Modelling residual mechanical properties of polymer composites after fire

A. G. Gibson, P. N. H. Wright, Y.-S. Wu, A. P. Mouritz, Z. Mathys and C. P. Gardiner

A thermomechanical modelling approach is proposed for estimating the residual properties of fibre reinforced polymer composites damaged by fire. The modelling was carried out in two parts: (i) prediction of the extent of thermal decomposition (or charring) using a thermal model; and (ii) prediction of the post-fire behaviour using a two layer model that combines the properties of the undamaged laminate and the residual char. Fire experiments were performed on glass–polyester, vinyl ester, and phenolic laminates using a cone calorimeter operated at heat fluxes in the range 25–100 kW m^{-2}, for times up to 30 min. After cooling to room temperature the thickness of the thermal damage layer was determined, along with values of the residual tensile, compressive and flexural properties. For the 'two layer' model it was found that the effective boundary between char material and undamaged laminate corresponded to the point where the residual resin content (RRC) of the laminate was 80%. Surprisingly, this value was found to hold for all three resin types tested. Using this RRC value, excellent agreement was found between the measured and predicted post-fire char thickness and the residual mechanical properties. The approach presented is the first reliable method for accurately predicting the residual properties of composites after fire.

PRC/1878

© 2003 IoM Communications Ltd. Published by Maney for the Institute of Materials, Minerals and Mining. A. G. Gibson (A.G.Gibson@ncl.ac.uk), P. N. H. Wright, and Y-S. Wu are in the Centre for Composite Materials Engineering, Stephenson Building, University of Newcastle upon Tyne, NE1 7RU, UK; A. P. Mouritz is in the The Sir Lawrence Wackett Centre for Aerospace Design Technology, Department of Aerospace Engineering, RMIT University, GPO Box 2476V, Melbourne, Victoria, Australia 3001; and Z. Mathys and C. P. Gardiner are at the DSTO, Aeronautical and Maritime Research Laboratory, PO Box 4331, Melbourne, Victoria, Australia 3001. This paper was presented at the 9th international conference on Fibre Reinforced Composites, FRC2002, held at the University of Newcastle upon Tyne on 26–28 March 2002. Manuscript accepted in final form 30 January 2003.

INTRODUCTION

A significant drawback in using organic matrix composites is their flammability and apparently poor fire resistance. Lack of predictive tools for their fire response is an important factor hindering these materials from entering many structural applications in land, marine and air transport, as well as civil engineering and infrastructure. The materials used in many transport applications must pass stringent safety regulations concerning fire performance.[1–6] Commonly used composites, particularly those with a styrene based resin matrix (e.g. polyester, vinyl ester), have difficultly passing the regulations because of their short ignition times, high heat release rates, and capacity to produce copious amounts of smoke and toxic products in a fire. Furthermore, the thermal softening, decomposition and cracking caused by fire can greatly reduce the mechanical properties of composites.

Various strategies have been adopted to mitigate some of the above problems, including the incorporation into the resin matrix of halogens to delay ignition, phosphorus additives to promote char formation, and antimony compounds to interfere with the combustion reaction. However, a limitation of these strategies is that an improvement to one fire property, such as ignitability, is usually accompanied by adverse effects to others, such as toxic product generation or mechanical properties. An alternative strategy has been to use phenolic resins, or other materials with a high main chain aromatic content. These generally have longer ignition times, lower heat release rates and lower toxic product generation than the styrene based resins, and a much higher proportion of the resin mass remains as carbonaceous char. Yet another strategy when low toxicity is required is to use resins such as modar and polyester in which the styrene solvent monomer has been replaced by methyl methacrylate. These resins, when combined with alumina trihydrate (ATH) filler, also show low heat release and low toxicity. There has been a lively debate recently concerning the relative merits of phenolics and the ATH filled resins in fire.[7] While various methods exist for improving the fire reaction properties of composites (ignitability, heat release etc.), the degradation of the mechanical properties, which is the prime concern of this paper, is less amenable to control by modification of the matrix.

Currently, despite the fact that the mechanical properties of unprotected composite structures are known to be severely degraded by fire,[8–12] there is

DOI 10.1179/146580103225009040

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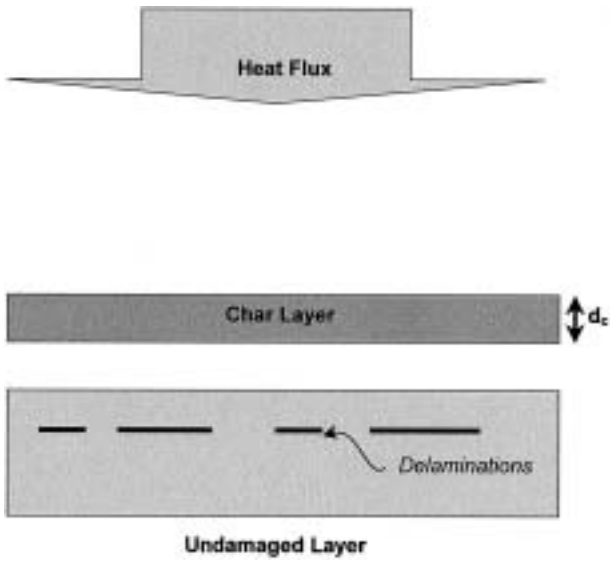
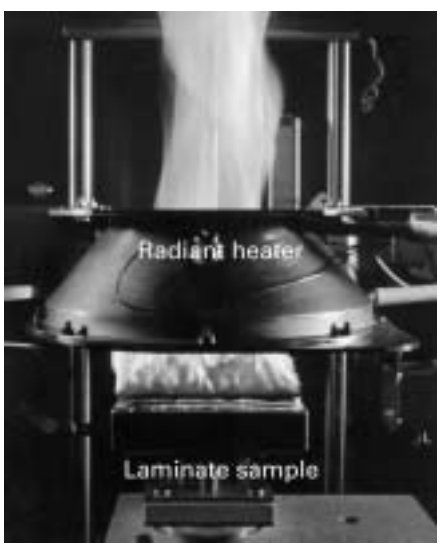


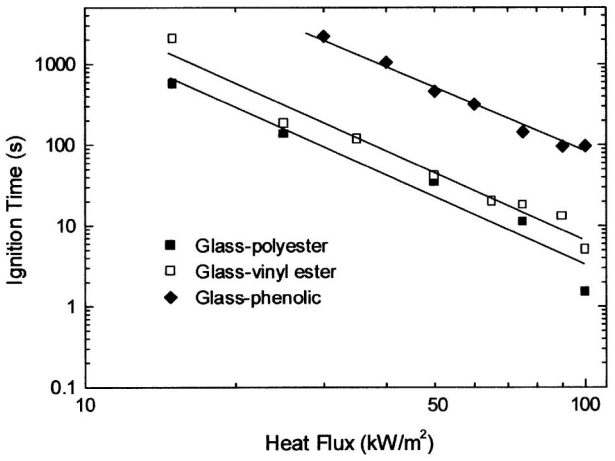
1 Schematic diagram of thermal damage profile through thickness of laminate

limited understanding of how this occurs and of the factors governing residual structural integrity. Figure 1 is a schematic diagram showing the principal features usually seen through the cross-section of a fire damaged laminate: residual char on the fire side, undamaged laminate on the cold side and, near to the boundary between the damaged and undamaged material, a region of delaminations.

Figure 2 shows a cone calorimeter, as employed in the present work to subject several types of glass fibre laminate to a known heat flux. On heating, the laminate surface temperature increases until resin decomposition begins to occur, and after a time, decomposition products are ignited. Figure 3 shows the relationship between the ignition time and the incident heat flux for the materials studied. After ignition, a front of decomposition advances into the bulk of the material. As shown schematically in Fig. 4, the residual resin content (RRC) declines over this region from 100% in the undamaged laminate to a



2 Exposure of composite laminate to reproducible heat flux using cone calorimeter



3 Log–log plot of ignition time against incident heat flux for cone calorimeter measurements on polyester, vinyl ester and phenolic laminates

lower value corresponding to the resin residue remaining in the char. As shown in Fig. 5, the structure of the char material differs substantially between 'styrenic' resins, which show little char residue, and phenolics.

The residual properties of the damaged laminates were measured at room temperature,[13–16] together with the char depth. It was found that the mechanical properties in tension and flexure could be simply related to the depth of char, as measured by microscopy of the cross-sections of damaged laminates. All the residual properties could be related to the char depth using a very straightforward 'two layer' mechanical model in which the components were assumed to be (i) undamaged laminate and (ii) residual char, each with characteristic values of Young's modulus and strength. Engineering expressions have been derived for all the key residual properties using this model.[13–16]

A group from the University of Newcastle developed a thermal model for the decomposition of composite laminates in fire.[17–19] This predicts the evolution of the temperature and resin content in the laminate with time for any surface boundary conditions. The model takes account of heat transport by conduction through the laminate, the effect of resin decomposition, which is an endothermic process, and the cooling effect of volatile resin decomposition products passing through the laminate. Application of the model requires knowledge of the decomposition process of the resin, which can generally be acquired through thermogravimetric analysis (TGA).

The purpose of the present collaboration, therefore, was to use the fire model to determine the char depth (i.e. the effective 'boundary' between damaged and undamaged laminate) in terms of residual resin content, for the samples studied by DSTO and RMIT. This enabled a quantitative model for residual properties to be developed.

THERMOMECHANICAL MODEL

Thermal model

The approach to modelling the residual mechanical properties of fire damaged laminates consists of two analysis steps using a thermal model followed by

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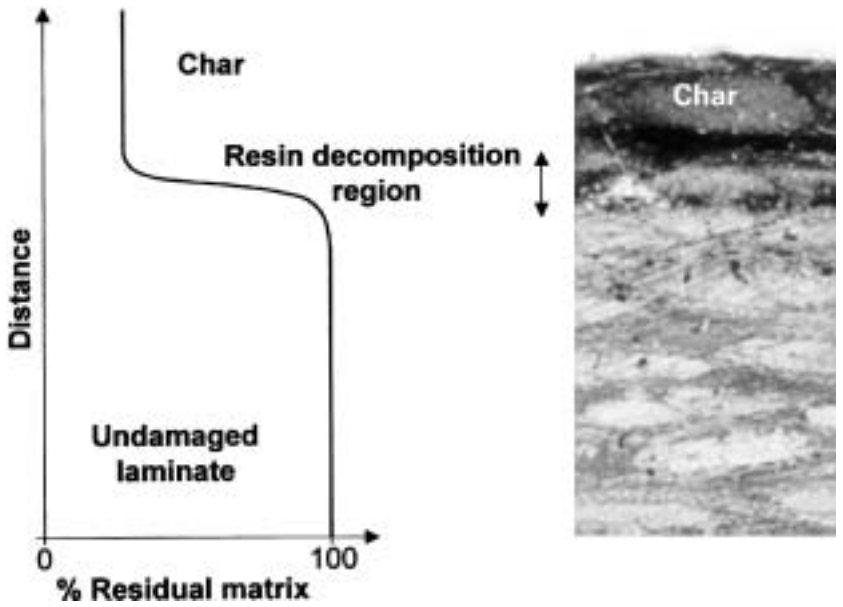
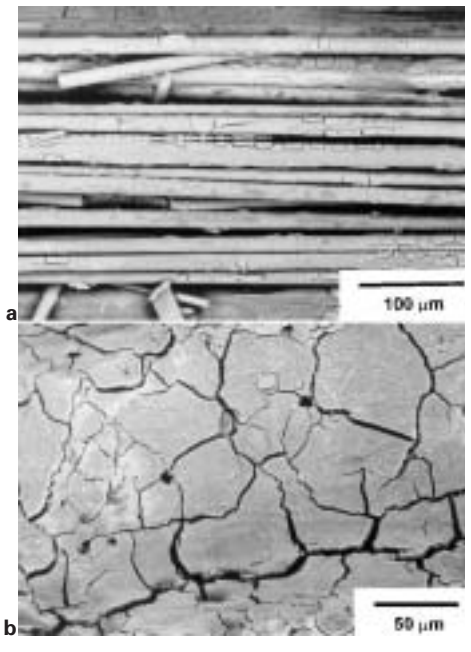


4 Three zone fire model comprising undamaged laminate, resin decomposition zone and residual char, together with cross-section through glass–polyester woven roving laminate exposed to heat flux of 50 kW m^{-2}

a two layer mechanical model. The thermal model, which is described first, allows the extent of thermal decomposition of a laminate in a fire to be determined.

There are several published models for the decomposition of organic materials in a fire, including wood, ablative re-entry protection materials, and composites.[17–22] Gibson and co-workers used a thermal model of this type to predict the decomposition of polymer composites in fire.[17–19] The model predicts the evolution of temperature and reduction in resin content of a laminate with time for any surface boundary condition.



5 Scanning electron micrographs showing microstructure of char in *a* glass–polyester and *b* glass–phenolic resin laminates; char observed in glass–vinyl ester laminates is very similar to that in *a*

As mentioned in the previous section, there are, in addition to the process of conduction, two other phenomena that can affect the energy transfer through composite laminates in fire: the decomposition of the matrix phase, which is a highly endothermic process; and the flow of volatile products from the decomposition region towards the hot face. These effects can be incorporated into a model for the thermal response by including terms for the energy fluxes due to decomposition and mass flow in the unsteady state heat conduction equation

$$\frac{\partial}{\partial x}\left(k\frac{\partial T}{\partial x}\right)+\dot{q}=\rho c_{\mathrm{p}}\frac{\partial T}{\partial t} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

The endothermic decomposition term is given, for polyester and vinyl ester resins, by a single overall thermally activated process

$$\frac{\partial m}{\partial t}=-A\left[\frac{(m-m_{\mathrm{f}})}{m_{\mathrm{o}}}\right]^{\mathrm{n}}e^{(-\mathrm{E/RT})} \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where m, t and T are the mass, time and temperature variables, respectively; A is the rate constant, E is the activation energy, n is the order of the reaction, and R is the gas constant.

Assuming thermal equilibrium between the decomposing laminate and the resultant gases, the enthalpy and mass flux of the reaction products define the energy flux due to mass transfer. The magnitude of the mass flux of decomposition products is known from the reaction kinetics and these products can be assumed to flow through the damaged material towards the fire, the undamaged material being impermeable. Generation of delamination cracks and their consequences are not considered, although they are known

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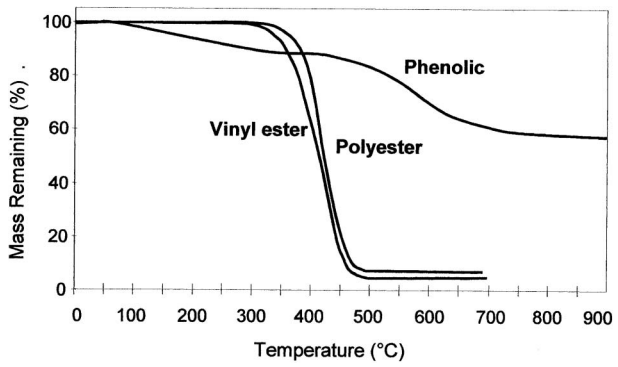

6 TGA curves at 25 K min^{-1} for isophthalic polyester, vinyl ester and phenolic resins in nitrogen atmosphere

to occur. The full governing equation is therefore

$$\rho C_P \frac{\partial T}{\partial t} = \frac{\partial}{\partial x}\left(k\frac{\partial T}{\partial x}\right) - \dot{M}_G \frac{\partial}{\partial x} h_G - \rho A \left[\frac{(m - m_f)}{m_o}\right]^n e^{-E/RT}(Q_P + h_C - h_G) \quad (3)$$

where T, t and x are temperature, time and through thickness coordinates, respectively; ρ, C_P and k are the density, specific heat and conductivity of the laminate, respectively; $\dot{M}_G$ is the mass flux; h_C and h_G are the respective enthalpies of the composite and evolved gas; and Q_P is the endothermic decomposition energy. The three terms on the right hand side relate to heat conduction, volatile convection and the decomposition endotherm, respectively.

The resin decomposition parameters were measured by TGA: Fig. 6 shows TGA curves for isophthalic polyester, vinyl ester and phenolic resins at a heating rate of 25 K min^{-1} in nitrogen. The two styrenic resins behave very similarly, beginning to decompose at ~350°C, the reaction being substantially complete at 480°C. They leave less than 7% of the initial resin mass as a carbonaceous char.

Phenolic resin, which has a higher aromatic content, leaves a larger proportion of char. It can also be seen that the kinetics of the decomposition process are quite different from those of the polyester: the reaction takes place in two distinct stages, a primary condensation, followed at a rather higher temperature by char formation. The thermal response of phenolic resin is preferably modelled by a two stage reaction, to account for this.[18] This can be accomplished by using an equation of the same form as equation (2) for each of the two stages.

A finite difference version of the thermal model has been validated for different resin systems by comparing the calculated and measured thermal responses during furnace fire tests.[17,18] The modelling parameters for this have been reported previously.[18] An FE based model has also been developed and reported.[19]

The boundary conditions for the application of the model in the present case assume an incident hot surface heat flux of 50 kW m^{-2}, with a surface emissivity of 80%. The cold face of the laminate was assumed to be fully insulated.

Post-fire mechanical model

Mouritz and Mathys[13–15] proposed a two layer model to estimate the residual mechanical properties of fire damaged laminates. In the model described here it is assumed the hot surface of a composite is uniformly heated by an incident heat flux, as illustrated in Fig. 1. (A model for non-uniform heating has also been proposed.[16]) Experimental observation reveals that a fire damaged laminate can be regarded, to a good approximation, as consisting of two layers:

(i) a thermally decomposed region where the resin is reduced to a carbonaceous char, and
(ii) a region that is undamaged (apart from some small delamination cracks close to the interface with the char zone).

In the present paper these two regions are simply called the 'char region' and 'unburnt region'. A two layer model is presented for estimating the residual tension, compression and flexure properties of laminates at room temperature that have the damage profile given in Fig. 1.

An underlying assumption of the two layer model is that the mechanical properties of the char and unburnt regions can be combined, as if they were a two layer laminate, to obtain the bulk stiffness and strength of a fire damaged material. To achieve this, a number of assumptions are made about the fire damage and its effect on mechanical properties, namely:

(i) the char region has a uniform thickness (defined as d_c in Fig. 1), which can be calculated using the thermal model or measured by microscopy
(ii) the mechanical properties of the unburnt region are the same as those of the original laminate
(iii) the mechanical properties of the unburnt region are constant throughout, and are not reduced by excessive heating of the resin matrix or the presence of the delamination cracks.

Using this approach, the residual tensile stiffness S_t of a laminate subject to uniformly distributed fire damage, as in Fig. 1, can be estimated using the simple expression

$$S_t = \left(\frac{d - d_c}{d}\right) S_o + \left(\frac{d_c}{d}\right) S_c \quad (4)$$

where d_c is the thickness of the char region, which is calculated using the thermal model; d is the original thickness of the laminate; and S_c and S_o are the tensile stiffness of the char and unburnt (original) material, respectively. The first term to the right hand side represents the tensile stiffness of the unburnt layer, while the second term gives the stiffness of the char layer.

Similarly, the tensile strength σ_t can be determined by

$$\sigma_t = \left(\frac{d - d_c}{d}\right) \sigma_{t(o)} + \left(\frac{d_c}{d}\right) \sigma_{t(c)} \quad (5)$$

where $\sigma_{t(c)}$ and $\sigma_{t(o)}$ are the tensile strengths of the char and unburnt regions.

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Similarly, the uniaxial compressive stiffness S_c of a fire damaged laminate can be determined using

$$S_c = \left(\frac{d-d_c}{d}\right) S_{c(o)} + \left(\frac{d_c}{d}\right) S_{c(c)} \quad . \quad . \quad . \quad . \quad . \quad (6)$$

where $S_{c(c)}$ and $S_{c(o)}$ are the compressive stiffnesses of the char and unburnt laminate.

The buckling load P_c can be determined using a modified version of the Euler buckling equation

$$P_c \approx C\pi^2 E_{c(o)} b(d-d_c)\left[\frac{0{\cdot}2887\,(d-d_c)}{L}\right]^2 + C\pi^2 E_{c(o)} b d_c \left[\frac{0{\cdot}2887 d_c}{L}\right]^2 \quad . \quad . \quad . \quad . \quad . \quad (7)$$

where $E_{c(o)}$ and $E_{c(c)}$ are the compressive moduli of the undamaged laminate and char, respectively, in the load direction; L and b are the length and width of the beam; and C is a constant determined by the restraint conditions at the beam ends ($C = 1$ when the ends of the beam are pin jointed).

Once P_c has been determined, the Euler buckling resistance of a fire damaged laminate beam σ_c can then be approximated by

$$\sigma_c \approx \frac{P_c}{bd} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

The post-fire flexural modulus and strength can also be determined using two layer analysis that combines the flexural properties of the char and undamaged regions. Mouritz and co-workers[13–16] proposed that when a fire damaged composite beam with a slender geometry is loaded in quarter point bending then the apparent flexural modulus E_f can be determined using

$$E_f = \left\{\frac{4(d-d_n)^3 + 4(d_n-d_c)^3}{d^3} + 4\frac{E_{f(c)}}{E_{f(o)}}\frac{[d_n^3-(d_n-d_c)^3]}{d^3}\right\} E_{f(o)} \quad . \quad . \quad . \quad (9)$$

where $E_{f(c)}$ and $E_{f(o)}$ are the flexural modulus of the char and undamaged laminate, respectively, and d_n is the distance from the outer surface of the char layer to the neutral stress axis of the beam, and is calculated using

$$d_n = \frac{E_{f(o)}d^2 - d_c^2(E_{f(o)} - E_{f(c)})}{2E_{f(o)}d + 2E_{f(c)}d_c - 2E_{f(o)}d_c} \quad . \quad . \quad . \quad . \quad . \quad (10)$$

The flexural failure load P_f of a fire damaged composite beam in quarter point loading can be estimated using

$$P_f = \frac{8}{L^*}\left\{\frac{\sigma_{f(o)}\cdot b}{3}\frac{(d-d_n)^3 + (d_n-d_c)^3}{(d-d_n)} + \frac{\sigma_{f(o)}\cdot b}{3}\frac{E_{f(c)}}{E_{f(o)}}\frac{[d_n^3-(d_n-d_c)^3]}{(d-d_n)}\right\} \quad . \quad . \quad . \quad (11)$$

where L^* is the length of the load span, b is the beam width, and $\sigma_{f(o)}$ is the flexural strength of the undamaged laminate.

Once P_f has been calculated, then the apparent flexural strength of a fire damaged laminate loaded in four point bending can be determined using

$$\sigma_f = \frac{3L_s P_f}{4bd} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (12)$$

where L_s is the length of the support span.

The appealing feature of the two layer model is the simplicity of the analysis. The post-fire properties can be simply approximated from the mechanical properties of the char and original laminate, and the depth of charring calculated using the thermal model. In many situations, as will be seen, the properties of the char material can be assumed to be negligible without much loss of accuracy, thus allowing further simplification.

EXPERIMENTAL

Composite materials

The ability to predict the post-fire mechanical properties using the thermomechanical model was evaluated for three common types of engineering composite: glass–polyester, glass–vinyl and glass–phenolic. All laminates were reinforced with an E-glass woven fabric having an areal density of 1·4 kg m^{-2}, produced by Colan Industries Pty Ltd. The resin in the glass–polyester was an isophthalic polyester (Synolite 0288-T-1) made by Dulux Australia. The vinyl ester resin (Derakane 411 C350) was supplied by Dow Chemicals. The matrix for the glass–phenolic was a low temperature, acid cure resole phenolic resin (Resinox® 1916) from the Huntsman Chemical Company Australia Ltd.

The laminates were fabricated using the hand layup method. The glass–polyester and vinyl ester laminates were allowed to post-cure at room temperature for several weeks prior to fire testing, without the use of elevated temperature. This is typically what occurs when large marine structures are manufactured from these resins. The fibre volume fraction was 0·35.

The glass–phenolic laminates were cured at room temperature for 24 h, followed by a post-cure at 60°C for 1 h and 80°C for 2 h. The fully cured phenolic laminate had a fibre volume fraction of 0·39.

All the laminate specimens were nominally 12·0 mm thick.

Fire testing

The laminates were exposed to a uniform heat flux for various times up to 30 min using the conical heating element of a cone calorimeter,[13–16] as shown in Fig. 2. The fire tests were performed at incident heat fluxes of 25, 50, 75 and 100 kW m^{-2}. These heat fluxes corresponded to source temperatures of ~570, 750, 875 and 970°C, respectively. The cold face of the specimens was thermally insulated.

After exposure of the laminate sample to the heat flux, an induction period (the ignition time) is observed before ignition occurs. This corresponds to the time for the laminate surface temperature to rise to a level where there are sufficient flammable decomposition products to support combustion. Following this, flashover occurs.

The ignition times of the laminates at different heat fluxes are plotted in Fig. 3. The superior fire resistance of the phenolic laminate over the two styrene based resin laminates is demonstrated by the much longer ignition times. Following ignition, the combustion

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process led to progressive resin degradation and char formation through the cross-section of the laminates. Following a measured period of exposure to the radiant source, the samples were extinguished and cooled to room temperature, before measurement of their residual mechanical properties.

Figure 4 shows a typical laminate in cross-section after fire testing, and a sketch of the change in residual matrix content. There are three regions. In order from the hot face, they are: residual char; damaged material (with partially decomposed resin); and undamaged laminate.

Figure 5 shows scanning electron micrographs of the structure of the char within *a* polyester and *b* phenolic laminates. The char region in the glass–polyester is largely depleted of resin, leaving mainly exposed fibres. The vinyl ester laminates showed similar behaviour. By contrast, the resin within the char region of the glass–phenolic resin can be seen to have left a substantial residue of heavily cracked carbonaceous char. In addition to the cracks, some holes can also be seen. These presumably originated from voids formed during the curing of the resin.

The decomposition zone between the char and undamaged region in all laminate types is characterised by the presence of a region of delaminations. These are probably caused by the pressure of volatile products acting in the laminate where the resin has been weakened by temperature and decomposition. The effects of the delaminations are not considered here in either the thermal model or the two layer model, although it is acknowledged that they may significantly influence both conductivity and mechanical properties.

The decomposition zone can extend for 1–2 mm of the cross-section, so determination of the 'effective' boundary between damaged and undamaged material can be subject to scatter of typically about ± 1 mm. The undamaged material was indistinguishable in appearance from the laminate before fire testing.

Thermogravimetric analysis

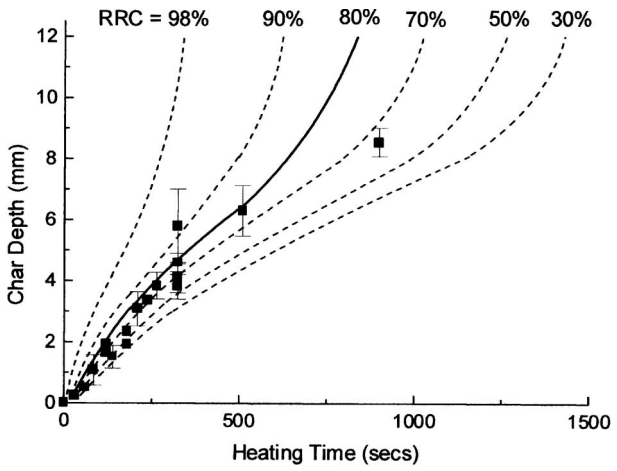
The thermal model requires knowledge of the decomposition reaction in the resin. This is generally most conveniently acquired by TGA. The resin decomposition parameters were determined from the TGA curves at a heating rate of 25 K min^{-1} in nitrogen, and are given in Fig. 6. The polyester and vinyl ester have very similar curves, both resins begin to decompose at 350°C and the reaction is substantially complete at 480°C, leaving less than 7% of the initial mass as a carbonaceous char. Phenolic resin, which has a higher aromatic content, leaves a larger proportion of char, as observed in Fig. 5*b*. The thermal response of the phenolic resin is preferably modelled by a two stage reaction to account for primary condensation followed by char formation.[18]

Mechanical testing

The post-fire tension, compression and flexural properties of the laminates were determined at room temperature after fire testing. The tensile stiffness and strength were measured according to the ASTM tensile test specification[23] using coupons with a gauge length of 100 mm and width of 25 mm. The tensile stiffness was determined instead of Young's modulus because of the difficulty in measuring the strain in a fire damaged laminate using strain gauges or an extensometer. The tensile stiffness was taken to be the gradient of the linear (elastic) portion of the load against crosshead displacement curve (expressed in N m^{-1}).

Compression tests were performed on slender composite beams, 150 mm long and 25 mm wide. The beam ends were simply supported between thick steel platens during compression loading. The compression stiffness of the laminate was determined as the slope of the applied load verses crosshead displacement curve in the linear (elastic) region. The Euler buckling strength was taken to be the applied stress at which the specimen began to buckle. Compression tests were only performed on the glass–polyester laminate.

The flexural modulus and strength of the laminates were determined using the ASTM four point bend method.[24] The specimens were 240 mm long and 25 mm wide, and were loaded at a crosshead speed of 5 mm min^{-1} in quarter point loading under failure. The flexural tests were performed with the burnt surface placed against the two load points so it experienced bending induced compression. A minimum of four specimens tested under identical fire conditions was used for the determination of the residual tension, compression and flexure properties of the laminates.



7 Thermal damage depth *v.* heating time for heat flux of 50 kW m^{-2}, for 12 mm thick glass–polyester laminates; curves show the RRC at interface between char and undamaged laminate determined using thermal model, for RRC values in range 30–98%

RESULTS AND DISCUSSION

It is assumed that heating the laminates in the cone calorimeter caused them to decompose into effectively a two layer material, as illustrated in Fig. 1. Figure 7 shows the effect of increasing heating time at constant heat flux on the thickness of the char layer d_c formed in glass–polyester. The data points indicate the char thickness values measured by microscopy. As expected, there is a steady increase in char with time, although there is vertical scatter among the measured char values because of some difficulty in accurately determining

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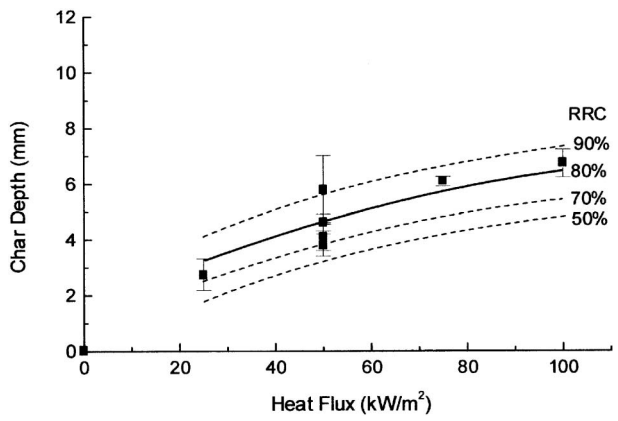
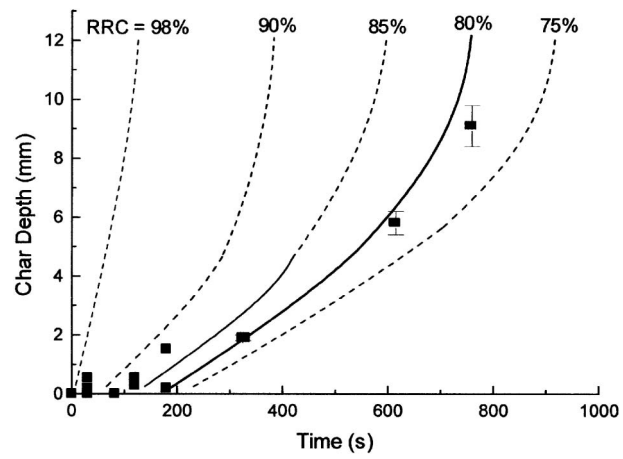


8 Effect of heat flux on char thickness for heating time of 325 s for glass–polyester laminates; curves show RRC at interface between char and undamaged laminate determined using thermal model



9 Thermal damage depth *v.* heating time, for heat flux of 50 kW m^{-2}, for 12 mm thick glass–phenolic laminates; curves show RRC at interface between char and undamaged laminate determined using thermal model, for RRC values in range 75–98%

the interface between the char and undamaged layers. The char layer thickness in the vinyl ester laminates behaved almost identically.

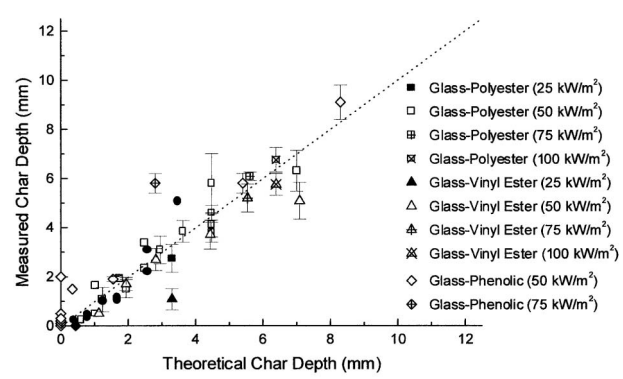
It was decided to investigate whether the effective boundary between the char and undamaged regions, the 'decomposition front', could be simply approximated in terms of a single stipulated value of RRC. The thermal model was used to calculate the heating times and heat fluxes at which the laminates reached a given RRC at different points through their thickness. Char depth *v.* heating time was modelled for a range of RRC values of 30–98%. These predictions are shown as solid curves alongside the measured data in Figure 7. Despite some scatter in the experimental data it can be seen that agreement is quite close for an RRC value of ~80%. The predicted char growth curves show three distinct regions. There is a very short initial lag, which corresponds presumably to the time required to heat the laminate to the decomposition temperature. Following this, there is a period of fairly steady char growth. Finally, as the damage front begins to approach the rear face and the undamaged laminate becomes thermally 'thin', the char growth rate accelerates.

Figure 8 shows the effect on char depth of varying heat flux for a constant exposure time of 325 s. Again the prediction for an RRC of 80% agrees well with the experimental data. It is interesting to note that the char growth rate does not increase linearly with heat flux, as might perhaps have been expected. For thick laminates in the 'steady growth' phase mentioned above the rate appears to be proportional to heat flux to the power of ~0·4.

Figure 9 shows the measured and modelled char rates for the phenolic laminates. Interestingly, although the curves show the three distinct regions as before, they are not the same shape as those for the polyester laminates, the most notable difference being the much longer induction period before char begins to grow. This appears to correspond to the longer ignition times observed in Fig. 3. It may also coincide with the completion of the first stage of the decomposition reaction and the onset of the second stage, as seen in the TGA curves in Fig. 6. Despite these differences, however, the experimental char growth results are again modelled quite well by an RRC value of 80%, and interestingly this value does appear to correspond approximately to the onset of the secondary reaction, as seen from the TGA results.

Figure 10 compares the measured and theoretical char thickness values for all the laminate materials studied. The theoretical char values were calculated using the thermal model for RRC 80%. It is seen that there is excellent agreement over a range of heat fluxes of 25–100 kW m^{-2}, and heating times up to 30 min.

The two layer model discussed in the section 'Post-fire mechanical model' was then used in conjunction with the thermal model (RRC = 80%) to provide predictions of a range of residual laminate properties after exposure to a heat flux of 50 kW m^{-2} for various periods. The predictions are compared with the measured residual properties in Figs. 11–16, where it can be seen that agreement is generally very good. Note that these properties should possibly be referred to as 'apparent' residual properties, as they are based on the original undamaged sample thickness.



10 Comparison of theoretical char depth, determined using thermal model with char thickness values measured by microscopy, for all laminate types studied at heat fluxes in range 25–100 kW m^{-2}

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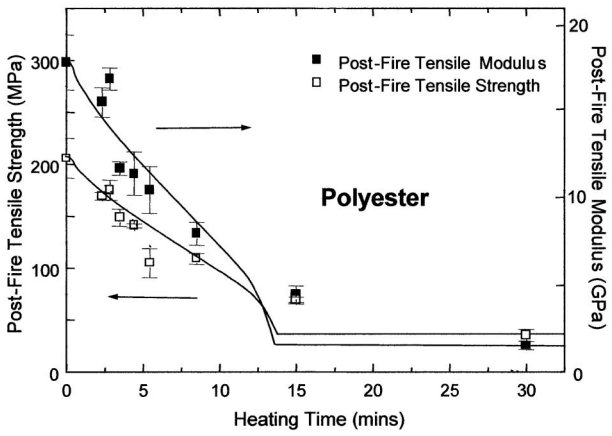
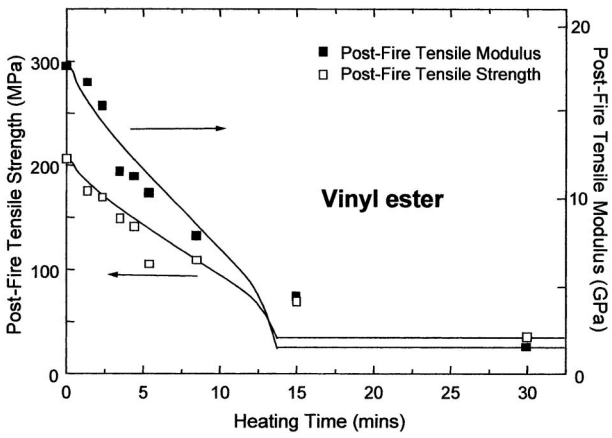
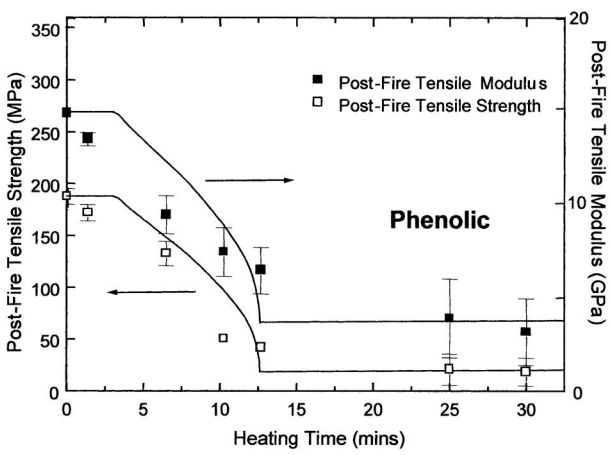


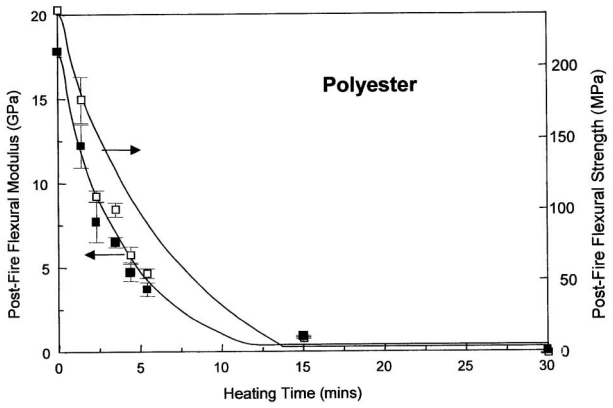
11 Change in tensile properties of glass–polyester laminate with heating time at heat flux of 50 kW m^{-1} (experimental points); curves show theoretical post-fire properties determined using two layer model



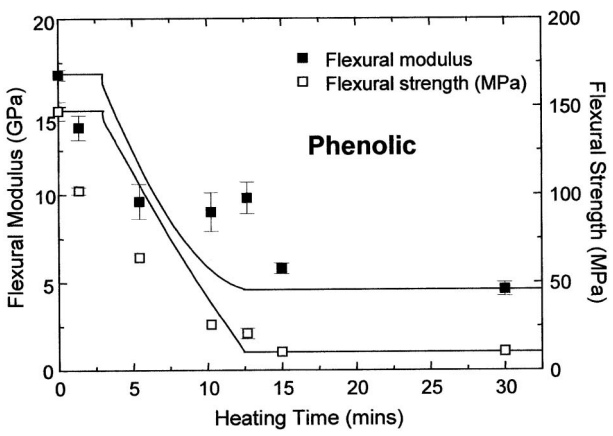
12 Change in tensile properties of glass–vinyl ester laminate with heating time at heat flux of 50 kW m^{-2} (experimental points); curves show theoretical post-fire properties determined using two layer model



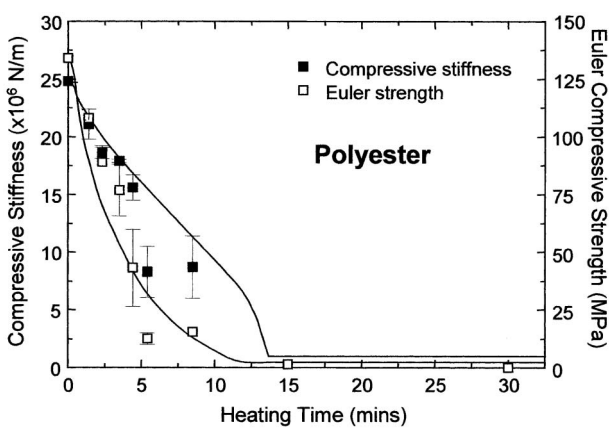
13 Change in flexural properties of glass–phenolic laminate with heating time at heat flux of 50 kW m^{-2} (experimental points); curves show theoretical post-fire properties determined using two layer model



14 Change in flexural properties of glass–polyester laminate with heating time at heat flux of 50 kW m^{-2} (experimental points); curves show theoretical post-fire properties determined using two layer model



15 Change in flexural properties of glass–phenolic laminate with heating time at heat flux of 50 kW m^{-2} (experimental points); curves show theoretical post-fire properties determined using two layer model



16 Change in compressive properties of glass–polyester laminate with heating time at heat flux of 50 kW m^{-2} (experimental points); curves show theoretical post-fire properties determined using two layer model

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Figures 11–16 show several interesting features. For instance there is a discontinuity in the model prediction, where the model predicts that the RRC = 80% point has reached the rear face of the laminate, i.e. all the material in the section is predicted to have been converted to the char phase, so the properties 'bottom out'. Although not negligible, the char properties are generally very poor compared with the undamaged values, strength and stiffness generally being less than 10% of the initial values. The only exception to this is the tensile and flexural modulus of the phenolic char, which is ~4 GPa. However, the residual strength of these particular phenolic laminates appears to be no higher than that of the others.

The phenolic resins also show a discontinuity at 3·1 min, the end of the induction period discussed previously. By contrast, the much shorter induction period for the styrenic resins is not long enough to be apparent on the property curves – damage appears almost immediately on fire exposure. Although the predicted property loss characteristics are different between the different materials, the times required for the properties to 'bottom out' are quite similar, being 13·7 min for the polyester laminates and 12·6 min for the phenolics. Despite their well known advantages in terms of smoke and toxicity, the phenolic resins differ little, and indeed are just very slightly inferior to the other resins in terms of residual properties.

It is interesting to speculate further on the decomposition characteristics of the phenolics. These resins usually contain voids resulting from the evolution of water during cure – the voids visible in the char structure in Fig. 5 probably resulted from this process. Both ignition time results, Fig. 3, and other cone calorimeter measurements suggest that in fire, the first stage decomposition reaction produces products that do not burn. This reaction is therefore likely to be an extension of post-cure, in which additional crosslinks are formed, the main byproduct of the condensation again being water. Water evolution may well account for the longer time to ignition of the phenolics and their generally lower flammability.

The second stage decomposition, by contrast, does produce flammable products, albeit with a lower level of heat release than those produced when polyesters or vinyl esters decompose. The second stage phenolic volatiles result from the coalescence of the crosslinked structure into a graphitic char, with the elimination of some of the methylene crosslinks, along with hydroxy groups from the original phenol molecules. The further loss of volatiles probably accounts for the bulk shrinkage and secondary cracks that can be seen in Fig. 5*b*, and the property reductions observed in Figs. 13 and 15.

The degradation of tensile properties in Figs. 11–13 occurs less rapidly than the loss of flexural properties in Figs. 14 and 15. This is because tensile behaviour is proportional to the thickness of uncharred material, whereas flexural stiffness is roughly determined by its cube. Flexural strength is related to its square.

Figure 16 shows compression behaviour. The compressive stiffness again falls off relatively slowly because it is linearly related to the thickness of undamaged material, whereas Euler buckling, being governed by flexural stiffness, and hence the cube of this quantity, falls off much more rapidly.

Despite the fact that property loss is related to the undamaged thickness to various powers, all these properties are seen to bottom out at the same time for each particular resin, even when the shape of the loss curve differs.

The relatively small difference between the residual properties with different resin systems suggests the possibility of offering general engineering guidelines on residual properties for use with a range of composite systems. This possibility will be explored in a future paper.

CONCLUDING REMARKS

A new modelling approach for predicting the post-fire tension, compression and flexural properties of composites has been presented. It is acknowledged that the two layer model (undamaged laminate plus char) is an approximation because it ignores the finite thickness of the decomposition region. Nevertheless this approach is useful in characterising the residual behaviour of laminates after fire. It also has the advantage of providing structural information in a form that is readily usable by designers.

The present results support the use of the modelling approach, and the thermal model for the decomposition response provides an additional insight into the degradation processes that take place through the thickness of the laminate. The decomposition reaction is similar in both polyester and vinyl ester laminates and, following a short induction time, involves progressive loss of flammable volatiles.

In contrast to the styrene containing resin, the decomposition mechanism in phenolic laminates takes place in two stages and is clearly different. The first stage reaction may involve only water loss and is associated with post-curing and the absence of ignition. The second reaction, which commences after a significant time lag, is a transformation to carbonaceous char, which involves both the production of flammable volatiles and the loss of mechanical properties.

Despite the differences between the resin types, the effective cutoff point between undamaged material and char appears to correspond to RRC = 80%.

It is intended to extend the investigation to take more accurate account of the presence of the decomposition region. Work is also under way on the response of loaded composite structures during fire.

ACKNOWLEDGEMENTS

The University of Newcastle authors would like to acknowledge EPSRC funding for work on *Fire Resistance of Loaded Composite Structures* as well as the support of the *EUCLID* programme on *Survivability, Durability and Performance of Composite Naval Structures* and the EU *COMPOSIT* network. Thanks are also extended to Mr C. Townsend (DSTO) for assistance with specimen fabrication and cone calorimetry.

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