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EFFECT OF CHLORINATION TREATMENT ON THE THERMOGRAVIMETRIC BEHAVIOUR OF WOOL FIBRES

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Abstract

The thermal behaviour of wool, untreated and chlorinated to various extents, was investigated. The kinetic parameters of the water loss and pyrolysis processes were computed and, based on their values, the way chlorination treatment affects wool fibre is discussed. As it appears, the chlorination process affects the fibre only superficially and not its internal chemical composition, as the values of the kinetic parameters of the thermal decomposition of wool fibre do not seem to be influenced at all by the treatment.

Keywords: chlorination, kinetic parameters, thermogravimetry, wool

Introduction

The chlorination of wool is a chemical treatment by which the fibre is stripped off its scales in order to decrease its felting potential and to allow production of machine washable wool garments. Depending on the amount of chlorine used, wool fibre may be damaged to various extents and may even lose completely its outer surface, cuticula [1]. As a consequence of the process the mechanical properties of wool are modified, the touch of the end products may be impaired, the fibres may yellow and also their dyeability is changed [2]. It may be expected that some chemical changes occur in the fibre.

The aim of the present paper is to study the applicability of thermal analysis (thermogravimetry) to investigate the effect of the chlorinating process, as it is performed now on an industrial scale, on the thermal behaviour of wool fibre. The study was performed by comparing the kinetic parameters calculated from thermogravimetric data of the untreated and treated fibres with the aim to analyze how chlorination affects the chemistry of the fibre.

Experimental

Ecru knitted fabrics of 27 μm wool, untreated and treated with 1, 2 and 3% chlorine (w/w of wool) were used.

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The chlorinating process was performed on the knitted fabric. The process was conducted by paddling the fabrics with 1, 2 and 3% chlorine in a solution of sodium hypochlorite, at pH=1.8...2.0 and temperature of 15...20°C, followed by an antichlorinating treatment at pH=8.5 with sodium sulphite, thoroughly rinsing with cold water and drying at room temperature.

From each fabric sample of 4–5 mg were cut and used for thermoanalytical experiments. A Netzsch TG 209 thermobalance, air flow of 10.00 $cm^3 min^{-1}$ and aluminium crucibles were used for thermogravimetric measurements. The temperature range was 20 to 500°C, and the heating rates were 10, 13, 15, 17 and 20 $K min^{-1}$.

Results and discussion

A typical thermogravimetric curve is given in Fig. 1. Two regions of major mass loss – from 30 to around 120°C and from 220 to 420°C – can be observed.

Both decomposition stages are quite complex from the point of view of the processes they involve.

The first process, occurring from 30 to 120°C and accompanied by a decrease of 7–10% in wool fibre mass, is ascribed to the loss of water. It is considered that there are three different types of water within the fibre i.e.: free water, loosely bonded water and chemically bonded water [3]. As a consequence, the loss of water, as recorded by the thermogravimetric curve, is the result of the overlapping of three different processes in which the three types of water are lost.

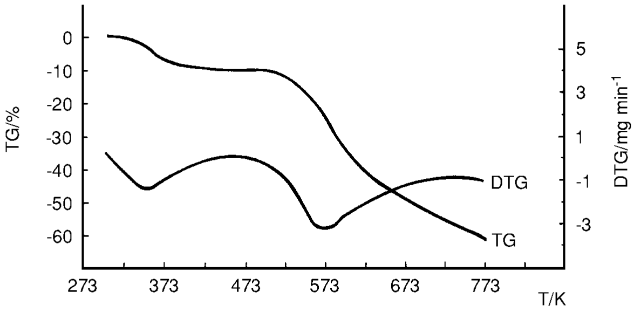

Fig. 1 TG and DTG curves of wool knitwear fabric

The second mass loss process, occurring from 220 to 420°C and accompanied by a 30–33% loss of wool fibre mass, is associated with the destruction of disulphide linkages and the elimination of H_2S [4]. During this process the helix structure is melted, followed by the thermal pyrolysis of the chain linkages, peptide bridges and some other lateral chains, which finally leads to skeletal degradation [5]. Consequently, this pyrolytic region includes several chemical reactions by which protein compounds are decomposed to lighter products and volatile compounds such as H_2S, CO_2, H_2O, HCN [6].

Based on the recorded mass loss data and the corresponding temperatures, the kinetic parameters of the two processes, (the reaction order, *n*, the activation energy, *E* and the pre-exponential factor, *A*) were calculated, by an integral method, for each experiment.

As it was discussed above, each of the two processes involves several overlapping reactions. Consequently, the computed kinetic parameters are not describing single reactions, but they are overall values. However, we assume that a change of the values of the calculated parameters should be due to some changes of the internal chemistry of the fibre itself, which results in a change of the mechanism of the dehydration and pyrolysis processes. 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 [8]. However, integral methods have the advantage of smoothing the experimental errors, which is very important when a material like wool is being analyzed [9].

The computational method that has been used was based on the following Eq. [7]:

$$\ln F(1-\alpha)=\frac{-E}{RT}+\ln A-\ln\beta+L \qquad (1)$$

where $F(1\text{-}\alpha)$ is the conversion integral given by Eq. (2) below, T is the temperature, β is the heating rate, R is the gas constant and L is a correction factor. The conversion integral was calculated in the reaction-order framework [8]:

$$F(1-\alpha)=\begin{cases}[1-(1-\alpha)^{1-n}]/(1-n), & n\neq 1\\ -\ln(1-\alpha), & n=1\end{cases} \qquad (2)$$

where n is the reaction order and α, the conversion degree, is given by:

$$\alpha=\frac{m_t-m_o}{m_f-m_o} \qquad (3)$$

where m_t is the mass at time t and m_o and m_f are the masses at the beginning and end of the process, respectively. For a proper choice of the reaction order, n, the plot of $\ln F(1-\alpha)$ *vs*. $1/T$ gives a straight line whose slope provides the value of the activation energy, E. The value of the pre-exponential factor, A, may, finally, be calculated from the intercept of the straight line. The calculus was performed by the Netzsch device software program.

The results obtained for the three parameters are given in Table 1.

From Table 1 one may notice first that for the whole range of heating rates the values of the kinetic parameters for the same sample are very close. According to the above discussion, we consider, thus, that the mechanism does not change when the heating rate changes from 10 to 20 K min^{-1}. Consequently, one may take the average values for the five experiments with the same wool sample in order to compare the effects of chlorinating treatment.

In Figs 2, 3 and 4 the average values of the three kinetic parameters for both processes are plotted *vs*. the percentage of the sodium hypochlorite used for treatment.

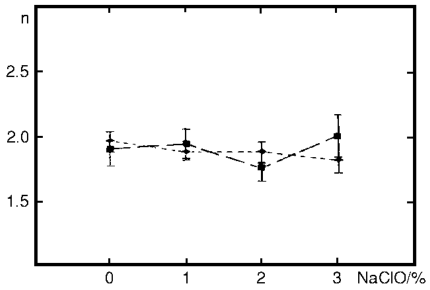

Fig. 2 Variation of the reaction order, *n*, with the intensity of the chlorinating process, for: ◆ – water desorption process; ■ – pyrolytic process

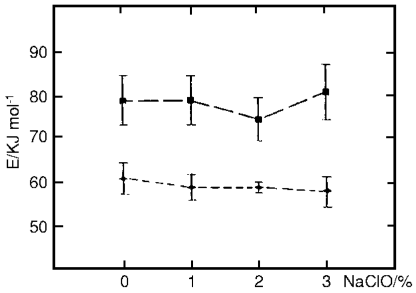

Fig. 3 Variation of the activation energy, *E*, with the intensity of the chlorinating process, for: ◆ – water desorption process; ■ – pyrolytic process

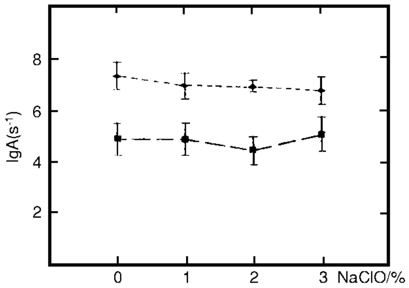

Fig. 4 Variation of the pre-exponential factor, lg*A*, with the intensity of the chlorinating process, for: ◆ – water desorption process; ■ – pyrolytic process

From Fig. 2 it may be noticed that the values of the reaction order parameter, *n*, are roughly equal to 2 for both the dehydration and pyrolytic processes. For the pyrolysis step this value might be explained by a model which takes into consideration the pyrolytic reactions together with the diffusion of the evolving gases, as reported

Table 1 The values of the kinetic parameters for the two mass losses steps and the temperature of the maximum reaction rate T_m (I – Water loss, II – Pyrolysis process)

Sample	Heating rate, β/K min^{-1}	Reaction order, *n*		Activ. energy, E/kJ mol^{-1}		Pre-exp. factor, lg*A*/s^{-1}		T_m/K	
		I	II	I	II	I	II	I	II
Untreated wool	10	2.01	1.73	64.9	69.4	8.0047	3.9360	339.7	557.0
	13	2.06	1.80	64.2	76.7	7.8883	4.7387	343.0	561.4
	15	1.97	1.97	59.8	81.4	7.2309	5.2262	343.7	564.8
	17	1.95	1.97	59.5	79.7	7.1747	5.0885	345.7	565.1
	20	1.84	2.09	55.4	86.0	6.5167	5.7314	350.1	568.1
Treated with 1% chlorine	10	1.95	1.76	63.7	70.3	7.7563	4.0167	341.3	558.0
	13	1.93	1.93	59.9	75.9	7.1260	4.6284	343.3	563.1
	15	1.78	2.03	55.4	81.5	6.4272	5.2099	346.8	565.5
	17	1.92	1.95	58.5	79.0	6.9228	5.0112	349.5	566.6
	20	1.87	2.07	56.0	86.8	6.5450	5.8134	353.9	568.9
Treated with 2% chlorine	10	1.87	1.58	58.7	65.6	6.9312	3.5773	341.7	557.0
	13	1.77	1.76	57.1	72.2	6.6993	4.2791	344.2	561.9
	15	2.00	1.80	60.2	75.8	7.2032	4.6530	347.5	562.4
	17	1.87	1.89	59.7	80.1	7.1008	5.1168	348.5	568.2
	20	1.92	1.82	57.5	77.5	6.7636	4.8996	350.9	568.8
Treated with 3% chlorine	10	1.85	1.82	59.6	71.3	7.1091	4.1027	340.7	557.9
	13	1.98	1.87	62.0	76.3	7.4782	4.6669	345.0	562.5
	15	1.84	2.00	58.3	81.2	6.8382	5.1932	347.7	566.8
	17	1.80	2.16	56.0	84.8	6.4580	5.5639	351.8	564.8
	20	1.68	2.24	52.1	89.0	5.9719	6.0134	352.0	569.9

previously [10]. One may assume that the water loss also occurs according to a similar mechanism.

One has to keep in mind that the analyzed process is the resultant of several overlapping processes and that it is probable that the values of the computed parameters are those of the slowest reaction. A support for this assumption seems be provided by some new results concerning a deeper analysis of the water desorption process. It was evidenced, thus, that three parallel reactions occur simultaneously. One of them, which involves the desorption of the strongly (chemically) bonded water, is of the second order and the other two processes, involving the desorption of the free and loosely bonded water, are of the first order [11].

Figures 3 and 4 show curves with a similar behaviour. As the variation of the values of the activation energy, E, and of the pre-exponential factor, A, follows the same paths, one may suppose that they are affected by a compensation effect due to the mathematical handling of the Arrhenius type relationship [12]. In order to overcome this, the values of the rate constant, k_T, have been computed by using the following equation:

$$k_T = A\exp(-E/RT) \qquad (4)$$

As the value of the temperature T, we have chosen the one that corresponds to the maximum value of the reaction rate, i.e. to the DTG peak, T_m, also given in Table 1. The values of the maximum rate constant, k_{Tm}, were computed for each experiment separately and then the averages were taken. The plot of these average values *vs.* the sodium hypochlorite amount used for the treatment is given in Fig. 5.

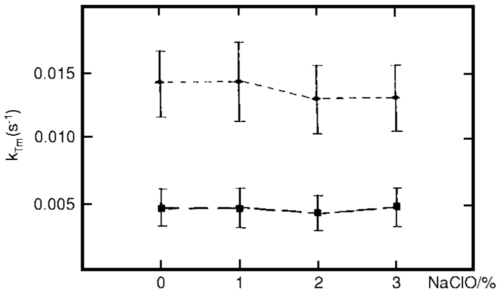

Fig. 5 Variation of the rate constant at the temperature corresponding to the maximum rate of the reaction, k_{Tm}, with the intensity of the chlorinating treatment for: ◆ – water desorption process; ■ – pyrolytic process

The plot in Fig. 5 allows us to conclude that, within the limits of the experimental errors, the maximum value of the rate constant, k_{Tm}, does not seem to be affected by the chlorinating treatment.

Summing up the results of the plots in Figs 2 and 5 respectively, it seems that neither the value of the reaction order, n, nor those of the maximum rate constant, k_{Tm}, are influenced by the chlorinating treatment.

As we have mentioned at the beginning, the values of the kinetic parameters computed above are considered as linked to the chemistry of the sample. If so, a change of the internal structure, whose thermal decomposition produces the TG curve, is expected to affect somehow the recorded curve and, consequently, its calculated parameters. As, within the limits of the experimental errors, no significant differences were noticed between the calculated values of the rate constants, one may conclude that the chlorinating process, performed as described, is either not affecting the inner chemistry of the wool fibre, or the modification is too small to influence the overall thermal decomposition process of wool fibre.

Conclusions

The thermal behaviour of untreated and chlorinated wool fibres was investigated by thermogravimetry. The kinetic parameters computed for the water desorption process and for the pyrolysis seem to be fairly constant over the range of the heating rates used in the investigations, and have been used for characterizing the recorded TG curves. The values of the reaction order, n, and of the maximum rate constant, k_{Tm}, have been found to be not affected by the intensity of the chlorinating treatment. Therefore we have concluded that the chlorinating process, conducted as described, does not influence the water desorption process and the pyrolysis of wool. As both processes are the resultant of several reactions, and, consequently, strongly related to the inner chemistry of the wool fibre, one may consider, also, that the wool chemistry is not affected by the chlorinating treatment.

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