Mehran University Research Journal of Engineering and Technology

https://doi.org/10.22581/muet1982.2301.06

2023, 42(1) 56-61

Sustainable flame retardant treatment for cotton fabric using non-formaldehyde cross-linking agent

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Received: 07 April 2022, Accepted: 15 December 2022, Published: 01 January 2023

KEYWORDS

Cotton Fabric

Flame Retardant

Cross-Linker

Sustainability

Non-Formaldehyde

ABSTRACT

Most flame-retardant finishing agents have been found to have an adverse effect on our environment and human skin because of the carcinogenic chemicals in their structure. Pyrovatex CP New is an Organophosphorus based flame retardant (FR) agent widely used in FR treatment of combustible. However, the main problem related to it is the release of high formaldehyde content (a known carcinogen). When used with methylated melamine (MM) an effective cross-linker. The objective of this research was to use citric acid (CA) and its integration with sodium hypophosphite (NaH_2PO_2) and two different co-catalyst Titanium dioxide (TiO_2) and phosphoric acid (PA) as a flame-retardant finishing for cotton fabrics. The flammability of cotton fabric was assessed by a manual vertical flammability test, it is found that the combination of co-catalysts in FR formulation lowers the flammability of cotton. The pyrolysis characteristics and char residue yield of the treated cotton shows that the flame retardancy improves as the amount of catalyst is increased. The whiteness index, crease recovery and tensile strength of the treated cotton fabric was also significantly improved with our suggested recipe formulation. The finished cotton has significant variations in terms of its tensile strength, crease recovery, and whiteness index.

1. Introduction

Fires in which death ascends is mainly from burns relating to textile. The severe burn injuries are difficult to treat medically and typically result in deep-rooted psychological ramifications thus affecting the medical, physical and societal conduct of burn patient. It is also noteworthy that the remedial expenditures for severe burn wounds are enormously high and involve lengthy periods of hospitalization. In the UK alone, about £250 million annually is spent on treating burns every year [1]. The flammability of textiles has always been thought of as a major hazard definitely but most textiles play an important role in everyday life. The abundantly present natural polymer in plants and other living things is called cellulose. There are several plant sources for cellulosic fibres, including cotton seeds. [2].

A prominent biopolymer in the globe is cotton [3]. It is the most significant and vital cellulosic fibre due to its huge planting area and global output. [4]. Due to its characteristics of breathability, smoothness, and hydrophilicity, it is widely utilised in home textile, clothing, and industries. Apart from many applications, the main disadvantage is the flammable nature that limits the use of cotton fabric. It burns easily and catches fire. Cotton undergoes degradation after the burning and forms highly combustible material levoglucosan [5]. Easy ignition and low thermal stability represent its weakness and limited use in textile [6, 7]. Acrylic, nylon, and polyester are a few other mixed textiles that are said to be less flammable. But since these synthetic materials melts when they burn, they inflict severe skin burns, making burning with them more dangerous [8]. The flammability of textiles has always been thought a major hazard: definitely, most textiles play an important role in everyday life (e.g. for medical purposes, for transportation, for protective garments, wearing purpose, the military), are flammable and probably risky materials [1]. To improve the flammability of cotton fabric different compounds had come into the market to reduce flammability. Nearly half a decade earlier, the era of the 1950s saw the progress of chemistry underpinning the majority of currently effective and lasting fire-retardant recoveries for textile fibers [9].

Pyrovatex and Proban are the two most used organophosphorus finishing agents due to their high resistance towards flammability and excellent durability of treated fabric [9]. The core issue with Pyrovatex is that formaldehyde is used in both its production and its use. [10], which is a carcinogenic compound [WHO]. Hence, the recent attention has been focused primarily on formaldehyde-free flame retardant [11].

In the recent past, the effectiveness of citric acid (CA) has been proven as a cross-linking agent and a mild fire retardant. CA is not only an efficient crosslinker but can also be used in the recipe formulation of fire -retardant finish due to carboxyl group and hydroxyl group in their structure [12]. CA, as a fire retardant, is less expensive, non-hazardous, effective, acceptable, and simpler to work with than other finishing agents [13].

The present study used CA and titanium dioxide (TiO_2) with phosphoric acid (PA) as co-catalyst to enhance the effect of flame retardancy by using the pad-dry-cure method. PA helps to initiate a flame retardant reaction [5]. TiO_2 on the other hand intact the whiteness of fabric, which usually deteriorates with PA and high curing temperatures.

2. Materials and Methods

2.1 Materials

Desized plain cotton fabric was kindly provided by popular textile mill, Karachi. Fabric weave parameters were 60 picks/inch, yarn count 20 Ne in weft, 60 ends/inch, yarn count 20 Ne in warp, and the fabric weight was 118.5g/m^2. CA, sodium hypophosphite (SHP), PA and TiO_2 were purchased from Al-Beruni chemicals, Hyderabad, Sindh (Pakistan). The samples of treated cotton fabric were preconditioned for 24 hours at 65% RH and 27°C before testing.

2.2 FR solution preparation

a) Solution without catalyst.

   10g/ml of CA and 9.6g/ml of SHP solution were prepared in 100ml of water. The pH of solution was maintained at under normal stirring for 150 minutes at room temperature.

b) Solution with TiO_2.

   Firstly 1% sol of TiO_2 stirred for 30mins at 60ºC temp and then 10g of CA and 9.6g of SHP solution in 100ml were mixed in 1% TiO_2 solution and again stirred for 120 mins. The detailed recipe formulation is given in Table 1.

Table 1

Recipe formulation

Samples	Citric acid (g/0.1L)	sodium hypophosphite (g/0.1L)	phosphoric acid (g/0.1L)	Titanium dioxide (g/0.1L)
C1	10	9.6	---------	--------
C2	10	9.6	3	--------
C3	10	9.6	3	1
C4	10	9.6	-------	1

2.3 Treatment of cotton fabric by applying the flame-retardant formulation

Table 1 shows the formulation of flame-retardant used for the coating. Flame retardant treatment was carried out by one bath pad-dry-cure method. The prepared solution was padded onto the fabric samples to obtain an 80% wet pick-up at room temperature. The sample C1 without any catalyst) were dried in a dryer at 85ºC for 10 min followed by curing at 170ºC for 6min, while all other samples were dried in a dryer at 110°C for 5min and cured at 180°C for 1.5min.

Using a weighing balance, the treated samples were weighed both before and after treatment. The pick-up % was calculated by applying the following equation.

$$\text{Pick up \%} = (w_o - w_1/w_o) \times 100 \quad (1)$$

Where w_o= weight of fabric after treatment and w_1= weight of fabric before treatment

Fig. 1 shows a few examples of treated samples. Untreated sample burnt quickly and completely, taking 7 sec. The fabric failed in flame resistance.

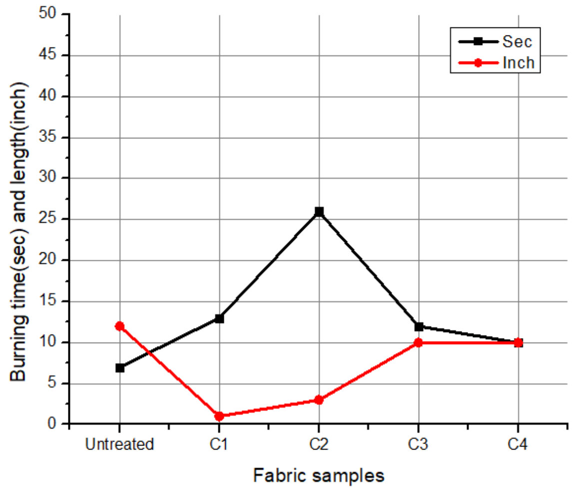

Fig. 1. Graphical representation of burning length and time of samples

3. Characterization

The flame retardant treated cotton fabric was assessed by using a manual Standard technique which is identical to the ASTM D-6413 method. Tensile strength of fabric was assessed by following the ASTM standard test method D-5035 which is raveled strip method by using a titan universal tensile testing machine in the textile engineering department, MUET, Jamshoro. Crease recovery of coated sample was assessed by following the standard of ASTM 66-2003 by using wrinkle recovery test apparatus. The whiteness of the coated sample was assessed by following the standard of ASTM-73 by using a spectrophotometer with D65 illuminant and 10° observer.

4. Results and Discussion

4.1 Flame retardancy analysis

The flame retardancy was characterized by two factors i.e., char length and burning time. The results of after treatment shown in Table 2.

Table 2

Burning time and burning length of sample

Samples	Burning time (sec)	Burning length (inches)
UT	7	12
C1	13	1
C2	26	3
C3	12	10
C4	10	10

CA was added in formulation for flame retardancy. The effectiveness of CA has been proven as a cross-linking agent as well as for fire retardants [14]. In the experiment, the impact of CA on flammability was examined. Although the use of CA and SHP helps to increase char yield, the presence of CA has less impact on it. SHP is increasing char yield while producing less combustible gas.

The result showed that the treatment of cotton fabric in the presence of PA as a co-catalyst decreases the flammability of cotton fabric. It is reported in the literature that PA as a co-catalyst increases the flame retardancy of fabric and the samples treated with FR solution needed to use PA as catalyst [15]. It given in Table 2 that the fabric treated with PA in formulation shows excellent flame retardancy to other samples. The burning length of C2 is 3 inches. The fixation percentage of FR on the fabric increased when PA used as a catalyst.

Previous research has shown that it is possible to add TiO_2 as a co-catalyst. [16]. TiO_2 was added in the formulation to increase flame retardancy of fabric. It was reported in the literature that TiO_2 as a co-catalyst reduces the flammability of cellulosic fabric [5]. The char length of fabric is increased when TiO_2 is increased from 0% to 1%. In the C3 sample, TiO_2 inhibits the propagation of flame and PA increases flame retardancy. The flame-retardant test was satisfactory for the specimen that was cured at a temperature from 150°C to 180°C.

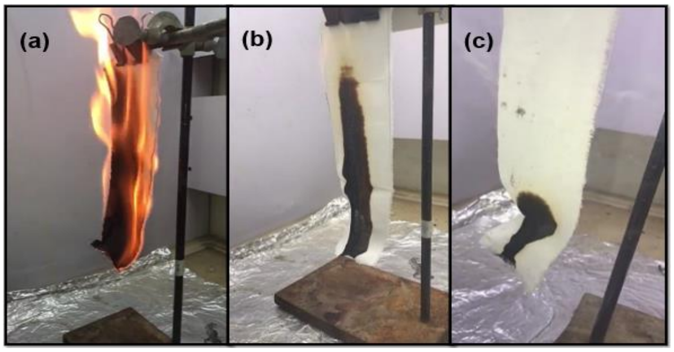

Fig. 2. Selected sample after flammability test (a) Untreated (b) With CA, SHP and TiO2 (c) With CA, SHP and PA

However, the effect was less after the neutralization process since the quantity of TiO_2 is decreased after neutralizing the propagation of flame. By adding TiO_2 into the formulations the fabrics flame-retardancy is improved. Previous studies have shown that adding TiO_2 as a co-catalyst can improve fabric properties [15].

Table 3

Tensile strength results

Sample No	Tensile strength(N) warp direction	Tensile strength(N) weft direction	Elongation at break(%) Warp direction	Elongation at break(%) Weft direction
UT	380.8	230.5	15.91	9.9
C1	350.5	222	3.72	2.62
C2	221.5	142.4	4.68	4.59
C3	288.8	156.16	4.01	3.39
C4	325	206.8	3.77	4.22

4.2 Mechanical Properties of Coated Fabric

Tensile strength of treated cotton was measured to evaluate the impact of treatment on cotton fabric; the results are given in Table 3. The result showed that the strength of the treated sample has decreased their strength. The tensile strengths of untreated fabric in warp and weft direction are 380.8 N and 230.5 N respectively. The elongations at a break in warp and weft directions are 15.91% and 9.9 %. It can be seen from Table 3 that sample C1 without any catalyst shows a slight reduction in the strength than untreated. Sample C2 shows considerably lower tensile strength and elongation than another treated sample. The reason for a reduction in strength is the acidic condition due to the presence of PA. Cotton fiber gets damaged by hydrolysis reaction that breaks down the cellulosic chain [8]. The application of the flame-retardant was enhanced by PA. Acid-catalyzed depolymerization causes permanent tenderizing and damage to cotton fibers by breaking down the cellulose chains. [16, 17]. C4 also shows a less serious change in by a change in the efficiency of the cross-linking reaction. TiO2 might increase the cross-linking reaction as a co-catalyst to enhance crosslinking performance. TiO2 helps to minimize the reduction in tensile strength because yarn friction is increased by surface-attached TiO2 particles, and it promotes the function of the crosslinked polymeric network by cross-linker between FR and cotton fabric. C3 with both PA and CA shows the average value of tensile strength as the PA decreases the strength but due to the use of TiO2 the strength is it considerably lower.

The angle of crease recovery of the untreated sample was evaluated as 51◦. It can be observed from Fig.4 that all treated samples have a good crease recovery angle because CA makes the supple polymeric film on the surface of the fabric [18]. It was discussed in the previous literature that all the polycarboxylic acids provide the formaldehyde-free crease-resistance finish [14]. C1 and C4 show better crease recovery as compared to C2 and C3, the main reason is the absence of PA. In the formulation, because PA makes the fabric stiff when cured at high temperature whereas C2 and C3 have some quantity of PA in the recipe, therefore, they have less crease recovery.

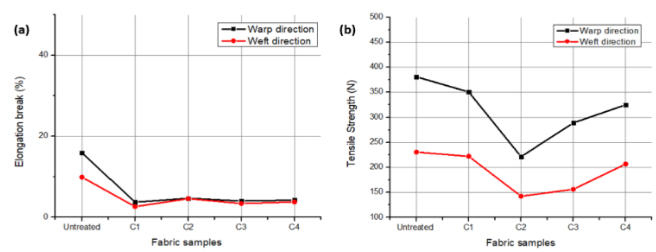

Fig. 3. Graphical representation of **(a)** Elongation break **(b)** Tensile strength of samples

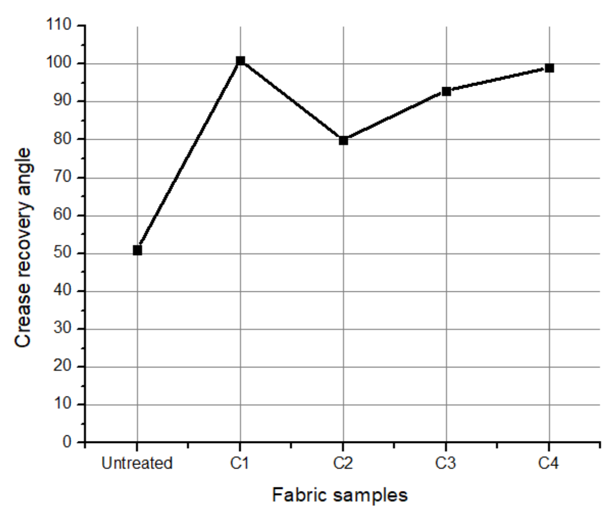

Fig. 4. Graphical representation of crease recovery angle

4.3 Whiteness Index

The whiteness index is referred to as the whiteness of textile fabric which denotes the characteristic of color perception by which color is being judged to approach the preferred white. It was discussed in the former literature that CA reports yellowness in the treated fabric [18]. The loss in whiteness may be attributed to the high temperature of curing and the acidic pH of the finishing solution. The whiteness index for the untreated sample is noted as 49. It can be observed from Fig.5 that samples treated with both catalysts improve the whiteness of the fabric as compared to other recipes without a catalyst. The cause of it is the presence of TiO_2 in the formulation. It was also reported that TiO_2 increases some whiteness of the fabric [8]. The white material enhances the effectiveness of the thermal and flame retardant insulation and secures the inner matrix elements. [19].

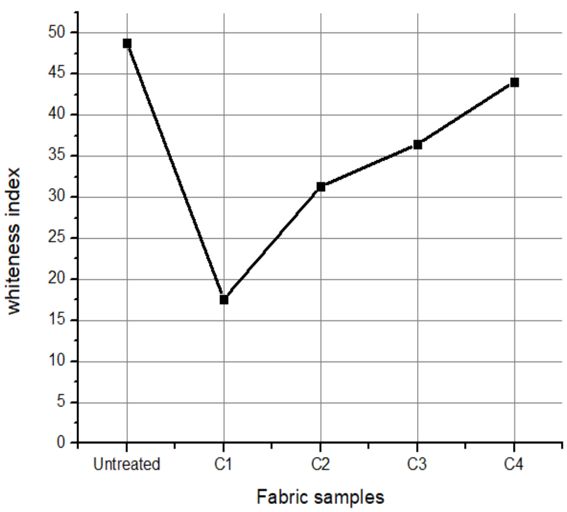

Fig. 2. Graphical representation of assessment of whiteness

5. Conclusion

This work was carried out to inspect the consequences of a cross-linker and catalyst on the flame-retardant performance of the cotton fabric. C2 sample shows the excellent flame its burning length is 3inch and burning time is more retardancy as compared to other treated samples. By the addition of TiO_2 with PA in the C3 sample, the char length and flame propagation are reduced. Sample C2 shows a considerably lower tensile strength than other treated samples due to the presence of PA it degrades the polymeric structure of cotton but C3 and C4 sample strength are more than C2 due to the presence of TiO_2. The whiteness of samples is affected by the high temperature of curing and the acidic pH of the finishing solution. The whiteness of the C4 sample is more than other treated samples due to the presence of TiO_2. It enhances the effectiveness of the thermal insulation and flame retardant, and it secures the inner matrix elements. C1 and C4 show better crease recovery as compared to C2 and C3 the main reason is the absence of PA. In the formulation, because PA makes the fabric stiff when cured at high temperature whereas C2 and C3 have some quantity of PA in a recipe, therefore, they have less crease recovery.

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