THERMO-MECHANICAL RESPONSES OF FLAME-RETARDED FIBRE REINFORCED COMPOSITES AFTER EXPOSURE TO CONVECTIVE AND RADIATIVE HEAT

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SUMMARY

This paper reports the thermal stability, fire resistance and effect of convective and radiative heat on residual mechanical performance of flame retardant fibre-reinforced epoxy composites. Kinetic and heat transfer models are used to predict mass loss during cone experiments. Mass loss due to thermal decomposition of the resin has been seen to be related to loss of mechanical properties after heat exposure.

Keywords: Epoxy; Flame retardants; Cone Calorimetry; Thermal stability; Flexural modulus.

INTRODUCTION

A crucial feature of any fibre-reinforced polymeric structural composite is the thermal and burning behaviour of its matrix resin [1,2], which affects the mechanical performance of the composite at elevated temperatures and may ultimately lead to complete loss of structural integrity. Hence, it is important to understand and predict the thermal, combustion and mechanical behaviour of composite materials at elevated temperatures. In order to assess the ignition and other fire related properties, it is necessary to know the thermal properties, such as thermal conductivity, density and specific heat of materials [3]. These thermal properties vary with temperature, govern the rate of rise of surface temperature and ultimately the time-to-ignition. Materials properties of a composite remain stable below the glass transition temperature, T_g, of the resin, which for thermosetting resins is in the range 80 – 150°C. At and above the T_g temperature, the resin softens, the resin-fibre interface weakens and the composites loses much of their stiffness and strength [4]. When the decomposition temperature of the resin is reached (>300°C), the resin undergoes a series of reactions, namely depolymerisation, decomposition, char oxidation, etc, producing both volatile combustible and incombustible products as well as char [5]. At this stage the mass loss of the resin has a relationship with the mechanical properties of the composite [6]. Mass loss, however, is also related to the temperature. Hence, by predicting the temperature of the material at any given time, the mass loss and mechanical performance of a composite can be predicted.

In this paper the thermal stability, fire resistance and effect of convective and radiative heat on residual mechanical performance of flame retardant fibre-reinforced epoxy composites have been discussed. The flame retardants comprise two components: an intumescent chemical (melamine phosphate) and a char former (cellulosic fibre, Visil Sateri), which have been added at different concentrations and relative ratios in the epoxy resin before laminate fabrication [7,8]. Thermal stability and flammability behaviour have been studied by thermogravimetric analysis and cone calorimetry. The effect of heat on mechanical property retention after exposure to convective (fan assisted furnace), and radiative (cone calorimeter) heat has also been investigated. Kinetic and thermal models have been used to predict the mass loss during cone experiments.

EXPERIMENTAL

Composite Materials

The composite laminates were fabricated using a wet lay-up method using an epoxy resin containing 1,4-butanediol diglycidylether, (Araldite LY5052) and a hardener based on modified cycloaliphatic amines (HY5052, Huntsman, Inc.); woven roving E glass (300 g/m^2, Glasplies, UK); Visil, a cellulosic fibre containing polysilicic acid, in pulverised form (from initial length 40 mm, 3.5 dtex and diameter 17 μm; Sateri Fibres, Finland) and an intumescent containing melamine phosphate (Antiblaze NH, Rhodia Specialities Ltd., now Albemarle). Eight ply control (Ep) and flame-retarded composite laminates (Ep-10, Ep-15 and Ep-20) were fabricated containing different amounts of intumescent and Visil by weight with respect to the resin content. Woven roving E-glass fabrics were impregnated with resin, stacked, vacuum bagged and cured at 80 ºC for 8 h under a pressure of 10^5 Pa. The mass fraction of the resin in the composites was approximately 50% (w/w). The details are given in Table 1.

Table 1: Mass percent composition and material properties of composite laminates

Sample	Mass (%)				Fibre Vol. Fraction (%)	Thick-ness (mm)	Glass Transition Temp.(ºC)	Heat of Decomp. (kJ/kg)
	Fibre (%)	Epoxy (%)	Visil (%)	Int. (%)				
Ep	50.0	50.0	0.0	0.0	32	2.73	130	198
Ep-10	50.0	45.0	2.5	2.5	32	3.06	130	395
Ep-15	50.0	42.5	3.75	3.75	32	3.28	130	331
Ep-20	50.0	40.0	2.5	7.5	28	2.84	130	254

Thermal Analysis

The thermal decomposition of fibre-reinforced composites was measured by means of thermogravimetric analysis (TGA) using an SDT 2960 simultaneous DTA–TGA instrument from room temperature to 800 ºC at heating rates of 10 and 200 ºC/min in air flowing at 100 cm^3/min. The heat of decomposition of the composites and specific heat capacity of both the composites and residual char were measured using differential scanning calorimetry (DSC) at 10 ºC/min in flowing N_2 (100 cm^3/min). These values are given in Table 1. The glass transition temperatures (T_g) of the composites were determined using a dynamic mechanical thermal analyzer (DMTA, Polymer Laboratories Ltd) by heating specimens (nominally 48 mm × 12 mm × 3 mm) from room temperature to 250 ºC at a heating rate of 10 °C/min under a fixed frequency load level of 10 Hz in air.

Flammability and Temperature Measurement Tests

The fire performance of fibre-reinforced epoxy composite panels measuring nominally 75 mm × 75 mm × 3 mm without and with flame retardant additives was evaluated using an FTT cone calorimeter at an applied heat flux of 50 kW/m^2. In order to evaluate the thermal barrier, *K*-type thermocouples were placed on the exposed and rear surfaces, and embedded in three positions through the thickness of the panels and connected to a Recorder® data logger. The temperature profiles were recorded as a function of exposure time.

In order to validate the heat transfer model discussed in a later section and the thermo-mechanical model developed by our collaborating research group [9], test specimens of control sample Ep and flame-retarded Ep-20 containing embedded thermocouples were partially heat damaged by exposing a circular area (1960 mm^2) to incident radiant heat fluxes of 13 and 34 kW/m^2 over varying time periods (up to 540 s) in the absence of a pilot flame. The experimental details are given elsewhere [6], but the temperature results are used here for validation of the model. It must be emphasised that these two samples due to embedded thermocouples had different thicknesses (Ep = 3.0 mm, Ep-20 = 3.5 mm) than the samples discussed above.

Mechanical Testing

The flexural modulus of glass fibre-reinforced specimens (120 mm × 15 mm × 3 mm) used to validate the theoretical models were measured in a three-point bending mode using a 100 N load cell in an Instron® 3369 tensometer with a load and displacement control, at a cross-head speed of 1 mm/min. The flexural modulus, E_f, was calculated using the Engineers' bending theory [10].

Convective heat damage: The effect of convective heat on the mechanical properties of fibre-reinforced composites was determined by heating the specimens from ambient temperature to desired temperatures (50, 75, 100, 125, 150, 200, 250 and 300 ºC) at a heating rate of 10 ºC/min inside a resistance-controlled and fan-assisted furnace. Upon reaching a desired temperature and allowing for equilibration (120 s), the flexural modulus of the specimen was determined at that elevated temperature. In another set of experiments, upon reaching a desired temperature and letting the specimens equilibrate for 120 s, the specimens were quenched by quickly removing them from the furnace and rapidly cooling them to ambient temperature before their residual flexural modulus was determined. The calculated modulii after thermal exposure were compared to the room temperature values of the same specimens in order to evaluate strength retention.

Radiative heat damage: In another set of experiments the effect of one-sided radiant heat on the mechanical properties of fibre-reinforced composites was determined by exposing samples to an incident heat flux of 50 kW/m^2 in the cone calorimeter. Test coupons of geometric dimensions 120 mm × 15 mm × 3 mm were partially heat damaged by exposing them to the radiant source (two replicates per sample) over different time periods (10, 20, 30 and 40 s) after which they were cooled to ambient temperatures before their flexural modulii were determined. The flexural load was applied on the heat damaged surface so that the damaged portion would bear the compressive strain. The obtained flexural modulus was then compared to the room temperature value of the same specimen.

RESULTS AND DISCUSSION

Thermal Analysis and Determination of Kinetic Parameters, Specific Heat Capacity and Other Physical Parameters

Fig. 1 shows TGA curves of fibre-reinforced composites at heating rates of 10 and 200 °C/min in an air atmosphere. The presence of glass fibre reinforcement does not significantly alter the thermal degradation profiles of epoxy resin formulations as shown elsewhere [8]. Cured epoxy resin in air undergoes three stages of mass loss in the temperature region of 100 to 680 °C. The first is a dehydration stage (100 - 250 °C) in which up to 2% mass loss is observed, the second stage, (300 - 500 °C), showing 70% mass loss, is attributed to the depolymerisation of polymeric chains to form a primary carbonaceous char and finally there is a char oxidation stage (500 - 680 °C) contributing 28% mass loss leaving no residual char at 800 °C [5,7,8]. The addition of flame retardant additives causes a considerable reduction in the onset degradation temperature and a compromised thermal stability at temperatures below 450 °C. However, at temperature above 450 °C, a noticeable enhancement in thermal stability of the epoxy resin is observed with higher residual char yields recorded at temperatures above 550 °C. TGA curves of composites shown here in Fig.1 represent all these steps, but the mass loss is proportional to resin content in the composites. TGA curves at 10°C/min show two-stage mass loss profiles (decomposition and char oxidation stages discussed above), while at 200°C/min heating rate these two steps are replaced by a one step process. The onset of decomposition has also shifted to higher temperatures at 200°C/min heating rate. This will change the kinetic parameters as well. Atmospheric and heating conditions are therefore crucial parameters for the development of a thermo-mechanical model that can be used to investigate the suitability of flame-retarded fibre-reinforced composites for high temperature service environments. Using established methods [11], the kinetic parameters (activation energy and Arrhenius frequency) were extracted from the 200 °C/min heating rate TGA curves and used for the heat transfer model discussed later.

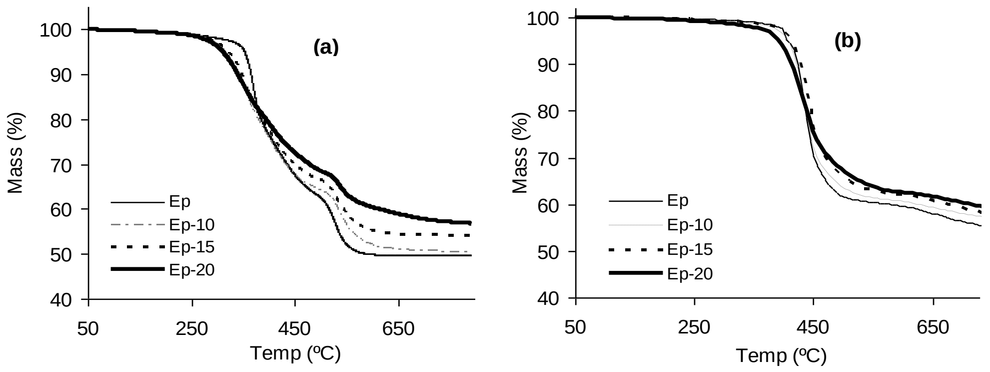

Figure 1. TGA curves of composites at 10 and 200 °C/min in flowing air

The temperature - dependent specific heat capacity of the virgin materials and the completely charred residual materials, shown in Fig. 2(a) were determined from dynamic scanning calorimetric (DSC) data using methods originally developed by Henderson et al [12]. The heat of decomposition was calculated by integrating the area between the apparent specific heat of virgin material and the actual specific heat of the decomposing material. These values are given in Table 1. It can be seen that the values are higher for flame retarded samples than the control sample, indicating their higher thermal stability.

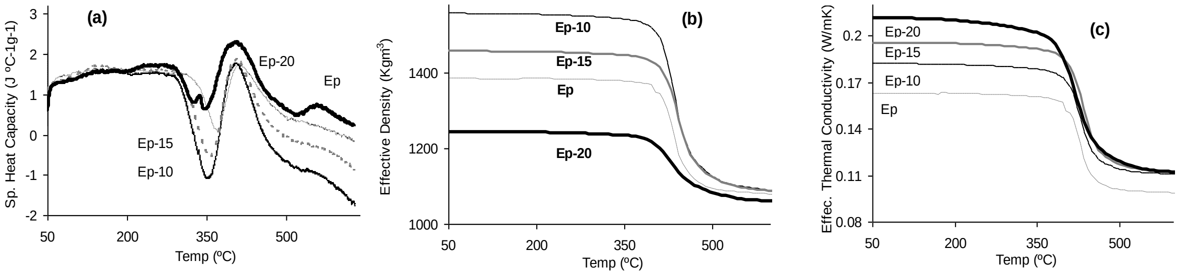

Figure 2. a) Specific heat capacity, b) effective density and c) effective thermal conductivity of different composites as a function of temperature.

By calculating the densities of the composites and their residual chars, the effective density as function of temperature could be plotted as shown in Fig. 2(b).

The glass transition temperatures (T_g) of the laminates were determined by dynamic mechanical thermal analysis (DMTA) and are given in Table 1. The T_g is an important material property with which the extent of cross-linking in polymeric matrices can be assessed. As the T_g values of the flame-retarded laminates are the same as that of the control sample, this shows that the presence of flame retardants even at concentration as high as 20% does not affect the curing behaviour of the epoxy resin.

Thermal conductivities of composites were determined using Lee's disc method. The overall mass conversion fractions as functions of temperature are used to estimate the effective thermal conductivity of composites at various stages of decomposition (see Fig.2 (c)).

Cone Calorimetry and Temperature Measurements

The fire performance of the composites was determined using cone calorimetry at an incident heat flux of 50 kW/m^2. Heat release rates and mass loss curves as functions of time are shown in Figs. 3(a) and (b) respectively. The time-to-ignition value for the flame-retarded composites was measured to be 24 – 31 s, a substantial reduction when compared to the control specimen, which ignited after 40 s. However, from the variation of HRR as function of time, Fig. 3(a), the flame-retarded composites exhibit a significantly lower heat release rate profile with up to 54% reduction in the peak value. However, the combustion period is somewhat prolonged relative to that of the control specimen. The overall reduction in the integrated area under the HRR versus time curves for EP-20 leads to a noticeable reduction (42 %) in the total heat release.

The superior fire performance properties of the flame-retarded composite are due to its resin matrix composition which yields lower mass fractions of combustible volatiles during decomposition as clearly observed in Fig. 3(b). The residual char yields for the flame-retarded composite is higher than that for the control, Ep, as expected from the proposed flame retardancy mechanism [5,7,8]. During thermal decomposition, intumescent and Visil chemically react with the epoxy resin to form a continuous char network above the pyrolysis zone. The presence of a physical and thermal barrier retards diffusion of combustible products and oxygen to the pyrolysis zone, ultimately causing a reduction in heat release rates. Material property-temperature dependencies of the fibre-reinforced composites are inevitably dependent on the residual mass after heat exposure, hence the flame-retarded specimens are expected to show improved mechanical stiffness (or modulus) retention.

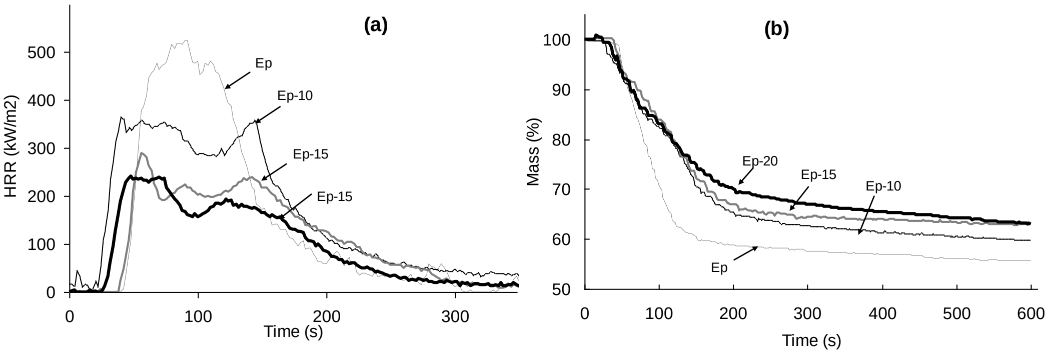

Figure 3: (a) Heat release rate and (b) mass loss curves as a function of time for composites from cone calorimetry measurements at 50 kW/m^2.

Temperature measurements recorded during heat exposure at the exposed surface show that once ignited, there is no difference in the surface temperature of the control and flame retarded samples (Fig.4(a)). However, there is a difference in rise of temperature through the thickness of the sample, in particular for the unexposed surface, where the flame-retarded samples exhibit a much lower temperature than the control sample. These data suggest that heat transfer through the thickness of the composites is slower for fire-retarded composites when compared to the control specimen. The retarded heat transfer through the fibre-reinforced structure for fire-retarded composites would mean prolonged structural integrity retention in case of a fire.

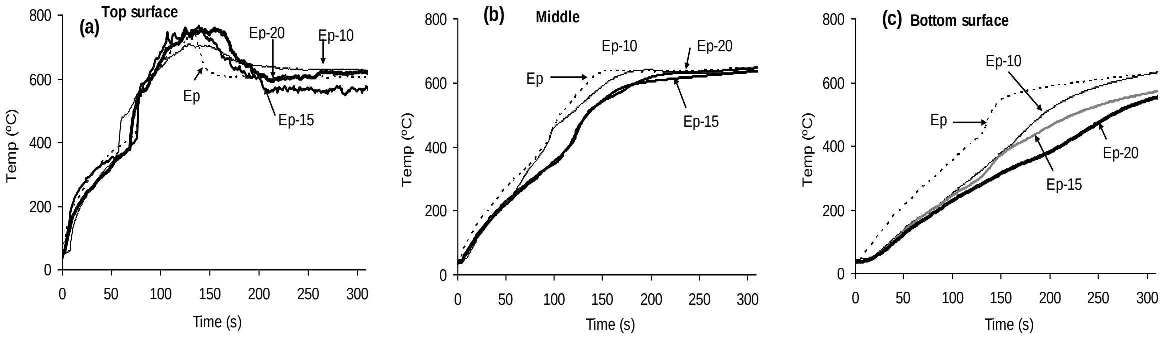

Figure 4. Temperature profiles in of composites at a) the exposed, b) middle and c) unheated surfaces of epoxy composites exposed to an incident heat flux of 50 kW/m^2.

Heat Transfer Model for Temperature Predictions

A one dimensional model for heat transfer into laminate type fibre-reinforced composites was originally developed by Henderson *et al* [12,13], and has since been modified and/or used by other researchers [14,15,16]. It is used here to calculate the temperature profile at any given time and through the laminate thickness. In the present work thermal decomposition of the resin matrix is assumed to follow a single stage Arrhenius rate dependency. The details of the model are given elsewhere [6].

The modeled temperature-time profiles for epoxy Ep and flame retarded Ep-20 samples are shown together with the experimentally measured data at 13 and 34 kW/m^2 in Figs. 5 and 6, respectively. While predicted temperature profiles are available for 100 points through the thickness, only the exposed and bottom surface profiles are shown to illustrate the overall predictive ability while maintaining the clarity of the graphs. At an incident heat flux of 13 kW/m^2 the temperatures at the exposed and the bottom surfaces are similar for the two specimens (see Fig. 5(a) and (b)), A low incident heat flux of 13 kW/m^2 is not enough to increase the laminate temperatures beyond 350 ºC, whereas the flame retardant additives are effective only above 450 ºC, as observed from TGA results for both laminates. Since the through-thickness temperatures of the laminates are below the decomposition temperatures, not much mass loss is observed hence the charring ability of the flame-retarded specimens is not realized. In general, there is a very good agreement between the experimental data and the predicted temperature profiles.

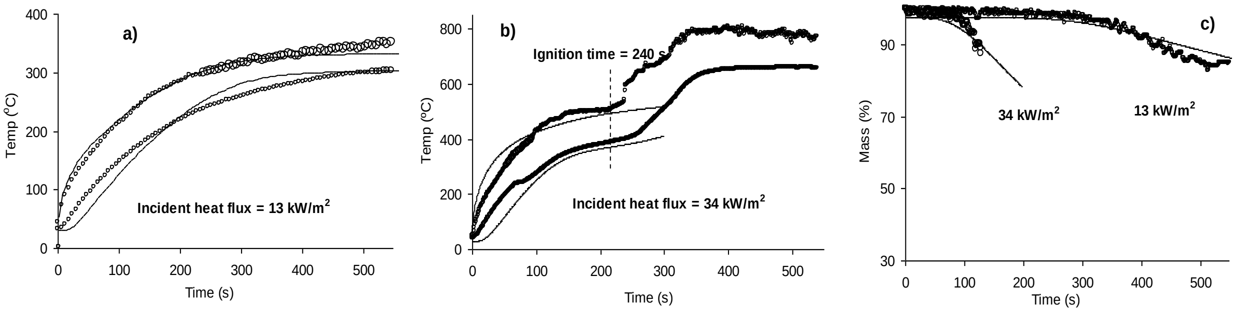

Figure 5. Experimental (data points) and predicted (solid lines) temperature profiles and mass loss data for control epoxy composite.

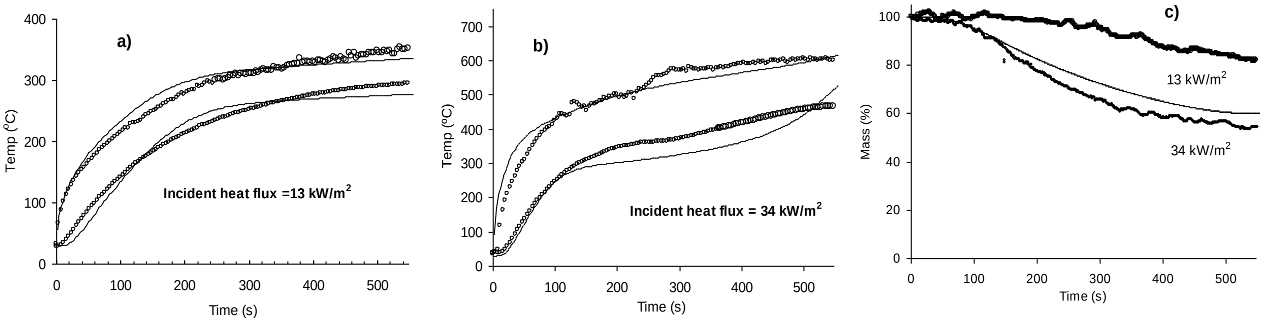

Figure 6. Experimental (data points) and predicted (solid lines) temperature profiles and mass loss data for Ep-20 composite.

When the specimens were exposed to a relatively higher incident heat flux of 34 kW/m^2, the exposed surface temperature of the control laminate reached 530 ºC after exposure for 240 s (Fig.5(b)), followed by auto-ignition. Once ignited, the overall through-thickness temperature of the specimen rapidly increased due to the heat feed from the flaming-combustion process with the exposed surface eventually reaching 770 ºC after 600 s exposure. The temperature profiles were predicted using our thermal model only until ignition since the current model does not have the flaming-combustion solving capabilities. The flame-retarded laminate, Ep-20 reached similar through thickness temperatures to those of the control sample during the initial 240 s, (i.e. the exposed surface reached 510 ºC), the rate at which the resin matrix decomposed was slower than that for the control as shown by TGA and cone calorimetric results. The temperature of the bottom surface reached 398 and 360 ºC after 240 s for Ep and Ep-20, respectively. These data suggest that heat transfer through the thickness of the composites is retarded for the flame-retarded composites relative to the control sample.

Figs.5 (c) and 6 (c) show experimentally obtained and theoretically predicted mass loss for Ep and Ep-20 after exposure to heat fluxes of 13 and 34 kW/m^2, respectively. The agreement between the experimental and predicted data is very good for both samples.

Mechanical Performance of Heat Damaged Composites

The effect of convective heat on the flexural modulus of composites was investigated by heating the samples in a fan-assisted furnace from ambient temperature to 300 ºC at a heating rate of 10 ºC/min. The elevated temperature flexural modulus of the composites were normalized with respective to corresponding room temperature values (13.8, 12.0, 13.1, and 11.7 GPa for Ep, EP-10, EP-15, and EP-20 respectively) to calculate flexural modulus retention. The results are shown in Fig. 7(a). The flexural modulus retention of the composites gradually decreases from temperatures as low as 50 ºC with a rapid acceleration due to the thermal softening of the resin occurring between 100 and 150 ºC. The flexural modulus retention of the composites was also determined after heating the coupons to a desired temperature followed by rapid cooling to ambient temperature. The specimens used were weighed before and after exposure to determine the extent of mass loss where it occurred. These values are important as they provide the high temperature residual material properties which are a required input into the thermal-mechanical model of composite structures.

There is a very good correlation between the flexural modulus retention and the fraction of combustible material remaining as seen from Fig 7(d). All the composites are thermally stable below 350 ºC. However, past the onset temperature of degradation there is a rapid loss of combustible material. The control composite (Ep) sharply loses mass at approximately 400 ºC and also its flexural modulus. At 425 ºC and beyond the mass fraction of Ep remaining is 50% of the initial mass which is attributed to the glass fibre mass fraction in the original composite. The flexural modulii of all samples exposed to temperatures beyond 425 ºC reduced to zero as result of the complete thermal degradation of the polymer matrix. Unlike the sudden mass loss observed for Ep at temperatures above 400 ºC, the flame-retardant composites show a gradual thermal degradation process, as also seen from thermogravimetric analysis and cone calorimetry experiments.

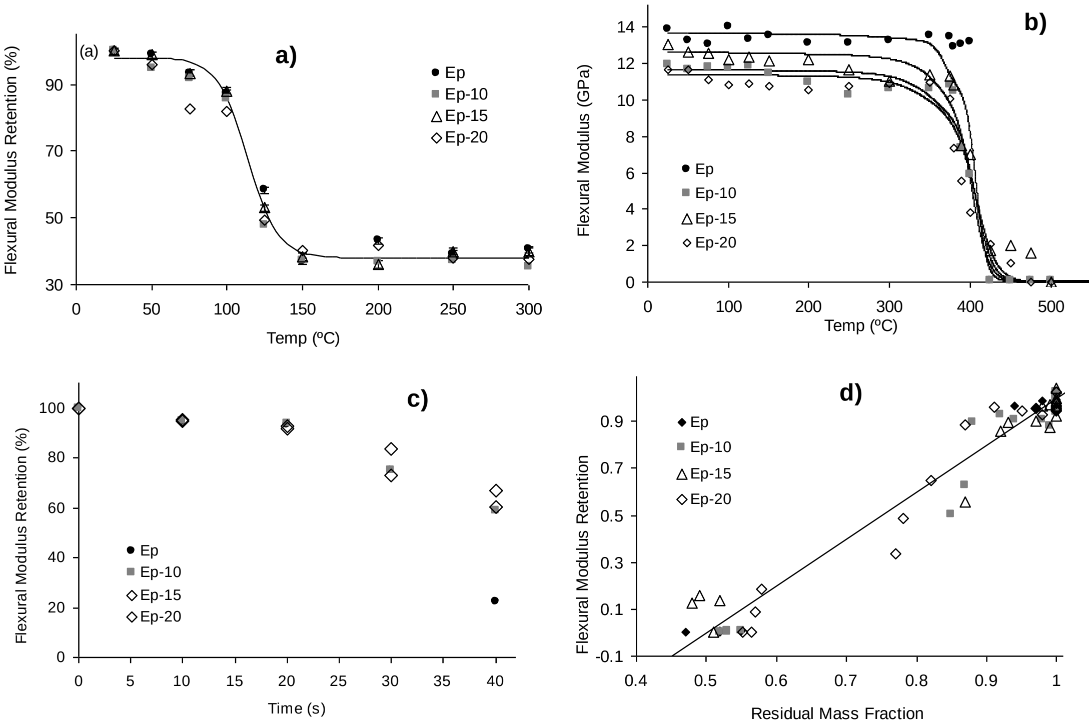

Figure 7: Residual flexural modulus retention of composites as measured a) at elevated temperatures, b) after exposure to elevated temperatures followed by rapid cooling to ambient temperature, c) after exposure to a 50 kW/m^2 heat flux, and d) flexural modulus retention after exposure to elevated temperatures followed by rapid cooling to ambient temperature versus the residual mass fraction.

The effect of radiative heat on the mechanical property retention of the composite laminates was investigated by exposing for a known period under a constant heat flux of 50 kW/m^2 in a cone calorimeter. For flexural tests of radiant heat damaged specimens, the compressive load was applied from the heat-exposed surface. Fig. 7(c) shows that the residual flexural modulus of all the composites is dependent on the heat-exposure period. A 5% loss in the original flexural modulus of all composite is observed after exposure periods of up to 20 s. After 30 s exposure, all samples lose approximately 25% of their original flexural modulus with the exception of Ep-20 which lost only 16%. When the samples are exposed for 40 s the control (Ep) retains only 22% of its original flexural modulus while Ep-10, Ep-15, and Ep-20 retain 59, 60, and 67% of their original flexural stiffness respectively. These results are promising in terms of the effect of flame retardants in improving the residual mass and thermo-mechanical properties. This relationship will be explored further in our future work.

CONCLUSIONS

Glass fibre-reinforced composites with flame retardant additives: charring agent and intumescent showed an improved thermal stability and fire performance compared to control sample from TGA and cone calorimetry results, respectively. The post-heat flexural modulus of the fibre-reinforced composites decreased after convective heat exposure but no significant differences were noted between flame-retarded composites and the control. The flame-retarded sample retained $\geq$ 60% of the original flexural stiffness when exposed to a 50 kW/m^2 radiative heat source for 40 s. The significantly improved fire performance of flame-retarded epoxy based composites emanates from the enhanced char formation due to the presence of a char promoter and intumescent additive. The resultant highly consolidated char networks that are observed for flame-retarded composites are responsible for holding together the fibre reinforcements thus significantly contributing to the residual mechanical properties of the fire or heat damaged composites. Using a heat transfer model, the through-thickness temperature profile of the laminates could be predicted. From these temperatures mass loss could also be predicted. The data acquired in this study will be used as input in our global quest to develop a predictive modelling tool that can be used to estimate the time-to-failure of loaded composite structures in fire.

ACKNOWLEDGEMENTS

The authors acknowledge the Engineering and Physical Sciences Research Council and DSTL-MoD (Ministry of Defence), UK for financial support.

References

1. Kandola B.K., Kandare E. *In* Eds, Horrocks AR, Price D. Advances in Fire Retardant Materials. Woodhead Publishers, UK, 2008, pp 398.
2. Mouritz A.P., Gibson A.G. Fire reaction of polymer matrix composites. Springer, 2006.
3. Drysdale D. An introduction to fire dynamics, 2nd ed. Wiley, Chichester, 1999.
4. Elmughrabi A.E., Robinson M., Gibson A.G. *Polym Degrad. Stab.*,**93,** 2008, 1877.
5. Kandola B.K., Horrocks A.R., Myler P., Blair D. In *Fire and Polymers*, ed. Nelson G.L., Wilkie C.A. ACS Symp. Ser. 2001, 344.
6. Kandare E., Kandola B.K., Myler P., McCarthy E., Edwards G., Jifeng Y., Wang Y.C. *J. Compos. Mater*. To be submitted, 2009.
7. Kandola B.K., Myler P., Horrocks A.R., El-Hadidi M., Blair D. *Fire Safety J.* **43**, 2008, 11.
8. Kandare E., Kandola B.K., Myler P., Gerard E. *J. Composite Materials*, submitted, 2009.
9. Li H., Li S., Wang Y.C., Kandare E., Kandola B.K., Myler P. To be pub'd, 2009.
10. Tsai S.W., Hahn H.T. Introduction to composite materials, Technomic Pub. Co. Inc. (1980) p. 167, Chapter 5.
11. Kandare E., Kandola B.K., Staggs J.E.J. *Polym. Degrad. Stab*. **92**, 2007, 1778.
12. Henderson J.B., Wiecek T.E. *J. Compos. Mater.* 21, 1987, 373.
13. Henderson J.B., Wiebelt J.A., Tant, M.R. *J. Compos. Mater.* 19, 1985, 579.
14. Feih S., Mathys Z., Gibson A.G., Mouritz A.P. *Composites. Part A.* 38, 2007, 354.
15. Lattimer B.Y., Quellette J., Trelles J. In: Couchman L. and Mouritz A.P. eds. Modelling of naval structures in fire, 2006.
16. Gibson A.G., Wu Y.S., Chandler H.W., Wilcox J.A.D., Bettess P. *Rev L'Inst Francais Petrole.* 50, 1995, 69.

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