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A kinetic model for the thermal decomposition of wool

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Abstract

A kinetic model which aims to describe the mass loss processes undergone by wool fibre subjected to controlled heating is proposed. The equations are tested on thermogravimetric recorded data and good agreement of the model with the experimental data is noted.

Keywords: DTA; Kinetics; Model; Oxidation; Pyrolysis; TGA; Wool

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1. Introduction

In a previous paper [1], thermogravimetry has been used to investgate the thermal behaviour of untreated and flame-retardant treated wool. For this purpose wool fibres of 23 μm diameter, treated with 0%, 2%, 4%, 6%, 8% or 10% K_2ZrF_6 (Zirpro method) were decomposed thermally. After the loss of water, two general processes accompanied by major mass losses were evident.

The first process is endothermic, occurring from 200 to 400°C and the second process is exothermic and occurs within the range 450–600°C. Both processes have been shown by many other researchers, who studied the thermal behaviour of wool [2,3]. As a result, a general scheme for the thermal degradation of wool may be proposed

$$\text{Wool} \xrightarrow{\text{(endo)}} \text{Pyrolysis products} \xrightarrow{\text{(exo)}} \text{Oxidation products}$$

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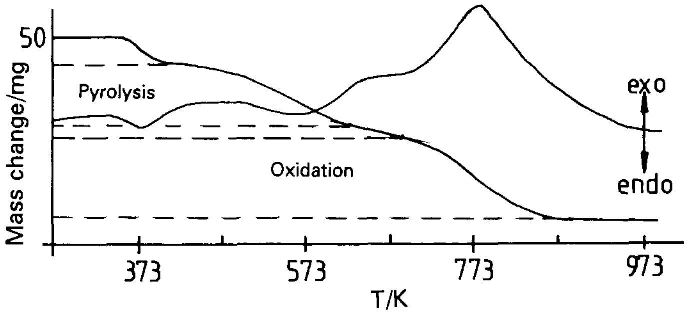

Fig. 1. DTA and TG curves recorded for wool on a Derivatograph Q 1500 D.

During the endothermic step it is supposed that macromolecular chains of protein compounds are decomposed to lighter products and volatile compounds, such as CO, NH_3 and H_2S are evolved [3]. Pyrolysis products then react with oxygen through several gas phase reactions, leading to various oxidation products.

The two processes probably overlap but as Fig. 1 shows, one may easily find an inflexion point on the TG curve which could be considered as the end of the pyrolysis and the beginning of the oxidation, in order to compute the appropriate degrees of conversion.

The TG data from Ref. [1] led to second-order kinetics for the first process and to first-order kinetics for the second process, but it has to be mentioned that through Ref. [1] we have assumed the reaction order model only to be of value. In the following we wish to propose a physical model to explain the recorded data.

2. Thermal decomposition model

Taking into account the mass loss and the endothermic profile, the first process may be roughly considered as a "vaporization" of volatile substances from wool fibre. During the heating of wool its helical structure melts [2] and pyrolysis of peptide bridges and S–S linkages together with the lateral chains begins. Consequently the wool fibre skeleton is damaged [2,3]. The various physical and chemical processes occurring from 200 to 400°C are recorded by TG as a unitary overlapping process of loss of volatiles.

The rate at which the volatiles are lost is supposed to be limited by their diffusion through the fibre. The process is relatively similar to "vaporization" of volatile substances from within the wool fibre. This assumption is supported by the TG curves recorded both in air and in nitrogen atmosphere being identical, as shown by Ingham [3].

We shall also take into account that each element of volume is producing gases by the reactions occurring within it, i.e. the amount of input gases is lower than that of the output gases for each considered volume. Therefore the model will take into account diffusion through the fibre accompanied by local mass production from chemical reactions.

A model describing this type of process is proposed (see the demonstration in Appendix A) using the equation

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = A(1-\alpha)^{n+1}\exp(-E/RT) \tag{1}$$

where α is the degree of conversion, n is the reaction order of the chemical reaction which produces gases, and A and E have their usual meanings.

Assuming that during the pyrolysis process wool fibres may be considered as cylinders of radius r_0 and length l, according to Appendix A the pre-exponential factor A is given by the equation

$$A = \frac{1}{2}k_0\pi l r_0^2 \tag{2}$$

where k_0 is the pre-exponential factor of the decomposition reaction rate constant.

Assuming, further, first-order kinetics for any of the decomposition reactions which produce gases, i.e. $n = 1$, one may finally write for the pyrolysis process the rate equation

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = \frac{1}{2}k_0\pi l r_0^2(1-\alpha)^2\exp(-E/RT) \tag{3}$$

Note that Eq. (3) exhibits apparently second-order kinetics for the pyrolysis of wool fibre as recorded by TG, in good agreement with our previous results for paper [1].

The exothermic oxidation process is considered to be dependent upon oxygen access to the fibre surface. The rate limiting step should be the diffusion of oxygen through the gaseous layer which surrounds the fibre. Let this layer thickness be x. The kinetics of the process may be assumed to be similar to those of metal oxidation (Tamman [4]), i.e.

$$\frac{\mathrm{d}x}{\mathrm{d}t} = \frac{D}{x} \tag{4}$$

where D is the diffusion coefficient of oxygen through the gas limiting layer.

Assuming that during the oxidation process the fibre has a spherical symmetry defined by a radius R_0, and that at a moment t the radius is R, one may write for x

$$x = R_0 - R \tag{5}$$

Let V_0 and V be the volumes of the wool fibre at the beginning and at time t. Obviously

$$V = V_0(1-\alpha) \tag{6}$$

where α is the degree of conversion. Taking into account the spherical symmetry, from Eqs. (5) and (6) one obtains

$$x = R_0[1-(1-\alpha)^{1/3}] \tag{7}$$

Taking into account Eq. (7), Eq. (4) becomes

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t}=\frac{3D'}{R_0^2}\frac{(1-\alpha)^{2/3}}{1-(1-\alpha)^{1/3}} \tag{8}$$

By using the notation

$$k''=\frac{3D'}{R_0^2}=D_0\exp(-E/RT) \tag{9}$$

one may finally write

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t}=D_0\frac{(1-\alpha)^{2/3}}{1-(1-\alpha)^{1/3}}\exp(-E/RT) \tag{10}$$

Eq. (10) points out that the oxidative process follows three-dimensional diffusion of the Jander type [4]. Eq. (10) shows different kinetics to those we proposed in Ref. [1]. In order to compare the kinetics, the experimental data from Ref. [1] obtained for untreated and flame-retardant treated (Zirpro [5]) wool have been used to compute the kinetic parameters (the pre-exponential factor A and the activation energy E) for the two different kinetic functions, i.e. the function given by Eq. (10) (Jander type kinetics) and that given in Ref. [1] (first-order kinetics). For the calculation we have used the integral method, as presented previously [6]. The correlation coefficients have been compared and the results are listed in Table 1.

As one may observe from Table 1, the recorded data fit the kinetics given by Eq. (10) better than first-order kinetics. We thus conclude that for the oxidative process Eq. (10) offers a more suitable description than does the first-order kinetics model. Summing up, Eqs. (3) and (10) could describe the pyrolytic and oxidative mass loss processes of untreated and Zirpro treated wool, in good agreement with the experimental recorded data, even though the assumptions made for the construction of the model were quite rough.

Table 1
Values of the kinetic parameters of the exothermal process computed for Jander type kinetics and for first-order kinetics ($n = 1$)

Sample: wool treated with K_2ZrF_6/%	Jander type kinetics			First-order kinetics		
	E/(kJ mol^{-1})	A/s^{-1}	r [a]	E/(kJ mol^{-1})	A/s^{-1}	r [a]
0	284	2.5×10^{16}	0.998	159	2.2×10^{9}	0.998
2	304	1.3×10^{18}	0.998	169	1.7×10^{10}	0.995
4	333	6.0×10^{19}	0.996	185	1.5×10^{11}	0.992
6	306	1.5×10^{18}	0.999	170	2.0×10^{10}	0.997
8	327	7.1×10^{18}	0.998	182	5.2×10^{10}	0.999
10	428	1.4×10^{25}	0.992	237	1.3×10^{14}	0.984

[a] Correlation coefficient.

Table 2
Values of the kinetic parameters for the endothermal and exothermal steps of the wool thermal decomposition process

Sample: wool treated with K_2ZrF_6/%	Endothermic step		Exothermic step	
	E/(kJ mol^{-1})[a]	A/s^{-1}	E/(kJ mol^{-1})[a]	A/s^{-1}
0	102	3.5×10^8	284	2.5×10^{16}
2	93	1.0×10^8	304	1.3×10^{18}
4	94	9.5×10^7	333	6.0×10^{19}
6	95	1.5×10^8	306	1.5×10^{18}
8	118	5.3×10^9	327	7.1×10^{18}
10	116	2.0×10^9	428	1.4×10^{25}

[a] Eq. (3). [b] Eq. (10).

The kinetic parameters computed for the two processes using Eqs. (3) and (10) and the epxerimental data from Ref. [1] are given in Table 2.

3. Conclusions

By assuming that pyrolysis and oxidation of wool are unitary processes from the point of view of wool losses, a kinetic model (i.e. Eqs. (3) and (10)) has been proposed to account for the thermal behaviour of the mass of wool fibre. In spite of several simplifying suppositions which have been made throughout the paper, the TG recorded data for untreated and flame-retardant treated wool show fairly good agreement with the proposed model. Work is in progress to find a correlation between the kinetic parameters computed above and the efficiency of the flame-retardant treatment.

Appendix A: Kinetic models for a diffusional process accompanied by chemical reaction

In the following we shall consider the analysis of diffusion accompanied by continuous production of gases from a chemical reaction and the derivation of the corresponding kinetic model.

Let us consider an element of volume of substance, $\mathrm{d}V$. The concentration of gases which diffuse into it is lower than the concentration of evolving gases, because of the gas production within the volume, due to the chemical reaction.

If one assumes that the rate of gas production is related to the chemical reaction occurring within the volume $\mathrm{d}V$, one may write

$$\frac{\mathrm{d}c}{\mathrm{d}t} = k_0 c^n \tag{A1a}$$

where n is the reaction order, c is the concentration of substance undergoing the decomposition reaction, and k_0 is the rate constant. Assuming that the whole volume of substance is constant compared with the mass m, and by introducing the volume V into the constant k, Eq. (A1a) may be rewritten as

$$\frac{\mathrm{d}c}{\mathrm{d}t} = km^n \tag{A1b}$$

Taking into account Eq. (A1b) one may write a general equation for diffusion under steady state conditions

$$\frac{\partial c}{\partial t} = D\nabla^2 c + km^n = 0 \tag{A2}$$

where D is the diffusion coefficient and ∇^2 is the Laplacian operator.

The evolving gases are assumed to leave the whole volume of substance through the outer surface; consequently the rate of diffusional mass loss recorded in the TG curve should be

$$\frac{\mathrm{d}m}{\mathrm{d}t} = -SJ \tag{A3}$$

where S is the area of the outer surface and J is the flux of diffusion.

For the sake of simplicity, in the following we shall consider the cases of cylindrical and of spherical symmetry only.

(a) Cylindrical symmetry

In this case Eq. (A2) becomes

$$\frac{\partial^2 c}{\partial r^2} + \frac{1}{r}\frac{\partial c}{\partial r} + \frac{k}{D} m^n = 0 \tag{A4}$$

Because

$$m = \rho \pi l r^2 \tag{A5}$$

where ρ is the density of the investigated material, l is the length of the cylinder and r is its radius, Eq. (A4) leads to

$$\frac{\partial^2 c}{\partial r^2} + \frac{1}{r}\frac{\partial c}{\partial r} + \frac{k}{D} (\rho \pi l)^n r^{2n} = 0 \tag{A6}$$

The solution of Eq. (A6) is

$$\frac{\partial c}{\partial r} = \mathrm{e}^{-\int \frac{1}{r}\mathrm{d}r}\left[C + \int \frac{k}{D}(\rho \pi l)^n r^{2n} \mathrm{e}^{\int \frac{1}{r}\mathrm{d}r}\right]\mathrm{d}r \tag{A7}$$

where C is the integration constant.

After performing the integration one obtains

$$\frac{\partial c}{\partial r} = \frac{1}{r}\left[C + \frac{k}{D}(\rho \pi l)^n \frac{1}{2n+2} r^{2n+2}\right] \tag{A8}$$

Because there is no further production of gases when the cylinder disappears, it turns out that for $r \to 0$ the condition $\partial c/\partial r \to 0$ has also to be fulfilled. Taking into account this condition, Eq. (A8) leads to the ratio $C/0$, and in order to avoid the division by 0 one has to consider that also $C = 0$. One may thus write

$$\frac{\partial c}{\partial r} = \frac{k}{D} m^n \frac{r}{2(n+1)} \tag{A9}$$

Taking into account that the flux J in the radial direction is

$$J = D\frac{\partial c}{\partial r} \tag{A10}$$

from Eq. (A3) and Eqs. (A9) and (A10) it turns out that

$$\frac{\mathrm{d}m}{\mathrm{d}t} = -SD\frac{k}{D} m^n \frac{r}{2(n+1)} \tag{A11}$$

Because the area of the outer surface of a cylinder is

$$S = 2\pi r l \tag{A12}$$

one finally obtains

$$\frac{\mathrm{d}m}{\mathrm{d}t} = -\pi r l k m^n \frac{r}{n+1} \tag{A13}$$

or, taking into account Eq. (A5)

$$\frac{\mathrm{d}m}{\mathrm{d}t} = -\frac{k}{n+1}\frac{1}{\rho} m^{n+1} \tag{A14}$$

(b) Spherical symmetry

In this case Eq. (A3) becomes

$$\frac{\partial^2 c}{\partial r^2} + \frac{2}{r}\frac{\partial c}{\partial r} + \frac{k}{D} m^n = 0 \tag{A15}$$

Because

$$m = \frac{4}{3}\pi \rho r^3 \tag{A16}$$

where r is the radius of the sphere, Eq. (A15) leads to

$$\frac{\partial^2 c}{\partial r^2} + \frac{2}{r}\frac{\partial c}{\partial r} + \frac{k}{D}\left(\frac{4}{3}\rho\pi\right)^n r^{3n} = 0 \tag{A17}$$

From Eq. (A17), through integration, one obtains

$$\frac{\partial c}{\partial r} = \frac{1}{r^2}\left[C + \frac{k}{D}\left(\frac{4}{3}\rho\pi\right)^n \frac{r^{2n+3}}{3(n+1)}\right] \tag{A18}$$

Assumptions similar to those for the cylindrical case allow one to write that $C = 0$ and, consequently

$$\frac{\partial c}{\partial r} = \frac{k}{D} m^n \frac{r}{3(n+1)} \tag{A19}$$

Taking into account that the flux J is given by Eq. (A10) and that the outer surface area of the sphere is

$$S = 4\pi r^2 \tag{A20}$$

one may write

$$\frac{\mathrm{d}m}{\mathrm{d}t} = -4\pi r^2 D \frac{k}{D} m^n \frac{r}{3(n+1)} \tag{A21}$$

After performing all the calculations

$$\frac{\mathrm{d}m}{\mathrm{d}t} = -\frac{k}{n+1}\frac{1}{\rho} m^{n+1} \tag{A22}$$

One may notice that Eq. (A22) is identical with Eq. (A14).

By defining the degree of conversion α, as [4]

$$\alpha = 1 - \frac{m}{m_0} \tag{A23}$$

where m_0 is the mass of substance at the beginning of the reaction, Eq. (A14) or (A22) becomes

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = \frac{k}{n+1}\frac{1}{\rho} m_0^n (1-\alpha)^{n+1} \tag{A24}$$

Taking into account that k is a rate constant, its dependence on temperature is given by Arrhenius law

$$k = A\mathrm{e}^{(-E/RT)} \tag{A25}$$

where A is the pre-exponential factor, E is the activation energy, T is the temperature and R is the gas constant.

Introducing the notation

$$Z = \frac{A}{n+1}\frac{m_0^n}{\rho} \tag{A26}$$

Eq. (A24) may finally be written as

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = Z(1-\alpha)^{n+1}\mathrm{e}^{(-E/RT)} \tag{A27}$$

Eq. (A27) may be considered as the kinetic model of a diffusional process accompanied by chemical reaction.

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