9 (7.3)	17.5 (−0.4)	47.3 (−19.1)	80 (818)
(viii)	4.1	110 (238)	15.4 (12.9)	16.8 (0.5)	57.6 (−28.6)	−203 (1073)
(ix)	6.0	466 (−21)	39.2 (−10.8)	24.1 (−4.3)	20.0 (1.3)	1020 (−213)

[a] Values in parentheses are the differences between calculated (presented here) and actual (from Table II) values. Except for residual mass, negative differences indicate a "less than additive" effect.
[b] As in Table I.

$$0.42Ep + 0.05Int = 278 \qquad (2)$$

$$0.42Ep + 0.05Vis = 329 \qquad (3)$$

$$0.40Ep + 0.05Vis + 0.05Int = 278 \qquad (4)$$

From eqs. (2)–(4), the effect on PHRR values for unit mass fractions of intumescent (Int), Visil (Vis), and (Vis + Int) can be calculated by substituting for Ep. Similar equations can be used for samples containing Kynol [samples (v) and (vi)]. The PHRR values calculated per unit of each additive with respect to unit resin are shown in Figure 6(a). Values for samples (ii)–(iv) are negative, indicating respective additive heat release rate–reducing properties. For Visil–intumescent combinations, respective calculated values (by averaging weighted component values) for each component are also given.

Figure 6(a) shows that unit mass fractions of intumescent and Visil alone reduce PHRR by 1620 and 600 kW/m^2, respectively. The combined effect of (Vis + Int) (−800 kW/m^2) is less than that of the additive compared with the calculated value of −1110 kW/m^2. However, Dabrowski et al.[18] showed that glass may react with phosphoric acid released from phosphate intumescents and so the simple eqs. (1)–(4) may be only approximate because they assume that glass is inert. Kynol and intumescent, on the other hand, increase the PHRR by 120 kW/m^2, whereas a decrease of 730 kW/m^2 is expected.

These unitized values are then used to calculate PHRR values for samples (iv), (vi), and (vii)–(ix) and are given in Table III. For sample (iv) the observed value is less than expected and for sample (vi) this difference is greater. Samples (vii) and (viii) show even greater differences that may be attributed to a layering effect of the Visil–Int fabrics present. In samples (i)–(vi) Vis and Int are additives and the glass-fiber mass fractions are the same [eight layers; see Experimental section], whereas in samples (vii)–(ix) the glass contents are different (see Experimental section), and so may exert varying filler effects, thus giving greater inconsistency in these latter results. Moreover, because Visil (or Kynol) and the intumescent in samples (iv)–(vi) are in pulverised additive forms, their high surface contact with resin will more likely affect the decomposition of resin and assist in crosslinking reactions, whereas in samples (viii) and (ix) there will be a reduced surface effect.

Other unitized parameters

Other parameters, THR, H_c, residual mass after 5 min, and smoke were calculated using equations similar to eqs. (1)–(4) by inserting respective values. For mass calculations, the mass of the glass was subtracted from the total mass residue and the results are given in Figure 6 and Table III.

THR values show effects similar to PHRR where, for example, the observed reduction in THR for Vis + Int [sample(iv)] is less than expected compared to the calculated value [see Fig. 6(b)], and increase for Ky + Int is also less than expected. For Visil-containing samples (iv), (vi), and (vii), THR is more than expected, whereas for Kynol-containing samples (v) and (ix), it is less than expected.

Residual mass values after 5 min for samples containing FR fiber and an intumescent are again slightly less than expected, as can be seen from Figure 6(c), which is contrary to results of thermal analytical studies as shown in Figure 1. This suggests that in an actual fire situation, although these additives help in char formation [see Fig. 4(b)], they do not work so efficiently under the slow heating conditions of TGA. For samples containing FR fiber and intumescent in fabric form, the lower than expected residual mass (see Table III) suggests that they do not mix and interact with resin fast enough to form a "char-bonded" structure.

Smoke results show trends similar to heat release parameters, as can be seen from Figure 6(d) and Table III, in that actual smoke reduction is less than calculated, although samples containing Visil show clearer comparative results than those of Kynol analogs.

CONCLUSIONS

Thermal analytical results indicate that there is resin–Kynol–intumescent interaction similar to the resin–Visil–intumescent interaction observed previously.[9,10] Moreover, resin–Visil–intumescent systems are comparable with and even better at enhancing residues at higher temperatures than the resin–Kynol–intumescent combination, where a high performance fiber is used. Cone calorimetric results also indicate similar behavior, in that when intumescent and FR fiber are used as additives, they reduce PHRR, THR, AvHRR, and smoke values. This effect is different from the one observed for similar polyester composites,[11] where, although PHRR and AvHRR were reduced, THR increased and HRR versus time curves became broader with higher flameout times. Thus, where in polyester laminates the presence of intumescent and FR fiber slowed but prolonged burning, in the epoxy samples reported here, overall burning tendencies are reduced. However, quantitative analysis of the separate and combined effect of the additives/components suggests that any interactions are less than additive, which is contrary to the thermal analytical results. A number of differences exist between the two sets of experiments with (i) the slow heating regime in thermal analysis, (ii) the effect of layered fabrics in com-
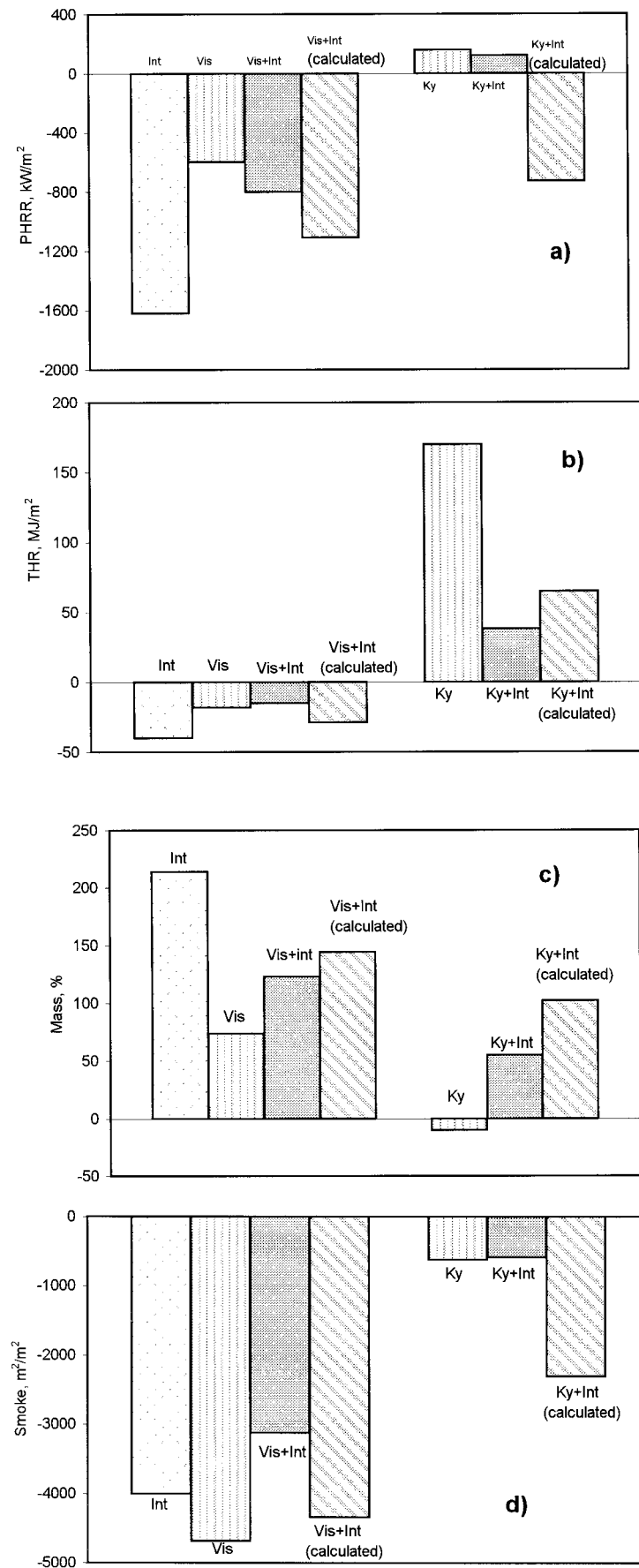
Figure 6 (a) Peak heat release rate (PHRR), (b) total heat release rate (THR), (c) residual mass after 5 min exposure, and (d) smoke production per unit mass fraction of additives in samples (ii)–(ix).

posites, and (iii) the assumed inertness of glass being of possible significance. Clearly, the observed less than additive fire performance in composites is of greatest concern and requires further investigation. The mechanical properties of these laminates and residual mechanical properties after heat/fire exposures are presented in a separate publication.

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