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## Modelling char formation in isothermal and non-isothermal thermogravimetric experiments

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### Abstract

We model char formation in isothermal and thermogravimetric (TG) experiments by a catalytic one-step reaction. For isothermal experiments there is an analytic solution and we show how the maximum amount of char formed, and the stability of the char, varies with the parameters in our model. For TG experiments we use the concept of a 'characteristic temperature' to provide bounds on parameter values and calculate the amount of char formed numerically. This approach can also be used to predict whether barrier-forming additives form char below or above the decomposition point of a polymeric solid.

*Keywords:* Char; Decomposition isothermal; Polymer, TGA

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### 1. Introduction

Many fires, especially those fuelled by polymers, are initiated and maintained through a non-linear feedback process in which a reactant gas is released from the decomposing polymer to fuel a gas phase (flame) reaction. Radiation from the flame then heats the neighbouring polymer further and completes the feedback cycle. The formation of char at the surface of the polymer exerts an inhibiting effect on this feedback, and has potential usefulness in fire control. In order to compare the effectiveness of additives in TG experiments and other flammability tests [1], parameter values for activation energies and pre-exponential factors are required in order to model the solid-phase decomposition reaction. These values can be obtained experimentally from thermogravimetric analysis (TG) [2]. Here we present a simple

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TG model to determine these values and consider the effect of a competing char-forming reaction.

Char-forming additives reduce the risk of ignition in two related ways. They form a protective layer over a decomposing polymer that reduces the heat flux to it, and they reduce the inflow of reactive species into the gas phase. We model the char-forming reaction by a one-step Arrhenius reaction which is first order with respect to the polymer and zero order with respect to the additive. The study of char-forming schemes in TG experiments has considerable industrial interest and can be applied to more general fire application tests. The usual problem in the analysis of data obtained from TG experiments is to determine the form of the rate functions and to calculate values for reaction parameters [3–5]. In this paper we model the rate functions by Arrhenius functions and vary the reaction parameters in order to see their effect on TG data. We are particularly interested in determining the effect of these variations on the formation and stability of char.

In the isothermal analysis in Section 3.1, we assume that the sample temperature remains uniform, so that the char does not act as a flux inhibitor; in Section 3.2, we consider the more general, non-isothermal, case. In either case there are two distinct ways of measuring the effectiveness of a given char-promoting additive: the maximum amount of ‘reduced char’ formed and the stability of the ‘reduced-polymer reduced-char’ co-product.

## 2. A simple TG model

We consider the thermal decomposition of a polymeric material  $\mathcal{P}$  under a constant heating rate  $\alpha$ . We assume that this reaction is first order with respect to  $\mathcal{P}$  and that it is a single-step Arrhenius reaction. The sample is assumed to be sufficiently small that its temperature is spatially uniform.

This system is modelled by an ‘ideal TG model’, expressed symbolically as



or, in differential form

$$\frac{d\mathcal{P}}{dt} = -A_0 \exp\left[\frac{-E_0}{RT}\right] \mathcal{P}$$

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

where  $\mathcal{V}$  represents gas-phase products,  $\mathcal{P}$  is the weight of polymeric material remaining at time  $t$  (kg),  $t$  is the time (s),  $A_0$  is the pre-exponential factor for the decomposition reaction ( $\text{s}^{-1}$ ),  $E_0$  is the activation energy for the decomposition reaction ( $\text{J mol}^{-1}$ ),  $R$  is the ideal gas constant ( $\text{J K}^{-1} \text{mol}^{-1}$ ),  $T$  is the temperature (K),  $\alpha$  is the heating rate ( $\text{K s}^{-1}$ ) and the initial conditions are

$$\mathcal{P}(0) = \mathcal{P}_0 \quad \text{and} \quad T(0) = T_0 \quad (1)$$

To identify and expose important parameters, it is convenient to non-dimensionalise by defining new variables  $\mathcal{P}^* = \mathcal{P}/\mathcal{P}_0$ ,  $T^* = T/T_0$ ,  $t^* = \alpha t/T_0$ , so that the system becomes

$$\frac{d\mathcal{P}^*}{dt^*} = -A_0^* \exp\left[\frac{-E_0^*}{T^*}\right] \mathcal{P}^* \quad (2)$$

$$\frac{dT^*}{dt^*} = 1 \quad (3)$$

where  $A_0^* = A_0 T_0/\alpha$  is a non-dimensionalised pre-exponential factor, and  $E_0^* = E_0/(RT_0)$  is a non-dimensionalised activation energy. The initial conditions are now

$$\mathcal{P}^*(0) = T^*(0) = 1 \quad (4)$$

A polymeric material can be characterised by the temperature at which its reactivity function,  $y = -d\mathcal{P}/dt$ , reaches its maximum value, e.g.  $d^2\mathcal{P}/dt^2 = 0$ ; we call this temperature the ‘characteristic temperature’. This happens when [6]

$$\frac{A_0}{\alpha} = \frac{E_0}{RT_m^2} \exp\left[\frac{E_0}{RT_m}\right] \quad (5)$$

where  $T_m$  is the ‘characteristic temperature’ of the polymeric material.

Eq. (5) can be written in the non-dimensionalised form

$$\ln(A_0^*) = \ln\left(\frac{E_0^*}{T_m^{*2}}\right) + \frac{E_0^*}{T_m^*} \quad (6)$$

Eq. (5) shows that there is a unique characteristic temperature for all non-zero values of  $\alpha$ . However if  $\ln(A_0^*) > \ln(E_0^*) + E_0^*$ , the polymeric material will not experience the characteristic temperature—this condition corresponds to the initial temperature being above the characteristic temperature.

Fig. 1 shows the variation of  $\ln(A_0^*)$  with  $E_0^*$  for fixed values of  $T_m^*$ . Values of the non-dimensionalised parameters were taken corresponding to  $T_0 = 298$  K,  $\alpha = 1/60$  K s<sup>-1</sup>,  $10^3 \leq A_0(\text{s}^{-1}) \leq 10^{15}$ , and  $50 \leq E_0(\text{kJ mol}^{-1}) \leq 250$ .

We seek the necessary parameter values so that  $600 \leq T_m \leq 773$ . This represents the range between processing temperature and degradation temperature for many polymers of industrial interest. From Eq. (5) we see that this happens when  $E_0$  and  $A_0$  are chosen so that

$$\frac{E_0}{(773)^2 R} \exp\left(\frac{E_0}{773 R}\right) \leq \frac{A_0}{\alpha} \leq \frac{E_0}{(600)^2 R} \exp\left(\frac{E_0}{600 R}\right) \quad (7)$$

### 3. Char-forming reaction schemes

When both char and volatiles are formed from the thermal decomposition of the polymer, we need to extend the mathematical model to contain both these products. Thus we consider isothermal and non-isothermal cases, and assume that in each case

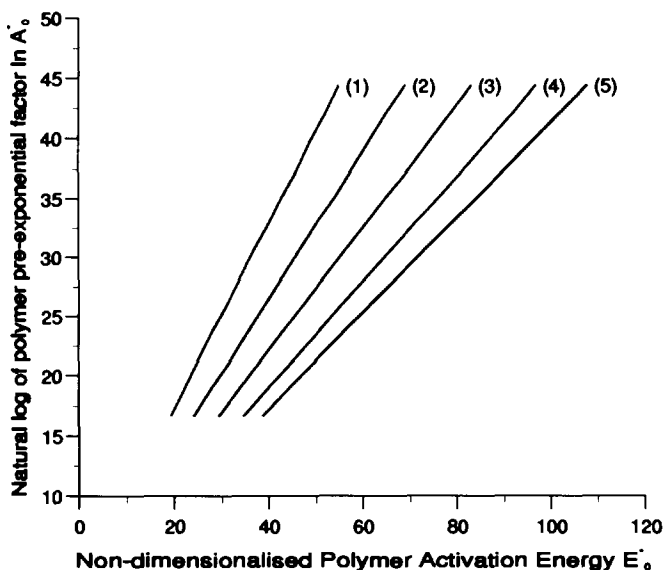


Fig. 1. Variation of  $\ln(A_0^*)$  with  $E_0^*$  for fixed  $T_m^*$ . With  $T_0 = 298$  K the values of  $T_m^*$  correspond to: (1)  $T_m^* = 1.342$  ( $T_m = 400$  K), (2)  $T_m^* = 1.679$  ( $T_m = 500$  K), (3)  $T_m^* = 2.013$  ( $T_m = 600$  K), (4)  $T_m^* = 2.349$  ( $T_m = 700$  K), and (5)  $T_m^* = 2.594$  ( $T_m = 773$  K).

the reaction scheme takes the form



Here  $\mathcal{P}$  is the polymeric material,  $\mathcal{B}$  is a char,  $\mathcal{V}$  represents gas-phase products,  $k_0$  is the reaction rate for the decomposition of the polymeric material to volatiles,  $k_1$  is the reaction rate for the conversion of polymeric material to char, and  $k_2$  is the reaction rate for the conversion of char to volatiles.

### 3.1. Isothermal conditions

Under isothermal conditions the reaction scheme for the char-forming system can be written as

$$\frac{d\mathcal{P}}{dt} = -(k_0 + k_1)\mathcal{P}$$

$$\frac{d\mathcal{B}}{dt} = k_1\mathcal{P} - k_2\mathcal{B}$$

$$\frac{d\mathcal{V}}{dt} = k_0\mathcal{P} + k_2\mathcal{B}$$

with initial conditions

$$\mathcal{P}(0) = \mathcal{P}_0, \quad \mathcal{B}(0) = 0 \quad \text{and} \quad \mathcal{V}(0) = 0 \quad (8)$$

We non-dimensionalise by defining  $s = k_0 t$ ,  $\mathcal{P}_0 \mathcal{P}^* = \mathcal{P}$ ,  $\mathcal{P}_0 \mathcal{B}^* = \mathcal{B}$ ,  $\mathcal{P}_0 \mathcal{V}^* = \mathcal{V}$ , where we call  $\mathcal{P}^*$  the ‘reduced polymer’,  $\mathcal{B}^*$  the ‘reduced char’ and  $\mathcal{V}^*$  the ‘reduced gaseous products’. This introduces two new parameters  $k_1^* = k_1/k_0$  and  $k_2^* = k_2/k_0$ .

The system becomes

$$\frac{d\mathcal{P}^*}{ds} = -(1 + k_1^*)\mathcal{P}^* \quad (9)$$

$$\frac{d\mathcal{B}^*}{ds} = \mathcal{P}^* - k_2^*\mathcal{B}^* \quad (10)$$

$$\frac{d\mathcal{V}^*}{ds} = \mathcal{P}^* + k_2^*\mathcal{B}^* \quad (11)$$

with initial conditions

$$\mathcal{P}^*(0) = 1, \quad \mathcal{B}^*(0) = \mathcal{V}^*(0) = 0 \quad (12)$$

There are two cases to consider:  $1 + k_1^* \neq k_2^*$  and  $1 + k_1^* = k_2^*$ . For the first case, the solution is

$$\mathcal{P}^*(s) = \exp\{- (1 + k_1^*)s\} \quad (13)$$

$$\mathcal{B}^*(s) = \frac{k_1^*}{k_2^* - (1 + k_1^*)} [\exp\{- (1 + k_1^*)s\} - \exp\{-k_2^*s\}] \quad (14)$$

$$\mathcal{V}^*(s) = 1 - \frac{k_2^* - 1}{k_2^* - (1 + k_1^*)} \exp\{- (1 + k_1^*)s\} + \frac{k_1^*}{k_2^* - (1 + k_1^*)} \exp\{-k_2^*s\} \quad (15)$$

and in the second case

$$\mathcal{P}^*(s) = \exp\{- (1 + k_1^*)s\} \quad (16)$$

$$\mathcal{B}^*(s) = k_1^* s \exp\{- (1 + k_1^*)s\} \quad (17)$$

$$\mathcal{V}^*(s) = 1 - (1 + k_1^* s) \exp\{- (1 + k_1^*)s\} \quad (18)$$

In what follows we consider the non-degenerate case,  $1 + k_1^* \neq k_2^*$ .

### 3.1.1. Char formation

In the design of char-forming additives, an important measure of effectiveness is the maximum amount of char formed. It is believed that the greater the degree of char formation under TG conditions the better the additive will be under ‘real’ conditions. The amount of ‘reduced char’ present in the TG system is seen from Eq. (14) to be maximised when

$$s = \frac{1}{1 + k_1^* - k_2^*} \ln \left( \frac{1 + k_1^*}{k_2^*} \right) \quad (19)$$

and is given by

$$\mathcal{B}_{\max} = \frac{k_1^*}{k_2^* - (1 + k_1^*)} \left\{ \left( \frac{k_2^*}{1 + k_1^*} \right)^{(1+k_1^*)/(1+k_1^*-k_2^*)} - \left( \frac{k_2^*}{1 + k_1^*} \right)^{k_2^*/(1+k_1^*-k_2^*)} \right\} \quad (20)$$

When  $k_2^* \ll 1$  this reduces to

$$\mathcal{B}_{\max} \approx \frac{k_1^*}{(1 + k_1^*)} \left\{ 1 - \left( \frac{k_2^*}{1 + k_1^*} \right) \right\} \quad (21)$$

from which we derive the criterion for the maximisation of ‘reduced char’ (that is the criterion for  $\mathcal{B}_{\max} \approx 1$ ), which is

$$k_1^* \gg 1 \gg k_2^* \quad (22)$$

The special case  $k_2^* = 0$  is of interest, as this provides a lower bound on the value of  $k_1^*$  required, and hence on  $k_1$ , to achieve a particular level of ‘reduced char’ in the system.

Thus, for example, if we want the maximum level of ‘reduced char’ formed to be 5% of the sample weight, then from Eq. (21) we have

$$\frac{k_1^*}{(1 + k_1^*)} \geq 0.05 \quad (23)$$

which gives the bound  $k_1^* \geq 1/19$ . In terms of our original variables this is  $k_1 \geq 1/19k_0$ .

### 3.1.2. Stability of the polymer–char co-product

In the absence of the char-forming pathway ( $k_1^* = 0$ ), the ‘reduced polymer’ has a half-life  $s = \ln 2$ . When  $k_1^* \neq 0$ , we can measure the effectiveness of the char-forming pathway by calculating the amount of ‘reduced polymer’ and ‘reduced char’ present at  $s = \ln 2$ . The char-forming additive is effective only if  $(\mathcal{P} + \mathcal{B})(\ln 2) > 0.5$ , regardless of the degree of ‘reduced char’ formation. From Eqs. (13) and (14) we have

$$(\mathcal{P} + \mathcal{B})(\ln 2) = \frac{k_2^* - 1}{k_2^* - (1 + k_1^*)} 2^{-(1+k_1^*)} - \frac{k_1^*}{k_2^* - (1 + k_1^*)} 2^{-k_2^*} \quad (24)$$

Level curves of  $(\mathcal{P} + \mathcal{B})(\ln 2)$  are shown in Figs. 2 and 3. From these we see that the char-forming reaction is only of interest if  $k_2^* < 1$ , that is when the char is thermally stable, which is compatible with the assumption made above.

### 3.2. Non-isothermal conditions

We next consider the system

$$\frac{d\mathcal{P}}{dt} = -(k_0(T) + k_1(T))\mathcal{P}$$

$$\frac{d\mathcal{B}}{dt} = k_1(T)\mathcal{P} - k_2(T)\mathcal{B}$$

$$\frac{d\mathcal{Y}}{dt} = k_0(T)\mathcal{P} + k_2(T)\mathcal{B}$$

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

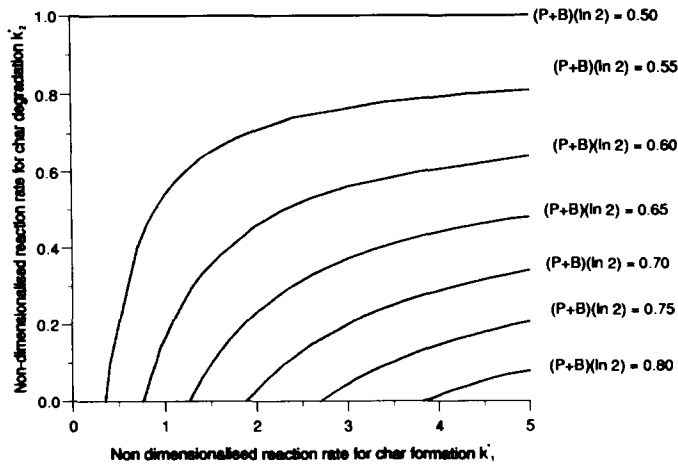


Fig. 2. Stability of the Polymer-Char co-product under isothermal conditions: Char Thermally stable.

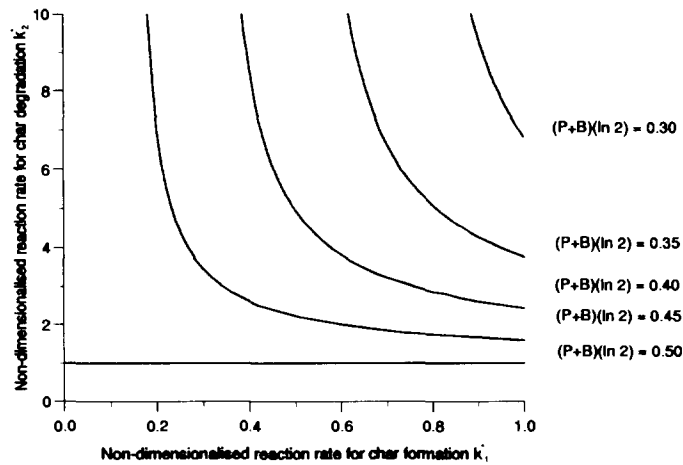


Fig. 3. Stability of the Polymer-Char co-product under isothermal conditions: Char Thermally unstable.

where the rate coefficients  $k_i(T)$  are now temperature dependent. We assume that all reactions are described by Arrhenius rate-coefficients, so that  $k_i(T) = A_i \exp[-E_i/RT]$ .

In order to simplify the analysis, we assume that the char undergoes negligible decomposition over the temperature range  $298 \leq T(\text{K}) \leq 698$ . We non-dimensionalise  $\mathcal{P}$ ,  $\mathcal{B}$ ,  $\mathcal{V}$ ,  $t$  and  $T$  by introducing the variables  $\mathcal{P}^*$ ,  $\mathcal{B}^*$ ,  $\mathcal{V}^*$  (as defined in Section 3.1), and  $t^*$  and  $T^*$  (as defined in Section 2). The system can then be written as

$$\frac{d\mathcal{P}^*}{dt^*} = -(A_0^* \exp[-E_0^*/T^*] + A_1^* \exp[-E_1^*/T^*])\mathcal{P}^* \tag{25}$$

$$\frac{d\mathcal{B}^*}{dt^*} = A_0^* \exp[-E_0^*/T^*] \mathcal{P}^* \quad (26)$$

$$\frac{d\mathcal{V}^*}{dt^*} = A_1^* \exp[-E_1^*/T^*] \mathcal{P}^* \quad (27)$$

$$\frac{dT^*}{dt^*} = 1 \quad (28)$$

where  $A_0^*$  and  $E_0^*$  have been defined previously.  $A_1^*$  and  $E_1^*$  are defined in the obvious way. The initial conditions are  $\mathcal{P}^*(0) = 1$ ,  $\mathcal{B}^*(0) = \mathcal{V}^*(0) = 0$  and  $T^*(0) = 1$ , with integration carried out over the time period  $0 \leq t^* \leq 698\alpha/T_0$ .

In the calculations that follow, we take  $\alpha = 1/60 \text{ K s}^{-1}$  and  $T_0 = 298 \text{ K}$ . Hence a material with a characteristic temperature  $T_m = 600 \text{ K}$  has a reduced characteristic temperature  $T_m^* = 2.013$ . We are interested in the amount of ‘reduced char’ formed at a temperature of  $700 \text{ K}$ , denoted  $\mathcal{B}(\chi)$ . This corresponds to ‘reduced temperature’ of  $2.349$ . In practice it is not possible to measure the weight of char formed in one TG run; what is measured is the weight of char and polymer. However the values taken for  $A_0$  and  $E_0$  in the following numerical experiments correspond to polymers that are fully decomposed by  $700 \text{ K}$ . Under these conditions  $\mathcal{B}(\chi)$  corresponds to an experimentally measurable parameter.

We define a ‘reduced characteristic temperature’,  $T_{mc}^*$ , for the decomposition of a polymeric material in the presence of a char-promoting pathway implicitly by

$$\begin{aligned} & \left[ A_0^* \exp\left(-\frac{E_0^*}{T_{mc}^*}\right) + A_1^* \exp\left(-\frac{E_1^*}{T_{mc}^*}\right) \right]^2 \\ & = \frac{A_0^* E_0^*}{T_{mc}^{*2}} \exp\left(-\frac{E_0^*}{T_{mc}^*}\right) + \frac{A_1^* E_1^*}{T_{mc}^{*2}} \exp\left(-\frac{E_1^*}{T_{mc}^*}\right) \end{aligned} \quad (29)$$

It is important to realise that our definition for  $T_{mc}^*$  is based upon the decomposition of the polymeric material, e.g.  $d^2 \mathcal{P}^*/dt^{*2} = 0$ , and not upon the decomposition of solid-phase material, e.g.  $d^2(\mathcal{P}^* + \mathcal{B}^*)/dt^{*2} = 0$ . Although the latter is easier to measure experimentally, we choose the former because we are interested in the temperature which characterises the decomposition of the polymeric material. Clearly if

$$A_0^* \exp\left(-\frac{E_0^*}{T_{mc}^*}\right) \gg A_1^* \exp\left(-\frac{E_1^*}{T_{mc}^*}\right)$$

then  $T_{mc}^* \rightarrow T_m^*$ .

Figure 4 shows the variation in  $T_{mc}^*$  and  $\mathcal{B}(\chi)$  with  $E_1^*$  for fixed values of the other parameters. We have taken  $A_0^* = 17.88 \times 10^{10}$ ,  $A_1^* = 17.88 \times 10^8$  and  $E_0^* = 48.836$ . The values of  $A_0^*$  and  $E_0^*$  have been chosen so that the dimensionalised characteristic temperature  $T_m$  is  $619.7 \text{ K}$ , with the values for  $\alpha$  and  $T_0$  given above.

The variation of  $T_{mc}^*$  and  $\mathcal{B}(\chi)$  illustrated in Fig. (4) has two features common to plots for different parameter values:  $T_{mc}^*$  increases with  $E_1^*$  but is bounded above by  $T_m^*$ , here by  $T_m^* = 2.080$ , whilst  $\mathcal{B}(\chi)$  decreases as  $E_1^*$  increases.



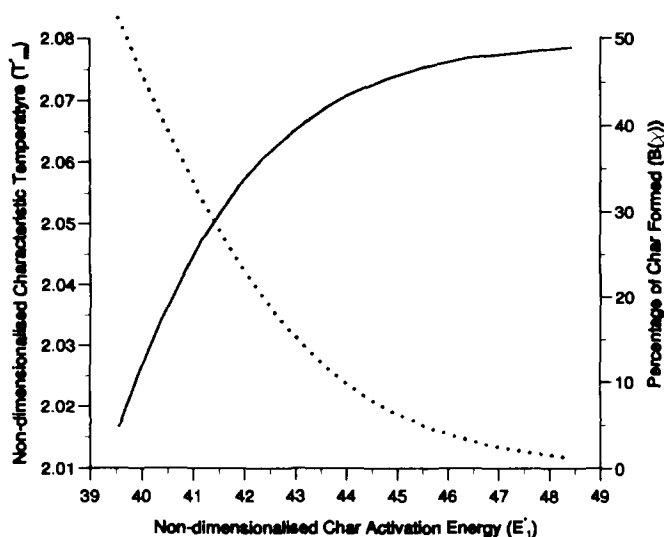


Fig. 4. Variation of  $T_{mc}^*$  and  $\beta(\chi)$  (dotted line) with  $E_1^*$  for typical parameter values.

For a particular material, e.g. given  $A_0^*$  and  $E_0^*$ , Eq. (29) provides bounds on additive parameters, i.e. the range of values for  $A_1^*$  and  $E_1^*$  which satisfy  $T_{mc}^* \geq 2.013$ , e.g.  $T_{mc} \geq 600$ . Fig. 5 shows such a plot for the values of  $A_0^*$  and  $E_0^*$  given above. Then having chosen  $A_1^*$  and  $E_1^*$  so that  $T_{mc}^* \geq 2.013$ , Eqs. (25)–(28) are integrated to give  $\beta(\chi)$ .

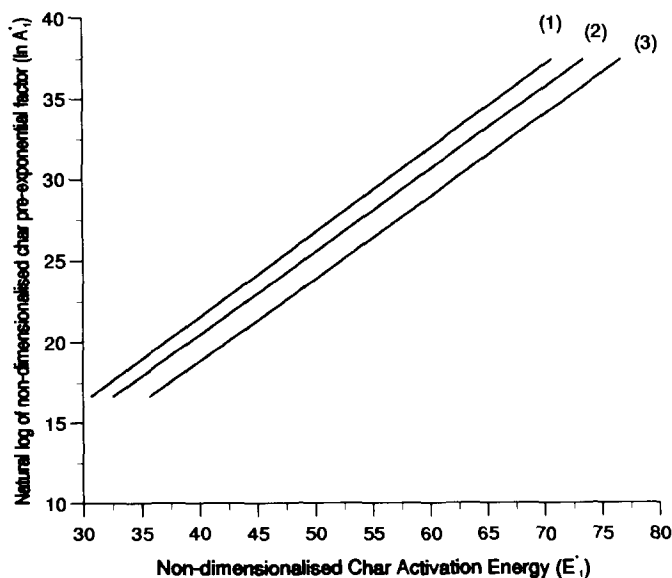


Fig. 5. Variation of  $T_{mc}^*$  with  $\ln(A_1^*)$  and  $E_1^*$  for  $A_0^* = 17.88 \times 10^{10}$  and  $E_0^* = 48.836$ . The lines are: (1)  $T_{mc}^* = 2.013$  ( $T_{mc} = 600$  K), (2)  $T_{mc}^* = 2.054$  ( $T_{mc} = 612$  K), and (3)  $T_{mc}^* = 2.074$  ( $T_{mc} = 618$  K).

In order to focus on the practical value of these results we consider an additive which is effective in promoting char formation for a given  $A_0^*$  and  $E_0^*$ , which determines a value for  $T_m^*$ . We investigate its performance with different materials which have the same value for  $T_m^*$ .

Suppose the additive has  $A_1^* = 17.88 \times 10^7$  and  $E_1^* = 36.324$ , and consider materials which have  $T_m^* = 2.085$ , corresponding to  $T_m = 620$ . From Eq. (6), it suffices to specify either  $A_0^*$  or  $E_0^*$ . Fig. 6 shows the variation of  $T_{mc}^*$  with  $\ln(A_0^*)$  and Fig. 7 shows the variation in  $\mathcal{B}(\chi)$  with  $\ln(A_0^*)$ . Although this variation in absolute terms is small, it has the curious feature that it has a local minimum. The behaviour exhibited in Figs. 6 and 7 has been found over a wide range of parameter values for  $A_0^*$ ,  $A_1^*$ ,  $E_0^*$  and  $E_1^*$ .

Alternatively, we may examine the behaviour of an additive by specifying  $A_1^*$  and  $E_1^*$  and either  $A_0^*$  or  $E_0^*$  and allowing the unspecified variable to change. In Fig. 8 we have taken  $A_1^* = 17.88 \times 10^7$  and  $E_1^* = 36.324$ , fixed  $A_0^* = 298 \times 10^6$  and allowed  $E_0^*$  to vary. From Eq. (5), we see that fixing  $A_0^*$  and increasing  $E_0^*$  corresponds to choosing materials with increasing values for  $T_m^*$ . Under these conditions we see that the higher the  $T_m^*$  the more effective the additive. This is not surprising because increasing stability (higher  $T_m^*$ ) corresponds to slower rates of decomposition which means that there is more material to catalyse into char.

#### 4. Discussion

We have used the concept of a ‘characteristic temperature’ to define values of  $A_0$  and  $E_0$  which correspond to ‘typical’ polymers of industrial interest. An analytic expression

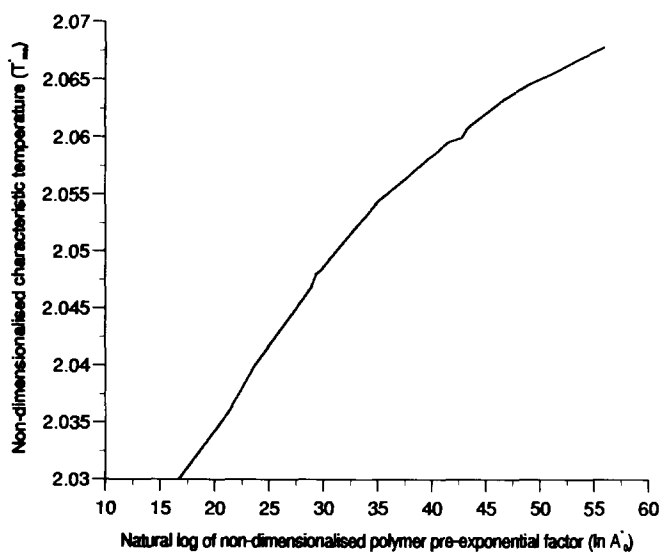


Fig. 6. Variation of  $T_{mc}^*$  for materials with  $T_m^* = 2.085$  ( $T_m = 620$ ) for a fixed additive as described in the text. The range in  $T_{mc}^*$  corresponds to a range  $606 \leq T_{mc} \leq 616$ .

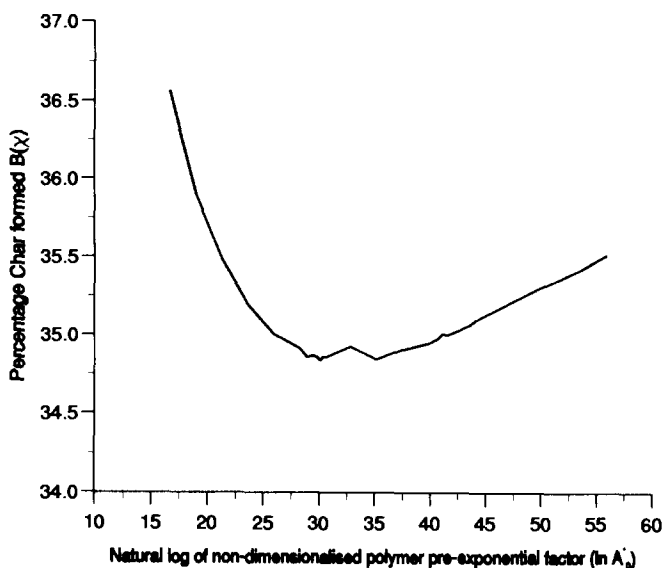


Fig. 7. Variation of  $B(\chi)$  for materials with  $T_m^* = 2.085(T_m = 620)$  for a fixed additive as described in the text.

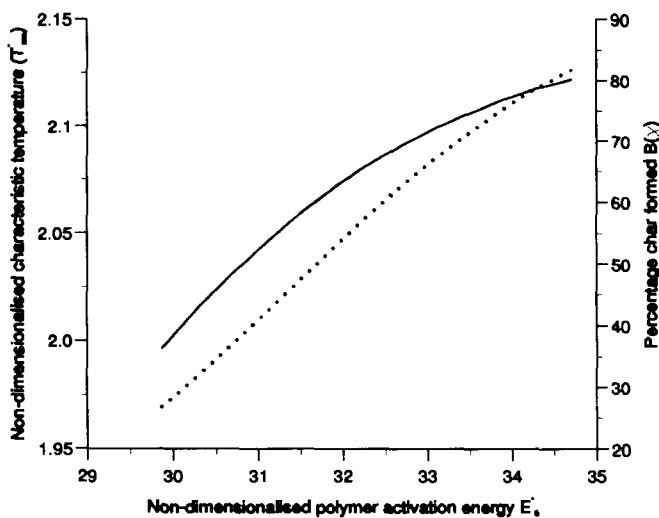


Fig. 8. Variation of  $T_m^*$  and  $B(\chi)$  (---) for fixed  $A_0^*$ ,  $A_1^*$  and  $E_1^*$  with  $E_0^*$ . The variation in  $T_m^*$  corresponds to a range  $590 \leq T_{m,c}(K) \leq 630$ .

is readily derived which allows calculation of these values (Eq. (7)). For fixed  $A_0$ , we derive a lower bound  $E_{0,l}$  and an upper bound  $E_{0,u}$  for  $E_0$ . In fact it is possible to derive better bounds  $E_{0,bl}$  and  $E_{0,bu}$ , such that  $E_{0,l} \leq E_{0,bl} \leq E_0 \leq E_{0,bu} \leq E_{0,u}$ . This is because, when  $T = 600$  K, a material which has  $T_m = 600$  has already undergone extensive

decomposition, typically of the order of 50%. Such a material would not be thermally stable at processing temperatures of around 600 K. A better requirement for the lower bound would be that little reaction has occurred by this temperature, i.e.  $\mathcal{P}^*(T^* = 2.013) \geq 0.95$ . Although a material which has  $T_m = 773$  has undergone extensive reaction, there remains a significant amount of the material which has not decomposed. In practice most materials have fully decomposed by this temperature. A better upper bound would be the criterion that  $\mathcal{P}^*(T^* = 2.781) \leq 0.05$ . For our purposes, the rough bounds obtained in this paper are sufficiently accurate.

As well as providing bounds on  $A_0$  and  $E_0$ , it is also possible to use the results of the section on thermal decomposition to produce bounds on  $A_1$  and  $E_1$  for possible additives. As we do not wish  $T_{mc} \leq 600$  K, it is clear that  $A_1$  and  $E_1$  must satisfy the relationship

$$\frac{A_1}{\alpha} \leq \frac{E_1}{(600)^2 R} \exp\left(\frac{E_1}{600 R}\right) \quad (30)$$

Using the argument mentioned above, this provides a lower bound on  $E_1$  (for fixed  $A_1$ ), which can be improved by using the condition that  $\mathcal{P}^*(T^* = 2.013) \geq 0.95$ .

We note in passing that Eq. (30) can be used to predict the kinetic effectiveness of barrier-forming additives. (Consideration of relative thermal conductivities is also required.) These additives decompose, producing a thermal barrier over a polymeric material: they do not interact chemically with the polymer to form a char. Clearly a given additive of this class will not be effective if it forms the barrier at a higher temperature than the decomposition temperature ( $T_m$ ) of the polymer. For a given polymer,  $T_m$  is readily calculated at a given heating rate, either experimentally or through knowledge of  $A_0$  and  $E_0$ . Additionally, for a given barrier-forming additive it is possible to calculate  $A_1$  and  $E_1$  from TG experiments on the additive. Hence Eq. (30) can be used to predict whether or not a given barrier-forming additive could work with a given polymer by simply replacing 600 by  $T_m$ .

In Section 3.1, we considered the case when the decomposition and char-forming reactions occur under isothermal conditions. In this case it is possible to write an analytic solution to the equations. The efficiency of the char-forming reaction in a TG experiment can be measured either in terms of the maximum amount of 'reduced char' formed or in terms of the stability of the 'reduced-polymer reduced-char' co-product. Consideration of the equation for the maximum amount of 'reduced char' formed (Eqs. (20), (21) and (23)) provides lower bounds on the value of  $k_1^*$  to achieve a given level of 'reduced char' formation. However char formation is only desirable if the 'reduced char' formed is thermally stable. The condition for this is that  $k_2^* < 1$  (Figs. 2 and 3). An important practical question is which of these criteria is the more important. Consider for example a case where we have two additives. The first promotes a higher level of 'reduced char' formation but the second is more thermally stable. Which is more effective in, for example, the cone calorimeter, or, a real fire? Is the best additive one of these extremes or a combination of the two? It is not possible to answer these important fire science problems from TG work alone, and although some correlation has been

made between TG and cone data [7], a more realistic model (experiment) of a fire situation is required.

In Section 3.2 we considered char-forming reactions under non-isothermal conditions. In order to simplify the problem we assumed that the char is thermally stable over the range  $298 \leq T(\text{K}) \leq 700$  and undergoes negligible decomposition. As  $A_j^* \propto A_j$  ( $j = 0, 1$ ),  $E_j^* \propto E_j^*$  ( $j = 0, 1$ ) and  $T_{\text{mc}} \propto T_{\text{mc}}^*$ , we can replace the non-dimensionalised variables with their dimensionalised counterparts. If we define ‘acceptable’ additives as having the property that  $T_{\text{mc}} \geq 600$  and  $\mathcal{B}(\chi) \geq 2$ , we find that replacing the condition  $T_{\text{mc}} \geq 600$  with the ‘improved’ condition  $\mathcal{P}^* \geq 0.95$  does not affect the substance of our results in this section. The values we have calculated for  $\mathcal{B}(\chi)$  are upper bounds, as we have ignored the decomposition of the char.

From Fig. 4 we see that, for fixed  $A_0$ ,  $A_1$  and  $E_0$ ,  $T_{\text{mc}}$  increases with  $E_1$  whilst  $\mathcal{B}(\chi)$  decreases with  $T_{\text{mc}}$ . For high values of  $E_1$  the value for  $T_{\text{mc}}$  approaches the corresponding value  $T_m$  for the polymeric material in the absence of the additive. Hence high values for  $\mathcal{B}(\chi)$  correspond to making the polymeric material less thermally stable. It also follows that the higher the value of  $T_m$  the greater the range of values that  $E_1$  can take, so that  $T_{\text{mc}} \geq 600$ , and hence the higher the range in  $\mathcal{B}(\chi)$ . This result is illustrated in Fig. 8.

From Figs. 6 and 7, we see that an additive which works ‘well’ for a material with a given  $T_m$  works well for other materials with the same  $T_m$ . Although  $T_{\text{mc}}$  steadily increases towards  $T_m$  with increasing  $A_0^*$ , there is very little variation in the value for  $\mathcal{B}(\chi)$ : just under 2% over a very wide range of materials. This behaviour, mathematically, rests upon our assumption that the chemical parameters of the char-forming reaction do not depend upon the material being retarded; this may be true for certain classes of compounds but is not true in general.

Throughout this paper we have treated  $A_1$  and  $E_1$  as experimentally controlled variables, and have investigated numerically the behaviour of different polymer–additive systems. The experimenter uses different additives and measures their effectiveness without knowledge of the values for  $A_1$  and  $E_1$ . An important question is how behaviour in a TG experiment correlates to behaviour in more realistic fire situations. One way to answer this question is to model more realistic fire situations and simulate behaviour numerically. This requires that the modeller knows values for polymer parameters such as  $A_0$  and  $E_0$  and additive parameters such as  $A_1$  and  $E_1$ .

$A_0$  and  $E_0$  can be determined from TG runs on the polymeric material in the absence of an additive by standard methods. The corresponding values for an additive which acts as a catalyst for a first-order reaction, as considered in this paper, are readily determined from isothermal TG runs. As  $A_0$  and  $E_0$  are known, it is possible to calculate  $k_0(T_j)$ , the polymeric decomposition rate at a specified temperature  $T_j$ . As an analytical solution exists (Eqs. (3) and (14)) for this system, the experimentally measured quantity  $\mathcal{P}^* + \mathcal{B}^*$  can be fitted to the analytic result to find optimum values of  $k_1^*(T_j)$  and  $k_2^*(T_j)$ . As we know  $k_0$ , we can then calculate  $k_1(T_j)$  and  $k_2(T_j)$ . The variation of  $k_1(T_j)$  and  $k_2(T_j)$  with temperature then gives us values for the formation of char ( $A_1$  and  $E_1$ ) and degradation of char ( $A_2$  and  $E_2$ ). If these experiments are performed at temperatures where char decomposition is very slow then this calculation becomes even easier. Knowledge of these parameters is of great importance in better

modelling the behaviour of the polymer–additive system in more realistic fire situations.

At a later date we plan to model char formation in more realistic fire situations and to compare results from these models to predictions made on the basis of TG work. In particular we plan to investigate the relative merits of promoting thermal stability of char or maximising the amount of char formed.

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