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FLAME RETARDANT COMPOSITE MATERIALS
Measurement and modelling of ignition properties

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Abstract

Flame retardant additives offer a potential short-term solution for reducing the combustibility of composites, and hence the reduction of the associated hazards. A brief review of fire modelling was performed to identify suitable mathematical expressions with which the results of the experimental flame retardant investigation were analysed. These were then used in a limited trial to compare the experimental and calculated ignition parameters. The comparison of simple mathematical equations with fire test results indicated that their ability to reasonably reproduce the experimental ignition parameters of the flame retardant treated composites is dependent on the mechanism of flame retardant activity, particularly the stage of combustion at which it is designed to be active.

Keywords: composite materials, flame retardants, ignition properties, mathematical estimation

Introduction

This paper reports the findings of a limited trial performed as part of a wider experimental study primarily focussed on assessing and mitigating the hazards associated with combustion of fibre reinforced composite materials [1]. A range of commercially available flame retardants were being methodically assessed in a selected composite system (epoxy resin 8552 with 8 plies of T800 carbon fibre reinforcement). The flame retardants were incorporated into the resin as individual additives at various levels (10, 20 and 40% by mass) and from this some combinations of flame retardants were selected and fire tested from 40 to 70% by resin mass. The latter set of materials were very difficult to process, so coupling agents were added to improve the viscosity of the uncured resin, and hence the quality of the cured panels.

The costs of materials, manufacturing, quality control and then fire testing of a large number of composite panels, as would be needed for an extensive comparison of flame retardants in the same baseline composite material, are significant. So the requirement for a quick, simple and cost effective screening technique was identified. The aim of the investigation reported here was to determine if simple fire equations could be used to give indicative results for flame retarded composites, and so fulfil this purpose.

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In the first instance a brief review of the literature on fire behaviour ‘modelling’ was performed [1]. This was done in order to identify an appropriate expression or equation to fulfil the requirement for a quick and simple method of generating values, indicative of experimental results. Two areas were selected for investigation, ignition and heat release, as these are important parameters in fire behaviour. If a material does not ignite, then the fire risk, particularly the fire propagation risk, is significantly reduced, and post ignition, the rate of heat release is a governing parameter of fire growth rate. This paper concentrates on the consideration of ignition properties and only the pertinent aspect of the literature review is detailed in the next section.

Brief literature review

List of symbols

A=rate constant
$\beta=L_v/C\Delta T$
C=heat capacity
C_p=specific heat capacity
C_2 – depends on radiant absorptance and volumetric heat capacity
k=thermal conductivity
L=thickness of sample
L_0=initial sample thickness
L_v=latent heat of vaporisation
m=mass
q''=rate of heat release
m''=mass loss rate, pyrolysis rate, or mass conversion rate
$q_p=q(T_p)$
$q^*=1/\Delta T\int_{T_a}^{T_p}q(T)\mathrm{d}T$
Q_i=ignition threshold
Q_{ext}=applied heat flux
$Q_{net}=(q''-q''_{cr})$ heat flux to the sample minus critical heat flux for ignition
ρ=density
t=time
t_i=time to ignition
T=temperature
T_a=ambient temperature
T_i=ingition temperature
T_{crit}=critical mass loss rate temperature
T_p=vaporisation temperature
$\Delta T=(T_i-T_a)$
$\theta=(T-T_a)/(T_p-T_a)$
$v'=\rho L_v/q\ \mathrm{d}s/\mathrm{d}t$
$v'^*=L_v/q_p(\mathrm{d}m''/\mathrm{d}t)_{crit}$

Ignition

When performing thermal analysis of a sample of material, consideration must be given to whether the sample is ‘thermally thick’, or ‘thermally thin’ [2, 3]. A sample can be considered thermally thin when temperature gradients may be neglected (i.e. the temperature may be assumed to be uniform through the thickness of the sample). A sample will be thermally thick when the temperature gradients may not be neglected. For thermally thin samples Eq. (1), relating heat transfer to temperature gradient may be assumed [2].

$$Q_{\mathrm{ext}}=mC_{\mathrm{p}}(\mathrm{d}T/\mathrm{d}t) \tag{1}$$

In order for ignition to occur a critical point has to be reached at which conditions for sustainable ignition are achieved. This critical point is reached when a sufficient rate of production of volatiles (i.e. pyrolysis rate) is reached, and maintained. This rate can be described in terms of production of volatiles, hence mass loss rate; or it can be described in terms of the surface temperature required to achieve the mass loss or volatile production rate. All of the ignition models identified in this review contain the value ΔT, the difference in temperature between ambient temperature, and that required for sustained ignition of the sample.

The ignition of thermally thin samples is mainly associated with the relaxed temperature profile, while for thick samples typically ignition requires attainment of higher temperatures at the surface alone [4]. Accordingly, thin samples require ignition heat inputs that are proportional to thickness and heat capacity. In contrast, thick samples require an amount of heat to ignite them that is determined by the conduction properties of the solid material, but independent of the thickness in the limit of the semi-infinite solid. The general conditions required for ignition are given in Eq. (2) [4].

$$Q_{\mathrm{i}}\equiv Q_{\mathrm{ext}}t_{\mathrm{i}}=C_2L \tag{2}$$

Most of the approximations for time to ignition appear to be based around similar equations, of which the simplest form appears to be Eq. (3) [2].

$$t_{\mathrm{i}} = \rho CL_0(T_{\mathrm{i}} - T_{\mathrm{a}})/Q_{\mathrm{net}} \tag{3}$$

A development of Eq. (3) allows calculation of time to ignition in relation to the external heat flux applied, as shown in Eq. (4) [5].

$$t_{\mathrm{i}}=\frac{\pi k\rho C}{4}\left(\frac{\Delta T}{Q_{\mathrm{ext}}}\right)^2 \tag{4}$$

When q'' is constant, that is there are no heat losses, then the ignition time can be obtained by using Eq. (5) [6]. However, when there are heat losses, this equation will underestimate the ignition time. A more realistic scenario for cone calorimeter tests is to assume that ignition occurs at a critical mass loss rate per unit area. In this case we can use the ablation model, Eq. (6) [6] and include Eq. (5) for the time taken for the surface to reach the ablation temperature, T_{p}. This results in the ignition time estimate expressed in Eq. (7) [6] assuming that the critical mass loss rate per unit area is less than the quasi-steady state value [6].

$$t_{\mathrm{i}}=k\rho C(T_{\mathrm{crit}}-T_{\mathrm{a}})^2/q^2 \tag{5}$$

$$\beta =1/(1-v')^2\mathrm{d}v'/\mathrm{d}t'+(1+\beta)v' \tag{6}$$

$$t_{\mathrm{i}}=\frac{k\rho C\Delta T^{2}}{q^{*2}}+\frac{\Delta Tk\rho L_{\mathrm{v}}}{q_{\mathrm{p}}^{2}}(1+\beta)\ln\left[\frac{1}{1-(1+\beta)v'^{*}/\beta}\right] \quad (7)$$

The ablation model in Eq. (6) is derived by taking the kinetic expression for the thermal degradation of a small sample, Eq. (8) [6] and integrating it with respect to y, through thickness co-ordinate, to give Eq. (9) [6]. When the sample is sufficiently thick Eq. (10) [6] can be taken as a good approximation to the temperature profile through the sample. Substituting the temperature profile, Eq. (10), into the integrated energy, Eq. (9), results in a good estimation for the regression, or mass loss rate. This regression rate expression is the ablation model already presented as Eq. (6) [6].

$$-\mathrm{d}m/\mathrm{d}T=Am^{\mathrm{n}}\exp(-T_{\mathrm{A}}/T) \quad (8)$$

$$\frac{\mathrm{d}\left[\int\limits_{s(t)}^{L}\theta\mathrm{d}y\right]}{\mathrm{d}t}+(1+\beta)\frac{\mathrm{d}s}{\mathrm{d}t}=\frac{q}{\rho C\Delta T} \quad (9)$$

where: $s(t)$=location of top surface;

$$\theta=\exp\{-[(q-\rho L_{\mathrm{v}}\mathrm{d}s/\mathrm{d}t)/k\Delta T](y-s)\} \quad (10)$$

Summary

It is clear from this brief review, there are three distinct levels of mathematical equations for consideration of fire behaviour of a material. These are equations defining specific properties, for example, thermal conductivity; basic equations defining a generic parameter or aspect of behaviour, for example, heat release rate; and complex sets of equations to be used in conjunction with boundary conditions, and intended for use in computer modelling applications. The finite difference and finite element models are inherently complex, costly, time consuming and require a significant amount of experimentally derived data as input. The equations describing the parameters, such as heat release rate, can be taken at different levels. For example, a generic equation can appear simple, but to solve these equations the data for the components must be available. If determination of the components is necessary prior to using the basic equation, then the situation can become very complex, as estimations of reaction rates are made by chemical kinetics, and attempts are made to account for the variable chemical species produced by the varied mechanisms of the free radical combustion reactions. To further this investigation it was decided to employ the generic parameter level of equation to determine whether the effects of using flame retardants could be predicted prior to experimentation.

Estimating critical ignition parameters

Model selection

Three Eqs were considered for use, (3), (11), a derivative of (3); and (4) [2, 5].

$$t_\mathrm{i}=\frac{\rho C_\mathrm{p} L_0 (T_\mathrm{i}-T_\mathrm{a})}{q''_\mathrm{net}} \tag{3}$$

$$t_\mathrm{i}=\frac{\rho C_\mathrm{p} L_0 (T_\mathrm{i}-T_\mathrm{a})}{Q_\mathrm{in}-Q_\mathrm{out}} \tag{11}$$

$$t_\mathrm{i}=\frac{\pi k\rho C}{4}\left(\frac{\Delta T}{Q_\mathrm{ext}}\right)^2 \tag{4}$$

Approximations (3) and (11) rely on prior knowledge of the temperature at which ignition occurs, the heat flux at which ignition occurs, or both. As this leaves two unknowns in Eq. (3), it is not a viable solution for this application. For adequate solution of Eq. (11), all aspects of the outgoing heat flux would need to be included, conductive, convective, radiative and re-radiative. This requires inclusion of chemical kinetic considerations, and the solution becomes very complex. Equation (4) includes only one unknown, ΔT, or (T_i–T_a). Ambient temperature (T_a) is known. By rearranging Eq. (4), T_i can be calculated according to Eq. (12), and this will give an indication of whether the flame retardant additives have an impact on ignition in terms of increasing the energy, or heat input required. Experimental ignition times (t_i) from cone calorimeter results can be used.

$$\Delta T=q''_\mathrm{ext}\sqrt{\left[\frac{4t_\mathrm{i}}{\pi k\rho C_\mathrm{p}}\right]} \tag{12}$$

Ignition model assumptions and limitations

The thermal conductivity, density and heat capacity were required for all materials. Initially the values were to be derived by calculating the proportional contributions of the reinforcement (*f*), matrix (*m*) and additive (*a*) to each of these properties, using the relative volume fraction Eq. (13) [7], where *x* represents the property (density, heat capacity or thermal conductivity). However, the combined system may respond differently when reacted from the values generated by individual components, so experimental measurements of the properties were performed. Measuring the properties also overcame the issue that, using Eq. (13) for thermal conductivity, calculations are restricted to the axial direction for the fibres.

$$x=v_\mathrm{f}x_\mathrm{f}+v_\mathrm{m}x_\mathrm{m}+v_\mathrm{a}x_\mathrm{a} \tag{13}$$

As this was a preliminary study, the estimation calculations and experimental work for comparison were only performed on a small number of specimens. The specimen set selected included the baseline composite material, as a control, and six other samples of the same composite, each with one of six different flame retardants additives in the resin. The flame retardants used covered both physical and chemical mechanisms of activity. At this preliminary study stage they were included as individual additives, rather than adding combinations of flame retardants, this was done to simplify the analysis of the results. The flame retardants were included in the composites at 20% resin mass. This level was selected as it was expected to be sufficiently high to show any effects from the flame retardant additives. To include the additives at higher percentage levels required the use of coupling agents so that the composites could be easily processed to achieve a good quality panel with even additive distribution. This was not desirable, as the introduction of a coupling agent may make analysis of the results more complicated.

Experimental

Cone calorimetry

Cone calorimetry according to ISO 5660 Pt.1 [8] at 35 kW m^{-2} was used as it was realised at this stage that it was not possible to obtain ignition times from literature for these particular sample materials under these experimental conditions, so the measured times to ignition were included in the calculations. In addition, indicative measurements of the density, heat capacity and thermal conductivity of the composite samples were made.

Density

Density was measured by determining the mass both in and out of water, with the aid of a sinker, according to BS 903: Method A1 [9].

Thermal conductivity

Measurements of thermal conductivity and specific heat capacity were performed using a MDSC (modulated differential scanning calorimetry) technique. Although reported measurement techniques and calibration methods were taken into consideration [10–15], the method followed for thermal conductivity was one supplied by the instrument manufacturer, TA Instruments. By this method the thermal conductivity was measured by ‘the use of open sample pans which results in the application of the temperature oscillation to only one side of the test specimen.’ This results in the materials’ characteristics at the heated surface dominating the measurement. This is significant for the measurement of the composite samples in question, as the manual addition and processing of the resins with the flame retardants will have inevitably led to some variations in distribution of the additives, potentially creating a source of inaccuracies in the measured thermal conductivity results. In practice small specimens of two thicknesses were used for each material; a thin piece approximately 0.5 mm thick, and a thicker piece approximately 2 mm thick were used, the latter typically being the full thickness of the cured composite. Specimens of both thicknesses were approximately disk shaped with diameters of 6 mm. Thermal conductivity measurements were taken from the back face of the specimen in order to determine heat transfer through the material. The thinner specimens were sufficiently thin to allow full heat transfer to the back face, while the thicker specimens were sufficiently thick to impede full heat transfer to the back face. Using the difference in measured values a thermal conductivity value for the material was calculated.

Heat capacity

The MDSC introduces heat through the base plate on which the specimen is mounted. By this method, specific heat capacity was measured directly. The base test temperature for all of the MDSC measurements made was 296 K. It is known that specific heat capacity does vary with temperature, and ideally the specific heat capacity for each material would have been measured at the temperature of activity, i.e. the combustion temperature for each of the flame retarded materials. However, as the materials may show different combustion temperatures due to the different flame retardant mechanisms, the resultant measurements of specific heat capacity at different temperatures would not be directly comparable. So the decision was made to make the specific heat capacity measurements all at one temperature to minimise additional variables, and increase the direct comparability of the calculated results. 296 K was selected as this was the assumed ambient temperature value used in the estimation calculations.

Ignition model calculations

The estimations were performed on a limited material set, comprising a control and six materials with selected flame retardants, with different mechanisms of action, as described in the previous section. The calculations were performed according to Eq. (12), with the ambient temperature value added to the right hand side of the equation, to leave the ignition temperature in Kelvin as the result for each material. The values required for this calculation (with the exception of ambient temperature, T_a, taken as 296 K, and incident heat flux, Q_{ext}, taken as 35 kW m^{-2}), and the results (predicted ignition temperature) are listed for each material in Table 1.

Results and discussion

Results

From the results for ignition temperature presented in Table 1, it is evident that the addition of aluminium trihydrate (ATH) has the greatest beneficial effect, significantly increasing the ignition temperature. The reasons for the different effects on ignition temperature are the different mechanisms of reaction of the flame retardants.

Table 1 Mean density, specific heat capacity, thermal conductivity and predicted ignition temperature calculation results

Sample	Ignition time t_i/s	Thermal conductivity k/W m^{-1} K	Density ρ/g cm^{-3}	Specific heat capacity C_p/J g^{-1} K^{-1}	Predicted ignition temperature T_i/K
CF/8552+20% aluminium trihydrate	124	0.413	1.831	0.934	819
CF/LY5052+20% dimelamine phosphate	74	0.299	1.617	1.118	758
CF/8552+20% urea	68	0.279	2.041	0.987	730
CF/8552 control	90	0.386	2.195	0.941	716
CF/8552+20% zinc borate	105	0.454	2.308	0.945	703
CF/8552+20% ammonium pentaborate	91	0.385	2.195	1.015	703
CF/8552+20% boric acid	67	0.433	2.082	0.932	649

Specific heat capacity was expected to be the dominant influence on time to ignition, but the MDSC measurements showed the solid state specific heat capacity values not to vary significantly between the flame retardant treated composites. There may have been more significant differences in specific heat capacity if measurements had been done in the vapour phase, where many of the additives show their flame retardant activity.

It was not expected that thermal conductivity would exert the most significant influence on ignition temperature, although it was expected to have some effect on ignition time. Materials with higher thermal conductivity would be expected to show longer times to ignition, as the higher thermal conductivity would allow the incident heat to be distributed throughout the specimen, so taking longer for the whole specimen to reach the temperature required for ignition. This is an acknowledged effect, and has been the author's experimental experience with composite materials, particularly when comparing otherwise identical epoxy composite materials with glass fibre (lower thermal conductivity) and carbon fibre (higher thermal conductivity) reinforcement [1].

This effect was confirmed by the samples with the ATH and zinc borate additives, where higher thermal conductivity values than the control sample gave extended ignition times. The extent of the increase in time to ignition could not be directly experimentally related to the thermal conductivity, as this could also be influenced by other parameters or mechanisms. Contrary to this association, the sample with the boric acid additive showed a decrease in time to ignition relative to the control, despite a higher measured thermal conductivity value, this could again be due to the influence of other mechanisms, possibly early formation of a glassy thermal barrier layer.

The two materials with the significantly lower measured thermal conductivity values, those with the urea and dimelamine phosphate additives, did show reduced time to ignition values, as would be expected. Low thermal conductivity leads to localised retention of incident heat near the surface, the consequence of which would be local rapid heating to the temperature required for ignition. The material with the ammonium pentaborate additive gave a similar thermal conductivity to the control material, and a very similar measured time to ignition. With the exception of the material containing boric acid, these results support indications of a relationship between thermal conductivity and time to ignition.

Discussion

Some of the behaviour indicated by the results can be explained through reference to the mechanisms of action of the flame retardant additives. Some of these mechanisms, including decomposition routes have been described in literature.

Aluminium trihydrate: $2Al(OH)_{3\,(s)} \rightarrow Al_2O_{3\,(gl)} + 3H_2O_{(g)}$ [16]

Boric acid: $2H_3BO_{3\,(s)} \rightarrow B_2O_{3\,(gl)} + 3H_2O_{(g)}$ [16]

Ammonium pentaborate: $(NH_4)_2B_{10}O_{16}\cdot 8H_2O \rightarrow 5B_2O_3 + 2NH_3 + 9H_2O$ [17]

Decomposition routes for the other compounds have had to be assumed:

Zinc borate: $2ZnO\cdot 6B_2O_3\cdot 7H_2O_{(s)}\rightarrow 2ZnO_{(s)}+6B_2O_{3\,(s)}+7H_2O_{(g)}$

Urea: $2NH_2CONH_{2\,(s)}+3O_{2\,(g)}\rightarrow 2CO_{2\,(g)}+2NH_{3\,(g)}+N_2O_{(g)}+H_2O_{(g)}$

Dimelamine phosphate: $(C_3H_6N_6)_2\cdot H_3PO_{4\,(s)}+6O_{2\,(g)}\rightarrow H_3PO_{4\,(s)}+6CO_{2\,(g)}+$
$+4NH_{3\,(g)}+4N_{2\,(g)}$

although there is information published on their mechanisms of flame retardant activity [18, 19].

ATH acts by progressive release of water vapour as the material is heated. There is absorption of heat, firstly to thermally decompose the ATH to produce water, then by the water still in the composite, which then removes the heat as it vaporises and is evolved from the surface. Finally, in the vapour phase above the surface the water absorbs heat that would otherwise be incident on the surface. All these mechanisms reduce the heat available to the composite, delaying the onset of its thermal degradation and the production of volatiles [16]. In addition to the heat absorption activity, water in the vapour phase acts to dilute volatiles produced from thermal decomposition of the composite, maintaining their concentration below that required for sustained ignition for a prolonged period. The elevated ignition temperature of the ATH treated composite over the control material, indicated that this mechanism of production of large amounts of water does increase the heat input required to achieve sustained ignition.

None of the other flame retardants appeared to significantly improve the ignition temperature performance of the composite. This is due to the different mechanisms involved in their reactions to fire.

Dimelamine phosphate treatment of the composite did show a calculated, (though less than ATH), increase in ignition temperature. Dimelamine phosphate has a char formation mechanism [20]. Char is created at the expense of volatile production on thermal decomposition. This preferential production of carbonaceous char in the initial stages of thermal decomposition reduces the production and transport of volatiles to the material surface, hence the potential for sustained ignition. The temperature required to produce sufficient flow of volatiles for sustained ignition (the ignition temperature), is therefore increased by this mechanism. Potential reasons for eventual production of sufficient volatiles for ignition may include insufficient loadings of dimelamine phosphate, or loss of the phosphoric acid char promoting catalyst by vaporisation. Higher loadings of the flame retardant, or an additional source of phosphorus, in the material may sustain char formation for longer, so increasing the ignition temperature further.

A marginally elevated ignition temperature was calculated for the urea treated composite. This could be due to production of some ammonia gas generating a cooling effect as it evolves from the surface, and diluting the volatiles immediately above the material surface. Zinc borate and boric acid both evolve some water on heating, which will generate some cooling and diluting effects. However, the residual flame retardant, largely dehydrated (zinc) borate absorbs heat within the solid material, as these are glass forming materials [21, 22]. When the loading levels are sufficiently high, these can form glasses in the exposed surface layers, creating both a thermal and impermeable gas barrier. The latter prevents oxygen penetration into, and volatile escape from the material, slowing oxidative decomposition and minimising volatile transport to the flame, eventually extinguishing it. These mechanisms are targeted towards extinguishing a combusting solid, rather than preventing ignition.

At this (20% by resin mass) additive loading level, the mechanisms of cooling and dilution in the vapour phase appeared to be the most effective method of increasing the temperature required for sustained ignition. Preferential production of carbonaceous char at the expense of volatile decomposition products also increased the temperature required for sustained ignition, but not as significantly as that obtained by water production. This char formation mechanism might have proved to have a greater impact on ignition temperature at higher additive loading levels. However, panels with higher loading levels were of a poorer quality, showing inconsistent dispersion of the additives, hence would have given inconsistent experimental results. Use of a coupling agent was considered, but this would have added another variable for consideration when interpreting the results.

Conclusions

The equation:

$$\Delta T = q''_{\mathrm{ext}} \sqrt{\left[\frac{4t_{\mathrm{i}}}{\pi k \rho C_{\mathrm{p}}}\right]} \tag{12}$$

generated plausible critical ignition temperatures for the range of flame retardants considered, and supported the mechanism known for ATH (cooling and dilution by gas phase water production) by indicating a significantly increased ignition temperature. The overall trend from the results gave indicative support for a relationship between thermal conductivity and time to ignition, with materials with lower thermal conductivity expected to ignite earlier than their higher thermal conductivity counterparts due to localised heating effects.

The aim of using this basic model to predict the effect of the flame retardants on ignition parameters without performing experimental measurements was not achieved, as the t_{i}, C_{p}, k and ρ, experimentally measured parameters were required for the calculation. However, the calculations did provide a useful confirmation of the stage of activity of the different mechanisms of action of the flame retardants. This is demonstrated by the good indication, by increased predicted ignition temperature, of the cooling and dilution effects of ATH, a flame retardant aimed primarily at retarding ignition. By comparison there was a lack of influence on predicted ignition temperature by the glass forming additives, zinc borate and boric acid, where the mechanisms are typically activated once the polymer is undergoing combustion.

In summary, the ignition equation was successful in indicating significant differences in ignition temperatures, and confirmed the expected link between low thermal conductivity and early ignition. However, the requirement for experimental work negated the benefit of using the calculations to estimate or indicate the behaviour of flame retarded panels without the cost of procuring and manufacturing the materials.

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