Thermochimica Acta 516 (2011) 29–34

Contents lists available at ScienceDirect

Thermochimica Acta

journal homepage: www.elsevier.com/locate/tca

Flame retardant wool using zirconium oxychloride in various acidic media optimized by RSM

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ARTICLE INFO

Article history:
Received 9 September 2010
Received in revised form
27 December 2010
Accepted 7 January 2011
Available online 20 January 2011

Keywords:
Wool
Flame retardant
Zirconium oxychloride
Acid
Response surface methodology

ABSTRACT

The flame retardant wool was prepared using zirconium oxychloride with various acids. The thermal degradation of wool treated with the flame retardant synergistic system, zirconium oxychloride, citric acid and hydrochloric acid, was studied by thermal analysis, mass loss, limiting oxygen index (LOI) and vertical flame test. The fabric surfaces were also observed by SEM. The wool treated with the flame-retardant shows an increase in the decomposition temperature, residual mass and LOI. Also the wool treated with hydrochloric acid showed improved flame retardant properties compared to the use of formic acid. The response surface methodology (RSM) was also used for the experimental plan with four variables on the results of flame retardancy. The statistical analysis confirms the optimum conditions obtained by the experimental results.

1. Introduction

The flammable nature of fibrous products is one of the major problems of the present time. Fires from textiles are 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].

Naturally occurring polyamide fibers, such as the sheep wool, display a high degree of natural flame retardancy [1]. Wool, a protein fiber, contains many kinds of α-amino acids such as cysteine, thiocarbamic acid, and cross-linking polypeptides with a helical structure [1].

The natural flame-resistant properties of the wool are connected with its relatively high nitrogen content (16%) [1], high moisture content (10–14%) [2], high ignition temperature (570–600 °C) [3], low heat of combustion, low flame temperature and high limiting oxygen index [4]. The performance of wool fabrics in the various test methods currently in use depends on the specified method and fabric construction. A horizontal method is much less severe than a 45° or a vertical test. Most wool fabrics will pass a horizontal test but may not pass some 45° or vertical tests. It follows that wool in some cases needs a flame-resist treatment in order to pass particular flammability specification and test method. Curtain and wall covering in public building, aircraft furnishings and blankets, furnishings and curtains in general transport, protective clothing and carpets of shag pile construction and low density are products which may require such treatment [5]. It has previously been proposed to apply titanium compounds to textile fibers as flame-retardant agents. Such compounds are not always suitable when wool fibers are used because they can cause yellowing. Moreover, although the process is satisfactory for many purposes, it is not entirely suitable for the manufacture of bleached wool.

Wool, when heated alone, pyrolyses by a complex series of reactions which yield a number of products at increasing temperatures. Initially at 230–240 °C rupture of the helical structure occurs and the major ordered part of the wool protein undergoes a solid to liquid phase change [6]. At 250–295 °C an endothermic reaction occurs associated with release of sulphur compounds due to the breaking of the cystine disulphide bonds and simultaneous release of hydrogen sulphide. Above 250 °C general pyrolytic decomposition occurs, including char-forming reaction with dehydration and loss of other volatiles. In the presence of air, formation of sulphur dioxide occurs between 270 °C and 320 °C [6]. Cleavage of the cystine disulphide bond is seen to play a very important role in the thermal degradation and combustion of keratin and it

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doi:10.1016/j.tca.2011.01.007

Table 1
Experimental for flame retardant wool based on CCD.

Run number	A: Zirconium oxychloride (%)	B: Temperature (°c)	C: Citric acid (%)	D: HCl (37%) (%)	Char length (cm)
1	10.60	95.00	12.80	5.65	1.3
2	5.60	77.00	12.80	5.65	1.4
3	8.10	70.86	9.55	8.00	1.35
4	8.10	86.00	9.55	8.00	1.05
5	8.10	86.00	9.55	4.05	1.25
6	10.60	77.00	6.30	10.35	1.3
7	8.10	86.00	9.55	8.00	1.1
8	8.10	86.00	9.55	8.00	1.0
9	8.10	101.14	9.55	8.00	1.0
10	8.10	86.00	9.55	8.00	1.05
11	8.10	86.00	9.55	8.00	1.0
12	12.30	86.00	9.55	8.00	1.5
13	5.60	95.00	6.30	10.35	1.65
14	5.60	95.00	12.80	10.35	1.45
15	3.90	86.00	9.55	8.00	1.85
16	8.10	86.00	15.02	8.00	1.45
17	8.10	86.00	4.08	8.00	1.15
18	10.60	77.00	12.80	10.35	1.3
19	5.60	7.00	6.30	5.65	2.0
20	10.60	95.00	6.30	5.65	1.5
21	8.10	86.00	9.55	11.95	1.1

has been suggested that the oxidation of cystine may be the initial exothermic reaction in the burning of wool [6]. Few reports have been published on the systematic study of the decomposition parameters of wool treated with flame retardant reagents [7,8].

The present study has optimized a process for improving the flame-resist properties of natural protein fibers which comprises depositing in the fibers a complexed zirconium compound and thermal degradation of treated wool and raw wool were investigated.

In recent years there have been a number of reports of treatments which enhance wool natural flame-resistant properties [9–13]. Benisek in the International Wool Secretariat Laboratories observed that mordanting treatments based on zirconium and titanium salts markedly improve wool flame resistance [9–11]. We have also reported the effect of zirconium oxychloride with formic acid on wool and showed an improvement in the flame retardant properties of wool fabrics [1].

Response surface methodology (RSM) may be used for an experimental plan with a number of variables on the results of flame retardancy. Response surface methodology is a collection of statistical and mathematical techniques useful for developing, improving and optimizing processes. The most extensive applications of RSM are in the particular situations where several input variables potentially influence some performance measure or quality characteristics of the process. Thus a performance measure quality characteristic is called the response. The input variables are sometimes called independent variables, and they are subject to the control of the scientist or engineer. The field of response surface methodology consists of the experimental strategy for exploring the space of the process or independent variables. Empirical statistical modeling may then be used to develop an appropriate approximating relationship between the yield and the process variables, and optimization methods for finding the values of the process variables that produce desirable values of the response [14].

In the work reported in this paper, a vertical flame test and Differential Scanning Calorimetric (DSC) and Thermogravimetry (TG) were used to study the flame resistance and thermal behavior of wool fabric. Also scanning electron microscopy (SEM) and Energy Dispersive X-ray Microanalysis (EDXS) were used to study the surface morphology of the treated wools.

2. Experimental

2.1. Materials

The wool fabric with plain woven structure from 48/2 Nm yarns was supplied by Iran Merino. The fabric was scoured with 0.5% of a nonionic detergent at 50 °C for 30 min (L:G = 40:1) and then washed with tap water, and dried at room temperature. The zirconium oxychloride (35% ZrO_2) used in this study was supplied by Shanghai Yancui Co, China. hydrochloric acid and citric acid were obtained from Merck, Germany.

2.2. Preparation and application of flame retardant

Hydrochloric acid and citric acid were mixed with $ZrOCl_2$ according to Table 1, after which water was added until each solution achieved a liquor to wool ratio L:G = 20:1.

Hydrochloric acid was added to each of the above flame retardant solutions in order to maintain a pH = 2 during the exhaustion process. The wool treatment was started at 40 °C for 20 min and the temperature was raised for 30 min to the specified temperature and heated for 45 min. After being exhausted, the treated samples were rinsed with tap water and dried at room temperature. Finally, the modified wools were subjected to vertical flame testing.

2.3. Flammability test

The criterion for flame retardation in the present work is that the fabric must pass the rigorous test prescribed by the United States Federal Aviation Administration (F.A.A. test) [15]. Briefly, this test requires the burning of a vertically held fabric in a draft-free cabinet, in accordance with Federal Test Method Standard 191, Method 5903. A minimum of three specimens must be tested and the averages results reported. A flame 76 mm (3.2 in.) high is applied to the fabric, which is held 19 mm (3/4 in.) above the top edge of the burner. The flame is held in position for 12 s and then removed. For a sample to pass the test, the average burn length must not exceed 20 cm (8 in.), and the average flame time after removal of the flame source must not exceed 15 s.

2.4. Limiting oxygen index (LOI)

The LOI value is the minimum amount of oxygen in an oxygen-nitrogen mixture required to support complete combustion of a