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A novel durable flame-retardant cotton fabric using sodium hypophosphite, nano TiO_2 and maleic acid

F. Lessan [a], M. Montazer [a,*], M.B. Moghadam [b]

[a] Textile Engineering Department, Center of Excellence in Textile, Amirkabir University of Technology (Tehran Polytechnic), Tehran, Iran
[b] Department of Statistics, Allameh Tabatabai University, Tehran, Iran

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ABSTRACT

This research mainly deals with a novel flame-retardant for woven cotton fabric using sodium hypophosphite (SHP), maleic acid (MA), triethanol amine (TEA) and nano TiO_2 through conventional pad-dry-cure method. Thermal gravimetric analysis (TGA) and differential thermal analysis (DTA) were employed to investigate the thermal decomposition behavior of the treated samples. The char length, char yield before and after 5 washing cycles, limited oxygen index (LOI) and whiteness index of the treated cotton fabrics were investigated. The central composite design (CCD) was also used for variables based on Design of Expert software. The results revealed the importance of SHP in which 5% SHP can increase the LOI from 18.6 to 23. This leads to obtain a lower initial decomposition temperature and a higher char formation. Also presence of 6% TEA greatly prevents the cotton fabric from yellowing during the curing process.

1. Introduction

Cotton is the widely used textile fiber with high flammability. Application of flame retardant products on cotton is an important textile issue [1,2] especially for protection of consumers in military and the airline industry [3]. For a long time, phosphorous compounds including tetrakis hydroxymethyl phosphonium chloride (THPC) and N-methylol dimethylphosphono propionamide (MDPA) with the trade names of "Pyrovatex CP" or "Pyrovatex CP New" have been the most useful approach to obtain durable flame-retardant finishes for cotton. They can react with the fiber or form cross-linked structures on the fiber [2–9]. These compounds influence the pyrolysis reaction, prevent the formation of levoglucosan and flammable volatiles, increase the formation of char and act as flame retardant for cellulose [3,10]. It is shown that the amount of phosphorus content on the treated cellulose is an important factor in flame retardant efficiency. In other words, a large amount of flame retardant led to more effectiveness in decreasing flammability of cellulose fiber [11]. The major disadvantage of these compounds is the potential of formaldehyde emission during curing and use of products by consumers. Formaldehyde is known as a carcinogen compound by World Health Organization thus development of formaldehyde-free durable flame retardants should be considered [3–5].

There have been a large number of studies in the past in order to application of other phosphorous containing compound to make textiles more flame resistance through enhance degradation of textiles at lower temperature and higher formation of char. Jinping et al. studied application of DMMEP (dimethyl 2-methacryloyloxy ethyl phosphate) on silk fabric and improved fire performance of the fabric. They observed that phosphorous compound decreased the initial decomposition temperature of treated silk fabric, and increased char formation [12]. Zhu et al. investigated flame-retardant finishing of cotton fibers using an organophosphorus nitrogen containing compound. They reported that temperatures for the flame-retardant fibers were lower, but the formed solid residue was higher than the untreated cotton [13]. Chen et al. used poly (2-hydroxy propylene spirocyclic pentaerythritol bisphosphonate) (PPPBP) for flame-retardant finishing of poly ethylene terephthalate (PET) and reduced its flammability. They indicated that the char is the critical factor in flame retardant PET fabrics [14]. Forouharshad et al. investigated flame retardancy of wool by zirconium oxychloride with diverse acidic media [15].

Sodium hypophosphite (SHP) is an phosphorus-based salt and well-known catalyst for cross-linking cellulose with poly carboxylic acids [16,17]. Wu and Yang studied the combination of MA and SHP in flame retardant finishing of cotton fleece fabric [17]. Yang and Wu investigated the flame retardant of cotton using a hydroxyalky-functional organophosphorus compound and BTCA, in the presence of SHP as a catalyst. They indicated that the polycarboxylic acid functions as a binder between the organophosphorus oligomer and cellulose and makes the organophosphorus

* Corresponding author. Tel.: +98 2164542657; fax: +98 2166400245.
E-mail address: tex5mm@aut.ac.ir (M. Montazer).

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compound a durable flame retardant finish agent on cotton fabric [4]. Cheng et al. studied flammability of cotton fleece using the phosphorus-containing maleic acid oligomers (PMAO) with SHP as the catalyst. They found that PMAO can be bound to cotton fleece by esterifying with cotton cellulose in the presence of SHP and reduces the fabric flammability [5]. However using carboxylic acid as cross-linking agent with SHP causes discoloration of white cotton fabrics during the curing process [18]. Therefore, it is necessary to prevent yellowing.

Nano sized TiO_2 is well known photocatalyst for many scientists due to its high chemical stability, non-toxicity and good heat resistance [19–25]. Chen and Wang were used nano TiO_2 as catalyst in cross-linking of cotton fabric with citric acid under the irradiation of UV light [26]. Nazari et al. were studied cross-linking of cotton with poly carboxylic acids using nano TiO_2 along with SHP and determined the optimum conditions by using a statistical model [27].

The aim of this study was to investigate the flame retardant action of SHP in the presence of nano TiO_2 and MA on cotton fabric. Due to fabric yellowing as a result of using MA and SHP at high temperature, triethanol amine (TEA) was also used. Various experiments with different concentrations of MA, TEA, Nano TiO_2 and operation times are designed by using central composite design. Also different response variables including whiteness index, char length in vertical flammability and char yield before and after 5 laundering cycles were studied. The correlation between variables and responses were found in poly nominal equations, using response surface method (RSM). Also other testings including LOI, TGA and DTA on some samples were carried out. Finally, optimum values of variables and responses were obtained based on the statistical method.

2. Experimental

2.1. Materials

The bleached plain weave 100% cotton fabric was used with weigh of 128 g/m^2, wrap density of 25 yarn/cm and weft density of 20 yarn/cm. MA, SHP and TEA were supplied by Merck Chemical Co. (Germany). Nonionic detergent (UltravonGP) purchased from ex-Ciba Co. (Switzerland). Nano titanium dioxide with the anatase crystalline structure and average particle size of 21 nm was purchased from Evonik Co. (Germany).

2.2. Experimental design

Table 1 shows the experiments designed with different concentrations of MA, TEA, Nano TiO_2 and operation times using central composite design. The influence of the variables on the results including whiteness index, char length in vertical flammability and char yield before and after 5 laundering cycles was adjusted using Eq. (1).

$$Y = b_0 + \sum b_i X_i + \sum b_{ij} X_i X_j + \sum c_i X_i^2 \quad i \geq j \;\; i, j = 1, 2, 3 \qquad (1)$$

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 [27].

2.3. Scouring

The cotton fabric samples were scoured using 1 g/l nonionic detergent at 60 °C for 20 min with a liquor to goods ratio (L:G) 40:1 followed by rinsing with cold water.

Table 1
Designed experiments using CCD and whiteness index values of different samples.

Sample	MA (%W/V)	TEA (%W/V)	TiO_2 (%W/V)	Time (min)	Whiteness index
1	7.5	2	0.25	45	56.5
2	7.5	6	0.75	15	60.5
3	7.5	2	0.25	15	51.8
4	0.0	4	0.50	30	62.9
5	15.0	8	0.50	30	53.2
6	15.0	4	1.00	30	49.5
7	7.5	6	0.25	45	62.9
8	22.5	2	0.75	45	−10.9
9	15.0	0	0.50	30	−16.5
10	7.5	2	0.75	45	62.7
11	15.0	4	0.50	30	46.9
12	15.0	4	0.50	30	44.0
13	15.0	4	0.50	60	50.1
14	7.5	2	0.75	15	61.0
15	15.0	4	0.50	30	41.4
16	30.0	4	0.50	30	1.8
17	22.5	6	0.25	15	34.3
18	15.0	4	0.50	30	43.9
19	7.5	6	0.25	15	57.6
20	22.5	2	0.75	15	18.8
21	22.5	6	0.25	45	39.2
22	7.5	6	0.75	45	61.6
23	15.0	4	0.00	30	52.4
24	15.0	4	0.50	30	45.9
25	22.5	6	0.75	15	35.6
26	22.5	6	0.75	45	42.4
27	22.5	2	0.25	45	−11.4
28	15.0	4	0.50	30	47.7
29	15.0	4	0.50	0	50.4
30	22.5	2	0.25	15	13.2
Untreated	0	0	0	0	81.5

2.4. FR treatment

The aqueous finishing dispersions were prepared by various amounts of MA, TEA and nano TiO_2 based on experimental design (Table 1) with a L:G = 20:1 in an ultrasonic bath. In all experiments the amount of SHP was adjusted one third of MA [17]. The scoured cotton fabric was then impregnated in the dispersed solution for different time. The treated cotton fabrics were padded with 100% wet pick-up and dried at 80 °C for 2 min to remove mobile water followed by curing at 180 °C for 2 min. The treated samples were rinsed in ultrasonic bath for 5 min to remove un-bonded nano TiO_2 from the fabric surface.

2.5. CIE whiteness index

The whiteness index of samples was measured to evaluate the influence of performed treatment on fabric whiteness. The reflectance values were determined using Spectrophotometer Color-Eye 7000A from Gretag Macbeth and the CIE whiteness index was calculated using Eq. (2).

$$\mathrm{WI(CIE)} = Y + 800(x_n - x) + 1700(y_n - y) \qquad (2)$$

where WI is the whiteness index, Y is the CIE tristimulus value, (x, y) and (x_n, y_n) are the CIE chromaticity coordinates of the samples and perfect diffuser respectively [28].

2.6. Vertical flammability

The vertical flammability of cotton fabrics was measured according to BS3119 Standard Method and char length of samples obtained.

Table 2
ANOVA for response surface related to whiteness index of different samples.

Source	Sum of squares	df	Mean square	*F*-value	*p*-Value Probe > *F*
Model	2.313E+006	7	3.305E+005	44.82	<0.0001 significant
A-MA	1.551E+006	1	1.551E+006	210.29	<0.0001
B-TEA	4.649E+005	1	4.649E+005	63.05	<0.0001
D-Time	162.48	1	162.48	0.022	0.8833
AB	1.255E+005	1	1.255E+005	17.02	0.0004
BD	24872.65	1	24872.65	3.37	0.0798
A^2	30685.55	1	30685.55	4.16	0.0535
B^2	1.289E+005	1	1.289E+005	17.48	0.0004
Residual	1.622E+005	22	7373.49		
Lack of fit	1.555E+005	17	9145.42	6.78	0.0219
Pure error	6744.54	5	1348.91		
Cor total	2.476E+006	29			

2.7. Char yield

The phosphorus containing compounds provide flame retardant functions following a condensed phase mechanism in which char formation is increased [10]. The measuring of char yield can be an appropriate factor for study the influence of FR [14,29]. In this order, the weight of each sample before and after complete burning was measured and char yield was calculated according to Eq. (3).

$$\text{Char yield} = \frac{W_2}{W_1} \times 100 \quad (3)$$

where W_1, W_2 are weight of sample before and after complete burning, respectively.

2.8. LOI

Limiting oxygen index (LOI) values of some samples were measured according to ASTM D2863-08 standard method. In this order, 5 specimens of each sample were prepared in 5 cm × 15 cm and a mixture of oxygen and nitrogen is passed up through a cylinder containing the fabric specimen supported vertically. The minimum fraction of oxygen in a mixture of oxygen and nitrogen in which one specimen will just sustain burning is determined and reported as the LOI value [30].

2.9. Thermal analysis

Thermo gravimetric analysis (TGA) and differential thermal analysis (DTA) were carried out using a Perkin Elmer TG-DTA analyzer, model Pyris1, operating under nitrogen atmosphere with initial sample weights of 8 mg. Once the sample has been prepared, it should be placed into the TGA sample pan and distributed evenly across the pan bottom. The standard platinum sample pan (0319-0264) is used for this application. The runs were performed over a temperature range of 50–600 °C at a heating rate of 10 °C/min under a continuous N_2 flow of 100 ml/min.

3. Results

3.1. Whiteness index

The values of CIE whiteness index of all the samples are presented in Table 1. It can be observed that the performed treatment in the absence of TEA totally resulted in yellowing of the samples due to the presence of MA and SHP at high temperature. However application of TEA greatly increased the fabric whiteness. The whiteness index of sample 13 is increased about 66.6 due to the presence of 4% TEA in the finishing bath than that of sample 9. In the presence of MA and SHP, unsaturated compounds are produced causing fabrics yellowing. TEA reduces the formation of unsaturated compounds and prevents fabrics yellowing [18]. This means that presence of TEA significantly improves the appearance of the treated fabrics. Increasing concentration of TEA to 6% caused an increasing in the whiteness index of the samples. However greater value of TEA concentration diminished the whiteness index. Therefore, there is an optimum amount for the TEA concentration. Increasing operation time also led to increase in located MA and SHP on the fabric and decrease the fabric whiteness. Furthermore, increasing of nanoTiO_2 led to increase the fabric whiteness index.

The analysis of variance (ANOVA) related to the whiteness index of the treated samples is given in Table 2. According to the ANOVA results, the fitted model of the samples whiteness indexes is shown in Eq. (4). It can be seen that the concentration of MA and TEA used in the finishing solution and operation time are effective factors on the fabric whiteness index.

$$(\text{R1} + 18.15)^{1.56} = 1040 - 40 \times \text{MA} + 76.2 \times \text{TEA} - 5.4 \times \text{Time} + 5.9 \times \text{MA} \times \text{TEA} + 1.3 \times \text{TEA} \times \text{Time} - 0.6 \times \text{MA}^2 - 16.8 \times \text{TEA}^2 \quad (4)$$

where R1 is the whiteness index.

Fig. 1 shows the response surface curve of the fabric whiteness. This indicated that the most whiteness index is related to the sample treated with 7.5% MA and 6% TEA for 30 min in ultrasonic bath and 0.5% nano titanium dioxide. Thus increasing of MA concentration and thereby increasing of SHP decreases the whiteness and increases the yellowness. Also increasing of TEA to the limited extent reduces the yellowness and increases the whiteness index of samples. The influences of MA and SHP on increasing yellowness are high and increasing of TEA cannot prevent yellowing completely.

3.2. Char length

Char length of samples was measured in the vertical flammability test and reported in Table 3. The results showed that

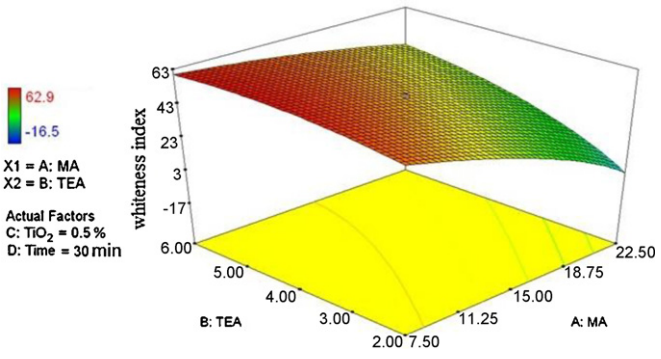

Fig. 1. Surface response curve related to whiteness index of samples.

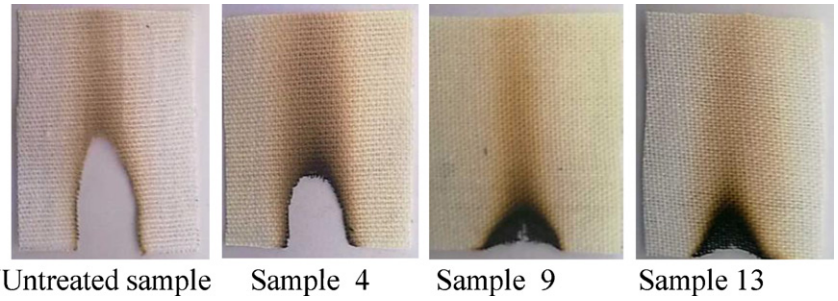

Fig. 2. The photograph related to vertical flame test of four different samples by BS3119.

the performed treatment was decreased the flammability of the samples. It can be concluded that increasing of MA and SHP concentrations leads to decrease the fabric flammability (see the results for sample 13). Also differences in the burning behavior and char length in vertical flame test for untreated sample and samples 4, 9, 13 can be seen in Fig. 2. In the case of untreated cotton, after removing the ignition source, the slight continuing of flame and no remaining observed. In samples 4, 9, 13 the flame immediately extinguished thus the char length is significantly decreased. However the samples 9 and 13 left behind a charred area after removing the ignition source. The results confirmed the impact of the existence of phosphorus deposited on the SHP treated samples that higher phosphorous increases the char formation. It is interesting to note also that the charred surface of the SHP treated samples was very uniform indicating that the phosphorus compound uniformly covered the fabric surface.

The ANOVA related to the char length of the treated samples is given in Table 4. According to the ANOVA results, the fitted model for the char length of samples is shown in Eq. (5). The most effective parameters in the char length of the samples are MA concentration and operation time. On the other hand, MA concentration is determined the SHP concentration. On these bases, it can be concluded that SHP concentration is an effective parameter in decreasing of flammability. The results are in accord with the others findings [17].

$$R2 = 11.5 - 0.1 \times MA - 0.03 \times Time \quad (5)$$

where R2 is char length of the samples.

Fig. 3 shows the response surface curve of the char length of the samples. The sample treated with 22.5% MA and 2%TEA has the lowest char length when treated with 0.5% nano titanium dioxide for 30 min in an ultrasonic bath. Also TEA has a little effect on the char length of the samples.

Table 3
Values related to char length and char yield of different samples.

Sample	Char length (mm)	Char yield	
		Before washing	After 5 wash cycles
1	11	16.50	14.01
2	10	16.22	9.20
3	10	16.92	14.07
4	11	9.49	3.07
5	9	18.21	15.74
6	8	21.83	19.94
7	9	15.48	6.85
8	8	23.35	21.61
9	7	23.44	20.46
10	8	19.25	13.10
11	8	19.64	17.07
12	9	20.93	20.31
13	7	23.05	20.82
14	11	16.77	13.52
15	9	21.14	19.25
16	7	22.22	22.10
17	7	23.95	22.21
18	8	20.74	17.25
19	10	16.31	9.58
20	7	23.66	22.96
21	8	22.85	22.74
22	10	17.12	9.97
23	8	19.64	19.07
24	7	20.42	19.27
25	7	22.50	22.02
26	9	23.10	22.69
27	8	23.03	21.19
28	8	19.76	18.01
29	12	20.24	17.96
30	9	22.19	21.34
Untreated	23	0.63	0.32

3.3. Char yield

The char yield of the treated samples before and after 5 laundering cycles is calculated and reported in Table 3 to evaluate the laundering stability of the finishing. It is observed that the char yield of the untreated sample before washing was 0.63%, and for the treated samples increased greatly however, it is reduced marginally after being subjected to 5 washing cycles. The char yield of the sample 13 was 23% before washing, that can be a measure to evaluate self-extinguishability of fabric, and decreased to 20.82% after 5 washing cycles. Hence, it can be concluded that the FR property of treated fabrics can withstand against laundering for at least after 5 cycles.

The ANOVA results for the char yield before and after washing are given in Tables 5 and 6 respectively. Accordingly, the fitted models for the char yield of the samples before and after washing are shown in Eqs. (6) and (7). It can be realized that the concentration of MA is the most important determining factor in the char yield before and after washing. Also the MA concentration is determined the SHP concentration, hence increasing SHP has greatly affected the formation of char. SHP acts in the condensed phase similar to the other phosphorus compounds and produces low flammable gases

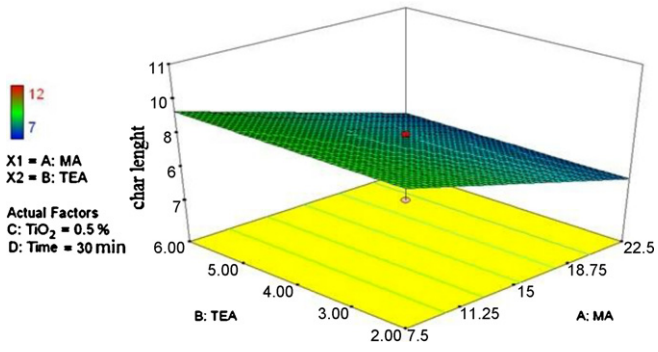

Fig. 3. Surface response curve related to char length of samples.

Table 4
ANOVA for response surface related to char length of different samples.

Source	Sum of squares	df	Mean Square	*F*-value	*p*-Value Probe > *F*
Model	28.17	2	14.08	12.47	0.0001 significant
A-MA	24.00	1	24.00	21.25	<0.0001
D-Time	4.17	1	4.17	3.69	0.0654
Residual	30.50	27	1.13		
Lack of fit	27.67	22	1.26	2.22	0.1917
Pure error	2.83	5	0.57		
Cor total	58.67	29			

Table 5
ANOVA for response surface related to char yield of different samples before washing.

Source	Sum of squares	df	Mean square	*F*-value	*p*-Value Probe > *F*
Model	295.07	6	49.18	60.14	<0.0001 significant
A-MA	237.64	1	237.64	290.62	<0.0001
B-TEA	8.88	1	8.88	10.86	0.0032
C-TiO_2	3.47	1	3.47	4.24	0.0510
D-Time	2.52	1	2.52	3.08	0.0924
A^2	37.23	1	37.23	45.53	<0.0001
D^2	2.62	1	2.62	3.20	0.0867
Residual	18.81	23	0.82		
Lack of fit	16.88	18	0.94	2.44	0.1644
Pure error	1.92	5	0.38		
Cor total	313.88	29			

Table 6
ANOVA for response surface related to char yield of different samples after 5 wash cycles.

Source	Sum of squares	df	Mean square	*F*-value	*p*-Value Probe > *F*
Model	777.49	4	194.37	167.42	<0.0001 significant
A-MA	646.05	1	646.05	556.46	<0.0001
B-TEA	28.12	1	28.12	24.22	<0.0001
AB	29.32	1	29.32	25.26	<0.0001
A^2	74.00	1	74.00	63.74	<0.0001
Residual	29.03	25	1.16		
Lack of fit	20.75	20	1.04	0.63	0.7929
Pure error	8.27	5	1.65		
Cor total	806.52	29			

increasing the char yield [3]. Also, increasing TEA concentration in the finishing solution reduces the char yield before and after washing. This may be due to the reduction of located SHP on the fabric surfaces.

$$R3 = 10.8 + 1.03 \times MA - 0.3 \times TEA - 0.02 \times MA^2 \quad (6)$$

$$R4 = 9.3 + 1.2 \times MA - 1.9 \times TEA + 0.09 \times MA \times TEA - 0.03 \times MA^2 \quad (7)$$

where R3 and R4 are char yield before and after 5 washing cycles.

Figs. 4 and 5 show the response surface curve of the char yield of untreated and 5 cycles-washed treated samples. These figures show that the sample treated with 22.5% MA and 2%TEA has the highest char formation value when treated with 0.5% nano titanium dioxide in an ultrasonic bath for 30 min. In addition, increasing MA concentration has an effective role in increasing of the char yield. However, increasing of TEA has no influence on the char formation.

3.4. LOI

LOI values of five different samples are presented in Table 7. For each sample, the LOI values of 5 specimens were measured and the average value with standard deviation are calculated and reported. The LOI value of the sample 4 is not much changed as it is treated without MA and SHP. The presence of 15% MA and 5% SHP in the finishing solution for the sample 13 shows the increase of the LOI value from 18.6 to 22.7 representing the effect of presence of phosphorous compound. The LOI value of the sample 13 is lower than that of the sample 9. This can be due to the presence of TEA in which causes a reduction in the linkages between the cellulose and SHP lowering the amount of phosphorus on the fabric. The LOI value of sample 23 in the absence of TiO_2 and presence of TEA is lower than that of the sample 9.

Table 7
Average of LOI values and standard deviation of them for 5 different samples.

Sample	Untreated	4	9	13	23
LOI	18.6	18.8	23.0	22.7	22.3
S.D.	0.29	0.37	0.38	0.16	0.44

3.5. TGA and DTA

In order to investigate effect of performed treatment on cellulose pyrolysis process, TGA and DTA curves of the five different samples are presented in Figs. 6 and 7 respectively. The pyrolysis is a complex reaction in which various reactions; endothermics bond rupture, volatilization, and exothermic bond formation can be happen simultaneously. However, the DTA thermogram shows only the net change [31]. The weight loss of samples in each pyrolysis stages can be known from TGA curve profile. At first, all TGA curves are liner that is related to the initial pyrolysis stage in which damage on cellulose occurs mostly in the amorphous region of the polymer, some physical properties of the fabric change and a little weight loss is observed. In second stage, high slope in curves observed related to large weight loss of sample. At this stage the pyrolysis of cellulose takes place in the crystalline region of the

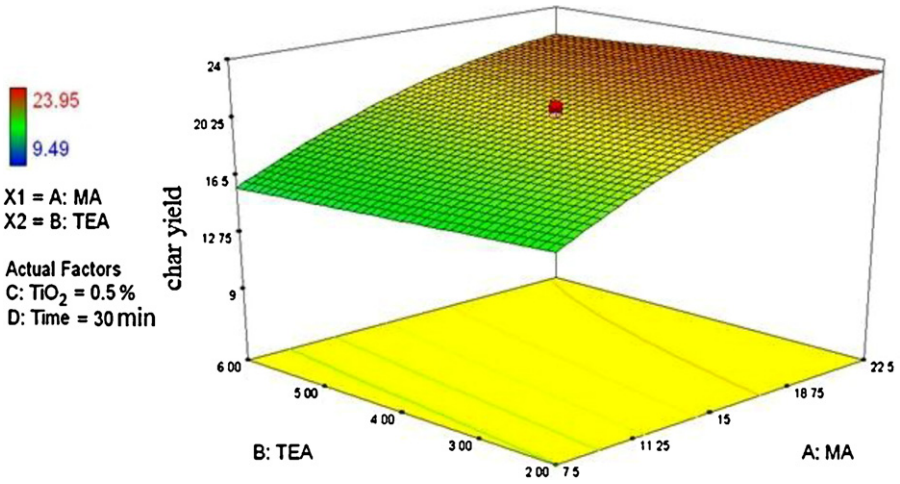

Fig. 4. Surface response curve related to char yield of unwashed samples.

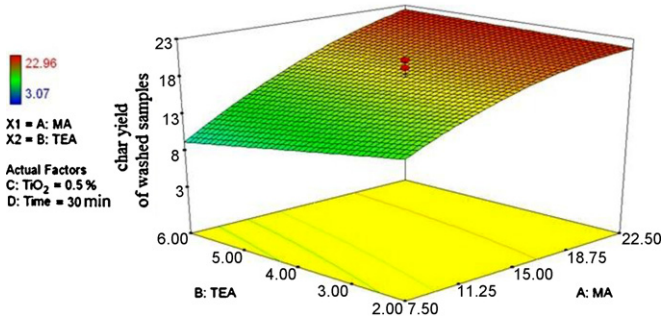

Fig. 5. Surface response curve related to char yield of 5 cycles-washed samples.

polymers. Finally curves are observed in liner form related to char pyrolysis.

The most important differences of the untreated and the treated fabrics in TGA curves were the initial decomposition temperature and the final char residue. It can be observed in Fig. 6 that the most weight loss is related to the untreated sample. In this sample the remained char is 7.5%. In sample 4, the weight of residual materials is rather higher than the untreated one and due to the addition of nano TiO_2 in the finishing bath, the final char increases to 15%. The final residual char increases at 600 °C and reaches to 28%, 27% and 26% for the samples 9, 13 and 23 respectively in comparing with sample 4. This can be explained by the addition of the phosphorous compound (SHP) which helps to form more non-flammable char residue [13]. The amount of char formed from the treated samples correlates well with the LOI values of the treated fabrics. The increased amount of char formed contributes to greater LOI values of the treated fabrics. The higher final char residue at high temperatures suggests that addition of SHP can change the pyrolysis mode of the cotton fabric when heated and SHP functions as an efficient char forming resulting a char with high resistance against heat at high temperatures. Thus, it can conclude that the phosphorous compound improved flame retardant property with increasing char content and the activation energy of cotton decomposition as reported by other researchers [9,29]. More study about mechanism and kinetic of thermal degradation in cotton fabric treated with this flame retarding system can be also considered.

The TGA curve of the untreated sample and sample 4 indicates the onset of the cellulose depolymerization at about 315 °C. The main stage of pyrolysis is in the range of 320–380 °C during which a rapid weight loss is occurred and much of the pyrolysis products such as levoglucosan is produced. The final stage of pyrolysis is occurred above 400 °C. These stages also exist in the FR-treated samples but due to the existence of the phosphorous compound in the treated samples (samples 9, 13 and 23) the initial decomposition temperatures (Table 8) of the treated fabrics are lower than that of the untreated cotton fabric and reduce from 315 °C to 304 °C. This phenomenon can be related to the accelerated initiation stage of pyrolysis and catalytic dehydration of cellulose by the phosphorus compound. From Table 8, it can be seen that T_{max} (maximum temperatures of degradation) for SHP treated cotton cellulose (samples 9, 13 and 23) are lower than the untreated cotton and sample 4, indicating dehydration and char formation reactions catalyzed by the phosphorus compound. Adding TiO_2 and TEA in sample 4 increases the T_{max} comparing with untreated cotton.

Also a large endothermic peak in DTA curves of the untreated samples is observed at main pyrolysis stage that related to the

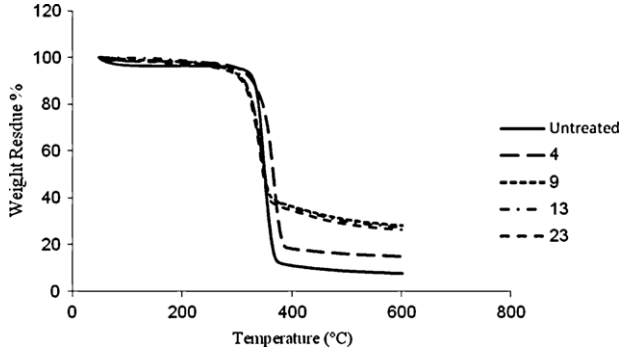

Fig. 6. TGA curve of different samples.

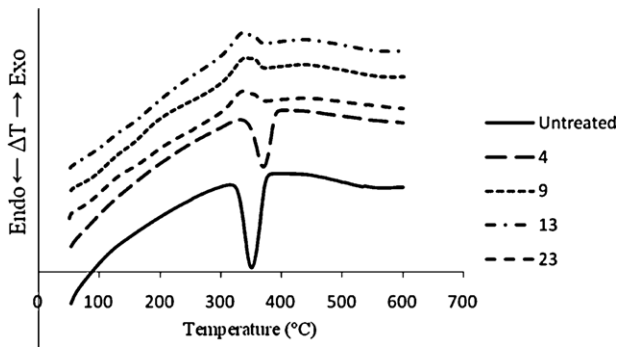

Fig. 7. DTA curve of different samples.

Table 8
Thermal data from Figs. 6 and 7.

Sample	Untreated	4	9	13	23
Initial decomposition temperature (°C)	315	315	304	304	304
Maximum temperature of degradation (T_{max}) (°C)	347	364	327	330	329
Char residue at 600 °C (%)	7.5	15	28	27	26

weight loss and vaporization of pyrolysis products [25]. The endothermic peak of sample 4 is weaker than the untreated one due to the existence of nano TiO_2 in the finishing solution. The sample treated with SHP shows an exothermic peak in the DTA curve due to the acceleration of pyrolysis termination stage by the salt [32]. Namely in termination stage of the sample treated with SHP, stronger bonds are formed and the generated heat neutralize the endothermic peak of the previous stage and finally an exothermic peak appears.

3.6. Optimization of variables and responses

Design of Expert software is used for optimization of results obtained from whiteness index, char length and char yield before and after washing. It is cleared that the optimum design point with desirability of 0.73 is for MA with concentration of 13.36% (w/v), nano TiO_2 0.68% (w/v), TEA 4.87% (w/v) and operation time 45 min. SHP concentration is still one third of MA concentration. The responses values of this sample will be: whiteness index of 54.5, char length of 8 mm, char yield before and after 5 washing cycles of 20.56 and 16.71% respectively.

4. Conclusion

In this research, the effect of SHP and nano TiO_2 as a novel flame retardant for cotton fabric was investigated. Some analysis including char length, char yield, LOI, TGA and DTA was studied in order to evaluate flame retardant property of treated samples. The presence of phosphorus deposited on the SHP treated samples is the most effective parameter in the char forming and decreasing the flammability of the treated fabrics. Also, nano TiO_2 is an effective compound in increasing the char formation. Totally, the performed treatment helps to form more non-flammable char residue and increases char formation after heating. The increased char formation is a measure of fabric self-extinguishability that slightly reduced after 5 washing cycles. The increased amount of char formed contributes to greater LOI values of the treated fabrics. The thermal analysis indicated the presence of SHP leads to decrease the initial and maximum decomposition temperatures and more char formation. On the other hand, without TEA performed treatment led to yellowing of the samples. However, application of TEA within the limited concentrations greatly improved the fabric whiteness. The SHP concentration was determined with MA concentration and was one third of MA concentration. According to RSM, the optimum concentration of MA is 13.36% (w/v) equal to 4.45% (w/v) concentration of SHP.

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