

A thermogravimetric study of flame-proofed wool

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Abstract

A thermogravimetric investigation of K_2ZrF_6 -treated and untreated wool was carried out in air atmosphere. Two regions of major mass losses were analysed and the kinetic parameters of the two decomposition processes were computed. The results suggest that a correlation between the calculated parameters and the treatment level may exist.

INTRODUCTION

The flammable nature of fibrous products is one of the major problems of the present time, fires from textiles causing many deaths and injuries, and considerable financial losses. Hazards from flammable fabrics have been recognized for many centuries, and repeated attempts have been made to control them [1].

Although wool is regarded as a natural flame resistant fibre, some flame-proofing treatments based on titanium or zirconium salts have been developed, in order to make wool fabrics conform to the most severe specifications [2].

Thermogravimetry is used widely as a method to investigate the thermal decomposition of polymers and to assess their relative stabilities [3]. In addition, considerable attention has been directed toward the use of the thermogravimetric data for the determination of kinetic parameters.

The aim of this work is to obtain the kinetic parameters of the thermal decomposition of wool and to study how the treatment with a zirconium salt affects them.

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EXPERIMENTAL

Materials

Wool fibres 25 μm thick, cleaned with CCl_4 , were used for the experiments. The zirconium treatment salt K_2ZrF_6 and the HCl solution used for adjusting the pH were both analytical grade.

Equipment

A derivatograph Q 1500 D, Paulik, Paulik and Erdey type (MOM Budapest), air atmosphere, platinum crucibles and alumina reference standard were used. DTA (250 μV sensitivity) and TG curves were recorded. The weight of each sample submitted to thermal destruction was about 50 mg.

A Pye Unicam atomic absorption spectrophotometer was used to determine the zirconium content in the wool.

Treatment

The wool was treated in a Linitest laboratory dyeing apparatus with 0%, 2%, 4%, 6%, 8%, 10% and 12% salt and 10% HCl (37%), to maintain a pH of 2.5, for 45 min at 60°C with a 40:1 liquid to solid ratio. After treatment the fibres were rinsed and dried in air at room temperature.

RESULTS AND DISCUSSION

Untreated and treated fibres were subjected to controlled heating in the derivatograph. An example of recorded DTA and TG curves is given in Fig. 1. The temperature ranges and mass losses (percentages) for the most important processes are given in Table 1.

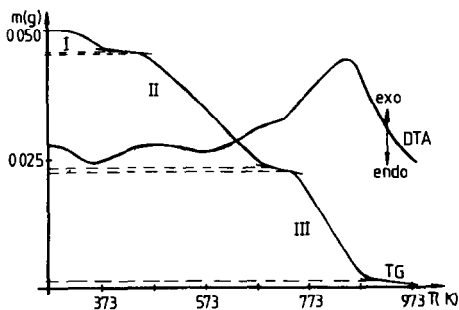


Fig. 1. TG and DTA curves recorded for wool.

TABLE 1

The mass losses and the corresponding temperature ranges from the TG curves

Sample treatment	Temperature range (°C)			Mass loss (%)		
	Process I	Process II	Process III	Process I	Process II	Process III
Unscoured	≤ 118	170–340	436–540	7.3	27.6	16.6
CCl ₄ cleaned	≤ 128	190–394	438–568	9.6	33.6	29.6
0%	≤ 140	212–385	445–605	9.6	33.6	34.4
2%	≤ 110	193–366	430–559	8.5	35.2	35.5
4%	≤ 120	203–380	449–570	8.0	35.2	33.6
6%	≤ 115	175–361	435–570	6.4	33.3	34.7
8%	≤ 160	222–391	466–595	5.2	31.3	32.7
10%	≤ 160	245–400	478–590	5.6	33.4	35.6
12%	≤ 115	194–363	410–557	8.7	32.0	36.0

Both Fig. 1 and Table 1 indicate that three processes take place which are accompanied by significant mass loss. The first, which ends at around 120–150°C, is an endothermic process and is clearly the loss of sorbed water. The kinetic parameters of this process are of some interest when differences between degradative treatments of wool are to be analysed.

The second important mass loss is associated with the destruction of disulphide linkages and the elimination of H₂S [4]. Previous studies have considered the destruction of the wool helix in a nitrogen atmosphere; because the present investigation takes place in air atmosphere, some oxidative reactions are also very likely. The recorded DTA curve exhibits a broad endothermic peak which is probably the result of an overlapping of several effects. Consequently, it may be considered that this second process is the result of the melting of the helix structure followed by the thermal pyrolysis of their chain linkages, peptide bridges and some other small lateral chains, which finally leads to skeletal degradation [5].

The third large mass loss is an exothermic process which may be ascribed to the oxidative destruction of the fibre.

The last two processes on the TG curve were analysed and their kinetic parameters were computed. The integral method was used for the calculations. The fundamental criticism of integral methods as applied to a single thermogravimetric curve is that the best values of the kinetic parameters are inevitably fitted to the data whether or not these parameters have any significance in the understanding of the mechanism [6]. However, integral methods have the advantage of smoothing the experimental errors, which is very important when a material like wool is being analysed [7].

The following equation was used in the calculation [8]:

$$\ln F(1 - \alpha) = -E/RT + \ln A - \ln \beta + L \quad (1)$$

TABLE 2

The kinetic parameters of the last two processes (II and III)

Sample treatment	Process II			Process III			Sum of energies
	<i>n</i>	<i>E</i> (kcal mol ⁻¹)	<i>A</i> (s ⁻¹)	<i>n</i>	<i>E</i> (kcal mol ⁻¹)	<i>A</i> (s ⁻¹)	
Unscoured	2	18.6	5 × 10 ⁶	1	43.1	2 × 10 ¹¹	61.7
CCl ₄ cleaned	2	19.6	7 × 10 ⁶	1	41.1	3 × 10 ¹⁰	60.7
0%	2	24.4	3 × 10 ⁸	1	37.9	2 × 10 ⁹	62.3
2%	2	22.2	1 × 10 ⁸	1	40.4	2 × 10 ¹⁰	62.6
4%	2	22.5	1 × 10 ⁸	1	44.3	1 × 10 ¹¹	66.8
6%	2	22.6	2 × 10 ⁸	1	40.7	2 × 10 ¹⁰	63.3
8%	2	28.3	5 × 10 ⁹	1	43.6	5 × 10 ¹⁰	71.9
10%	2	27.7	2 × 10 ⁹	1	56.6	1 × 10 ¹⁴	84.3
12%	2	22.5	1 × 10 ⁸	1	32.9	2 × 10 ⁸	55.4

where $F(1 - \alpha)$ is the conversion integral given by eqn. (2) below, E is the activation energy, A is the preexponential factor, β is the heating rate, T is the temperature, R is the gas constant and L is a correction factor. The conversion integral was calculated in the reaction-order framework [9]:

$$F(1 - \alpha) = \int_0^\alpha (1 - x)^{-n} dx = \begin{cases} \frac{1 - (1 - \alpha)^{1-n}}{1 - n} & n \neq 1 \\ -\ln(1 - \alpha) & n = 1 \end{cases} \quad (2)$$

where n is the reaction order and α , the conversion, is given by $\alpha = (m_t - m_0)/(m_f - m_0)$, where m_t is the mass at time t , and m_0 and m_f are the masses at the beginning and end of the process, respectively.

The plot of $\ln F(1 - \alpha)$ versus $1/RT$ gives a straight line whose slope provides the activation energy E . The use of the least-squares method to draw the straight line allows the correlation coefficient to be calculated. Different correlation coefficients are obtained for different values of the reaction order n , and the one whose absolute value is the closest to unity gives the reaction order which best fits the process. The value of the preexponential factor A may finally be calculated from the intercept of the straight line. The values of these parameters calculated for the last two processes are given in Table 2. It can be seen that the computed reaction order is 2 for the first process and 1 for the second process. Thus, the pyrolysis of wool is a second-order reaction and its oxidative destruction is first order. In addition, the values of the preexponential factor A are of the same magnitude for all the studied systems. This fact supports the supposition that the compensation effect does not affect the results [9].

With respect to the values of E , even if they are not true activation energies as understood by homogeneous kinetics, they are considered to reflect strongly the energies involved in the processes [9].

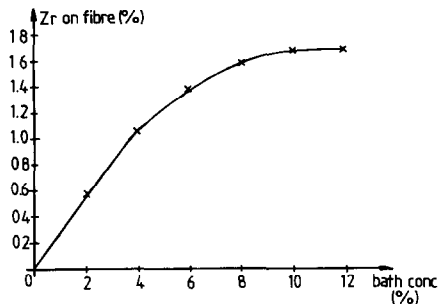


Fig. 2. Adsorption isotherm of zirconium by wool fibre.

The last column in Table 2 was obtained by summing the values obtained for E . This sum may be regarded as being related to the total thermal energy required to destroy the wool fibre. The high value obtained for unscoured wool, which is close to those of the treated wool, may be explained by effects caused by mineral impurities. The values obtained with high concentrations (10% and 12%) of zirconium salt, are considered anomalous, the zirconium complex which is probably formed in the solution being only part of the explanation. A determination of the zirconium content of the wool fibres was made by atomic absorption spectrophotometry. The results are plotted versus the bath concentration, and a Langmuir-type adsorption isotherm was obtained, see Fig. 2. It should be noted that during these experiments, saturation of the fibre is reached for bath concentrations of about 8%.

The shape of the obtained curve also corroborates the hypothesis that zirconium ions are linked by active sites (carboxyl terminal groups) from the non-crystalline part of the wool [10]. A plot of the values of the energy sum against the zirconium content of the fibre, as given in Fig. 3, displays a fairly linear relationship between the amount of sorbed zirconium ion and the total energy required to destroy the fibre. Again, 10% and 12% treated

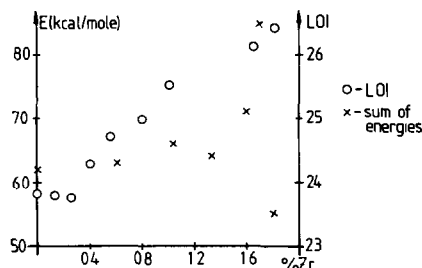


Fig. 3. The dependence of the sum of energies and of the LOI value on the zirconium content of the fibres.

wools behave anomalously. Thus, one may suppose that the sorbed ions help new linkages to be established in the wool fibre; consequently, more energy will be required to break the fibre.

Figure 3 also shows limiting oxygen index (LOI) values of the wool fibre versus the zirconium content of the wool, as given in ref. 11. The values of LOI and of the sum of the energies have a similar dependence on the zirconium content of the fibre. This suggests that a relationship between LOI and the sum of energies might exist.

CONCLUSIONS

The TG investigation of wool fibre revealed three major regions of weight loss. The kinetic parameters of the last two, which are considered to be the regions within which wool fibre decomposes, were used to characterize the level of the K_2ZrF_6 flame-proofing treatment. It was also shown that the sum of the two values of parameter E , calculated for each of these two processes, increases when the amount of zirconium ion sorbed by the fibre increases. This suggests that the ions lead to the formation of new linkages inside the fibre, probably by forming a complex.

A possible relationship between LOI and the sum of the energies was suggested by the similarity of their plots against the zirconium content of the fibre. An explanation of this may be given if one considers that the energy of burning of wool provides the major contribution to the LOI value.

To summarize, one may consider that the sum of the two values of parameter E might be used as an index to characterize the level of a treatment with zirconium salt.

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