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Author post-print (accepted) deposited by Coventry University's Repository

Original citation & hyperlink:

Kandola, BK, Krishnan, L, Ebdon, JR & Myler, P 2020, 'Structure-property relationships in structural glass fibre reinforced composites from unsaturated polyester and inherently fire retardant phenolic resin matrix blends', *Composites Part B: Engineering*, vol. 182, 107607.

<https://dx.doi.org/10.1016/j.compositesb.2019.107607>

DOI 10.1016/j.compositesb.2019.107607

ISSN 1359-8368

ESSN 1879-1069

Publisher: Elsevier

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DOI: 10.1016/j.compositesb.2019.107607

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Structure-property relationships in structural glass fibre reinforced composites from unsaturated polyester and inherently fire retardant phenolic resin matrix blends

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Abstract

The effects of matrices from co-cured blends of an unsaturated polyester (UP) with inherently fire-retardant and char-forming phenolic resoles (PH) on the mechanical and fire performances of resultant glass fibre-reinforced composites have been investigated. Three different phenolic resoles with increasing order of compatibility with UP have been used. These are: (i) an ethanol soluble resin, (PH-S), (ii) an epoxy-functionalized resin (PH-Ep), and (iii) an allyl-functionalized resin (PH-Al). The mechanical properties of the composites increased with increasing compatibility with two resin types as might be expected, but not previously demonstrated. However, even with the least compatible resin (PH-S), the impact properties were unaffected and the flexural/tensile properties while reduced, were still acceptable for certain applications. Fire properties were however, in reverse order as previously observed in cast resin samples from these composites. Moreover, the reduction in flammability was less compared to those of the cast resin samples, reported previously, explained here based on the insulating effect of glass fibre reinforcement.

Keywords: A. Polymer-matrix composites (PMCs); A. Glass fibres; B. Mechanical properties; Fire properties

1. Introduction

Unsaturated polyester resin based composites are commonly used in marine structures owing to their favourable water resistance and mechanical properties. This resin however, has poor fire performance and burns with heavy smoke and soot. Commonly used methods of fire retardance, namely (i) using inorganic, halogen- and/or phosphorus-containing fire retardant (FR) additives and (ii) chemical modification of the resin backbone with FR (usually halogenated) chemicals have limitations in terms of the effects of additives on the processability, particularly for the resin infusion technique, and on the mechanical properties of the derived composites [1, 2]. Halogenated resins / FRs also have environmental concerns associated with them. For applications where good fire performance is required, usually phenolic composites are used. However, due to the brittleness of phenolic resins, they are not usually suitable for primary structures. Another well known method of fire retarding polymers, but less exploited in composites industry is polymer blending, used for preparing new materials that combine the good properties of both components [3]. Polymers can be ‘miscible’ or ‘immiscible’, depending on the thermodynamics of polymer – polymer interactions and kinetics of the mixing process [4]. Most polymer pairs are immiscible and form a phase - separated system. In case of thermoset resins, blending (prior to curing) by physical means such as mechanical stirring with a high shear force leads to the formation of interpenetrating networks (IPNs) i.e., two or more networks are at least partially interlaced on a polymer scale but not chemically bonded to each other [5-7]. A resultant property of a resin blend mainly depends on the chemical miscibility of the blended materials and the processing conditions [8].

Miscibility can be improved in several ways, e.g., by chemical modification, copolymerization, introduction of groups able to form specific interactions, etc. [9-11] or by the addition of a compatibiliser. Since chemical modification or co-polymerization changes intrinsic properties of the resins, these are not commercially acceptable options. Compatibilization is a preferred option. Some resin pairs are intrinsically compatible, e.g., epoxy - phenolic [8], UP- epoxy [6, 12, 13] resin blends, mainly due to their compatible curing chemistries. UP and phenolics however, cure by different chemistries, UP by free radical polymerization and phenolics by condensation reaction, hence are incompatible. The most commonly used compatibilization strategies include: (i) use of a common solvent [14], (ii) the chemical functionalization of at least one of the components of the blend [15] and (iii) use of an external compatibilizer (such

as a surfactant) [16]. In this context at Bolton we have been attempting to blend UP with different phenolics using strategies (i) and (ii) with a view that the blend will have improved fire and mechanical performances [3,17]. However, the challenge in co-curing is not only owing to different curing chemistries, as mentioned above, but also different curing temperatures. UP cures at room temperature, whereas phenolics cure above 130 °C. While co-curing, the curing conditions need to be carefully monitored so that any formaldehyde or water released during phenolic curing is not entrapped within the already semi cured UP to create weak spots. The schematic of formation of IPN structures is shown in Fig. 1.

Here we have blended UP with three different commercially available resoles comprising (i) containing a compatibilizing solvent, ethanol (PH-S); and chemically modified to contain (ii) hydrophobic and reactive epoxy groups (PH-Ep) and (iii) free-radically reactive allyl groups (PH-Al). The evidence of increasing compatibility (PH-Al > PH-Ep > PH) of these phenolic resins with UP has been demonstrated by differential scanning calorimetry (DSC), differential mechanical thermal analysis (DMTA), solid state ¹³C-NMR and scanning electron microscopy (SEM) studies in our previous work [3, 17] and is summarised here in Fig. 2. Digital images of cast resins and SEM images of fractured surfaces show much less evidence of microscopic heterogeneity in the case of the more compatible systems. DMTA measurements of glass transition temperatures (T_g) show two T_g values for UP/PH-S and UP/PH-Ep with a less well-defined second one in the latter, and only a single T_g in the most compatible system (UP/PH-Al) [3]. Moreover, these co-cured resin blends are significantly more fire retardant than unmodified UP, indicated in Fig. 2 by their LOI values. The least compatible resin blend, UP/PH-S, however showed the best fire retardancy by cone calorimetry, whereas the most compatible UP/PH-Al performed less well [17]. We believe that the reasons for this lie in the inhomogeneity of UP/PH-S, in which cured PH domains are dispersed largely within a matrix of cured UP, the former acting as nucleating centres for char formation in a surrounding UP matrix. This mechanism is discussed in details in ref [17]. The mechanical properties of these resins however, are expected to be in reverse order, i.e., the most compatible blend to have the best mechanical properties.

Here glass fibre-reinforced composites with UP/PH ratios of 70/30 and 50/50 wt-% have been prepared from these blended resins and their mechanical and fire performances evaluated in terms of the chemical compatibility between the two resin types and the latter compared with

those of previously reported for cast resins. For one resin (UP/PH-A1), the effect of different PH content from 20-50 wt-% was studied, from which it could be observed that with 50 wt-% PH the best FR properties for a particular blend and with 30 wt-% the best balance of FR and mechanical properties could be achieved [18], hence these two ratios were chosen for all resin types.

2. Experimental

2.1 Materials

Unsaturated Polyester (UP):

Crystic® 2.406PA (Scott Bader), an unsaturated, phthalic anhydride-based UP and pre-accelerated with cobalt octoate; Catalyst M, methyl ethyl ketone peroxide based (Scott Bader).

Phenolic resins:

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

Epoxy functionalised phenolic (**PH-Ep**): Plyophen 23983 (Sumitomo-Bakelite Europe N.V.), an isopropanol-based, epoxy-functionalized, phenolic resole containing 16–18 wt% isopropanol and <6 wt% water.

Allyl functionalised phenolic (**PH-A1**): Methylon 75108 (Sumitomo-Bakelite Europe N.V.), a solvent-free, allyl-functionalized, phenolic resole.

Fibre reinforcement:

Woven roving E-glass fibre, 300 gm/m² (Glasplies)

2.2 Composite preparation

Blends of UP/PH with 70/30 and 50/50 wt-% ratios were prepared by mixing required quantities of UP and the PH resin with mechanical stirring and then degassing under vacuum for 15 min. A methyl ethyl ketone peroxide catalyst (2 wt % w.r.t. resin) was added into the resin mixture and stirred for another 10 min.

Eight layers of woven E-glass fabric, impregnated individually with UP resin or UP/PH resin blend (50% each by weight), were stacked, vacuum bagged and cured using curing

conditions given in Table 1. Composite panels of 300 mm x 300 mm were prepared, from which specimens of required dimensions were cut using a high speed circular saw blade for each mechanical and fire test. The glass-fibre reinforced composite (GFRC) of pure PH could not be prepared because of its low viscosity at high temperatures, which led to too much leak-out when curing.

2.3. Mechanical property measurements

2.3.1. Flexural testing

A three-point bending flexural test was carried out according to BS EN ISO14125 [19] using an Instron 3369 universal testing machine. A 100 N load cell with a compression rate of 1 mm/min was used on the samples with a span length of 100 mm. Tests were undertaken within the elastic range of the material due to limited number of samples. Three replicate specimens of the size 150 mm x 20 mm x thickness as in Table 1 for each sample were tested and the results averaged.

2.3.2. Tensile testing

Tensile testing was carried out according to BS EN ISO 527 [20] using an Instron 3369 universal testing machine. The gauge length of each specimen was 100 mm and polymeric tabs were bonded at their ends to improve the gripping and ensure failure within the gauge region. The tests were conducted using a 50 kN load cell with a crosshead speed 1 mm/min. Tensile modulus and strength values were calculated from stress-strain curves using an extensometer, selective samples had strain gauges bonded to their surfaces to verify the results. Three replicate specimens of the size 150 mm x 20 mm x thickness as in Table 1 for each sample were tested and results averaged.

2.3.3. Impact drop weight testing

The impact properties of the samples were investigated using an Instron Dynatub Mini-Tower drop weight impact machine in accordance with ASTM D7136 [21]. The samples, sized 75 x 75 mm², were fully clamped circumferentially by a 50 mm diameter holder. The clamped samples were impacted by dropping a steel 16 mm diameter hemispherical impactor from 100 mm height to create an impact energy level low enough to avoid significant surface damage so further testing of the samples could be carried out for post-fire impact testing. A high-speed

data acquisition system (Dynatup® Impulse™ software data capture system) was used to obtain load - central displacement curves. Three replicate specimens of each sample were tested and the results averaged.

2.4 Fire Testing

2.4.1. Cone calorimetry

A Fire Testing Technology cone calorimeter was used according to ISO 5660 / ASTM E1354 standard to perform experiments on horizontally oriented samples of dimensions 75mm x 75mm x thickness as in Table 1 at 50 kW/m² external heat flux. Smaller than usual samples were used here in order to allow comparisons with the results of previously reported experiments [17] carried out on similarly small samples. Moreover, reported results for composites in this paper are discussed in comparative terms with respect to control UP; hence the use of 75 mm square plaques may not be that important in terms of compliance to ISO 5660 standard. The samples were wrapped in aluminium foil and tested within a retainer frame. All experiments were conducted in triplicate and results were reproducible to $\pm 10\%$.

2.4.2. UL-94 testing

The fire performances of the composite was evaluated using a UL-94 flame-spread test according to ISO 1210 in both vertical and horizontal orientations. Flame spread rates in both vertical and horizontal orientations were also measured by slightly modifying the testing methodology, by recording the time taken by the flame to reach a specified distance. The first 10 mm of sample burning was not taken into account and so times of burning were recorded once the flame had reached a line drawn at 10 mm from the edge against which flame of 20 mm height was applied for 10 s as specified in the test and discussed above. A video film was taken of the burning of each sample from which times to reach 50 (t_1) and 100 mm (t_2) marks and/or to achieve flameout were noted. Two replicate specimens of each sample were burnt and results averaged. The burning behaviour of each sample was observed and noted.

3. Results and Discussion

All composite samples were visually good with a uniform plain surface without any voids. During curing the colour of the blended resins changed from light brown to dark brown.

Compositions of different composites are given in Table 1. With one phenolic type (Ph-A1), different UP/PH blend ratios were prepared. The results showed that mechanical properties decreased with increasing phenolic content, whereas the flammability increased. Two ratios have been selected to discuss here in more detail: 50/50, so that maximum FR effect from phenolic can be obtained, and 70/30 being better from the processability point of view as well as the optimum ratio for the best mechanical and fire properties.

Since the resin contents in all samples were slightly different, selected mechanical properties (flexural and tensile moduli, E) have been normalised w.r.t. fibre volume fraction (FVF) using Equation 1:

$$E_{Normalised} = \frac{E_{Absolute}}{FVF} * 40 \dots\dots\dots \text{Eq 1}$$

and selected fire properties (cone parameter (CP)) w.r.t. 40 wt% resin content using Equation 2:

$$CP_{Normalised} = \frac{CP_{Absolute}}{\text{Resin wt \%}} * 40 \dots\dots\dots \text{Eq 2}$$

3.1 Mechanical performances of fibre-reinforced composites

3.1.1 Flexural performance of UP and UP/ PH composites

The flexural test was performed in the elastic region, from which modulus values, E , were calculated using Engineer’s bending theory [22], using Equation 3:

$$E = \frac{Kl^3}{4bh^3} \dots\dots\dots \text{Eq 3}$$

in which K is the slope of load-displacement curve, l is the test span, h the thickness, and b the width of the specimen.

Typical average stress versus strain curves of selected samples are shown in Fig. 3 and the calculated modulus values of all samples are given in Table 2. The normalised modulus values

with respect to 40 % fibre volume are also listed because the composites have slightly different weight % of the resin and it is well known that the flexural performance of composites very much depends on the matrix mechanical properties, matrix content and also on the effectiveness of reinforcement. It must though be noted that flexural properties are not conventionally normalised because these are significantly influenced by the matrix compared to tensile properties, which are dominated by the reinforcement.

As can be seen from the results that the presence of PH-S in composites UP/PH-S:70/30 and 50/50 blends reduced the flexural modulus of UP from 18.0 to 11.4 and 14.4 GPa, respectively, which are 37 and 20 % reductions w.r.t. UP composite. The reduction in initial modulus can be explained due to the influence of the phenolic resin. In theory if the two resins are incompatible and there is a phase separation, there should be significant reduction in flexural modulus. In the case of UP/PH-S, the PH-S is a non-functionalised resin and there is no active functional group to react with UP resin, hence poor compatibility between the two [3]. Despite the incompatibility, the reduction in initial modulus is not too high, which may indicate that there is a little physical phase separation and that an interpenetrating network is formed, which behaves nearly as a homogenous material, and/or that the domain sizes of the PH domains are small such that they act much like a particulate filler in the UP. Moreover, the increase in phenolic content from 30 to 50% has a limited effect on the modulus.

The reduction in flexural modulus in composite samples containing PH-Ep is less (13 and 2% in 70/30 and 50/50 blends, respectively) than in those containing PH-S. This can be explained on the basis that epoxy functionalised phenolic resin is more compatible with UP than is the non-functionalised one (PH-S) [3], the epoxy functional groups of the phenolic resin may have reacted during curing with any terminal carboxylic acid groups of the UP. Hence the homogeneity of the matrix will be higher than that from the UP/PH-S blend. UP/PH-Al samples on the other hand have flexural modulus values similar to that of UP, i.e., 17.8 and 18.4 GPa for 70/30 and 50/50 blends, respectively. The reason for this may be that the allyl groups in PH-Al 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, resulting in a highly co-cross-linked structure [3], hence a very homogeneous matrix. This shows that the flexural modulus increases with the increase in homogeneity of the co-cured cross-linked structure.

In UP/PH-S and UP/PH-EP composite samples it can also be seen that each 70/30 blend has a lower modulus than that of the respective 50/50 blend. This can be explained by supposing that the UP resin in the blended composite acts as a plasticising component because of the absence/lack of the chemical bonding between the UP and PH. This plasticising effect is less with lower UP content in the 50/50 blend.

3.1.2 Tensile properties

Typical stress-strain curves for GFRCs from UP, and from one UP/PH (PH-S) resin blend with both 70/30 and 50/50 ratio are shown in Fig. 4. It can be seen that the stress-strain curves are initially linear i.e. indicate elastic behaviour in which the composites behaved like a homogeneous material with the fibres and matrix experiencing the same strain. From this first linear part the initial modulus was calculated and results for all samples are presented in Table 2 along with normalized values with respect to 40% FVF. Above the first elastic range the slope of the curve changed due to partial decoupling of the stress and strain in the matrix and fibre, followed by a small non-linear deformation prior to failure.

The initial tensile modulus of UP is 13.2 (N, normalized values) GPa, and for all samples from blended resin samples is in the range 11.2 – 13.9 GPa, with no particular trend. In GFRC composites, fibre is the major factor affecting the tensile properties of the composite, hence there is a little effect of the matrix type, particularly in the elastic range as opposed to in the flexural mode where the matrix is the load carrying component [23]. It is well known that in composites, the tensile properties are affected not only by the properties of the reinforcing fibres/fabrics but also by the interfacial adhesion between the reinforcing fibre and the polymer matrix [24]. Better fibre-matrix adhesion gives better load-transfer between fibre reinforcement and matrix resulting in a better mechanical performance [24]. The effect of matrix can be seen from stress-at-failure values, where the value decreased from UP (375 MPa) in the order UP/PH-S (256 – 281 MPa) > UP/PH-Ep (268 – 298 MPa) > UP/PH-Al (371 MPa). This can be explained based on the compatibility of the two resins in the blend. As the compatibility increases, the homogeneity of the cross-linked matrix increases, which may affect the final strain-to failure.

Overall the results show that there is not a significant reduction in tensile properties, despite reduction in stress-to failure values. All samples though followed the same trend in stress-strain

curves upto ~5% strain, which is well above the usual design strain of the composites, indicating that these blends can be used for structural applications.

3.1.3. Impact properties

The load-displacement curves of all composites subjected to 1J impact are shown in Fig. 5. This energy level was used as it caused some visible damage to the UP GFRC as shown in Table 3. Higher impact energy levels were not used to avoid excessive damage to the samples as the samples were to be tested for their fire performance and post-fire impact tolerance. The data from the load *vs.* deflection impact curves of the composite laminate samples were used to calculate the impact modulus and the load - displacement trend (indicating toughness), the values are given in Table 3. The samples were examined after the test to measure the visible impact damage on the composite surface (tub hitting surface). After impact testing, the morphologies of the damaged area on the tested samples were measured using a digital camera. Images and the results are presented in Table 3.

From Table 3, in UP composite sample a visible impression of the tub of about 7.1 mm² area after impact testing can be seen, however there is no physical damage, i.e., no delamination or fibre breakage. In the case of an impact test, the material damage is associated with a stress or strain regime, while fracture is the fragmentation of material by cracking and is determined by energy considerations i.e., the fracture will occur if the growth of a crack results in a lower energy of the system [25], i.e., the energy required to overcome the cohesive force of the molecules is equal to the dissipation of the strain energy that is released by the crack [26].

From Fig. 5 it can be clearly seen that the load *vs.* deflection curve of the GFRC of UP is smooth and uniform, which indicates that there is little associated damage caused by the drop weight during test; the impact modulus is 19.6 GPa. The impact modulus value is higher than that of flexural and tensile modulus values in GFRC composites because it varies with different factors such as material variables, loading and environmental conditions and impactor geometries. Amongst the material variables, the mechanical properties of fibre and matrix, particularly the failure strains, interface properties and fibre configuration play important roles in determining impact damage resistance and damage tolerance of the composites [26].

The composites of UP/PH-S:70/30 and 50/50 samples after impact test show no impressions or physical damages and it can be supported with their smooth load vs. deflection curves (see Fig. 5 for 70/30 sample). The initial slopes and shapes of the curves are similar to those of the UP. The impact moduli of UP/PH-Ep:70/30 and 50/50 composites are 19.4 GPa and 19.5 GPa respectively which are similar to that of UP (19.6 GPa), indicating that the GFRC of UP and UP/PH-S have similar impact resistance.

Composites of UP/PH-Ep:70/30 and 50/50 samples in Table 3 are seen to have the damaged areas of 113 mm² and 8.3 mm² respectively. The load vs. deflection curve of UP/PH-Ep:70/30 (Fig. 5) indicates slightly reduced transmitted force and greater deformation than that of the UP. Further increase in the PH-Ep content to 50% resulted in a broader curve, which means that the UP/PH-Ep blend composite can potentially absorb more impact energy than that of UP and is less brittle and better at resisting damage. The damage seen in Table 3 is more localised on the impact surface and could have been because of resin deficiency on the surface. The impact modulus values are also similar, which supports this argument.

The samples of UP/PH-Al blend composites do not show visible physical damages or impression on their surfaces (Table 3). Due to the good compatibility between UP and PH-Al, the presence of PH-Al in the blends does not produce an adverse effect on impact resistance. The load vs. deflection curves of UP/PH-Al blended composites are shorter and broader than that of the UP composite. The increase in the PH-Al content also produces a broader curve, which indicates that the UP/PH-Al blend composite can potentially absorb more impact energy than that of UP. The composites of UP/PH-Al blended samples show smooth load vs. deflection curves without any irregularities indicating little internal damage and have similar impact modulus values to that of UP.

From the above discussions, it is concluded that the overall mechanical performance (flexural, tensile and impact modulus) of the GFRC samples are in the following order:

$$\text{UP/PH-Al} > \text{UP/PH-Ep} > \text{UP/PH-S}$$

This order is also supported by the DMTA results of cast resin, previously presented [3].

3.2. Fire performance of Glass fibre -reinforced UP/PH blended composites

3.2.1. Cone calorimetry

The cone calorimetric results from GFRC composite samples tested at 50 kW/m² heat flux are listed in Table 4 and selected results shown in Fig. 6. Since all laminates had different resin contents varying from 33 to 45 % (Table 1), in order to compare the effect of resin type and composition in the GFRC laminates of different blends with that of the UP, the cone results are normalised with respect of a 40 wt. % resin content and the values are listed in parenthesis in Table 4 and also in the text written in parenthesis after the actual values and indicated by the letter N.

The UP GFRC sample ignited after 38 s (time-to-ignition, TTI) of continuous radiant heat exposure, after which the heat release rate started rising reaching a PHRR (peak heat release rate) value of 491 (479 N, normalised to 40 wt. % resin content) kW/m², the sample continued to burn until 146 s with a THR (total heat release) of 32.6 (30.3 N) MJ/m². After the flame out at 146 s, all of UP resin had burnt out, leaving 59.8 % residue of unburnt glass fibre (0.8% carbonaceous residue after compensating for glass fibre content). In the image of the residue in Fig. 6(a), only glass fibres can be seen with no char in between.

In all co-blended UP/PH composite samples no spalling during burning was observed. Spalling usually occurs owing to release of water if the phenolic resin is not fully cured. Since with the curing conditions used for these resins complete curing occurs, as discussed in detail in our previous publications [3,17], no spalling occurred. For co-blended UP/P-S and UP/PH-Ep composite samples, TTI is little affected by the presence of the phenolic resin, the values being similar to, or slightly less, than that of UP composite. On the other hand; the composites from UP/PH-Al have slightly greater TTI than that of UP composite sample. It may be due to the fact that the UP/PH-Al blend is co-crosslinked [3,17], and hence displays the ignition behaviour of a homogeneous material, whereas in UP/PH-S and UP/PH-Al composites, the two resins not being intimately crosslinked, the UP component ignites first.

The PHRR in the UP/PH-S:70/30 composite has been reduced to 428 (418 N) kW/m² (Fig.6), THR to 26.9 (26.2 N) MJ/m², TSR to 1482 (1446) m²/m² and char yield increased to 5 % (3.4 % N) compared with the values for the UP composite. In the 50/50 blend composite PHRR, THR, EHC and TSR are further reduced, whereas the amount of charred residue has increased.

The composite sample from UP/PH-Ep:70/30 ignites at 42 s and burns with a PHRR of 415 (461 N) kW/m² and flames out at 132 s. It also has a THR of 25.9 (25.3 N) MJ/m² and TSR of 1689 (1648 N) m²/m². The UP/PH-Ep: 50/50 composite has lower PHRR, THR and TSR than those of UP/PH-Ep:70/30 (see Table 4). This is simply because of the lower resin (and therefore higher glass fibre) content in the UP/PH-Ep:50/50 composite.

The UP/PH-Al composite samples have higher TTI of 46 s in UP/PH-Al:70/30 and 48 s in UP/PH-Al:50/50 compared with the composite of UP (38 s). The other parameters such as PHRR, THR, EHC and TSR are reduced, reducing further with increased phenolic content.

The above analysis of results shows that the flammabilities of all composite samples containing phenolic resins are lower than that of the composites containing UP resin. The lower flammability of phenolic is due to the greater number of relatively thermally stable aromatic rings in their chemical structures [17, 27,28] which, on heating, cross-link and char, whereas the UP resin decomposes more readily into combustible volatiles, which burn. The normalised values represented in Table 4 can be used to compare the effect of phenolic resin type on the reduction of flammability of the composites. In Fig. 7 the percentage change in each parameter with respect to those of the control UP GFRC are given, along with the corresponding data for the pure cured cast resins, taken from our previous publication [17].

The effect of phenolic resin type in terms of increasing TTI:

$$\text{PH-Al} > \text{PH-Ep} \approx \text{PH-S}$$

In terms of reducing PHRR, THR, TSR and increasing char residue:

$$\text{PH-S} > \text{PH-Ep} > \text{PH-Al}$$

The fire growth rate indices (FIGRA), the ratio of peak heat release rate to time to peak heat release rate for all the GFRC samples are listed in the Table 5. Higher FIGRA means higher fire risk and faster flame spread [29]. From the cone results of GFRC samples, the normalised (40 wt.% resin) FIGRA value for the UP composite is 8.9 kW/m²s and for the GFRC of UP/PH-S:70/30 is 5.5 kW/m²s which is much lower than that of the UP composite due to the 30 % PH-S content. The higher phenolic content of the UP/PH-S blend gives a lower FIGRA value. These lower FIGRA numbers indicate that the presence of phenolic resin in the blended resin composites can provide effective flame retardance to the composite and hence reduce the fire

risk. The GFRC of UP/PH-Ep and UP/PH-Al samples show lower FIGRA values than that of UP composite (see Table 4). Another important parameter to measure the propensity of fire development under real fire conditions is the maximum average rate of heat emission (MAHRE) [29]. The MAHRE parameter is defined as the peak value of the cumulative heat emission divided by time. The values are given in Table 4, which show a similar trend i.e. more reduction in composites from UP/PH-S blends than those in UP/PH-Ep and UP/PH-Al blends.

In order to compare the effect of phenolic resins in reducing the flammability of the UP in composites with those in cast resins reported previously [17], in Fig. 7 the percent reduction in each cone parameter for the respective cast resin system (taken from ref 17) are also reported. The direct comparison shows that the trends of changes in all parameter for different samples are similar in both cases, however the reductions for the composite laminates are much less than those for the respective cast resin samples. This may be explained as arising from the presence of 55-67 wt.% glass fibres in the composites, which being a thermal insulator, reduces the overall burning of the composite compared to neat resin, hence even the control sample is not as flammable as the cast resin. In the fibre-reinforced composites, the volatiles released during composite burning are contained in the composite because of the layered structure (glass fibres in composites) hence, char formation is reduced and this is the probable reason for the blends system not being as effective in the composites as it is in the blended cast resins.

As can be seen from these trends that amongst the three groups of samples, UP/PH-S samples show higher fire retardancy in terms of reduction in PHRR than that UP/PH-Ep and UP/PH-Al samples. In UP/PH-Ep and UP/PH-Al blended composites, presence of functionalised phenolic resins showed lower char yield than that of UP/PH-S. A possible reason for the greater fire retardancy of the UP/PH-S blended resin compared to the others has been explained in detail in our previous publication [17].

3.2.2. Impact performance of heat damaged composites

Impact tests were carried out on residual samples obtained after cone experiments (see inset images in Fig. 6) using similar conditions as in Section 3.1.3. The results given in Table 3 show that the UP composite has only glass fibre remaining, with no stiffness after the cone test, whereas samples of UP/PH show some retention of stiffness. This can be seen clearly from

Table 3 where % retention values of modulus with respect to modulus of unburnt sample are also given.

The UP/PH-S:70/30 and 50/50 composites after exposure to cone calorimeter have impact modulus values of 2.8 GPa and 3.1 GPa respectively, which means 14 % and 15 % modulus retention w.r.t. the respective impact modulus values of unburned samples (see Table 3). The higher retention in UP/PH-S composites may be due to the consolidated char formed by the PH-S resin, which gives the stiffness to the composite structure. There was no visible physical damage observed on the residual sample.

The UP/PH-Ep:70/30 and UP/PH-Ep:50/50 composite samples show impact moduli of 2.51 GPa and 3.4 GPa, respectively, retaining 12 % and 17 % of impact modulus. There were no visible physical damages observed on the tested samples.

The heat damaged UP/PH-Al:70/30 and UP/PH-Al:50/50 composite samples have impact moduli 3.42 GPa and 3.75 GPa respectively and show 17 % and 19 % modulus retention. The burnt samples also did not show physical damage on their surfaces after the impact tests. From Table 3, it is observed that all of the co-blended samples of higher phenolic content show higher percentage impact modulus retention because of greater char formation, suggesting that the presence of resole phenolic resin in the co-blended composite samples of UP/PH leads to better mechanical properties retention than in that containing UP alone.

3.2.3. UL -94 results

The composite samples were tested under both vertical and horizontal UL-94 modes. In both tests the samples were marked at 25 and 100 mm intervals from the exposed end and from time taken for flame to reach from the first mark to the other one, the burning rates could be calculated. All results are listed in Table 5. In vertical orientation, the UP composite burned completely and hence, could not pass the minimum classification of the UL-94 test [30] (Table 5). All composite samples from UP/ PH blended matrices also failed in both vertical and horizontal burning tests. In the horizontal UL-94 test, the HB rating was given to the samples, which means in a sample either the burning rate does not exceed 75 mm/min or it self-extinguishes before 100 mm [31]. In this case the whole sample burnt after the first ignition, but burning rate was lower than 75 mm/min.

As can be seen from Table 5, the burning rates in horizontal and vertical tests for the UP composite is higher than for all blended samples. In the vertical orientation, the UP sample has 83.8 mm/min burning rate, which is reduced to 80 mm/min for the UP/PH-S:70/30 composite and 35.1 mm/min, for the UP/PH-S:50/50 composite, i.e., > 50 % reduction in the latter. All types of resole phenolic resins show the same trend i.e., the burning rate decreases with phenolic resin presence, decreasing further with increasing phenolic content.

On comparing the effect of different phenolic resin types it can be seen that the trend in the UL-94 results is different than that for cone results. The UP/PH-Al:70/30 composite sample displays a vertical burning rate of 57.2 mm/min (UP composite = 83.8 mm/min), which is slightly lower than those of UP/PH-S:70/30 and UP/PH-Ep:70/30 composites. This can be explained on the basis of the TTI values seen in the cone results (Table 4), where UP/PH-Al samples have higher TTI values than all other samples. The delayed ignition leads to lower surface flame spread compared to that of UP/PH-S and UP/PH-Ep composites. The low flame spread is one of most important international maritime organisation (IMO) test requirements needed for composites in marine applications. Hence UP/PH-Al composites with lower flame spread could be better for marine applications and hence need further investigation. Based on UL-94 results the composite samples show the following trend for rate of burning:

$$\text{UP/PH-Al} < \text{UP/PH-Ep} < \text{UP/PH-S} < \text{UP}$$

In horizontal tests the burning rate is very low for all samples including the UP sample (17.1 mm/min). All phenolic resin containing samples have lower burning rates than that of the UP composite, which decreases with increasing phenolic resin content, but the effect of resin type is not significant. All UP/PH:70/30 have burning rates of ~ 14-15 mm/min and UP/ PH:50/50 of ~10.5-11 mm/min.

4. Conclusions

The results show that the fire resistance of composites from UP can be improved by blending and co-curing UP with phenolic resoles. The GFRC of UP/PH-S (UP with non-functionalised phenolic) resin blend shows higher fire resistance but lower mechanical properties, the latter being due to poor compatibility between UP and PH-S. The properties however, are still good to be used for certain applications such as automotive/marine transport and chemical plant industries. Whereas, GFRCs from UP with functionalised phenolic resin, PH-Ep (epoxy functionalised) and PH-Al (allyl functionalised) show comparatively lower flame retardancy

but with little deterioration in mechanical properties. The reductions in flammability values of different composites from blended resins compared to that of from UP are though less than respective reductions for the cast resins, which is due to the presence of glass fibre which acts a thermal insulator and may also entrap/delay the release of some volatiles produced during burning of the resin. All composite laminates though failed the UL-94 test and even in horizontal tests burnt along the whole length, but the rate of flame spread in composite samples made with UP-PH blended resins was lower, indicating that these samples may behave better in tests involving surface flame spread. Overall this work has shown that composites can be produced from co-blended UP-phenolic resins, which with carefully chosen resin and associated curing conditions will have improved fire and acceptable to good mechanical properties.

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. We also thank Mr Chen Zhou at the University of Bolton for carrying out some tensile tests.

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Captions to Figures

Fig.1. Schematic of IPN formation on co-curing two resins

Fig. 2. Digital images, scanning electron micrographs, DMTA (tan δ vs temp curves, arrows indicate T_g s) and LOI results of cast resins of a) UP and PH resins and b) UP/PH:50/50 blends (results taken from refs [3, 17])

Fig. 3. Stress vs. strain curves for GFRC of UP and 70/30 blends of UP/PH-S, UP/PH-Ep and UP/PH-Al under flexural mode

Fig. 4. Stress vs. strain curves for GFRCs of UP and UP/PH-S blends in tensile mode

Fig. 5. Load vs. deflection curves of GFRC laminates of UP and of 70/30 blends of UP/PH-S, UP/PH-Ep and UP/PH-Al from drop-weight impact testing

Fig. 6. Digital images of charred residues of GFRC composites of a) UP, b) UP/PH-S:70/30, c) UP/PH-S:50/50, d) UP/PH-Ep:70/30, e) UP/PH-Ep:50/50, f) UP/PH-Al:70/30, g) UP/PH-Al:50/50 after cone experiment at 50 kW/m² heat flux

Fig. 7. Percent change in cone parameters w.r.t UP: comparison of cone results for GFRCs (normalised to 40 wt%) and cast resins [15] with those of UP

Captions to Tables

Table 1. Composition of the GFRCs from UP and UP/Res-PH blends

Table 2. Mechanical properties of the GFRCs from UP and UP-PH composites

Table 3. Digital images of impact damage and damage observations on the front (impacted) of all GFRC samples after 1.02kg drop-weight impact testing

Table 4. Cone results for GFRCs of UP and UP/Res-PH blends exposed to 50 kW/m² heat flux

Table 5. UL -94 test results of GFRC samples of UP and of UP/ PH co-blended matrices

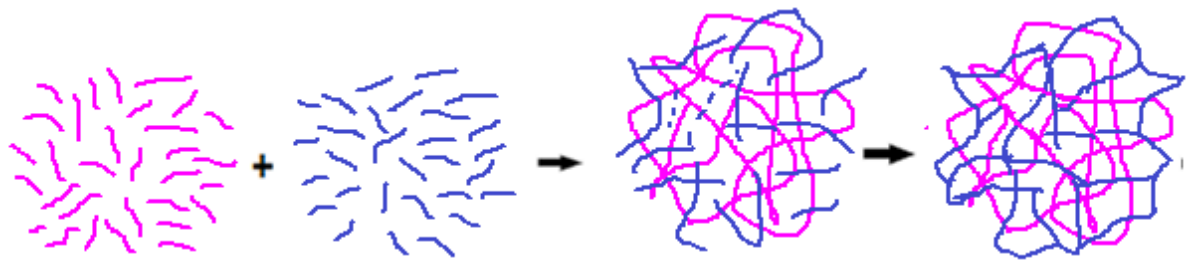


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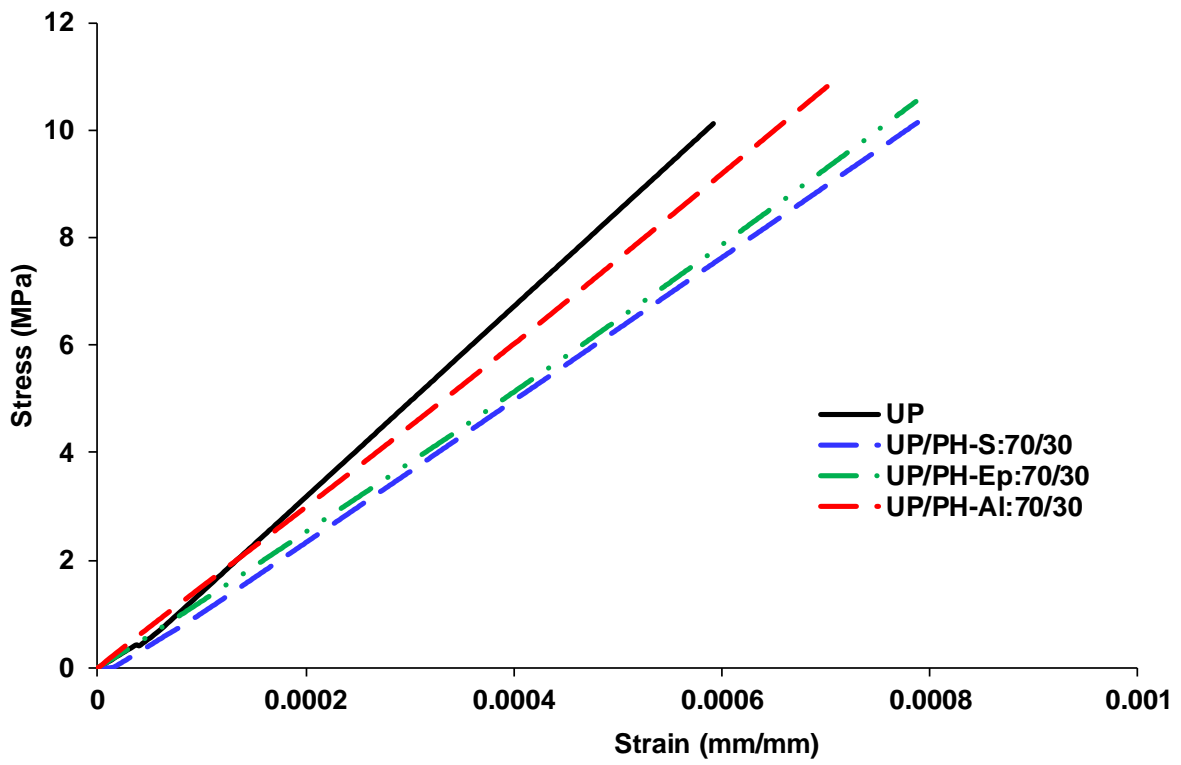


Fig. 3. Stress vs. strain curves for GFRC of UP and 70/30 blends of UP/PH-S, UP/PH-Ep and UP/PH-Al under flexural mode

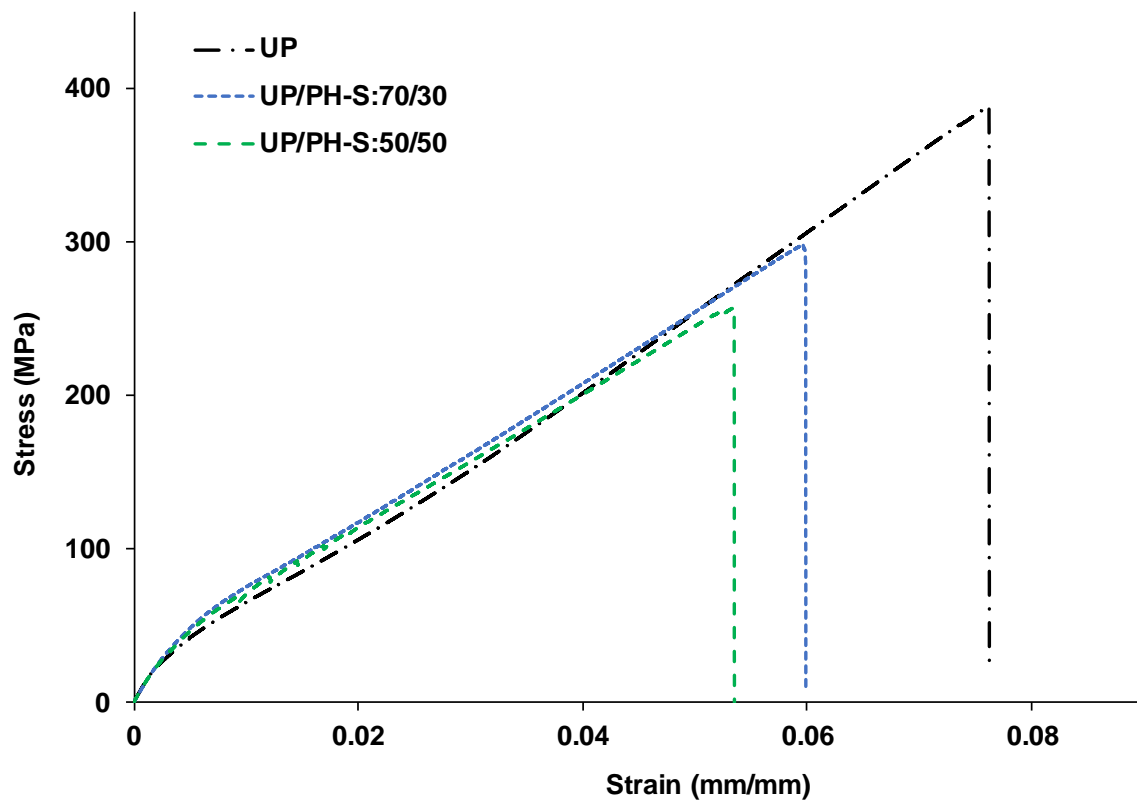


Fig. 4. Stress vs. strain curves for GFRCs of UP and UP/PH-S blends in tensile mode

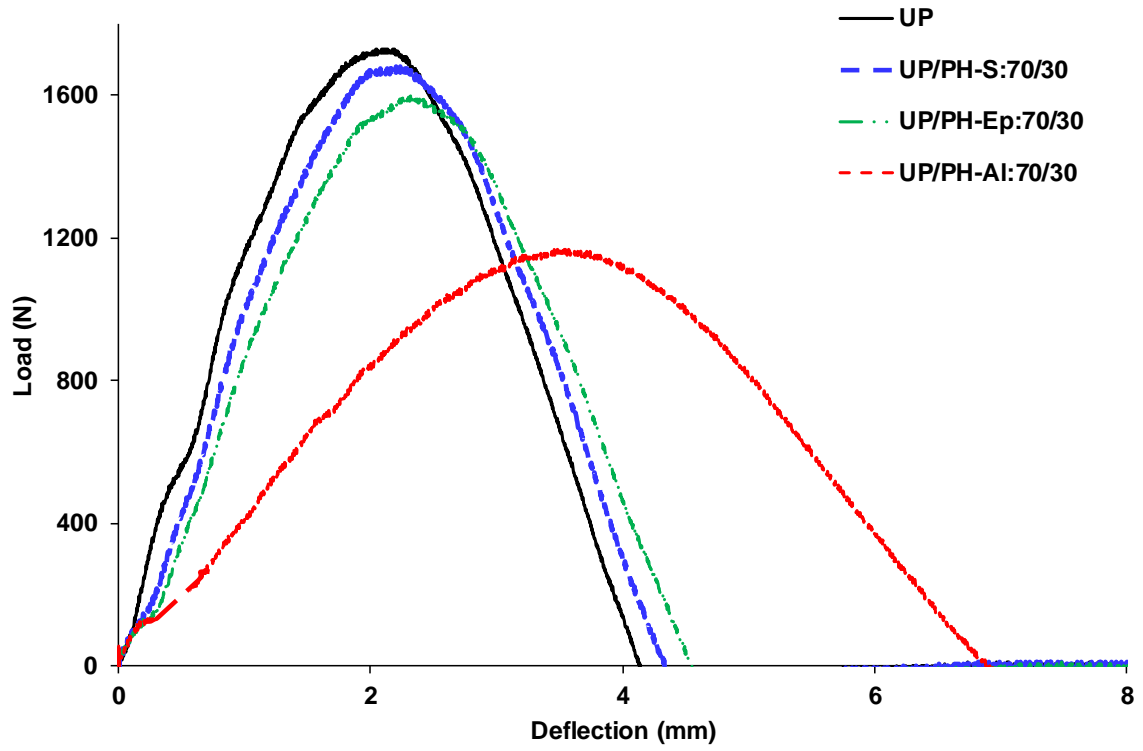


Fig. 5. Load vs. deflection curves of GFRC laminates of UP and of 70/30 blends of UP/PH-S, UP/PH-Ep and UP/PH-Al from drop-weight impact testing

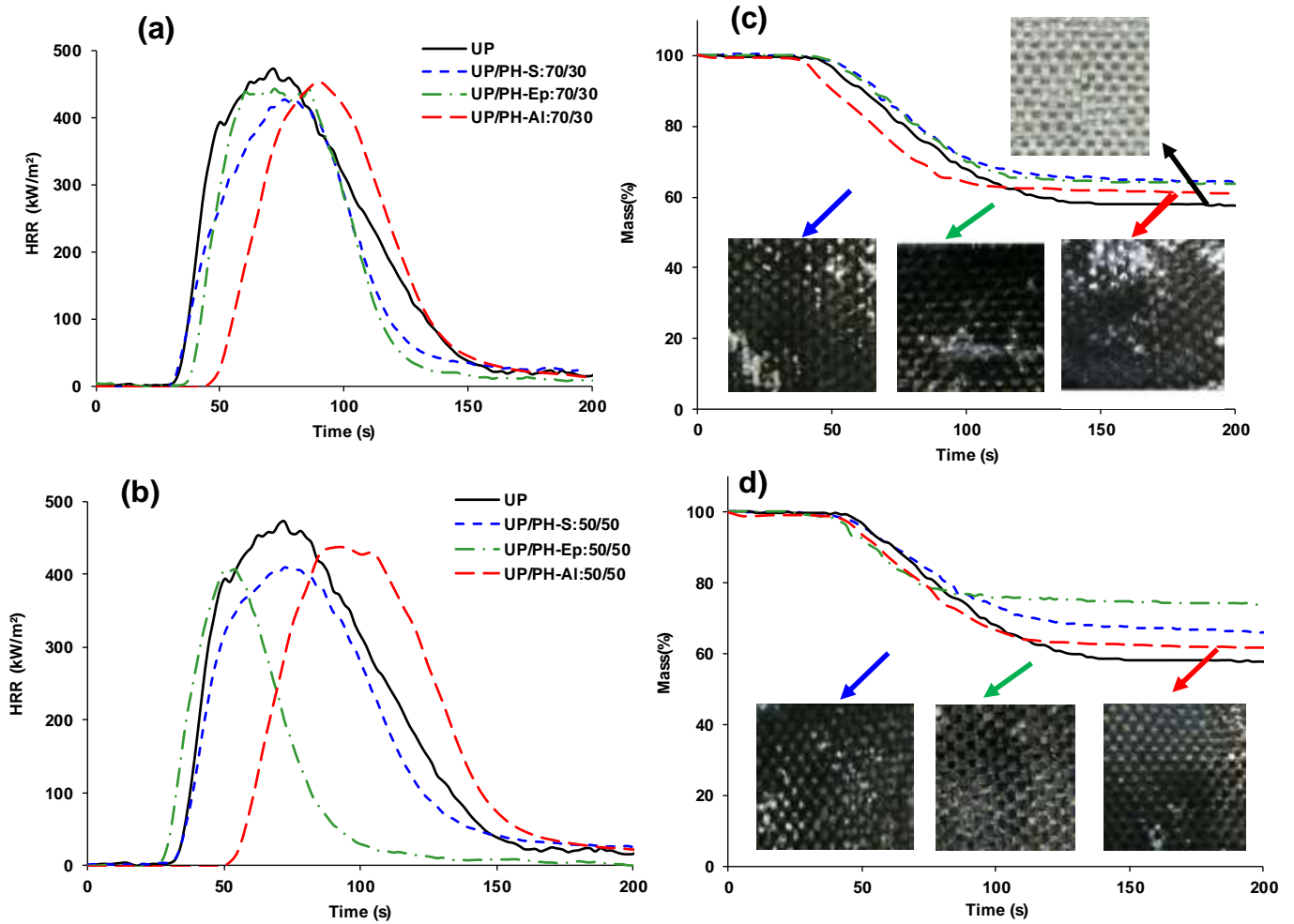


Fig. 6. Heat release rate (a,b) and mass loss (c,d) vs time curves, and digital images of charred residues (inset images, colours of arrows indicating respective samples) of GFRC composites of UP, UP/PH: 70/30 and 50/50 blends at 50 kW/m² heat flux

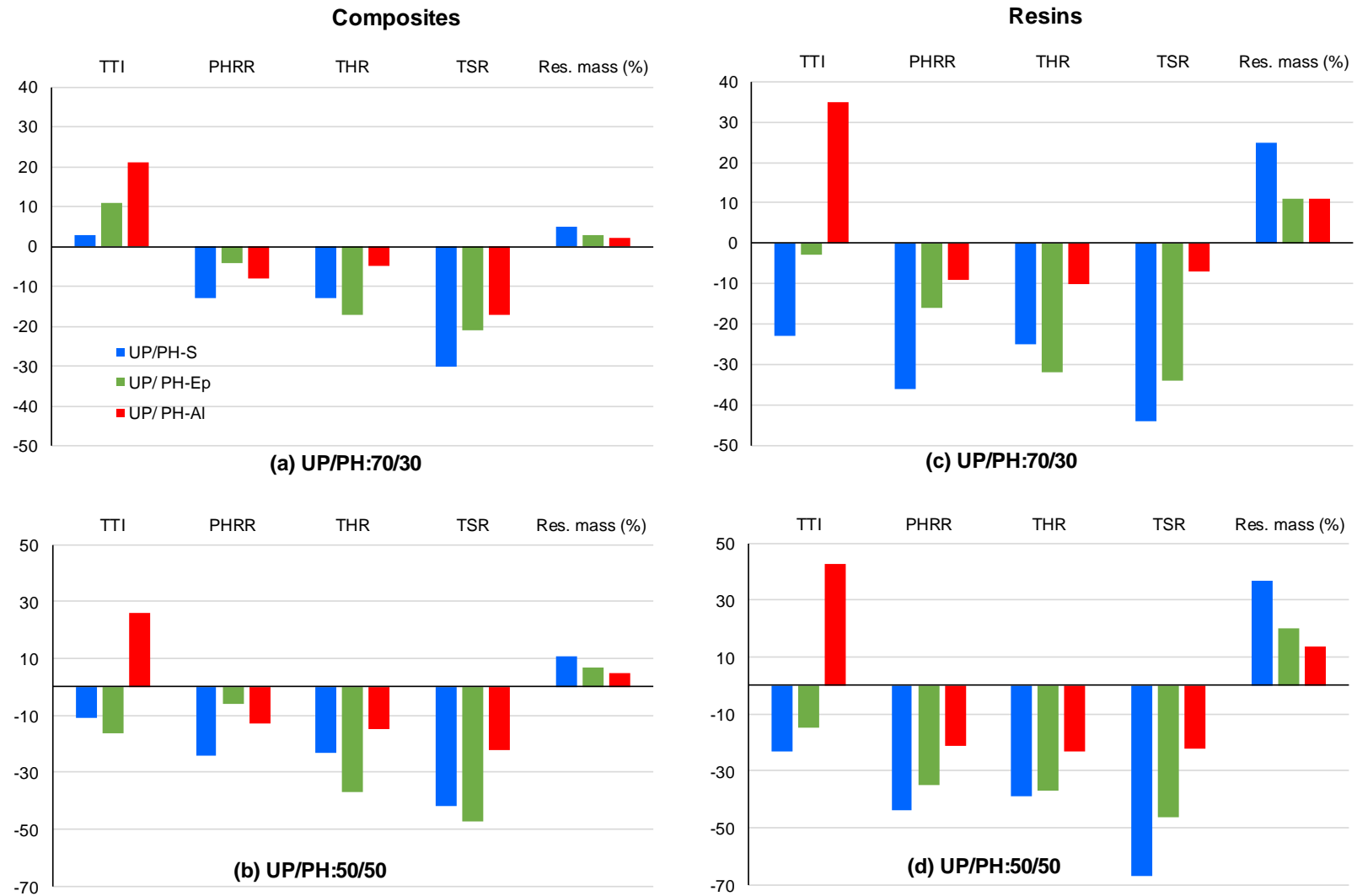


Fig. 7. Percent change in cone parameters w.r.t UP: comparison of cone results for GFRCs (normalised to 40 wt%) and cast resins [15] with those of UP

Table 1. Composition of the GFRCs from UP and UP/Res-PH blends







Sample ID	Thick. (mm)	Fibre wt.%	Resin wt.%	Fibre Vol Fraction, %	Curing conditions
UP	2.4	59	41	39	RT 24 h, 80°C 6 h
UP/PH-S:70/30	2.5	59	41	38	50°C 6 h, 80°C 24 h, 90°C 9 h, 130°C 1 h, 160°C 1 h
UP/PH-S:50/50	2.6	55	45	33	80°C 24 h, 100°C 1 h, 130°C 1 h, 160°C 1 h
UP/PH-Ep:70/30	2.6	59	41	38	50°C 6 h, 70°C 8 h, 80°C 8 h, 100°C 6 h, 130°C 2 h, 160°C 2 h
UP/PH-Ep:50/50	2.1	67	33	45	50°C 6 h, 70°C 8 h, 80°C 8 h, 100°C 6 h, 130°C 2 h, 160°C 2 h
UP/PH-Al:70/30	2.4	59	41	38	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
UP/PH-Al:50/50	2.3	58	42	36	50°C 6 h, 80°C 12 h, 100°C 8 h, 120°C 6 h, 130°C 6 h, 150°C 2 h, 190°C 2 h

Table 2. Mechanical properties of the GFRCs from UP and UP-PH composites

Sample	Flexural Mod (GPa)			Tensile properties			
	Absolute value	Normalised to 40% FVF	% Change*	Initial Tensile Mod. (GPa)			Stress-at-failure (MPa)
				Absolute value	Normalised to 40% FVF	% Change*	
UP	17.7 ± 0.6	18.0 ± 0.6	0	12.9 ± 0.8	13.2 ± 0.8	0	375 ± 13
UP/PH-S:70/30	10.9 ± 0.6	11.4 ± 0.5	-37	11.6 ± 0.5	12.2 ± 0.5	-8	281 ± 13
UP/PH-S:50/50	11.8 ± 0.5	14.4 ± 0.5	-20	11.6 ± 0.4	13.9 ± 0.4	+5	256 ± 2
UP/PH-Ep:70/30	15.0 ± 0.6	15.7 ± 1.4	-13	10.5 ± 1.0	11.2 ± 1.0	-16	298 ± 6
UP/PH-Ep:50/50	19.7 ± 0.7	17.6 ± 0.2	-2	11.0 ± 0.5	11.6 ± 0.5	-12	268 ± 4
UP/PH-Al:70/30	17.0 ± 0.6	17.8 ± 1.0	-1	10.8 ± 0.3	12.0 ± 0.3	-9	317 ± 8
UP/PH-Al:50/50	16.4 ± 0.5	18.4 ± 0.4	+2	NA			NA

Note: * = The % reduction (-) or %increase (+) w.r.t. normalised flexural modulus of UP composite values; NA = results not available.

Table 3. Digital images of impact damage and damage observations on the front (impacted) of all GFRC samples after 1.02 kg drop-weight impact testing

Sample ID	Before burning		Impact modulus of unburnt samples (GPa)	Change w.r.t. UP (%)	After burning		Impact modulus of cone tested samples (GPa)	Impact modulus retention (%)	Residual char (%)
	Images	Damaged observation and area (mm ²)			Images	Damaged observation and area (mm ²)			
UP		V 7.1 ± 1.2	19.6 ± 0.6	0		X -	0.35 ± 0.05	2	1
UP/PH-S:70/30		X -	19.4 ± 0.6	-1		X -	2.81 ± 0.02	14	25
UP/PH-S:50/50		X -	19.5 ± 0.6	-1		X -	3.10 ± 0.05	16	37

UP/PH- Ep:70/30		D	113.0 ± 2.5	20.3 ± 0.5	4		X	-	2.51 ± 0.05	12	11
UP/PH- Ep:50/50		V	8.3 ± 1.6	22.4 ± 1.0	14		X	-	3.44 ± 0.15	15	20
UP/PH- Al:70/30		X	-	19.7 ± 0.5	1		X	-	3.42 ± 0.05	17	11
UP/PH- Al:50/50		X	-	19.3 ± 0.2	-2		X	-	3.75 ± 0.15	19	14

Note: X = no physical damage appears, V= visible impression seen on the surface (by the impact tub at a local area), D = surface damages on the composite laminates.

The % reduction (-) or % increased (+) w.r.t. impact modulus of UP composite values

Table 4. Cone results for GFRCs of UP and UP/Res-PH blends exposed to 50 kW/m² heat flux

Sample	Resin wt. (%)	TTI (s)	FO (s)	PHRR (kW/m ²)	THR (MJ/m ²)	TSR (m ² /m ²)	Res. mass (%)	FIGRA (kW/m ² s)	MAHRE (kW/m ²)
UP	41	38	146	491(479)	32.6 (30.3)	2233 (2077)	59.8 (0.8)	9.1 (8.9)	255 (249)
UP/PH-S:70/30	41	39	140	428 (418)	26.9 (26.2)	1482 (1446)	64.0 (5.0)	5.6 (5.5)	203 (198)
UP/PH-S:50/50	45	34	168	411 (365)	26.4 (23.5)	1344 (1195)	65.8 (10.8)	5.1 (4.5)	210 (187)
UP/PH-Ep:70/30	41	42	132	415 (461)	25.9 (25.3)	1689 (1648)	62.0 (3.0)	6.4 (6.2)	238 (232)
UP/PH-Ep:50/50	33	32	101	382 (448)	15.8 (19.2)	916 (1110)	73.6 (6.6)	6.3 (7.6)	191 (232)
UP/PH-Al:70/30	41	46	131	454 (443)	29.4 (28.7)	1769 (1726)	59.9 (0.9)	6.9 (6.7)	237 (231)
UP/PH-Al:50/50	42	48	140	436 (415)	27.1 (25.8)	1699 (1618)	63.0 (5.0)	5.2 (5.0)	253 (241)

Note: TTI = time-to-ignition; FO = flame out; PHRR = peak heat release rate; THR = total heat release; TSR = total smoke release; FIGRA = fire growth rate index

The variation in values for different parameters are: TTI = ± 3; FO = ± 6; PHRR = ± 26; THR = ± 1.2; EHC = ± 1.4; TSR = ±104; Res.mass = ±1.6, FIGRA= ±0.6, MAHRE = ± 17

The values within the parentheses are the normalised values with respect to 40 wt. % resin using Equation 2; the residual mass values are after compensating for the glass fibre content for each sample as in Table 1

Table 5. UL -94 test results of GFRC samples of UP and of UP/ PH co-blended matrices

Samples	Horizontal burning (HB) rate (mm/min)	UL94 rating for HB test	Vertical burning (VB) rate (mm/min)	UL94 rating for VB test
UP	17.1 ± 0.1	HB	83.8 ± 2.3	FAIL
UP/PH-S:70/30	15.2 ± 0.7	HB	80 ± 1.7	FAIL
UP/PH-S:50/50	10.5 ± 0.5	HB	35.1 ± 1.3	FAIL
UP/PH-Ep:70/30	15.2 ± 0.3	HB	78.6 ± 2.0	FAIL
UP/PH-Ep:50/50	10.9 ± 0.2	HB	33.2 ± 1.8	FAIL
UP/PH-Al:70/30	13.6 ± 0.2	HB	57.2 ± 0.9	FAIL
UP/PH-Al:50/50	11.2 ± 0.1	HB	32.4 ± 1.9	FAIL