Study on the thermal stability of wool treated with flame-retardant reagents

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Abstract

The thermal degradation of wool treated with flame-retardant reagents synthesized in our laboratory, namely, $(NH_4)_3H_2PO_4$ $[Al(H_2PO_4)_5]$, $(NH_4)_3Cl[Ca(H_2PO_4)_4]$, $(NH_4)_3Cl$ $[Mg(H_2PO_4)_4]$, $(NH_4)_3H_2PO_4[Zn(H_2PO_4)_4]$, $K(NH_4)_2Cl[Zn(H_2PO_4)_4]$, $Na_3Cl[Zn(H_2PO_4)_4]$ and $H_3PO_4[Zn(H_2PO_4)_2]$ was studied by thermal analysis, infrared spectroscopy and by measurement of the limiting oxygen index (LOI). The kinetic parameters were obtained using the equations of Brodio and Kissinger. The activation energies were calculated for the decomposition of untreated wool and wool treated with flame-retardant reagents. Experimental data showed that for the wool treated with flame-retardant reagents there were increases in char yield and LOI, and decreases in the activation energy and the temperature of decomposition.

Keywords: DTA; Flame-retardant; Pyrolysis; TA; Thermal degradation; Wool

1. Introduction

Wool is a protein composed of the –NH–Co– group. The natural flame-resistant properties of the wool are connected with its relatively high nitrogen content (16%), high ignition temperature (773 K), low heat of combustion, low flame temperature and high limiting oxygen index [1]. With the development of science and technology and the improvement of the standard of life, improvement of the natural flame-resistance of wool has provoked people's interest.

Many reports have been published on the use of flame-retardant reagents for wool [1–3]. As far as we know, however, the systematic study of the kinetic parameters of

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wool treated with flame-retardant reagents has not yet been reported. In this paper, seven flame-retardant reagents prepared in our laboratory were applied at pH < 3 in order to exhaust the negatively charged complexes on the positively charged amino groups inside the wool fibres. The thermal degradation of wool with and without flame-resistant treatment was then studied by thermal analysis, infrared spectroscopy and by measurement of the LOI.

2. Experimental

2.1. Material

The following samples of wool with and without flame-retardant treatment were selected for the present study. Sample (I) was New Zealand wool. It was washed with carbon tetrachloride and water and then dried at 330 K, Samples (II)–(VIII) were obtained by dipping the dried wool into an aqueous solution (concentration 0.06–0.10 mol L^{-1}) of one of seven flame-retardant reagents synthesized in our laboratory [1], namely: $(NH_4)_3H_2PO_4[Al(H_2PO_4)_5]$, $(NH_4)_3Cl[Ca(H_2PO_4)_4]$, $(NH_4)_3Cl$ $[Mg(H_2PO_4)_4]$, $(NH_4)_3H_2PO_4[Zn(H_2PO_4)_4]$, $K(NH_4)_2Cl[Zn(H_2PO_4)_4]$, Na_3Cl $[Zn(H_2PO_4)_4]$ and $H_3PO_4[Zn(H_2PO_4)_2]$. The weight ratio of liquor to wool was 30:1. Each reaction mixture was boiled for 30 min.

2.2. Thermal analysis

Differential thermal analysis (DTA) and thermogravimetry (TG) were carried out on a DT-40 thermal analyzer (Shimadzu, Japan). DTA and TG were performed under static air at a scanning rate of 10 K min^{-1}. α-Al$_2$O$_3$ was taken as the reference material.

2.3. Infrared spectrometry

Fourier transform infrared (FTIR) analysis was performed on a Bio-Rad FTS-40 FTIR spectrophotometer at a resolution of 4 cm^{-1}; wool residues obtained by heating wool, with and without flame-retardant treatment, in a DTA cell at 473, 523, 573, 623 and 673 K were analyzed by the KBr technique.

3. Results and discussion

From Table 1 it is evident that the residual char and the LOI values for wool with flame-retardant treatment (samples (II)–(VIII)) are more than those for the untreated wool. These data suggest that the combustibility of the treated wool is reduced.

The results from thermal analysis of wool with and without flame-retardant treatment are also presented in Table 1. A typical trace is shown in Fig. 1. The second exotherm is at 787, 758, 770, 739, 728, 740, 765 and 758 K for wool samples I–VIII, respectively. As explained by Wang et al. [3] the weight loss between 523 and 698 K

Table 1
The thermal properties of wool with and without flame-retardant treatment

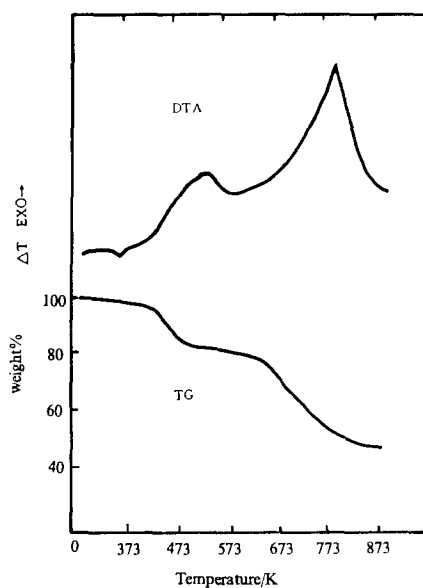| Sample no.	Char yield/w%	LOI	Second exotherm		
			Exotherm/K	Activation energy/(kJ mol^{-1})	
				Kissinger	Brodio
I	0.8	24.0	787	160.7	
II	2.4	27.0	758	127.2	125.5
III	3.3	28.0	770	113.6	117.2
IV	4.4	27.5	739	113.0	118.9
V	8.3	31.0	728	113.7	113.8
VI	9.5	33.5	740	126.1	125.5
VII	5.1	32.5	765	121.2	113.9
VIII	6.0	31.0	758	111.4	116.4

Fig. 1. Thermal analysis of wool in air, rate of heating 10 K min^{-1}.

resulted from the decomposition of cystine and terminal amino groups and from decarboxylation. The second weight loss between 700 and 870 K was due to the carbonization of the wool with and without flame-retardant treatment and the oxidation of the charred residue.

The kinetic parameters for the second stage of pyrolysis of the wool with and without flame-retardant treatment were determined using the methods described by Brodio [4] and Kissinger [5].
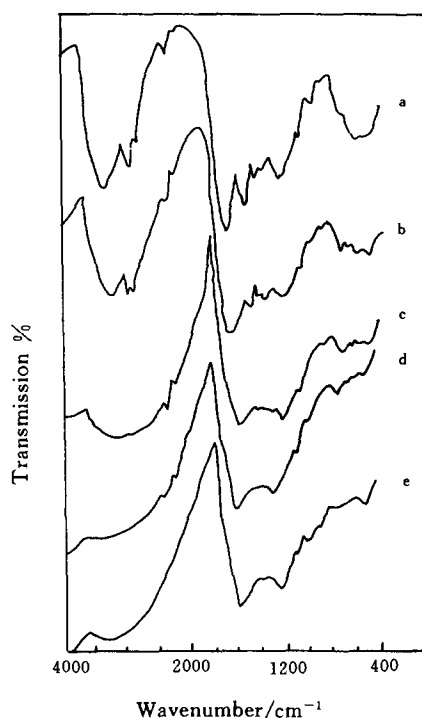
Fig. 2. The change on heating in air of the Fourier transform IR spectrum of wool; a–e, wool charred at 473, 523, 573, 623 and 673 K, respectively.

It can be seen from Table 1 that the energies of activation for the wool with flame-retardant treatment (II)–(VIII) are low compared with those of the untreated wool.

The IR spectra at 473, 523, 573, 623 and 673 K for untreated wool in air are shown in Fig. 2 [6]. The changes in the IR spectra are explained as follows. The N–H bending frequency at 1520 cm^{-1} shows a reduction in intensity, as would be expected with increasing loss of ammonia from the char. The CH_2– and CH_3–stretching at 2950 and 2924 cm^{-1} do not show much reduction in intensity until 673 K, indicating that the evolution of volatile hydrocarbons commences only at higher temperatures. The carbonyl stretching frequently at 1631 cm^{-1} shows less reduction in intensity, but by 673 K the maximum absorption shifts to 1600 cm^{-1}, suggesting the formation of C=C [6].

The IR spectra for wool treated with $(NH_4)_3Cl[Mg(H_2PO_4)_4]$ are shown in Fig. 3; the band at 2429 cm^{-1} (O–H) disappears and the band of PO_4^{3-} appears at 1080 cm^{-1}.

All of the complex reagents mentioned above are composed of cations such as H^+, Na^+ and NH_4^+, anions such as Cl^- and $H_2PO_4^-$ and complex anions such as $[Ca(H_2PO_4)_4]^{2-}$ and $[Al(H_2PO_4)_5]^{2-}$. In addition, the amino groups inside the wool fibre can form the cation $-NH_3^+$ under acid conditions. Hence, treatment with the
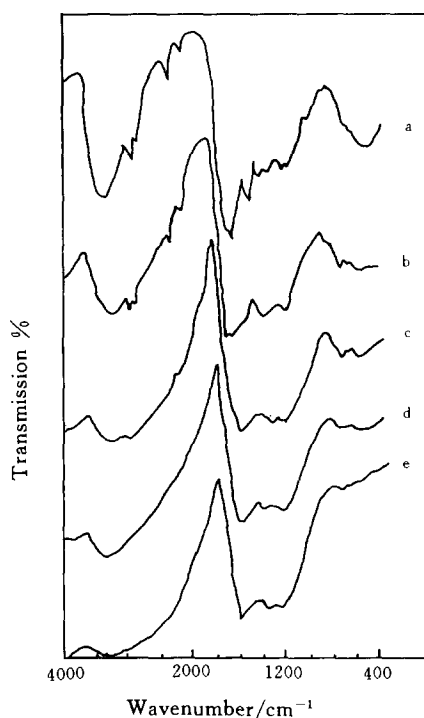
Fig. 3. The change on heating in air of the Fourier transform IR spectrum of wool treated with $(NH_4)_3Cl$ $[Mg(H_2PO_4)_4]$; a–e, wool charred at 473, 523, 573, 623 and 673 K, respectively.

fire-retardant reagents mentioned above results in the binding of complex anions to the positively charged amino group at pH $\leq$ 3. The pyrolysis of the wool treated with phosphorus-containing flame-retardant reagents forms a glass-like melt which isolates the air from the wool to achieve the flame-retardant effect [7].

References

[1] J.L. Tian, Huaxue Shijie, 1 (1988) 8.
[2] A.R. Horrocks, J. Soc. Dyers Colour., 16 (1986) 62.
[3] J.Q. Wang and D.M. Feng, Polym. Deg. Stab., 43 (1994) 93.
[4] A. Brodio, J. Polym. Sci. Part A–2, (1969) 1761.
[5] H.E. Kissinger, Anal. Chem., 29(11) (1957) 1702.
[6] P.E. Ingham, J. Appl. Polym. Sci. 15 (1971) 3025.
[7] C.M. Tian, H.Z. Guo, H.Y. Zhang, J.Z. Xu and J.R. Shi, Thermochim. Acta 253 (1995) 243.