# Fire Performance Evaluation of Different Resins for Potential Application in Fire Resistant Structural Marine Composites

BALJINDER KANDOLA and LATHA KRISHNAN Institute for Materials Research and Innovation, University of Bolton Deane Road Bolton, BL3 5AB, UK

# ABSTRACT

This work explores the possibility of reducing the flammability of unsaturated polyester (UP) resin, commonly used in marine composites, by co-blending with less combustible and char-forming resins such as phenol-formaldehyde, melamine-formaldehyde and furans. The compatibility and curing properties of UP, other resins and their blends in 50:50 wt-% ratios have been have been studied by differential scanning calorimetry (DSC) and dynamic mechanical thermal analysis (DMTA) techniques. Based on the successful establishment of curing conditions, plaques of resins have been cast and cured. Thermal stability has been studied by thermogravimetry (TGA), whereas the fire performance evaluation was carried out by limiting oxygen index (LOI) and cone calorimetry at 50kW/m<sup>2</sup> heat flux. According to a fire risk assessment based on cone calorimetric data, the resole phenolic resins and their blends with UP achieved the highest fire safety rating.

KEYWORDS: thermoset resins, marine composites, flammability, heat release rate, smoke

# INTRODUCTION

The use of glass-fibre-reinforced polymeric composites (GRPs), mainly of unsaturated polyesters or vinyl ester resins, in ship and boat building is widespread due to their good corrosion resistance [1] and minimal maintenance requirement properties. For small commercial vessels, yachts, life boats and navy vessels their use is widespread. Although large vessels are constructed primarily of steel, composites are used in part for ship superstructures [1] and interior components. However, along with the improvements to materials and construction methods, the prime concern is to ensure that vessels are safe for their passengers and crew. Fire safety is a very important part of that overall safety concern. All commercial passenger and cargo ships have to comply with the fire performance requirements contained in the IMO/HSC Code [2]. The fire tests acceptance criteria defined in the IMO/FTP code [3] advise that for areas of moderate and major fire hazard (e.g., machinery spaces and storerooms), the materials used should be 'Fire resisting', i.e., they should prevent fire and smoke propagation during a defined period of time. Composites used for load - bearing structures should also be able to maintain their load-bearing capacity within the specified period of time (30 or 60 min).

At present, three main methods are used to render GRP composite structures fire retardant [4,5], each one has its own strengths and weaknesses. The first method is to use mineral and ceramic wool, or phenolic foam, as an outer protective surface, particularly for composites used for deck and bulkhead structures for naval applications [6]. However, the main disadvantage of this approach is that such a surface adds significant weight and can also act as an absorbent for spilled fuel during a fire. The second method is to use a fire-retardant (usually intumescent) paint or coating. Both of these methods provide passive protection to the structure by acting as heat barriers, insulating and reflecting the radiant heat back towards the heat source which delays the heat-up rate and reduces the overall temperature on the reverse side of the substrate. They however, have no effect on the combustibility of the underlying GRP laminate. The third method involves chemical or physical modification of the basic resin matrix. Polyester or vinyl ester resins are usually modified by attachment of suitable halogen atoms to the polymeric backbone of the resin. Invariably with halogenated resins, halogen synergists such as the antimony trioxide or zinc hydroxy stannate are used. The main disadvantage of this solution is that such halogen-containing resins release toxic and corrosive gases and, owing to increasing environmental awareness and strict environmental legislation, are falling out of favour. Hydrated mineral fillers such as alumina trihydrate (ATH), magnesium hydroxide and calcium carbonate can also be added to

the resin to decrease flammability [7]. However, whilst these mineral fillers do not release toxic gases on thermal decomposition, the disadvantage is that the high concentrations required to significantly improve fire retardancy can greatly impair the mechanical properties of the composite. Ammonium polyphosphate and red phosphorus are excellent halogen-free flame retardants for all types of thermoset resins [8]. Zinc borate and stannates are most often used as smoke suppressants. However, in fully developed fires with low ventilation, a flame retardant concentration of 20% (w/w) with or without zinc borate is not sufficient to suppress both flammability and smoke formation. The recent development over the last ten years has been the use of nanoscopic additives, such as organically modified clays, which when uniformly dispersed within the polymer matrix (5-10%, w/w) can reduce the peak heat release value by up to 70% for many resin systems. However, in most cases they do not pass commercial combustion tests such as LOI and UL-94. Moreover the main disadvantage of using additives is that these components when added to the resin, affect its processability and the modified resin is difficult to be used in the resin transfer moulding technique, commonly used for polyester and vinyl ester resin composites.

An example of current practice for fire-resistant composite structures used for masts in naval ships is shown in Fig. 1 where all three strategies discussed above are currently used. Since for naval ships the fire threats from internal and external blasts and weapon-induced fire are higher than for civilian ships, the fire performance requirements for the former are also high. It must be emphasized here that the structure shown in Fig 1 is being chosen as an example and is by no means the only relevant structure and application. The structure shown in Fig.1 is designed to survive these attacks and complies with SOLAS/IMO requirements. The layered structure contains a balsa core sandwiched between two glass fibre-reinforced vinyl ester (a commercially available flame-retardant version: most probably a halogenated resin) laminates, coated with an intumescent layer and then with a phenolic foam layer bonded to it. Although satisfactory with respect to regulations this is a far from ideal solution in terms of weight and cost. The manufacturing process requires three distinct stages, lamination, painting and foam application. This requires time and resources to complete. In addition, the overall density and hence weight of the layered composite structure is quite high compared to the unprotected GRP structure, thus negating the attraction of using lightweight advanced composites. The weight and inherent effort in construction could be reduced by using an inherently noncombustible resin material, which is the focus of the research work carried out at Bolton. The major objective is to develop a modified polymeric matrix to reduce the combustibility of the vinyl ester or polyester resins currently used in marine composites, by blending with inherently flame retardant resins, which will increase the thermal stability and char-forming capacity of the matrix. The physical and chemical properties of the resins need to be optimised to enable the resin to be infusible for resin transfer moulding, low temperature curing, to maximize compatibility and bonding with glass fibres, and to permit up-scaling to produce large laminates.

Polymer blending is designed to generate materials with optimized chemical, structural, mechanical, morphological and biological properties. 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. The polymer blends will gain the good properties of each polymer.



Fig. 1 Schematic of the layered composite structure used for naval ship masts

In this paper the thermal stability and fire performance of different resins are studied to identify the best candidates for blending with UP. DSC has been used to study their curing behaviour and compatability with UP. Resins selected are phenolic, melamine-formaldehyde and furan types. Phenolic (phenolformaldehyde) resins are well known to have excellent flame retardance, good heat resistance, and low smoke/toxic gas evolution on burning [5]. Based on phenol/formaldehyde ratios, resole or novolac resins are obtained. The most widely used phenolic resins for composites are resoles due to their low-viscosity and hence, easy processability. However, despite having good fire retardant properties, the phenolics are not commonly used for in composites for structural applications because of their brittleness. Here two types of resoles and one type of novolac resins have been used. One of the phenolic and the novolac resins have been chemically modified to make them compatible with the unsaturated polyester. It must be noted that the main problem of blending UP and PH resins is their incompatibility due to their different curing mechanisms, which can lead to phase separation and hence, poor mechanical properties of the composite produced. The compatibility can be improved by functionalizing one of the resins, phenolic in this case [9,10]. Melamine formaldehyde resins, similar to phenol-formaldehyde (phenolic) are less flammable and produce minimal smoke. Furan resins also on heating undergo cross-linking and produce char, and their combustibility is low compared to unsaturated polyester resins, hence have also been selected for blending. Here the flammability of these resins and their 50:50 (wt-%) blends with unsaturated polyester are studied.

## EXPERIMENTAL

#### Materials

**Unsaturated Polyester (UP):** a pre-accelerated, unsaturated phthalic anhydride- based resin was sourced from Scott-Bader. A methyl ethyl ketone peroxide based catalyst (Catalyst M) for curing the resin was also sourced from Scott Bader.

#### **Phenolics:**

Resole (Res): Following two resins were sourced from Sumitomo Bakelite Europe N.V:

- (i) Durez 33156 (D): An ethanol based phenolic resole
- (ii) Methylon 75108 (M), a solvent free, allyl functionalized resole type phenolic resin.

**Novolac** (Nov): A methacrylated novolac resin, prepared by chemically modifying resin D31459, sourced from Sumitomo Bakelite Europe N.V.

**Melamine formaldehyde (MF) :** a spray dried resin (MF 600b) was sourced from Momentive, Albany, New York. The resin was dissolved in di ethylene glycol solvent for use in this work.

**Furan resin :** Furobond resin **(FB)** was sourced from Transfurans Chemicals (TFC), Belgium. The catalyst used to cure the resin, p-toluenesulfonic acid monohydrate was sourced from Fisher Scientific, UK

#### Sample preparation

A sample of cured UP resin was prepared by mixing the resin with 2 wt-% of catalyst M with a mechanical stirrer in a 100 ml beaker. The mixture was then poured into 5.5 cm diameter circular or 10 x10 cm square aluminium open moulds to a depth of 3 mm. The specimens were then allowed to cure at room temperature for 24 h and post-cured at 80°C in an oven for 4 h. Samples of resole phenolic resins were directly transferred to moulds, again to depths of 3 mm and stored at room temperature for 24 h (to allow much of the solvent to evaporate) followed by cure and post cure by increasing the temperature slowly up to 200°C; detailed curing conditions are given in Table 1. Nov, MF and FB resins were similarly prepared, ie, first a formulation was prepared by adding appropriate solvent/catalyst and then transferred to a mould and cured using appropriate curing conditions (Table 1).

The formulations of resin blends were prepared by mixing 50 wt-% UP and 50 wt-% of Res/Nov/MF/FB resins with mechanical stirring and then degassing under vacuum for 15 min. A methyl ethyl ketone catalyst (2 wt-% w.r.t. UP resin) was added into the resin mixture and stirred for another 10 min. Subsequently the resins were transferred to the moulds and cured using appropriate curing conditions, given in Table 1. In each case sample thickness was  $\sim$  3mm.

## Curing behaviour and compatibility study

A DSC Q2000 was used to test the samples (2-10 mg) at a heating rate of  $5^{\circ}$ C/min within the range of 30-350°C. The curing peaks and heat of reaction during curing (J/g) from the curves were measured.

A DMA Q800 was used to test the samples using a single cantilever clamp and multi-frequency-strain experiment set up (0.1% strain and 1 Hz frequency). The specimen was heated at 10°C/min within the range 30-350°C. Tan  $\delta$  and storage modulus were measured and recorded. For each sample two test specimens were tested.

# **Thermal Analytical Study**

Thermogravimetric analysis (TGA) was performed on all cured samples of UP, other resins and their blends using an SDT2960 from TA instrument. It was used to study thermal stability of samples from room temperature to 900°C using 10 -12 mg samples heated at a constant heating rate of 10°C/min under air with flow rate 100 ml/min. For each sample two test specimens were used.

# Limiting Oxygen Index (LOI)

The limited oxygen index (LOI) of all cured, cast resins and their blended samples was studied using a Stanton Redcroft apparatus equipped with an oxygen analyser. Three test specimens of  $\sim 3$  mm thickness, 10 mm width, and 100 mm length were cut from the cured resin plaques. The sample was suspended vertically and ignited with a flame. The condition at which the sample just burnt like a candle was used to determine the LOI value of that particular sample.

# **Cone Calorimetry**

The flammability of all cast resin samples and their blends were evaluated using a cone calorimeter (Fire Testing technology, UK). Circular samples measuring 5.5 cm dia. with a nominal thickness of 3 mm, were fire tested in the horizontal mode with an ignition source at an applied heat flux of 50 kW/m2. The 50 kW/m2 heat flux, which is used in many standards, was chosen to simulate a well developed fire.

Previously in our laboratories, a comparative study of the cone calorimetric behaviour of round and standard square ( $10 \text{ cm} \times 10 \text{ cm}$ ) samples was undertaken in order to understand the effect of geometry on flammability properties of polymeric materials. Circular specimens with a four-fold reduction in area gave similar results for the peak heat release rates (PHRR), total heat release (THR) and effective heat of combustion (EHC). Smoke, CO and CO2 production results were found to be different from those measured for the larger specimens since these parameters are independent of exposed specimen surface area. However, in this work, these data were used for comparison purposes only with respect to control specimens, hence there was no need for adjustments.

# **RESULTS AND DISCUSSIONS**

## Curing and compatibility study by DSC

The DSC curves for all samples shown in Fig.2 have been analysed to study the curing behaviour of resins such as temperature range for curing, cure peak temperature, percentage of cure etc. This information has been used to optimize cure conditions for resins and composites (Table 1) and also to study the compatibility of the component resins in the blends.

The DSC of uncured UP in Fig. 2 shows an exothermic curing reaction of the resin starting at room temperature and peaking at 82°C. Based on this, the curing of the resin, initiated by a radical initiator (catalyst M), was carried out at room temperature for 24 h, followed by post curing at 80°C for 6 h to achieve 100% curing. The curing reaction in UP is a radical polymerization reaction [5].



Fig.2 DSC curves of uncured UP, phenolic (Res-D, Res-M, Nov), MF and furan (FB) resins

	DEC			
Resin	Endo, peak max (°C)	peaks Exo, peak max (°C)	Curing conditions for cast resin	<i>Tg</i> from DMTA (°C)
UP	-	81	RT 24h, 80°C 6h	92
Res-D	70,144	250	50°C 6h,80°C 12h,160°3h	269
JP/ Res-D	106	194	80°C 24h,100°C 1h,130°C 1h,160°C 1h	92,197
Res-M	176	224	100°C 8h,120°C 6h,130°C 6h, 150°C 2h,180° C 2h	285
JP/ Res-M	-	81,175,226	50°C 6h,80°C 12h, 100°C 8h,120°C 6h, 130°C	117
			2h,150°C 2h,180° C 2h	
Nov	-	67	RT 24h, 80°C 6h	171
UP/ Nov	-	57	RT 24h, 80°C 6h	120
MF	-	94	RT 24h, 80°C 6h	152
UP/MF	-	80	RT 24h, 80°C 6h	89
FB	111	137	RT 24h, 80°C 48h, 100°C 4h	94
UP/FB	157	183	RT 24h, 80°C 48h, 100°C 4h	68

Table 1.DSC peaks, curing conditions and Tg of uncured resins

Resole phenolic resins typically show an exothermic peak at much higher temperature than UP [9,11,12]. The curing of phenolics occurs by polycondensation, producing water and formaldehyde, which evaporate endothermally. The DSC curves of both Res-D and Res-M resins in Fig. 2(a) show endothermic as well

as exothermic peaks. The endothermic peaks representing evolution of water and formaldehyde during curing are very sharp. The peak temperature values for exothermic peaks reported in Table 2 indicate that these resins cure at much higher temperature than UP. The DSC curve of Res-M clearly shows that the exothermic curing reaction starts at about 180°C and is complete at about 280°C. Such temperatures are much higher than those observed for UP and 100% of curing is obtained only at 180°C, ie., 100°C higher than for UP. The detailed curing study is given elsewhere [10]. The onset of curing for Res-D is not as clear as it is for Res-M as the large endothermic peak of the solvent evaporation masks the exothermic signal. However, both resins require temperatures as high as 160 - 180°C in order to be fully cured. For blended resins, curing conditions used were very similar to the ones used for the respective resole phenolic resin.

The DSC curve of methacrylated novolac (Fig.2(b)) shows an exothermic peak with maximum at  $67^{\circ}$ C, indicating that it can be cured under conditions similar to UP, as also observed by Cherian et al for a modified novolac resin [13]. The novolac resin similar to resoles does not need any initiator. The curing conditions used for the resin and the blend with UP were similar to those for UP (Table 1).

Spray dried melamine formaldehyde resin with diethylene glycol solvent (MF600b) showed an endothermic and a small exothermic peak (Fig. 2(c)). Melamine formadehyde resins cure by addition, followed by polycondensation reaction [14]. Curing condition for the blended sample was similar to that of the UP.

The DSC curve of Furan (FB) resin (Fig. 2(d)) shows an endothermic followed by an exothermic peak with peak maxima at 111 and 137°C, respectively. This resin also cures by polycondensation reaction [15]. The exothermic reaction is by ring-opening of furan. The blended resin has shown similar trend to the FB (Table 1). Similar curing conditions to UP can be used for FB and its blend with UP, however both need post curing at 100°C for 4h (Table 1).

# Differential Mechanical Analysis (DMA)

The DMTA was performed on all cast resin samples. From the Tan  $\delta$  versus temperature curves, the glass transition temperature,  $T_g$  for each sample was determined, the values are reported in Table 1. All pure resins display a single  $T_g$ . Phenolic resins, as expected have much higher  $T_g$  than UP. The  $T_g$  of FB is very similar to UP. All bended resins except UP/Res-D have a single  $T_g$ , indicating their combatibility. The UP/Res-D displays two  $T_g$  values, indicating poor compatibility between two resins. The  $T_g$  values of blends are in between the values of individual resins. For UP/FB, the value however is lower than of each resin type.

# Thermogravimetric analysis (TGA)

TGA can be used to examine the thermal stability and decomposition behaviours of the resins. Mass loss curves as a function of temperature for all samples are shown in Fig. 3 and the analysed results are given in Table 2.

The onset of decomposition temperature, represented by the temperature where 10% mass loss occurs ( $T_{10\%}$ ) for UP in Table 2 is 310 °C, 50% mass loss occurs ( $T_{50\%}$ ) at 371 °C and complete decomposition occurs at 545 °C. This resin undergoes complete decomposition through chain scission reactions, releasing mostly styrene and other volatiles [16], leaving no char residue at the end of reaction (Table 2). All phenolic resins are more thermally stable than UP, as can be seen from Fig. 3 (a-c) and Table 2, i.e., onset of decomposition is higher, the highest being for Res-M (422 °C), and  $T_{100\%}$  for Res-M, Res-D and Nov being 700, 602 and 580 °C, respectively. Phenolic resins on heating, after initial chain scission reactions cross-link and result in carbonaceous char residues [16]. As can be seen from Fig. 3(a), the Res-D has much higher residual mass at each temperature compared to UP. Res-M's thermal stability in terms of residual mass at each temperature is lower than Res-D, whereas that of Nov is the least. This indicates that their thermal stability should follow the order:

$$\text{Res-D} > \text{Res-M} > \text{Nov}$$

MF on the other hand is less thermally stable than UP at temperatures < 400 °C, the T<sub>10%</sub> being 130 °C and T<sub>50%</sub> being 334 °C. However, above 400 °C, this resin is more thermally stable due to its cross-linking tendency. T<sub>100%</sub> is at 633 °C, compared to 545 °C in UP.

The furan FB resin is more thermally stable than UP at all temperatures,  $T_{10\%}$ ,  $T_{50\%}$  and  $T_{100\%}$  for this resin are 332, 676 and 802 °C, respectively. Furan resins, similar to phenolic resins on heating undergo cross-linking reactions leading to char formation. The char residues of all samples at 650 oC are reported in Table 2. On comparing TGA curves of all resins in Fig. 3(f), the char formation tendency of the resins can be ranked as:

$$FB > Res-D > Res-M > Nov > MF > UP$$

In principle, the flammability should follow the reverse order. The furan resin however, shows less thermal stability than UP at temperatures less than 400oC and my show lower time-to-ignition in cone experiments.

Thermal degradation behaviour of all blends is in between those of the UP and the respective blended resin.



Fig.3 TGA curves of cured UP, phenolic (Res-D, Res-M, Nov), MF, furan (FB) resins and their 50:50 (wt-%) blend with UP

Resin	T <sub>10%</sub> (°C)	T <sub>50%</sub> (°C)	T <sub>100%</sub> (°C)	Char residue at 650 °C (%)	LOI (%)
UP	310	371	545	0.5	17.9
Res-D	336	599	700	27.1	23.0
UP/Res-D	296	544	685	11.2	19.8
Res-M	422	508	602	0.5	22.4
UP/Res-M	338	439	580	0.2	19.7
Nov	391	451	576	0.5	21.3
UP/Nov	327	394	560	0.2	19.7
MF	130	334	633	1.7	22.1
UP/MF	201	369	630	0.2	19.2
FB	332	676	802	58.3	23.1
UP/FB	346	451	735	21.5	18.9

Table 2.TGA analysis and LOI of cured UP, phenolic (Res-D, Res-M, Nov), MF, furan (FB) resins and their 50:50 (wt-%) blend with UP

## Limiting Oxygen Index

The limiting oxygen index (LOI) is the minimum concentration of oxygen, expressed as a percentage that will support combustion of a polymer. Resistance to flaming increases as value of LOI increases. The LOI values of all samples are given in Table 2. The pure UP resin is combustible and has a LOI value of 17.9 %. All phenolic resins have higher LOI values than UP, and as expected from TGA results, the Res-D has highest value (23.0%), followed by Res-M (22.4%) and Nov (21.3%). MF has a value 22.1%, whereas FB has 23.1%.

From LOI results, the flammability of the resins can be ranked as:

$$FB \approx Res-D < Res-M \approx MF < Nov$$

The LOI value for blends is in between those of the respective resins.

#### **Cone Calorimetry**

The heat release rate (HRR), rate of smoke release (RSR) and % mass versus time curves for all resins are plotted in Figures 4 (a), (b) and (c), while all derived parameters i.e. time-to-ignition (TTI), flame out time (FO), peak heat release rate (PHRR), total heat release (THR), effective heat of combustion (EHC), average specific extinction area (ASEA) a measure of the amount of smoke produced and % residual weight (CY) for resins and UP/resin blends are given in Table 3.

As can be seen from Fig. 4 and Table 3, UP resin ignited at 37s and burnt until 180s, producing 83.7 MJ/m<sup>2</sup> total heat (THR) with a peak value at 1131 kW/m<sup>2</sup>. Except for Res-M (TTI = 49s), all phenolic resins had similar TTI to that of the UP. TTI values of phenolic resins are very low, indicating that despite phenolics' expected inherent flame retardant properties, the resins ignite within a short period of time. However, once ignited, they burn slowly with lower peak (PHRR) and total heat release (THR) as compared to UP (Fig. 4(a)). Among the resoles, the Res-D has lower PHRR (522 kW/m<sup>2</sup>) and THR (38.4 MJ/m<sup>2</sup>) compared to the Res-M (720 kW/m<sup>2</sup> and 52.3 MJ/m<sup>2</sup>, respectively). The lower flammability of phenolics is due to greater number of stable aromatic benzene rings in their chemical structures [5,10] which on heating cross-link and form stable char, whereas the UP resin decomposes into combustible volatiles, which burn. This is also evident from mass loss vs time curves in Fig. 4(c), where resole resins show lower mass loss and produce more char yield at the end of the experiment (Res-D = 42.8%, Res-M=22.4%) compared to UP (1.7%). Methacrylated novolac (Nov) on the other hand, though less flammable than UP, is more

flammable than the resoles, showing PHRR of 801 kW/m<sup>2</sup> and THR of 62.1 MJ/m<sup>2</sup> (Fig. 4(a), Table 3). The cross-linking tendency of this resin is slightly less than those of the resoles as seen from lower char yield value (19.3%) at the end of the experiment.

Sample	Mass (g)	TTI (s)	PHRR (kW/m <sup>2</sup> )	THR (MJ/m <sup>2</sup> )	EHC (MJ/kg)	ASEA (m <sup>2</sup> /kg)	CY (%)	FPI ((s)/(kW/m <sup>2</sup> ))	FIGRA (kW/m <sup>2</sup> )/(s))
UP	10.4	37	1131	83.7	20.3	1137	1.7	0.033	10.1
Res-D	7.9	35	522	38.4	22.5	454	42.8	0.057	5.5
UP/ Res-D	8.6	36	583	54.9	18.9	867	23.3	0.062	5.7
Res-M	7.2	49	720	52.3	19.8	984	22.4	0.068	7.4
UP/Res-M	9.0	35	809	66.7	20.9	1070	17.1	0.043	7.9
Nov	9.1	35	801	62.1	20.9	1226	19.3	0.044	8.1
UP/Nov	8.8	31	840	62	20.3	1196	8.7	0.037	8.7
MF	6.4	16	531	53.8	18.2	0	17.6	0.030	5.5
UP/MF	6.1	16	674	71	19.5	498	1.3	0.024	6.6
FB	9.3	25	981	38.6	17.3	709	44.2	0.025	18.9
UP/FB	9.0	18	993	57.2	18.1	709	20.2	0.018	15.5

Table 3.Derived cone results of cast resin samples of UP, phenolic (Res-D, Res-M, Nov), MF, furan (FB) resins and their 50:50 (wt-%) blends with UP at 50 kW/m<sup>2</sup>

Note: The variation in values for different parameters are as:  $TTI = \pm 2$ ;  $PHRR = \pm 33$ ;  $THR = \pm 6.1$ ;  $EHC = \pm 0.6\%$ ; ASEA =  $\pm 39$ ;  $CY = \pm 1.9$ . FPI = TTI/PHRR; FIGRA=PHRR/tPHRR

MF ignited earlier (TTI = 16s) than UP, burnt for a longer time (FO = 200s), but produced lower peak (531 kW/m<sup>2</sup>) and THR (53.8 MJ/m<sup>2</sup>) as seen from Fig.4(b) and Table 3. FB on the other hand ignited early (TTI = 25s) but burnt for a shorter time (flameout at 118s), producing large peak (981 kW/m<sup>2</sup>), but lower total heat release rate (38.6 MJ/m<sup>2</sup>). The better charring tendency of FB is evident from lower mass loss in Fig. 4(d) and higher char yield value (44.2%) in Table 3.

Mass loss vs time curves in Fig. 4(c) show that Res-D has lower mass loss at any time than Res-M and Nov, leaving 42.8% char at the end of experiment compared to 22.4 and 19.3% in Res-M and Nov, respectively. In all phenolic resins the mass loss starts at similar time as of UP. FB and MF resins on the other hand ignited earlier and started losing mass earlier than UP, however their charring tendency is evident by high residual chars (FB=44.2%, MF=17.6%, Table 3) obtained at the end of the test. The charring tendency of different resins from this experiment can be ranked as:

$$FB > Res-D > Res-M > Nov > MF > UP$$

This trend is similar to that observed by TGA experiment. The fire ranking however, depends upon many factors, such as TTI, heat release rate etc, hence may not follow the same trend. The detailed analysis of these results leading to possible mechanisms of their degradation are given in our forthcoming publications [17].



Fig.4. a, b) HRR; c,d) mass loss and e,f) rate of smoke release versus time curves for UP, phenolic (Res-D, Res-M, Nov), MF and furan (FB) resins at 50 kW/m<sup>2</sup> external heat flux

An important aspect of fire safety of materials is low smoke production. UP is well known to be burning with heavy smoke and soot [4,5]. As can be seen from Fig. 4 (e and f), the smoke production is maximum in UP, total being 1137 m<sup>2</sup>/kg (Table 3). Amongst phenolics, Res-D produced minimum smoke (454 m<sup>2</sup>/kg), followed by Res-M (984 m<sup>2</sup>/kg) and Nov (1226 m<sup>2</sup>/kg). MF produced minimal smoke. FB also had a very low value (709 m<sup>2</sup>/kg).

The flammability and smoke production in all blends is in between those of the UP and blended resin as can be seen from Table 3.

# **Fire Safety Rating**

Two other fire parameters that can be used to rank the fire safety of materials are the fire performance index (FPI) and the fire growth rate (FIGRA). The fire performance index is defined as the ratio of the

time-to-ignition to the peak heat release rate (TTI/PHRR). There is a correlation between FPI and the time to flashover; i.e., a lower FPI value suggests an accelerated flashover event [18]. Therefore materials with low FPI values generally pose elevated fire risks. Based on FPI results in Table 3, the fire safety of different resins can be ranked as:

$$\text{Res-M} < \text{Res-D} < \text{Nov} < \text{UP} < \text{MF} < \text{FB}$$

The FIGRA (Fire Growth Rate Index) indicates the burning propensity of a material, calculated from the ratio of PHRR and time to PHRR for all samples in Table 3. Lower the FIGRA value, lower the fire growth in a material. Based on FIGRA values, the fire safety of resins can be ranked as:

$$\text{Res-D} \approx \text{MF} < \text{Res-M} < \text{Nov} < \text{UP} < \text{FB}$$

The relative overall fire performance of different resins can be evaluated by plotting the total heat release against the fire growth rate values calculated by dividing PHRR by TTI [19], as shown here in Fig. 5. Fire safe materials should have low THR and PHRR/TTI values; i.e. these samples should fall close to the coordinates (0;0) on a 2-D plot. While none of the resins falls within this region, all phenolic resins and their blends with UP fall within the region considered as having higher fire safety than UP. MF, FB and their blends have lower fire safety than UP.



Fig.5 A 2-D fire safety assessment grid for UP, phenolic (Res-D, Res-M, Nov), MF, furan (FB) resins and their 50:50 (wt-%) blends with UP, exposed to a 50kW/m<sup>2</sup> heat flux.

#### CONCLUSIONS

This work has demonstrated that it is feasible to co-cure unsaturated polyester (and probably vinyl ester) with an appropriate char forming resin such as phenolic, melamine-formaldehyde or furan. Thermal stability of all char forming resins, evaluated by thermogravimetric analysis, was seen to be higher than that of the UP. For fire performance evaluation, the order of ranking differed based on the test used, i.e., LOI or cone aclorimetry; or the parameter chosen from one test, i.e., cone calorimetry in this case. For overall fire performance evaluation, the total heat release was plotted against the fire growth rate values calculated by

dividing PHRR by TTI, and the results indicated that resole phenolic resins and their blends with UP have highest fire safety rating. The future work involves evaluation of fire performance of composite laminates prepared from these resins according to IMO/SOLAS requirements.

### Acknowledgements

The authors thank the Engineering and Physical Sciences Research Council (EPSRC Grant EP/H020675/1), UK for financial support of this work, 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.

## REFERENCES

- [1] Egglestone, G.T. and Turley, D.M., *Fire Mater.* 1994, **18**, 255.
- [2] SOLAS, Consolidated Edition, 2004, consolidated text of the International Convention for the Safety of Life at Sea, 1974, and its Protocol of 1978: articles, annexes and certificates.
- [3] Fire Test Procedure (FTP) Code, International Code for Application of Fire Test Procedures, Resolution MSC.61 (67), International Maritime Organization, London, 1998.
- [4] Kandola, B. K. and Horrocks, A. R., "Composites" in *Fire Retardant Materials*, Horrocks, A.R. and Price D, Eds, Woodhead Publishing Ltd, Cambridge, 2001, Chapter 6, p 182.
- [5] Kandola, B.K. and Kandare, E., "Composites having improved fire resistance" *in "Advances in Fire Retardant Materials"*, Horrocks, A.R. and Price, D., Eds, Woodhead Publishing Ltd, Cambridge, 2008, Chapter 15.
- [6] Kovlar, P.F. and Bullock, D.E., in *"Recent Advances in Flame Retardancy of Polymeric Materials"*, ed. Lewin M. ; Proc. of the 1993 Conf, BCC, Stamford, Conn., 1993, p 87.
- [7] Hanafi, W.Z.A.W. and Hornsby, P.R., "*Plastic and Rubber Processing and Applications*", 1993, **19**, p 175.
- [8] Hörold, S. Polym. Degdn. Stab., 1999, 64, p 427.
- [9] Kandola, B.K., Deli, D. and Ebdon, J.R., "Compatibilised Polymer Blends", UK Patent Application No. 1121498.8
- [10] Deli, D., Kandola, B.K., Ebdon, J.R. and Krishnan, L., *J Material Science*, 2013, 48, p6929.
- [11] Munoz, J.C., Ku, H., Cardona, F. and Rogers, D., J Mater Process Techn, 2008, 202 (1-3), p486.
- [12] Kay, R. and Westwood, A.R., European Polymer Journal, 1975, 11 (1), p25.
- [13] Cherian, A.B. and Thachil, E.T., J Appl Polym Sci, 2006, 100, p457.
- [14] Merline, D.J., Vukusic, S. and Abdala, A.A., *Polymer Journal*, 2012, p1.
- [15] Mohanty, A. K., Misra, M. and Hinrichsen, G., Macromol. Mater. Eng., 2000, 276/277, p1.
- [16] Kandola, B.K., Horrocks, A.R., Myler, P., Blair, D. K. In *Fire and Polymers*, Nelson, GL., Wilkie, C.A., Eds. *ACS Symp. Ser.*,2011, **797**, p344.
- [17] Kandola, B.K., Deli, D., Krishnan, L. and Ebdon, J.R., *J Material Science*, under review.
- [18] Katsoulis, C., Kandare, E, and Kandola, B.K., *J Fire Sci.*, 2011, **29**(4), p361.
- [19] Petrella RV., J. Fire Sci., 1994, **12**, p14.