

The effect of intumescent on the burning behaviour of polyester-resin-containing composites

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Abstract

Recently we have shown that the introduction of an intumescent/flame retardant fibre system to a rigid composite comprising a textile reinforcing element (e.g. woven glass fabric layers) and a resin may generate additional char with respect to the additive contributions of all components present when studied using thermogravimetric techniques. This paper presents the results of cone calorimetric experiments of a series of composites comprising a combination of glass reinforcing elements, selected intumescent (based on melamine phosphate), the flame retardant Visil fibre and selected unsaturated polyester resins. Results show that the introduction of the intumescent/Visil can significantly reduce the peak heat release values and in some cases the peak smoke intensities evolved by composite samples exposed to 50 kW m⁻² heat flux. Furthermore, mass loss rates are reduced and residual chars are increased. There is a clear indication that we have established a novel route to increasing the fire resistant properties of rigid composites. © 2002 Published by Elsevier Science Ltd.

Keywords: A. Glass fibres; B. Mechanical properties; A. Resins; Flammability

1. Introduction

Unsaturated polyesters are widely used as resin components in composites used in naval constructions, offshore applications, waterpipes, chemical containments, building construction, automotive, etc. Their processing involves a radical polymerisation between a prepolymer that contains unsaturated groups and styrene that serves both as diluent for the prepolymer and as cross-linking agent. Unsaturated polyesters are very popular because of their low cost, easy processing, low densities, good corrosion resistance and high strength-to-weight ratios. However, standard unsaturated polyester resins are highly flammable and produce large quantities of smoke and toxic gases [1–3]. Their increasing commercial utilization demands the development of flame retardant systems to reduce fire hazards. Two common methods of flame retarding composites are use of thermal surface barriers like intumescent paints and ceramic fibres [4] or flame retardant additives [2]. Intumescent systems apart from being used as paints can also be used as additives in bulk polymers [5,6].

Our previous research [7–10] has shown that certain intu-

mescent in contact with char-forming fibrous polymers form complex, interactive, fibrous-intumescent chars. The interactive pyrolytic mechanisms of both components create a char-bonded structure, which is unusually resistant to oxidation. Flame retardant viscose fibres containing polysilicate (Visil, Sateri Fibres, Finland) or organophosphorus (Viscose FR, Lenzing, Austria)-based flame retardants char interactively with intumescent containing phosphate or polyphosphate components. During exposure to heat and flame, both fibre and intumescent components within the textile composite interact during thermal degradation stages to form a 'char-bonded' structure which has a greater mass than expected from the char yields of the individual components with respect to the original masses present. These have enabled textile composite materials to develop unusually high levels of flame and heat resistance. Recently, we have shown that the introduction of these intumescent/flame retardant fibre systems to thermoset (epoxy, polyester and phenolic) resins results in physical and chemical interaction of three components leading to enhanced char formation [11,12]. Based on this a patent has been filed for fibre reinforced (e.g. glass) rigid composite structures containing intumescent/flame retardant cellulosic fibre, which show superior flame retardant properties [13]. The intumescent/FR fibre combinations may be introduced either as a pulverized additive to the resin or as an additional textile fabric

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Table 1
Materials used in novel composite structures

Composite phase	Material no.	Description of material
Matrix resins:	i	A-polyester (Scott Bader): Orthophthalic, Crystic 471 PALV
	ii	B-polyester (Scott Bader): Isophthalic, Crystic 491 PA
Reinforcement fibre:	iii	E-glass in the form of woven roving (300 gm ⁻²)
	iv	E-glass in the form of random mat (300 gm ⁻²)
	v	E-glass in the form nonwoven web (450 gm ⁻²)
Intumescent components:	vi	Int1-Antiblaze NW (Rhodia Specialities Ltd): contains melamine phosphate and dipentaerythritol between 1:1–2:1 mass ratio
	vii	Int2-Antiblaze NH (Rhodia Specialities Ltd): contains melamine phosphate
Flame-retardant fibre:	viii	Visil (Sateri Fibres, Finland): cellulosic fibre containing polysilicic acid, in pulverised form
	ix	Visil, nonwoven web (120 gm ⁻²)
FR fibre/intumescent:	x	Visil-Int1 (180 gm ⁻²)
	xi	Visil-Int2 (180 gm ⁻²)
	xii	Visil-Int2 (240 gm ⁻²) (prepared by padding on to Visil nonwoven fabric both intumescent (50/100% w.r.t. fibre wt) and Vinamul 3303 resin (15% w.r.t. intumescent)

layer to the composite structure [13]. In the present work, the mechanical and fire performance of different polyester composite laminates containing flame retardant cellulosic fibre/intumescent both in fabric form and additives, are presented.

2. Experimental

2.1. Samples

Materials used for the preparation of various laminates are given in Table 1. Two types of laminates have been prepared—one containing no glass fibre reinforcement (A1–A10) and the other containing E-glass fibre in the form of random mat (B1–B4, C1–C6) and woven roving (D1–D4). The description of samples, respective components used, amount of components present (mass fractions) and thicknesses of the laminates are given in Tables 2–4.

2.1.1. Composite preparation

The laminates were prepared by a hand lay up technique, which involved impregnating required number of layers of respective fabrics with resin, pressing them all to the same thickness and curing at room temperature for 48 h.

2.2. Testing equipment

2.2.1. Mechanical performance

To establish the potential usefulness of each composite in terms of a structural component and whether the addition of an intumescent and/or fibre components reduces mechanical properties, the generic mechanical (flexural and tensile) properties were measured using coupons (200 × 20 mm²) with end tabs for tensile testing. A small proportion of these coupons had strain gauges bonded on their surfaces to verify the testing machine results.

The flexural performance was measured in a four point bending mode and by using engineers' bending theory [14] stress, modulus and strain were calculated. Tests were

Table 2
Composite samples without glass fabric reinforcement

Sample no.	Materials used from Table 1	Sample	Mass fraction (%)		Thickness (mm)	LOI (%)
			Fibre and/or Int	Resin		
A1	i	Resin A	–	100	2.2	18.0
A2	i, ix	Four layers of Visil/resin A	14.4	85.6	2.8	18.8
A3	i, x	Four layers of Visil-NW/resin A	19.2	80.8	3.3	20.6
A4	i, xi	Four layers of Visil-NH/resin A	18.7	81.3	3.4	20.9
A5	i, v	One layer of glass/resin A	14.2	85.8	2.2	18.3
A6	ii	Resin B	–	100	2.9	–
A7	ii, ix	Four layers of Visil/resin B	19.4	80.6	2.0	–
A8	ii, x	Four layers of Visil-NW/resin B	24.0	76.0	2.6	–
A9	ii, xi	Four layers of Visil-NH/resin B	23.4	76.6	2.8	–
A10	ii, v	One layer of glass/resin B	19.7	80.3	1.5	–

Table 3

Composite samples with glass fabric reinforcement (note: samples C5 and C6 were prepared to get their thickness similar to C4)

Sample no.	Materials used from Table 1	Sample details
Series B (represents 'standard' glass-reinforced composites)		
B1	i, iv	Two layers of random glass/resin A
B2/C1	i, iv	Four layers of random glass/resin A
B3	i, iv	Six layers of random glass/resin A
B4	i, iv	Eight layers of random glass/resin A
Series C		
C1	i, iv	Four layers of random glass/resin A
C2	i, iv, vii	Four layers of random glass/resin A + Int2 (Int 10% w.r.t. resin A wt)
C3	i, iv, vii, viii	Four layers of random glass/resin A + Visil + Int (Visil + Int, 20% w.r.t. resin A wt)
C4	i, iv, xii	Three layers of random glass and two layers of Visil-Int2 fabric sandwiched in between/resin
C5	i, iv, vii	Five layers of random glass/resin A + Int2 (Int 10% w.r.t. resin A wt)
C6	i, iv	Seven layers of random glass/resin A
Series D		
D1	i, iii	Four layers of woven glass/resin A
D2	i, iii, vii	Four layers of woven glass/resin A + Int2 (Int 10% w.r.t. resin A wt)
D3	i, iii, vii, viii	Four layers of random glass/resin A + Visil + Int (Visil + Int, 20% w.r.t. resin A wt)
D4	i, iii, xii	Three layers of woven glass and two layers of Visil- Int2 fabric sandwiched in between/resin

undertaken within the elastic range of the material in order to enable further tests to be carried out on the coupons.

The tensile tests were conducted on a Dartec Universal testing machine with load and displacement control, at a cross-head speed of 1 mm min⁻¹ and load cell of 50 kN. The gauge length of each specimen was 100 mm and polymeric tabs were bonded on to their ends for gripping and to ensure failure within the gauge region. The loads and displacements were measured via a load cell and linear

variable differential transformers (LVDT) connected to an Intercol data logging system. Where strain gauges are attached (orthogonal), pairs were bonded to the outer surface and attached to the same data logging system.

2.2.2. Flammability

Limiting oxygen index (LOI): A Stanton-Redcroft LOI FTA analyser was used to determine LOI values according to a standard procedure [15].

Table 4

Details of composite samples with glass fabric reinforcement

Sample no.	Vol. fraction glass (%)	Mass fraction (%)				Thickness (mm)	LOI (%)
		Glass	Resin	Visil	Int		
B1	23.9	40.2	59.8	–	–	1.4	–
B2	24.1	40.4	59.6	–	–	2.7	–
B3	24.0	40.3	59.7	–	–	4.1	–
B4	25.3	42.0	58.0	–	–	5.7	–
C1	23.7	39.9	60.1	–	–	2.7	19.3
C2	16.4	29.5	64.2	–	6.3	3.8	22.6
C3	14.0	25.8	62.0	6.1	6.1	4.6	22.6
C4	10.0	19.2	72.5	8.3 ^a	8.3 ^a	5.0	21.5
C5	18.4	32.5	61.4	–	6.1	4.6	22.6
C6	26.7	43.8	56.2	–	–	4.7	20.5
D1	40.0	62.7	37.3	–	–	1.0	–
D2	38.5	57.2	38.8	–	3.8	1.2	–
D3	31.5	49.6	42.2	4.1	4.1	1.5	–
D4	8.7	21.7	65.1	13.2 ^a	13.2 ^a	4.3	–

^a Visil-Int2 fabric.

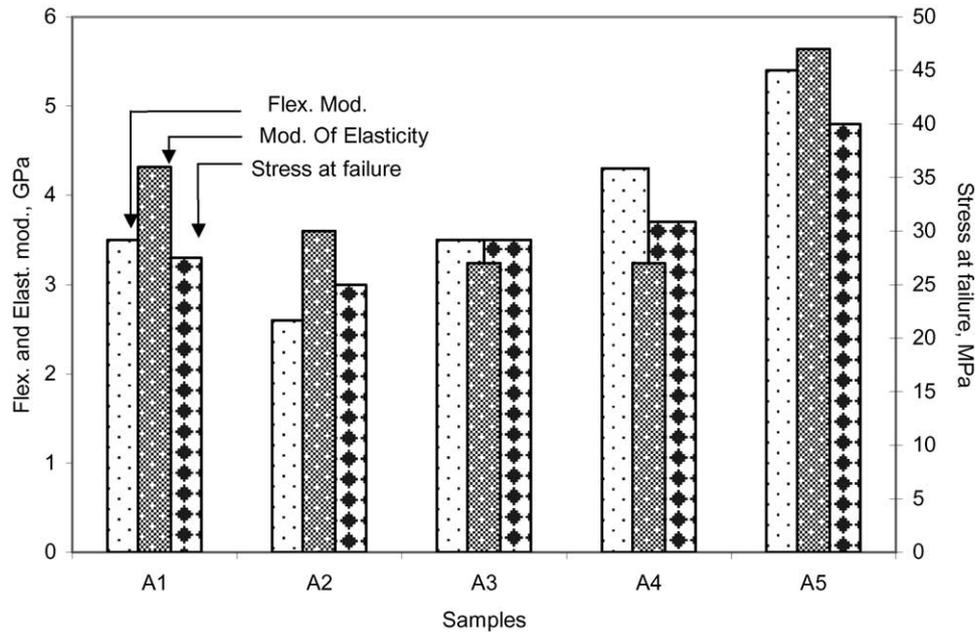


Fig. 1. Flexural and tensile properties of composite samples without glass reinforcement.

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 conditions to expose $100 \times 100 \text{ mm}^2$ fabric samples according to ISO 5660 [16].

3. Results and discussion

3.1. Samples without glass reinforcement (A1–A10)

Flexural and tensile testing results of samples A1–A10 showed that when Visil and Visil-Int fabrics are used as reinforcement (samples A2–A4, A7–A9) both tensile and flexural moduli are in the range 2.6–4.3 GPa and are similar to those for pure resins (A1 and A6,

range 2.2–3.7 GPa), but are slightly less than when nonwoven glass fibre is present (A5 and A10, range 4.4–5.4 GPa). As an example, the results for samples A1–A5 are shown in Fig. 1.

LOI, which is a measure of flammability of the samples, is the minimum concentration of oxygen in oxygen/nitrogen mixture that will just support combustion. The results for A1–A5 samples are given in Table 2. When Visil fabric is used for the preparation of the laminate (sample A2), there is little effect on the value of LOI compared to pure resin (sample A1, LOI = 18.0). However, when Visil-Int fabric is used in samples A2 and A3, the LOI values increase to 20.6 and 20.9, respectively. The presence of glass fibre (sample A5) does not affect the LOI compared to the pure resin value.

Cone calorimetry: The various parameters recorded by the cone calorimeter are given in Table 5 and selected

Table 5
Cone calorimetric results for composite samples without glass fabric reinforcement at 50 kW m^{-2} heat flux

Sample	TTI (s)	Flameout (s)	Peak HRR (kW m^{-2})	THR (MJ m^{-2})	Average values from ignition to 5 min				Smoke at 600 s ($\text{m}^2 \text{ m}^{-2}$)
					HRR (kW m^{-2})	H_c (MJ kg^{-1})	CO yield (kg kg^{-1})	CO ₂ yield (kg kg^{-1})	
A1	29	570	729	59.5	183	20.1	0.06	1.8	4547
A2	32	550	422	63.1	193	18.7	0.05	1.80	5447
A3	38	616	307	71.4	200	16.7	0.05	1.57	5656
A4	30	622	311	77.0	213	17.5	0.05	1.55	4894
A5	37	479	337	50.5	157	19.9	0.05	1.86	3701
A6	34	606	1133	78.4	234	13.9	0.09	4.17	4554
A7	31	463	600	51.2	165	20.0	0.05	1.96	2192
A8	38	614	466	60.6	180	18.7	0.04	1.60	3137
A9	45	595	457	55.8	166	18.5	0.05	1.60	3062
A10	36	337	487	38.0	123	20.9	0.05	1.94	2018

results are shown in Fig. 2(a–f). As can be seen from Table 5, time to ignition (TTI) for all the samples is quite similar and is not affected by Visil or Visil-Int addition. However, total time to burn (flameout) varies depending on the amount of resin in the sample. Generally samples with Visil and/or intumescent (A2–A4, A7–A9) burn slowly and for longer time compared to pure resin (A1, A6) and resin with glass (A5, A10) composites. Moreover, curves for heat release rate (HRR) (Fig. 2(a)), CO, CO₂ and smoke production (Fig. 2(d)) show that for pure resin (A1, A6), there is a sharp peak representing rapid volatilisation leading to high peak HRR and shorter duration of burning. When Visil and Visil-Int (A2–A4, A7–A9) are present, the peak becomes less intense and curve is broader indicating reduction in volatilisation due to condensed phase activity of Visil and Visil-Int [8–10]. This effect is seen more in samples containing Visil-Int fabric (A3, A4, A8, A9) where the peak is reduced further than Visil containing samples (A2, A6) and another peak appears in these samples, which indicates that condensed phase activity of Visil-Int component helps in char formation [12], which then oxidises and burns. In glass-containing samples (A5, A10) similar reduction in volatilisation is observed, which is purely a physical effect where glass acts as a filler and slows down the migration of volatile products to the burning zone.

HRRs for samples A1–A5 as function of time are shown in Fig. 2(a) and peak heat release and average HRR values of all the samples are given in Table 5. Peak HRR values for pure resins A1 and A6 are 729 and 1133 kW m⁻², respectively, which is reduced to 422 (A2) and 600 kW m⁻² (A7), when Visil fibre is present. Peak heat release values are further reduced on addition of Visil-Int fibre combination in samples A3 (307 kW m⁻²), A4 (311 kW m⁻²), A8 (466 kW m⁻²) and A9 (457 kW m⁻²). These values are even lower than for respective samples when glass fibre only is used (samples A5 and A10 with values 337 and 487 kW m⁻², respectively). Moreover, this reduction in peak HRR occurs despite very low Visil/Int content in these samples (Table 2). However, total heat release (THR) and average HRR values for these samples containing Visil and Visil-Int fibre are higher than for pure resin and sample containing glass fibre (Table 5). The reason is that these samples burn slowly but for longer times. Effective heat of combustion, which is the quantity of heat produced by combustion of a unit quantity of a material, decreases with addition of Visil fabric in the resin (samples A2 and A7), and further reduces on addition of Visil-Int fabrics (samples A3, A4, A8, A9) as can be seen from Table 5.

Thermal stabilities of the samples as represented by mass loss curves (Fig. 2(b)) are also affected by Visil-Int contents. The latter samples are more thermally stable and more char is left behind at any given time. The residual mass at 5 min are shown in Fig. 2(c). This

supports our previous findings by thermal analytical studies that these components produce more char than expected [11,12].

Carbon monoxide and carbon dioxide production for all samples are given in Table 5. The total amount produced for Visil and Visil-Int containing samples is less than for pure resin, but as the burning behaviour of the samples change, CO and CO₂ production also changes with a series of lower intensity peaks at longer times. Generally Visil and Visil-Int containing samples produce CO and CO₂ in lower amounts but for longer times.

Smoke production varies and depends upon burning behaviour of the samples. Samples with Visil-Int combinations produce less smoke initially but evolution carries on for longer times as can be seen from Fig. 2(d). Hence, total smoke produced after 10 min is higher than for pure resin and glass-containing samples (Table 5).

3.2. Samples with glass reinforcement

Based on results of A-series, one resin ((i) from Table 1) and one intumescent (Int2 (material vii) from Table 1) were selected for investigation in combination with glass reinforcement. Three series of samples were prepared. Samples B1–B5 contain only glass reinforcement without any additives and were prepared to observe the effect of thickness of the laminates on their performances. Samples C1–C6 contain glass as random mat and D1–D4 as woven roving reinforcement. The mechanical performance and cone results of these samples are shown in Figs. 3–6 and Table 6.

3.2.1. Standard glass reinforced composite laminates (B1–B4): effect of thickness

Flexural and tensile properties: Flexural moduli of samples B1–B4 are in the range 7.7–10.2 GPa and increases as glass content increases (Table 3), whereas, tensile moduli (range 6.3–7.5 GPa) are less affected by thickness. This may be due to fact that flexural properties depend upon the placement of reinforcement within the thickness of the sample [17] whereas, for tensile properties, position is independent of thickness.

Cone calorimetry: Cone results of samples B1–B4 show that as thickness (Table 3) of the laminates increases, TTI and also duration of burning (flameout time) increases. When sample thickness becomes equivalent to being thermally thick (i.e. the heat wave penetration depth is less than the physical depth) stage, TTI is less affected and burning slows down [18]. HRR curves are shown in Fig. 3(a). Peak HRR values decrease with thickness (from 451 kW m⁻² in sample B1 to 260 kW m⁻² in sample B4, but as thick samples burn for longer times, THR and AvHRR values increase. Sample B4 is more thermally thick than B1–B3, burns more slowly initially and for a longer time (Table 6), hence, average HRR after 5 min is lower than for sample

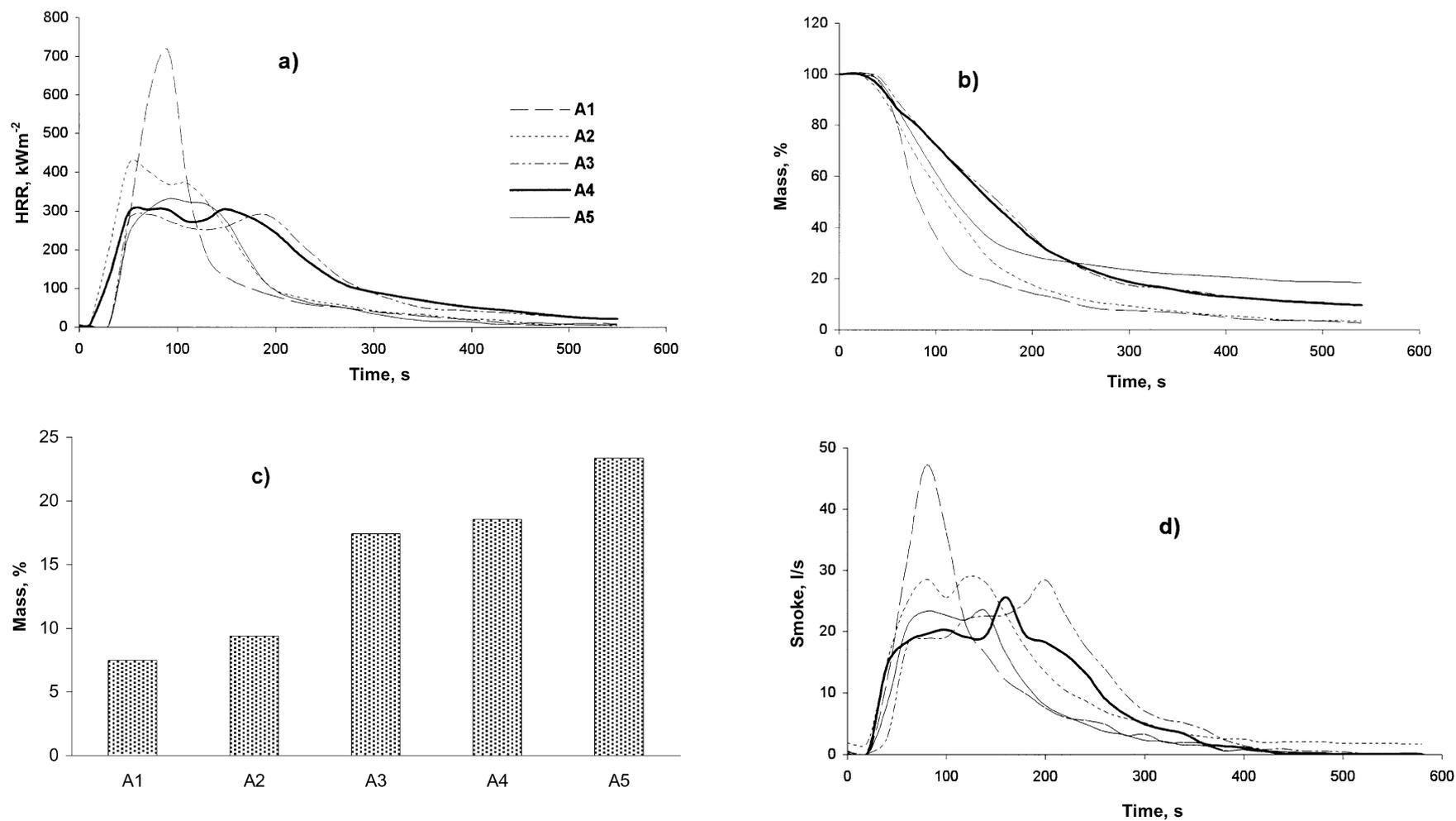


Fig. 2. Cone calorimetric parameters of A1 (---), A2 (---), A3 (---), A4 (—) and A5 (—) samples at 50 kW m^{-2} heat flux: (a) HRR versus time; (b) mass loss versus time; (c) residual mass after 5 min; (d) smoke production versus time.

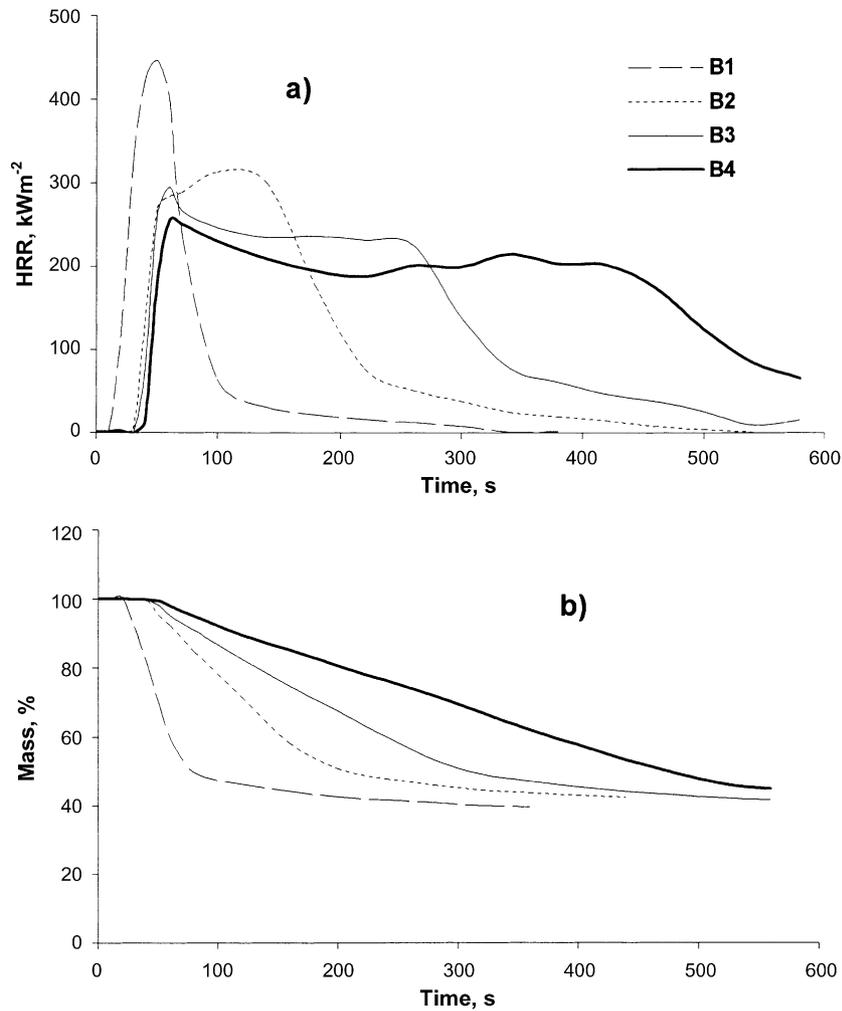


Fig. 3. Cone calorimetric parameters of B1 (---), B2 (···), B3 (—), and B4 (—) samples at 50 kW m⁻² heat flux: (a) HRR and (b) mass loss versus time.

B3. Effective heats of combustions for these samples, as expected remain constant (Table 6) since the same unit mass is burning at a particular time. Mass loss curves in Fig. 3(b) show that thermally and physically thin samples burn quickly losing mass quickly, whereas for thicker samples mass loss rates are slower. CO, CO₂ and smoke production are spread over longer times, i.e. initially, values are reduced but the total values increase with increase in thickness because they burn for longer times as can be seen from smoke results in Table 6.

3.2.2. Samples C1–C6

Samples C1–C3 have the same amount of resin and glass content (four layers of glass) with and without selected additives (intumescent and Visil/intumescent), and have different thicknesses (Table 4). As can be seen from above discussion, thickness of the laminates affects both the mechanical and fire performance. Hence, samples C5 and C6 were prepared to give thicknesses similar to sample C3 although component contents are different. Sample C4

contains Visil-NH fabric as in samples A4 and A9. Mechanical testing results are shown in Fig. 4(a), which show that the trends of the flexural and tensile moduli are the same. Both flexural and tensile moduli decrease slightly with additives. But when the moduli are normalised with respect to glass content, the moduli of the samples containing additives (C2 and C3) are higher than control sample C1 as can be seen from Fig. 4(b), where unit tensile moduli of these samples are presented.

LOI: LOI results are given in Table 4. Intumescent presence slightly increases the value of LOI with respect to standard sample (C1) from 19.3 to 22.6 (C2 and C5) and is not affected by thickness of the laminate (samples C2 and C5) and additional presence of Visil (C3 with LOI 22.6). The sample C4 sample containing Visil-NH fabric has a similar LOI value of 21.5.

Cone calorimetry: Cone results in Table 6 show that TTI is not much affected by the presence of additives but flame-out time is different for all samples depending upon the resin content and thickness of the laminate. HRR curves are

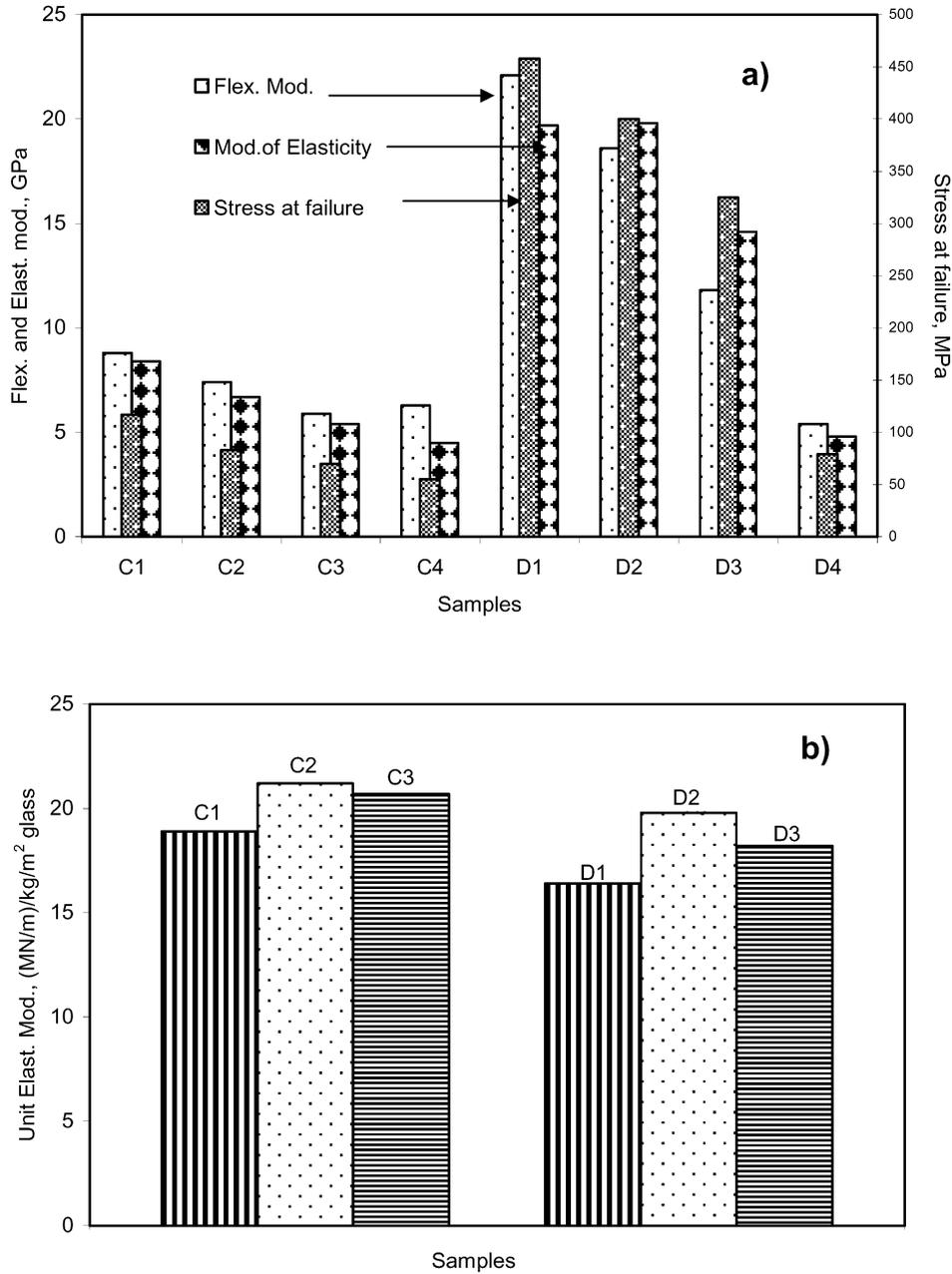


Fig. 4. (a) Flexural and tensile properties; (b) unit tensile moduli of composite samples with glass reinforcement.

shown in Fig. 5(a and b). In Fig. 5(a) samples have the same amount of resin (C1–C3) (Table 6) and show that presence of intumescent (sample C2) decreases the peak HRR value of resin only (C1) from 314 kW m^{-2} . Further addition of Visil (sample C3) reduces it further to 246 kW m^{-2} . However, with additives present, the HRR curves are broader. Average HRR for 300 s and THR values increase which reflect the added fuel content of the Visil component. The effective heat of combustion decreases from sample C1 to C3 from 19.9 to 16.0 MJ kg^{-1} , showing the influence of additives on the release of volatiles during pyrolysis.

As can be seen from discussion for samples B1–B4, thickness of the samples influences burning behaviour and hence, HRR considerably. In Fig. 5(b), the samples have the same thickness but different resin and glass contents (C3, C5 and C6). Peak HRR is higher in sample C5 but THR and AvHRR are quite similar in all samples. Effective heat of combustion, however, shows the same trend as samples C1–C3, i.e. for the sample with no additive (C6) it is 19.7 MJ kg^{-1} , which reduces with addition of intumescent (C5) and Visil/intumescent (C3) to 17.3 and 16.0 MJ kg^{-1} , respectively. This reflects the effect the additives have on volatile fuel formation.

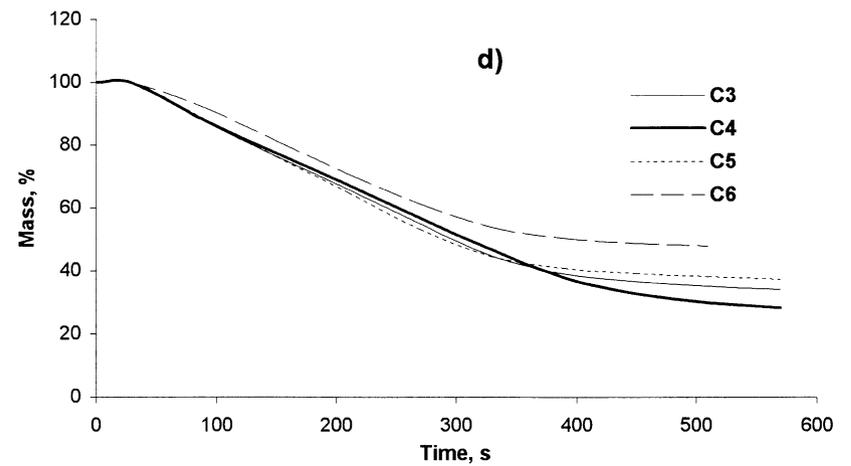
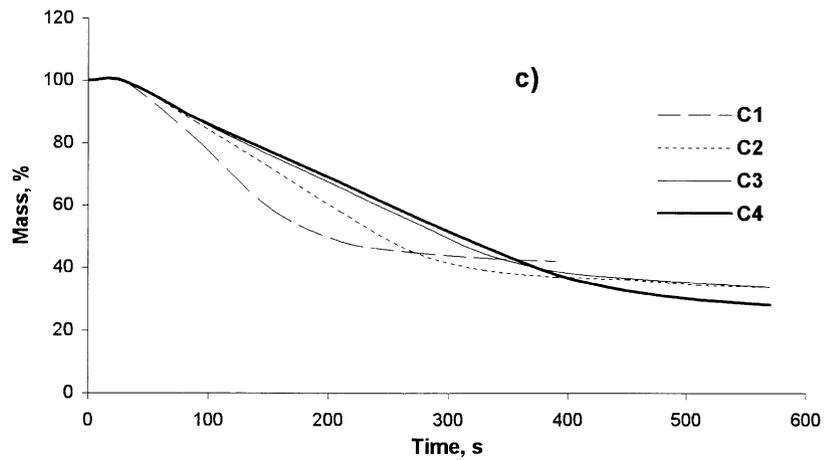
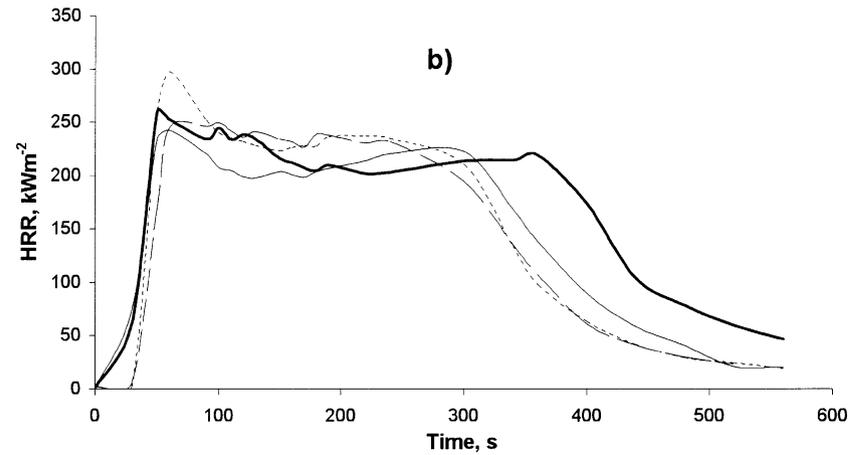
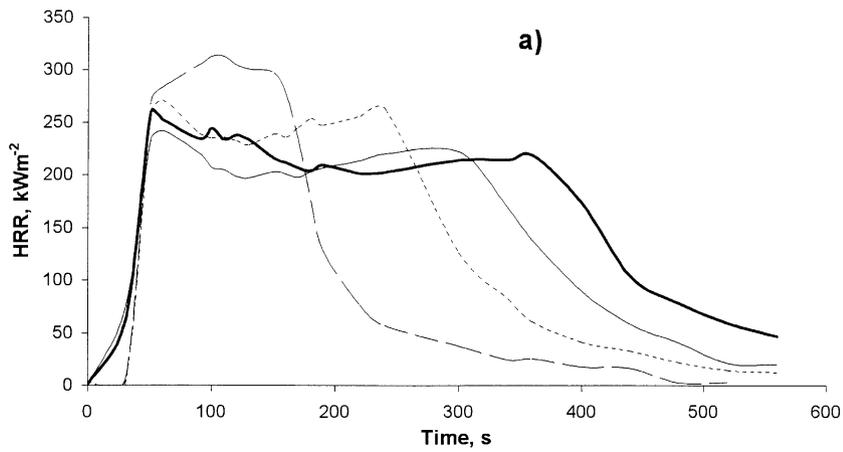


Fig. 5. Cone calorimetric parameters of C1, C6 (---), C2, C5 (···), C3 (—), and C4 (—) samples at 50 kW m^{-2} heat flux: (a,b) HRR and (c,d) mass loss versus time.

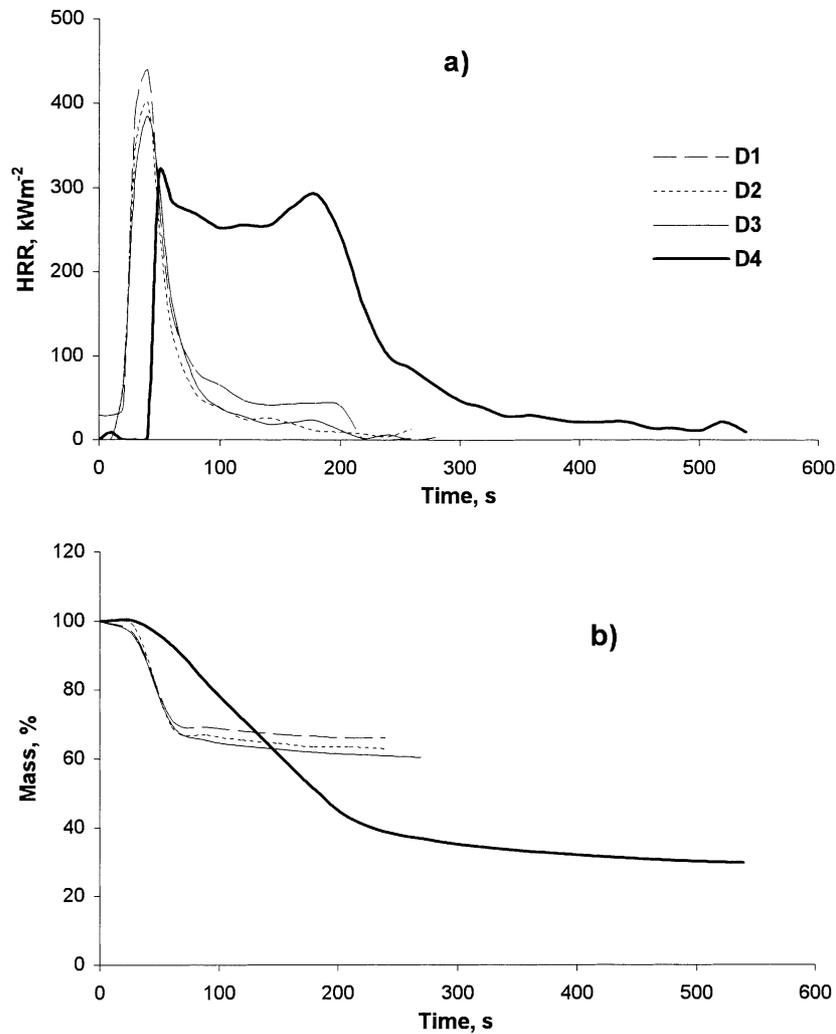


Fig. 6. Cone calorimetric parameters of D1 (---), D2 (···), D3 (—), and D4 (—) samples at 50 kW m⁻² heat flux: (a) HRR and (b) mass loss versus time.

Table 6

Cone calorimetric results for composite samples with glass fabric reinforcement at 50 kW m⁻² heat flux

Sample	TTI (s)	Flameout (s)	Peak HRR (kW m ⁻²)	THR (MJ m ⁻²)	Average values from ignition to 5 min				Smoke (m ² m ⁻²)	
					HRR (kW m ⁻²)	H _c (MJ kg ⁻¹)	CO yield (kg kg ⁻¹)	CO ₂ yield (kg kg ⁻¹)	at 120 s	at 600 s
B1	17	428	451	26.9	88	20.3	0.06	1.57	1264	1336
B2/C1	37	490	314	52.3	162	19.9	0.05	1.68	1403	2695
B3	40	660	309	73.8	215	19.2	0.04	1.67	1155	3845
B4	44	793	260	99.8	177	19.1	0.04	1.63	1027	5213
C2	38	680	276	74.1	206	17.6	0.05	1.58	1239	4071
C3	30	665	246	80.3	190	16.0	0.04	1.46	1223	4725
C4	30	710	264	94.9	197	17.2	0.04	1.55	1184	5241
C5	41	712	297	80.6	206	17.3	0.03	1.54	1283	4600
C6	44	581	269	75.8	196	19.7	0.04	1.67	986	3594
D1	26	217	477	21.4	81	19.8	0.06	1.83	598	607
D2	19	214	402	16.3	61	19.0	0.01	1.44	735	736
D3	22	239	387	17.6	62	18.6	0.08	1.54	748	753
D4	48	543	356	58.7	176	17.6	0.05	1.60	1152	2981

Table 7
NBS smoke test under flaming conditions for duration of 240 s

Samples	Max. specific optical density	Time to $D_s = 16$ (s)	Smoke obscuration index
C1	687	40	170,153
C2	623	28	204,538
C3	230	54	16,821
C4	503	38	88,453
C5	300	44	31,346
C6	527	48	86,322

Mass loss curves in Fig. 5(c and d) indicate that presence of intumescent (C2) and Visil/intumescent (C3) make them more thermally stable by slowing down volatilisation and burning. CO, CO₂ and smoke production for these samples also show the same variations as HRR values. Average CO and CO₂ values produced after 300 s are not much altered with additives (Table 6), reflecting total carbon contents. Total smoke production if considered for a shorter period (120 s), decreases on addition of intumescent (C2) and Visil/intumescent (C3) but over the longer time period (600 s), the values increase as can be seen from Table 6.

NBS smoke chamber test [19] results for these samples are shown in Table 7. Results indicate that on addition of intumescent in sample C2, maximum optical density is reduced from 687 to 623 (sample C1). On further addition of Visil, it is reduced to 230 in sample C3. For sample C4, the value (503) is still lower than from sample C1. These values are for 240 s which correlate with smoke results for cone for 120 and 300 s, where a decreasing trend is observed with the presence of additives, indicating reduction in volatiles formation. However, since the additives increase carbon content (char formation), average and total smoke production increase over a longer period (e.g. 600 s).

3.2.3. Samples D1–D4

These samples contain glass fabric in the form of woven roving and are meant to have improved tensile properties compared with C-series samples, which is evident from the mechanical testing results shown in Fig. 4(a) and the presence of additives shows similar effects to those in the C-series (Fig. 4(b)). However, for samples D2 and D3 flexural moduli are lower than tensile moduli, which may be due to the presence of voids in the laminates as woven glass mat is used in these samples.

Cone calorimetric results in Fig. 6(a and b) and Table 6 also show similar trends with respect to composition. In spite of thicknesses of the samples being varied (Table 4), TTI and flameout times for all the samples are quite similar. Peak HRR values for these samples are higher than for C-series samples, since they are thinner and hence, burn more quickly, but the effect of additives is similar, i.e. presence of intumescent decreases peak HRR from 477

(sample D1) to 402 kW m⁻² (sample D2), which is further reduced to 387 kW m⁻² with additional presence of Visil (sample D3). THR and average HRR values also decrease with additives, contrary to results in C-series. This is due to a thickness effect, since these are thermally and physically thin, they quickly volatilise and burn for a shorter time compared to C-series, as can be seen from their flameout times in Table 6. Effective heat of combustion shows the same trend but the decrease in values with additives is less than the C-series (Table 6). CO, CO₂ and smoke production are less than C-series samples, but trends are similar.

Samples C4 and D4 which contain Visil-Int fabric are mechanically weaker than samples C3 and D3 containing these components as additives in resins. Since the glass content for these samples are different, they cannot be directly compared, although peak HRR values in the former samples are reduced but THR and AvHRR values are increased as they burn for longer times, reflecting greater thickness and hence mass of combustible material. CO, CO₂ and smoke emissions also increase.

Normalised HRR values: In order to compare the burning behaviour of samples containing additives, HRR parameters for all the samples in Table 6 were normalised to unit mass fraction of the resin (while ignoring glass and additive masses) and are shown in Fig. 7. Fig. 7(a) shows the thickness affect, PHRR decreases whereas, THR increases with increase in thickness. This effect is more evident in samples D1 and B2, which contain the same amounts of glass but in different forms. These are woven roving and random mat, respectively (Table 3) and have different thicknesses (Table 4). Samples B1–B5 have different thicknesses because of different layers of glass. Thus glass layers are acting as fillers by slowing down the migration of the resin to the burning zone.

In Fig. 7(b), PHRR and THR values of samples C1–C6, normalised to unit mass fraction of resin are shown, where effect of additives is more evident. When the thicknesses of the samples are different (same amount of glass (Table 3)), intumescent without and with Visil presence reduces PHRR by 18 and 24%, and increases THR by 33 and 48%, respectively. However, when thicknesses are same (but different glass amounts, and hence filler effects) intumescent presences has no effect on PHRR, additional presence of

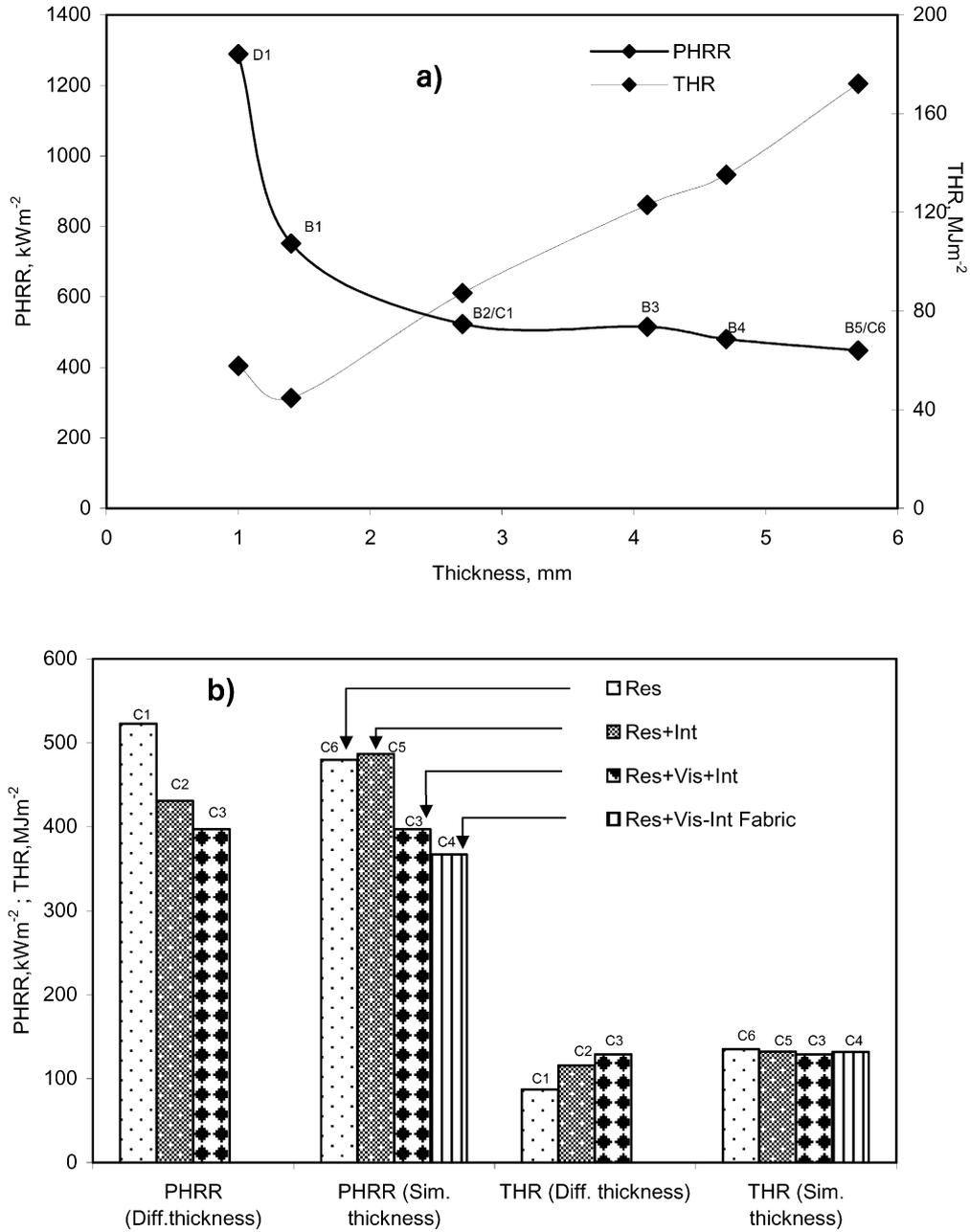


Fig. 7. Effect of (a) thickness and (b) additives on derived heat release parameters.

Visil reduces it to 17%. THR for samples with similar thicknesses is not affected.

4. Conclusions

Cone results for series A show that Visil-Int fabric inclusion significantly decreases the flaming behaviour of resin. The intumescent component in Visil-Int fabric acts in the condensed phase, reducing volatilisation and increasing char formation. However, Visil-Int fabric does not act as mechanical reinforcement, as seen from test results.

Flexural results are not much affected compared to pure resin. This shows that they have rigidity but not strength as evident from tensile results. However, when these components are used along with glass fabric either as additives in the resin or as a fabric as an extra layer, they do not reduce mechanical performance as shown in Fig. 4(b). Unfortunately, their presence does not reduce burning behaviour as significantly as was previously expected by thermal analytical results [11,12]. It is possible that glass itself acts as a filler which physically impedes burning by acting as a barrier to volatile formation and its migration to the burning zone. This effect can be seen in the B-series

samples, where by increasing thickness of the sample, burning behaviour is changed. When Visil-Int as additive or in fabric form is present along with glass fabric, the low content of intumescent (3–6% (Table 4)) cannot generate enough condensed phase activity to add further to the physical effect of the glass. Future work will involve increasing intumescent content to observe this effect.

It can be suggested, however, that samples in A-series can be used for applications, where strength is not a significant issue, as it will replace glass, which is more expensive and dense, or they can be used as protective coatings on the thick laminates.

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References

- [1] Scudamore MJ. Fire performance studies on glass-reinforced plastic laminates. *Fire Mater* 1994;18:313.
- [2] Egglestone GT, Turley DM. Flammability of GRP for use in ship superstructures. *Fire Mater* 1994;18:255.
- [3] Mouritz AP, Mathys Z. Post-fire mechanical properties of marine polymer composites. *Compos Struct* 1999;47:643.
- [4] Sorathia U, Rollhauser M, Hughes WA. Improved fire safety of composites for naval applications. *Fire Mater* 1992;16:119.
- [5] Kovar RF, Bullock DE. In: Lewin M, editor. Multifunctional intumescent composite firebarriers, Recent advances in flame retardancy of polymeric materials, vol. IV. Stamford: BCC, 1993. p. 87.
- [6] Bras ML, Camino G, Bourbigot S, Delobel R, editors. Fire retardancy of polymers. The use of intumescence. Cambridge: RSC, 1998.
- [7] Horrocks AR, Anand SC, Hill B. Fire and heat resistant materials. UK Pat. 2279084B, 21.06.1995.
- [8] Horrocks AR, Anand SC, Sanderson D. Complex char formation in flame retarded fibre-intumescent combinations: I. Scanning electron microscopic studies. *Polymer* 1996;37:3197.
- [9] Kandola BK, Horrocks AR. Complex char formation in flame retarded fibre-intumescent combinations: II. Thermal analytical studies. *Polym Degrad Stab* 1996;54:289.
- [10] Kandola BK, Horrocks AR. Complex char formation in flame retarded fibre-intumescent combinations: III. Physical and chemical nature of char. *Text Res J* 1999;69(5):374.
- [11] Kandola BK, Horrocks AR, Myler P, Blair D. Flame retardant properties of novel fibre-reinforced composite materials. Flame retardants 2000, Westminster, London/UK: Queen Elizabeth II Conference Centre/Interscience Communication Ltd, 2000. p. 217.
- [12] Kandola BK, Horrocks AR, Myler P, Blair D. Thermal characterization of thermoset matrix resins. In: Nelson GL, Wilkie CA, editors. Fire and polymers, ACS Symposium Series. ACS, Washington, DC, 2001. p. 344.
- [13] Horrocks AR, Myler P, Kandola BK, Blair D. Fire and heat resistant materials. Patent Application PCT/GB00/04703 December, 2000.
- [14] Tsai SW, Hahn HT. Introduction to composite materials. Technomic Publ. Co. Inc, Pennsylvania, 1980. Chapter 5, p. 167–216.
- [15] ASTM D 2863-87. Standard test method for measuring the minimum oxygen concentration to support candle-like combustion of plastics (oxygen index). ASTM, Philadelphia, PA, USA.
- [16] ISO 5660-1. Fire tests—reaction to fire—part 1: rate of heat release from building products (Cone calorimetric method), Geneva, Switzerland: International Standards Organisation, 1993.
- [17] Kitching R, Tan AL, Abu-Mansour TMN. The influence of through thickness properties on glass reinforced plastic laminated structures. *J Compos Struct* 1984;2:105–51.
- [18] Babrauskas V, Parker WJ. Ignitability measurements with the cone calorimeter. *Fire Mater* 1987;11:31–43.
- [19] ASTM E 662-83. Standard test method for specific optical density of smoke generated by solid materials. ASTM, Philadelphia, PA, USA.