Use of high performance fibres and intumescents as char promoters in glass-reinforced polyester composites

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Abstract

This work reports the development of novel glass fibre-reinforced composite materials containing a commercially available polyester resin, a phosphate - based intumescent and inherently flame retardant polybenzimidazole (PBI, Celanese), cellulosic (Visil, Sateri), phenol-formaldehyde (Kynol) and oxidised acrylic (Panox) fibres. The intumescent and flame retardant fibre components are added as additives in pulverized form to the resin component of the composite laminate. Thermal stability, char formation and flammability properties of these novel structures are studied by cone calorimetry. The results are discussed in terms of the effect that these char-forming fibres have on promoting further char formation and hence, altering the burning behaviour of resin-intumescent composites.

Keywords : Polyester ; Composites ; Intumescents ; Flame retardant fibres ; Flammability ; Cone calorimetry

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1. Introduction

Certain intumescent systems, when dispersed with flame retardant cellulosic eg Visil (Sateri, Finland), Viscose FR (Lenzing), Proban-treated cotton (Rhodia Specialities Ltd) ; aramid eg, Nomex (DuPont) ; phenolic eg, Kynol (Kynol, Japan) ; melamine-formaldehyde eg, Basofil (BASF, Germany) ; oxidised acrylic eg, Panox (Sigri) and hetero-aromatic eg, PBI (Celanese) fibres, form a char bonded structure which enhances their flame and heat resistant properties [1-4]. These have enabled textile composite materials to develop unusually high levels of flame and heat resistance. We have used these interactive fibre-intumescent systems to enhance the char - forming property of polymeric resins in glass-reinforced rigid composites [5]. Thermal analytical results have indicated that when these components are added to thermoset (polyester, epoxy and phenolic) resins, there are chemical and physical interactions beween all three components resulting in increased char formation [6]. Based on this study, novel glass-reinforced polyester and epoxy composites containing different intumescents and FR fibres were also prepared. FR fibre and intumescent components in these structures were added both as additives in pulverized form and as fibres interdispersed with intumescent as a fabric scrim for partial replacement of glass fibre [7-9]. In this paper similar composite laminates have been prepared, where Visil fibre is replaced with PBI, Kynol and oxidised acrylic fibres. The flammability of these laminates has been evaluated by cone calorimetry and effects of different types of fibres on resin-intumescent combinations have been compared.

2. Experimental

2.1. Composite laminate samples

2.1.1. Materials

Resin :	Polyester resin - Orthophthalic, Crystic 471 PALV (Scott Bader)
Reinforcing fibre :	E-glass in the form of woven roving (300 gm^{-2})
Intumescent:	Antiblaze, NH (Rhodia Specialties Ltd) – contains melamine phosphate

Flame-retardant fibres in pulverised form :

(i) Polybenzimidazole, PBI (Celanese)

(ii) Visil (Sateri Fibres, Finland) – cellulosic fibre containing polysilicic acid

(iii) Kynol, KF – 10 BT (Kynol, Japan)

(iv) Oxidised acrylic, Panox (Sigri) fibre

2.1.2. Samples

Samples (i) – (xi) with 8 layers of woven glass and resin containing following additives were prepared :

(i) Res - resin (no additive)

(ii) Res/Int - resin + intumescent, NH (Int, 10% w.r.t.resin)

(iii) Res/PBI - resin + PBI (PBI, 10% w.r.t.resin)

(iv) Res/PBI/Int - resin + PBI + Int (PBI + Int, 20% w.r.t.resin)

(v) Res/Vis - resin + Visil (Visil, 10% w.r.t.resin)

(vi) Res/Vis/Int - resin + Visil + Int (Visil + Int, 20% w.r.t.resin)

(vii) Res/Ky - resin + Kynol (Kynol, 10% w.r.t.resin)

(viii) Res/Ky/Int - resin + Kynol + Int (Kynol + Int, 20% w.r.t.resin)

(ix) Res/Ox.acr - resin + oxidised acrylic (oxidised acrylic, 10% w.r.t.resin)

(x) Res/Ox.acr/Int - resin + oxidised acrylic + Int (acrylic + Int, 20% w.r.t.resin)

2.1.3. Composite preparation

The laminates were prepared by a hand lay - up technique by impregnating glass fabric with resin and/or additives, stacking them up, pressing them all to the same thickness and curing at room temperature for 48 h. The description of these samples, amount of components present (mass fractions) and thicknesses of the laminates are given in Table 1.

2.2. Testing Equipment

Thermal analysis : For simultaneous DTA/TGA analysis a TA Instruments SDT 2960 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 pulverised fibres were used in this study. The following combinations were studied :

- Resin, intumescent and fibre individually

- Resin / intumescent - 1 : 1 mass ratio
- FR fibre/intumescent - 1 : 1 mass ratio
- Resin // FR fibre / intumescent - 1 : 0.5 : 0.5 mass ratio

Flammability testing : 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 x 100 mm fabric samples according to ISO 5660 [10].

3. Results and discussion

3.1. Thermal analysis of component mixtures

Thermal analytical results and thermal degradation mechanisms of polyester resin, Visil, intumescent Antiblaze NH (melamine phosphate) used in the present study and their different combinations are discussed in detail in our previous communications [6,7,9]. As for the present work, in some samples ((v), (vi) and (ix)) Visil fibre is replaced by a number of aromatic or semi-aromatic fibres - Kynol, PBI, oxidised acrylic, thermal analytical studies of all the combinations with these fibres were carried out and here results are compared with the combinations containing Visil fibre. The results for mixtures of all fibres and intumescent with and without resin were different from individual components indicating chemical interaction leading to formation of a complex char. In Fig.1a char yield differences between expected and calculated average values from TGA curves of individual components of fibre-intumescent mixtures are plotted as functions of temperature. As can be seen from Fig.1a, the Kynol and PBI - melamine phosphate mixtures show evidence of greater interaction than Visil – melamine phosphate at temperatures above 470 ^{0}C. Oxidised acrylic - melamine phosphate mixture is less thermally stable than expected below 560^{0}C, and after that the thermal stability increases.

When compatibility of each fibre with resin/intumescent system is studied, it can be seen from Fig 1b that all combinations show less than expected char formation upto 400^{0}C and more-than-expected char formation in the temperature range 400 - 800 ^{0}C. PBI combination becomes less thermally stable above 750 ^{0}C. All fibres increase thermal stability of resin/intumescent system and form 16-20 % more char than expected whereas, intumescent only increases this efficiency of resin to 9%, as seen from Fig.1b . This indicates some interaction between the cross-linking resin and the char- forming fibres. Detailed modes of possible interaction have been discussed elsewhere [6] This chemical interaction between these components indicates that composite laminates produced from these components should have superior flame retardant properties.

3.2. Cone calorimetric results for composite laminates

The various parameters recorded by the cone calorimeter are given in Table 2 and selected results are shown in Figs. 2- 4. As can be seen from Table 2, times to ignition (TTI) for all the samples are quite similar (24 to 36 s) and are not affected by presence of additives.

3.2.1. Heat release rates

Heat release rate versus time curves for samples (i) to (iv) are given in Fig.2a and peak heat release, total heat release and average heat release values for 4 minutes for all samples are given in Table 2. These results show that presence of intumescent reduces the PHRR value of resin only sample from 370 (Sample (i)) to 267 kW/m^2 (Sample (ii)). PBI fibre (Sample (iii)) reduces the PHRR to 248 kW/m^2. However, when both PBI fibre and intumescent are present (Sample (iv)), the value is reduced to 206 kW/m^2. The shape of the curves in Fig.2a also suggests this, showing earlier ignition and reductions in peak intensities. Moreover, shapes of the curves are not changed significantly, resulting in decreases in total areas under the curves. This is seen from AvHRR and THR values from Table 2, which are considerably reduced for the sample containing fibre and intumescent, which means that this combination is reducing the burning propensity of resin. These results are in contrast to our earlier work [8] and also in this work for Visil fibre - containing samples, where Visil fibre (Sample (v) marginally reduces PHRR, but increases AvHRR and THR values as seen from Table 2. Presence of both Visil and intumescent (Sample (vi)) reduce all values compared to only Visil -

containing samples, but THR and AvHRR values are greater than control sample values. Kynol shows an effect similar to Visil fibre, whereas, a combination of Kynol and intumescent (Sample (viii)) is effective in reducing the PHRR value to 260 kW/m^2. Presence of oxidised acrylic fibre only (Sample (ix)) reduces all values compared to resin only sample. However, when both oxidised acrylic fibre and intumescent are present (Sample (x)), the THR and AvHRR values are increased compared to fibre - containing sample only, but are less than for the control sample. For comparison of the effect of different fibres and intumescent, HRR versus time curves for samples (i), (iv), (vi), (viii) and (x) are given in Fig. 2b. Fig.2b and results in Table 2 indicate that the PBI/Int combination is most effective in reducing PHRR, THR and AvHRR values, followed by oxidised acrylic, Kynol and Visil.

3.2.2. Effective heat of combustion (H_c)

The effective heat of combustion over a given time frame (4 min in Table 2) is the quantity of heat produced by combustion of a unit mass of a material. It is measured in the cone calorimeter throughout the burn period from the simultaneous HRR and mass loss responses and may thus be used to measure possible flame retarding effects of components present. The effective heat of combustion decreases with presence of intumescent (Sample (ii)) compared to resin only sample (Sample (i)). Addition of PBI fibre (Sample (iii)) reduces the value, whereas, Visil, Kynol and acrylic fibres increase the value compared to resin only. When fibre and intumescent both are present, values are reduced compared to resin and resin fibre combinations. However values are similar for all types of fibre/intumescent combinations, i.e. here the type of fibre has less effect.

3.2.3. Mass loss

The char retained after burning a polymer is also a measure of its flammability and so the mass loss curves give insight into the fire performance of the samples. Typical mass loss curves for selected samples are given in Fig.3a and results support thermal analytical results that addition of intumescent and fibre components promote char formation of the resin. Fig.3b shows changes in mass after 4 minutes cone exposure of all samples compared to the control (resin only) sample (Sample (i)), where it can be seen that Visil and Kynol, with and without intumescent, are not as effective char promoters as PBI and oxidised acrylic fibres, where 14 and 18 %, respectively in absence of intumescent and 16 and 14% char mass increases occur in presence of intumescent. This is not in agreement with thermal analytical results as seen in Fig. 1b, which indicate that all fibres are more effective than PBI in char promotion. This may be due to different nature of two tests. Moreover samples tested for thermal analysis have different component ratios (see Section 2.2) than those prepared for cone test (see Table 1). Rapid heating conditions in cone change the decomposition mechanism of different components and hence, interactions, compared to slow heating results from thermal analytical experiments. However, interaction between different components leading to enhanced char formation, indicated in Fig.1 is also seen from cone results in Fig.3.

3.2.4. Smoke production

Smoke reduction a crucial property for polyester samples and emissions for all samples were recorded. PBI and oxidised acrylic fibres when present alone reduce smoke values as can be seen from Table 2, whereas, Visil and Kynol increase them. However, when intumescent is present, the values are reduced compared to resin only sample, except for oxidised acrylic combinations, where values are increased.

3.2.5. The fire growth rate index, FIGRA

The fire growth rate index [11] combines peak fire size (PHRR) and time to achieve this (time to peak, TTP) and is helpful in ranking the materials in terms of potential fire safety.

FIGRA index = PHRR / TTP (kW/s) [11]

The FIGRA index values calculated for all the samples are given in Table 3. As the results show presence of intumescent decreases this value. All fibres help in decreasing this value compared to resin only, to different extent. However, when fibre and intumescent both are present, there is futher reduction in the values. The order is :

PBI/Int ≅ Ky/Int < Ox.acr/Int < Vis/Int

Hence, PBI and Kynol fibres are more effective in reducing burning propensity of resin-intumescent mixture, followed by oxidised acrylic and then Visil.

3.2.6. Unitised HRR values

From Table 1 it can be seen that all these samples have different mass fractions of resin and so cone results may be resolved with respect to each component if we assume additivity of components heat release values. This then enables assessments to be made whether more complex mixtures are showing evidence of true heat release reductions or not. Thus from the cone results given in Table 2 , for sample (i), the following equation for PHRR can be written, assuming that the 0.63 mass fraction of glass has zero fuel level :

$$0.37\ H_{Res} = 370 \qquad \text{- - - - - (1)}$$

to yield $H_{Res} = 1000$ kW/m^2 per unit mass fraction, where H_{Res} is the PHRR for per unit of pure resin. In a similar manner, the following equations for samples (ii) - (iv) hold :

$$0.36\ H_{Res} + 0.038\ H_{Int} = 267 \qquad \text{- - - - - (2)}$$

$$0.34\ H_{Res} + 0.036\ H_{PBI} = 248 \qquad \text{- - - - - (3)}$$

$$0.35\ H_{Res} + 0.036\ H_{PBI} + 0.036\ H_{Int} = 206 \qquad \text{- - - - - (4)}$$

Where H_{Int} and H_{PBI} are respective PHRR values per unit mass of intumescent and PBI. From equations (2) and (3), the unit PHRR or 'H' values of Int and PBI can be calculated by substituting for H_{Res}. These values are then inserted into left hand side of equation (4) to calculate PHRR for Sample (iv), whereas, the value on right hand side (206 kW/m^2) is the experimental PHRR value. Similar equations can be used for samples containing other fibres (Samples (v) - (x)). These unitised values are then used to calculate the PHRR value for samples (iv), (vi), (viii) and (x) and are given in Table 3. For all samples the calculated values are less than those listed in Table 2. The difference between observed (experimental, from Table 2) and calculated values (from Table 3) are plotted in Fig. 4a. Similarly other cone parameters THR, H_c and smoke were calculated for these same samples using equations similar to (1) -

(4) for calculation of respective component unitised values. The results are given in Table 3 and Figs. 4b - d.

From Fig. 4a it can be seen that experimental PHRR values for samples (iv), (vi), (viii) and (x) are higher than expected from additive calculations. However, the differences are in the increasing order. The order with respect to fibre type is :

PBI < Kynol < Oxidised acrylic < Visil

Which indicates that PBI has the greatest effect of minimising resin PHRR. For THR values (after 4min) (see Fig. 3b), presence of PBI has a synergistic effect in that the calculated value is less than control giving a negative differential value. This is follwed by Visil, Kynol and then oxidised acrylic in ability to reduce resin and hence composite THR. Using a similar argument, all fibres except Visil reduce effective heat of combustion (H_c) of resin-intumescent system synergistically as seen from Fig.3c and the order is similar to the one for PHRR above.

From these derived parameters of PHRR, THR and H_c, it can be concluded that ability of each char-forming fibre to reduce the flammability of the resin-intumescent mixture is :

PBI > Kynol > Oxidised acrylic > Visil

Extending this analytical procedure to smoke generation, PBI also assists in reducing smoke production synergistically as seen from Fig.4d. Visil produces smoke slightly more than expected, followed by Kynol and oxidised acrylic.

4. Conclusions

Thermal analytical results have indicated that there is a resin-PBI or Kynol or oxidised acrylic-intumescent interaction similar to resin-Visil-intumescent interaction observed previously [5,6]. Cone calorimetric results also indicate similar behaviour, where it is seen that when intumescent and FR fibre are used as additives, they reduce PHRR, THR, AvHRR and smoke values. This effect is different than the one observed for thermally and physically thick polyester composites comprising Visil [8] where, although PHRR and AvHRR were reduced, THR increased and HRR vs time curves became broader with higher flameout times. Derived cone parameters help in analysing the separate and combined effect of the additives / components and results suggest that in some cases interactions are less than additive which, however is contrary to thermal analytical results reported elsewhere [5-7,9]. This may be due to different nature of two tests, in particular the slow heating regime in thermal analysis, the effect of layered glass fabrics in composites and the assumed inertness of glass. However, since cone calorimetric results are more representative of real fire behaviours, they are perhaps more indicative of the fire performance enhancing effects of the fibre/intumescent combinations reported. In conclusion, the effect of addition of a char-forming high performance fibre in reducing the flammability of resin in presence of intumescent is:

PBI > Kynol > Oxidised acrylic > Visil

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Captions

Fig.1. TGA results : percentage mass difference (actual - averaged) as a function of temperatures of all fibres with a) Int and b) mixture of Res and Int.

Fig. 2. HRR versus time curves for samples a) (i) - (iv) and b) (i), (iv), (vi), (viii) and (x) at 50 kW/m^2 heat flux.

Fig.3. a) Mass loss vesus time curves for samples (i)-(iv) at 50kW/m^2 heat flux and b) change in residual mass of samples (ii) - (x) compared to sample (i).

Fig.4. Differences between experimental and calculated values of a) PHRR, b) THR, c) H_c and d) smoke production of Res/Fibre/Int combinations. Negative differece indicates synergy of respective fibre with Res/Int combination.

Table 1. Physical properties of composite laminate samples (i) – (x).

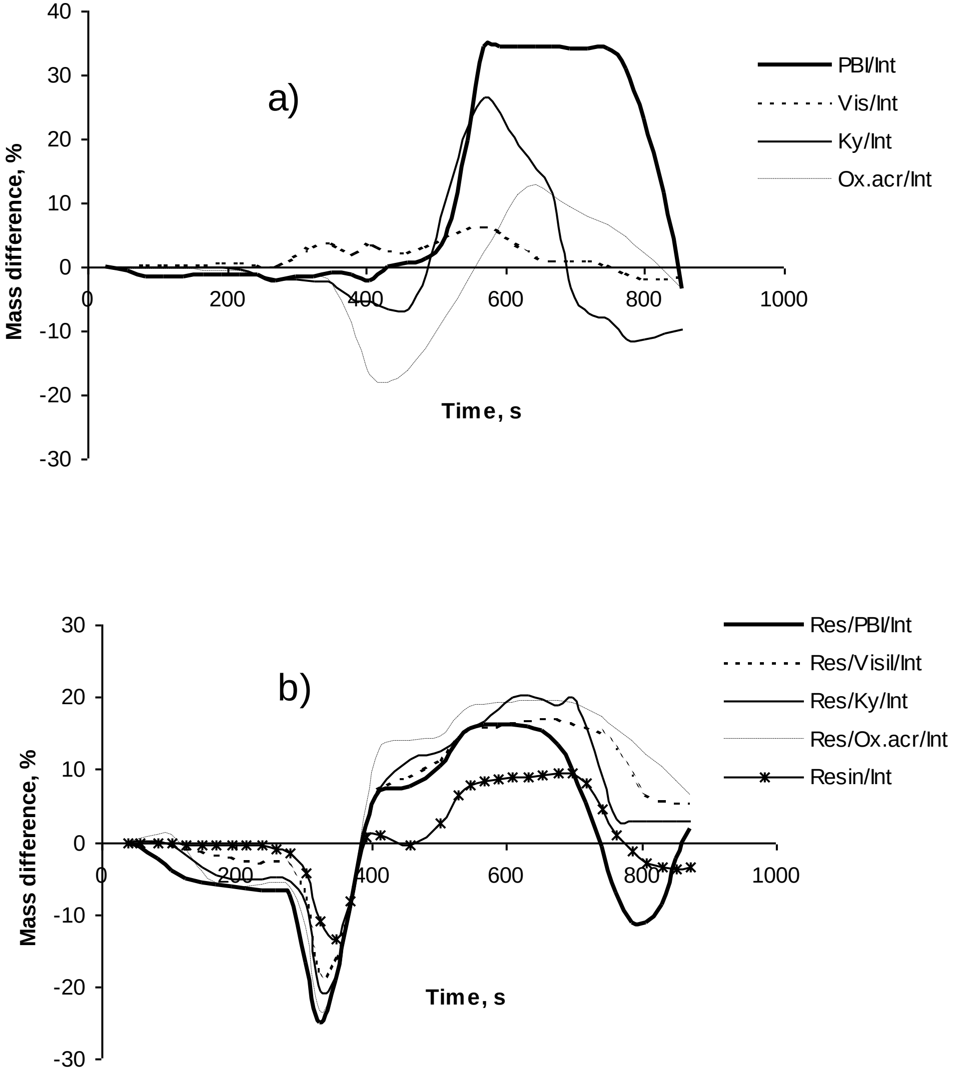
Samples	Mass Fraction (%)				Thickness
	Glass	Resin	Fibre	Intumescent	(mm)
(i). Res	63.0	37.0	-	-	2.3
(ii) Res/Int	60.2	36.0	-	3.8	2.3
(iii) Res/PBI	62.6	34.0	3.6	-	2.3
(iv) Res/PBI/Int	57.8	35.0	3.6	3.6	2.4
(v) Res/Vis	60.5	36.0	3.5	-	2.4
(vi) Res/Vis/Int	57.0	36.0	3.5	3.5	2.5
(vii) Res/Ky	59.1	37.0	3.9	-	2.3
(viii) Res/Ky/Int	56.2	36.0	3.9	3.9	2.3
(ix) Res/Ox.acr	61.4	35.0	3.6	-	2.4
(x) Res/Ox.acr/Int	57.6	35.0	3.7	3.7	2.4

Table 2. Cone calorimetric results for composite samples (i)-(x) at 50 kW/m^2.

Samples	TTI (s)	PHRR (kW/m^2)	TTP (s)	FIGRA kW/s	THR (MJ/m^2)	Av.HRR 4 min (kWm^{-2})	H_c 4 min (MJ/kg)	Smoke after 4 min (m^2/m^2)
(i) Res	33	370	35	10.6	27.9	116	18.1	1347
(ii) Res/Int.	24	267	40	6.7	24.9	103	16.8	1212
(iii) Res/PBI	28	248	30	8.2	25.4	105	17.7	1263
(iv) Res/PBI/Int	28	206	70	2.9	22.5	93	16.9	1068
(v) Res/Vis	31	356	35	10.2	36.5	151	18.3	1823
(vi) Res/Vis/Int	32	348	37	9.4	35.0	145	17.5	1756
(vii) Res/Ky	32	325	40	8.1	30.8	128	19.2	1429
(viii) Res/Ky/Int	32	260	90	2.9	31.5	130	17.5	1605
(ix) Res/Ox.acr	36	287	41	7.0	21.7	90	18.3	949
(x) Res/Ox.acr/Int	28	256	29	8.8	26.3	109	17.4	1353

Table 3. Calculated cone parameters for composite samples using component unitised values

Sample	PHRR (kW/m^2)	THR (MJ/m^2)	H_c (MJ/kg)	Smoke (m^2/ m^2)
(iv) Res/PBI/Int	170	24.1	17.4	1206
(vi) Res/Vis/Int	270	34.5	16.8	1733
(viii) Res/Ky/Int	220	27.7	17.9	1291
(x) Res/Ox.acr/Int	194	19.5	17.5	845



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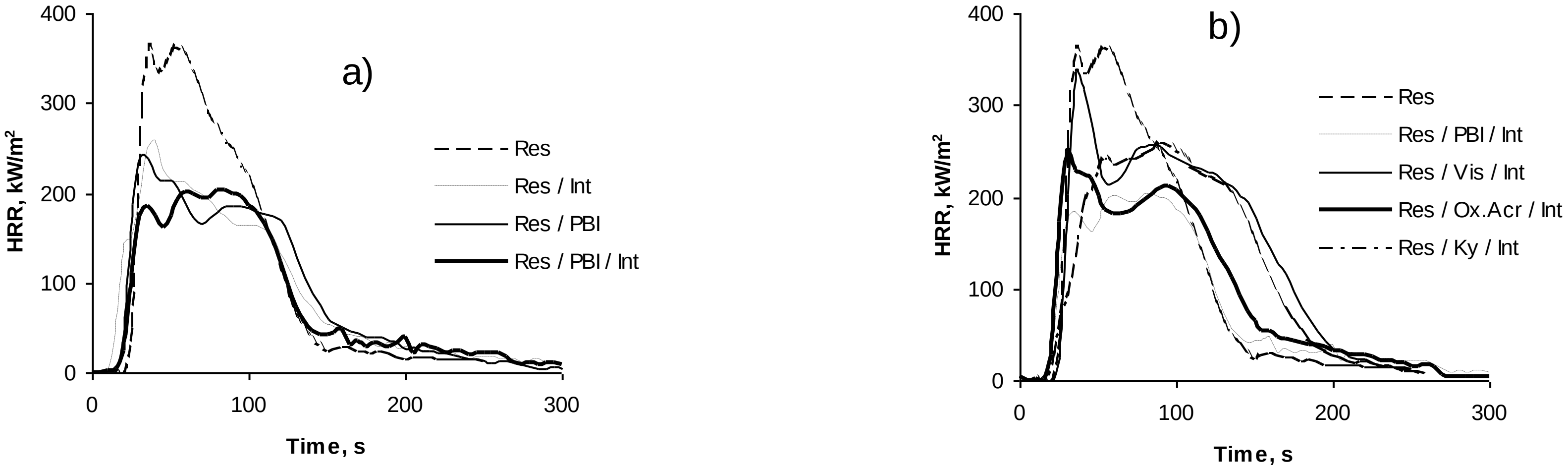

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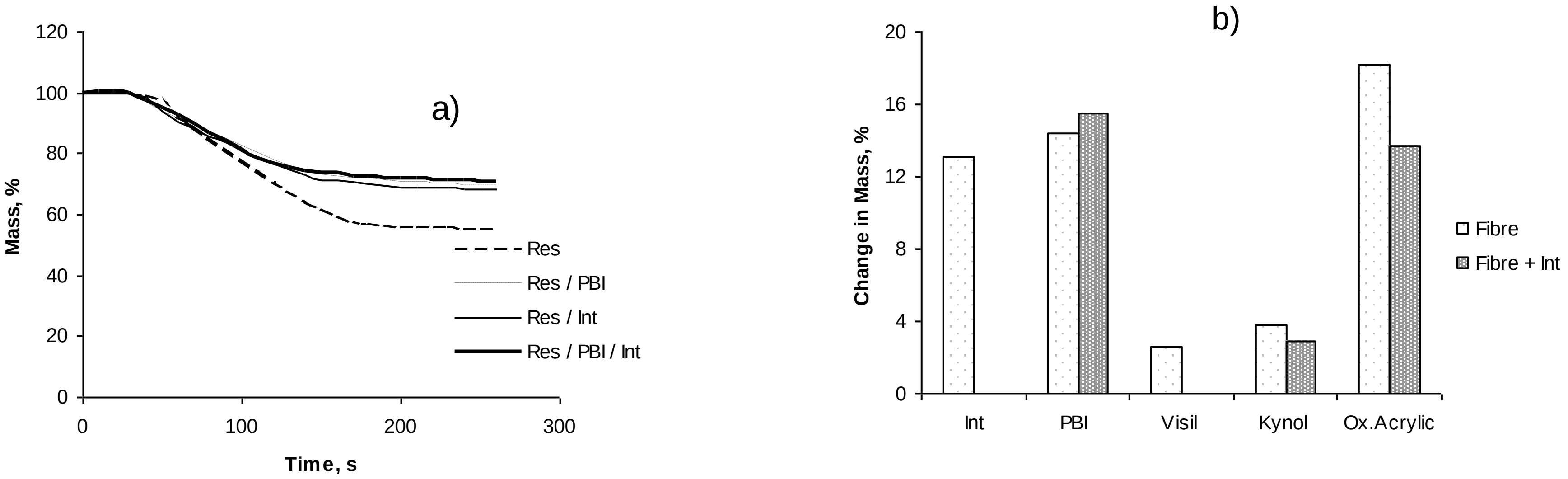

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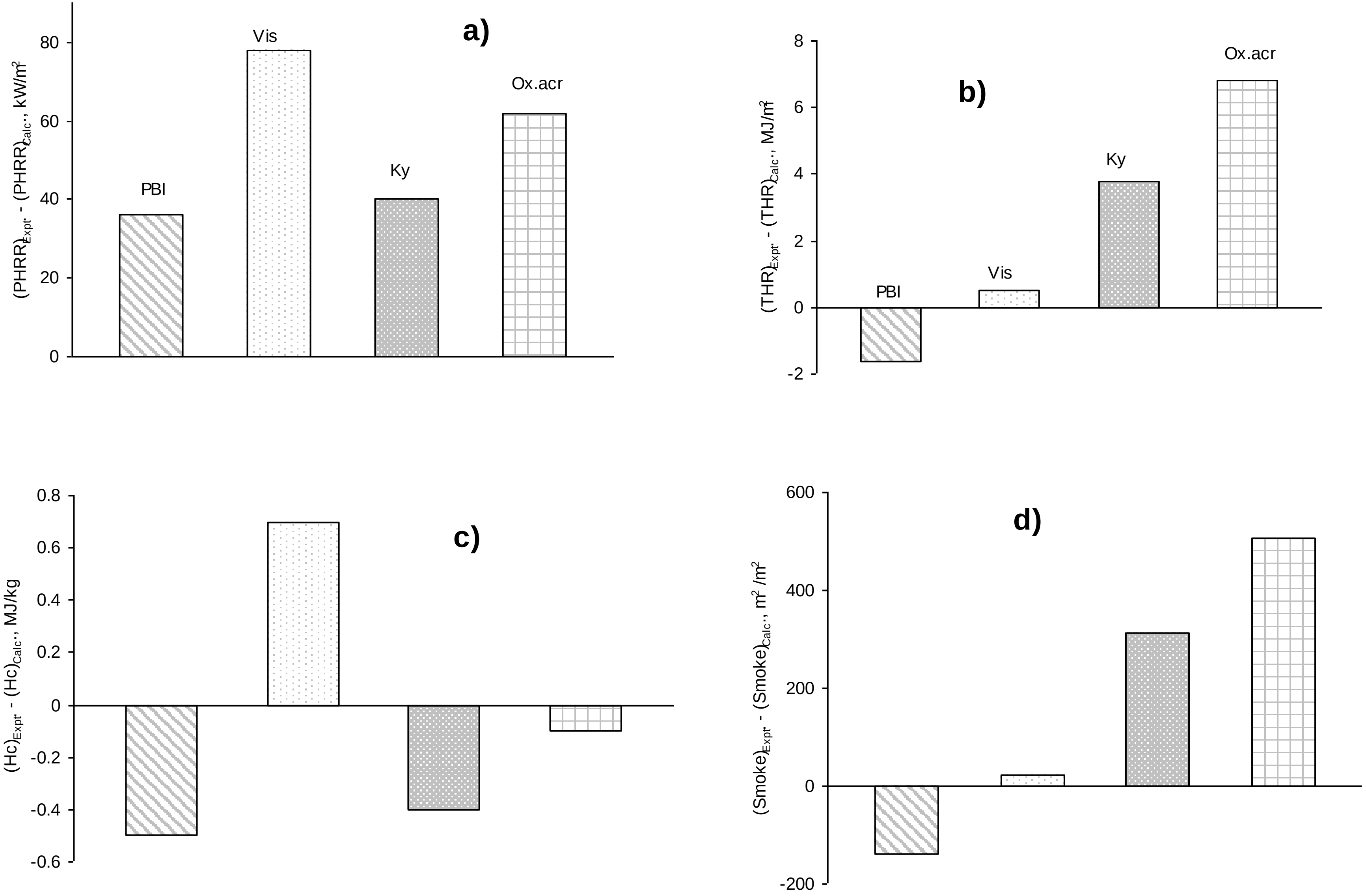

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