

DEVELOPMENT OF SUSTAINABLE FLAME RETARDANTS FOR COTTON FABRICS BY POLYMERIZATION OF TRIMETHYL PHOSPHATE WITH SUCCINIC ACID, UREA AND GLYOXAL

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This paper evaluates two sets of sustainable flame retardant recipes for cotton fabrics through polymerization of trimethyl phosphate (TMP) with succinic acid, urea and glyoxal. In the first set of recipes, succinic acid and TMP were polymerized. In the second set, urea and glyoxal were polymerized with TMP. For these recipes, the effects of temperature, initiator, and catalyst were studied under normal atmosphere, nitrogen atmosphere, and inert atmosphere. The developed recipes were applied on cotton fabric samples and evaluated in terms of char-length and char-width. Based on char-length and char-width, selected samples were tested regarding limiting oxygen index, crease recovery angle, air permeability, shrinkage, smoldering cigarette test, phosphorus concentration, formaldehyde content, antimicrobial testing, energy dispersive X-ray spectroscopy (EDX) analysis and scanning electron microscopy (SEM) analysis. The performance of the new recipes was evaluated against the formaldehyde based commercial recipes, involving Pyrovatex. The research identified two optimum recipes to be used under nitrogen atmosphere. The optimized recipe of TMP, urea and glyoxal exhibited better results than the Pyrovatex based recipes.

Keywords: hazardous chemicals, flame retardant, phosphorus, nitrogen atmosphere, char length, textile finishing

INTRODUCTION

Many social organizations have started customer awareness movements around the world. For instance, Greenpeace's Detox campaign is encouraging famous global textile brands to ensure the elimination of hazardous chemicals from the textile production and final products in their supply chain networks.¹ Consequently, the top textile brands are redesigning their supply chains due to the increased concerns about hazardous chemicals. Hence, the top brands will ultimately exclude all the unsustainable suppliers.² The textile industry involves the consumption of numerous chemicals around the world. Flame retardants are one of the major chemical finishes used in the textile materials. Cotton fabrics have many attractive properties and numerous applications. Unfortunately, they are highly flammable, which may increase the probability of horrible fire incidences.³⁻⁴ All these issues have triggered the

scientific community to develop new environment-friendly flame retardants for cotton fabrics. Most of the existing commercial flame retardants involve the usage or discharge of toxic substances, such as halogens, formaldehyde, and dicyandiamide.

Halogen based flame retardants have been restricted in many countries. Still, several papers have developed halogenated flame retardants due to their effectiveness. For instance, Abou-Okeil *et al.*⁵ developed a halogen based flame retardant using phosphorusoxychloride, which was comparable to Pyrovatex based commercial flame retardants. Due to the restriction of halogenated substances in many countries, the textile industry has successfully adopted many phosphorus based durable flame retardants, such as n-methylol dimethylphosphonopropionamide (commercially known as Pyrovatex). Pyrovatex based flame retardants use or release formaldehyde during

application or consumer use. Formaldehyde is a toxic substance, causing many health issues, including cancer.⁶ In addition to the halogenated and phosphorus based flame retardants, several emerging technologies, such as nanotechnology and bio-macromolecules, have offered ecofriendly alternatives. Nanotechnology based flame retardants involve several issues, such as durability and toxic nanoparticles.⁷ The use of bio-macromolecules (*e.g.* plant based and protein based) also has many disadvantages, such as lower char-length,⁸ unacceptable LOI,⁹⁻¹⁰ lower durability, poor washing fastness, high cost, and limited sources for bulk production.¹¹ Such issues related to the flame retardants based on the nanotechnology and bio-macromolecules restrict their acceptance by the textile industry.

The development or modification of phosphorus based flame retardants is the current focus of the scientific community. Unfortunately, toxic substances, such as formaldehyde and dicyandiamide, have been used in the production or application of several phosphorus based flame retardants. For instance, Zheng *et al.*¹² and Zhang *et al.*¹³ used formaldehyde during the production of phosphorus based flame retardants. The formaldehyde release can be reduced using butane tetra carboxylic acid, but this substance has several issues, such as low tensile strength, and very high cost.¹⁴ Many papers described the development of formaldehyde-free flame retardants. Wang *et al.*¹¹ developed a phosphorus based flame retardant without the use of formaldehyde. However, toxic dicyandiamide was used as a catalyst. They reported the release of ammonia during the application. Zheng *et al.*¹⁵ developed a phosphorus based flame retardant without the use of formaldehyde. They used methylene phosphonic acid, urea, ethanol and dicyandiamide. Lu *et al.*¹⁶ developed formaldehyde free phosphorus based flame retardant using diphosphonic acid, hydroxyethylidene, and ethanol, while dicyandiamide was used as catalyst. Jia *et al.*¹⁷ developed a phosphorus based flame retardant using pentaerythritol, phosphoric acid, ethanol, urea and dicyandiamide. Lu *et al.*¹⁸ developed a phosphorus based durable flame retardant using urea, ammonium polyphosphate and dicyandiamide as a catalyst. From the literature review, it can be concluded that most of the efficient flame retardants involve toxic substances, such as halogens, formaldehyde, and dicyandiamide.

Trimethyl phosphate is a phosphorus based, halogen free, and formaldehyde free flame retarding agent, which has been reported as an effective flame retarding agent. Chung *et al.*¹⁹ studied the flame retardant properties of polyurethane using TMP. They used TMP for the degradation of polyurethane and indicated that the degraded product was changed to phosphorus containing oligourethanes. Tsunekawa *et al.*²⁰ used TMP to improve the conductivity of lithium-ion batteries. Wang *et al.*²¹ used TMP to decrease the flammability of lithium-ion batteries. In addition, TMP has been used as fire retardant in plastics manufacturing.²² MacDonald *et al.*²³ used TMP as flame retardant and concluded that the TMP is a good alternative to halogenated flame retardants. Hence, TMP can be used as an effective ingredient in flame retardant recipes, if its performance can be enhanced for cotton fabric.

Typically, crosslinkers are used to enhance the durability and certain other performance properties of cotton fabric. Nevertheless, most of the cross-linkers reported in the literature are toxic and contain formaldehyde. However, succinic acid is a bio-based formaldehyde free alternative finishing agent for cotton fabrics.²⁴⁻²⁵ Chen and Wang²⁶ used succinic acid as crosslinking agent for cotton cellulose using nano titanium dioxide as a catalyst and achieved an effective crosslinking reaction between succinic acid and cellulose. Several studies also reported the use of glyoxal as a formaldehyde free crosslinker for cotton fabrics.²⁷⁻²⁸ Lee and Kim²⁸ treated cotton fabrics with a glyoxal-glycol mixture as a formaldehyde free durable press finish by the pad-dry-cure method and indicated improved whiteness, good strength retention, and good wrinkle recovery angle. Fouda *et al.*²⁹ treated cotton fabric with glyoxal and indicated good tensile strength and antibacterial activity in the presence of chitosan. Glyoxal has many advantages, such as wide availability, low cost, good functionality, and good solubility in water.³⁰ Kittinaovarat *et al.*³⁰ treated fabric with glyoxal and indicated better durable press performance and antibacterial ability than those of fabric treated with chitosan. The reaction between glyoxal and urea makes DHEU (dihydroxy ethylene urea), which reacts with formaldehyde to make dimethylol dihydroxy ethylene urea (DMDHEU). DMDHEU and its modified products are the most widely used resins in the textile industry.²³ However, they release carcinogenic formaldehyde, which is a great

concern for brands and consumers. This paper uses potassium persulfate as initiator. Choi³¹ used potassium persulfate as a free radical initiator for the polymerization of a formaldehyde free durable press finish for cotton fabrics. They indicated good properties. El-Shafei *et al.*³² used potassium persulfate as a free radical initiator to polymerize the chitosan and butyl acrylate for cotton fabrics.

This paper uses TMP with two sets of recipes. Succinic acid was polymerized with TMP and potassium persulfate in the first set of recipes, while the urea-glyoxal mixture was polymerized with TMP in the second set of recipes under various conditions. The performance of the proposed flame retardant recipes was compared against the Pyrovatex based flame retardant recipes.

EXPERIMENTAL

In this research, 100% bleached cotton fabric samples were used in all the recipes. The bleached cotton fabric was purchased from Kamal Textile Faisalabad, Pakistan. The proposed new recipes used trimethyl phosphate (TMP) as halogen free flame retarding agent, sodium hypophosphite (SHP) as catalyst for succinic acid recipes, succinic acid (SA), urea (U), and glyoxal (G) as formaldehyde free crosslinkers, potassium persulfate (PPS) as initiator, and acetic acid and sodium bicarbonate to adjust pH. All these chemicals for the proposed new recipes were purchased from Sigma Aldrich. All the chemicals were laboratory grade and were used as received without any purification. For comparison purpose, the Pyrovatex based commercial recipes used Pyrovatex CP new (PVTX) as commercial flame retardant obtained from Huntsman. Knittex-CHN (CHN) as formaldehyde based catalyst and phosphoric acid (PA) as enhancer were obtained from Huntsman.

The polymerization was performed under normal atmosphere, inert atmosphere, and nitrogen atmosphere. Inert atmosphere means vacuum condition, in which all the air is pumped out. In nitrogen atmosphere, the vacuum is first created by removing all the air and then nitrogen is filled into the flask.

Two separate sets of recipes were developed based on different crosslinkers. In the first set of recipes, the succinic acid was used as crosslinker with TMP (Table 2). In the second set of recipes, the combination of urea and glyoxal was used as crosslinker with TMP (Table 3). Table 2 and Table 3 provide full details about all the recipes developed for the cotton fabric samples. After the polymerization of one hour, the resultant flame retardant recipes were applied on the cotton fabric samples, using the padding process at 80% pick-up. The percentage values for the fire retardant in the tables (1-5) represent fire retardant

concentration in water. After padding, the fabric was dried at 100 °C for three minutes and cured at 180 °C for two minutes. Then, the fabric was washed with 0.5% detergent solution at the 80% pick-up and later dried at 100 °C for three minutes.

Before testing, all the fabric samples were conditioned for 24 hours at 20 °C temperature (T °C) and 65% relative humidity. The polymerization recipes were optimized considering the char-length and char-width that were determined using the vertical burning test (BS 5438 Test 2B). Then, the following tests were performed on some selected recipes: limiting oxygen index (LOI %) (ASTM D2863) by using LOI apparatus (YZS-100A), crease recovery angle in degrees (CRA) (BS EN 22313 test method) by using a Shirley crease recovery tester (SH-149), air permeability retention (%) (ASTM D737) by the air permeability apparatus, model HY0461L, warp-wise shrinkage (%) and weft-wise shrinkage (%) (AATCC test method 135), smoldering cigarette test before and after five washes (minutes) (EN 1021), phosphorus concentration (ppm) (using Olsen's method), formaldehyde content in fabric (ppm), energy dispersive X-ray spectroscopy (EDX) analysis, antimicrobial testing (AATCC 147 test method) and scanning electron microscopy (SEM) analysis (after four minutes of gold coating) performed by using a Seron SEM model AIS1800C, Korea. Fourier transform infrared spectroscopy (FTIR) analysis (32 background scans in the wavelength range from 650 to 4000 cm⁻¹) was performed by using Agilent CARY 630 apparatus. The TGA of samples was performed to record the mass loss during heating from 25 °C to 600 °C, at a heating rate of 10 °C/min. A NETZSCH TG 209F1 Libra (Germany) evolution analyzer was used to perform TGA.

RESULTS AND DISCUSSION

This section summarizes and interprets the results obtained after synthesis and application of the two sets of proposed recipes. The proposed recipes were compared against two commercial recipes involving Pyrovatex CP new and phosphoric acid. Besides, the effect of using only TMP or only a crosslinker (*i.e.* succinic acid, urea, or glyoxal) was tested under different concentrations. When using only TMP or a crosslinker, the fabric samples burned completely (Table 1).

Table 2 summarizes the char-length and char-width for the recipes involving succinic acid and TMP. Under normal atmosphere (Case 1), the catalyst and initiator were not used, and the temperature was different for each recipe. In this case, the samples burned fully for each recipe. In Case 2 to Case 5, the polymerization was performed in nitrogen atmosphere. In Case 2, the

TMP quantity, succinic acid quantity, and the temperatures for all the recipes were kept identical to those in Case 1. In Case 2, the samples burned fully for each recipe. In Case 3, the temperature was kept constant at 75 °C, and the effects of incorporating the catalyst and the initiator were evaluated. It is important to mention here that the catalyst is essential for carboxylic acids, like succinic acid, as reported by other researchers. Similarly, during our fire retardant polymerization, it was also concluded that the catalyst is essential.

In recipe TS11, the catalyst was used, but no initiator. For this recipe, the sample burned fully. Using 0.5% initiator (PPS) provided the best char-length (recipe TS13). This optimum quantity was used in Case 4, which included variable temperatures. In this case, the concentrations of TMP, catalyst, crosslinker, and initiator were the same as in recipe TS13 in Case 3. In Case 4, recipe TS17 provides superior char-length to that of the other recipes with temperatures of 75 °C (recipe TS17 and recipe TS13 are identical). Hence, 75 °C is still the optimum temperature for the best char-length. It may be due to the fact that below 75 °C, like 50 °C or lower, the temperature is too low for the polymerization to start under optimum conditions, and may be at 90 °C or above, certain side reactions occur, which is not desired.

Hence, this optimum temperature was used to evaluate the effects of variable concentrations of different chemicals in the recipes (Case 5). In recipe TS20, when the concentration of TMP was kept identical as in the best recipe selected previously and the concentrations of the catalyst, crosslinker, and initiator were decreased. The char-length and char-width were inferior to those of recipe TS17 or TS13. Recipe TS21 is the same as recipe TS17 or TS13. In recipe TS22, the concentrations of the catalyst, crosslinker, and initiator were increased. Still, recipe TS21 (or TS17 or TS13) gave the best char-length and char-width. In recipe TS23, the quantity of TMP was decreased to 50% and the concentrations of other chemicals were the same as in recipe TS21 (or TS17 or TS13). Recipe TS23 gave 16% higher char-length than TS21 (or TS17 or TS13). In recipe TS24, the quantity of TMP was increased to 33% and the concentrations of the other chemicals were the same as in recipe TS21 (or TS17 or TS13). Recipe TS24 gave 1% worse char-length than TS21 (or TS17 or TS13). Hence,

recipe TS21 (or TS17 or TS13) was the best recipe under nitrogen atmosphere.

In Case 6, the polymerization was performed in inert atmosphere. In this atmosphere, all the recipes were kept the same as in Case 4. Under inert atmosphere, the recipe TS27 provided the best char-length. Still, the recipe TS21 (or TS17 or TS13) provided superior char-length and char-width under nitrogen atmosphere to those of recipe TS27 under inert atmosphere. Hence, the nitrogen environment is more favorable in the case of succinic acid.

Table 3 summarizes the char-length and char-width for the recipes involving the polymerization of TMP with urea and glyoxal. Polymerization under each atmosphere with different temperatures and constant pH provided good char-length. However, nitrogen atmosphere provided the best char-length (Case 1 to Case 3, in Table 3). Recipe TGU7 provided the best char-length at 40 °C. This optimum temperature was used to test the effect of variable pH under nitrogen atmosphere (Case 4). Still, recipe TGU7 provided the best char-length. It is important to note that recipe TGU7 and recipe TGU17 are the same. Hence, this recipe provided the optimum values for pH during polymerization, as well as during application on the cotton samples. In Case 4, the sample burned fully at other pH values. In Case 5, the concentrations of TMP, urea, and glyoxal were changed under the nitrogen atmosphere and optimum temperature. Still, recipe TGU7 (or TGU17 or TGU23) provided the best char-length. Hence, the nitrogen atmosphere provided the best recipe.

For the first set of recipes involving polymerization of TMP with succinic acid, the best selected recipe was TS21 (or TS17 or TS13). For the second set of recipes involving polymerization of TMP with urea and glyoxal, the best selected recipe was TGU23 (or TGU7 or TGU17). Both selected recipes provided an acceptable char-length. It can be observed that the best recipe with urea and glyoxal provided 61% superior char-length to that of the best recipe with succinic acid. It can be noted that one more recipe with urea and glyoxal (TGU2) under normal atmosphere provided 36% superior char-length and 41% superior char-width to those of the best recipe with succinic acid.

Table 1
 Char-length and char-width corresponding to recipes with Pyrovatex, TMP, urea, and glyoxal

Recipe	Flame retardant	Catalyst	Crosslinker	Polymerization temperature (°C)	Initiator	Weight add-on (%)	Char-length (mm)	Char-width (mm)
PVTX1	20% PVTX	1.5% CHN	2.5% PA	-	-	9.3	98±0.2	32±0.1
PVTX2	40% PVTX	2.2% CHN	6% PA	-	-	9.4	64±0.1	28±0.1
TMP1	5% TMP	-	-	-	-	9.1	Fully burned	Fully burned
TMP2	10% TMP	-	-	-	-	9.2	Fully burned	Fully burned
TMP3	20% TMP	-	-	-	-	9.4	Fully burned	Fully burned
TMP4	40% TMP	-	-	-	-	9.4	Fully burned	Fully burned
SA1	-	-	5% SA	-	-	9.1	Fully burned	Fully burned
SA2	-	-	10% SA	-	-	9.2	Fully burned	Fully burned
SA3	-	-	15% SA	-	-	9.4	Fully burned	Fully burned
Urea1	-	-	5% urea	-	-	9.1	Fully burned	Fully burned
Urea2	-	-	10% urea	-	-	9.3	Fully burned	Fully burned
Urea3	-	-	15% urea	-	-	9.2	Fully burned	Fully burned
Glyoxal 1	-	-	5% glyoxal	-	-	9.1	Fully burned	Fully burned
Glyoxal 2	-	-	10% glyoxal	-	-	9.4	Fully burned	Fully burned
Glyoxal 3	-	-	15% glyoxal	-	-	9.4	Fully burned	Fully burned

Table 2
Char-length and char-width corresponding to recipes with TMP and succinic acid

Recipe	Flame retardant	Catalyst	Cross-linker	T (°C)	Initiator	Weight add-on (%)	Char-length (mm)	Char-width (mm)
Case 1. Polymerization under normal atmosphere, at different temperatures, with no catalyst/initiator								
TS1	10% TMP	-	10% SA	25	-	9.3	Fully burned	Fully burned
TS2	10% TMP	-	10% SA	50	-	9.1	Fully burned	Fully burned
TS3	10% TMP	-	10% SA	75	-	9.2	Fully burned	Fully burned
TS4	10% TMP	-	10% SA	90	-	9.1	Fully burned	Fully burned
TS5	10% TMP	-	10% SA	100	-	9.2	Fully burned	Fully burned
Case 2. Polymerization under nitrogen atmosphere, at different temperatures, with no catalyst/initiator								
TS6	10% TMP	-	10% SA	25	-	9.2	Fully burned	Fully burned
TS7	10% TMP	-	10% SA	50	-	9.4	Fully burned	Fully burned
TS8	10% TMP	-	10% SA	75	-	9.4	Fully burned	Fully burned
TS9	10% TMP	-	10% SA	90	-	9.1	Fully burned	Fully burned
TS10	10% TMP	-	10% SA	100	-	9.3	Fully burned	Fully burned
Case 3. Polymerization under nitrogen atmosphere, at optimum temperature, with catalyst and initiator								
TS11	10% TMP	8% SHP	10% SA	75	-	9.1	Fully burned	Fully burned
TS12	10% TMP	8% SHP	10% SA	75	0.4% PPS	9.4	83±0.5	29±0.4
TS13	10% TMP	8% SHP	10% SA	75	0.5% PPS	9.2	76±0.3	27±0.1
TS14	10% TMP	8% SHP	10% SA	75	0.6% PPS	9.4	81±0.4	31±0.5
Case 4. Polymerization under nitrogen atmosphere, at different temperatures, with catalyst and initiator								
TS15	10% TMP	8% SHP	10% SA	25	0.5% PPS	9.2	105±0.4	49±0.3
TS16	10% TMP	8% SHP	10% SA	50	0.5% PPS	9.1	88±0.7	41±0.6
TS17	10% TMP	8% SHP	10% SA	75	0.5% PPS	9.2	76±0.3	27±0.1
TS18	10% TMP	8% SHP	10% SA	90	0.5% PPS	9.3	84±0.9	29±0.6
TS19	10% TMP	8% SHP	10% SA	100	0.5% PPS	9.3	89±0.4	29±0.3
Case 5. Polymerization under nitrogen atmosphere, at optimum temperature and different concentrations								
TS20	10% TMP	4% SHP	5% SA	75	0.25% PPS	9.4	79±0.8	28±0.6
TS21	10% TMP	8% SHP	10% SA	75	0.50% PPS	9.2	76±0.3	27±0.1
TS22	10% TMP	12% SHP	15% SA	75	0.75% PPS	9.3	78±0.9	27±0.7
TS23	5% TMP	8% SHP	10% SA	75	0.50% PPS	9.3	91±0.1	37±0.7
TS24	15% TMP	8% SHP	10% SA	75	0.50% PPS	9.3	77±0.3	27±0.6
Case 6. Polymerization under inert (vacuum) atmosphere, at different temperatures, with catalyst and initiator								
TS25	10% TMP	8% SHP	10% SA	25	0.5% PPS	9.2	114±0.3	53±0.8
TS26	10% TMP	8% SHP	10% SA	50	0.5% PPS	9.3	116±0.4	56±0.5
TS27	10% TMP	8% SHP	10% SA	75	0.5% PPS	9.1	105±0.4	31±0.5
TS28	10% TMP	8% SHP	10% SA	90	0.5% PPS	9.4	119±0.5	36±0.6
TS29	10% TMP	8% SHP	10% SA	100	0.5% PPS	9.4	118±0.6	41±0.4

It may be due to the fact that succinic acid is a dicarboxylic acid and definitely will be less effective than a tricarboxylic acid, like citric acid, while DHEU has the capability of forming efficient ether linkages.

The pH plays an important role in polymerization, therefore, it was evaluated in Case 4. Typically, DHEU synthesis and polymerization reactions are carried out under alkaline conditions. In this paper, when polymerization was carried out under acidic conditions (TGU18 and TGU19), the treated cotton fabric samples burned completely. Usually, crosslinkers are applied onto cotton fabric under acidic conditions. In this paper, when the application pH was changed to alkaline conditions

(TGU16 and TGU19), the treated fabric burned completely. Hence, recipe TS21 (or TS17 or TS13) and recipe TGU23 (or TGU7 or TGU17) were selected for further testing. Table 4 summarizes the results of the tests performed on these specific recipes.

Limiting oxygen index (LOI)

It can be observed that, when only a single crosslinker or TMP was used, the LOI value was too low. The fabric samples treated with Pyrovatex provided good LOI (recipes PVTX1 and PVTX2). However, the LOIs for recipe TGU23 (with urea and glyoxal) and recipe TS21 (with succinic acid) were comparable with that of the 40% Pyrovatex based recipe, as demonstrated

by the char-length and char-width results as well. The Pyrovatex based recipe with lower concentration (20%) performed inferior to the proposed recipes. Hence, the proposed recipes provide the best alternatives to the formaldehyde based Pyrovatex.

Smoldering cigarette test

The recipe involving only a single crosslinker or TMP, or 20% Pyrovatex (PVTX1), showed less performance in the smoldering cigarette test, compared with recipe PVTX2 (with 40% Pyrovatex), recipe TGU23 (with urea and glyoxal) and recipe TS21 (with succinic acid).

Therefore, this test result is also in line with the char-length and LOI tests.

Before washing, recipe TGU23 (with urea and glyoxal) and recipe TS21 (with succinic acid) showed flame-resistance comparable to that of the recipe having 40% Pyrovatex and superior to that of the 20% Pyrovatex based recipe. After five washing cycles, the Pyrovatex based fabric showed 1% decrease in flame resistance, while recipe TGU23 (with urea and glyoxal) and recipe TS21 (with succinic acid) showed a more significant decrease in flame resistance, related to the smoldering cigarette test. Recipe TGU23 (with urea and glyoxal) showed better flame resistance than recipe TS21 (with succinic acid).

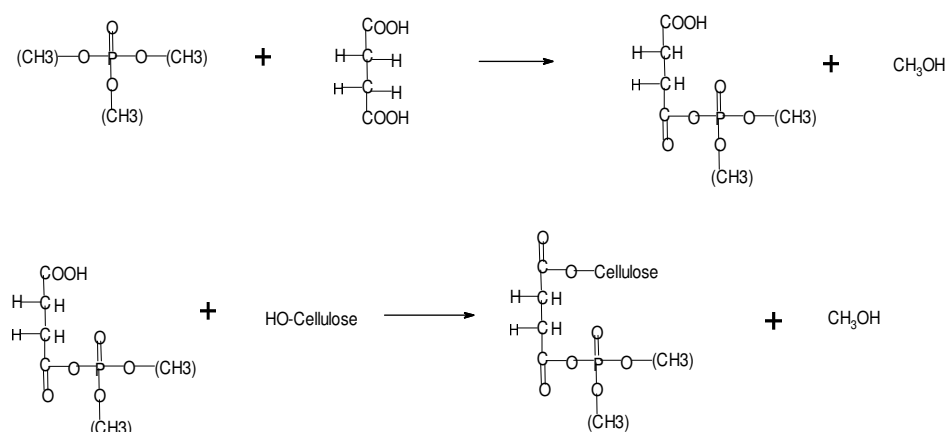


Figure 1: Reaction mechanism of TMP and succinic acid with cotton

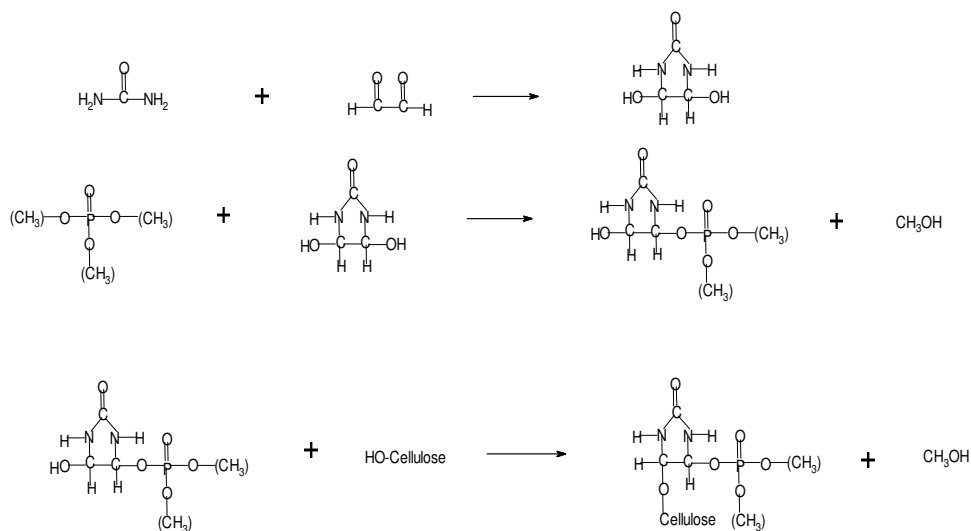


Figure 2: Reaction mechanism of TMP, urea and glyoxal with cellulose

Table 3
Char-length and char-width corresponding to recipes with TMP, urea, and glyoxal

Recipe	Flame retardant	Crosslinker	pH during polymerization	pH during application	T (°C)	Weight add-on (%)	Char-length (mm)	Char-width (mm)
Case 1. Polymerization with normal atmosphere, different temperatures, and constant pH								
TGU1	10% TMP		9.5	4.5	30	9.2	115±0.5	19±0.7
TGU2	10% TMP		9.5	4.5	40	9.4	49±0.5	16±0.2
TGU3	10% TMP	10% urea, 10% glyoxal	9.5	4.5	60	9.1	129±0.2	34±0.5
TGU4	10% TMP		9.5	4.5	80	9.1	96±0.1	31±0.6
TGU5	10% TMP		9.5	4.5	90	9.3	69±0.8	19±0.7
Case 2. Polymerization with nitrogen atmosphere, different temperatures, and constant pH								
TGU6	10% TMP		9.5	4.5	30	9.1	79±0.6	19±0.5
TGU7	10% TMP		9.5	4.5	40	9.3	30±0.1	36±0.4
TGU8	10% TMP	10% urea, 10% glyoxal	9.5	4.5	60	9.2	99±0.9	18±0.8
TGU9	10% TMP		9.5	4.5	80	9.2	71±0.5	33±0.5
TGU10	10% TMP		9.5	4.5	90	9.3	75±0.4	36±0.7
Case 3. Polymerization with inert (vacuum) atmosphere, different temperatures, and constant pH								
TGU11	10% TMP		9.5	4.5	30	9.2	140±0.8	35±0.3
TGU12	10% TMP		9.5	4.5	40	9.3	59±0.5	39±0.3
TGU13	10% TMP	10% urea, 10% glyoxal	9.5	4.5	60	9.1	93±0.6	36±0.4
TGU14	10% TMP		9.5	4.5	80	9.1	125±0.8	20±0.2
TGU15	10% TMP		9.5	4.5	90	9.3	75±0.6	26±0.3
Case 4. Polymerization with nitrogen atmosphere, optimum temperature, and variable pH								
TGU16	10% TMP		9.5	9.5	40	9.1	Fully burned	Fully burned
TGU17	10% TMP		9.5	4.5	40	9.3	30±0.1	36±0.4
TGU18	10% TMP	10% urea, 10% glyoxal	4.5	4.5	40	9.2	Fully burned	Fully burned
TGU19	10% TMP		4.5	9.5	40	9.2	Fully burned	Fully burned
Case 5. Polymerization with nitrogen atmosphere, different concentrations, and optimum temperature								
TGU20	10% TMP	5% urea, 5% glyoxal	9.5	4.5	40	9.4	180±0.5	26±0.6
TGU21	10% TMP	15% urea, 15% glyoxal	9.5	4.5	40	9.2	56±0.4	24±0.7
TGU22	5% TMP		9.5	4.5	40	9.3	56±0.8	24±0.4
TGU23	10% TMP	10% urea, 10% glyoxal	9.5	4.5	40	9.3	30±0.1	36±0.1
TGU24	15% TMP		9.5	4.5	40	9.1	31±0.2	36±0.2

Table 4
Performance of selected fabric samples at fundamental tests

Test	No sample	Control sample	10% succinic acid	10% urea and glyoxal	10% TMP	Recipe PVTX1 (with 20% Pyrovatex)	Recipe PVTX2 (with 40% Pyrovatex)	Recipe TGU23 (with urea and glyoxal)	Recipe TS21 (with succinic acid)
Limiting oxygen index (LOI) (%)	N/A	18.3	18.3	18.4	19.6	27.5	33	33.9	32.8
CRA (degree) crease recovery angle (CRA)	N/A	138	192	171	143	160	170	195	188
Air permeability retention (%)	N/A	100	81	83	87	85.5	69.3	83.8	78
Warp-wise shrinkage (%)	N/A	7.7	1.6	1.3	3.6	3.3	2.8	2.6	2.7
Weft-wise shrinkage (%)	N/A	6.1	1.5	1.3	3.4	3.3	2.8	2.1	2.6
Smoldering cigarette test before washing (minutes)	N/A	10	12	11	12	17	25	27	24
Smoldering cigarette test after washing (minutes)	N/A	10	12	11	12	16	24	16	16
Phosphorus concentration (ppm)	N/A	0	0	0	26276	17689	34344	30955	28987
Formaldehyde content in fabric (ppm)	N/A	0	0	0	0	32	41	0	0

N/A – not applicable or available

Crease recovery angle (CRA)

The recipes containing only a specific crosslinker indicated better CRA than the recipes with the flame-retarding agent (TMP). This indicates that the succinic acid and the urea-glyoxal mixture are effective crosslinkers for cotton, and TMP alone does not contribute to an improved CRA. These results are quite obvious as the main function of crosslinkers is to improve the crease recovery angle. However, using only a specific crosslinker performed worse in terms of other properties (*i.e.* LOI, smoldering cigarette test, char-length, and char-width), which are important for flame-retardancy. Hence, the addition of a crosslinker to the flame-retarding agent enhanced the flame-retardancy and CRA simultaneously. Succinic acid formed ester bonds with TMP and cotton, as shown in Figure 1. It is mainly due to this covalent bonding that the treated fabric's crease recovery is higher than that of untreated cotton fabric. However, in the case of urea and glyoxal, it first forms dihydroxyethylene urea, which then forms ether linkages with TMP and cotton, as exhibited in Figure 2. Therefore, treated cotton fabric (TMP and urea-glyoxal) exhibited superior crease recovery to that of untreated cotton fabric, mainly due to the newly developed ether linkage. Pyrovatex also improved CRA due its covalent bonding with cotton fabric (*i.e.* recipe PVTX1 and recipe PVTX2). However, recipe TGU23 (TMP with urea and glyoxal) and recipe TS21 (TMP with succinic acid) indicated better CRA than the Pyrovatex based recipes.

Air permeability retention

Air permeability retention for the untreated cotton fabric sample was considered the best (100%). Air permeability decreases as the chemical concentration increases because of increased blockage of air passage through the coated fabric. The air permeability retention values of all the selected recipes, except recipe PVTX2, were comparable to each other. One reason that recipe PVTX2 resulted in less air permeability retention is its concentration of chemicals (*i.e.* 40% Pyrovatex, 2.2% CHN catalyst, and 6% phosphoric acid). Recipe TGU23 (TMP with urea and glyoxal) showed 7% higher air permeability than recipe TS21 (TMP with succinic acid).

Shrinkage

The recipes containing only a crosslinker indicated the least shrinkage, and the recipe

containing only TMP (*i.e.* flame-retarding agent) indicated the worse shrinkage. It is quite obvious that the more significant the crosslinking of cotton, the lower will be the shrinkage. Recipes TGU23 (TMP with urea and glyoxal) and recipe TS21 (TMP with succinic acid) indicated considerably less shrinkage than the Pyrovatex based flame retardants (recipes PVTX1 and PVTX2). It is clear that the crosslinkers (*i.e.* succinic acid, urea, glyoxal) decreased the shrinkage in the proposed recipes.

Phosphorus concentration and formaldehyde content in fabric

In the phosphorus based flame retardants, the phosphorus is the key element that improves the flame retardancy. Succinic acid, urea, and glyoxal do not contain any phosphorus. Formaldehyde based recipes (recipes PVTX1 and PVTX2) contain acceptable amount of phosphorus, depending on the quantity of Pyrovatex. For a good flame retardant, 17000 ppm is the recommended quantity of phosphorus. The best formaldehyde-free recipes, TGU23 (with urea and glyoxal) and TS21 (with succinic acid), contain more than the acceptable amount of phosphorus. Concerning the formaldehyde content in the cotton fabric, recipe PVTX1 (with 20% Pyrovatex) indicated 32 ppm formaldehyde and recipe PVTX2 (with 40% Pyrovatex) indicated 41 ppm formaldehyde. In contrast, the best two recipes, TGU23 (with urea and glyoxal) and TS21 (with succinic acid), indicated zero formaldehyde.

Fourier transform infrared spectroscopy (FTIR)

FTIR analysis was also performed on selected seven recipes. For recipe TS21 (Fig. 3c), a prominent ester peak was observed at 1248 cm^{-1} , and P-O-C stretch can easily be detected at $920\text{--}1088\text{ cm}^{-1}$. It can be observed that there is no such peak of the ester for the remaining recipes (Figs. 3 and 4). In addition, for recipe TGU23, a prominent ether peak was observed at 1250 cm^{-1} (Fig. 4d).

TGA analysis

Figure 5 presents the TGA curves of untreated cotton fabric, cotton fabric treated with 10% SA, 10% urea, 10% glyoxal, 10% TMP, recipe TS21 (best recipe of TMP with SA), recipe TGU23 (best recipe of TMP with urea and glyoxal) and 20% Pyrovatex. The untreated cotton fabric (see curve 1), 10% SA treated cotton fabric (curve 2),

10% urea (curve 3) and 10% glyoxal (curve 4) have decomposition temperatures starting at 337 °C. The cotton fabrics treated with the fire retardants have lower decomposition temperature because of the catalytic dehydration of cellulose by the fire retardants. The decomposition temperature of recipe TGU23 treated fabric (306 °C, curve 7) was higher than that corresponding to recipes TS21 (300 °C, curve 6), 20% Pyrovatex (280 °C, curve 8) and TMP 10% (250 °C, curve

5). However, the amount of char formed was higher for recipe TGU23 treated fabric (39.98%, curve 7) than for recipe TS21 (34.98%, curve 6), 20% Pyrovatex (28.79%, curve 8) and 10% TMP (23.56%, curve 5). Overall, recipe TGU23 treated cotton fabric exhibited better thermal stability than that treated with recipe TS21, 20% Pyrovatex and 10% TMP. These results are in line with the best char length and width exhibited by TGU23 treated fabric.

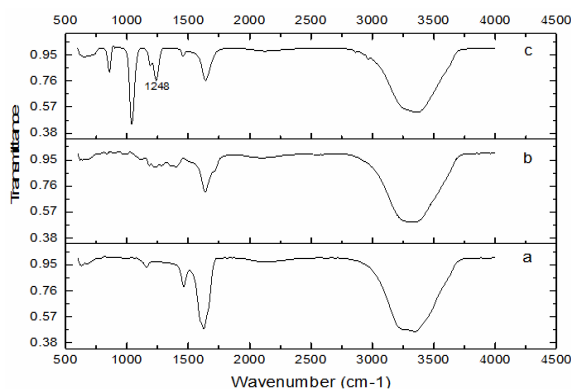


Figure 3: FTIR analysis of samples treated with (a) 10% TMP, (b) 10% SA, (c) recipe TS21

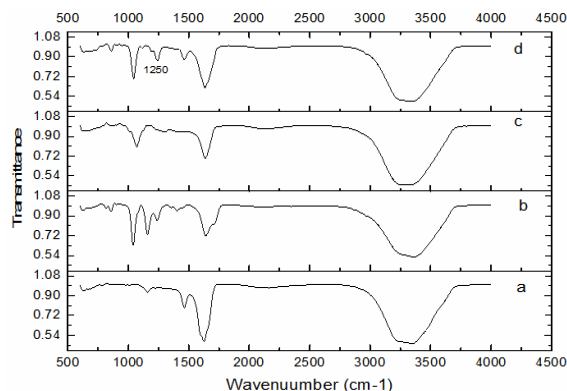


Figure 4: FTIR analysis of samples treated with (a) 10% TMP, (b) 10% urea, (c) 10% glyoxal, (d) TGU23

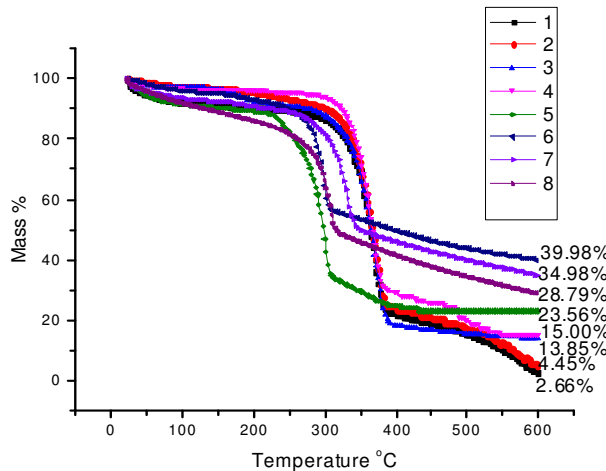


Figure 5: TGA analysis of (1) untreated cotton fabric, and samples treated with (2) 10% SA, (3) 10% urea, (4) 10% glyoxal, (5) 10% TMP, (6) recipe TGU23, (7) recipe TS21, (8) 20% PVTX

Energy dispersive X-ray spectroscopy (EDX) analysis

EDX analysis is used to obtain X-ray spectra of solids. It is a vital technique to identify the elements in the materials. The EDX analysis was performed on seven recipes, as described in Figure 6. It can be observed that there is no peak of phosphorus in the control fabric or in the recipe with a crosslinker (*i.e.* 10% succinic acid, 10%

urea and 10% glyoxal). Hence, using only crosslinker did not impart flame retardancy. In contrast, prominent phosphorus peaks can be observed when using only TMP and for the best recipes TS21 (with succinic acid) and TGU23 (with urea and glyoxal). Hence, EDX analysis confirmed the presence of phosphorus in the proposed flame retardant recipes. Recipe TGU23 (with urea and glyoxal) showed higher

phosphorus of 23.32%, which is responsible for its superior fire retardancy as well.

SEM analysis

SEM analysis was performed on three selected samples, specifically, untreated cotton, the sample

treated with recipe TS21 (the best recipe using TMP and succinic acid) and the fabric treated with TGU23 (the best recipe using TMP with urea and glyoxal). It can be observed that the surface of the untreated cotton sample is clear and smooth.

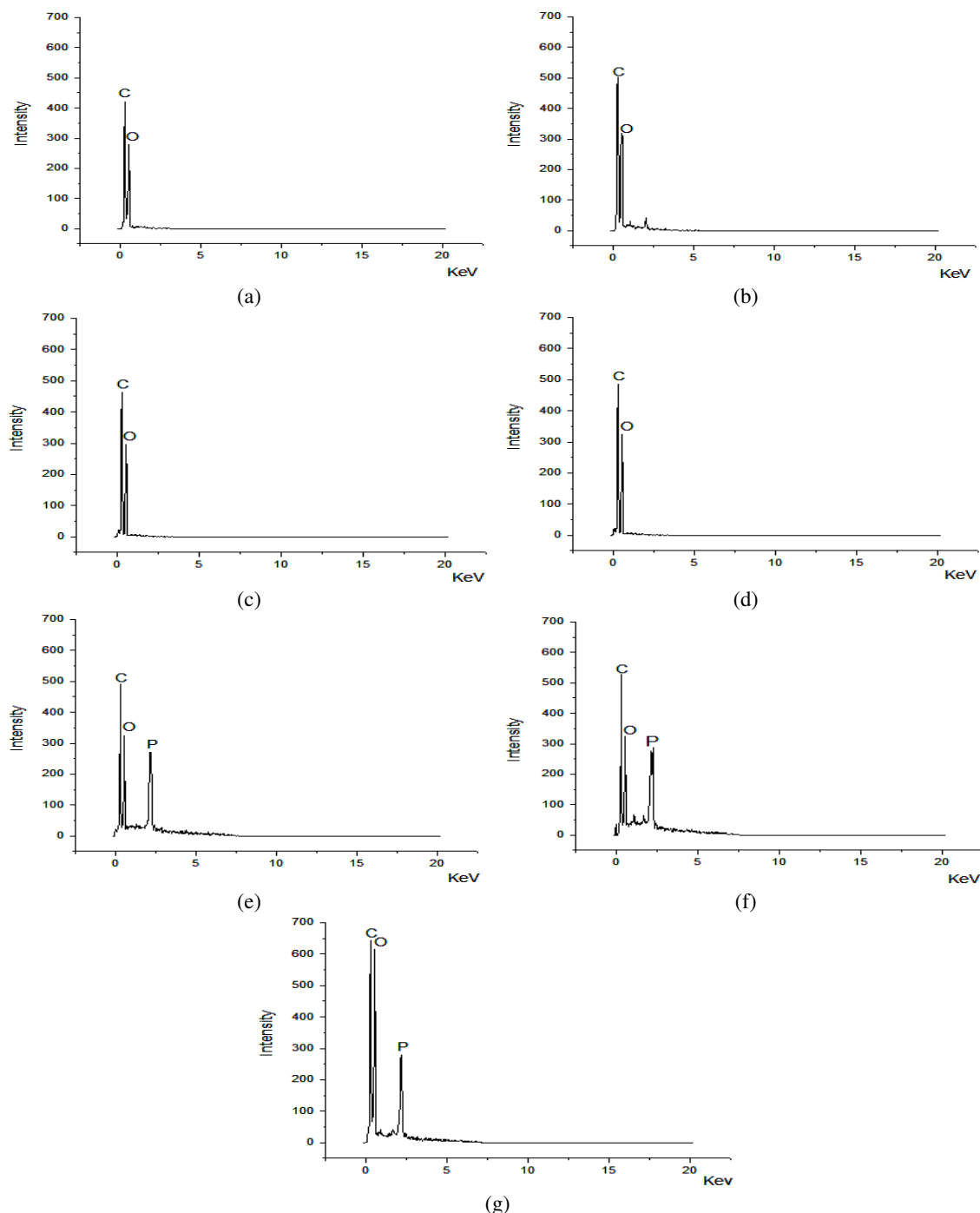


Figure 6: EDX analysis of (a) control fabric, and samples treated with (b) 10% succinic acid, (c) 10% urea, (d) 10% glyoxal, (e) 10% TMP, (f) recipe TS21 (with succinic acid), (g) recipe TGU23 (with urea and glyoxal)

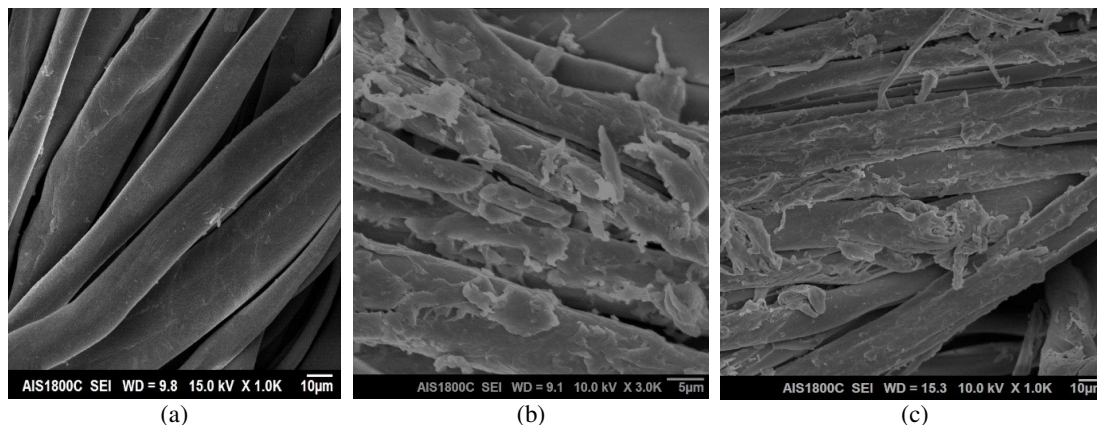


Figure 7: SEM images of (a) untreated cotton fabric sample, and samples treated with (b) recipe TS21 (with succinic acid), (c) recipe TGU23 (with urea and glyoxal)

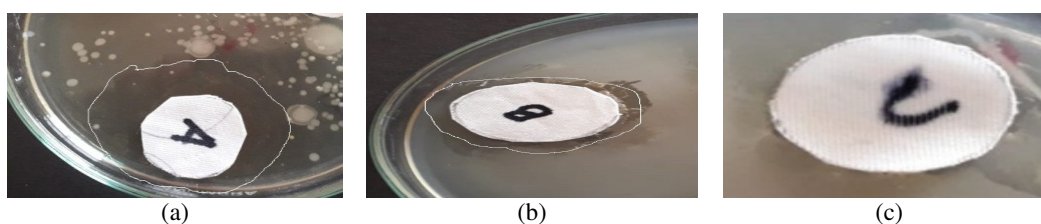


Figure 8: Antimicrobial test of (a) recipe TS21 (with succinic acid), (b) recipe TGU23 (with urea and glyoxal), (c) untreated cotton fabric

However, the surface of the sample treated with the above two best polymerization involving recipes reveals the coating on the fabric, which is evidence that the fire retardant has been successfully applied onto the cotton fabric (Fig. 7).

Antimicrobial performance of finished cotton fabric

The antimicrobial test was performed on the untreated cotton sample, and on samples treated with recipe TS21 (the best recipe using TMP with succinic acid) and TGU23 (the best recipe using TMP with urea and glyoxal). It can be observed that the untreated cotton sample showed no antimicrobial activity, as expected. However, the sample treated with the best recipe using TMP with succinic acid (TS21) exhibited 0.91 mm width of the clear zone of inhibition, and the best recipe using TMP with urea and glyoxal (TGU23) showed 0.34 mm width of the clear zone of inhibition (Fig. 8). Hence, the proposed recipes showed good antimicrobial performance.

CONCLUSION

This research successfully develops two efficient flame retardant recipes, using trimethyl

phosphate (TMP) with bio-based crosslinker succinic acid, as well as TMP with urea-glyoxal under different polymerization atmospheres and conditions. When treated under normal atmosphere and without using catalyst or initiator, the fabric sample was fully burned for each assessed recipe involving succinic acid and TMP. Similarly, when nitrogen atmosphere was used for the treatment, the fabric sample was fully burned for each of the prepared recipes. However, the addition of catalyst (SHP) and initiator (PPS) to the recipes with TMP and succinic acid improved the flame retardancy. The optimum result in the case of succinic acid was obtained when 10% succinic acid was polymerized with 10% TMP, along with catalyst 8% SHP and 0.5% PPS at 75 °C under nitrogen atmosphere. The char-length for this best recipe was higher than that corresponding to the 40% Pyrovatex based recipe and lower than that of the 20% Pyrovatex based recipe. Similarly, in the case of polymerization between TMP, urea, and glyoxal, the best results were obtained under nitrogen atmosphere. The above-mentioned optimized recipes also exhibited improved performance in terms of LOI, shrinkage control, antimicrobial and crease recovery properties. EDX analysis confirmed the presence

of adequate phosphorus amounts in the two best recipes. SEM analysis indicated the successful application of the identified recipes on the fabric samples. Both recipes are non-toxic and formaldehyde free. However, the succinic acid based recipe is more sustainable, as it is a bio-based product. Hence, the proposed recipes provide potential alternatives to the existing hazardous flame retardants for textile materials.

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