Optimization of Zirconium Acetate on the Flame Retardant Properties of Wool

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ABSTRACT: The thermal degradation of wool treated with the flame retardant synergistic system, zirconium acetate, acid citric, and hydrochloric acid, was studied by thermal analysis, mass loss, the limiting oxygen index (LOI), and the vertical flame test. SEM pictures were provided to study the morphology of the treated samples. The flame-retardant treated wool indicated a decrease in the temperature of decomposition, an increase in the residual mass and LOI, comparing with the untreated wool. The central composite design (CCD) was used for the experimental plan with four variables on the results of flame retardant. Statistical analysis confirmed the optimum conditions obtained by the experimental results. © 2012 Wiley Periodicals, Inc. J Appl Polym Sci 125: 1261–1266, 2012

Key words: flame retardant; wool; zirconium acetate; central composite design; TG; DSC; LOI

INTRODUCTION

Wool is the most flame-resistant fiber among other natural fibers. Wool has the most complex fiber structure optimized through evolution to provide thermal protection to mammals. Several factors in this structure are also responsible for wool natural flame resistance. Specifically, wool has high ignition temperature (570–600°C) among other common natural fibers,[1] high limiting oxygen index (25–26%),[2] low heat of combustion, low heat release, high nitrogen content (14%),[2] high moisture content,[3] dose not melt or drip, and form a self-insulating char preventing further flame spread. While most textile fibers are polymer containing mainly carbon and hydrogen that can burn easily. Wool also contains high levels of nitrogen and sulphur while, many fire retardants used are high in nitrogen. Wool therefore, requires higher levels of oxygen in the surrounding atmosphere to accelerate combustion. The limiting concentration of oxygen required to support combustion of wool in standard tests is higher than the ambient oxygen in air (21%). Therefore, it is difficult to ignite wool, but once ignited, the flame spreads slowly and it is easy to extinguish.[1]

Wool fibers are assembled from keratinized cells. The elongated cortical cells in the centre of the fiber are protected from the environment by a layer of cuticle cells. These outer layer cells contain high level of sulphur. Also, the fiber is held together by a lightly cross-linked cell membrane complex. When wool is heated to the point of combustion this structure tends to foam providing an insulating layer of pyrolysed material separating heat and oxygen from the fuel. Wool has traditionally been chosen in diverse applications, including nightwear, protective garment, transportation and military requirements due to its natural low flammability characteristics.

Fabric structure and density are important parameters considering the flammability performance of textile products. Heavy and dense fabrics with a flat surface along with air excluding design are known to give the best performance.

The evolution of increasingly severe mandatory flammability regulation in many aspects of domestic, social and business life has meant that even inherently low flammability fibers, such as wool, required a flame retardant treatment for some applications. Typical applications subject to mandatory flammability requirements include children nightwear, domestic and commercial furnishings, public transportation, and protective clothing. Initially, fire retardant treatment for wool were based on the impregnation of borates, phosphorus, and to a limited degree the organic phosphorus compounds more commonly associated with cellulosic fibers.

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TABLE I
Central Composite Design for Flame Retardant of Wool

Run number	A: Zirconium acetate (%)	B: Temperature (°C)	C: Citric acid (%)	D: HCl (37%) (%)	Char length (cm)
1	7.95	86.00	9.55	8.00	1.1
2	7.95	70.86	9.55	8.00	1.95
3	5.60	95.00	6.30	10.35	1.95
4	7.95	86.00	9.55	4.05	2
5	7.95	86.00	9.55	8.00	1.05
6	7.95	101.14	9.55	8.00	0.85
7	5.60	77.00	6.30	5.65	2.9
8	7.95	86.00	9.55	8.00	1.2
9	7.95	86.00	9.55	8.00	1.1
10	10.30	95.00	12.80	5.65	1.2
11	7.95	86.86	9.55	11.95	1.2
12	7.95	86.00	15.02	8.00	1.25
13	7.95	86.00	4.08	8.00	1.75
14	5.60	95.00	12.80	10.35	2.6
15	7.95	86.00	9.55	8.00	1.1
16	10.30	95.00	6.30	5.65	1.75
17	4.00	86.00	9.55	8.00	2.95
18	10.30	77.00	12.80	10.35	0.65
19	5.60	77.00	12.80	5.65	2.95
20	11.90	86.00	9.55	8.00	0.65
21	10.30	77.00	6.30	10.35	1.15

The introduction of stricter flammability requirements for airline furnishings resulted from a review of general aviation standards coinciding with the release of wide bodied aircraft in the early 1970s. Many flammability treatments available at the time did not satisfy the new requirements, therefore a new flame retardant treatment based on the reaction of zirconium or titanium salts with wool were introduced. This treatment was developed under the general name of "Zirpro," to cover a variety of flammability standards and care claims. The zirpro treatment can combine flame resistance with shrink resistance, oil and water repellency and in some instances, dyeing. Zirpro treatments are based on the exhaustion of negatively charged zirconium salts, under acid conditions, onto positively charged wool. These results in the deposition of only about 3% of flame retardant inside the fiber with negligible effect on properties such as handle.[4] These treatments stabilize and further crosslink the protein structure. The best treatments are colorless, do not alter wool natural properties, such as handle and moisture adsorption, and tend to be deposited near the surface of the fiber. These treatments tend to increase and strengthen the insulating foam produced as wool is decomposed by heat. Zirpro treated wool also has good durability to washing and dry-cleaning.

In recent years there have been a number of reports of treatments which enhance wool natural flame-resistant properties.[4–10] We also studied the effect of zirconium oxychloride with formic acid or hydrochloric acid on wool in previous research showed enhanced flame retardant properties of wool fabrics.[4,5] In this work, vertical flame test, differential scanning calorimetric (DSC) and thermogravimetry (TG) analysis were used to study the flame resistance and thermal behavior of the treated wool. Also scanning electron microscopy (SEM) and energy dispersive X-ray microanalysis (EDXS) were used to study morphology and elemental analysis of the treated wool fabrics.

EXPERIMENTAL

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% nonionic detergent at 50°C for 30 min ($L : R = 40 : 1$) and then washed with tap water, and dried at room temperature. The zirconium acetate (ZrAc) (22% ZrO_2) used in this study was supplied by Shanghai Yancui, China. Hydrochloric acid and citric acid were obtained from Merck, Germany.

Preparation of flame retardant

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

Flame retardant wool

Hydrochloric acid was added to each flame retardants to maintain a pH of 2 during the exhaustion.

Treatment of samples was started at 40°C for 20 min and the temperature was raised for 30 min to specified temperature according to the CCD and heated for 45 min. After being exhausted, the treated samples were rinsed with tap water and dried at room temperature. Finally, the modified fabrics were used for vertical flame test.

Flammability test

Here, the rigorous test was prescribed by the United States Federal Aviation Administration (F.A.A. test) were adapted for the flame retardant testing of the fabrics.[10] 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 results averaged. A flame 3/2 in. high is applied to the fabric, which is held 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 8 in. (20 cm), and the average flame time after removal of the flame source must not exceed 15 s.

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 vertically held sample that burns downward from the top. The higher the LOI value, the more efficient is the flame-retardant treatment. The LOI values were determined in accordance with ASTM D2863-06 by means of a General Model Stanton Redcroft FTA flammability unit.[11]

Thermogravimetry (TG)

Trials were performed in a TGA-PL thermo gravimeter analyzer (Polymer Laboratories, UK) using a platinum crucible of 70 µL. The following analytical conditions were used: initial temperature: 30°C; final temperature: 600°C; heating rate: 10°C min^{-1}; purging gas: nitrogen 50 mL min^{-1}.

Differential scanning calorimetric (DSC)

Trials were performed in a DSC-Maia-200 F3 unit (Netzsch, Germany). Micropunched aluminum pans of 40 µL were used. Condition: initial temperature: 20°C; final temperature: 600°C; heating rate: 10°C min^{-1}; purging gas: nitrogen 50 mL min^{-1}.

TABLE II
Range of Variables

Variable	Lower limited	Upper limited
Temperature (°C)	77.00	95.00
Zirconium acetate (%)	5.60	10.30
Citric acid (%)	6.30	12.80
Hydrochloric acid (%)	5.65	10.35

Scanning electron microscopy (SEM-EDXS)

Morphology of the samples was observed by scanning electron microscopy (VEGA TESCAN, Czech Republic). Samples were fixed to SEM holders and coated with a thin layer of gold prior to SEM investigation.

Reflectance measurement

The reflectance of the treated samples was recorded using a Gretag Macbeth COLOREYE 7000A spectrophotometer integrated with an IBM personal computer. CIELAB color coordinates (L^*, a^*, b^*, C^*, and h) were calculated from the reflectance data for 10°C observer and illuminant D65.

Experimental design

The central composite design used for experimental plan with four variables is shown in Table I. Four variables including zirconium acetate, formic acid and citric acid amount, and temperature were studied. In which their ranges are shown in Table II. Also the influence of the variable on the results Char Length (C.L.) in centimeter is fitted in to following second order polynomial function:

$$C.L. = b_0 + \sum b_i x_i + \sum b_{ij} x_i x_j + \sum c_i x_i^2$$
$$i \geq j$$
$$i = 1, 2, 3, 4$$

In this equation, b_0 is an independent term according to the mean value of the experimental plan, b_i are regression coefficients that explain the influence of the variables in their linear form, b_{ij} are regression coefficients of the interaction terms between variables, and c_i are the coefficients of quadratic form of variables. The estimation equation regression coefficients b_i, b_{ij}, c_i along with determination coefficient R^2 are shown in Table III.

RESULTS AND DISCUSSION

Thermal behavior

Figures 1 and 2 shows the comparisons of TG and DSC curves of raw and treated wool with 10.07% ZrAc, 12.66% citric acid, and 10.32% hydrochloric

TABLE III
Regression Coefficients and Determination Coefficient

C.L. coefficient	Char length
b_0	26.37955
b_1	−0.63284
b_2	−0.37078
b_3	−0.38686
b_4	−0.43420
c_1	0.049296
c_2	1.61503E-003
c_3	0.015732
c_4	0.036492
b_{12}	3.23445E-003
b_{13}	−0.028642
b_{14}	−0.055823
b_{23}	2.35043E-003
b_{24}	1.06175E-003
b_{34}	0.010638E-004
R^2	0.9921

Figure 2 Comparison of DSC curve of pure wool and treated wool.

acid at 77°C. Thermal data were derived as shown in Table IV; the three peaks indicated, and the corresponding assignments, are given in the table. An initial broad endothermic process is observed from 30 to 160°C. This is considered to be due to moisture evaporation and accompanied by a decrease of 7% in wool fibers mass and dehydration of wool is ascribed to the loss of water. It is considered that there are three different types of water within the fiber i.e., free water, loosely bonded water, and chemically bonded water. As a consequence, the loss of water, as recorded by the thermo gravimetric curve, is the result of the overlapping of three different processes in which the three types of water are lost.

The second important endothermic process occurred from 190 to 350°C and accompanied by an about 34% loss of wool fiber mass. The hydrogen-bond peptide helical structure ruptures and the ordered regions of the wool undergo a solid-to-liquid phase change; also cleavage of the disulphide bonds occur and a number of volatiles are released including hydrogen sulfide and sulfur dioxide.[9] The
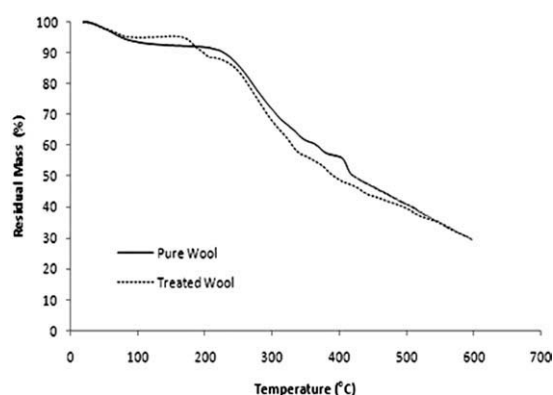
TG response in Figure 1 for each of the two samples show that onset of decomposition occurs with the following order: raw wool > treated wool. This order is expected since there is a relationship between their respective pyrolysis mechanisms. As presented in Figure 1, compared with raw wool, TG curve of the treated sample shows a low decomposition temperature and an increased mass loss, as can be seen in Table IV. In fact, the presence of ZrAc and citric acid, which reacts on condensed phase, catalyzes the thermal decomposition of the wool.

The third process is an exothermic reaction that the char oxidation reactions dominate. The presence of the flame retardants appear to have resulted in a cross-linked complex, which can be achieved in graphite-like structure, and possibly aromatic char which has a higher-than-expected resistance to oxidation.[9] Data in Table IV clearly indicate that the Zirpro flame retardant promotes the char formation as expected. It is also evident from Table IV that the residual char and the LOI values are higher for the flame-retardant treatment wool. Char formation in the condensed phase is recognized as an effective way of protecting the underlying polymer from fire attack. These data suggest that the combust ability of the treated wool is lower. Also it can be seen from the DSC curves that the enthalpies decreased from 140.2 J g^{-1} for raw wool to 111.9 J g^{-1} for the treated wool at the third process.

Statistical analysis

The analysis of variance (ANOVA) is given in Table V. It can be concluded that all of the terms in this model are significant. Also, the suitable P-value test, which did not pass 0.050, showed that the model was suitable and worked well.

Figure 1 Comparison of TG curve of pure wool and treated wool.

TABLE IV
The Thermal Properties of Wool with and Without Flame-Retardant Treatment

| | Second pyrolysis process | | Third pyrolysis process | | | |
Sample	Temperature range (°C)	Mass loss (%)	Temperature range (°C)	Residual mass (%)	Enthalpy (J g^{-1})	LOI (%)
Pure wool	190–326	34.08	391–597	29.40	140.2	25.4
Treated Wool[a]	166–330	40.02	385–599	31.06	111.9	26.5

[a] Sample was obtained with 10.07% ZrAc, 12.66% citric acid, and 10.32% hydrochloric acid at 77°C.

According to the ANOVA results, a suitable model is as shown in equation:

$$C.L. = +(26.38) + (-0.63 \times A) + (-0.37 \times B) \\ + (-0.39 \times C) + (-0.43 \times D) + (3.23E - 003 \times A \times B) \\ + (-0.03 \times A \times C) + (-0.06 \times A \times D) \\ + (2.35E - 003 \times B \times C) + (1.06E - 003 \times B \times D) \\ + (0.01E - 004 \times C \times D) + (0.05 \times A^2) \\ + (1.61E - 003 \times B^2) + (0.002 \times C^2) + (0.04 \times D^2)$$

In this equation, A, B, C, and D are zirconium acetate (wt %), temperature (°C), citric acid (o.w.w. %), and formic acid (o.w.w. %), respectively.

Figure 3 also shows the response surface of the model. By using Design Expert software the optimum design point with total desirability of 100% is: the temperature of 77.14°C, zirconium acetate of 10.07%, citric acid of 12.66%, and hydrochloric acid of 10.32%.

Color indices

The L*, a*, b*, C*, and h values of zirconium treated wool and untreated, are given in Table VI. The lightness (L*) values showed an increase for the sample treated with zirconium acetate. There was a relatively small change in a*, b*, C*, and h for wool treated sample. The results showed that treated wool with zirconium acetate has not been significantly affected in yellowing.

SEM pictures

The SEM pictures have been used to show the effects of zirconium salt on the surface of the fibers. The results in Figure 4(a) show a normal morphological form of the raw wool and scales can be clearly seen. In Figure 4(b,c), several particles can be seen on the surface of the wool-treated sample. For the treated wool, there are no significant changes on the fiber surface; however, some particles on the fiber surface related to the zirconium. The wool sample treated with 10.07 wt % of zirconium acetate indicated an aggregation of zirconium on the edge of scales and scattering on the fiber surface randomly. Existence of zirconium and other elements on the wool treated surfaces is investigated by EDXS analysis and is reported in Table VII following the analysis of one of the particles observed in Figure 4.

TABLE V
ANOVA for Response Surface Quadratic Model

| Source	Sum of squares	DF	Mean square	F value	P-value Prob > F
Model	10.92	14	0.78	53.58	<0.0001
A-ZrAc	2.64	1	2.64	181.71	<0.0001
B-Temp	0.60	1	0.60	41.56	0.0007
C-Citric acid	0.10	1	0.10	7.13	0.0370
D-Formic acid	0.32	1	0.32	21.98	0.0034
AB	0.016	1	0.016	1.07	0.3418
AC	0.38	1	0.38	26.30	0.0022
AD	0.31	1	0.31	21.64	0.0035
BC	0.038	1	0.038	2.60	0.1581
BD	1.671E-003	1	1.671E-003	0.11	0.7463
CD	0.053	1	0.053	3.63	0.1055
A^2	1.11	1	1.11	76.09	0.0001
B^2	0.26	1	0.26	17.57	0.0057
C^2	0.41	1	0.41	28.35	0.0018
D^2	0.61	1	0.61	41.70	0.0007
Residual	0.087	6	0.015		
Lack of fit	0.075	2	0.038	12.56	0.0189
Pure Error	0.012	4	3.000E-003		
Cor Total	11.01	20			
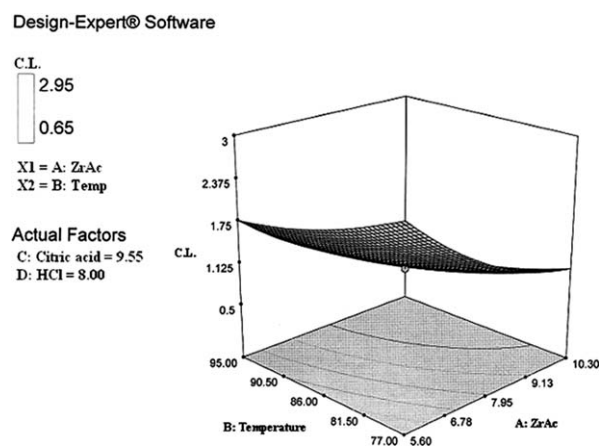
Figure 3 3D plot of A and B with their continue plot.

TABLE VI
Color Coordinates of Raw, Washed, and Treated Wool

Sample	L^*	a^*	b^*	C^*	h	Char length (cm)
Raw wool	84.19	0.71	15.75	15.77	87.42	3.25
Washed wool	83.30	0.70	17.57	17.58	87.73	4
Treated wool[a]	85.41	0.69	16.18	16.19	87.55	0.6

[a] Sample was obtained with 10.07% ZrAc, 12.66% citric acid, and 10.32% hydrochloric acid at 77°C.

CONCLUSION

The treatment of wool with ZrAc and citric acid accelerates the formation of combustible gases from the fiber. The gases are decomposed at a temperature below the ignition temperature, then the gases escape unburned. Three major regions of weight loss were obtained based on the thermal analysis of the wool products. During the progress of thermal degradation, ZrAc and citric acid catalyze the pyrolysis reaction, lower the decomposition temperature and increase the LOI and residual mass. Also, the vertical flame tests indicate that the treatment of wool with zirconium acetate increases the flame retardancy of wool to the great extent. Finally, zirconium acetate does not have any negative effect on the wool color. Statistical analysis by Design of Expert indicated that application of 10.07% ZrAc, 12.66% citric acid, and 10.32% hydrochloric acid at 77°C on wool produces optimum flame retardant wool with desirability of 100%. In SEM images, particles of zir-
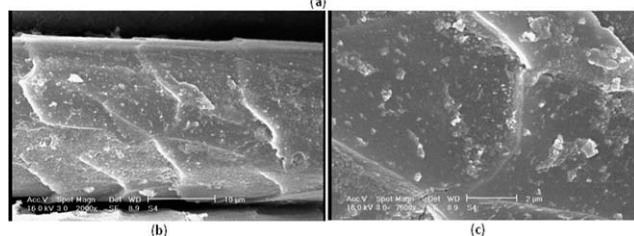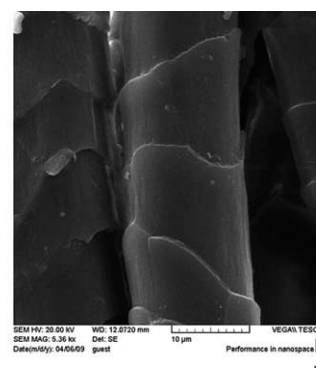

Figure 4 SEMs of (a) raw wool (b,c) wool treated with 10.07% ZrAc, 12.66% citric acid, and 10.32% hydrochloric acid at 77°C ($L : R = 20 : 1$).

TABLE VII
Elements Analyzed of Wool Treated (Normalized, wt %)

Sample	Zr	S	Cl	Au	Total
Treated wool[a]	4.43	2.31	0.34	92.91	100

[a] Sample was obtained with 10.07% ZrAc, 12.66% citric acid, and 10.32% hydrochloric acid at 77°C.

conium on the edge of scales and the change of morphology in comparison with raw wool are observed.

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