



Blends of unsaturated polyester and phenolic resins for application as fire-resistant matrices in fibre-reinforced composites: Effects of added flame retardants



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ABSTRACT

The flame retardance of co-cured blends of an unsaturated polyester with various phenolic resoles is improved by the addition of the phosphorus-containing flame retardants: resorcinol bis(diphenyl phosphate), bisphenol-A bis(diphenyl phosphate) and 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide. Cone calorimetric studies indicate reductions in important parameters such as total heat released and peak heat release rate. However, although the improved flame retardancy is accompanied by increased char yields, smoke evolution is also increased indicating contributions from both condensed-phase and gas-phase mechanisms of flame retardance. Improvements in flame retardance are particularly marked in systems in which the unsaturated polyester is at least partly compatible with the phenolic resole; TGA studies indicate that this may be due to better retention of the flame retardant in the condensed phase in the more compatible systems.

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1. Introduction

Unsaturated polyester (UP) resins, cured (crosslinked) with styrene, are widely used as the matrix resins in composites, especially those reinforced with glass fibre cloths or mats and now widely employed in the transport sector in applications such as car bodies, train cabs, boat hulls, seat frames and motor housings [1]. The main advantages of thermoset UP resins in such applications are their relatively low cost, good mechanical properties (when fibre-reinforced), and reasonable resistance to water, oils and other chemicals [2]. However, cured UP resins thermally degrade rapidly at temperatures above 300 °C to give volatile products (mainly styrene initially) that are easily ignited, and which burn readily with the evolution of considerable smoke [3]. For this reason, UP resins are generally compounded with halogen- and/or phosphorus-containing flame-retardant (FR) additives, often used at concentrations of 20% w/w or above to ensure efficacy but with consequent deleterious effects upon physical and mechanical properties [4,5]. Alternatively, the UP resin backbone may be chemically modified with FR groups, (a reactive strategy) [6], or be crosslinked using an FR monomer in partial replacement of the styrene [7,8], but either strategy significantly increases cost.

We have been investigating an alternative approach to improving the flame retardance of UP resins, namely by blending and co-curing them with inherently flame-retardant resins such as char-forming phenol-formaldehyde and melamine-formaldehyde resins [9–11]. This type of approach is well-established with high-performance thermosetting resins, e.g. the blending of epoxy with phenolic resins [12], but thus far, relatively little has been published ahead of our work on the blending of UPs with phenolics, owing to the inherent physical incompatibility of relatively hydrophobic UP resins with relatively hydrophilic formaldehyde-based resins, and to the fact that the former cure by a low-temperature (typically 40–80 °C) free-radical chain reaction whereas the latter cure via a high temperature (ca. 150 °C) polycondensation, often with an acid catalyst [13–16].

Despite the shortage of precedents and the seeming difficulties to be overcome, we have shown that UP resins may be successfully blended and co-cured with phenolic resoles (PH), i.e. phenolic resins made using an excess of formaldehyde and thus containing unreacted methylol groups, especially if a compatibilizing solvent, such as ethanol, is used in the initial blending process, or if the resoles have been chemically modified to contain hydrophobic and/or free-radically reactive groups, such as epoxy (UP/epoxy-PH blends) and allyl groups (UP/allyl-PH blends) [9,10]. The evidence of increased compatibility comes from SEM images of fracture surfaces, which show much less evidence of microscopic heterogeneity in the case of the more compatible systems, from DMTA

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measurements of glass transition temperatures (T_g) with the most compatible system (UP/allyl-PH) showing only a single T_g , and, in the case of UP/allyl-PH blends, also from solid-state ^{13}C NMR spectra, which indicate significant copolymerization of allyl groups in allyl-PH with the styrene and the in-chain double bonds of the UP [10]. Moreover, these co-cured resin blends are significantly more flame retardant than unmodified UPs, burn with lower evolution of heat and the formation of more char, have physical and mechanical properties that in several respects are superior to those of unmodified UPs, and can satisfactorily be used to make glass-reinforced composite panels [10,11].

However, we have been surprised to find that unexpectedly it is the least compatible resin blends, i.e. those based on UP plus an unmodified resole (PH) and which give rise to co-cured products with poor physical and mechanical properties, that are the most flame retardant, whereas those based on epoxy-PH and allyl-PH resoles, which have better physical and mechanical properties, are less flame retardant [11]. We believe that the reasons for this lie in the greater extent of cure of the unmodified resole in blends with UP, providing a greater thermally protective effect for the latter.

In this paper we describe further studies of the flame retardance of UP/resole co-cured blends, concentrating upon the effects of additional flame retardants. The FRs we have chosen to study are resorcinol bis(diphenyl phosphate) (RDP), bisphenol-A bis(diphenyl phosphate) (BADP) and 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO). RDP and BADP are well-established for use in polymer systems such as polycarbonate and polycarbonate blends [17,18], in which they are believed to act via both gas- and condensed phase mechanisms, whereas DOPO is a predominantly gas-phase flame retardant used mainly in epoxy resin-based materials [19].

2. Experimental

2.1. Materials

Crystic 2-406 PA, Scott-Bader: a pre-accelerated (cobalt octoate), phthalic anhydride-based unsaturated polyester (UP) resin containing 35–40% w/w styrene.

Catalyst M, Scott-Bader: a free-radical catalyst for UP curing consisting of methyl ethyl ketone peroxide dissolved in methyl ethyl ketone.

Durez 33156, Sumitomo-Bakelite NV: an ethanol-soluble resole containing 20–29% w/w ethanol, hereinafter referred to as “PH”.

Plyophen 223983, Sumitomo-Bakelite NV: an isopropanol-soluble, epoxy-functionalized resole containing 16–18% w/w isopropanol and <6% w/w water, hereinafter referred to as “epoxy-PH”.

Methylon 75108, Sumitomo-Bakelite NV: a solvent-free, allyl-functionalized resole, hereinafter referred to as “allyl-PH”.

Resorcinol bis(diphenyl phosphate) (RDP), Chemtura UK.

Bisphenol-A bis(diphenyl phosphate) (BADP), Chemtura UK.

9,10-Dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO), Tokyo Chemical Industry UK Ltd.

All of the above materials were used as received.

2.2. Casting and curing of resins and resin blends

2.2.1. UP resin

Samples of cured UP resin were prepared by mixing the resin with 2% w/w of catalyst M with a mechanical stirrer in a 100 ml beaker. The mixture was then poured into 5.5 cm diameter circular aluminium open moulds to a depth of 3 mm. The specimens were then allowed to cure at room temperature for 24 h and post-cured at 80 °C in an oven for 6 h.

2.2.2. PH resins

Samples of PH resins were directly transferred to 5.5 cm dia. moulds, again to depths of 3 mm, cured and then post cured for various times and at various temperatures up to 180 °C. In situations in which FR was added (i.e. RDP, BADP or DOPO), this was stirred into the resin until dissolved prior to transfer of the resin to the mould. For RDP and BADP, concentrations of 20% w/w FR/total resin (corresponding to 2.2% w/w and 1.8% w/w P/total resin, respectively) were employed, whereas for DOPO, the concentration was 10% w/w FR/total resin (corresponding to 1.6% w/w P/total resin).

2.2.3. Resin blends

Resin blends were prepared by mixing 70:30 and 50:50% w/w UP/resole for 10 min in a 100 ml beaker using a high-speed, overhead, electric stirrer fitted with a four-component blade (IKA RW16 at 900 rpm); additional FR was included where required. Catalyst M (2% w/w w.r.t. UP) was then added to the resin mixture and stirring continued for a further 10 min. The resulting mixtures were then transferred to 5.5 cm dia. moulds also (depth 3 mm), cured and then post cured by increasing the temperature again in stages to 180 °C.

2.2.4. Curing regimes

The precise curing regimes used for the various resin mixtures, with and without FR, are listed in Table 1.

These curing regimes were established by a process of trial and error so as to accommodate (a) initial evaporation of any solvent prior to significant cure (so as not to produce voids in the final cured product), (b) the relatively low temperature radical curing/co-curing stage for the UP, (c) the final higher temperature co-condensation of any residual methylol groups in the resole and, in so-doing, to obtain a rigid, visibly homogeneous product with optimised physical and mechanical properties [11]. It can be seen from Table 1 that for UP samples containing FRs, long cure times and high final post-cure temperatures (up to 160 °C in the case of UP with RDP) were required in order to obtain a satisfactory product, i.e. one that was rigid and non-tacky. All blends of UP with resoles also required long cure times and high final post-cure temperatures. However, for blends containing RDP and BADP, the final post cure temperatures were required to be no higher than those required in the absence of FRs (160 °C), whereas when DOPO was used as the FR, a final post-cure temperature of 180 °C was necessary. There was no apparent loss of FR through migration to the surface (blooming) during the curing of samples containing FR, indicating that the FRs were satisfactorily incorporated in the cured resins and resin mixtures.

The cured and co-cured resin samples were used in cone calorimetric experiments, and small portions of them were used also in TGA experiments.

2.3. Cone calorimetry

A cone calorimeter (Fire Testing Technology Ltd., UK) was used to assess flammability parameters for cured resins. Circular samples measuring 5.5 cm dia. with a nominal thickness of 3 mm, were fire tested in the horizontal mode with an ignition source at an applied heat flux of 50 kW/m². Before testing, the bottom surface and the edges of the samples were wrapped with aluminium foil to ensure that only the top surface would be directly exposed to the heat source. A minimum of three tests were performed for each formulation.

Previously in our laboratories, a comparative study of the cone calorimetric behaviour of round and standard square (10 cm × 10 cm) samples was undertaken in order to understand

Table 1
Curing conditions.

Sample no.	System	Curing conditions
1	UP	RT 24 h, 80 °C 6 h
2	UP: RDP	RT 24 h, 80 °C 6 h, 120 °C 2 h, 160 °C 2 h
3	UP: BADP	RT 24 h, 80 °C 6 h, 120 °C 2 h, 140 °C 2 h
4	UP: DOPO	RT 24 h, 80 °C 6 h, 100 °C 2 h, 120 °C 3 h
5	UP/PH: 70/30	50 °C 6 h, 80 °C 24 h, 90 °C 9 h, 130 °C 1 h, 160 °C 1 h
6	UP/PH: 70/30-RDP	Same as no. 5
7	UP/PH: 70/30-BADP	50 °C 6 h, 80 °C 24 h, 90 °C 9 h, 100 °C 3 h, 130 °C 1 h, 160 °C 1 h
8	UP/PH: 70/30-DOPO	50 °C 6 h, 80 °C 12 h, 90 °C 8 h, 110 °C 6 h, 130 °C 6 h, 150 °C 2 h, 180 °C 2 h
9	UP/PH: 50/50	80 °C 24 h, 100 °C 1 h, 130 °C 1 h, 160 °C 1 h
10	UP/PH: 50/50-RDP	Same as no. 9
11	UP/PH: 50/50-BADP	Same as no. 9
12	UP/PH: 50/50-DOPO	50 °C 6 h, 80 °C 12 h, 90 °C 8 h, 100 °C 6 h, 130 °C 3 h, 150 °C 2 h, 180 °C 2 h
13	PH	50 °C 6 h, 80 °C 12 h, 160 °C 3 h
14	PH: RDP	50 °C 18 h, 80 °C 24 h, 100 °C 3 h, 130 °C 1 h, 160 °C 1 h
15	PH: BADP	Same as no. 14
16	PH: DOPO	Same as no. 12
17	UP/epoxy-PH: 70/30	50 °C 6 h, 70 °C 8 h, 80 °C 8 h, 100 °C 6 h, 130 °C 2 h, 160 °C 2 h
18	UP/epoxy-PH: 70/30-RDP	Same as no. 17
19	UP/epoxy-PH: 70/30-BADP	Same as no. 17
20	UP/epoxy-PH: 70/30-DOPO	50 °C 6 h, 70 °C 12 h, 90 °C 8 h, 110 °C 6 h, 130 °C 6 h, 150 °C 2 h, 180 °C 2 h
21	UP/epoxy-PH: 50/50	Same as no. 17
22	UP/epoxy-PH: 50/50-RDP	Same as no. 17
23	UP/epoxy-PH: 50/50-BADP	Same as no. 17
24	UP/epoxy-PH: 50/50-DOPO	50 °C 6 h, 80 °C 12 h, 90 °C 8 h, 110 °C 6 h, 130 °C 6 h, 150 °C 2 h, 180 °C 2 h
25	Epoxy-PH	Same as no. 17
26	Epoxy-PH: RDP	Same as no. 25
27	Epoxy-PH: BADP	Same as no. 25
28	Epoxy-PH: DOPO	Same as no. 24
29	UP/allyl-PH: 70/30	50 °C 6 h, 80 °C 12 h, 100 °C 8 h, 120 °C 6 h, 130 °C 6 h, 150 °C 2 h, 180 °C 2 h
30	UP/allyl-PH: 70/30-RDP	Same as no. 29
31	UP/allyl-PH: 70/30-BADP	Same as no. 29
32	UP/allyl-PH: 70/30-DOPO	Same as no. 24
33	UP/allyl-PH: 50/50	Same as no. 29
34	UP/allyl-PH: 50/50-RDP	Same as no. 29
35	UP/allyl-PH: 50/50-BADP	Same as no. 29
36	UP/allyl-PH: 50/50-DOPO	50 °C 6 h, 80 °C 12 h, 90 °C 8 h, 110 °C 6 h, 130 °C 6 h, 150 °C 2 h, 180 °C 2 h
37	Allyl-PH	100 °C 8 h, 120 °C 6 h, 130 °C 6 h, 150 °C 2 h, 180 °C 2 h
38	Allyl-PH: RDP	Same as no. 29
39	Allyl-PH: BADP	Same as no. 29
40	Allyl-PH: DOPO	Same as no. 36

Note: In flame retarded systems, RDP and BADP = 20% (w/w); DOPO = 10% (w/w).

the effect of geometry on flammability properties of polymeric materials [20]. Circular specimens with a four-fold reduction in area gave similar results for the peak heat release rates (PHRR), total heat release (THR) and effective heat of combustion (EHC). Smoke, CO and CO₂ production results were found to be different from those measured for the larger specimens since these parameters are independent of exposed specimen surface area. However, in this work, these data were used for comparison purposes only

with respect to control specimens, hence there was no need for adjustments.

2.4. Thermogravimetric analysis

Thermogravimetric (TGA) analysis of all cured resins and their blends were performed on a TA Instruments, SDT 2960, from RT to 900 °C using 15 ± 1 mg samples heated at a constant rate of 10 °C/min in air at a flow rate of 100 ± 5 ml/min. The experiments were performed in duplicate and showed good reproducibility. Averaged data are presented.

3. Results and discussion

3.1. Cone calorimetric assessments of flame retardance

Cone calorimetry was used to obtain the following flammability parameters for cured resins and co-cured resin blends, both with and without added FR: time to ignition (TTI in s); time to flame out (FO in s), peak heat release rate (PHRR in kW/m²), total heat released (THR in kW/m²), effective heat of combustion (EHC in MJ/kg), total smoke released (TSR in m²/m²) and char residue (% w/w). These parameters for all resin systems, with and without FR, are given in Tables 2–4.

Typical cone calorimetric outputs in the form of plots of heat release rate (HRR) and mass vs. time are shown in Fig. 1 for co-cured blends of UP (70% w/w) with allyl-PH (30% w/w) with and without FR (i.e. for the blends that are of most technological interest to us owing to having better processability and mechanical properties than the 50:50% w/w blends). From these curves it can be seen in particular that addition of FR to UP/allyl-PH 70/30% w/w decreases THR and PHRR and increases final char yield, with DOPO being notably effective.

All of the cone calorimetric data are presented in Tables 2–4. The flammability parameters for cured UP, for the cured PH, epoxy-PH and allyl-PH resoles (denoted as PH2, PH3 and PH4 in our earlier papers [10,11]), and for co-cured blends of UP with PH, epoxy-PH and allyl-PH, have been discussed at length previously [11]. Suffice it to note here that cured PH, epoxy-PH and allyl-PH are all significantly less flammable than cured UP and that additions of PH, epoxy-PH and allyl-PH to UP all produce significant improvements in flame retardance, e.g. addition of 30% w/w PH to UP reduces PHRR by about 380 kW/m², reduces THR by 20 MJ/m², reduces TSR by about 1700 m²/m², and increases char yield from ca. 1% w/w to 25% w/w. With 30% w/w epoxy-PH, PHRR is reduced by about 170 kW/m²; THR by 25 MJ/m², TSR by about 1300 m²/m², and residue increased to 11% w/w. For 30% w/w added allyl-PH, the corresponding reductions in PHRR, THR and TSR are 75 kW/m², 8 MJ/m² and 270 m²/m², respectively, with a 10% w/w increase in residue, indicating the point made earlier, that the least compatible resole (PH) produces the greatest improvement in flame retardance of the UP, whilst allyl-PH, despite being the most compatible resole, produces the least (although still a significant) improvement. Similar trends are seen in the data for 50:50% w/w co-cured UP/resole blends. The mechanism of flame retardance in these blends is predominantly condensed phase as indicated by the significant reductions in smoke output during combustion and the large increases in char yield compared with those of cured UP, since smoke is normally taken to be an indicator of suppressed gas phase oxidation [21]. In only one respect do additions of allyl-PH outperform additions of PH and epoxy-PH in terms of their flame retardance, and that is in times to ignition (TTI): the TTIs are 31, 39 and 54 s, respectively for 70:30% w/w UP/PH, UP/epoxy-PH and UP/allyl-PH. Again, similar trends are shown for the 50:50% w/w blends. The overall slightly disappointing results obtained for the

Table 2
Cone calorimetric parameters for cured UP, cured PH and co-cured UP/PH blends, with and without FR (In this and Tables 3 and 4, FR = flame retardant, TTI = time to ignition, FO = time to flame out, PHRR = peak heat release rate, THR = total heat released, EHC = effective heat of combustion; TSR = total smoke released, Char = residue remaining at end of cone calorimetric experiment).

System	TTI/s	FO/s	PHRR/kW m ⁻²	THR/MJ m ⁻²	EHC/MJ kg ⁻¹	TSR/m ² m ⁻²	Char/% w/w
UP	40	178	1050	79	19.7	4090	1
UP: RDP	49	131	840	44	11.9	5430	2
UP: BADP	48	150	800	53	13.1	6230	6
UP: DOPO	44	148	850	54	12.6	6130	1
UP/PH: 70/30	31	178	668	59	20.6	2307	25
UP/PH: 70/30-RDP	49	176	503	45	12.7	4248	17
UP/PH: 70/30-BADP	46	201	476	56	15.0	4897	16
UP/PH: 70/30-DOPO	27	175	429	54	14.9	4580	13
UP/PH: 50/50	31	156	584	48	21.5	1357	37
UP/PH: 50/50-RDP	37	154	522	41	16.0	2573	26
UP/PH: 50/50-BADP	32	171	537	47	16.9	2867	26
UP/PH: 50/50-DOPO	23	209	506	64	14.8	5584	21
PH	33	156	467	38	22.6	594	46
PH: RDP	39	131	519	30	16.0	1411	43
PH: BADP	40	140	555	35	19.0	1539	42
PH: DOPO	19	157	536	45	20.8	1362	43

Note: The variation in values for different parameters are: TTI = ±3; FO = ±4; PHRR = ±32; THR = ±2.3; EHC = ±0.7; TSR = ±156; Char = ±5.

Table 3
Cone calorimetric parameters for cured epoxy-PH and co-cured UP/epoxy-PH blends, with and without FR.

System	TTI/s	FO/s	PHRR/kW m ⁻²	THR/MJ m ⁻²	EHC/MJ kg ⁻¹	TSR/m ² m ⁻²	Char/% w/w
UP/epoxy-PH: 70/30	39	148	885	54	18.0	2699	11
UP/epoxy-PH: 70/30-RDP	44	143	558	38	12.2	4040	17
UP/epoxy-PH: 70/30-BADP	42	157	565	45	16.0	4302	14
UP/epoxy-PH: 70/30-DOPO	20	149	509	46	14.1	3645	14
UP/epoxy-PH: 50/50	34	151	682	50	18.9	2203	20
UP/epoxy-PH: 50/50-RDP	45	139	528	36	12.0	3602	22
UP/epoxy-PH: 50/50-BADP	44	145	549	40	14.0	3665	19
UP/epoxy-PH: 50/50-DOPO	24	115	542	36	14.0	2756	18
Epoxy-PH	35	145	489	34	23.4	603	48
Epoxy-PH: RDP	40	113	539	26	15.0	1510	40
Epoxy-PH: BADP	38	119	514	28	15.6	1777	38
Epoxy-PH: DOPO	22	115	502	30	17.4	1345	42

Note: The variation in values for different parameters are: TTI = ±2; FO = ±4; PHRR = ±32; THR = ±1.5; EHC = ±2.0; TSR = ±156; Char = ±2.

UP/allyl-PH blends are the main reason for investigating the influence on flammability of added flame retardants as mentioned above.

Table 2 indicates that additions of RDP, BADP and DOPO to cured UP all improve flame retardance significantly, with small increases in TTI and significant decreases in PHRR and THR. However, all three FRs operate almost exclusively in the gas phase in UP as indicated by large increases in total smoke and only marginal increases in char. In cured PH, additions of all three FRs can be seen to slightly increase PHRR. However, RDP and BADP do produce marginal reductions in THR, whereas DOPO increases THR also. All

three FRs increase smoke (TSR) and, interestingly, reduce char yields. Thus, at best, all three FRs could be said to be ineffective as flame retardants for cured PH. For cured epoxy-PH, the story is similar: the FRs have virtually no effect on PHRR, produce only slight decreases in THR, again with increases in smoke and reductions in char yield (Table 3). In cured allyl-PH, the FRs have a more positive effect on flame retardance (Table 4), with DOPO, especially, producing a large reduction in PHRR, albeit accompanied by a significant increase in smoke and only a small increase in char yield, consistent with DOPO acting mainly as a gas phase flame retardant. RDP and BADP are also marginally effective as FRs in

Table 4
Cone calorimetric parameters for cured allyl-PH and co-cured UP/allyl-PH blends, with and without FR.

System	TTI/s	FO/s	PHRR/kW m ⁻²	THR/MJ m ⁻²	EHC/MJ kg ⁻¹	TSR/m ² m ⁻²	Char/% w/w
UP/allyl-PH: 70/30	54	179	960	71	19.6	3820	11
UP/allyl-PH: 70/30-RDP	52	153	620	41	12.3	4440	14
UP/allyl-PH: 70/30-BADP	51	156	680	46	13.6	4890	13
UP/allyl-PH: 70/30-DOPO	55	213	540	47	13.5	4650	17
UP/allyl-PH: 50/50	57	201	800	61	18.0	3170	14
UP/allyl-PH: 50/50-RDP	47	151	570	40	13.6	3660	23
UP/allyl-PH: 50/50-BADP	51	153	590	42	13.5	4180	19
UP/allyl-PH: 50/50-DOPO	47	194	530	44	12.5	4220	18
Allyl-PH	72	216	880	48	20.1	2210	27
Allyl-PH: RDP	61	143	780	33	14.2	2410	37
Allyl-PH: BADP	67	130	830	35	16.4	2410	37
Allyl-PH: DOPO	83	171	540	32	11.8	3060	33

Note: The variation in values for different parameters are: TTI = ±3; FO = ±3; PHRR = ±32; THR = ±2.5; EHC = ±0.7; TSR = ±156; Char = ±4.

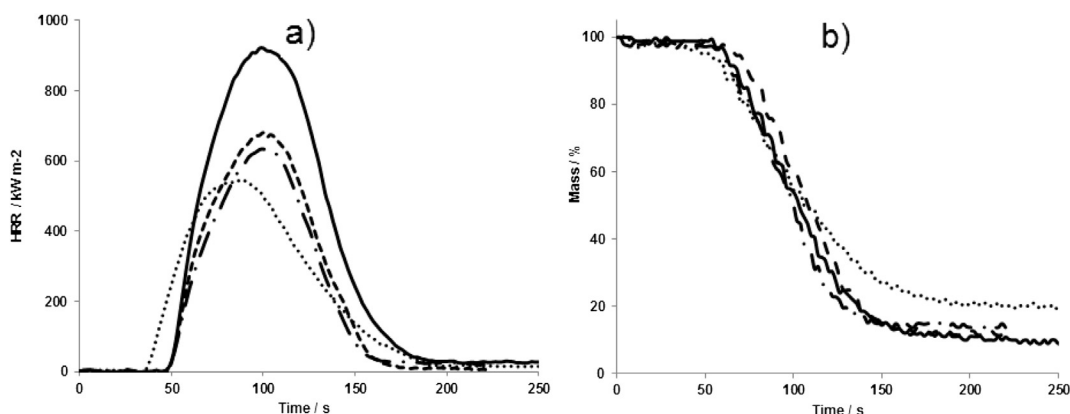


Fig. 1. Plots of heat release rate (HRR) and mass vs. time from cone calorimetric experiments on co-cured UP/allyl-PH 70:30% w/w blends with no FR (—), with 20% w/w RDP (- · - ·), with 20% w/w BADP (- - - -) and with 10% w/w DOPO (· · · · ·).

cured allyl-PH (small reductions in PHRR, and larger reductions in THR). RDP and BADP produce slightly more char and slightly less smoke in cured allyl-PH than does DOPO, indicating that these two FRs are acting in both gas and condensed phases.

Given that the FRs are effective in both cured UP and cured allyl-PH, but less so in cured PH and cured epoxy-PH, it is not surprising to note that, in general, the FRs are more effective in co-cured UP/allyl-PH blends than they are in co-cured UP/PH and UP/epoxy-PH blends. For example, additions of the FRs to 70:30% w/w blends of UP/allyl-PH produce large reductions in PHRR and THR, albeit with some increase in smoke and only marginal increases in char. At a 70:30% w/w blend ratio, the TTI is also not much affected. The performances of RDP, BADP and DOPO in the UP/allyl-PH system are similar, indicating that in this system the balances between gas phase and condensed phase mechanisms of flame retardance are also similar. This is surprising given that DOPO is normally regarded as being a gas phase flame retardant, and is significantly more volatile than either RDP or BADP, as indicated by the fact that heating these flame retardants on their own at 10 °C per min on the TGA machine under nitrogen gives the following results: DOPO, 10% wt loss by 250 °C; RDP, 10% wt loss by 350 °C; BADP, 10% wt loss by 430 °C.

3.2. Thermo-oxidative stabilities

In order to better understand the influence of the added FRs upon flame retardance, we have examined also the thermo-oxidative stabilities of the UP/resole blends, with and without added FR, by TGA under air atmosphere.

TGA weight loss curves in air for 70:30% w/w blends of UP/PH, UP/epoxy-PH and UP/allyl-PH (the blend compositions of most technological interest to us owing to having better processability and mechanical properties than the 50:50% w/w blends), with and without added FR, are presented in Fig. 2 (a1), (b1) and (c1). It can be seen from Fig. 2 (a1) that in all cases addition of FR to the UP/PH co-cured blend leads to greatly increased weight loss over the temperature range 350–600 °C and that above 600 °C, only RDP and DOPO produce significant increases in char. From this we conclude that additions of the FRs to UP/PH inhibit char formation in the range 400–600 °C but that what char remains is slightly more oxidatively resistant above 600 °C. For the UP/epoxy-PH blends (Fig. 2 (b1)), only RDP appears to destabilize significantly the blend, and then only below 400 °C; all FRs produce significant increases in char above 400 °C and this char is also more oxidatively stable than that produced from UP/epoxy-PH without FR. The behaviours of the UP/allyl-PH blends with and without added FR

(Fig. 2 (c1)) are similar to those of UP/epoxy-PH. However, in this blend no char remains above 600 °C unless FR is present; so it could be said that in UP/allyl-PH, added FR rather more effectively catalyses char formation and increases its oxidative stability.

The effects of the FRs on weight loss under air are more clearly seen in Fig. 2 (a2), (b2) and (c2) in which the weight loss data for the resin blends without FRs have been subtracted from those recorded with FRs. From Fig. 2 (a2) it is even more apparent that there is significantly more weight loss below 600 °C from UP/PH when FRs are present. Much of this additional weight loss is undoubtedly due to volatilization of the FRs as the blends soften ahead of any combustion, lending further support to the findings from cone calorimetry that the FRs are largely ineffective in UP/PH and that the only marginal increases in flame retardance they produce arise largely from gas phase mechanisms. However, there is some small reduction in weight loss above 600 °C for UP/PH with RDP and DOPO. For UP/epoxy-PH (Fig. 2 (b2)), only RDP appears to be prematurely lost to any significant extent, and then only below about 400 °C; all the FRs lead to increased stability (reduced weight loss) above 450 °C, consistent with a greater contribution of condensed phase mechanisms to FR in these systems. The behaviour of UP/allyl-PH (Fig. 2 (c2)) is similar to that of UP/epoxy-PH, except that weight loss above 450 °C is reduced even more when the FRs are present; this is consistent with the greater effectiveness of the FRs in flame retarding UP/allyl-PH blends than they are in flame retarding the two other UP/resole blends, and also that in co-cured UP/allyl-PH blends, condensed phase mechanisms of flame retardance are significant, as indicated by the cone calorimetric data for this system (Table 4).

Further evidence that the FRs are functioning in the co-cured UP/resole blends mainly in the gas phase with respect to the UP component of blends and significantly in the condensed phase only with respect to the phenolic component is contained within the TGA weight loss curves in air for cured samples of the separate blend components: UP, PH, epoxy-PH and allyl-PH (Fig. 3). The weight loss curves for cured UP with the various FRs are similar to that for UP with no added FR, with only marginal increases in char when FR is present (Fig. 3(a)). However, for cured PH, epoxy-PH and allyl-PH, introduction of FRs leads to increased char formation and extends the range of temperatures over which some of this char at least remains unoxidized, i.e. from 700 °C to about 800 °C for PH and epoxy-PH, and from 600 °C to 800 °C for allyl-PH (Fig. 3(b), (c) and (d)). The extension in the temperature range of char stability is particularly striking for allyl-PH and is consistent with the particular efficacy of the FRs in UP/allyl-PH blends.

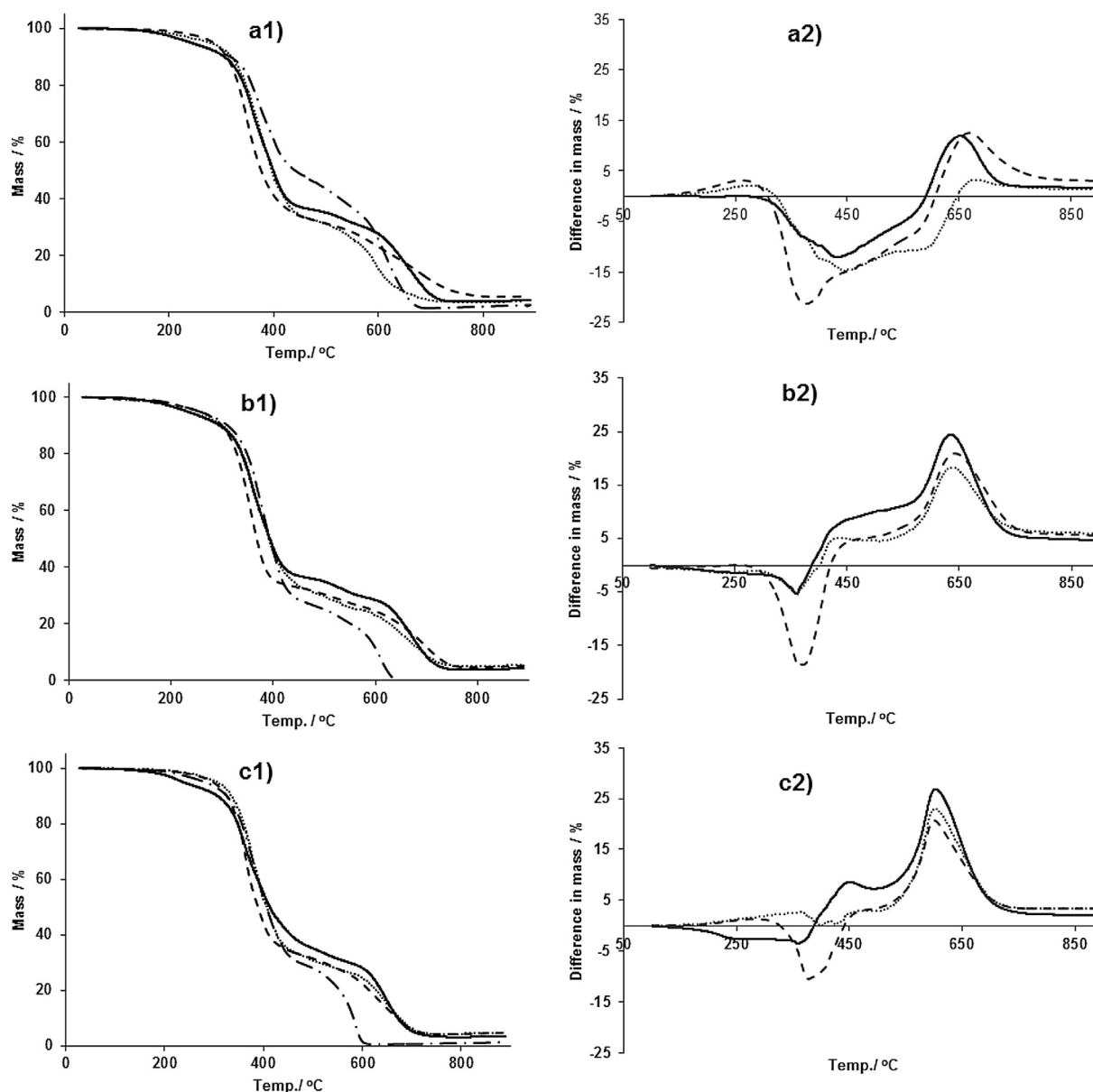


Fig. 2. TGA weight loss curves (a1, b1 & c1) and TGA weight loss difference curves, i.e., weight loss for blend with FR minus weight loss for blend without FR, (a2, b2 & c2) in air for co-cured 70:30% w/w UP/resole blends with no FR (— · — · —), with 20% w/w RDP (— · — · —), with 20% w/w BADP (·····) and with 10% w/w DOPO (—). (a1 & a2 = UP/PH, b1 & b2 = UP/epoxy-PH, and c1 & c2 = UP/allyl-PH).

3.3. The chemistry of FR action in co-cured UP/resole blends

P-containing flame retardants function by one of two general mechanisms: gas phase and condensed phase [22]. In the gas phase mechanism, a volatile P-containing oxidation product from the thermolysis of the FR acts as a free radical chain stopper in the gas phase. Such a product is the $\bullet\text{P}=\text{O}$ radical, which is produced readily from DOPO by a radical transfer reaction followed by thermal rearrangement (Scheme 1) [23].

Similar radicals can be produced by thermolysis of other phosphonates, and of alkyl and aryl phosphates and phosphine oxides [24–26]. Clearly, from the results presented here, this is the major mode of action of RDP, BADP and, especially, DOPO in flame retarding UP and co-cured UP/PH blends, and a contributor also to flame retardation of co-cured UP/epoxy-PH and UP/allyl-PH blends.

The condensed-phase mechanism of flame retardance by P-containing flame retardants is believed to involve primarily high

temperature oxidation of the P-containing FR in the liquid state producing polyphosphoric acids and anhydrides, which then dehydrate portions of the polymer producing H_3PO_4 and leading to increased C=C unsaturation in the polymer and, ultimately, to increased carbon-rich char formation; this mechanism of flame-retardance has been shown to be particularly important for polymers containing —OH groups, such as cellulose derivatives [27]. However, strong Brönsted acids, such as H_3PO_4 , in an organic medium, can act also as initiators for cationic crosslinking reactions involving C=C bonds, e.g. Scheme 2.

Cured UP contains no groups that can readily be dehydrated and is also too thermally labile (over 90% decomposition occurs below 400 °C [11]) for there to be much material remaining at temperatures at which polyphosphoric acids and anhydrides are formed, hence only a gas-phase mechanism of flame retardance applies in this case. However, in the co-cured UP/resole blends there are, within the cured resole matrices, oxymethylene linkages that can

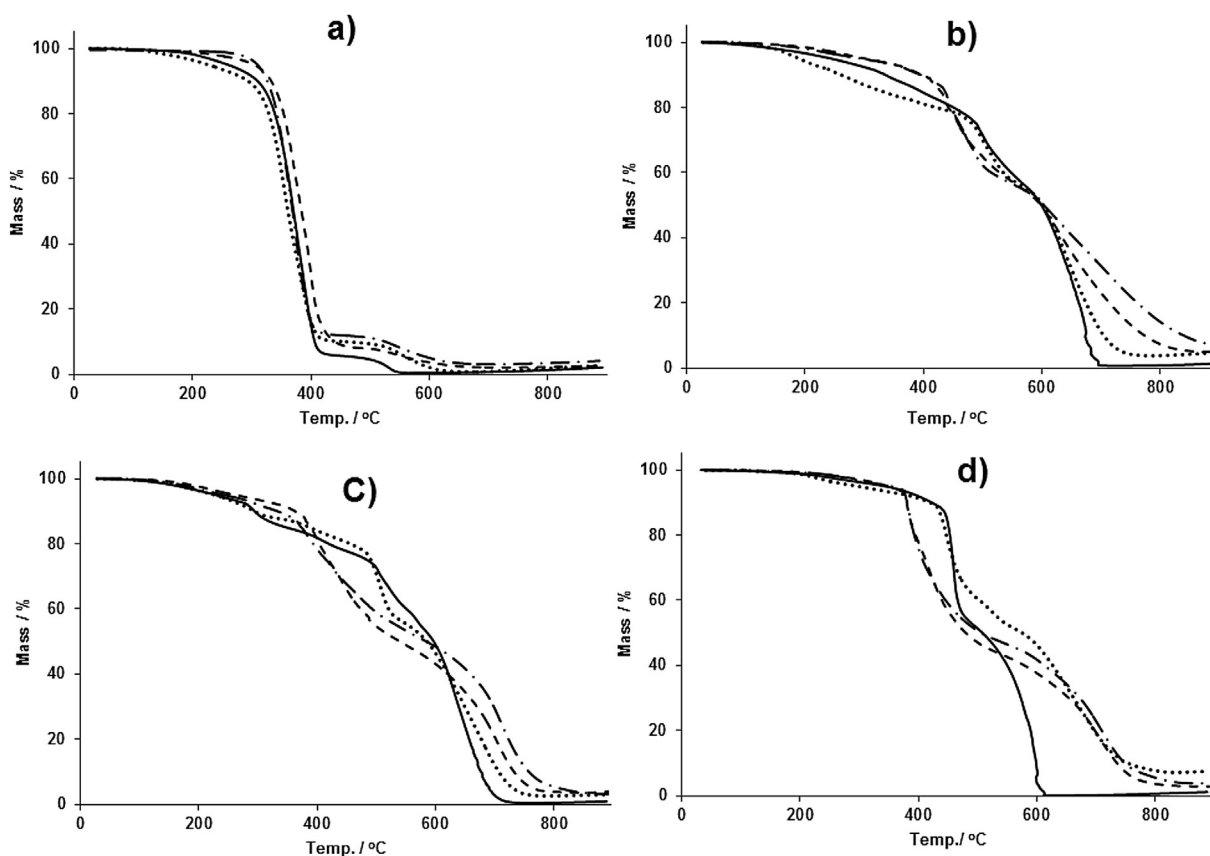
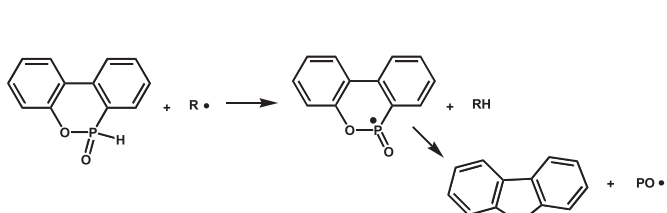
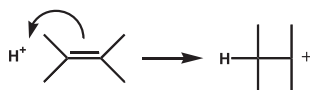


Fig. 3. TGA weight loss curves in air for (a) cured UP, (b) cured PH, (c) cured epoxy-PH and (d) cured allyl-PH, with no FR (—), with 20% w/w RDP (---), with 20% BADP (····) and with 10% DOPO (-·-·-·).

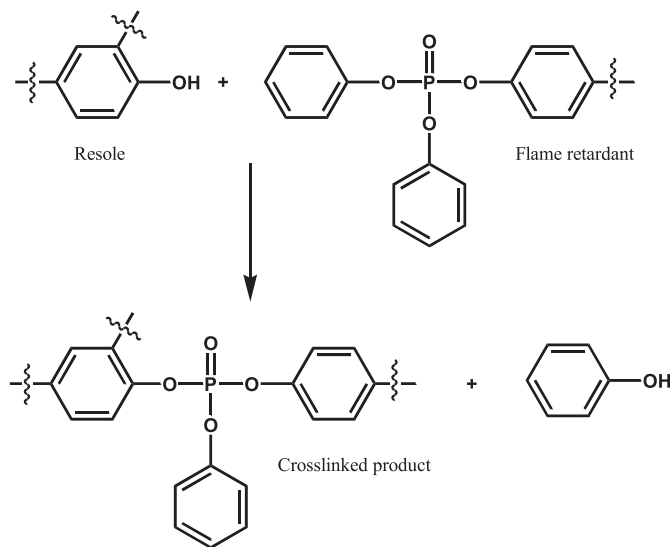


Note: R• may be H•, HO•, an alkyl radical, an alkoxy radical or any other reactive radical involved in the gas phase chain oxidation process.

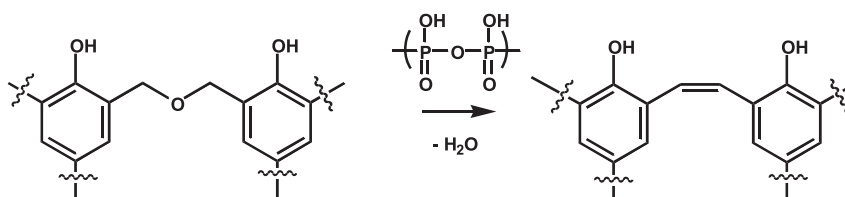
Scheme 1. Production of •P=O radical from DOPO by a radical transfer step followed by elimination.



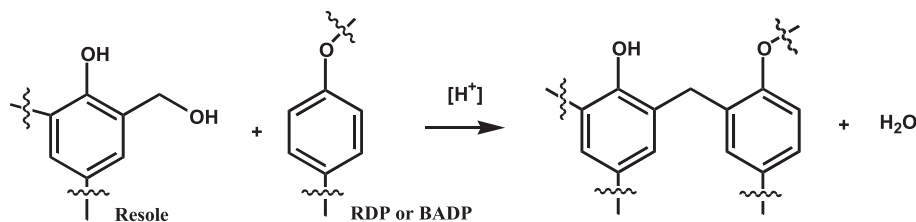
Scheme 2. Cationic crosslinking of C=C bonds initiated by H⁺.



Scheme 4. Crosslinking of resole via transesterification with RDP or BADP.



Scheme 3. Dehydration of oxymethylene bridges by phosphorus polyacids and anhydrides.



Scheme 5. Condensation of RDP or BADP with resole methylol group.

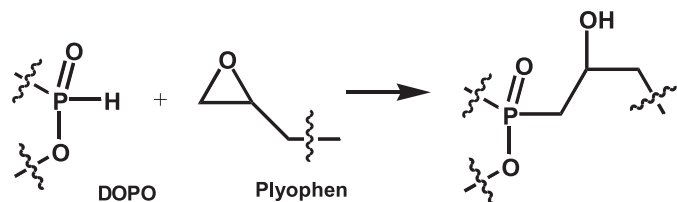
be dehydrated to give olefinic methine linkages, leading to increased C=C conjugation, greater thermal stability and providing a precursor to carbonaceous char formation (Scheme 3).

In phenolics, there are also possibilities of char catalysis via trans-esterification of phenolic OH groups with phosphate esters such as RDP and BADP (Scheme 4). Reactions such as these have been suggested, for example, as important contributors to condensed phase flame retardant action of RDP and BADP in polycarbonate-based polymer systems [28].

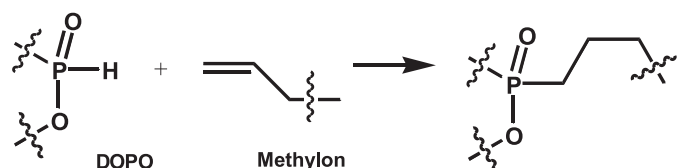
A further contributor to condensed-phase action of these FRs in co-cured UP/resole blends may be chemical reaction of the FR with one or both of the resin components during preparation and curing of the blend, especially given the high temperature involved in fully curing the resole component. Thus, aromatic groups in all three FRs may react with methylol groups present in the resoles via the type of reaction involved in the curing of the resoles themselves, especially RDP and BADP, given that they also are phenolic compounds (Scheme 5).

In co-cured UP/epoxy-PH blends, there is the additional possibility that the epoxy groups in epoxy-PH react with the P–H bonds of DOPO in a nucleophilic substitution reaction leading to ring-opening of the epoxy and attachment of the DOPO (Scheme 6). In co-cured UP/allyl-PH blends, reaction of DOPO may be possible with the C=C bonds of the allyl groups via an “ene” type reaction, with similar results (Scheme 7).

Reactions such as these would explain the retention, and apparent condensed-phase flame-retardant action, of much of the DOPO in the co-cured UP/epoxy-PH and UP/allyl-PH blends. It should be noted though that, at this point in our work, the reactions indicated in the above reaction schemes are largely matters of conjecture; work to elucidate gas phase and condensed mechanisms of flame retardance in these systems is continuing.



Scheme 6. Reaction of DOPO with epoxy group of epoxy-PH.



Scheme 7. Reaction of DOPO with allyl group of allyl-PH.

4. Conclusions

The flame retardance of naturally flame retardant co-cured blends of UP with epoxy-PH and with allyl-PH can usefully be improved by the addition of an organic P-containing FR such as RDP, BADP or DOPO. The flame-retardant action of these FR additives involves both gas-phase and condensed-phase components as indicated by increased yields of both smoke and char on combustion. The FRs are, however, least effective in co-cured UP/PH blends. The reasons for this are not clear, but may be associated with the decreased compatibility of UP with PH compared with UP/epoxy-PH and UP/allyl-PH. In UP/PH it is possible that the FR is excluded to a large extent from the PH phase and, residing largely in the UP phase, is released at relatively low temperatures into the gas phase during pyrolysis and combustion. The improvements in fire performance that follow from additions of FRs to UP/allyl-PH blends, i.e. the blends that are of most interest to us from the technological point of view, are shown schematically in the Fire Safety Assessment Grid (plot of THR vs. PHRR/TTI in which, THR is total heat released, PHRR is peak heat release rate, and TTI is time to ignition) presented in Fig. 4. Given that it is the 70:30% w/w co-cured blend of UP and allyl-PH that possesses the best combination of physical and mechanical properties, DOPO would seem to be, on balance, the flame retardant additive of choice for this system; it can be seen from Table 1 that in the 70:30% w/w blend, addition of 10% w/w DOPO leads to a marginal increase in TTI, a 44% reduction in PHRR, a 32% reduction in THR and a 55% increase in char residue, albeit with a 22% increase in TSR (total smoke released).

Effects of the additional FRs upon the physical and mechanical properties of the co-cured blends and fibre-reinforced composites derived from them are currently being investigated, as are further aspects of pyrolysis and combustion.

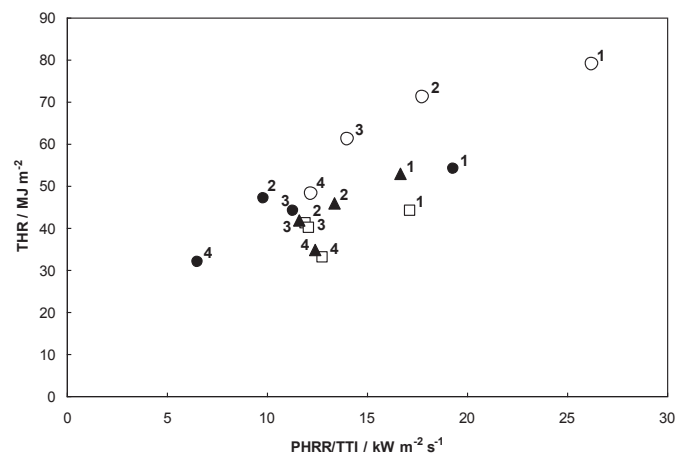


Fig. 4. Fire Safety Assessment Grid (THR vs. PHRR/TTI) for cured UP, cured allyl-PH and cured UP/allyl-PH blends without FR: ○; with RDP (20% w/w): □; with BADP (20% w/w): ▲; and with DOPO (10% w/w): ●. Key to numbers: 1 = cured UP, 2 = co-cured UP/allyl-PH 70:30; 3 = co-cured UP/allyl-PH 50:50 and 4 = cured allyl-PH.

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