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Preparation of flame retardant wool using zirconium acetate optimized by CCD

M. Forouharshad[a,*], M. Montazer[b,*], M.B. Moghadam[c], O. Saligheh[d]

[a] Textile Department, Islamic Azad University South Tehran Branch, Tehran, Iran
[b] Textile Department, Amirkabir University of Technology, Center of Excellence in Textile, Tehran, Iran
[c] Associate Professor, Department of Statistics, Allameh-Tabataba'i University, Tehran, Iran
[d] Textile Department, Islamic Azad University South Tehran Branch, Young Researchers Club, Tehran, Iran

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ABSTRACT

The thermal degradation of wool treated with the flame retardant synergistic system, zirconium acetate, citric acid and formic acid, was studied by thermal analysis, mass loss, limited oxygen index (LOI) and vertical flame test. The surfaces of the wool samples were observed by SEM. The treated wool samples show an increase in the temperature of decomposition, residual mass and LOI in comparison with the untreated wool. The central composite design (CCD) was used for the experimental plan with four variables on the results of flame retardancy. Statistical analysis confirms the optimum conditions obtained by the experimental results.

1. Introduction

The burning behavior of fibers is influenced by a number of thermal transition temperatures and thermodynamic parameters. There are four thermal transitions for fibers with their physical glass (T_g) and melting (T_m) transitions, if appropriate, which may be compared with their chemically related transition of pyrolysis (T_p) and ignition and the onset of flaming combustion (T_c) [1]. In addition, typical values of flame temperature and heats of combustion exist. Generally, the lower the respective T_c (and usually T_p) temperature and the hotter the flame, the more flammable is the fiber. This generalization is typified by the natural cellulosic fibers cotton, viscose and flax as well as some synthetic fibers like the acrylics. Limit oxygen index (LOI) are measures of the inherent burning character of a material and may be expressed as a percentage or decimal [1]. Fibers having LOI values of 21% or 0.21 or below ignite easily and burn rapidly in air. Those with LOI values above 21% ignite and burn more slowly and generally when LOI values rise above approximately 26–28%, fibers and textiles may be considered to be flame retardant and will pass most small flame fabric ignition tests in the horizontal and vertical orientations [1].

The dyeing and finishing of wool continues to pose a challenge for textile and protein chemists because the complexity of its chemical and physical structure and the need to find effective processes are in competition in recent years with its almost constant world tonnage production and diminishing share of world fiber markets and textile economy. Within the area of flammability of all so-called conventional fibers, wool has the highest inherent non-flammability and for some end-uses, where high densities of structure and horizontal orientation (e.g. carpets) are required in the product, wool fabrics will often pass the required flame-retardancy tests untreated [1]. Wool has a relatively high LOI value of about 25 [2] and a low flame temperature of about 680 °C [1]. Its high ignition temperature of 570–600 °C [3] is a consequence of its higher moisture regain (8–16% depending upon relative humidity) [4], high nitrogen (15–16%) [4] and sulphur (3–4%) content and low hydrogen (6–7%) content by weight [1]. While organo-sulphur compounds are generally flame retardant to some degree, the disulphide-containing cystine links are easily oxidisable and so this can offset some of the anticipated natural flame retardancy. Pre-oxidation of wool and hence cystine to cysteic acid residues restores this expected retardant activity and oxidized wools can have greater inherent flame retardancy as a consequence [1].

The performance of wool fabrics in the various test methods currently in use depends on the specified test 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

* Corresponding authors. Tel.: +98 21 22 11 52 67; fax: +98 21 22 11 52 67.
E-mail addresses: Forouharmahdi@gmail.com (M. Forouharshad), tex5mm@aut.ac.ir (M. Montazer).

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Table 1
Central composite design for flame retardant application on wool.

Run number	A: Zirconium acetate (%)	B: Temperature (°C)	C: Citric acid (%)	D: Formic acid (37%) (%)	Char length (cm)
1	4.00	86.00	9.55	8.00	2.6
2	10.30	77.00	6.30	10.35	1.2
3	10.30	77.00	12.80	10.35	1
4	7.95	86.00	15.02	8.00	1.6
5	7.95	86.00	9.55	4.05	1.65
6	5.60	77.00	6.30	5.65	2.4
7	7.95	101.14	9.55	8.00	0.95
8	7.95	86.00	9.55	8.00	1.2
9	10.30	95.00	6.30	5.65	1.7
10	7.95	86.00	9.55	11.95	1.45
11	7.95	70.86	9.55	8.00	1.85
12	5.60	95.00	12.80	10.35	2.25
13	11.90	86.00	9.55	8.00	0.8
14	7.95	86.00	9.55	8.00	1.15
15	7.95	86.00	9.55	8.00	1.05
16	7.95	86.00	9.55	8.00	1.2
17	7.95	86.00	4.08	8.00	1.55
18	5.60	77.00	12.80	5.65	2.5
19	5.60	95.00	6.30	10.35	1.95
20	7.95	86.00	9.55	8.00	1.15
21	10.30	95.00	12.80	5.65	1.65

some cases needs a flame-resist treatment in order to pass particular flammability specifications and test methods. 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 treatment [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.

In recent years there have been a number of reports of treatments which enhance wool's natural flame-resistant properties [5–9]. The review by Horrocks discusses comprehensively developments in flame retardants for wool up to 1986 and very little has changed since that time. Given that a number of traditional non-durable finishes based on boric acid–borax (1:2, w/w) mixtures and sulphamic acid (as the ammonium salt) and phosphor compound are still used [10].

We also studied the effect of zirconium oxychloride with formic acid on wool in previous research which showed improvement in flame retardancy properties of wool fabrics [10].

The most commonly used durable flame retardants are based on Benisek's Zirpro (IWS) system. Major advantages of this treatment are the absence of any discoloration or other effect on wool aesthetics, coupled with its application via a simple exhaust process [1].

The Zirpro process is based upon the exhaustion of negatively charged complexes of zirconium or titanium onto positively charged wool fibers under acidic conditions. The Zirpro treatment can be applied to wool at any processing stage from loose fiber to fabric using exhaustion techniques either during or after dyeing [1]. In the work reported in this note, vertical flame testing and Differential Scanning Calorimetric (DSC) and Thermogravimetry (TG) analysis were used to study the flame resistance and thermal behavior. Also scanning electron microscopy (SEM) and Energy Dispersive X-ray Microanalysis (EDXS) were used to study the morphology of 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% non-ionic detergent at 50 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 Co., China. Formic acid and citric acid were obtained from Merck, Germany.

2.2. Preparation and application of flame retardant

Formic acid and citric acid were mixed with ZrAc according to Table 1, after which water was added until solution achieved a 20:1 ratio of liquor to wool.

2.3. Flame retardate application on wool

Formic acid was added to each of the above flame retardants in order to maintain a pH of 3 during the exhaustion procedure. Treating of samples was started at 40 °C for 20 min and the temperature was raised for 30 min to 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 used for vertical flame test.

2.4. 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) [11]. 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. (35 mm) high is applied to the fabric, which is held (3/4) in. (19 mm) 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.

2.5. 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

Table 2
Range of variables.

Variable	Lower limited	Upper limited
Temperature (°C)	77	95
Zirconium acetate (%)	5.60	10.30
Citric acid (%)	6.30	12.80
Formic acid (37%) (%)	5.65	10.35

treatment. The LOI values were determined in accordance with ASTM D2863-06 by means of a General Model Stanton Redcroft FTA Flammability unit.

2.6. Thermogravimetry (TG)

Trials were performed in a TGA-PL thermogravimetric analyzer (Polymer Laboratories, UK) using a platinum crucible of 70 μL. The following analytical conditions were used, sample mass: 5.290 mg; initial temperature: 30 °C; final temperature: 600 °C; heating rate: 10 °C min^{-1}; purging gas: nitrogen 50 mL min^{-1}.

2.7. Differential scanning calorimetric (DSC)

Trials were performed in a DSC-Maia-200 F3 unit (Netzsch, Germany). Micropunched aluminum pans of 40 μL were used. Teh testing condition were: sample mass: 12.36 mg; initial temperature: 20 °C; final temperature: 600 °C; heating rate: 10 °C min^{-1}; purging gas: nitrogen 50 mL min^{-1}.

2.8. Scanning electron microscopy (SEM)

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.

2.9. Experimental design

The central composite designs used for experimental plan along with obtained response are shown in Table 1. Four variables including zirconium acetate, formic acid and citric acid amount, and temperature were studied. In which their ranges are shown in Table 2. Also the influence of the variable on the results Char Length (C.L.) in centimeter is fitted in to following second order polynomial function (Eq. (1)):

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

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 3.

3. Results and discussion

3.1. Thermal behavior

Figs. 1 and 2 show the comparisons of TG and DSC curves of raw wool and treated wool (wool treated with 10.15% ZrAc, 12.78% citric acid, and 9.31% formic acid at 95 °C). The thermal parameters can be obtained from these figures and listed in Tables 4 and 5. Each

Table 3
Regression coefficients and determination coefficient.

C.L. coefficient	Char length
b_0	21.15760
b_1	−0.98433
b_2	−0.31253
b_3	−0.36032
b_4	0.32560
c_1	0.039545
c_2	1.38669E−003
c_3	0.016492
c_4	0.029942
b_{12}	8.12244E−003
b_{13}	−0.010638
b_{14}	−0.058637
b_{23}	1.49573E−003
b_{24}	−4.32119E−003
b_{34}	8.18331E−004
R^2	0.9925

Table 4
The thermal properties of second pyrolysis process of wool with and without flame-retardant treatment.

Sample	Temperature range (°C)	Mass loss (%)
Pure wool	190–326	34.08
Treated wool[a]	211–334	37.54

[a] Sample was obtained with 10.15% ZrAc, 12.78% citric acid, and 9.31% formic acid at 95 °C.

figure indicates that three processes take place in the wool pyrolysis progress. An initial broad endotherm process is observed from 30 °C 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 thermogravimetric 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, occurring from 190 °C to 350 °C and is 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 occurs and a number of volatiles are released including hydrogen sulfide and sulphur

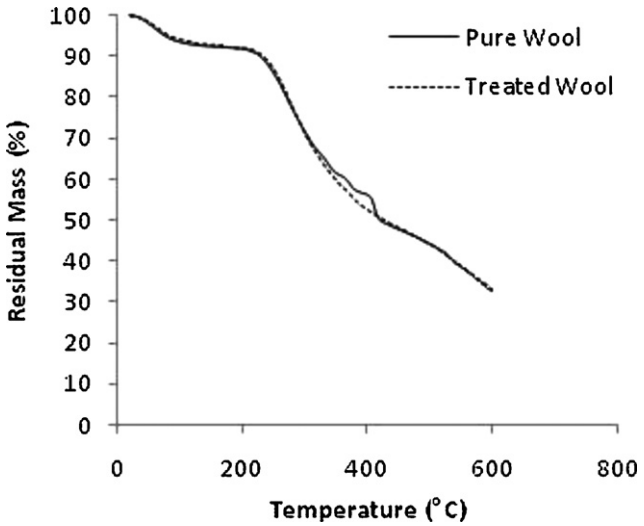

Fig. 1. Comparison of TG curve of pure wool and treated wool.

Table 5
The thermal properties of wool with and without flame-retardant treatment.

Sample	Temperature range (°C)	Residual mass (%)	LOI (%)	Enthalpy (J g^{-1})
Pure wool	391–597	30.80	25.4	140.2
Treated wool[a]	448–599	33.06	25.8	122.2

[a] Sample was obtained with 10.15% ZrAc, 12.78% citric acid, and 9.31% formic acid at 95 °C.

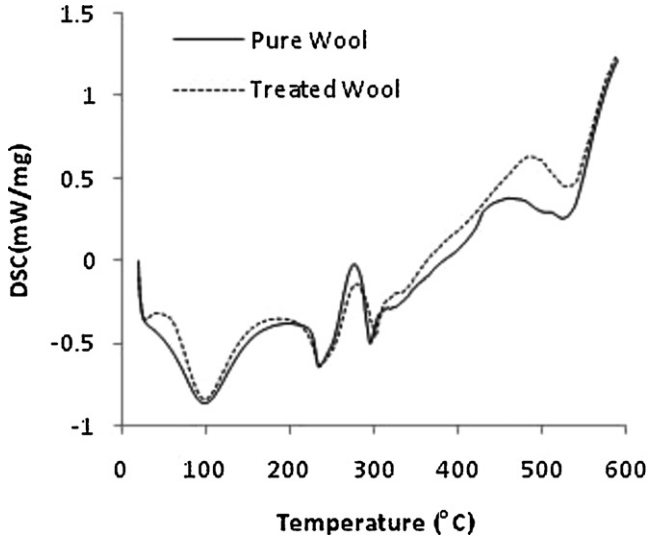

Fig. 2. Comparison of DSC curve of pure wool and treated wool.

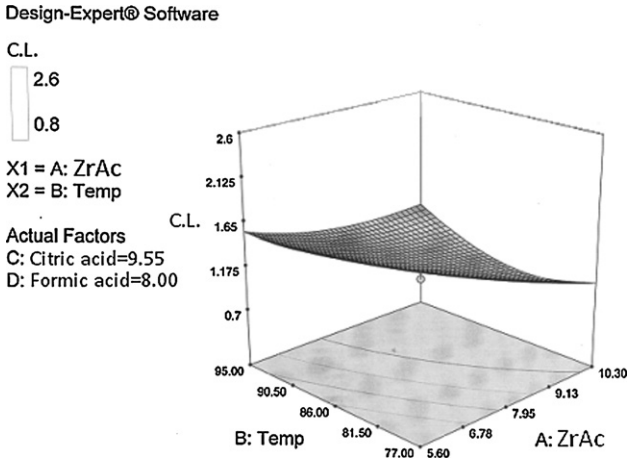

Fig. 3. 3D plot of A and B with their continue plot.

dioxide [12]. The TG response in Fig. 1 for each of the two samples show that onset of decomposition occurs in the order raw wool < treated wool. This order is expected since there is a relationship between their respective pyrolysis mechanisms. As presented in Fig. 1, the TG curve of treated sample shows a high decomposition temperature and an increased mass loss compared with raw wool which can be seen from Table 4. It is the fact that the presence of ZrAc and citric acid, which reacts on condensed phase, could increase the number and extent of reactions forming volatile products.

The third process is an exothermic reaction that the char oxidation reactions dominate. The presence of the flame retardants appears to have resulted in a cross-linked complex, which can be achieved in graphite-like structure, and possibly aromatic char which has a high-than-expected resistance to oxidation [12]. From Table 4 it is evident that the residual char and the LOI values for wool with flame-retardant treatment are more than those of the untreated wool. These data suggest that the combustibility of treated wool is reduced. Also the DSC curves show a decrease in enthalpies from 140.2 J g^{-1} for raw wool to 122.2 J g^{-1} for treated wool for this third process which is in correspondence with the increase in LOI parameter.

These results confirm that the influences of ZrAc are lower than those of the $ZrOCl_2$ on wool flame retardant which has already been reported in our previous paper [10]. This could be attributed to the presence of Cl on the $ZrOCl_2$ treated wool also zirconium oxychloride can link with reactive groups (–OH, –NH) in the wool to form a cyclic structure which could be a char precursor but ZrAc on the other hand lacks the ZrO presence and so may not be able to react in the same manner. The results of LOI are also similar to the results of TGA and DSC as the LOI is 29.3 for $ZrOCl_2$ and 25.8 for ZrAc treated wools [10].

Table 6
ANOVA for response surface quadratic model.

Source	Sum of squares	DF	Mean square	*F*-Value	*P*-Value Prob > *F*
Model	5.64	14	0.40	56.35	<0.0001
A: ZrAc	1.62	1	1.62	226.69	<0.0001
B: Temp	0.41	1	0.41	56.67	0.0003
C: Citric acid	4.012E−003	1	4.012E−003	0.56	0.4820
D: Formic acid	0.020	1	0.020	2.80	0.1454
AB	0.098	1	0.098	13.68	0.0101
AC	0.053	1	0.053	7.39	0.0347
AD	0.35	1	0.35	48.62	0.0004
BC	0.015	1	0.015	2.14	0.1936
BD	0.028	1	0.028	3.87	0.0966
CD	3.125E−004	1	3.125E−004	0.044	0.8413
A2	0.71	1	0.71	99.73	<0.0001
B2	0.19	1	0.19	26.38	0.0021
C2	0.45	1	0.45	63.45	0.0002
D2	0.41	1	0.41	57.18	0.0003
Residual	0.043	6	7.146E−003		
Lack of fit	0.028	2	0.014	3.72	0.1224
Pure error	0.015	4	3.750E−003		
Cor total	5.68	20			

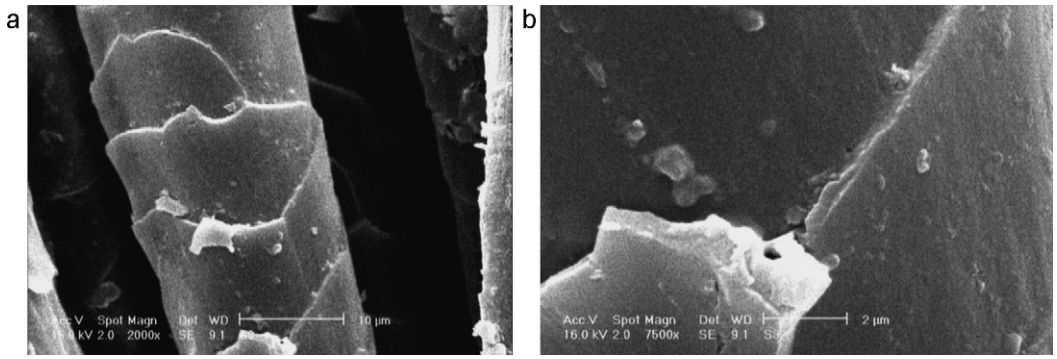

Fig. 4. SEM of wool treated with 10.15% ZrAc, 12.78% citric acid, and 9.31% formic acid at 95 °C. (L:R = 20:1).

Table 7
Elements analyzed of wool treated (normalized) (wt%).

Sample	Zr	S	Cl	Au	Total
Treated wool[a]	6.23	5.09	0.28	88.40	100

[a] Sample was obtained with 10.15% ZrAc, 12.78% citric acid, and 9.31% formic acid at 95 °C.

3.2. Statistical analysis

The analysis of variance (ANOVA) is given in Table 6. It can be concluded that all of the terms in this model are significant. Also the lack of fit test with the *P*-value of 0.1224 shows the model is significant and it is fitted well. According to the ANOVA results, the fitted model is:

$$\begin{aligned}\text{C.L.} = {} & +(21.15760)+(-0.98433\times A)+(-0.31253\times B)\\ & +(-0.36032\times C)+(0.32560\times D)+(8.12244E-003\times A\\ & \times B)+(-0.010638\times A\times C)+(-0.058637\times A\times D)\\ & +(1.49573E-003\times B\times C)+(-4.32119E-003\times B\times D)\\ & +(8.18331E-004\times C\times D)+(0.039545\times A^2)\\ & +(1.38669E-003\times B^2)+(0.016492\times C^2)\\ & +(0.029942\times D^2)\end{aligned}$$

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.

Fig. 3 also shows the response surface of the model. By using Design Expert Package software the optimum design point with total desirability of 100% is about temperature of 94.61 °C, zirconium acetate of 10.15%, citric acid of 12.78%, and formic acid of 9.31%.

3.3. SEM

SEM was utilized in considering of a possible zirconium acetate effect on the wool fabric surfaces. For the treated wool some particles are observed on the fiber surface (Fig. 4). The wool sample treated with 10.15 wt% of zirconium acetate indicated an aggregation of zirconium compounds on the edge of scales and scattering on the fiber surface randomly. Existence of zirconium element and other elements on the wool treated surfaces is investigated by EDXS analysis and is reported in Table 7.

4. Conclusions

The thermal behavior of wool fiber revealed three major regions of weight loss. During the progress of thermal degradation, ZrAc, citric acid and formic acid may interfere with the pyrolysis reactions causing a higher onset decomposition temperature and higher mass loss in the second stage. The results of vertical flame test indicate that the treatment of wool with zirconium acetate increases the flame retardancy of wool to the great extent. Statistical analysis by DOE indicated that application of 10.15% ZrAc, 12.78% citric acid, and 9.31% formic acid at 94.61 °C on wool produces an optimum design point with desirability of 100%. SEM pictures confirm the presence of zirconium compounds on the edge of scales and the change of morphology in comparison with raw wool.

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