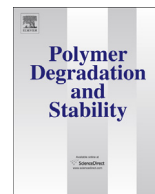




Contents lists available at ScienceDirect

Polymer Degradation and Stability

journal homepage: www.elsevier.com/locate/polydegstab

Blends of unsaturated polyester and phenolic resins for application as fire-resistant matrices in fibre-reinforced composites. Part 2: Effects of resin structure, compatibility and composition on fire performance

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ARTICLE INFO

Article history:

Received 20 May 2014

Received in revised form

7 October 2014

Accepted 2 November 2014

Available online xxx

Keywords:

Unsaturated polyester

Phenolic resole

Blend

Fire performance

Thermal stability

Cone calorimetry

ABSTRACT

The effects of co-curing blends of an unsaturated polyester (UP) with inherently fire-retardant and char-forming phenolic resoles (PH) on the thermal stability and fire retardancy of the resulting resins have been investigated. To overcome the challenge of UP/PH incompatibility, arising from their different chemical structures and curing mechanisms (radical vs. condensation), different phenolic resoles have been used: ethanol-soluble, epoxy-functionalized, and allyl-functionalized. A traditional water-based resole has also been used to give a reference non-compatible system. In Part 1 of this series of publications it was shown that the compatibility of the two resins increases with functionalization; the allyl-functionalized resole showing the best compatibility with UP. Limiting oxygen index measurements and cone calorimetry have shown that fire performance of the functionalized PH resins and their blends with UP is worse than that from the unfunctionalized PH resin, but still significantly better than that of the UP. To understand this behaviour, thermal analyses coupled with infrared spectroscopy of volatile degradation products have been used on all resins and their blends, based on which, mechanisms of their decomposition and interactions are proposed, and the effects of these on flammability are discussed.

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1. Introduction

Fire, smoke and toxicity standards for glass fibre-reinforced polymeric composites (GRPs) based on unsaturated polyesters (UP) and used in marine and mass transit systems especially, are closely monitored. UP resins burn readily in air, their aromatic contents from species such as styrene and phthalic acid functionalities, cause significant smoke generation [1]. Typical halogenated flame-retardant formulations used for UP systems serve the purpose of reducing flammability but consequent increases in the corrosiveness, toxicity and the smoke content of the resultant combustion products are major disadvantages. Inorganic additives such as alumina trihydrate reduce flammability and smoke production, but for them to be effective, very high quantities (typically >50 wt%) are required, which cause processing problems and adversely affect the mechanical properties of laminates based on these resins [2–4]. Even chemically reactive type flame-retardant

additives are usually required in concentrations >30 wt% to be effective enough to pass commercial flammability tests [2,3]. An environmentally friendly alternative is to blend the resin with another inherently flame-retardant and char-forming resin such as a phenolic [2,3,5] or melamine formaldehyde resin.

Polymer blending is designed to generate materials with optimized chemical, structural, mechanical, morphological or biological properties. Ideally, in a polymer blend the components are chosen such that the weaknesses of one polymer can, to a certain extent, be masked by the strengths of the other and vice versa [6]. Preparation of different ratios of blended polymers requires many combinations and each has to be individually characterized [7]. In a polymer blend two or more polymer chains having constitutionally or configurationally differing features are in intimate combination but not bonded to each other. Polymer blends will typically display the good properties of each polymer. UP resins can be blended with epoxy resins [8–10]; similarly phenolic resins can be blended easily with epoxies [11]. Blending of UP with phenolic resins, however, is a challenge owing to the different curing mechanisms of these two resins: resoles (phenolic resins bearing reactive methylol groups) cure by condensation reactions

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with the elimination of water (incompatible with UP) and novolacs (phenolic resins to which a formaldehyde derivative, e.g. hexamethylenetetramine, has to be added to effect cure) are cured, usually under pressure to prevent the release of volatiles, at temperatures of up to 180–200 °C [12]. UP resins, on the other hand, are cured by a free radical process after the addition of a crosslinking monomer such as styrene, usually at temperatures below 80 °C [13]. Nevertheless, interpenetrated cured structures have been formed from UP and some phenolic resoles by vigorous dispersive mechanical stirring followed by a multistage curing regime [13,14].

The main aims of this research are to reduce the flammability of UP by blending with compatibilized phenolic resoles (PH) [15], to study the effects of different PH on the flammability/fire retardancy of UP, and to understand the mechanisms of decomposition of different types of blends and how these impact upon fire performance. Compatibilization strategies include the use of a common solvent, or the chemical functionalization of at least one of the components of the blend [13,15]. Four different commercially available PH resoles, PH1, PH2, PH3 and PH4 have been selected and blended with a UP. PH1 is water soluble; PH2, although having structure similar to that of PH1, is ethanol-soluble; PH3 is epoxy-functionalized; and PH4 is functionalized mainly with allyl groups. PH1 was chosen so that we could blend a traditional water-based resole with UP to give a reference, non-compatible system, whilst the three other resoles have been shown to have increased compatibility with UP in that PH2 employs a solvent (ethanol) with which both resins are compatible, PH3 is also isopropanol-based but in addition has the epoxy functionality, which may react during curing with any terminal carboxylic acid groups in the UP, and the allyl groups in PH4 have the potential to co-cure, free radically, with the carbon–carbon double bonds in the UP backbone and the styrene crosslinking monomer present in the UP. In Part I of this series of publications [13], the physical and chemical properties of cured UP/PH mixtures have been investigated, principally by differential scanning calorimetry (DSC), differential mechanical thermal analysis (DMTA), solid-state ¹³C NMR spectroscopy and scanning electron microscopy (SEM). The results have shown that the compatibility of UP with PH increases in the order PH4 > PH3 > PH2 > PH1. In this part we describe our studies of the effects of PH structure and blend compatibility on fire performance.

2. Experimental

2.1. Materials

The following materials were obtained from commercial sources:

Crystic[®] 2.406PA, Scott-Bader: an unsaturated, phthalic anhydride-based UP containing 35–40 wt% styrene, pre-accelerated with cobalt octoate.

Catalyst M, Scott-Bader: a methyl ethyl ketone peroxide-based radical catalyst for UP curing.

Durez 33166, Sumitomo-Bakelite Europe N.V: a water-based phenolic resole containing 25–30 wt% water (PH1).

Durez 33156, Sumitomo-Bakelite Europe N.V: an ethanol-based phenolic resole containing 20–29 wt% ethanol (PH2).

Plyphen 23983, Sumitomo-Bakelite Europe N.V: an isopropanol-based, epoxy-functionalized, phenolic resole containing 16–18 wt% isopropanol and <6 wt% water (PH3).

Methylon 75108, Sumitomo-Bakelite Europe N.V: a solvent-free, allyl-functionalized, phenolic resole (PH4).

The chemical structures of these products have been given before [13]; all were used as received.

2.2. Casting and curing of resins and resin mixtures

A sample of cured UP resin was prepared by mixing 60 g resin with 2 wt% of catalyst M with a mechanical stirrer in a 100 mL beaker. 11 g of this mixture was then poured into a 5.5 cm diameter circular aluminium open mould to a depth of 3 mm. The specimen was then allowed to cure at room temperature for 24 h and post-cured at 80 °C in an oven for 4 h. Samples of PH resins (Table 1) were directly transferred to 5.5 cm diameter circular moulds (11 g in each case), again to depths of 3 mm, cured and then post cured by increasing the temperature slowly up to 200 °C; detailed curing conditions are given in Part 1 of this series of papers [13].

The formulations of the major resin blends (Table 1) were prepared by mixing UP and each PH in 70/30 or 50/50 wt% ratios with a mechanical stirrer (IKA[®] RW 16 overhead electric, four bladed propeller stirrer) at high shear (900 rpm) in a 100 mL beaker. The required quantity of catalyst M (2 wt% with respect to UP) was added to the resin mixture which was stirred for a further 10 min. The resulting resin mixtures (11 g for each specimen) were transferred to aluminium moulds, cured at RT for 24 h and then post cured by increasing the temperature slowly up to 190 °C; detailed curing conditions are again given in Part 1 [13].

2.3. Flammability study

2.3.1. Limiting oxygen indices

The limiting oxygen indices (LOI) of all cured resins and their blends were measured according to a standard method (BS 2782) using a Fire Testing Technology (FTT) LOI instrument equipped with an oxygen analyzer. At least five specimens of dimensions 100 mm × 10 mm × ca. 3 mm were tested for each sample.

2.3.2. Cone calorimetry

A cone calorimeter (Fire Testing Technology Ltd, UK) was used to assess the flammability parameters of the UP-based systems studied in this work. Circular samples measuring 55 mm in diameter with a nominal thickness of ca. 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 surfaces and the edges of the samples were wrapped with aluminium foil to ensure that only the top surfaces 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 round and standard square samples (100 mm × 100 mm) was undertaken in order to understand the effect of geometry on flammability properties of polymeric materials [16]. 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 standard specimens since these parameters are dependent on exposed specimen surface area. However, in the study reported here, these data were used for comparison purposes with respect to the control specimens hence there was no need for adjustments.

2.3.3. Thermogravimetry-FTIR study

Thermogravimetric analyses (TGA) of all cured resins and their blends were performed on an SDT 2960 simultaneous DTA (differential thermal analysis) – TGA instrument from room temperature to 800 °C using 15 ± 1 mg samples heated at a constant rate of 10 °C/min in both air and nitrogen flowing at 100 ± 5 mL/min. The experiments were performed in duplicate and showed good reproducibility. Averaged data is presented. During the experiments in nitrogen and some of the experiments in air, the SDT 2960 simultaneous thermogravimetric analyzer was linked to a Nicolet

Table 1Limiting oxygen index and cone results of cast resin samples of UP, PH1, PH2, PH3, PH4 and their blends at 50 kW/m².

Sample	LOI	Cone results						Char residue from TGA at 575 °C	
		TTI (s)	FO (s)	PHRR (kW/m ²)	THR (MJ/m ²)	TSR (m ² /m ²)	Residue (%)	In air (%)	In N ₂ (%)
UP	17.9	40	178	1053	78.9	4090	1	0.4	4.3
PH1	31.8	84	175	534	41.0	965	46	54.1	61.8
UP/PH1:70/30	20.7 (22.1)	34 (53)	117 (177)	962 (897)	51.0 (67.5)	1700 (3152)	18 (15)	28.9 (16.5)	25.9 (33.0)
UP/PH1:50/50	21.3 (24.9)	37 (62)	153 (176)	787 (793)	44.6 (60.1)	1683 (2527)	26 (24)	42.3 (27.3)	39.3 (27.3)
PH2	23.0	33	156	452	37.6	594	46	55.5	58.6
UP/PH2:70/30	19.5 (19.4)	31 (38)	178 (171)	630 (872)	62.3 (66.5)	2307 (3278)	24 (15)	32.9 (16.9)	20.4 (20.6)
UP/PH2:50/50	19.8 (20.4)	31 (37)	156 (167)	568 (752)	48.4 (58.2)	1357 (2342)	37 (24)	43.3 (27.9)	36.8 (31.5)
PH3	23.1	35	145	489	34.2	603	48	54.9	58.0
UP/PH3:70/30	18.7 (19.5)	39 (39)	148 (168)	885 (883)	54.3 (65.5)	2699 (3043)	11 (16)	17.3 (16.7)	19.0 (20.4)
UP/PH3:50/50	19.7 (20.5)	34 (38)	151 (162)	682 (771)	49.6 (56.6)	2203 (2346)	20 (25)	32.6 (27.6)	35.5 (31.1)
PH4	22.2	72	216	804	47.8	2209	27	28.8	42.8
UP/PH4:70/30	19.0 (19.2)	54 (50)	179 (189)	955 (978)	70.7 (69.6)	3819 (2929)	11 (9)	13.5 (8.9)	19.6 (15.9)
UP/PH4:50/50	19.6 (20.1)	57 (56)	201 (197)	828 (928)	61 (63.3)	3166 (3149)	14 (14)	4.0 (14.6)	27.1 (23.6)

Note: 1. The variation in values for different parameters are as: TTI = ±2; PHRR = ±32; THR = ±2.3; TSR = ±150; residue % = ±4.
2. The values in parentheses and in italics are calculated from those of the components.

Smart iTR iS10 FTIR spectrophotometer for the analysis of gases evolved during decomposition.

3. Results and discussion

3.1. Flammability of resins and resin blends

3.1.1. Limiting oxygen index (LOI)

Measurement of limiting oxygen index (LOI), the minimum concentration of oxygen expressed as a percentage that can support candle like flaming combustion of a polymer, is a quantitative method whereby the relative flammabilities of materials can be evaluated. An increase in the LOI value suggests an improvement in the resistance to ignition of materials being investigated. LOI values of all samples are given in Table 1. UP has a much lower LOI (17.9%) than any of the PH, which is as expected. In general, all phenolic resins have LOIs higher than that of UP, indicating the lower flammability of phenolics. The order of LOI values for the pure cured resins is:

PH1 > PH2 > PH3 > PH4 > UP

This indicates that the unfunctionalized resins (PH1 and PH2) may have lower flammability than the functionalized resins and that the flammability increases with an increase in functionality.

PH1 has an exceptionally high LOI (31.8%). PH1 and PH2 are similar in structure, the only difference is the solvent. While PH1 is water-based, PH2 is initially dispersed in ethanol; the presence of residual ethanol trapped in cured PH2 may account for its slightly higher ignitability (lower LOI). On the other hand, in PH3 some of the methylol group functionality is replaced by epoxy functionality, whilst in PH4 there are very few methylol groups, this resin relying principally upon high temperature cure of allyl groups in its normal commercial application as a surface coating material. Reducing the methylol content reduces the number of potential conventional (methylol plus methylol or methylol plus phenol) crosslinking sites within the cured phenolic component. Hence, the less cross-linked PH3 and PH4 resins have, as expected, lower LOIs.

The LOIs of the blends are between those of UP and PH and increase with increasing phenolic content, as can be seen in Table 1. The values for UP/PH1 blends are lower than weighted averages calculated from the values of the components (Table 1); this pattern has been reported before for incompatible blends of UP and PH and may be a consequence of the incompatibility, the unblended domains of UP acting as sources of ignition [14]. The values for all

other blends are close to calculated values considering the probable error.

3.1.2. Cone calorimetry

Resins: The cone calorimetric fire performances of UP, phenolic resins and their blends were evaluated at 50 kW/m² heat flux. During burning of the PH1 and the UP/PH1 blend resins some spalling was observed. Phenolic resoles in general during curing release water, which can create voids in the cured samples. These voids during burning cause spalling, and delamination in the case of fibre-reinforced composites. In cured PH1 and UP/PH1 cast resins voids were visible and could not be avoided during the preparation stage, which is understandable as this is a water based resin. However, all other phenolic resins and their blends could be cured to give samples without any voids. Hence, these burnt smoothly without any spalling. The heat release rate (HRR), % mass and rate of smoke release (RSR) vs. time curves for all resins are plotted in Fig. 1, while all derived parameters, i.e. time-to-ignition (TTI), flame-out time (FO), peak heat-release rate (PHRR), total heat release (THR), total smoke release (TSR) and %residual mass for resins and UP/PH blends are given in Table 1.

As can be seen from Fig. 1(a) and Table 1, UP resin ignited at 40 s and burnt until 178 s, producing 78.9 MJ/m² THR with a PHRR of 1053 kW/m². Amongst the four phenolic resins, PH1 has highest TTI (84 s), followed by PH4 (72 s), while PH2 and PH3 ignite after 33 and 35 s, respectively. This trend is different from that expected from the LOI results. PH4, which has lowest LOI among the phenolic resins, has a much higher TTI than that of either PH2 or PH3. In general, even though phenolic resins are expected to have inherent flame-retardant properties, their TTIs are quite low. However, once ignited they burn slowly, with lower PHRR and THR compared with those of UP, as can be seen from Fig. 1(a). The lower flammability of phenolics is due to the greater number of relatively stable aromatic rings in their chemical structures [2,15,17] which, on heating, cross-link and char, whereas the UP resin decomposes into combustible volatiles, which burn. PH2 has the lowest PHRR of 452 kW/m² with a THR of 37.6 MJ/m². PH3 has a slightly higher PHRR (489 kW/m²) than that of PH2, but the THR is lower (34.2 MJ/m²) than that of PH2. PH4, on the other hand, has much higher PHRR (804 kW/m²) and THR (47.8 MJ/m²). This shows that PH2, PH3 and PH1 have lower flammability, whereas PH4 is more flammable despite its higher TTI. The char-forming ability of phenolics also follows the same trend as can be seen from Fig. 1(b) and the char yields given in Table 1. While UP is completely burnt away at the end of the experiment, the mass loss rates in all phenolics are lower than that

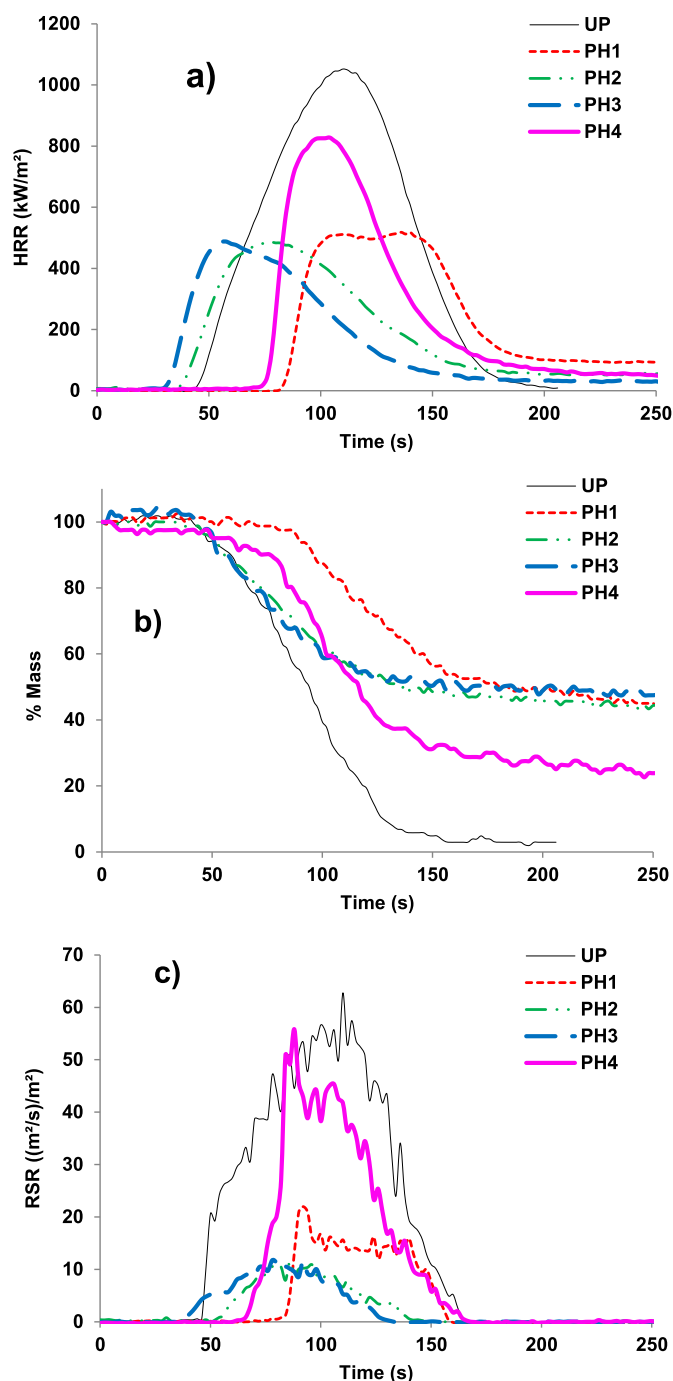


Fig. 1. a) HRR; b) mass loss and c) rate of smoke release versus time curves for UP, PH1, PH2, PH3 and PH4 resins at 50 kW/m² external heat flux.

of UP. PH1, PH2 and PH3 give 46–48 wt% residual char, whereas PH4 has higher mass loss rate than the other phenolic resins (see Fig. 1(b)) and leaves only 27% char residue at the end of the cone experiment. The smoke production in these PH resins also follows the same trend (Fig. 1(c)). High char-forming resins produce low smoke 594–965 m²/m², whereas PH4 produces much higher smoke, 2209 m²/m², although this is still lower than that of UP (4090 m²/m²), (see Table 1).

It is to be noted that PH1 is used only for comparative purposes. Since this is water based, it will normally not be used for blending with UP. Hence, the results for blends of UP with PH1, although

useful for studying the effect of compatibility, are not subsequently discussed in the same depth as those for blends with the other PH resins.

Resin blends: In UP/PH blends, as can be seen from Table 1, TTI is little affected by the presence of the phenolic resin in the cases of PH1, PH2 and PH3, the values being similar to, or slightly lower than, that of UP. This is more clearly seen from the calculated average values in Table 1 and in Fig. 2(a) in which the difference between TTI for the blend and that of the UP is plotted. This indicates that since these blends are not intimately co-cross-linked, and that the UP ignites first. In the UP/PH4 blend, on the other hand, the TTI is much higher than that of UP and almost the same as the calculated average value. This could be due to the fact that the blend is co-cross-linked [13], and hence displays the ignition behaviour of a homogeneous material.

Most other parameters for the blends are between those of the pure phenolics and pure UP, and the influence of the PH increases with increasing PH content, as can be seen from Fig. 2. The results for UP/PH2 however, are particularly interesting: PHRR, THR and TSR values for the blend are much lower than expected based on consideration of average values or these parameters calculated from the results for the individual components, as shown in Table 1. These differences are not so pronounced in UP/PH1 and UP/PH3 blends, in particular not for 70/30 wt% ratios of components. The differences are least in UP/PH4; for the 70/30 wt% blend, values of PHRR, THR and TSR are similar (considering probable error) to the calculated values. The differences between measured and calculated average mass loss rates also follow the same trend, which is reflected by the higher than expected char yields in UP/PH1 and UP/PH2 shown in Table 1 and Fig. 2(e). The much higher than expected char yields for UP/PH2 blends can be clearly seen in Fig. 2(e). These results indicate that during thermal degradation of UP/PH2, there is some kind of interaction between the degradation products from each component. Whereas in UP/PH4 blends, which are more compatible and probably more fully co-cross-linked [13], the flammability is greater, although still lower than that of UP. In terms of smoke production, PH2 blends produce lower TSR than PH3 and PH4 blends. The trend in TSR is similar to those of the other flammability parameters.

In order to try to understand these trends in fire behaviour of UP/PH blends, thermogravimetric analyses (mass loss as a function of temperature) coupled with infrared spectroscopic analyses of gases evolved during degradation (TGA-FTIR) have been performed.

3.2. Thermal stability

The thermal stability and degradation behaviour of the cured UP, the various PH and their blends have been studied by simultaneous DTA-TGA in both nitrogen and air atmospheres. Plots of mass loss as a function of temperature for all resins in nitrogen and in air are shown in Figs. 3 and 5 and the analyzed results of TGA, DTG (differential thermogravimetric analysis) and DTA in both atmospheres are tabulated in Table 2.

3.2.1. UP in nitrogen

The TGA mass loss curve of UP in nitrogen in Fig. 3(a) shows that up to ca. 180 °C, there is 0.9% mass loss, which can be attributed to volatilization of absorbed moisture, solvent and/or any unreacted monomers. There is a single-stage mass loss for UP between 183 and 462 °C with 94.8% mass loss and DTG max at 383 °C, representing decomposition of the resin, in which polystyrene cross-links decompose releasing styrene and other volatiles, and the residual polyester backbone degrades [17–20]. That this is a single-stage decomposition is corroborated also by the appearance of a

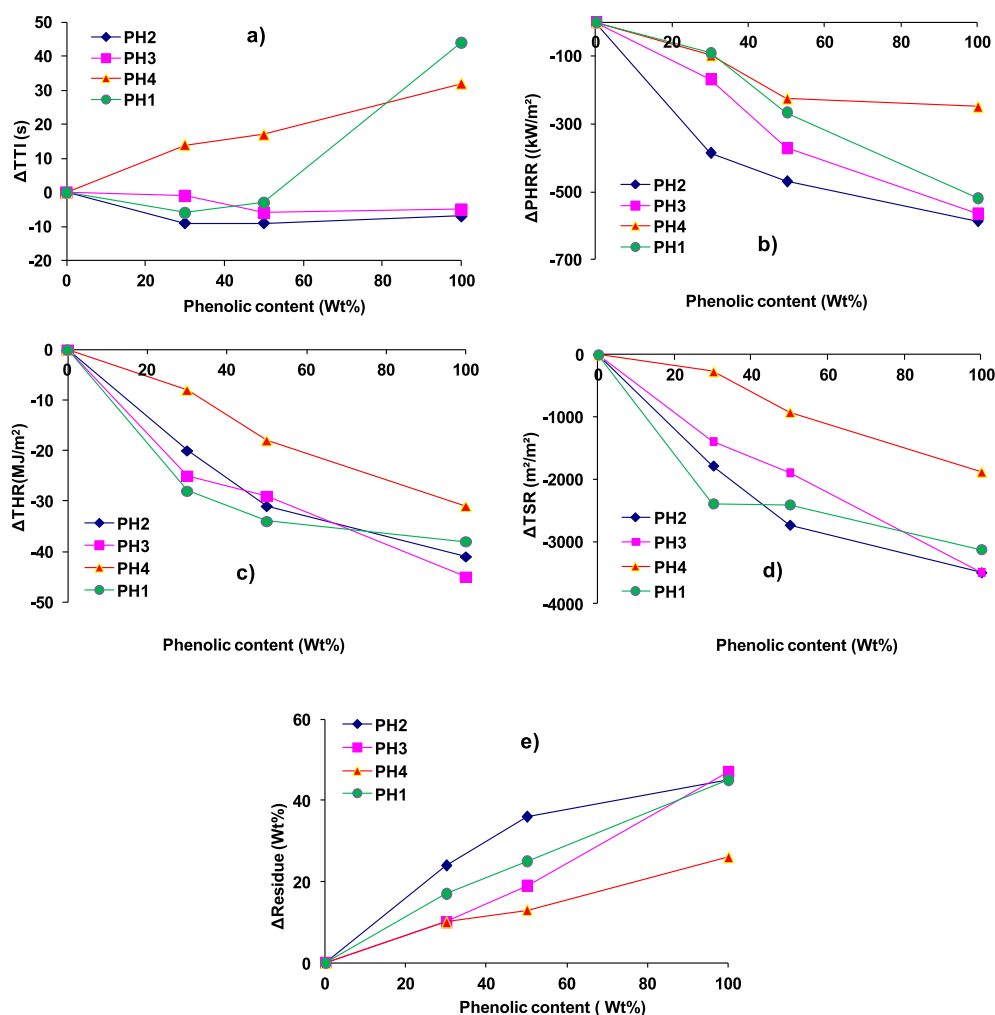


Fig. 2. Effect of phenolic content on a) TTI, b) PHRR, c) THR, d) total smoke production and e) %residual mass in UP-PH blends.

single endothermic DTA peak at 369 °C (Table 2(a)). The reactions contributing to this degradation process are discussed later.

3.2.2. UP in air

As seen from Fig. 3(a), the TGA curve for UP in air indicates two main stages of mass loss. The first one, representing decomposition of the resin, is very similar to that in nitrogen up to 435 °C with 93.1% mass loss, except that UP clearly degrades slightly more readily in air than in nitrogen (10% mass loss by 308 °C in air as opposed to 325 °C in nitrogen), which is to be expected given that polystyrene and linear polyesters (model compounds for the sequences in UP) both degrade more readily in air than in nitrogen owing to free-radical, auto-oxidative, contributions to degradation. (For example, in separate TGA experiments, we have shown that polystyrene loses 10% mass by 354 °C in air vs. 404 °C in nitrogen, and that poly(ethylene terephthalate) loses 10% mass by 391 °C in air vs. 407 °C in nitrogen.) In polystyrene, auto-oxidation is initiated at carbons alpha to the phenyl rings [21], whereas in polyesters it is initiated at carbons alpha to ester and ether links [22]. A general mechanism for such auto-oxidations was first proposed by Bolland and Gee [23]. The second stage of mass loss in UP in the temperature range 435–566 °C (with DTG maximum at 532 °C) with 5.6% mass loss, represents solid-state oxidation of char [18]. The decomposition stage is accompanied also by a small endothermic DTA peak at 352 °C, which is overlapped by a subsequent large

exothermic DTA peak having a maximum at 404 °C; the exothermic peak arises from oxidation of volatile degradation products. The char oxidation stage is represented by an exothermic peak with maximum at 533 °C. As can be seen from Fig. 3(a), the resin decomposes completely by 575 °C, leaving no char residue. The detailed mechanisms of these reactions have been discussed elsewhere [17,20] and are summarised in a later section.

3.2.3. PH resins in nitrogen

The pyrolysis behaviours of all phenolic resins in nitrogen (Fig. 3(b–d)) are similar, showing principally two stages of mass loss, the temperature range and %mass loss for each of which depend upon resin type. In all resins there is a small mass loss (ca. 4%) below ca. 315 °C in PH1 and PH2, ca. 266 °C in PH3 and ca. 366 °C in PH4. This mass loss could be due to volatilization of adsorbed moisture, water of reaction (post curing or dehydration) and any unreacted oligomers. In PH3 there is further mass loss of 8.3% in the temperature range 266–357 °C, giving rise to a DTG peak maximum at 302 °C and accompanied by an endothermic DTA peak with a maximum at 301 °C. This mass loss could be due to breakdown of epoxy groups for which, in epoxy resins, a free-radical mechanism has been suggested [24]. The main decomposition reactions are represented by the second stage, which is multi-step in PH1, PH2 and PH3, as can be seen from the multiple DTG and DTA peaks, listed in Table 2(a). The mass losses in this region in PH1, PH2 and PH3 are

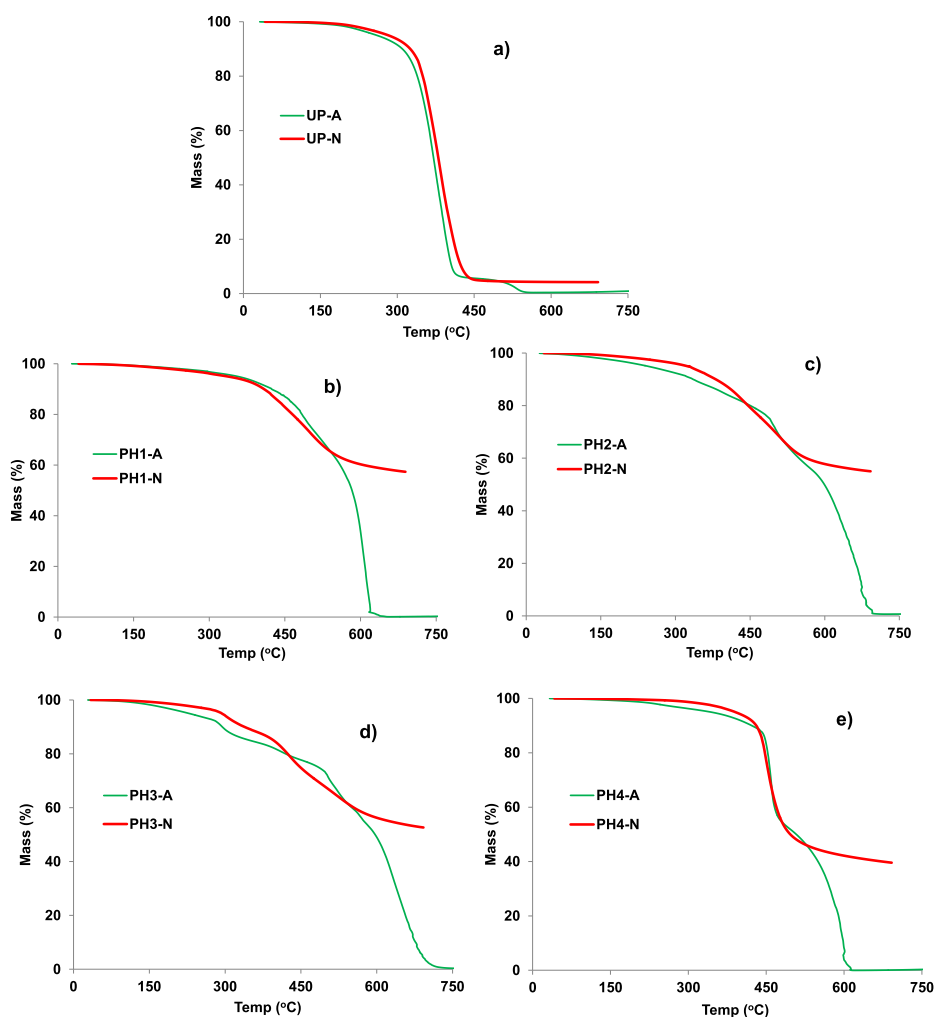


Fig. 3. TGA curves of cured UP and phenolic (PH1, PH2, PH3, PH4) resins in air and N₂.

similar, i.e., 38.3, 41.0 and 35.9%, respectively, whereas in PH4 it is much higher (57.2%). This can be explained by the different type of crosslinking initially present in PH4 and by the further reactions that take place in PH4 when it is heated. The char residue left at the end of the TGA experiments in resins PH1, PH2, PH3 and PH4 are 57, 55, 53 and 40%, respectively (see Fig. 3). These results correlate well with the LOI and the cone parameters presented in Table 1, in that they demonstrate the well-known relationship between char yield and flammability [25]. PH4, while degrading more comprehensively than the other PH resins, decomposes at a higher temperature as evident from endothermic peak maximum at higher temperature (454 °C) compared to ca. 400 °C in the other three resins. We believe this is because PH4 is intended for surface coatings applications, and cures principally via free radical polymerization of its allyl groups

[26], rather than by reactions between methylol groups and phenolic rings, as indicated in Fig. 4. Moreover, this curing almost certainly continues through the early stages of TGA heating since we have detected unreacted allyl groups in our relatively low-temperature cured PH4 prior to TGA analysis by solid-state ¹³C NMR spectroscopy [13]. In common with other chain-reaction linked polymers, PH4 begins to degrade significantly only when the temperature approaches 400 °C, at which point the previously polymerized allyl groups depolymerize with rapid disintegration of the network and the units from which it is comprised. This difference in network structure is probably the reason also why the char yield from PH4 is significantly less than those from PH1, 2 and 3.

3.2.4. PH resins in air

In air, the mass loss behaviour for the first small mass loss and subsequent decomposition stages are similar to the respective behaviour of each resin in nitrogen, ignoring small variations in degradation temperature and mass loss, which will be due to auto-oxidation reactions as with UP. There is an additional char oxidation stage in all resins in which >50% mass loss occurs.

The DTA curves of all resins in air show only exothermic peaks (Table 2(b)). The broad endothermic peaks representing decomposition reactions and product volatilization are masked by the exothermic base line deviations/peaks representing oxidation of the evolved decomposition products. In PH1 there is no clear peak,

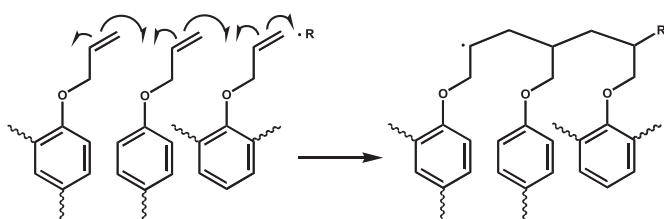


Fig. 4. Crosslinking of PH4 via radical polymerization of allyl groups.

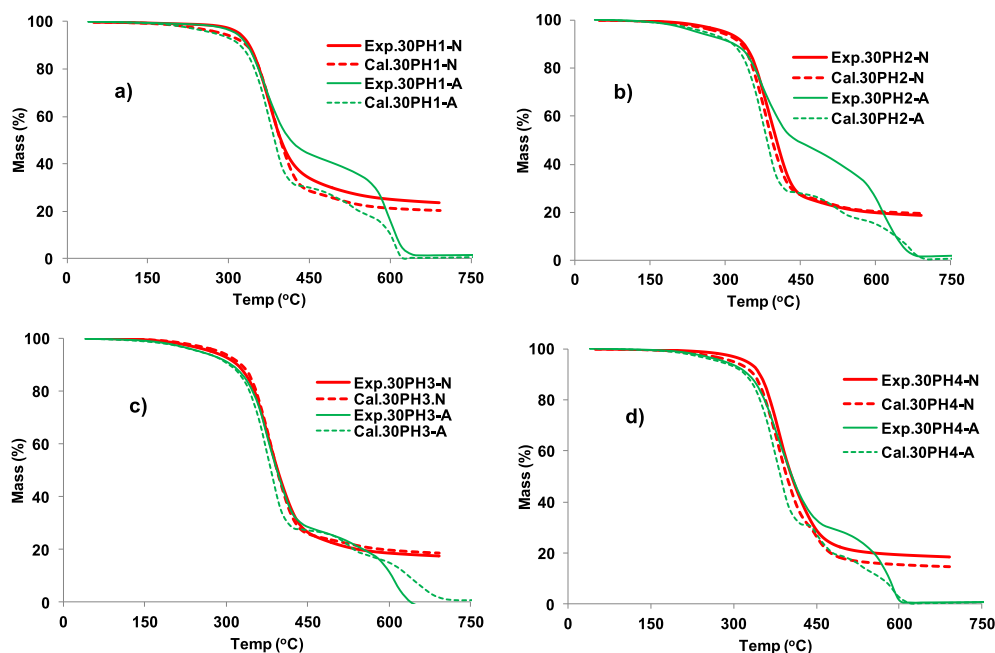


Fig. 5. TGA curves of 70:30 blends of UP and phenolic (PH1, PH2, PH3, PH4) resins in air and N₂.

whereas both PH2 and PH3 display an exothermic peak at 505 °C; in PH4 this peak occurs at a lower temperature (457 °C). The subsequent large exothermic peak due to the oxidation of the char is at a lower temperature in PH1 (601 °C) than in PH2 (671 °C), while in PH3 and PH4 there are double peaks at 569 + 629 °C and 593 + 611 °C, respectively. The decomposition of phenolic resin is reported to start with the release of water arising from further condensation reactions [27–29]. The released water may then assist in oxidation of methylene links to carbonyl groups [27,30], which subsequently decompose, releasing CO, CO₂ and other volatile products leaving, ultimately, char.

As can be seen from Table 2(b), the mass losses in the various stages for the various PH resins are different, which indicate slight differences in their modes of degradation. All PH resins degraded completely in air, leaving no residual char. The temperatures at which zero residue was observed are 610, 697, 718 and 615 °C for PH1, PH2, PH3 and PH4, respectively. The masses of residues at 575 °C (the temperature at which UP is completely decomposed) for all phenolic resins are given in Table 1. For PH1, PH2 and PH3, the amounts of residue at 575 °C are similar (*ca.* 55%), whereas for PH4 the amount of

residue is much lower (28.8%). Moreover, in PH1, PH2 and PH3, these residual amounts are only slightly higher in nitrogen than they are in air, whereas in PH4 the residual amount is much higher in nitrogen (42.8%). This indicates that PH4 is more readily oxidised than PH1, PH2 and PH3, which is consistent with PH4 undergoing a radical chain oxidation process, similar to that for UP, whereas PH1, PH2 and PH3, being more highly cross-linked and containing no readily depolymerizable chains, are more resistant to oxidation.

3.2.5. UP/PH blends in nitrogen and air

TGA mass loss vs. temperature curves for blends, in both nitrogen and air, lie between those of the constituent UP and PH resins, as can be seen by comparing the TGA mass loss curves for the 70:30 wt% UP/PH blends, shown in Fig. 5(a–d), with those for the constituent resins in Fig. 3. In Fig. 5, the calculated mass losses ((mass fraction of UP × measured mass loss of cured UP) + (mass fraction of PH resin × measured mass loss of cured PH)) are also presented. As can be seen from the figure, the experimental curves in nitrogen are very similar to the calculated ones. However, in air the thermal stabilities of UP/PH1 and UP/PH2 are greater than

Table 2(a)

DTA – TGA analysis in nitrogen.

Sample	Resin	UP/PH: 70/30				UP/PH: 50/50							
		Temp range (°C)	Mass loss (%)	DTG max (°C)	DTA (Endo) peak max (°C)	Temp range (°C)	Mass loss (%)	DTG max (°C)	DTA (Endo) peak max (°C)	Temp range (°C)	Mass loss (%)	DTG max (°C)	DTA (Endo) peak max (°C)
UP	RT-183	0.9											
	183–462	94.8	383	369									
PH1	RT-318	4.4	299	305	RT-260	1.6				RT-205	3.7		
	318–690	38.3	423,446,502	402	260–691	74.6	379	370	205–691	59.9	359	358	
PH2	RT-315	4.6	270	277	RT-280	1.3	399	375	RT-280	4.4			
	315–690	41.0	315(s),346(s), 439,500	317(s),347(s),399	280–691	74.7			161–691	61.6	376	362	
PH3	RT-266	2.3			RT-268	5.4			RT-263	1.6			
	266–357	8.3	302	301	268–691	77.1	380	373	263–691	65.7	376	365	
PH4	RT-366	3.6			RT-260	3.7			RT-285	1.7			
	366–691	57.2	451	454	177–691	77.9	382	381	285–691	73.3	380, 443	370, 445(s)	

Note: s = small (shoulder peak).

Table 2(b)
DTA – TGA analysis in air.

Sample	Resin				UP/PH: 70/30				UP/PH: 50/50			
	Temp range (°C)	Mass loss (%)	DTG max (°C)	DTA (Exo) peak max (°C)	Temp range (°C)	Mass loss (%)	DTG max (°C)	DTA (Exo) peak max (°C)	Temp range (°C)	Mass loss (%)	DTG max (°C)	DTA (Exo) peak max (°C)
UP	RT-183	0.9										
	183–435	93.1	373	352(En,s); 404								
	435–566	5.6	532	533								
PH1	RT-318	4.4			RT-260	1.6			RT-260	3.7		
	318–517	28.0	459	*	260–491	57.9	371	353(En)	260–549	48.4	353,408, 430	*
	517–629	67.6	601	592	491–660	39.3	603	603	549–601	45.7	600	602
PH2	RT-315	8.3			RT-278	7.2	222		RT-287	8.5	221	
	315–422	10.3	336, 393	*	278–523	52.2	371,402(s)		287–526	25.1; 12.2	353,490	418, 490
	422–567	25.8	494	504	523–699	39.1	611	611	526–716	52.1	619	617
PH3	RT-266	7.0			RT-268	5.9			RT-263	6.2	217	
	266–454	8.8; 6.9	293, 410	*	268–507	69.5	365,399(s)	*, 434	263–510	54.0	362	*
	454–552	17.8	504	505	507–687	26.3	610	608	510–710	38.6	612	610
PH4	RT-372	3.9		*	RT-260	4.3		*	RT-276	4.2	241	*
	372–490	44.0	459	457	260–486	67.2	379	417	276–494	62.7	365,444	444
	490–624	52.1	597,610(s)	593,611(s)	489–623	28.5	587	583	494–607	33.1	567	563

Note: s = small (shoulder peak); En = endothermic peak (all other peaks are exothermic)

* = Very broad endothermic peak, masked by baseline shift and following exothermic peak.

expected, whereas for UP/PH3 and UP/PH4 they are as expected. For more clarity, the differences between expected and calculated mass losses for both 70:30 and 50:50 wt% blends are plotted as a function of temperature in Fig. 6, which show that in air atmosphere blends of UP with PH1 and PH2 give much higher residual char than expected, whereas blends of PH3 have lower than expected stability between 560 and 700 °C. PH4 blends display similar behaviour to those of PH3, but at much lower temperatures. This indicates that UP/PH1 and UP/PH2 blends are more oxidatively resistant than

expected and thus their flammabilities should also be better than values calculated from those of the component resins. This greater than expected oxidative resistance of UP/PH1 and UP/PH2 may be a consequence of esterification reactions between unreacted methylol groups in the PH with carboxylic acid chain ends in the UP, although at higher temperatures, transesterifications between methylol groups and carboxylate links within the UP might also occur (Reactions 1 and 2, respectively, in Fig. 7). It should be noted however that such reactions would compete with reactions

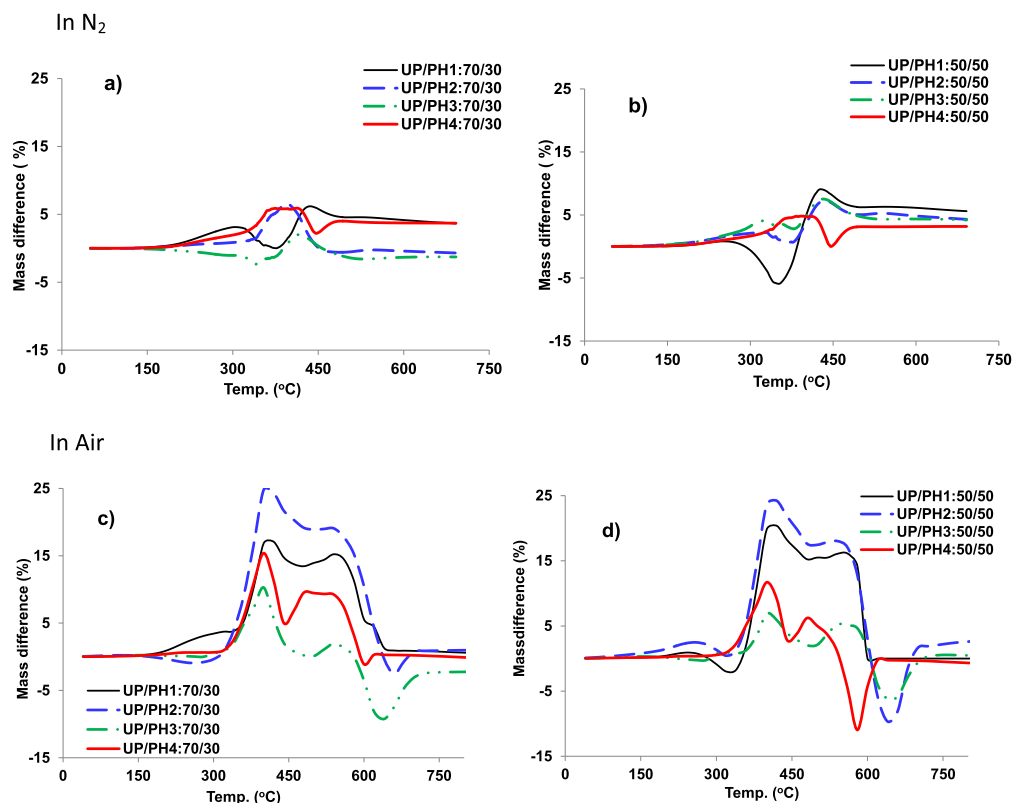


Fig. 6. Mass difference between experimental and calculated curves as a function of temperature for UP/PH:70/30 and UP/PH:50/50 in a), b) N₂ and c), d) air.

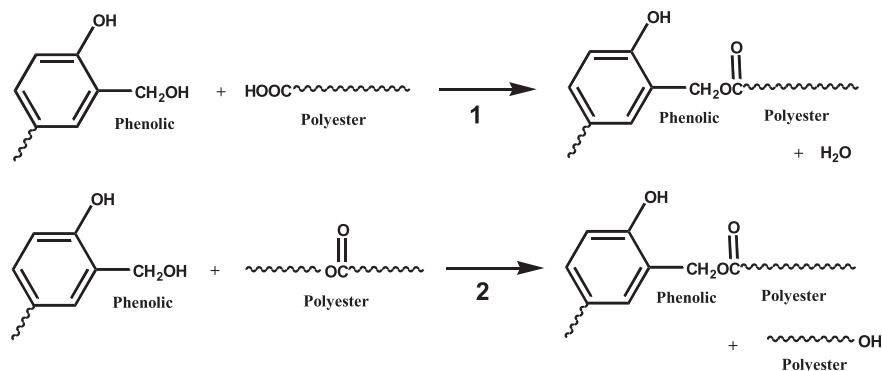


Fig. 7. Possible esterifications (Reaction 1) and transesterifications (Reaction 2) between PH and UP resins.

between methylol groups and the ortho and para positions of phenolic nuclei, so their probabilities might be quite low. Esterifications and transesterifications are less likely for UP/PH3 and UP/PH4, owing to the replacement of most methylol groups with epoxy groups in the case of the former and allyl groups in the case of the latter (although there are possible reactions between epoxy groups and carboxylic acid groups in the case of UP/PH3). Even so, although such reactions would lead to additional crosslinking in UP/PH1 and UP/PH2, it is not obvious that such crosslinking would automatically lead to greater oxidative stability. This behaviour of UP/PH1 and UP/PH2 is discussed more fully later.

However, in terms of thermal stability and thermo-oxidative stability (reduced mass loss rates), all blends are better than UP, the best value being shown by UP/PH1. The UP/PH blends also show

the same trends in flammability as in their thermal and thermo-oxidative stability.

3.3. Evolved gas analysis

TG-FTIR was used to analyse the gases evolved during the thermal decomposition of UP, PH resins and their blends in both nitrogen and air. In nitrogen, the pyrolysis products can easily be identified; in air, evolved gas analysis serves mainly to give an indication of the extent of oxidation of volatiles. Fig. 8 shows IR absorbance spectra recorded for volatile products of degradation of UP and one phenolic resin (PH2) at different temperatures in nitrogen and air. The intensities of bands in these spectra and those of other resins and resin blends were used to construct the plots of amount of degradation product versus

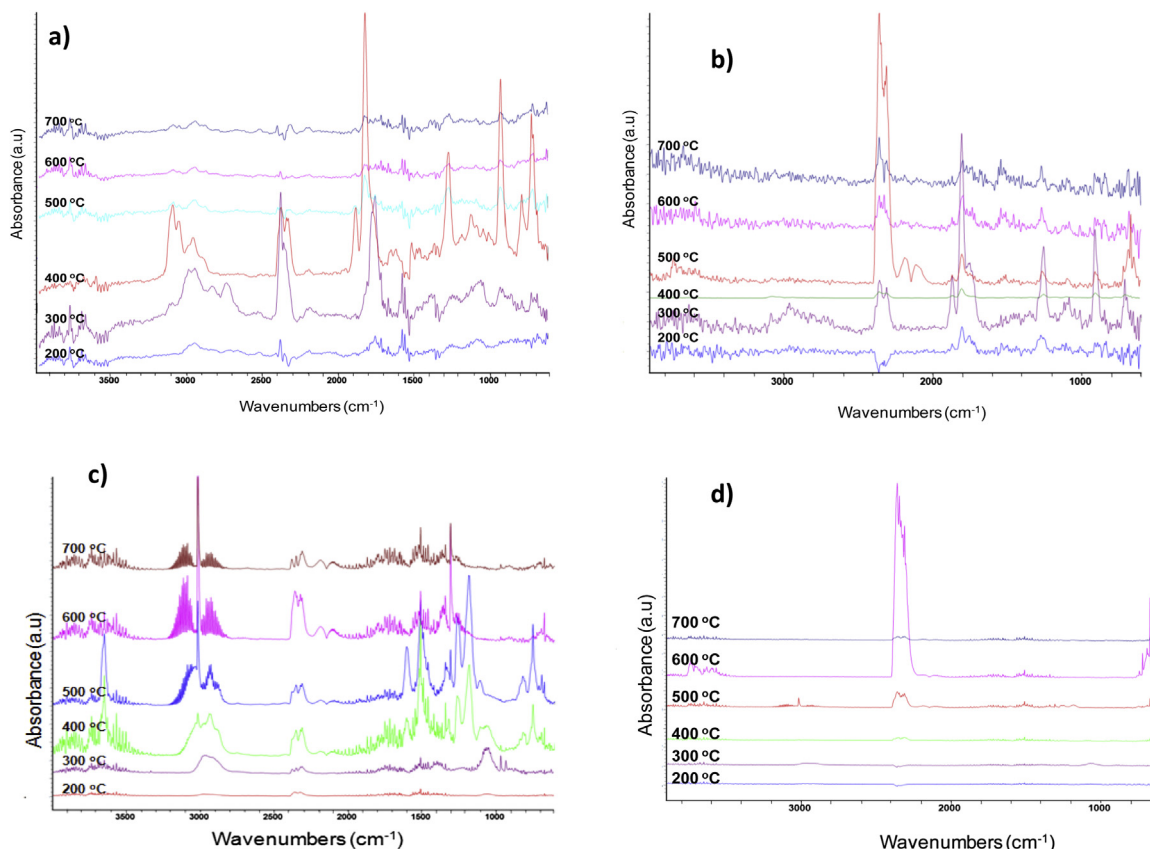


Fig. 8. FTIR of evolved gases: a) UP in N₂, b) UP in air, c) PH2 in N₂ and d) PH2 in air.

temperature presented in Figs. 9 and 10. Band assignments are based mainly on the library of FTIR spectra of gases contained within the NIST WebBook [31] and on other literature [32–34] and these and the implications of the plots based on them are discussed below.

3.3.1. UP resin

In the spectra recorded of gases evolved under nitrogen (Fig. 8(a)), the following assignments have been made:

CO₂: 2360 cm⁻¹, C=O stretch; 710 cm⁻¹, O=C=O bending vibration. The peak at 2360 cm⁻¹ has been used for quantitative analysis in Figs. 9 and 10.

Phthalic anhydride: 1866 cm⁻¹, C=O symmetric stretch; 1770 cm⁻¹, C=O asymmetric stretch. The peak at 1866 cm⁻¹ has been used for quantitative analysis.

Styrene: 700 cm⁻¹, C–H bending vibration of phenyl ring.

Compounds containing aliphatic (C–H) groups: 2980–2880 cm⁻¹, C–H stretch. Within these bands, the intensity at the peak maximum of 2925 cm⁻¹ has been used for quantitative analysis.

Benzenoid groups (compounds containing mono benzene ring such as styrene, phthalic anhydride, etc): 1600 cm⁻¹, ring-breathing mode.

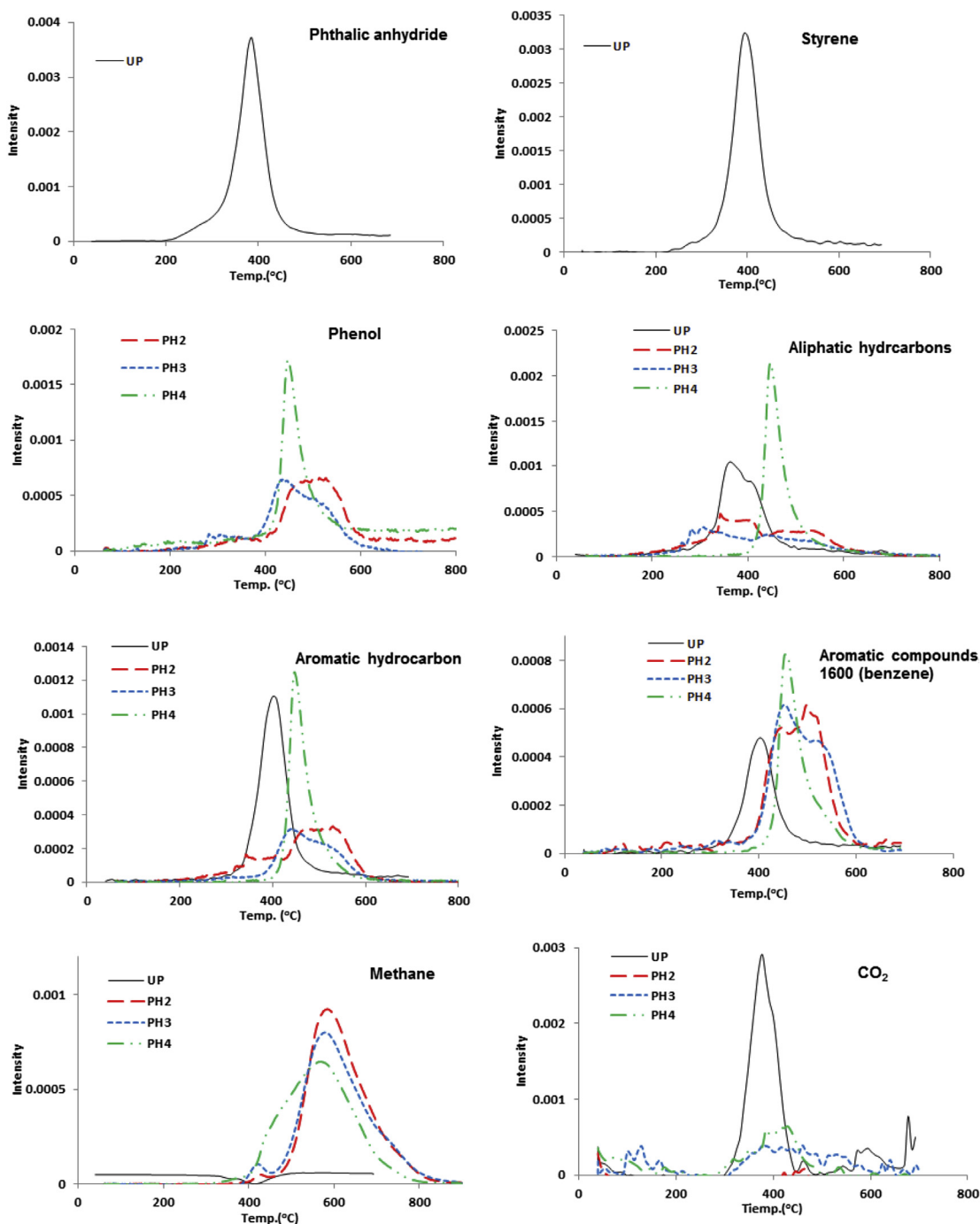


Fig. 9. Absorbances of pyrolysis products for UP, PH2, PH3 and PH4 as a function of temperature.

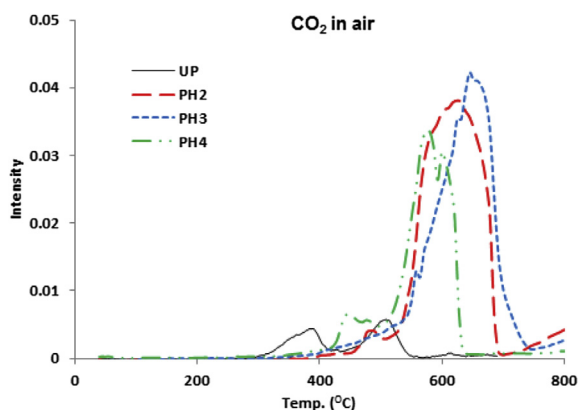


Fig. 10. Absorbance of CO₂ for UP, PH2, PH3 and PH4 as a function of temperature obtained from TGA-FTIR in air.

Aromatic groups (compounds containing aromatic C–H): 3020–3200 cm⁻¹. Within these bands, the intensity at the peak maximum of 3025 cm⁻¹ has been used for quantitative analysis.

As can be seen from Fig. 9, evolution of phthalic acid and styrene from UP begin at ~200 and 255 °C, respectively, with maximum rates of evolution at 385 and 400 °C. CO₂ evolution begins at 290 °C with maximum rate at ca. 380 °C. Compounds containing aliphatic C–H start to appear at 220 °C (maximum rate at 365 °C), whilst compounds containing aromatic C–H start to appear at ca. 270 °C (maximum rate at 400 °C). Total amounts of the various volatiles, measured from areas under the concentration vs. time peaks, are given in Table 3. Phthalic anhydride is believed to be eliminated from UP resins via a cyclo-elimination process (Reaction 1 in Fig. 11) [35], whilst styrene (and styrene oligomers) arise from depolymerization of the oligostyrene cross-links (Reaction 2 in Fig. 11), with initial bond breakage probably occurring at the relatively weak C–C bond adjacent to the polyester backbone (Bond A). A further homolytic scission at bond C and consequent conversion of the single bond, B, to a double bond, will release more styrene and reconstitute linear polyester sequences.

The total aromatic C–H band intensity measured at 3025 cm⁻¹ will reflect the concentrations of all aromatic products eliminated from UP, particularly styrene, styrene oligomers and phthalic anhydride. Hence the growth and decay of this band in the FT-IR spectra mirrors, as expected, that at 700 cm⁻¹ assigned to styrene and that at 1866 cm⁻¹ assigned to phthalic anhydride. The same applies also to the band assigned to phenyl rings at 1600 cm⁻¹.

Polyesters thermally degrade via a variety of chain scission and rearrangement reactions [17,20]. The fact that the polyester backbones in the UP used here are derived from three aliphatic diols (ethylene glycol, propylene glycol and diethylene glycol) probably accounts for the aliphatic fragments (as measured from C–H band intensity at 2925 cm⁻¹) appearing in the TG-FTIR traces over a range of temperatures, with two rate maxima, although some of this aliphatic intensity will arise from styrene monomer and oligomers. A further product released during the thermal decomposition of polyesters is CO₂, which arises from decarboxylation of acid and ester groups. The trace of CO₂ concentration vs. temperature in Fig. 10 shows that this reaction takes place between ca. 285 °C and 445 °C, with a maximum rate at ca. 375 °C. Two of the steps that have been proposed for polyester thermal degradation [17,20] are shown as Reactions 3 and 4 in Fig. 11.

Above 350 °C in air, the major volatile product observed from UP is CO₂. This is because the majority of degradation products oxidise in air. The concentration vs. temperature curve for CO₂ evolution in air is shown in Fig. 10. Two stages of CO₂ evolution can be seen: the first between 290 and 430 °C, with a maximum at ca. 385 °C, and the second between 430 and 562 °C. The first of these two stages represents decarboxylation (the same as in thermal decomposition in nitrogen), and the second, char oxidation. Total CO₂ evolved is given in Table 3.

3.3.2. PH resins

It is reported in the literature [36–38] that the volatiles evolved during the thermal degradation of phenolic resins include water, alcohols, formaldehyde, CO₂, methane, phenol, and various other aromatic compounds.

The volatiles identified in our FTIR spectra recorded on degrading PH resins include CO₂, compounds containing aliphatic C–H, and aromatic species, all with peaks in similar positions to those in the spectra of the volatile degradation products from UP. However, additional assignments can be made:

Water: Small peak at 3911–3489 cm⁻¹, with maximum at 3750 cm⁻¹

Formaldehyde: Small peak at 1720–1740 cm⁻¹, C=O stretch.

Phenol: 3700–3603 cm⁻¹, with maximum at 3647 cm⁻¹, O–H stretch.

Methane: 3300–2650 cm⁻¹, with maximum at 3016 cm⁻¹, C–H stretch [31]. In instances in which methane is a major constituent of the evolved gases, the characteristic P and R rotational fine structure of the methane spectrum is seen and measurement of methane band intensity from the central peak presents no problems. However, in some spectra, the peaks from

Table 3
Quantitative analysis of peaks of Figs. 9 and 10.

Sample	Gas evolved (FTIR peak (cm ⁻¹)); intensity × 100								CO ₂ evolved in air
	CO ₂ (2360) ±0.05	Phenol (3647) ±0.19	Phthalic anhydride (1866) ±0.18	Styrene (709) ±0.49	Methane (3016) ±0	Benzenoid compounds ^a (1600) ±0.17	Aromatic groups ^b (3025) ±0.29	Aliphatic groups (2925) ±0.19	
UP	1.91	0.0	2.68	2.53	0.10	0.39	1.11	1.49	6.49
PH2	0.60	1.01	0	0	1.48	0.84	0.66	1.08	47.16
PH3	0.63	1.13	0	0	1.41	0.93	0.48	0.89	46.22
PH4	0.46	1.10	0	0	1.30	0.44	0.75	1.24	31.28
UP/PH2:50/50	2.04 (1.25)	0.74 (0.51)	0.82 (1.34)	1.32 (1.27)	1.27 (0.79)	0.47 (0.62)	0.54 (0.88)	0.85 (1.28)	28.37 (26.82)
UP/PH3:50/50	2.77 (1.27)	0.73 (0.56)	1.27 (1.34)	1.91 (1.27)	1.08 (0.76)	0.74 (0.66)	0.61 (0.79)	0.94 (1.19)	23.35 (26.36)
UP/PH4:50/50	2.01 (1.18)	0.62 (0.55)	0.98 (1.34)	1.42 (1.27)	0.97 (0.70)	0.36 (0.42)	1.03 (0.93)	1.24 (1.36)	22.98 (18.88)

Note: The reported values are averages of two runs.

The values in brackets and in italics are the calculated averages from individual components.

^a Benzenoid compounds containing mono benzene ring, such as phenol, styrene, phthalic anhydride etc.

^b Aromatic groups could include all possible aromatic groups.

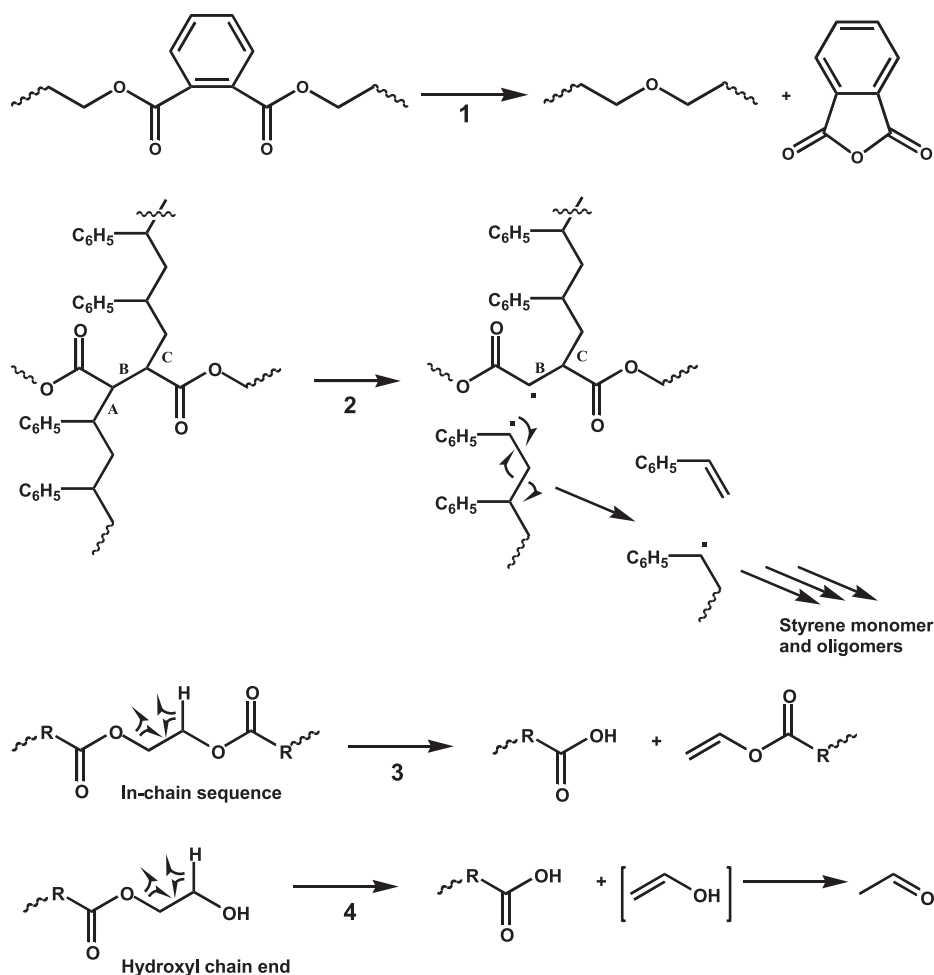


Fig. 11. Steps in the thermal degradation of UP. Reactions 1–4 correspond to the main decomposition stage in Table 2(a and b).

methane are obscured by those from other aliphatics; in these cases, no attempts have been made to measure methane concentration.

Elimination of water from PH resins arises from additional crosslinking reactions that take place between methylol groups and phenol rings during TGA heating beyond the initial curing temperature, as mentioned above (although at higher temperatures, other dehydration reactions may also contribute to the elimination of water), whilst elimination of formaldehyde arises from conversion of dimethylene ether links to methylene links (Reactions 1–4 in Fig. 12)

Methane is a product of high temperature “cracking” in which residual hydrogen is eliminated from the developing carbon-rich char in the form of the most thermodynamically stable hydrocarbon, in fact at 550 °C and above, methane appears to be the only significant aliphatic hydrocarbon pyrolysis product from the PH resins. The rapid breakage of C–H and C–C bonds at high temperatures, leading to a pseudo-steady state flux of hydrogen atoms and small hydrocarbon radicals, will favour the elimination of hydrogen in the form of the most thermodynamically stable small molecule; this will be methane, which has a standard Gibbs energy of formation, $\Delta_f G^\circ$, of about -51 kJ mol^{-1} (for comparison, $\Delta_f G^\circ$ (ethane) = -33 kJ mol^{-1} , $\Delta_f G^\circ$ (hydrogen) = 0 kJ mol^{-1} [by definition]; $\Delta_f G^\circ$ (ethane) = $+68 \text{ kJ mol}^{-1}$ and $\Delta_f G^\circ$ (ethyne) = $+209 \text{ kJ mol}^{-1}$) [39].

In all PH resins, similar patterns of FT-IR peaks for evolved gases were observed, however, these gases were evolved at different

temperatures and their concentration vs. temperature profiles were different. As can be seen from Fig. 9, phenol evolution from PH4 occurs over a narrower temperature range than from PH2 and PH3. Moreover in PH4 there is a single sharp concentration vs. temperature peak whereas in PH2 and PH3 the peaks are broad indicating that in PH4, phenol is more readily liberated. The quantity released is also higher in PH4 than in PH2 and PH3 (Table 3). This is a further indication that, because crosslinking of PH4 is primarily via polymerization of allyl groups (Fig. 4), the decomposition of PH4 occurs over a narrow temperature range as the allyl chains undergo depolymerization.

CO_2 is produced in all samples at $>300 \text{ }^\circ\text{C}$. However, the quantities are small; no sharp peak for CO_2 evolution can be seen in the relevant plots in Fig. 9. It has been suggested that CO_2 may arise from the decarboxylation of minor carbonyl-containing oxidized structures in phenolic resins [40].

Evolution of compounds containing aliphatic C–H starts at around $200 \text{ }^\circ\text{C}$ in PH2 and PH3, and these compounds are evolved in two stages. The behaviour is very similar in both resins. In PH4, however, evolution starts at ca. $400 \text{ }^\circ\text{C}$ and compounds containing aliphatic C–H are produced in one stage (maximum rate at $450 \text{ }^\circ\text{C}$) and in large quantity compared to the other two resins (Table 3), again consistent with the different degradation pathway for PH4. Methane production in PH4 is also very different. In all resins it is detected at $>400 \text{ }^\circ\text{C}$, but in PH4 there is a more rapid release.

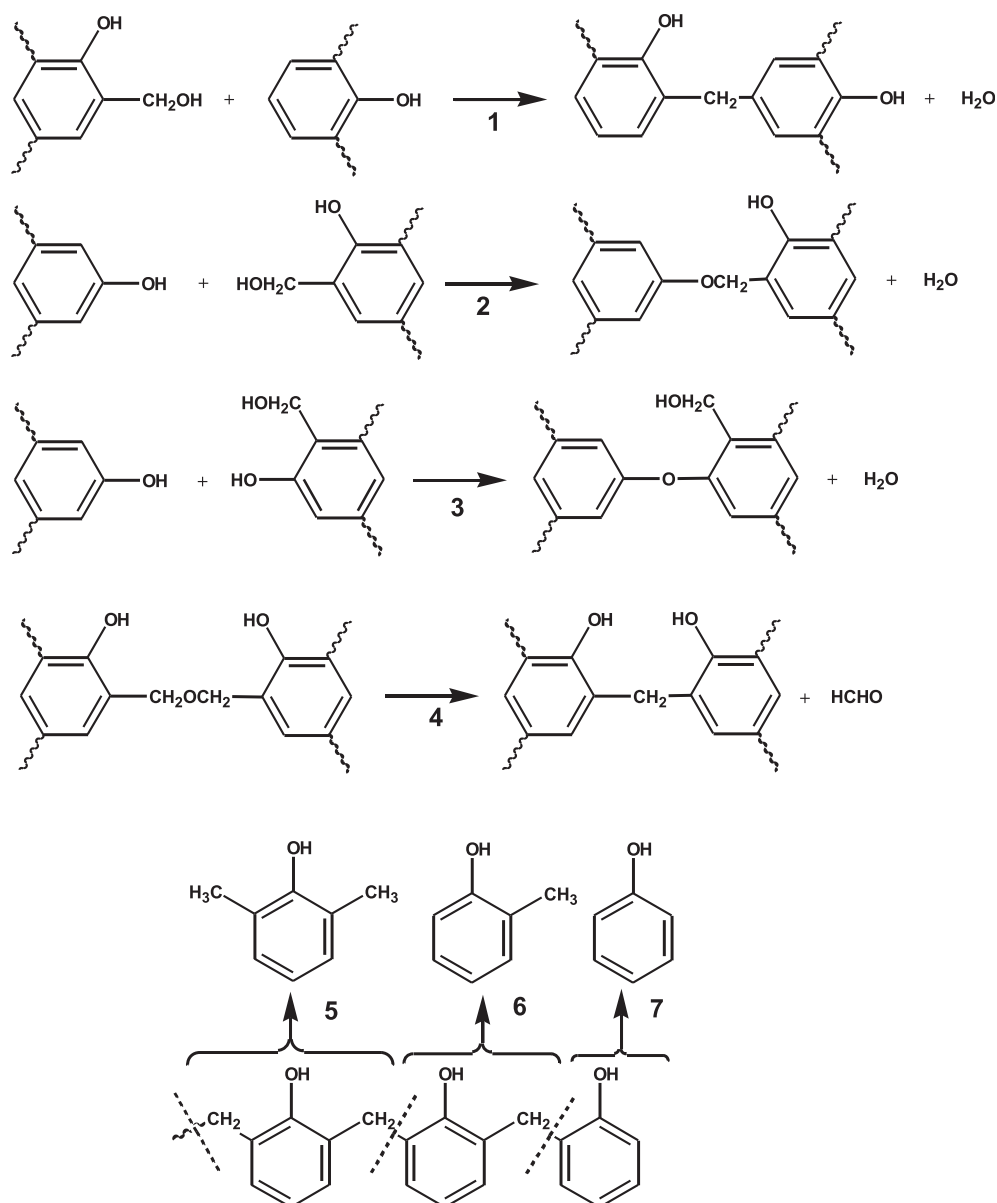


Fig. 12. Reactions suggested for liberation of water (Reactions 1, 2 and 3), formaldehyde (Reaction 4) and phenolic compounds (Reactions 5, 6 and 7) from PH resins during further heating beyond the curing temperature. Reactions 1–4 correspond to stage 1 (plus 2 in PH3) and 5–7 to stage 2 (stage 3 in PH3) of mass loss in Table 2(a and b).

For both PH2 and PH3, the rates of release curves for total aromatics, as measured from the intensities of aromatic C–H stretching bands at 3025 cm^{-1} and the phenyl ring breathing band at 1600 cm^{-1} , are very similar in terms of overall shape, relative intensity and position on the temperature axis, to the rate of release curves measured for the phenolic products from the O–H stretching band at 3647 cm^{-1} . This suggests that the majority of the aromatic fragments released during pyrolysis are phenolic, including cresols and xylenols, produced by cleavage of the PH resins at methylene linking groups (Reactions 5–7 in Fig. 12) [37]. We cannot rule out, however, that some of the aromatic products released at the higher temperatures are phenols stripped of OH groups, as has previously been suggested for the final stage of the resole degradation process [40].

In air, the oxidation of the evolved products occurs much earlier in PH4 than in PH2 and PH3, indicated by CO_2 production in Fig. 10, possibly because PH4 produces less char and so the char oxidation stage makes less of a contribution to CO_2 production.

3.3.3. UP/PH resin blends

All the species identified in gases evolved during degradation of UP and PH resins in nitrogen, are found also in the gaseous degradation products from UP/PH resin blends, as can be seen from Fig. 9. However, while the yields of most products from the blends, such as phenol, methane, phthalic anhydride and styrene, lie between those of respective resin components, yields of CO_2 are much higher than expected on the basis of resin composition; at present we have no explanation for this behaviour.

Quantitative analyses (Table 3) show that yields of phenols and phthalic anhydrides in blends are slightly lower than expected from calculated averages, while the yield of styrene is slightly higher. This may be a consequence of inter-resin reactions (esterifications and transesterifications) as shown in Fig. 7.

In air, the yield of CO_2 is much higher for UP/PH4 blends than for the other blends; possibly this is a consequence of the higher aliphatic content of PH4 in form of the allyl groups compared with PH1, PH2 and PH3.

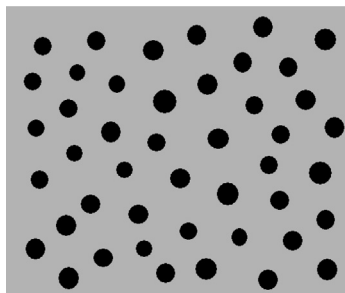


Fig. 13. The Zhang and Horrocks “Islands in the Sea” model [40] for char formation in a matrix polymer (■) nucleated by incompatible domains of a char-promoting species (●).

4. Conclusions

In this work, the thermal stabilities and flammability characteristics of a cured unsaturated polyester (UP), cured samples of four different phenolic resoles, PH1, PH2, PH3 and PH4, and co-cured blends of UP with PH1, PH2, PH3 and PH4 have been compared. The thermal and thermo-oxidative stabilities of all the blends were intermediate between those of the pure phenolics and UP. The stabilities of the unfunctionalized phenolic resins (PH1 and PH2) and blends based upon them are marginally better than products incorporating the functionalized resoles, PH3 and PH4.

The greater thermal and thermo-oxidative stabilities of UP/PH blends than of UP alone, translate into better fire performances for the blends as measured by LOI and cone calorimetric parameters, all of which show significantly higher LOI and significantly lower PHRR, THR and TSR than UP. The far greater char yields in the case of the blends compared with UP indicate that the major mechanism of fire retardance in these blends is a condensed phase one in which the phenolic component acts as the char former.

Interestingly, it is the phenolics that are the least compatible with UP (PH1 and PH2) that, on balance, confer the best fire performance on UP, whilst the most compatible (PH4) performs less well. It is tempting to believe that this might be due to esterification and transesterification reactions taking place between residual methylol groups in PH1 and PH2 (i.e. those not reacted during the initial curing process) with UP during cone or TGA heating. However, it is not obvious that such transesterified structures (Fig. 7) would be especially thermally or thermo-oxidatively stable. More probable, in our view, is that it is the inhomogeneity of UP/PH1 and UP/PH2 blends, in which cured PH domains are dispersed largely within a matrix of cured UP [13], which is the important factor. In support of this hypothesis, we note that the behaviour observed here for UP/PH1 and UP/PH2 blends is reminiscent of the effects observed when char-forming additives are added to non-char forming polymers at critical concentrations above which they become effective in shielding parts of the surrounding polymer matrix from pyrolysis and promoting more extensive char formation. Such behaviour has been observed, for example, in polypropylenes and polyamides containing incompatible, inorganic phosphorus-based, flame-retardant additives. Literature in this area has been reviewed by Zhang and Horrocks who have proposed an “Islands in the Sea” model to explain this behaviour (Fig. 13), in which domains of a char-promoting flame retardant act as nucleating centres for char formation in a surrounding polymer matrix of a different type when present at a concentration above a percolation threshold [41]. The “Islands in the Sea” model, however, would predict a non-linear dependence of a particular flame-retardant parameter upon concentration of nucleating centre in which

flame retardance would be minimal below the percolation threshold and only significant above it. This behaviour cannot be clearly discerned in any of the data displayed in Fig. 13, although there is a suggestion of such behaviour in the plots of ΔTTI and $\Delta PHRR$ vs. blend composition for UP/PH1 co-cured blends. This is an aspect of the fire performance of UP/PH blends that requires further study.

Our work in this area continues, especially on alternative functionalizations of PH resins to aid co-curing with UP, on other char-forming resin additives, and on the mechanical properties of co-cured UP resin blends and of composite structures based upon them.

Acknowledgements

We thank the UK Engineering and Physical Sciences Research Council (EPSRC) for the financial support of this work (Grant No. EP/H020675/1), Scott-Bader and Sumitomo-Bakelite Europe NV for the provision of materials and facilities, and Dean Bugg and Jan Schreurs of the aforementioned companies for technical advice.

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