

# Global kinetics of thermal degradation of flame-retarded epoxy resin formulations

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## Abstract

A predictive mathematical model to describe mass loss profiles of flame-retardant (FR) containing epoxy resin formulations is proposed. Mass loss is due to thermal degradation of the constituent components and can be described by a generic kinetic scheme with a given set of thermokinetic constants in the form of ordinary differential equations. The scope of this work is to determine the kinetic parameters of the thermal degradation of a known flame-retarded epoxy resin composition by using thermogravimetric analysis and using the acquired data to predict the degradation profiles for other formulations. The mass loss profiles of Visil and intumescent epoxy resin containing formulations were predicted by solving coupled systems of ordinary differential equations and then using Powell minimisation to find the optimal Arrhenius parameters, taking into account the mass ratio of the components in the mixture. The calculated kinetic constants for one formulation (85% resin–15% FR additives) are used to predict the mass loss profiles for other formulations (80% resin–20% FR additives and 90% resin–10% FR additives) with the assumption that the degradation mechanism does not change. The predicted thermal degradation profiles are compared with experimental data acquired using standard laboratory equipment in order to validate the proposed mechanisms. The kinetic parameters obtained adequately describe mass loss history of composite materials studied, even when extremely simplified kinetic schemes have been used.

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*Keywords:* Thermal degradation; Powell minimisation algorithm; Kinetic parameters; Flame-retarded epoxy resin

## 1. Introduction

Polymer matrix composites (PMCs) are widely used in automotive, aerospace and marine applications because of their high specific strength (weight to stiffness ratio) [1–3]. The most favourable characteristic of PMCs in automotive and aerospace industries is their lightness which leads to a lower fuel consumption. On the other hand, their resistance to corrosion allows PMCs to be used in the marine industry, for piping and chemical storage. Alongside the lingering concern about their end use recyclability, is the inherent flammability problem of the polymer matrices; they easily ignite and their combustion often leads to the evolution of toxic gases [4].

A feasible solution to improving the fire resistance of polymer matrix formulations is via incorporation of both non-reactive and reactive fire-retardant additives [5–7]. The additives which normally constitute 15–20% of the composite weight may form either an intrinsic part of the composite itself, or be employed in an external, add-on manner.

This study is part of a larger research project into the prediction of combustion-induced mechanical property degradation of flame-retardant structural composites. We are developing a micromechanics model to predict the degradation in mechanical properties of PMCs with temperature. In order to provide a model that adequately simulates the real world behaviour of composites under fire, the transport phenomena (mass, heat and momentum transfer) have to be described appropriately. Some of this information can be extracted from examining the global intrinsic kinetic constants during both thermal and oxidative degradations of resin formulations.

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Intumescent chemical fire-retardant systems are often used to improve the fire resistance of polymers [8–11]. The active ingredients used are generally an acid source such as ammonium polyphosphate (APP) or an inorganic acid such as boric acid, a source of carbon such as char forming polymers or polyols and a blowing agent such as melamine [12]. These additives are designed to swell into a thick, robust foam of low conductivity and low density following exposure to a heat source, restricting the flow of combustible volatiles and oxygen into the pyrolysis zone. The char layer formed at the surface of the material serves to slow down heat transfer into the interior of the polymeric material thus protecting the material from fire damage.

The flame retardancy of modified polymeric materials does not only depend on the thermal stability of the constituent elements, but also on their rate of degradation, rate of char formation and the amount of residual char. Intumescent formulations need to be optimised with regards to their proportions, physical and chemical properties so that they can efficiently form a protective char layer. While it is possible to use parametric designs for thermogravimetric analysis (TGA) to investigate the thermal stabilising efficiency of different mixtures, the cost of performing these experiments can be averted through the use of a predictive global mathematical tool that is based on a simplified model of a complex thermal decomposition scheme.

The aim of this study is to obtain a global mechanism and mathematical model that accurately describe the decomposition kinetics of epoxy resin formulations containing varying amounts of flame-retardant viscose fibres, Visil and an intumescent (Antiblaze, NH). Thermogravimetric curves were measured at a heating rate of 10 °C/min for the epoxy resin, Visil and intumescent individually and also for their physical mixtures. A multi-step kinetic scheme was evaluated for one of the formulations and the obtained kinetic constants used to predict the mass loss profiles for different other formulations at the same heating rate assuming the decomposition mechanism is composition invariant.

## 2. Experimental

### 2.1. Materials and physical experiments

Bisphenol-F epoxy trifunctional resin (Hexcel Composites Ltd), Visil, a cellulosic fibre containing polysilicic acid, in pulverised form (Sateri Fibres, Finland) and an intumescent (Antiblaze NH) containing melamine phosphate (Rhodia Specialities Ltd., now Albemarle) were used as received. Formulations analysed are presented in Table 1. Thermogravimetric analysis and differential thermal analysis (DTA) were performed on an SDT 2960 simultaneous DTA–TGA instrument from 50 to 1000 °C using 10 ± 1 mg samples heated at 10 °C/min with air as the purge gas (flow rate, 100 ± 5 mL/min). The experiments were performed in triplicates and showed good reproducibility. Derivatised thermogravimetric (DTG) curves have been used to precisely define mass loss stages and for the validation of the mathematical models.

Table 1  
Epoxy, Visil and intumescent formulations analysed

Sample	Resin [%]	Visil [%]	Intumescent [%]
Resin	100	0	0
Visil	0	100	0
Intumescent	0	0	100
Resin + 5% Visil + 5% Intumescent	90	5	5
Resin + 7.5% Visil + 7.5% Intumescent	85	7.5	7.5
Resin + 10% Visil + 10% Intumescent	80	10	10

### 2.2. Mathematical modelling

In solid state reactions, the rate of thermal decomposition of a reactant can be approximated via a kinetic scheme:  $d\mathbf{m}/dt = \mathbf{f}(\mathbf{m})$ , where  $\mathbf{m}$  is a vector of mass fractions, and  $\mathbf{f}$  is a vector-valued function representing the degradation mechanism. When the reaction is assumed to be first order, the rate of decomposition is directly proportional to the concentration of the reactant,  $m$  and becomes

$$\frac{d\mathbf{m}}{dt} = |\mathbf{K} \mathbf{m}| \quad (1)$$

where  $|\mathbf{K}|$  is a matrix of Arrhenius reaction rates.

First order decomposition rate constants are usually assumed to have Arrhenius dependency on temperature and are directly proportional to the mass fraction of the reactants,  $m$ . The rate constants are given as

$$k_i = A_i \exp(-E_i/RT), \quad i = 1 \dots \infty, \quad (2)$$

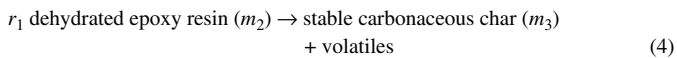
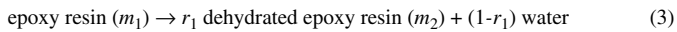
where  $A$  is the pre-exponential factor,  $E$  is the activation energy and  $T$  is the sample temperature. The sample temperature is a known function of time  $t$ :  $T = T_0 + \beta t$ , where  $T_0$  is the initial temperature and  $\beta$  is the heating rate.

The determination of kinetic parameters involves generating several candidate solutions derived from anticipated decomposition chemistry followed by proposition of a decomposition mechanism consisting of sequential reactions in the form of Eq. (1) to yield a series of ordinary differential equations (ODEs) for respective mass fractions. The ODEs are coupled and solved numerically using the Runge–Kutta algorithm. The parameters sought, viz., stoichiometric coefficients  $A$  and  $E$  are estimated using literature methods [13] and then optimised via Powell's algorithm [14]. Optimised kinetic parameters were obtained for the resin, Visil and the intumescent independently and also for the physical mixture containing 85% resin, 7.5% Visil and 7.5% intumescent. The kinetic constants obtained for the latter were then used to predict mass loss profiles for other formulations in Maple 6.0<sup>®</sup> using an ODE solver for stiff equations (Isode) assuming that the kinetic parameters are independent of the mixture composition. The predictive model was then validated against experimental data.

### 3. Results

#### 3.1. Chemical kinetics

The decomposition profiles of the epoxy resin, Visil and the intumescent have been modelled at various heating rates with the assumption that the volatiles are released at discrete stages following a series of successive decomposition processes [14]. The proposed simplified decomposition mechanism for epoxy resin derived from publications by Rose and co-workers [15,16] is shown in Scheme 1 below:



Scheme 1. Simplified decomposition scheme for the epoxy resin.

Scheme 1 above can be represented by a system of ordinary differential equations which contain 8 unknown kinetic parameters governing the mass loss rate for a defined heating rate,  $\beta$ , in this case 10 K/min:

$$\frac{dT}{dt} = \beta$$

$$\frac{dm_1}{dt} = -k_1 m_1$$

$$\frac{dm_2}{dt} = r_1 k_1 m_1 - k_2 m_2$$

$$\frac{dm_3}{dt} = k_3 m_2 - k_4 m_3$$

Each of the reaction rates above is assumed to have an Arrhenius type dependence of the form in Eq. (2). Initial conditions describing the experimental environment are defined;  $T(0) = T_0$ ,  $m_1 = 1$ ,  $m_2 = 0$ ,  $m_3 = 0$  and  $\beta = 10$  K/min. Different volatile species are released sequentially over the whole

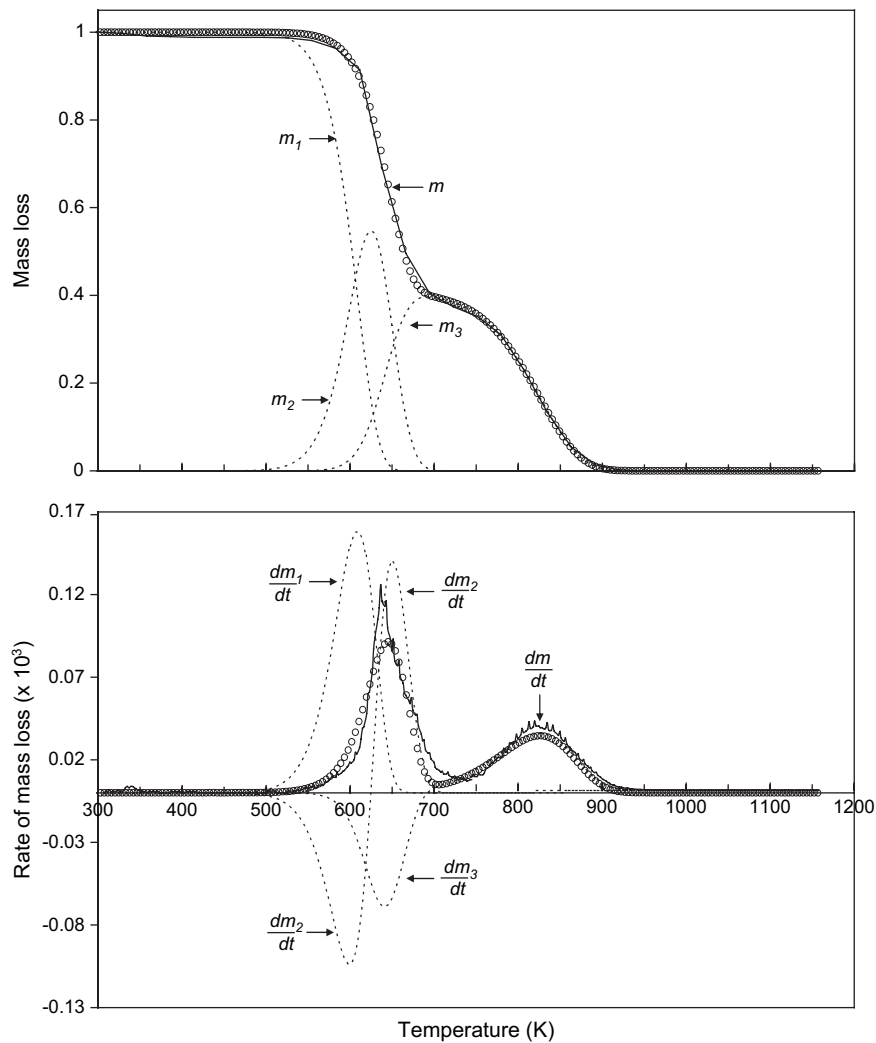


Fig. 1. Mass fractions and their temperature derivatives as functions of temperature as measured (lines) and calculated (circles) for the epoxy resin at a heating rate of 10 K/min (kinetic parameters are given in Table 2).

Table 2  
Optimised kinetic parameters for the resin

Kinetic constants	ln A	$E/R (\times 10^3)$ [K]
$k_1$	19.7	15.0
$k_2$	11.3	11.1
$k_3$	19.0	15.9
$k_4$	11.6	14.2

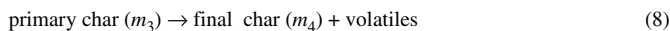
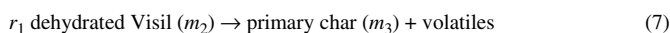
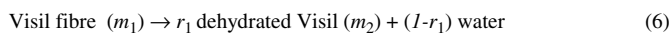
heating program and the overall mass loss rate is calculated from a linear combination of these individual rates:

$$\frac{dm_{\text{overall}}}{dt} = \sum_{i=1}^3 \frac{dm_i}{dt}$$

Fig. 1 shows calculated and measured mass fractions and rates of volatile release as functions of temperature for the epoxy resin. Good agreement is observed between the measured and calculated profiles. In the first stage (500–650 K) the resin is dehydrated and the amount of water lost is estimated from experimental data to be about 2% of the original weight. The dehydration of epoxy resin leads to the formation of a moisture free polymeric material,  $m_2$ , in the same temperature range. This is then followed by a conversion process to form a more stable carbonaceous material,  $m_3$ , with loss of volatiles in the temperature range of 550–700 K. Above 700 K the stable carbonaceous char further degrades to completion leaving no residue above 900 K.

Optimised apparent kinetic constants for the degradation of epoxy resin are shown in Table 2. While the obtained kinetic parameters are useful in describing the degradation profile in accordance with specified assumptions, a comparative study to other work is impractical since the materials, reaction models and mechanism assumed vary between authors. We also note that the uniqueness of the fit is not guaranteed given that we are attempting to describe a multi-faceted chemical reaction by using a grossly simplified mass loss model. However, for the purposes of this work, the results are sufficient.

Three stages of degradation are observed in the TGA curve of Visil fibre leading to the proposition of a decomposition scheme shown below (Scheme 2):



Scheme 2. Simplified decomposition scheme for Visil fibre.

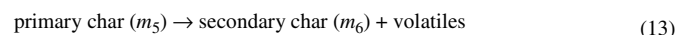
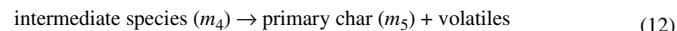
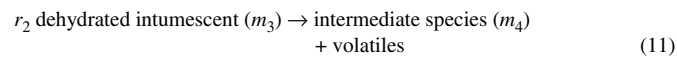
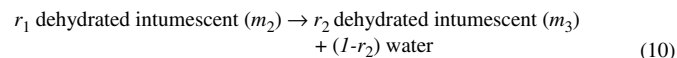
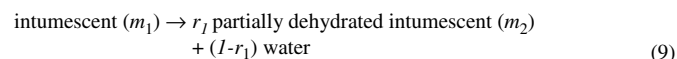
Initial conditions describing the experimental environment are defined here:  $T(0) = T_0$ ,  $m_1 = 1$ ,  $m_2 = 0$ ,  $m_3 = 0$ ,  $m_4 = 0$  and  $\beta = 10$  K/min. The calculated kinetic parameters for Visil fibre are presented in Table 3. Fig. 2 shows the calculated and measured mass fractions and rates of volatile release as functions of temperature for the cellulosic fibre. Following the first stage (dehydration) is the formation of a primary char,  $m_3$  (500–620 K) from the dehydrated

Table 3  
Optimised kinetic parameters for the Visil fibre

Kinetic constants	ln A	$E/R (\times 10^3)$ [K]
$k_1$	18.8	7.9
$k_2$	19.9	14.8
$k_3$	17.3	13.3
$k_4$	7.1	9.6
$k_5$	12.7	13.9

species  $m_2$ . Between 620 and 800 K,  $m_3$  begins to decompose forming a secondary and final char  $m_4$ . The calculated data and experimentally obtained data show an excellent agreement.

The thermal decomposition of the intumescent system is known to proceed via a number of distinct stages forming a complex mixture of volatiles and subsequently residual char. The possible stages describing the decomposition process are depicted in Scheme 3, illustrated below for prescribed initial conditions:  $T(0) = T_0$ ,  $m_1 = 1$ ,  $m_2 = 0$ ,  $m_3 = 0$ ,  $m_4 = 0$ ,  $m_5 = 0$ ,  $m_6 = 0$  and  $\beta = 10$  K/min.



Scheme 3. Simplified decomposition scheme for the intumescent.

Fig. 3 shows calculated and measured mass fractions and rates of volatile release as functions of temperature for the intumescent. Reasonable agreement is observed between the measured and calculated profiles. The decomposition stages are extensively discussed in a Ph.D. thesis published by Neisinger [14]. Physisorbed moisture is lost in two stages, viz. 500–560 K and 560–630 K regions to produce melamine pyrophosphate and melamine polyphosphate, respectively. The dehydration processes lead to the formation of  $m_3$ , melamine polyphosphate which then decomposes into an intermediate species melam ultraphosphate with the release of water, ammonia and melamine in the temperature region of 620–750 K. Unidentified phosphate–ultraphosphate–melamine type structures,  $m_5$ , are then formed via loss of volatiles in the temperature range of 730–830 K.  $m_4$  and  $m_5$  decompose in the same temperature region to yield  $m_6$  which is stable between 900 and 1100 K [17–19]. The optimised kinetic constants are presented in Table 4.

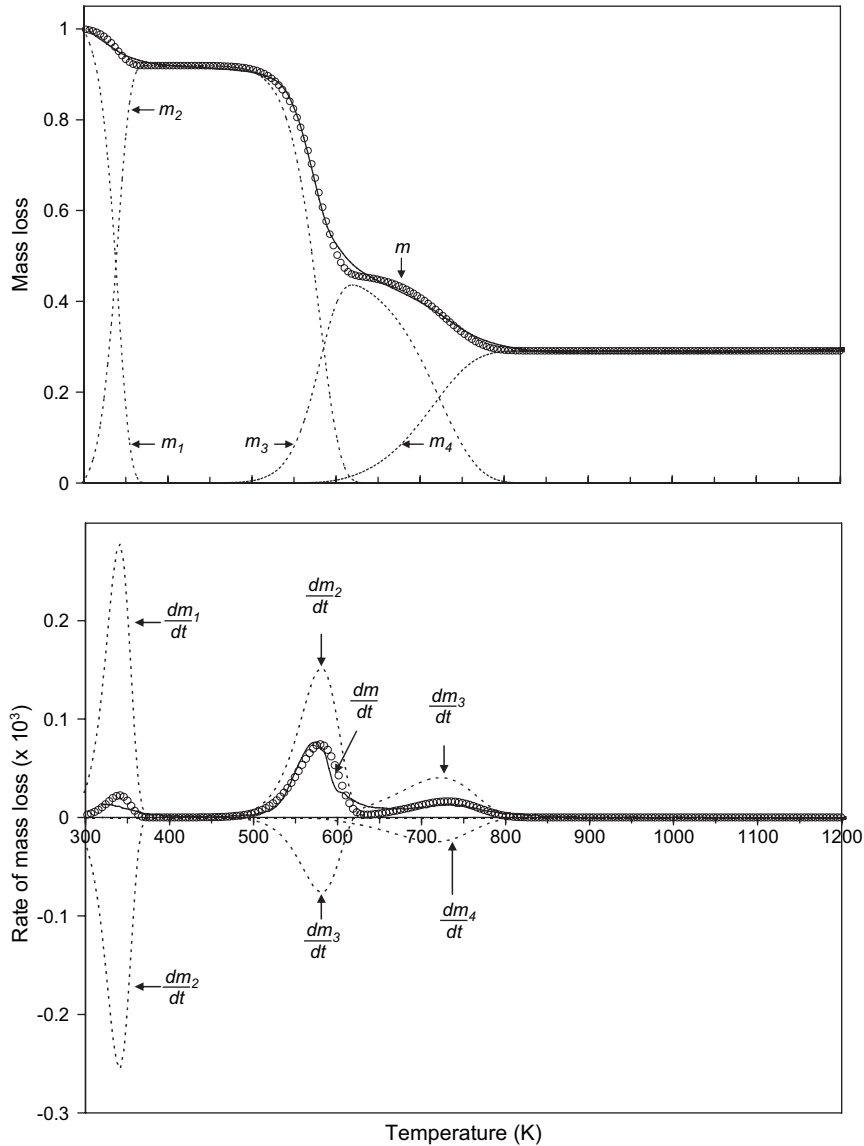


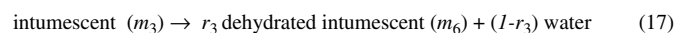
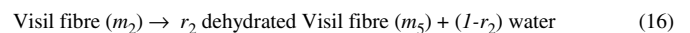
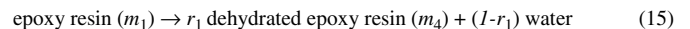
Fig. 2. Mass fractions and their temperature derivatives as functions of temperature as measured (lines) and calculated (circles) for Visil at a heating rate of 10 K/min (kinetic parameters are given in Table 3).

### 3.2. Predictive modelling

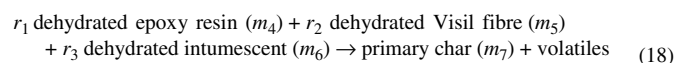
Having obtained kinetic constants for the individual components of the anticipated flame-retarded resin formulations, a model for the resin–Visil–intumescent system is proposed. While Neiningner [14] proved that Visil and the intumescent somewhat participate in interactive reactions to form a stabilised char, a more simplified, non-interactive scheme for the mixture is proposed to reduce the complexity of the problem at hand. It would be expected, however, that interactions must occur between certain species during the degradation process.

In this study, the three components are presumed to dehydrate independently, followed by collective primary char formation. The primary char then decomposes into a secondary and a final char with release of volatiles.

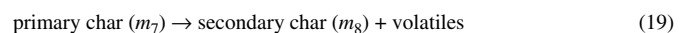
#### Stage 1: Dehydration



#### Stage 2: Cumulative char formation



#### Stage 3: Char oxidation



Scheme 4. Simplified decomposition scheme for resin–Visil fibre–intumescent physical mixtures.

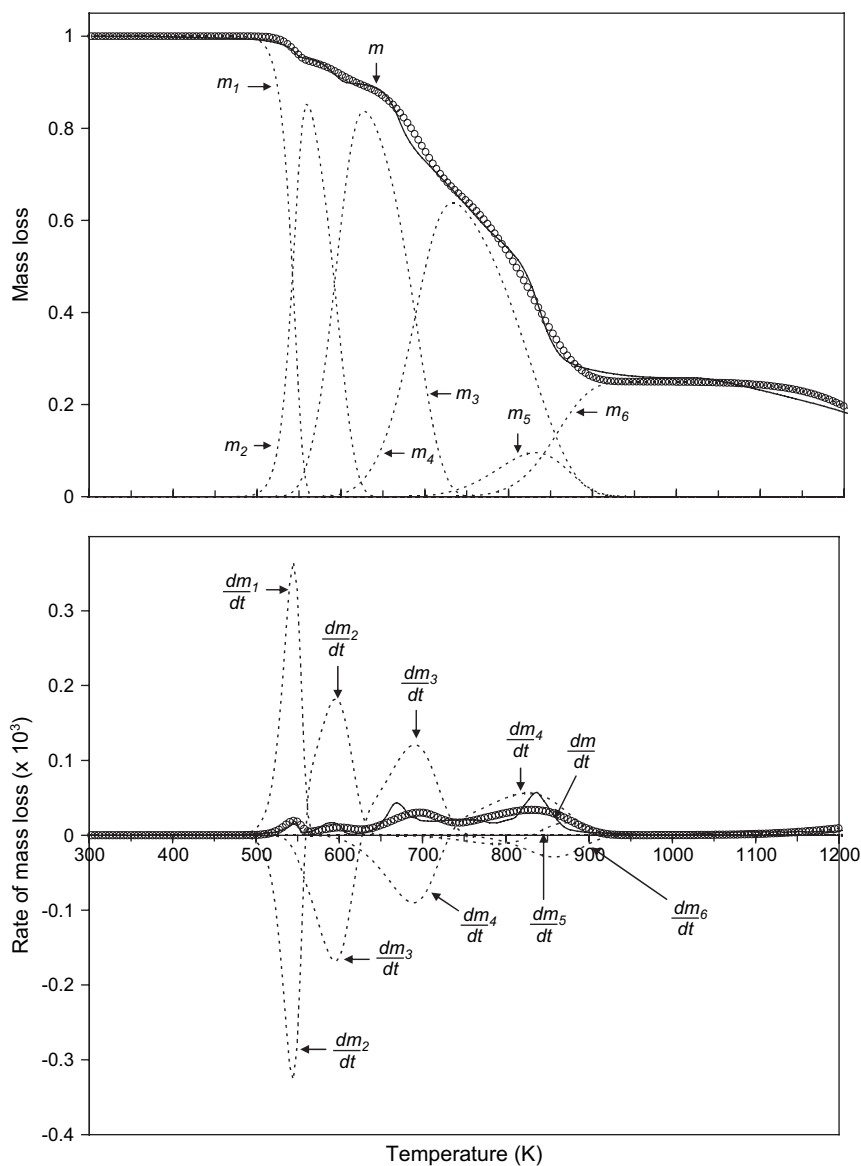


Fig. 3. Mass fractions and their temperature derivatives as functions of temperature as measured (lines) and calculated (circles) for the intumescent at a heating rate of 10 K/min (kinetic parameters are given in Table 4).

Table 4  
Optimised kinetic parameters for the intumescent

Kinetic constants	$\ln A$	$E/R (\times 10^3) [K]$
$k_1$	48.0	28.4
$k_2$	22.7	16.4
$k_3$	17.4	15.8
$k_4$	16.1	15.8
$k_5$	13.6	16.5
$k_6$	5.2	9.7
$k_7$	10.6	13.4
$k_8$	9.5	13.3
$k_9$	14.7	26.1

Several schemes to adequately describe the chemistry involved including interactive ones were attempted based upon an intelligent trial and error approach and the one shown above emerged the best. Scheme 4 describes the best simplified degradation mechanism of a physical mixture containing the resin, Visil and the intumescent.  $m_1$ ,  $m_2$  and  $m_3$  correspond to the mass fractions of the resin, Visil and intumescent in the physical mixture while  $r_i$  ( $i = 1, 3$ ) are the dehydrated fractions of  $m_i$ . Initial conditions are described as follows:  $T(0) = T_0$ ,  $m_1 = m_{i=1}$ ,  $m_2 = m_{i=2}$ ,  $m_3 = m_{i=3}$ ,  $m_4 = 0$ ,  $m_5 = 0$ ,  $m_6 = 0$ ,  $m_7 = 0$ ,  $m_8 = 0$  and  $\beta = 10$  K/min.

The complete and detailed description of this degradation process involves the solution to a system of coupled ordinary differential presented below:

$$\frac{dT}{dt} = \beta$$

$$\frac{dm_1}{dt} = -k_1 m_1$$

$$\frac{dm_2}{dt} = -k_2 m_2$$

$$\frac{dm_3}{dt} = -k_3 m_3$$

$$\frac{dm_4}{dt} = r_1 k_1 m_1 - k_4 m_4 - k_5 m_4$$

$$\frac{dm_5}{dt} = r_2 k_2 m_2 - k_6 m_5 - k_7 m_5$$

$$\frac{dm_6}{dt} = r_3 k_3 m_3 - k_8 m_6 - k_9 m_6$$

$$\frac{dm_7}{dt} = k_5 m_4 + k_7 m_5 + k_9 m_6 - k_{10} m_7 - k_{11} m_7$$

$$\frac{dm_8}{dt} = k_{11} m_7$$

Table 5  
Optimised kinetic parameters for the 85% resin + 7.5% Visil + 7.5% intumescent formulation

Kinetic constants	ln A	E/R ( $\times 10^3$ ) [K]
$k_1$	10.6	7.0
$k_2$	16.0	8.6
$k_3$	6.3	28.2
$k_4$	10.1	10.3
$k_5$	15.9	14.0
$k_6$	12.9	11.8
$k_7$	11.3	13.0
$k_8$	-7.5	16.1
$k_9$	9.9	14.4
$k_{10}$	10.9	14.2
$k_{11}$	4.6	10.0

The ordinary differential equations describing the formation and in some cases subsequent decomposition of species  $m_1$  through  $m_8$  involve 11 pairs of kinetic parameters for a physical mixture containing 85% resin, 7.5% Visil and 7.5% intumescent. The initial kinetic constant values used in the optimization program are from the schemes of individual components at the same heating rate of 10 K/min. The calculated parameters are presented in Table 5 and are used for predictive modelling purposes.

The calculated and measured mass fractions as functions of temperature for the physical mixture containing 85% resin, 7.5% Visil and 7.5% intumescent are shown in Fig. 4. An excellent agreement is observed between the measured and calculated profiles. The initial mass loss in the temperature range of 400–450 K is attributed to the dehydration of the constituent species,  $m_1$ ,  $m_2$  and  $m_3$  to form  $m_4$ ,  $m_5$  and  $m_6$ , respectively. The first stage is then followed by the decomposition of  $m_4$ ,  $m_5$  and  $m_6$  into collective char,  $m_7$ , with the loss of volatiles in the temperature region of 500–700 K. The primary char,  $m_7$ , is then converted into a secondary and a final char above 800 K [13].

The calculated kinetic parameters for the physical mixture described above are used to predict the mass loss profiles for other formulations containing varying proportions of the resin, Visil and the intumescent. While the simplified models may hardly describe the real degradation mechanism, they are appropriate for an approximation of different decomposition stages, which are normally observed as peaks in the derivative curves of mass loss [20]. We note here, the main assumption is that the proposed mechanism is not composition dependent at least in the range of formulations studied in this work.

Figs. 5 and 6 show mass fractions as a function of temperature for the 80% resin + 10% Visil + 10% intumescent and 90% resin + 5% Visil + 5% intumescent mixtures, respectively. A good agreement between the predicted data and the experimentally obtained data suggests that the

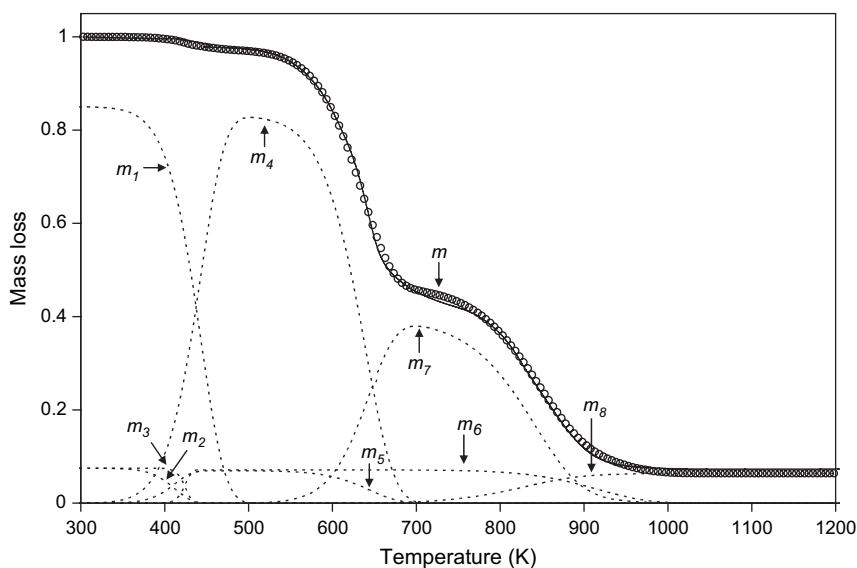


Fig. 4. Mass fractions as functions of temperature as measured (lines) and calculated (circles) for the 85% resin + 7.5% Visil + 7.5% intumescent formulation at a heating rate of 10 K/min (kinetic parameters are given in Table 5).



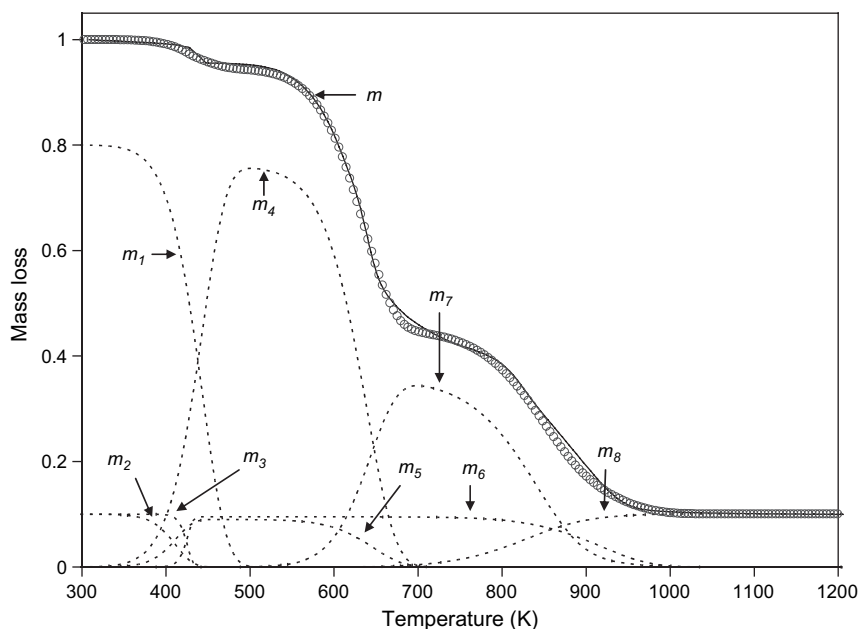


Fig. 5. Mass fractions as functions of temperature as measured (lines) and predicted (circles) for the 80% resin + 10% Visil + 10% intumescent formulation at a heating rate of 10 K/min.

proposed mechanism adequately describes the degradation process. The successful application of a scheme comprised of parallel reactions subsequently forming a cumulative char,  $m_7$ , suggests that there may be little or no chemical interactions between the constituent elements below 600 K. Thus a simple decomposition model used in this study, where there are insignificant chemical interactions in the lower temperature regime, is capable of reproducing mass loss profiles despite the possible limitations of this approach.

Fig. 7 shows, for comparative purposes, mass loss as a function of temperature for the 80% resin + 10% Visil + 10% intumescent and 85% resin + 7.5% Visil + 7.5% intumescent mixtures, respectively. A high confidence level of applicability

of the mathematical model is affirmed by the existence of subtle differences between the experimental and the simulated TGA curves. The mass loss profiles are therefore highly sensitive to the mechanistic scheme as well as the kinetic parameters employed.

In order to optimise flame-retardant formulations to achieve a high efficiency, it would require assessing TGA data for each possible formulation independently; this would advise an enormous experimental design resulting in the production of a fit surface. Even though the use of experimental design methods would suffice, the type of modelling work discussed in this paper would render unnecessary performance of TGA experiments. Predictive modelling is relatively faster (models a different

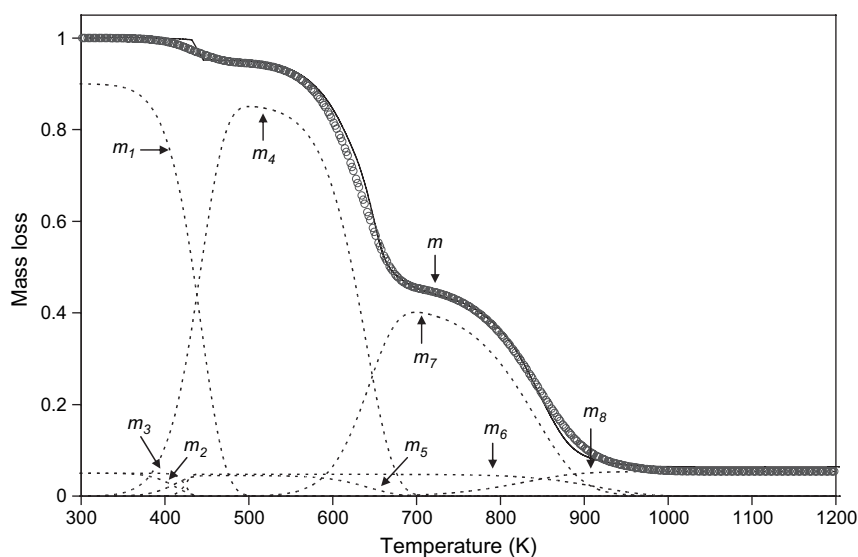


Fig. 6. Mass fractions as functions of temperature as measured (lines) and predicted (circles) for 90% resin + 5% Visil + 5% intumescent formulation at a heating rate of 10 K/min.



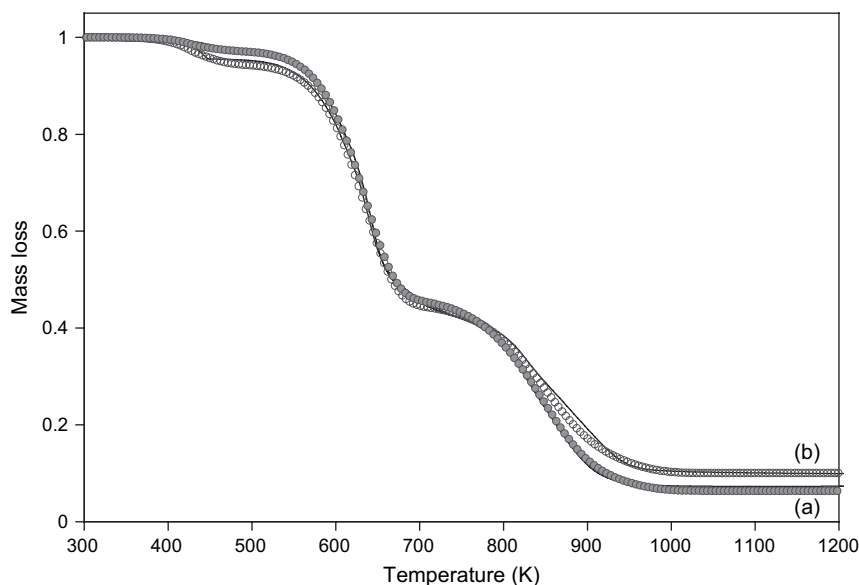


Fig. 7. Mass fractions as functions of temperature as measured (lines) and calculated/predicted (circles) for (a) 80% resin + 10% Visil + 10% intumescent and (b) 85% resin + 7.5% Visil + 7.5% intumescent formulations at a heating rate of 10 K/min.

formulation within 100 s) and can be used to screen formulations, hence becoming a rapid design tool. As long as results from predictive model agree with experimental measurements within a specified range of variation in respect to resin formulations, alone that is enough credibility to prove its reliability within that defined range.

#### 4. Conclusion

In this study thermogravimetric mass losses have been used as the measure against which the accuracy and validity of the mathematical model are evaluated. Kinetic parameters were optimised for one specified formulation to achieve near-perfect agreement between the simulated and experimental data. While a simplified mathematical model which obviously did not adequately describe the real chemistry during material decomposition is used, a reasonably high level of agreement between model predictions and experimental data for other formulations is encouraging. The mathematical predictive model developed in this study is capable of predicting the combustion and charring stages with a high degree of accuracy. The residual yield is predictable and is found to be composition dependent. Development of a predictive model would allow a faster and easier selection of optimum additive fractions in the formulation of highly flame-retarded polymer matrices for use in composite fabrication.

#### Acknowledgements

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