Failure model for phenolic and polyester pultrusions under load in fire

R. C. Easby[1], S. Feih[2], C. Konstantis[1], G. La Delfa[1], V. Urso Miano[1], A. Elmughrabi[1], A. P. Mouritz[2] and A. G. Gibson*[1]

The failure of polyester and phenolic pultrusions under tensile and compressive load and a one sided heat flux of 50 kW m^{-2} has been studied. A thermal/mechanical model, based on the Henderson equation and laminate theory, has been used to model their behaviour. In tension, significant load bearing capacity was retained over a period of 800 s, due to the residual strength of the glass fibres. However, pultruded composites are susceptible to compressive failure in fire, due to the loss of properties when the resin T_g is reached. The fire reaction properties reported here showed the phenolic pultrusions to perform better than polyesters in all fire reaction properties (time to ignition, heat release, smoke and toxic product generation). The measurements under load in fire showed that the phenolic system decayed at a slower rate than the polyester, due mainly to the very shallow glass transition of the phenolic, but also the char forming characteristic of the phenolic. The behaviour described here for phenolic pultrusions is superior to that reported for some phenolic laminates, the main reason probably being their lower water content.

Keywords: Phenolic, Polyester, Pultrusion, Fire

Introduction

This work was undertaken in collaboration with Fiberline Composites and involved polyester and phenolic pultruded sections. Pultruded composites are increasingly employed for structural applications, some of which may be sensitive to fire. For that reason, glass/phenolic pultrusions, which have better fire reaction properties (smoke, heat release, time to ignition, etc.), are sometimes used as an alternative to the more commonly employed glass/polyester. The purpose of this investigation was to develop a methodology for the fire characterisation and modelling of pultruded composites and to compare the structural behaviour of phenolic and polyester pultrusions under load in fire.

Recently, an improved structural approach has been developed for studying the behaviour of composites under load in fire.[1–9] This involves the application of a constant, one sided heat flux to a small laminate sample under constant tensile or compressive stress. The heat flux can be provided either by a radiant electrical element[1,2,4–6] or a calibrated gas burner.[3,7] Mechanical measurements are aided by a thermal model, based on the approach adopted by Henderson[10] for the prediction of the temperature evolution through composite laminates.

Experimental

Pultruded glass/phenolic and glass/polyester sections were supplied by Fiberline Composites. These were in the form of structural box sections in which the laminate was 8 mm thick. Like many types of pultruded section, these products were manufactured with a three layer structure as shown in Fig. 1. In this form of construction, a unidirectional core provides the main strength and stiffness of the section. The core is protected on both sides from mechanical and chemical damage by layer of continuous strand mat (swirl mat), in which the fibre orientation lies randomly in the plane of the laminate. The total thickness of the laminate section in this case was 8 mm, the skin thickness being 1·5 mm. Flat specimens cut from these sections can therefore be regarded as 'subelements' of a typical pultruded composite structure.

The Fiberline products were manufactured using the 'die injection' version of the pultrusion process, in which no wet resin is exposed to the working environment. General engineering properties of the sections are given in Ref. 11. The phenolic resin was an acid cured resin and the polyester resin was conventional halogenated polyester of the type widely used in structural applications.
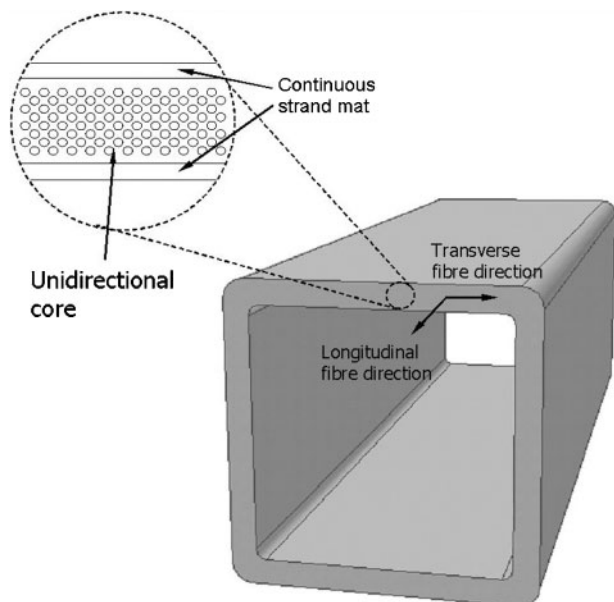
Fire reaction properties

The fire reaction properties of the pultruded laminates were measured using a cone calorimeter[12] and are compared in Table 1. The results underline the well known differences between phenolic and polyester resin

[1]Newcastle University, Newcastle upon Tyne, UK
[2]Royal Melbourne Institute of Technology, Melbourne, Vic., Australia

*Corresponding author, email a.g.gibson@newcastle.ac.uk

1 Three layer structure commonly employed in pultruded sections: unidirectional core and continuous strand mat (CSM) skins; testpieces were cut from this section

fire reaction properties, namely, extended time to ignition, reduced heat release rate and reduced toxic product evolution in the case of the phenolic. As mentioned above, one aim of this study was to investigate whether the fire reaction benefits of using phenolic resin would also be reflected in better mechanical performances of the phenolic pultrusions, both at high temperature and in fire.

Mechanical properties

To model the structural behaviour of a composite laminate in fire, material constants such as longitudinal and transverse stiffness, tensile and compressive strengths are needed as functions of temperature.[3,4,7] Experiments were therefore developed and carried out to measure these properties up to high temperature.[7] The results of these tests needed to be fitted as a function of temperature, so a fitting function was required. Between ambient temperature and the point at which they begin to decompose, many thermosetting resins go through a single large transition, the glass transition. The following empirical fitting function has been proposed,[2–9] based on the shape of the hyperbolic tan function

$$P(T) = P_U - \left(\frac{P_U - P_R}{2}\right)\left\{1 + \tanh\left[k\left(T - T_g'\right)\right]\right\} \quad (1)$$

where P_U and P_R are the unrelaxed and relaxed property value respectively, k is a constant describing the breath of relaxation, T is the absolute temperature and T_g is the
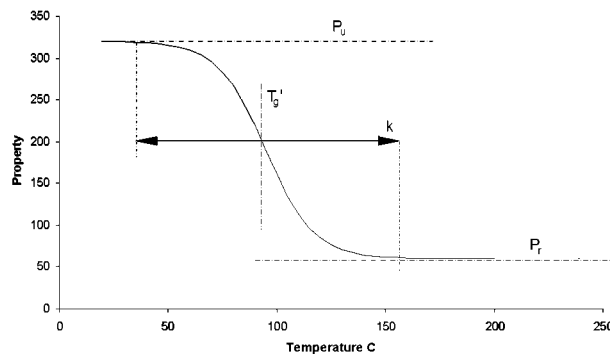
2 Schematic of property variation *v.* temperature with four parameter relationship of equation (1)
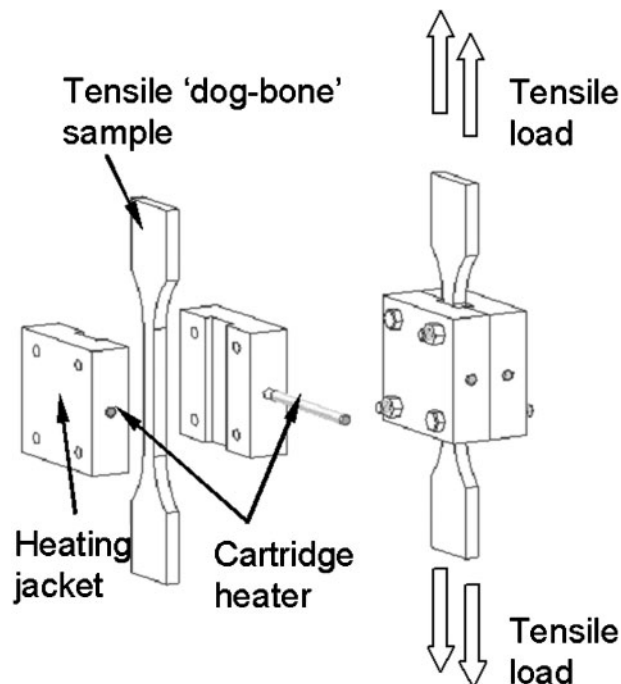
3 Temperature controlled heating jig for measurement of tensile strength at high temperature: only gauge length region of sample is heated, to avoid grip failures

absolute temperature of the mechanical glass transition. This relationship is shown schematically in Fig. 2.

Tensile strength

Dog bone shape samples were used for tensile testing of pultruded material specimens, several tests being carried out over a temperature range from 25°C up to 400°C. Instead of performing the tensile measurements in an oven, a small jig was designed (Fig. 3), comprising an aluminium jacket containing a cartridge heater. This was used to maintain a uniform temperature along the gauge

Table 1 Fire reaction properties (cone calorimeter, 75 kW m⁻²) for phenolic and FR polyester pultrusions

	Phenolic	Polyester
Time to ignition, s	150	17
Peak heat release rate, kW m⁻²	124	309
Average HRR (over 10 min) , kW m⁻²	72	112
Average smoke production (specific extension area), m² kg⁻¹	197	828
Average mass loss rate, g s⁻¹	0·044	0·066
Average CO yield, kg kg⁻¹	0·02	0·06
Average CO₂ yield, kg kg⁻¹	1·8	1·7
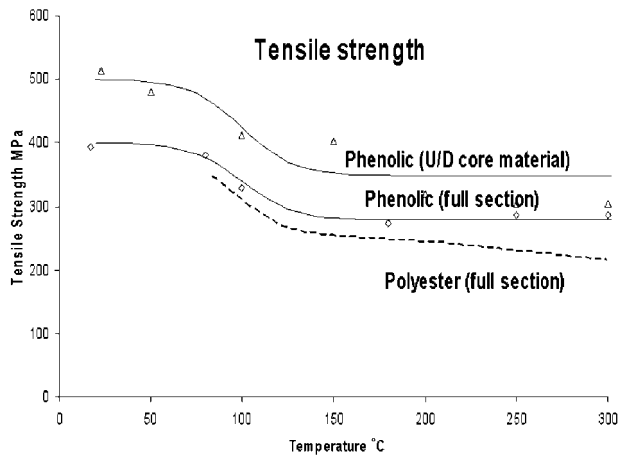
4 **Tensile strength of pultruded phenolic and polyester sections as function of temperature**

length during the test, an arrangement that enabled the specimen ends to be kept cold, thus preventing the material from slipping in the grips. Longitudinal tests were carried out on both the full three layer section of the pultrusion and on the unidirectional core material, with the skins removed, the results being shown in Fig. 4.

The room temperature tensile strength of unidirectional composites is often modelled using the well known 'law of mixtures' relationship

$$\sigma* = \sigma_f^* V_f + \sigma'_m (1 - V_f) \qquad (2)$$

where $\sigma*$ is the failure strength of the composite, σ_f^* is the failure strength of the fibres, σ'_m is the stress in the matrix at the failure strain of the fibres and V_f is the fibre volume fraction.

It can be seen from Fig. 4 that the fall in the strength of the unidirectional composite due to the resin glass transition is significantly greater than that predicted by putting $\sigma' = 0$ in equation (2). This effect was not found to be due to any spurious experimental effects, such as grip slippage. It therefore required some special consideration. The most probable explanation is the loss of the 'composite' effect. Below the resin T_g, the 'uniform strain' assumption applies, so all the reinforcement is subjected to the same strain level, by virtue of being encapsulated in the resin. The result of this will be that most of the fibres will fail at the average failure strain of the fibres. However, nominally unidirectional reinforcement will, in reality, be imperfectly aligned due to variations in the way the fibre tows are packed into the die during manufacture. There may also be 'path differences' between the lengths of fibre incorporated into a particular product sample. Once the resin modulus has fallen to a low value, there effects will become prominent in increasing the range of composite strains over which the fibres will fail, the overall result being a fall in the failure stress of the composite to a value lower than that of the $\sigma* V_f$ term in equation (2). This effect, which has not been widely discussed in literature, warrants further investigation and modelling.

At high temperature, both the polyester and the phenolic pultrusions maintained a high value of tensile strength,[5] although at lower level than that predicted by equation (2). This is largely determined by the fibre strength. The strength of the polyester samples was
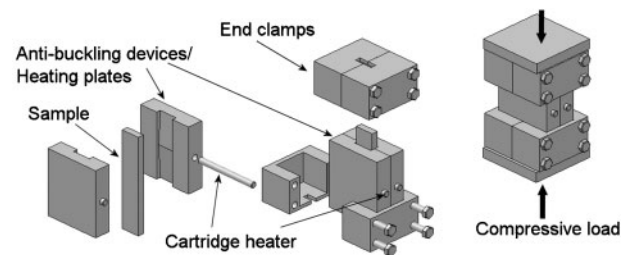
5 **Jig for measurement of compressive strength at high temperature, showing combined temperature controlled heating block and antibuckling guide**

found to fall off more rapidly, and to a lower level than that of the phenolic ones. The transition region for the phenolic appears much broader than that for the polyester.

Compressive strength

A compression testing jig was designed to provide both temperature control and buckling suppression. This is shown in Fig. 5. The samples were heated in the jig to the desired temperature, then loaded up to compressive failure. Tests were again performed at temperatures from 20°C up to 400°C. The compressive stress–strain curves were all found to follow the familiar saw tooth profile associated with compression tests on composites. The failure mechanism in compression is different from that in tension and involves the formation of a localised band of kinked material,[13] probably triggered by the shear deformation of any slightly misaligned material. Figure 6 shows the compressive strength of the phenolic and polyester pultrusions against temperature. The curves show a steep drop for temperatures above the transition region, there being little benefit in this case from the high temperature strength of the glass. Once again, the transition region for the phenolic appears to be broader than that for the polyester.

Longitudinal and transverse stiffness

Flexural modulus measurements were carried out using three point bend creep tests with rectangular specimens having a length/depth ratio of at least 16. The bending
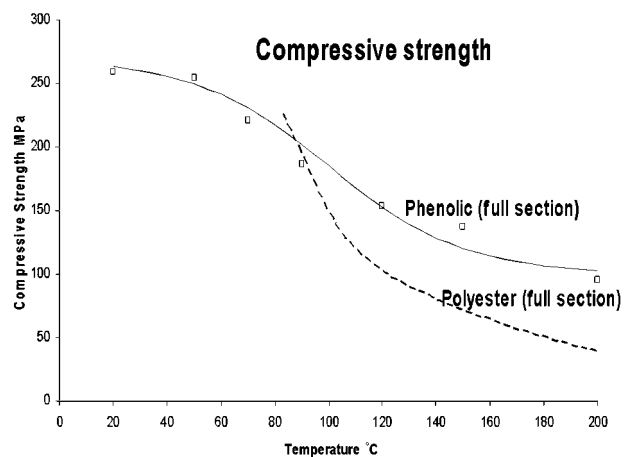
6 **Compressive strength of pultruded phenolic and polyester sections as function of temperature**
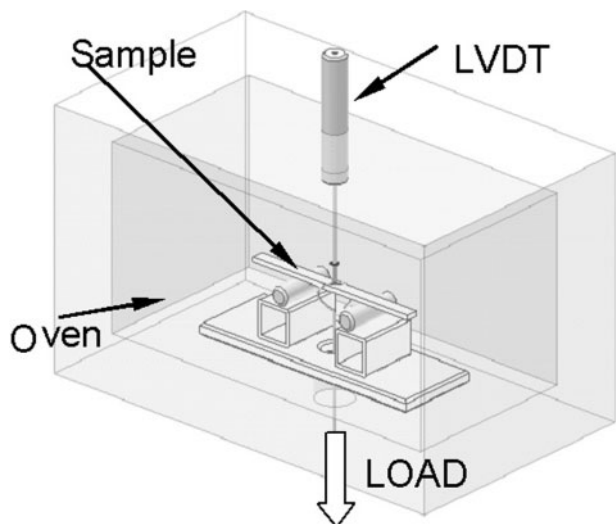
7 Temperature controlled rig for measurement of flexural modulus
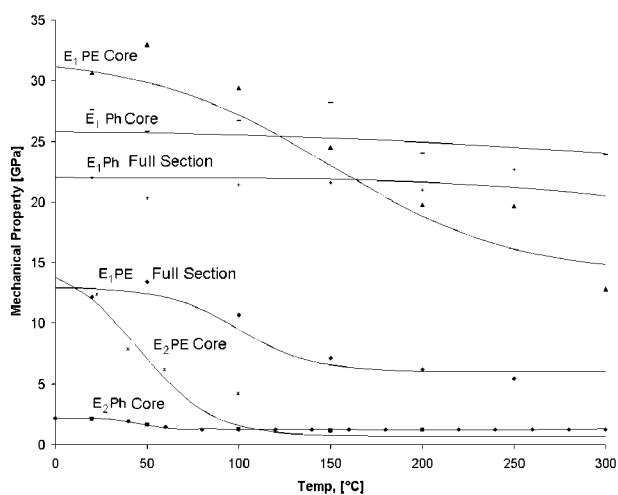
8 Flexural moduli (100 s) of pultruded phenolic and polyester sections as function of temperature

rig was placed inside a temperature controlled oven, as shown in Fig. 7. Once a stable value of the required temperature had been reached, the load was applied in a form of a dead weight. The deflection was measured with an LVDT transducer and recorded after 100 s loading time, enabling the 100 s Young modulus to be found. Figure 8 shows the longitudinal and transverse moduli E_1 and E_2 respectively as function of temperature for the polyester and phenolic pultrusions. Measurements were performed for both the full section
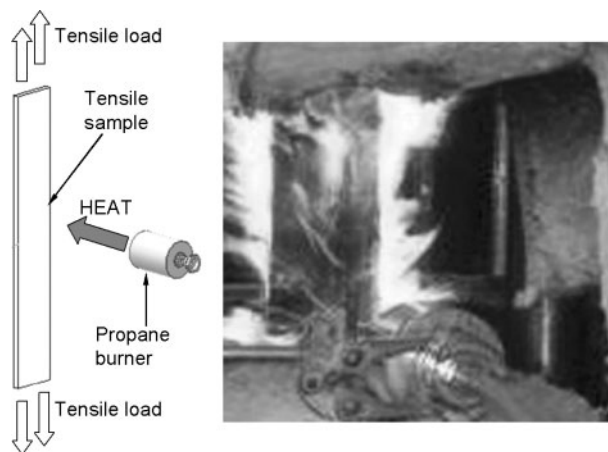
9 Test sample under tensile load subject to one sided heat flux using propane burner: rear face insulation of sample is not shown here

material and the core. In the case of the polyester pultrusion, the data show the familiar drop in magnitude as it passes through the transition region. The modulus drop for the polyester, like the fall in tensile strength, is larger than would be predicted by the law of mixtures of moduli, again implying effects due to fibre misalignment. The phenolic material shows a much smaller fall in stiffness, even in the resin sensitive transverse direction and again, the transition region can be seen to be very broad. The parameters used to describe all the composite mechanical properties as functions of temperature, using equation (1), are given in Table 2.

Fire testing under load

Rectangular tensile specimens for fire testing under load were machined, 500 mm long and 75 mm wide. The test configuration is shown in Fig. 9. The samples were subjected to a constant tensile load and simultaneous heat flux from the propane burner, which was calibrated *in situ*, as 50 kW m^{-2} based on hot face temperature and distance from the front of the burner to the front of the sample. The heat flux was kept constant throughout the test by monitoring a hot face thermocouple. The rear face of the sample was insulated with kaowool to prevent heat loss and to achieve the most reproducible thermal boundary condition. The time taken for the sample to fail, from the moment the burner was turned on, was recorded as time to failure for several loads. Ultimate tensile strength was also determined, and denoted with a failure time of 1 s.

The fire testing arrangement under compressive load is shown in Fig. 10. Samples, 120 mm long and 100 mm

Table 2 Parameters used to describe mechanical properties as functions of temperature: P_U and P_R are expressed in MPa for strengths and GPa for stiffness values

Material	Polyester				Phenolic			
Parameter	P_U, MPa	P_R, GPa	T_g, °C	k	P_U, MPa	P_R, GPa	T_g, °C	k
σ_{T1} (core)	354	242	150	0·03	500	347	100	0·035
σ_{T1} (full material)	230	220	150	0·03	400	278	100	0·035
σ_{C1} (full material)	320	60	95	0·045	270	100	100	0·02
E_1 (core)	32	14	150	0·01	26	22	300	0·005
E_1 (full material)	13	6	100	0·025	22	19	300	0·05
E_2 (core)	15·2	0·7	45	0·025	2·12	1·2	50	0·06
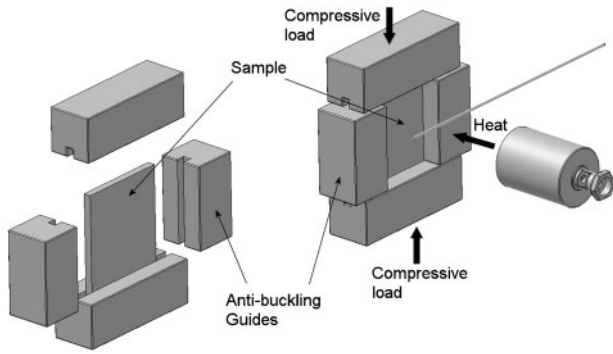
10 Fire test in compression, using propane burner as one sided heating source: note use of antibuckling guides; rear face of sample was thermally insulated

wide, were cut from the 10 mm thick pultruded laminate and were held in a constrained compression jig, similar in principle, to the Boeing compression after impact test jig.[14] The purpose of this was to suppress global buckling of the samples during testing while at the same time allowing samples with a large surface area to be exposed to heat flux.

Once in place, the samples were loaded with a constant compressive load, exposed to a propane burner flame and calibrated by means of a slug type heat flux meter to produce a heat flux of 50 kW m^{-2} at the specimen surface. The time to compressive failure of the sample was recorded for several different applied loads.

Results

Time to failure measurements were performed for both phenolic and polyester pultrusions under one sided heat flux. Both tensile and compressive failure events were observed to occur with little warning. The tensile stress rupture curves (Fig. 11), for both types of material, exhibit a fairly high level of residual strength, due to glass retaining a proportion of its strength at high temperatures. By contrast, the compressive stress rupture

curves show a more rapid decline in strength, to a lower final value. This limited residual strength in compression has been observed with other composites systems in fire[1,3,4,6] and is mainly attributable to the bulk of the matrix material reaching its glass transition temperature.

Modelling

Thermal model

A thermal model, based on the Henderson equation,[10] has been developed to predict the temperature distribution in a composite exposed to heat flux. The model is, in essence, a one-dimensional heat transfer relationship, which takes account of conduction, resin pyrolysis and the effect of the decomposition products passing through the laminate. The one-dimensional governing equation described previously[2–9] is expressed as

$$\rho C_\mathrm{P} \frac{\partial T}{\partial t} =$$

$$\underbrace{\frac{\partial}{\partial x}\left(k\frac{\partial T}{\partial x}\right)}_{\substack{\text{Heat}\\\text{conduction}}} - \underbrace{\frac{\partial}{\partial x}\left(\dot{M}_\mathrm{G}\,h_\mathrm{G}\right)}_{\substack{\text{Mass flow of}\\\text{volatile products}}} - \underbrace{\frac{\partial \rho}{\partial t}(Q+h_\mathrm{C}-h_\mathrm{G})}_{\substack{\text{Endothemic reaction of}\\\text{resin decomposite}}} \quad (3)$$

where $\dot{M}_\mathrm{G}$ is the mass flux (kg m^{-2} s^{-1}) of the volatile gas; ρ, C_p and k are the density (kg m^{-3}), the specific heat (J kg^{-1} K^{-1}) and the thermal conductivity (W m K^{-1}) of the material in the through thickness direction x; T is the temperature (K); t is the time (s); Q, h_C and h_G are the heat of decomposition (J kg^{-1}), enthalpy of the solid phase (J kg^{-1}) and enthalpy of the volatile gas (J kg^{-1}) respectively.

The composite transport properties in equation (3) evolve as functions of temperature and resin decomposition. The second term takes account of the cooling effect of decomposition reaction gases diffusing through the laminate thickness.

The heat consumed by the decomposition of the resin is modelled by the third term on the right hand side of equation (3). Thermogravimetric analysis (TGA) was used to determine the mass loss rate under controlled
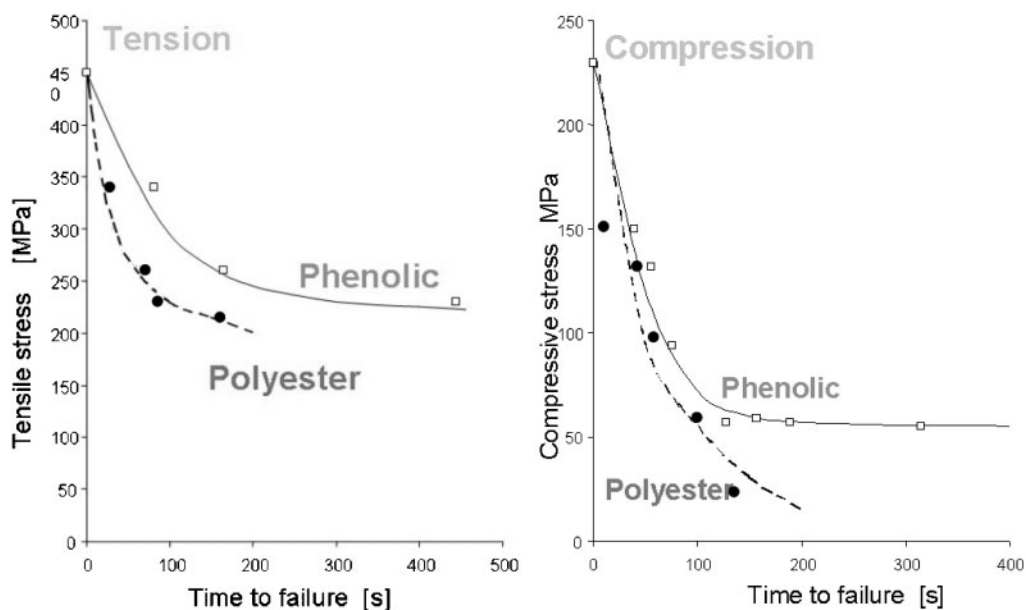
11 Measured and modelled fire test results for phenolic and polyester sections under tensile and compressive load at heat flux of 50 kW m^{-2}
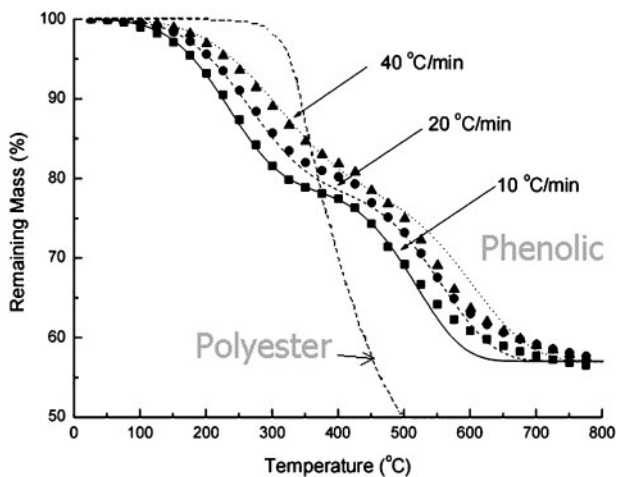
12 **Thermogravimetric analysis curves, showing comparison between decomposition of phenolic and polyester resin**

heating conditions, and the relevant material parameters may be evaluated using the Arrhenius rate equation

$$\frac{\partial m}{\partial t} = -Am_o \left(\frac{m-m_f}{m_o} \right)^n \exp\left(\frac{E}{RT} \right) \qquad (4)$$

where m, m_o and m_f are the current mass, the initial mass and the final mass (kg), A is the pre-exponential rate factor (s^{-1}), n is the order of the reaction, E is the activation energy ($J\ mol^{-1}$), R is the gas constant ($8\cdot314\ J\ mol^{-1}\ K^{-1}$) and T is the temperature (K).

TGA analysis

As mentioned above, TGA provides the main input parameters for the thermal model: A, n and E. The analysis also provides a measure of the amount of the char left when the resin is spent. The polyester resin TGA parameters are shown in Table 3.

The decomposition process of the phenolic resin takes place two stages. The process can be modelled using two sets of kinetic parameters and two Arrhenius

Table 3 Kinetic parameters for decomposition of polyester resin

A (polyester), s^{-1}	$1\cdot29 \times 10^{13}$
E (polyester), $J\ mol^{-1}\ K^{-1}$	2×10^5

Table 4 Kinetic parameters for decomposition of phenolic resin

|	
A (phase I), s^{-1}	5
E (phase I), $J\ mol^{-1}\ K^{-1}$	$27\cdot2 \times 10^3$
A (phase II), s^{-1}	68
E (phase II), $J\ mol^{-1}\ K^{-1}$	$65\cdot2 \times 10^3$
Mass remaining after phase I, %	87

equations. The rate parameters are shown in Table 4. A carbonaceous residue of $\sim 55\%$ is left when the decomposition is complete. This char formation is a useful attribute of phenolic resin, as it is capable of bearing some load. Also, of course, material remaining as char does not contribute to heat release. By contrast, the polyester resin decomposes in one stage and its residual resin content is $\sim 6\%$, so any resin is left to carry any load. The TGA curves for the phenolic and polyester resins are compared in Fig. 12.
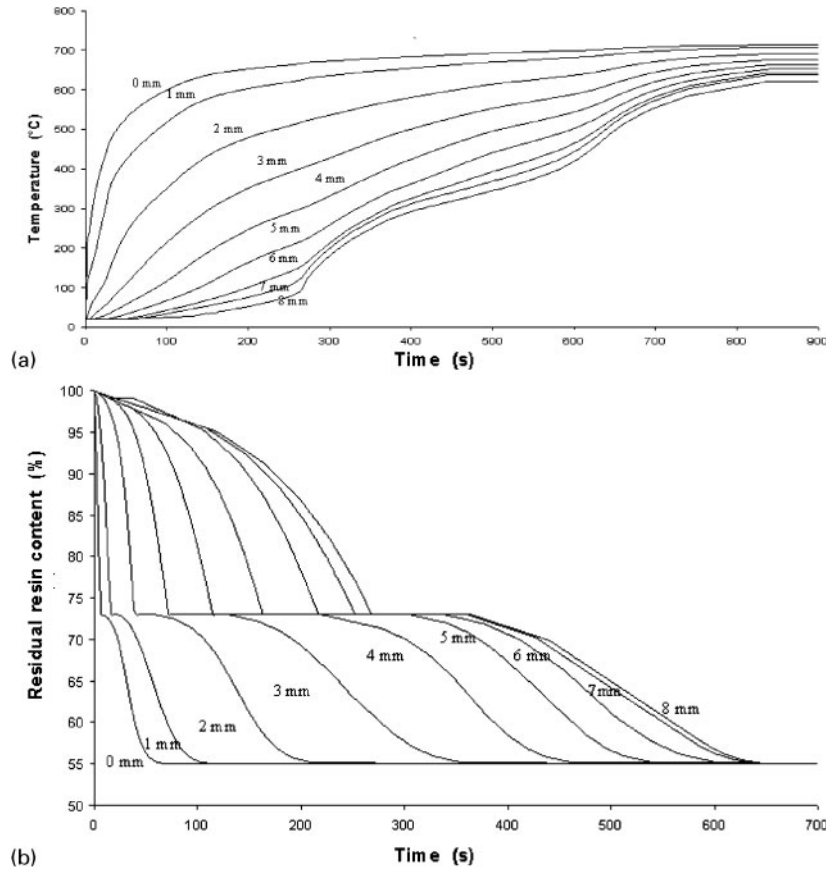
Thermal and residual resin profiles

Figures 13 and 14 show the modelled profiles of temperature and residual resin content through the polyester and phenolic laminates as a function of time. The temperature profiles show an initial plateau, which corresponds to the absorption of heat by the resin decomposition process. In the phenolic case, the residual resin profiles show some evidence initially of the two stage decomposition process. The char formation in the phenolic case ensures that the 'resin' content falls only to $\sim 55\%$, whereas in the polyester case, the residual content is almost 0.

Modelling behaviour under load

The laminate analysis failure model requires input from the thermal model described in the previous section, namely, temperature evolution and residual resin content through the thickness of the material. It also
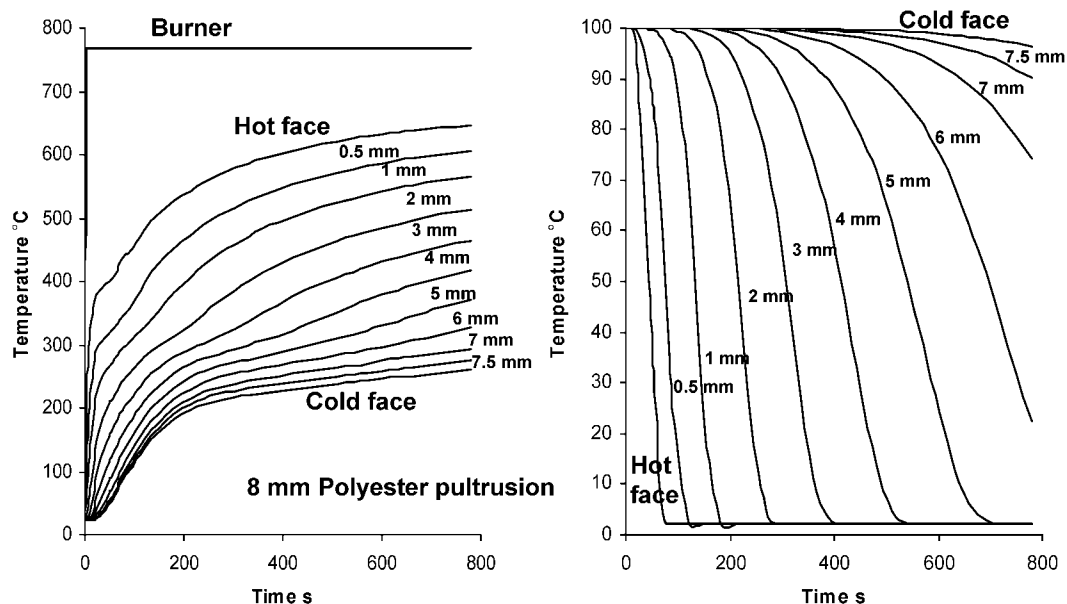
13 **Modelled thermal profiles (left) and residual resin profiles (right) at various depths for 8 mm thick three layer pultruded polyester glass laminate, subject to one sided heat flux of 50 kW m^{-2}**

14 *a* modelled thermal profiles and *b* residual resin profiles at various depths for 8 mm thick three layer pultruded phenolic glass laminate, subject to one sided heat flux of 50 kW m^{-2}

requires mechanical properties as functions of temperature, detailed above. The calculation steps involved in the model are shown in Fig. 15.

The transformed stiffness matrix $\bar{Q}$ of each layer of the composite is calculated as function of temperature. The $\bar{Q}$ matrix is used to calculate the A, B and D matrices as function of temperature

$$A = \sum_{k=1}^{n} \int_{h_{k-1}}^{h_k} \bar{Q} \, dx;$$

$$B = \sum_{k=1}^{n} \int_{h_{k-1}}^{h_k} \bar{Q} x \, dx; \quad D = \sum_{k=1}^{n} \int_{h_{k-1}}^{h_k} \bar{Q} x^2 \, dx \tag{5}$$

In this case, account needs to be taken of the variation of properties through each ply, due to the changes in temperature and residual resin content. This requires a numerical integration in addition to the conventional ply by ply summation. The applied loads (in plane forces and bending moments) are related to the resulting deformations (mid plane strains and curvatures) through the familiar 'ABD' matrix relationship

$$\begin{bmatrix} N \\ M \end{bmatrix} = \begin{bmatrix} A & B \\ B & D \end{bmatrix} \begin{bmatrix} \varepsilon_0 \\ k \end{bmatrix} \tag{6}$$

where N and M are the matrices of normal loads and bending moments, and ε_0 and k are the mid plane strains and curvatures. When the input parameters are loads, it is often preferable to employ the fully inverted version

$$\begin{bmatrix} \varepsilon_0 \\ k \end{bmatrix} = \begin{bmatrix} A' & B' \\ B' & D' \end{bmatrix} \begin{bmatrix} N \\ M \end{bmatrix} \tag{7}$$

In order to use laminate theory, the material has been considered to be composed of three layers, with the properties of each layer varying with temperature and resin content. The data for the core were determined experimentally, but it was not possible for the continuous strand mat (CSM) outer layers because they were too thin to separate from the core. These data were
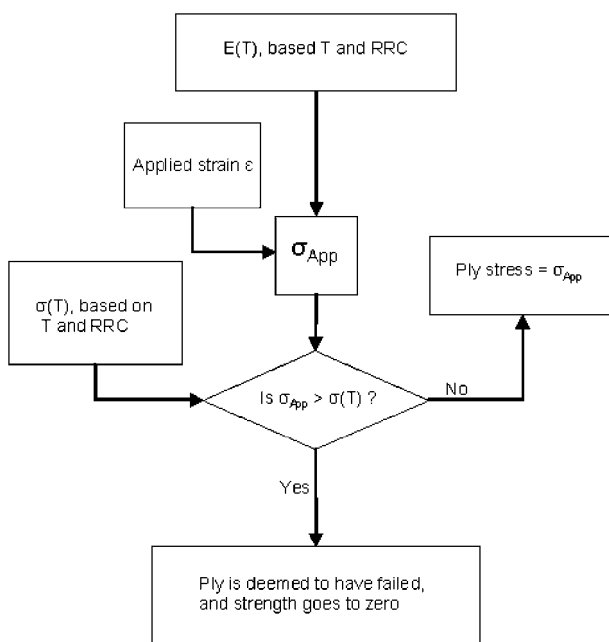
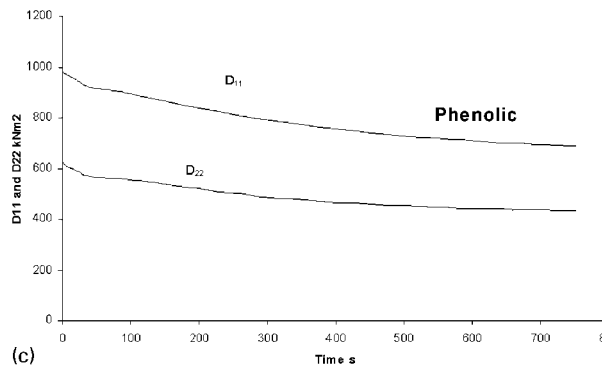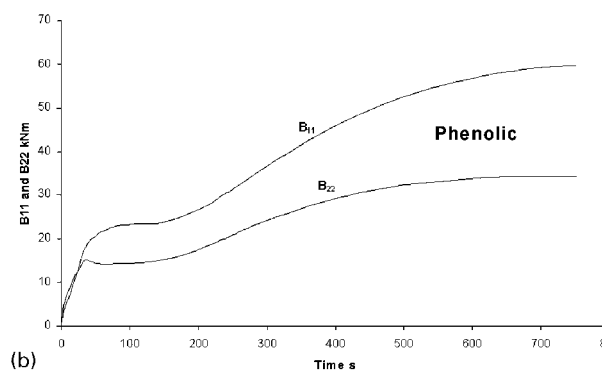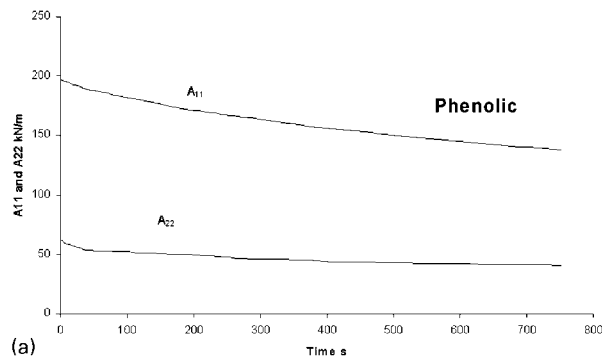15 Flow chart of model for fire behaviour under load
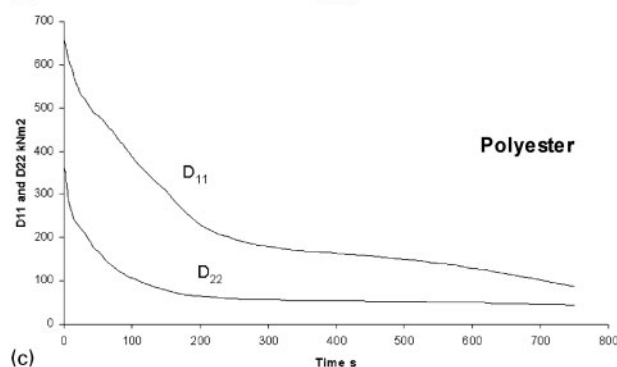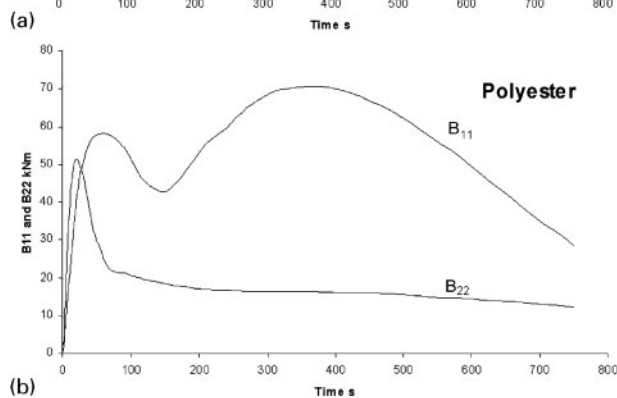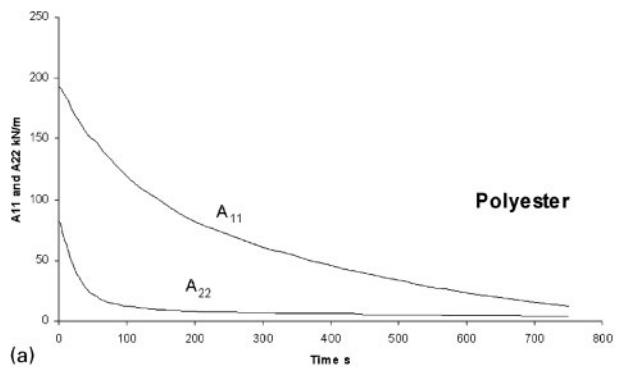
(a)

(b)

(c)

a A_{11} (upper curve) and A_{22} (lower curve); *b* B_{11} (upper curve) and B_{22} (lower curve); *c* D_{11} (upper curve) and D_{22} (lower curve)

16 Modelled evolution of *ABD* matrix components with time for 8 mm thick polyester pultrusion exposed to one sided heat flux of 50 kW m^{-2}

a A_{11} (upper curve) and A_{22} (lower curve); *b* B_{11} (upper curve) and B_{22} (lower curve); *c* D_{11} (upper curve) and D_{22} (lower curve)

17 Modelled evolution of *ABD* matrix components with time for 8 mm thick phenolic pultrusion exposed to one sided heat flux of 50 kW m^{-2}

calculated using a combination of sandwich beam theory and data from literature. The data describing compressive strength as a function of temperature were determined entirely experimentally, as described above. In this case, splitting the material into its three layers was deemed unnecessary. This was due to the almost negligible effect the CSM needle weave layers would have on the materials' compressive strength. The sandwich beam method considers the material as a typical sandwich beam and utilises the expression

$$E_{\mathrm{Full}} = E_{\mathrm{UD}} \frac{t_1^3}{t_2^3} + E_{\mathrm{CSM}} \left(\frac{t_2^3}{t_2^3} - \frac{t_1^3}{t_2^3} \right) \quad (8)$$

where E_{Full} is the flexural modulus of the full section of material, E_{UD} is the flexural modulus of the core material and E_{CSM} is the flexural modulus of the skin material. The thickness of the full section is t_2 and the thickness of the core material is t_1. This calculates the flexural modulus for the CSM skins from the flexural modulus of both the core material E_{UD} and the full

section E_{Full} (both obtained experimentally). The resulting flexural modulus E_{CSM} is the same in both perpendicular and longitudinal directions.

It was found that all the mechanical properties of the core and skin material could be described with equation (1). As mentioned above, the fitting parameters are shown in Table 2.

ABD matrix evolution

Figure 16 shows the evolution of the *ABD* matrix components for an 8 mm polyester pultrusion using the laminate failure model and Fig. 17 shows the corresponding predictions for the 8 mm phenolic pultrusion.

The *A* matrix components, which relate in plane loads and deformations, decline over time reflecting the decline in overall mechanical properties. This decline is much more marked in the polyester material when compared to the phenolic, due to phenolic composites retaining elastic properties up to higher temperatures. The *B* matrix components describe the interaction
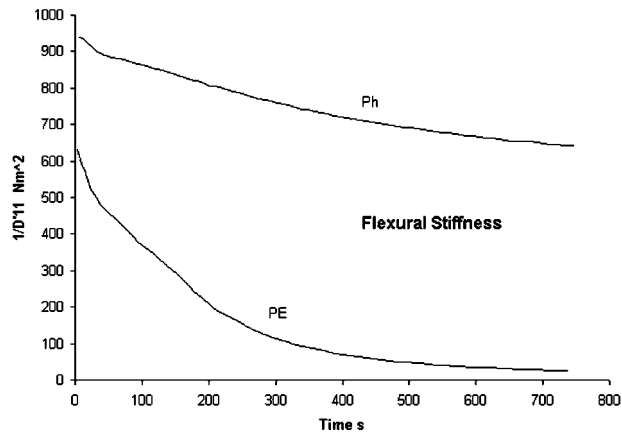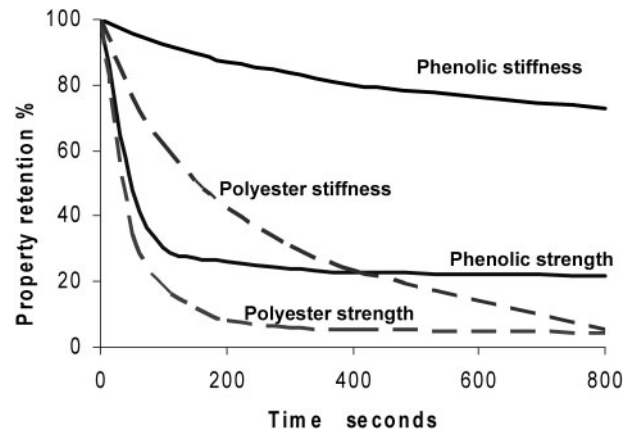
18 Modelled evolution of flexural stiffness $1/D'_{11}$ for 8 mm thick phenolic and polyester pultrusions, exposed to one sided heat flux of 50 kW m^{-2}

19 Normalised comparison of property retention for 8 mm thick phenolic and polyester pultrusions, exposed to one sided heat flux of 50 kW m^{-2}: phenolic: continuous curves; polyester: broken curves

between the in plane loads and out of plane bending and twisting. This value is initially 0 due to the symmetry of the material in the through thickness direction. The B terms rise to a peak as the CSM skin is burnt away causing a symmetrical imbalance. A second, larger peak is caused by further asymmetry as the UD core material is degraded. Finally, in the case of the polyester pultrusions, the B matrix terms decay as the full section of the product passes its glass transition and begins to decompose. This double peak in the case of B_{11} is not observed in laminates having a uniform structure throughout. Monolithic glass/polyester and glass/vinyl ester laminates showed only one single large peak.[3,4,9,15] The phenolic pultrusions also show a double peak, but the contribution of the CSM skins is less strong, and the final decay has only just begun to set in by the end of the simulation period, indicating significantly better stiffness retention.

The D matrix components, governing bending resistance, decline with time for both resin systems, but again, the phenolic system shows a much slower rate of decline than the polyester. The influence of the progressive asymmetry can be seen with the small shoulders that can be observed on the curves. These coincide with the peaks in the B matrix curves.

The bending stiffness of laminates is related primarily to the term $1/D'_{11}$ in the inverted ABD matrix (equation (7)). Figure 18 shows the evolution of $1/D'_{11}$ for the polyester and phenolic pultrusions. This is equivalent to the flexural stiffness parameter 'EI'. Once again this declines over time reflecting the decline in overall mechanical properties. As with the D matrix components, a shoulder is visible on the curves, again reflecting the progressive asymmetry. As with the A matrix parameters, this decline is far more significant in the polyester material, due to the phenolic material maintaining its mechanical properties at higher temperatures.

Finally, Fig. 19 shows a comparison of the property retention of the two types of laminate, normalised to percentage values. The pultruded laminates tested in this project are, under normal circumstances, part of much larger pultruded sections. It has been assumed in preparing the data for Fig. 19 that the key strength parameter is the compressive strength, since most structural pultrusions will be loaded either in compression or

flexure, which involves compression of some surfaces. This is the parameter that has been normalised to produce the strength curves. The key stiffness parameter was considered to be the A matrix leading term, so this too was normalised. Figure 19 underlines some interesting conclusions. The first is that strength falls away much more steeply than stiffness in fire. The second is that the phenolic system does show significantly improved behaviour, compared to polyester. In the polyester case, both stiffness and strength decay within 800 s to very low values. By contrast, 72% of the phenolic stiffness and 22% of the strength are retained at that time. It appears therefore that, in a structural application, phenolic pultrusions can retain useful properties in fire, especially if the main requirement is stiffness. The strength would be acceptable after 800 s if a sufficiently large safety factor[4,6] were used. Safety factors of this magnitude are not uncommon in some composite structures.

It should be borne in mind that the generally favourable results reported here for phenolic pultrusions do not apply universally to phenolic laminates. Some phenolic composites, particularly those produced by low temperature curing,[16] can be prone to severe delamination behaviour during fire, due mainly to the pressure generated by the vaporisation of water that can be present in the laminate from the curing operation. It has been shown[16] that it is necessary to remove this water to achieve good fire properties. In the case of pultrusions, the elevated temperature cycle involved in cure appears to be very effective in accomplishing this. A secondary factor may be fibre architecture: it may be that the woven fabric reinforcement often employed in cold cured laminates contains more intrinsic weak points for delamination than the three layer structure of mats and unidirectional composite used in pultrusions.

Conclusions

The thermal model based on the Henderson equation can predict temperature evolution through a pultruded composite and the empirical tanh function (equation (1)) can be used to describe mechanical properties. Both polyester and phenolic pultrusions retained a significant residual strength under tensile load, due to

the residual strength of the glass fibres. However, pultruded composites, like other organic matrix composites, are particularly susceptible to compressive failure when subjected to fire, due to the loss of properties when the resin T_g is reached.

The fire reaction properties reported here showed the phenolic pultrusions to perform better than polyesters in all fire reaction properties (time to ignition, heat release, smoke and toxic product generation).

The mechanical measurements under load in fire showed that phenolic pultrusions decayed at a much slower rate than the polyester, due mainly to the very shallow glass transition of the phenolic, but also the char forming characteristic of the phenolic. It appears that phenolics can retain a substantial degree of stiffness in fire (72%) along with 22% of strength after 800 s. These conclusions of course apply to 8 mm thick sections in a 50 kW m^{-2} fire. The model described here would probably be capable of modelling other thickness or heat flux conditions.

The fire integrity reported here for phenolic pultrusions is superior to that reported elsewhere for phenolic laminates.[16] The main factor influencing integrity appears to be water content. A secondary factor is fibre architecture.

Acknowledgement

References

1. J. Bausano, S. Boyd, J. Lesko and S. Case: Proc. Composites in Fire-3 Conf., Newcastle, UK, September 2003, University of Newcastle upon Tyne, Paper 4.
2. A. G. Gibson, P. N. H. Wright, Y-S. Wu, A. P. Mouritz, Z. Mathys and C. P. Gardiner: *Plast. Rubber Compos.*, 2003, **32**, 81–90.
3. A. G. Gibson, Y. S. Wu, J. T. Evans and A. P. Mouritz: *J. Compos. Mater.*, **38**, 2004, 1283–1307.
4. A. G. Gibson, A. P. Mouritz and Z. Mathys: *J. Compos. Mater.*, **38**, 2004, 1283–1306.
5. S. Feih, Z. Mathys, A. G. Gibson and A. P. Mouritz: *J. Compos. Mater.*, 2007, **41**, 2387–2410.
6. S. Feih, Z. Mathys, A. G. Gibson and A. P. Mouritz: *Composites Part A*, 2007, **38**, 2354–2365.
7. R. C. Easby: 'Fire behaviour of pultruded composites under load', PhD thesis, University of Newcastle, Newcastle, UK, 2006.
8. L. Couchman and A. P. Mouritz (eds.): 'Modeling of naval composite structures in fire', 109–142; 2006, Melbourne, Vic., Acclaim Printing.
9. A. P. Mouritz and A. G. Gibson: 'Fire properties of polymer composite materials'; 2006, Dordrecht, Springer
10. J. B. Henderson, J. A. Wiebelt, and M. R. Tant: *J. Compos. Mater.*, 1985, **19**, 579–594.
11. Fiberline Composites A/S: 'Fiberline design manual'; 2007, Middelfart, Fiberline Composites A/S.
12. V. Babrauskas: *Fire Mater.*, 1994, **8**, 81–95.
13. B. Budiansky and N. A. Fleck: *J. Mech. Phys. Solids*, 1993, **41**, 183–211.
14. 'Advanced composite compression tests', BSS 7260, The Boeing Company, Seattle, WA, 1986.
15. T. N. A. Browne: 'A model for the structural integrity of composite laminates in fire', PhD thesis, University of Newcastle upon Tyne, Newcastle, UK, 2006.
16. S. Feih, Z. Mathys, G. Mathys, A. G. Gibson, M. Robinson and A. P. Mouritz: *Polym. Degrad. Stabil.*, 2007, to be published.