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Development of eco-friendly flame retardant finishing system for cotton fabrics

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ABSTRACT

Most of textiles in use have limiting oxygen index (LOI) lower than 21, while cotton have 18.9, which means that they can burn easily once the fire has started. Currently, there is some difficulty in making durable flame retardant (FR) treatments for cotton fabric using an ordinary one-step wet process, which are nontoxic to the environment and humans.

The goal of this research is to impart cotton fabrics flame retardant properties via partial carboxymethylation followed by ester crosslinking with phosphoric acid in presence of urea. This research has also aimed to investigate the optimum treatment conditions that allow the selective and controlled deposition of urea onto carboxymethylated cotton fabric. In this regards the effect of process parameters on the physicochemical and performance properties of treated cotton fabric will elucidate. The treated fabric were monitored for nitrogen and phosphorous content besides, limiting oxygen index (LOI), char length, char residue, whiteness index, retained tensile strength and elongation at break. The treated cotton fabrics show LOI and char length 38, 4.7 cm respectively, compared with 18 and 11 cm for untreated fabric. The existence of new polyphosphate-cellulose interaction and other functional groups introduced into cotton fabrics were confirmed by FTIR spectroscopy and TGA.

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KEYWORDS

Carboxymethylation;
Cotton fabrics;
Functional finishing;
Flame retardant;
Limiting oxygen index
(LOI);
Polyphosphate.

INTRODUCTION

Cotton cellulose has desirable properties such as high water absorbency and moisture, being comfortable to wear and easy to dye. For these reasons, the apparel industry is predominantly cotton based, and the share of cotton in total fibre consumption is about 50%^[1].

Cotton is composed almost entirely of cellulose (90–96% based on weight of fibres). The impurities in cotton fibre range from 4% to 10%. The impurities include protein (1.0–2.1%), wax (0.4–1.7%), ash (inorganic salts) (0.7–1.8%), pectin (0.4–1.9%) and others (resins, pigments, hemi-cellulose) (1.5–2.5%)^[1,10].

Cotton is a highly combustible textile fibre. The

flammability of a cotton fabric largely depends on the construction and density of the fabric. Fires, on average, result in upwards of 20,000 injuries per year, and annual property loss reaches billions of dollars^[11].

Since most of textiles in use have limiting oxygen index (LOI) lower than 21, while cotton have 18.9, which means that they can burn easily once the fire has started, flame retardant finishing (FR) serve a vital purpose in protection against textile related fires and are used throughout the world in various applications such as textiles, plastics and building materials. Currently, there is some difficulty in making durable FR treatments for 100% cotton fabric using an ordinary one-step wet process, which are nontoxic to the environment and humans^[11, 12].

The use of durable and environmentally friendly flame retardants is of growing importance in several industries including textiles and plastics. With the increasing environmental and health concerns surrounding the use of halogenated flame retardants, the push to find alternatives due to current and pending legislation is rising. While some substitutes have been found to be effective in suppressing flame, there are concerns surrounding other properties, such as the durability and cost of these materials^[11].

The ability to create novel inorganic-organic-metal ordered structures with molecular level precision opens the possibility of developing multifunctional textiles for a myriad of applications including flame retardant^[13]. Due to the high curvature and heterogeneous nature of textile fibers, existing surface modification technologies are not capable of providing complete coverage of a fiber/fabric surface. The use of self-assembly techniques offer the possibility of achieving fully conformal, uniform functionalization of textile fibers of any continuous shape^[13]. On the other hand, chemical modifications can be obtained by using many compounds such as phosphorous-based compounds, which generate gases less toxic than those evolve from halogenated compounds^[13].

The goal of this research is to impart cotton fabrics flame retardant properties via partial carboxymethylation followed by ester crosslinking with phosphoric acid in presence of urea. This re-

search has also aimed to investigate the optimum processing conditions that allow the selective and controlled deposition of urea onto carboxymethylated cotton fabric. In this regards the effect of process parameters on the physicochemical and performance properties of treated cotton fabric will elucidate.

EXPERIMENTAL

Materials and chemicals

Grey loomstate cotton fabric (100 %), plane weave, 3/1 of weight 265 g/m² was supplied by Misr Company for Spinning and Weaving, El Mehala El-Kobra, Egypt. Monochloroacetic acid (C₂H₃ClO₂, 99%) from Sigma Aldrich company. Sodium hydroxide, sodium carbonate, sodium silicate, hydrogen peroxide (30%), orthophosphoric acid (85 %), Egyptol[®](non-ionic wetting agent based on ethylene oxide condensate), were supplied from El Gomhoria Company, Cairo, Egypt.

Desizing and scouring

The cotton fabrics were desized and scoured by using the exhaustion technique as follows: cotton fabric samples was treated with an aqueous solution containing sodium hydroxide (6 g/l), Egyptol (2 g/l) using liquor to goods ratio of 50:1 at 95°C for 30 min. After scouring, the samples were washed several times with boiling water followed by washing with cold water and finally dried at ambient conditions.

Bleaching

Scoured cotton fabrics were treated with an aqueous solution containing hydrogen peroxide (6 g/L) of pure hydrogen peroxide, sodium silicate (2 g/L) and organic stabilizer (1 g/L). The pH was adjusted to 10.5 using aqueous sodium hydroxide solution. A liquor to goods ratio of 50:1 was used and the bleaching process was carried out at 95 °C for 45 min. The fabric was then washed several times with boiling water, followed by washing with cold water and finally dried at ambient conditions.

Carboxymethylation of cotton fabrics (CMC fabric)

Cotton fabric was partially carboxymethylated

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by a method reported by Hashem *et al*^[14-17].

Treatment with ammonium polyphosphate

Samples of carboxymethylated cotton fabrics (CMC) having (335 meq/100 g fabric) were padded in different concentration of orthophosphoric acid (25-100 ml/L) squeezed and dried at 100 °C for 5 min. Another samples of CMC were padded in different concentration of urea (100-400 gm/L) squeezed and dried at 100 °C for 5 min. Finally, the treated fabrics washed with cold water and dried at ambient conditions.

The CMC samples treated with different concentration of orthophosphoric acid were padded again in aqueous solution of urea 400 gm/L, squeezed and dried at different temperature (100-130 °C) for different time (5-11 min).

Testing and analysis

Determination of carboxylic content

The anionic content of the carboxymethylated samples was quantitatively determined by acid base titration and is reported in the units of meq/100 g fabric. The method was adopted from previous work^[14,17].

Determination of nitrogen content

Nitrogen content of the samples was determined by the Kjeldhal method^[18].

Determination of phosphorous content

Phosphorous content of the treated samples was determined using atomic absorption Type Berken Elemar Lambada 2

FTIR analysis

Fourier Transform Infrared spectra are generated by the absorption of electromagnetic radiation in the frequency range 400 to 4000 cm⁻¹. FTIR spectra were recorded using Thermo Avtar 370 spectrometer.

Thermogravetric analysis (TGA & DTA)

TGA & DTA were done by thermal analyzer (TGA-50 Shimadzu instrument) at heating rate of 10 °C to 850 °C under N₂ gas with flow rate 20 %.

Determination of limiting oxygen index (LOI) of treated and untreated cotton fabrics

The property of flame-retardancy was monitored according to the vertical burning test method (AA TCC Test Method (34-1969), 1972).

Char residue

The weight of each sample before and after burning was measured^[19, 20] and char yield was calculated according to following Equation.

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

Where W₁, W₂ are the weight of samples before and after burning, respectively

Char length

The vertical flammability of cotton fabrics was used to measured char length according to BS3119 standard method.

Tensile strength and elongation at break

Tensile strength of the samples was determined according to ASTM Standard Test Method D-5035. A Q-Test 1/5 Tensile Tester was used. The average value of two measurements for each samples in the warp direction were recorded as the fabric breaking load (Lb).

Whiteness index

The whiteness index was measured using Ultra scan Pro Hunter lab.

RESULTS AND DISCUSSION

Flame retardancy mechanism for textiles - Tentative mechanism

Flame retardancy mechanism of textiles is proceeds via two interconnected routes the first route is chemical route which is further divided to two different mechanism condensed phase and gas phase mechanism, the other route is physical one as in Figure 1^[21].

Phosphorous based flame retardancy undergoes with both condensed phase and/or gas phase flame retardant action. The range of phosphorous-based flame retardant products is extremely wide, including phosphates, phosphonates, phosphinates, phos-

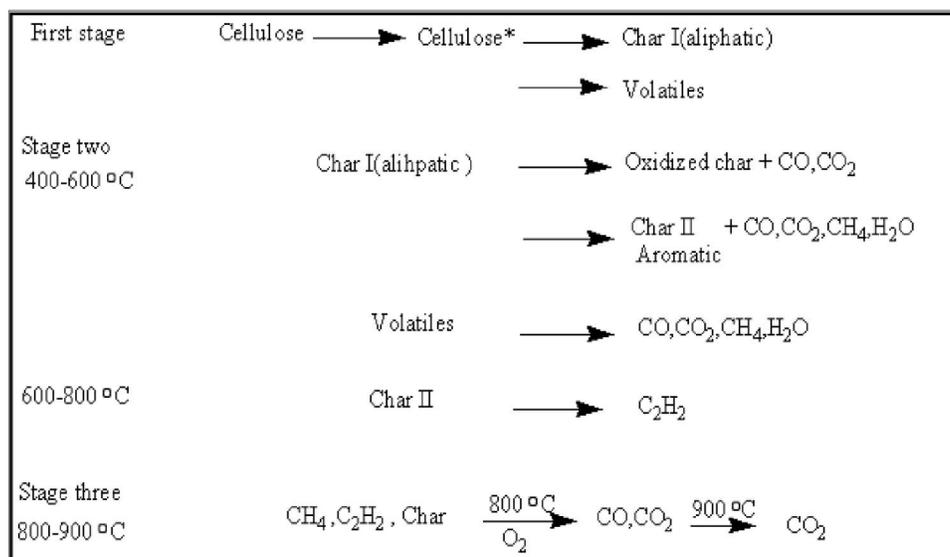
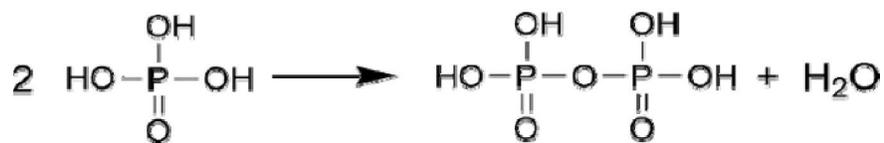


Figure 1 : Reaction mechanism of flame retardancy

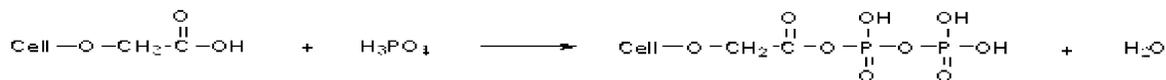
phine oxides, phosphates and red phosphorus^[22]. All of these compounds undergo thermal decomposition and production of phosphoric acid which rapidly condensate to generate pyrophosphate and release water as shown in Equation 1.



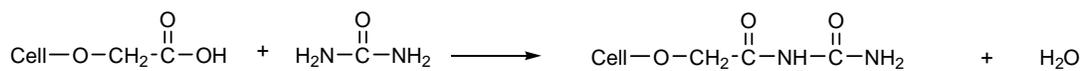
Equation 1

Each of phosphorous and nitrogen exhibit flame retardancy for fiber but when they combined they exhibit synergistic effects. The basis of this type is the interaction between phosphorus and nitrogen in C.M.C to impart fire retardancy. In this work urea and O-phosphoric acid were used to avoid environmental and health problems for skin^[23, 24].

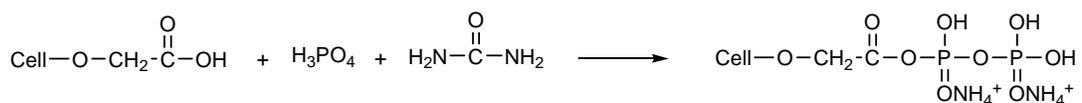
In this work it is clear that urea exhibit thermal poly condensation of orthophosphoric acid to form poly phosphoric acid which is good dehydrating agent for cellulose. The polyphosphoric group works as thermal barrier layer for cellulose. Char forming shows that it contains effective P-N combination as shown in equation2, 3,4^[25, 26].



Equation 2



Equation 3



Equation 4

Effect of monochloroacetic acid concentration

Cotton cellulose reacts with monochloroacetic acid in presence of sodium hydroxide to bring about

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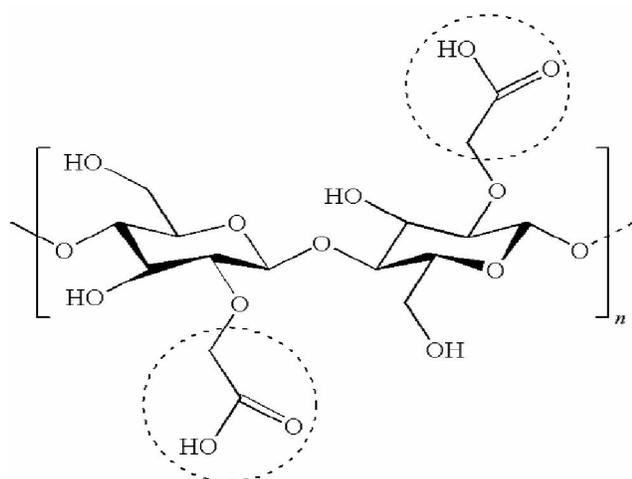


Figure 2 : Structure of carboxymethylated cotton fabric^[14-17]

partially carboxymethylated cotton (PCMC) as suggested by structure in Figure 2^[14-17]. TABLE 1 shows that as the concentration of sodium salt of monochloroacetic acid (MCAA) increased from 0.5 N to 3 N, the carboxylic content of the treated cotton fabrics increased from 102 meq/100 g fabric to 335 meq/100 g fabric. Enhancement of the reaction between MCAA and cotton fabric as the concentration of the former increases could be interpreted in terms

of greater availability of MCAA molecules near cellulose hydroxyls at higher MCAA concentrations. It is understandable that cellulose hydroxyls are immobile and their reaction relies on the presence of MCAA molecules in their proximity; a situation which can be accomplished at higher MCAA concentration.

Effect of ortho-phosphoric acid concentration

TABLE 2 shows the relation between H_3PO_4 concentration and the flame retardancy properties and strength properties as well as fabric whiteness index. Flame retardancy properties were monitored via determination of LOI, char length and char residue. The phosphorus content of the treated fabrics was also determined.

It is seen from TABLE 2 that, by increasing the concentration of H_3PO_4 the phosphorous content of the treated PCMCF increased. Meanwhile, both tensile strength, elongation at break and whiteness index decreased. Decrement in tensile strength and elongation at break is attributed to acid hydrolyses of cellulose and increasing the amount of hemi cellulose^[22].

TABLE 1 : Effect of monochloroacetic acid - sodium salt (MCAA) on carboxylic content of treated cotton fabrics

Concentration of MCAA (N)	Carboxylic content (meq/100 g fabric)
0.5	102.36
1	136.4
2	200
3	335

Conditions used: Cotton fabric samples in 15 wt% aqueous NaOH, squeezed to a wet pick up of 100%, dried at 60°C for 5 min, then padded in aqueous solution of sodium salt of monochloroacetic acid, squeezed to 100 % wet pick up, sealed in plastic bags and heated at 80°C for 1 h.

TABLE 2 : Effect of H_3PO_4 concentration on the flame retardancy and physical properties of treated cotton fabrics

H_3PO_4 Conc. (ml/L)	phosphorous content (ppm)	LOI	Char length (cm)	Char residue (%)	Tensile strength (kg.f)	Elongation at break (%)	Whiteness index
blank	0	18	11	50	84	27	73
25 (21.25)*	800	18	10	50.4	80	26	69
50 (42.5)	876	18	10	50.6	74	27	65
75 (63.75)	924	18	10	50.8	70	26	65
100 (85)	1230	20.2	9.4	51	65	22	65

* Values in brackets represent concentration of H_3PO_4 in g/L

Conditions Used: Carboxylic content 335 meq/100 gm cellulose, dried at 85 C for 5 min, cured at 100°C for 5 min. The fabrics were evaluated after five washing.

Washing Bath (Five washing): 100 ml water and 1 ml Egyptol® for 3 minutes at 60 °C

TABLE 3 : Effect of urea concentration on the flame retardancy and physical properties of treated cotton fabrics

Urea Conc. (g/L)	Nitrogen content (%)	LOI	Char length (cm)	Char residue (%)	Tensile strength (kg.f)	Elongation at break (%)	Whiteness index
blank	0	18	11	50	84	27	73
100	0.09	18	10	50.01	84	27	71
200	0.24	18.9	10	50.09	82	26	73
300	0.75	19.2	10	50.2	85	25	73
400	0.94	20.8	9.7	50.29	86	22	74

Conditions Used: carboxylic content 335 meq/100 gm cellulose, dried at 85 C for 5 min, cured at 100^oC for 5 min. The fabrics were evaluated after five washing, Washing Bath (Five washing): 100 ml water and 1 ml Egyptol[®] for 3 minutes at 60 °C

TABLE 4: Binary effect of urea and different concentration of H₃PO₄ on the flame retardancy and physical properties of treated cotton fabrics

H ₃ PO ₄ Conc. (ml/L)	Phosphorous content (ppm)	LOI	Char length (cm)	Char residue (%)	Tensile strength (kg.f)	Elongation at break (%)	Whiteness index
blank	0	18	11	50	84	27	73
25 (21.25)*	2217	22.4	7	52.07	78	25	70
50 (42.5)	2434	22.6	6.9	52.14	80	25	67
75 (63.75)	3160	22.9	6.7	52.56	80	24	66
100 (85)	3489	24.5	6.3	52.88	78	22	66

* Values in brackets represent concentration of H₃PO₄ in g/L

Conditions Used: carboxylic content 335 meq/100 gm cellulose, urea 400 g/L, dried at 85 C for 5 min, cured at 100^oC for 5 min. The fabrics were evaluated after five washing, Washing Bath (Five washing): 100 ml water and 1 ml Egyptol[®] for 3 minutes at 60 °C

It is further observed from results in TABLE 2 that, the LOI remain practically intact except when the concentration of H₃PO₄ reached 100 ml/L, the LOI slightly increased to 20.2. Char length of the treated fabrics slightly decreased as the concentration of H₃PO₄ increased whereas char residue decreased marginally.

Results of TABLE 2 make it clear that, utilization of H₃PO₄ alone does not impart flame retardancy to the CMCF whatever the concentration used.

Effect of urea concentration

PCMC fabric was treated with different concentration of urea (100-400gm/L) at higher temperature. The fabric was monitored for nitrogen content, flame retardancy properties as well as strength properties as whiteness index. Results obtained are set out in TABLE 3. Results of TABLE 2 depict the following: i) by increasing the concentration of urea the nitrogen content of the treated fabric gradually increased. ii) LOI of the treated fabrics slightly increased as the concentration of urea increased. LOI

attained its maximum value on using urea with concentration 400 g/L. At this concentration LOI of the treated fabric recorded 20.8 which is still far from those values of LOI required for flame proofing characteristics. iii) Char length gradually decreased as the concentration of urea increased whereas char residue remains practically the same. iv) Both tensile strength and elongation at break improved as the concentration of urea increased whereas W.I. remains practically intact^[23, 24].

Effect of binary solution urea and H₃PO₄

Based on the results obtained previously in TABLES 2 and 3 and the flame retardancy mechanism proposed in equation 2 and equation 3, studying the binary effect of urea and H₃PO₄ on the flame retardancy and physical properties of treated cotton fabrics is necessary.

Results of TABLE 4 depict the following: 1) by increasing the concentration of O-phosphoric acid the LOI of the treated fabrics increased. The same holds true for the char residue whereas char length

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TABLE 5 : Effect of curing temperature on the flame retardancy and physical properties of treated cotton fabrics

Curing temp. (°C)	LOI	Char length (cm)	Char residue (%)	Tensile strength (kg.f)	Elongation at break (%)	Whiteness index
Untreated	18	11	50	84	27	73
100	24.5	6.3	52.88	87	22	65
110	26	5.7	52.97	82	23	64
120	30	5.2	53.04	70	21	60
130	32	4.9	53.16	64	18	56

Conditions Used: carboxylic content 335 meq/100 gm cellulose, containing H_3PO_4 100 g/L, urea 400 g/L, dried at 85 °C for 5 min, curing time 5 min. The fabrics were evaluated after five washing, Washing Bath (Five washing): 100 ml water and 1 ml Egyptol® for 3 minutes at 60

TABLE 6 : Effect of curing time on the flame retardancy and physical properties of treated cotton fabrics

Curing time (min)	LOI	Char length (cm)	Char residue (%)	Tensile strength (kg.f)	Elongation at break (%)	Whiteness index
Untreated	18	11	50	84	27	73
5	26	5.7	52.97	82	23	64
7	32.4	5.2	54.34	71	21	61
9	34	4.7	54.76	62	17	55
11	38	3.9	55.01	55	16	51

Conditions Used: carboxylic content 335 meq/100 gm cellulose, H_3PO_4 100 g/L, urea 400 g/L, dried at 85 °C for 5 min, curing at 120 °C. The fabrics were evaluated after five washing, Washing Bath (Five washing): 100 ml water and 1 ml Egyptol® for 3 minutes at 60 °C

sharply decreased. 2) A sailed feature observed in TABLE 4 is the steady of fabric tensile strength as the concentration of H_3PO_4 increased in the presence of 400 g/L urea. A point which indicated that the reaction of H_3PO_4 with urea under our experimental conditions used to form ammonium polyphosphate was preferred than the hydrolysis reaction cotton cellulose with H_3PO_4 . 3) It is also seen from results in TABLE 4 that, the W.I. marginally decreased as the concentration of H_3PO_4 increased. 4) Higher flame retardant properties of the treated cotton fabrics were observed when the concentration of H_3PO_4 was 100 ml/L and urea concentration was kept at 400 g/L.

Effect of curing temperature

TABLE 5 shows the effect of curing temperature on the reaction between H_3PO_4 , urea and treated cotton to form ammonium polyphosphate onto cotton. It is clear that by increasing the fixation temperature from 100 -130 °C, the limiting oxygen index sharply increased from 24.5 to 32 and the char residue very marginally increased from 52.88 % to 53. 16 % . It

is further noted that the char length decrease from 6.3 cm to 4.9 cm and the tensile strength and elongation at break decreased. The fabric W.I. decreased by about 10 % from its initial value as the curing temperature increased.

Although higher curing temperature is favor for formation of polyphosphate, it is also favor for acid hydrolysis to cotton cellulose, which account for the decrement in T.S and W.I. Increasing the reaction of CMC fabric with urea and H_3PO_4 as the temperature increased could be associated with the favorable effect of the temperature on diffusion of urea and H_3PO_4 , and their mobility and their probable collision with cellulose molecules.

Effect of curing time

TABLE 6 shows reaction duration of urea, H_3PO_4 on the treated fabric. It is seen from result in TABLE 6 that; increasing the curing time up to 11 min brings about increasing in LOI from 26 – 38 and the char residue also increased to 55 %. It is further noted that the char length decreased as the curing time increased. The same holds true for the tensile strength

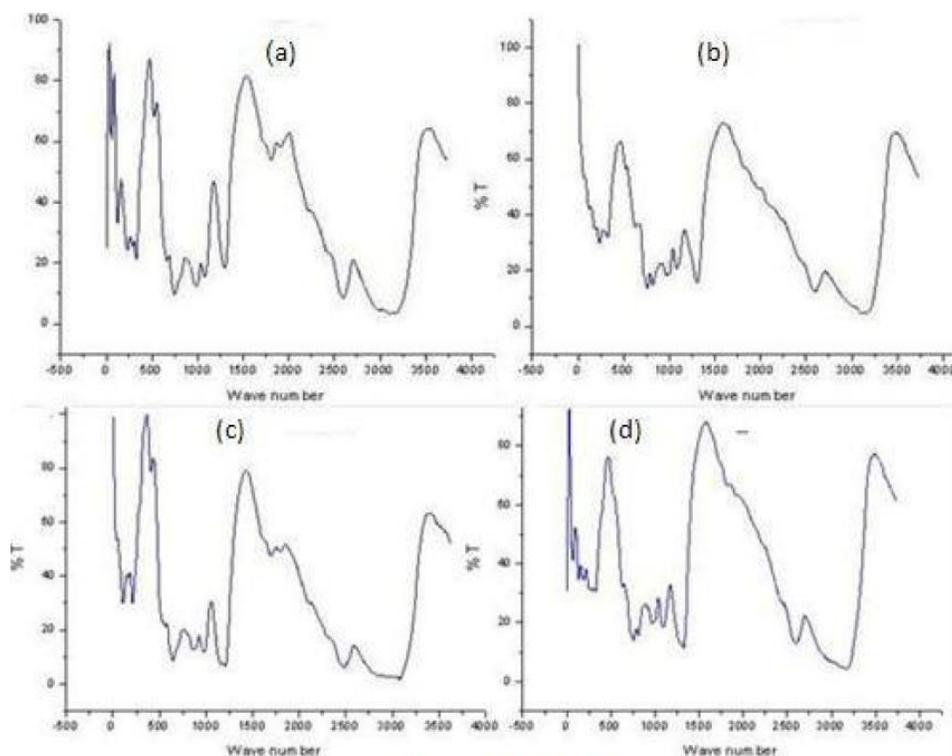


Figure 3 : FTIR of samples a :CMC, b: CMC treated with orthophosphoric acid, c: CMC treated with urea, d:CMC treated with orthophosphoric acid and urea

and elongation at break, which decreased by approximately 35 % and 40 % respectively. The fabric W.I. also decreased from 73 to 51 as the curing time increased up to 11 min.

Although, longer time provides better opportunity for better contact among reactants and therefore, higher extent of reaction, fabrics tender after prolonging time are adversely effects. A close examination of results in TABLE 6 shows that, after 7 min curing at 130°C, the flame retardant properties of cotton fabric is very high and at the same time the other fabric properties including T.S, elongation an break as well as W.I remain at very acceptable level.

FTIR analysis

The FTIR spectrum of carboxymetylated treated fabrics is shown in Figure (3-a). In addition to the cellulose peaks a new peaks indicate the presence of summarized follows: carboxylic group: 3531 cm^{-1} (carboxylic O-H stretching); 1653 cm^{-1} (-C=O stretching of carboxylic acid); 1120 cm^{-1} (-C-O-C- asymmetric bridge stretching), 701 cm^{-1} (-O-C=O bending in carboxylic acid)^[14,17].

The FTIR spectrum of CMC samples treated with

O-phosphoric acid is shown in Figure (3-b). A new peaks formed is assigned as follows: 1188 cm^{-1} and 1131 cm^{-1} (P=O stretching); 711 cm^{-1} (P-O-C)^[26].

The FTIR spectrum of CMC cotton samples treated with urea is shown in Figure (3-c). A new peaks formed is assigned as follows: 1451 cm^{-1} (N-C-N stretching), 3477 cm^{-1} (N-H₂ stretching)^[23,24].

The FTIR spectrum of CMC samples treated with O-phosphoric acid and urea is shown in Figure(3-d). A new peaks formed is assigned as follows: 1127 cm^{-1} (P=O stretching); 1005 cm^{-1} (P-O-C); 3453 cm^{-1} (O-H stretching); 3304 cm^{-1} (N-H vibration stretching); 1674 cm^{-1} (N-H vibration bending)^[25].

Thermal gravimetric analysis

Figures (7-10) and TABLE 7 show TGA of CMC, CMC fabrics treated with H₃PO₄, CMC fabrics treated with urea and CMC fabrics treated with urea and H₃PO₄, respectively. It seen that, in all samples, the first weight loss (amounted 4.4 - 5.4 %) is due to loss of absorbed moisture at temperature less than 80°C. The char formed at temperature higher than 370°C. In Figure (4-b), TGA of CMC fabrics treated with H₃PO₄ only, it is seen that, the thermal degra-

TABLE 7 : Thermal decomposition of cotton fabrics before and after different treatment

Sample Treatment	1 st step		2 nd step		3 rd step	
	Td (°C)	Wt. loss (%)	Td (°C)	Wt. loss (%)	Td (°C)	Wt. loss (%)
Carboxymethylated fabric (CMCF)	75	5.24	371	79.28	-	-
Treated H ₃ PO ₄	70	5.37	258	55.44	-	-
Treated with urea	66	4.46	179.71	15.15	352	65.84
Treated with H ₃ PO ₄ and urea	68	4.45	175.08	13.86	317	58.39

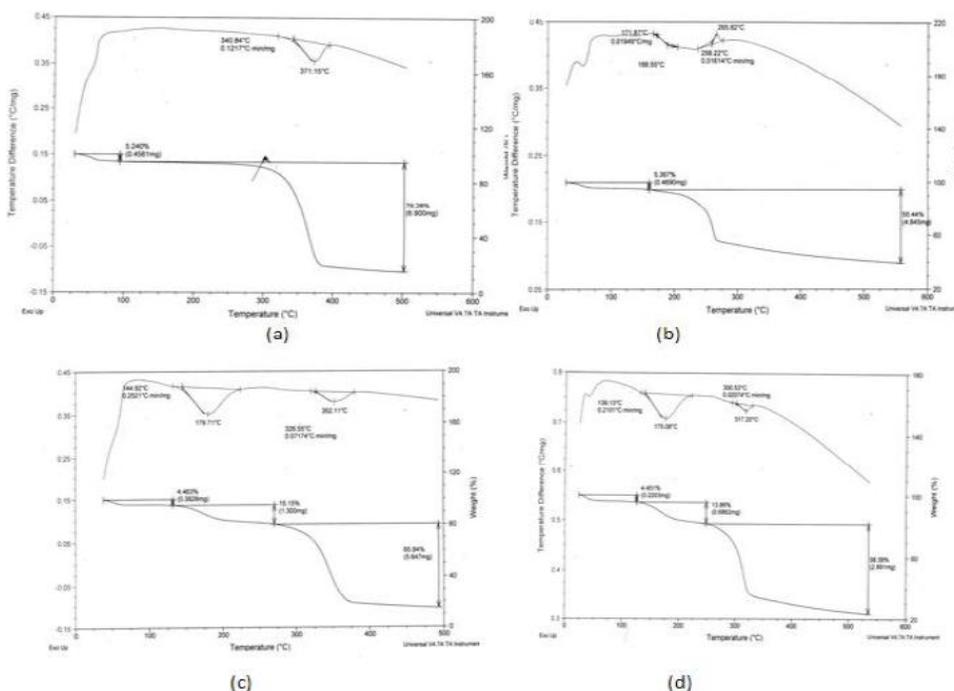


Figure 4 : TGA&DTA of samples a :CMC, b: CMC treated with orthophosphoric acid, c: CMC treated with urea, d:CMC treated with orthophosphoric acid and urea

dation at 258°C and the weight loss was reduced to 55% is due to releasing phosphoric acid that catalyzed the dehydration and the phosphorylation as well as inhibit the C₆-C₁ intermolecular rearrangement that produces levoglucosan thus promotes char forming^[14, 17, 26].

Figure (4-c) shows TGA of CMC fabrics treated with urea. It is seen that, treated fabrics decompose at three steps: the first represent the release of absorbed water at 66 °C and amounted 4.46 %. The second peak represents the release of ammonia at 179 °C and amounted 15%. The third peak represents the formation of char at 352 °C and amounted 65%^[23, 24].

Figure (4-d) shows TGA of CMC fabric treated

with H₃PO₄ and urea. It is seen from figure that, the second peak is corresponding to weight loss at 175°C is probably due to partially degradation of the crystalline of cellulose accompanied by loss some of NH₃^[26].

CONCLUSION

In this work the flame retardancy of cotton fabric was improved via introducing anionic functional group on cellulose fabric and introducing on it ammonium poly-phosphate group.

It is clear that all flammability properties were improved while physical properties were slightly decreases.

The treated fabrics were assessed by FTIR, TGA and DTA and clarify presence of carboxylic group and ammonium polyphosphate on the treated fabrics.

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