Synthesis of a Novel Highly Efficient Flame-Retardant Coating for Cotton Fabrics With Low Combustion Toxicity and Antibacterial Properties

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Research Article

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Posted Date: March 22nd, 2021

DOI: https://doi.org/10.21203/rs.3.rs-315407/v1

Version of Record: A version of this preprint was published at Cellulose on July 15th, 2021. See the published version at https://doi.org/10.1007/s10570-021-04076-2.

Synthesis of a novel highly efficient flame-retardant coating for cotton fabrics with low combustion toxicity and antibacterial properties

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Abstract

Synthesis of multi-function flame retardants is widely increasing to fulfil industrial and economic goals. In this work, a novel flame retardant, melamine salt of tannic phosphate (MTP) was prepared and characterized. MTP was mixed with polyvinyl alcohol (PVA) solution and used as a coating for cotton fabrics. In addition, tannic acid (TA) and melamine phosphate (MP) were mixed with PVA solution and applied as a coating for cotton fabrics. Vertical and horizontal flammability tests showed that the flame did not propagate in samples treated with PVA/MTP. In contrast, samples treated with PVA/TA/MP burnt completely. Limiting oxygen index (LOI) data indicated that samples treated with PVA/30%MTP reached LOI value 68.4%, while control sample had LOI value 17.1%. Smoke density results presented that PVA/MTP succeeded in reducing the maximum specific optical density (Ds_{max}) of cotton fabrics. FTIR gas analyzer results manifested that addition of PVA/MTP to cotton fabrics decreased the emission of CO, CO_2, C_3H_8, C_2H_6, C_6H_{14} and formaldehyde in the gas phase. Fractional effective dose (FED) and lethal toxic potency (LC_{50}) showed that samples coated with PVA/MTP are less toxic than blank. In addition, these fabrics exhibited a remarkable antibacterial property against gram-positive and gram-negative bacteria.

Keywords

Tannic acid, flame retardant, cotton fabric, smoke suppression, mechanical properties, antibacterial properties

1. Introduction

Cotton fabrics are excessively used in applications like clothing and house furniture due to their fabulous properties which includes comfortableness, biodegradability, hydrophilicity and good breathability (Chen et al. 2021; Zhu et al. 2020a). However, cotton fabrics are highly flammable and this problem restricts their industrial applications. For instance, LOI of cotton fabric is in the range 16-18%, which makes fabrics able to combust at ambient conditions (where O_2 in air is 20.95%) (Chen et al. 2020). To overcome this problem, many studies gave great interest to improve the flame retardancy using different kinds of flame retardant materials. As cotton fabric is naturally occurring material, an after finish method is used to improve its flame retardancy (Pan et al. 2015). Halogenated flame retardants such as pentabromodiphenyl ether, decabromodiphenyl ether and (Polychlorinated Biphenyl) showed good flame retardancy characteristics. However, the environmental regulations in many countries restricted their use because these materials manifested harmful effects to human and animals (Van der Veen and De Boer, 2012). Metal hydroxides such as $Al(OH)_3$ and $Mg(OH)_2$ were introduced as alternatives for halogenated flame retardants because they can take in a large amount of heat at high temperatures. But these materials should be added at high concentrations to obtain good flame retardancy action. The high loading levels of these materials deteriorate the mechanical properties (Hu et al. 2020; Zhu et al. 2020b; Laoutid et al. 2009). Intumescent flame retardants (IFRs) were used by many researchers to improve the flame retardancy of cotton fabrics because they are environmentally friendly (halogen free compounds) and produce low amounts of smoke and toxic gases (Wang et al. 2021). Traditional IFRs are consisting of acid source (like phosphoric acid), charring agent (like pentaerythritol) and bellowing agent (such as melamine). The ingredients of IFR system are decomposed during the combustion process of polymer composite to form insulating, cellular and intumescent char layer on polymer surface which protect the polymer from the effect of heat and flame. Moreover, it reduces the evolving of volatile organic compounds to the combustion zone (Wang et al. 2021; Chan et al. 2018; Fang et al. 2015). Recently, much research work was directed to combine the IFRs ingredients in one molecule to reduce the polarity of traditional IFRs and preparing single molecule intumescent flame retardant (SMIFR) (Makhlouf et al. 2020; Yang et al. 2019; Jian et al. 2019). In our previous work we prepared different melamine salts such as melamine salt of montmorillonite phosphate (MMP), melamine salt of pentaerythritol phosphate montmorillonite (MPPM) and melamine salt of chitosan phosphate (MCHP) as SMIFR and it showed good flame retardancy action on polypropylene and polyethylene (Makhlouf et al. 2017a, 2017b; Hassan et al. 2016).

Tannic acid (TA) is one of hydrolyzable tannins, commercial available and has an estimated chemical structure $C_{76}H_{52}O_{46}$. It is composed of inner layer containing glucose ring and outer layers consisting of gallic acid units. TA is used in different industries such as inks, plastic resins, adhesives, surface coatings and dyes. Besides; it is used in water treatment process (Das et al. 2020; Ramakrishnan and Krishnan, 1994). Pantoja-Castro and González-Rodríguez (2011) used the thermogravimetric analysis technique to differentiate between TA and condensed tannins. The authors reported that tannins were decomposed through three decomposition steps meanwhile TA showed five decomposition steps. This was referred to that TA has less complex structure and its bonds may be easily broken to form smaller structures. Also, the char residue at 600 °C was higher in case of condensed tannins due to tannins have more carbon atoms in their chemical structure than TA. Pyrolysis of tannins at 600 °C yields mainly catechol as a peculiar fragment (Nam et al. 2017; Galletti and Reeves,1992). On the other hand, TA produces 1,2- benzene diol and 1,2,3-benzene triol from degradation of the outer layer that containing gallic acid units. The inner layer was characterized by stability to higher temperatures and at temperature >700 °C, it crosslinked to form intumescent carbonaceous char (Nam et al. 2017; Xia et al. 2015). Tributsch and Fiechter (2008) stated that the presence of tannins in the bark of trees makes them naturally fire resistant due to tannins have antioxidant effects and are able to neutralize radicals through their electron donation properties. Therefore, tannins seem to be a new bio based materials that can be used in the development of fire retardant additives (Das et al. 2020; Singh and Kumar, 2020; Nam et al. 2017). Nam et al. (2017) treated cotton fabric with TA and TA/sodium hydroxide solution as IFR. The authors stated that, in one hand, treating cotton samples with 20% TA alone was able to alter the combustion behaviour of cotton. Microscale calorimeter results showed that 20%TA decreased the heat release capacity (HRC) of cotton by 35.8% and increased the char residue from 6.3% to 16.9%. However, TA alone was not sufficient to make improvement in the LOI value of cotton fabric. On the other hand, when treating cotton fabrics with 20%TA/1% sodium hydroxide LOI value increased to 30.2%, and the HRC of control sample was reduced by 81.8% and the char residue was increased to 21.5%. But the durability, mechanical and vertical flammability properties were not studied. According to our literature survey, combining TA as charring agent with other IFR ingredients to prepare SMIFR to impart different functions (such as flame retardancy and antibacterial effects) to cotton fabric was not studied.

Fire toxicity is considered the main reason of death and harm from unexpected fires. In the UK, during the period from 1955 to 2015, there has been a gradual transfer for the reason of

death from burn to toxic gases, and the injuries due to fire toxicity increased greatly (Stec, 2017; Stull, 2008). The exposure to toxic gases (such as CO, CO_2, NO_x, SO_2, acrolein, HCHO, NH_3, HCl and HBr) which are produced from fatal fires drive to set of physiological and behavioural effects. For instance, physical incapacitation and loss of sense of direction can take place when the person is subjected to these gases, and these effects are likely threat life because they can hinder safe escape. In the last decades, chemical analysis (without refuge to experiments on animals) was used to predict the main effects for fire toxicity like incapacitation by quantifying the toxic gases evolved during different fire conditions in small scale tests (Stec, 2017). Fractional Effective Dose (FED) is used in creating toxic potency data using chemical analysis of fire effluents, by taking into account the toxic effects of CO, CO_2, HCl, HBr, NO_x, SO_2, anoxia and other toxic gases. FED is defined as the ratio of the concentration and time product for a toxic gas released in a given test to the concentration and time product of that toxicant that has been statistically defined from distinct experimental data to cause lethality in 50% of test animals during a fixed exposure and post exposure time (Stec, 2017; Chow et al.2020). FED was calculated following to Eq. (1) (ISO 13344: 1996); Chow et al. 2020).

$$\mathrm{FED} = \frac{[\mathrm{CO}]}{[5000]} + \frac{[\mathrm{HCN}]}{150} + \frac{[\mathrm{HCl}]}{3800} + \frac{[\mathrm{HBr}]}{3000} + \frac{[\mathrm{NO}]}{1000} + \frac{[\mathrm{NO_2}]}{200} \qquad \text{Eq. (1)}$$

But this equation was not sufficient to consider the effect of CO_2 concentration on fire toxicity. Therefore, FED calculations were updated (see Eq. 2) by including CO_2 concentration; and the slope (m) and intercept (b) of plotting the curve of [CO] against [CO_2] to describe the growing up of CO toxicity as the [CO_2] increases. In addition, O_2 concentration was included in this update (ISO 13344:2015).

$$\mathrm{FED} = \frac{\mathrm{m}[\mathrm{CO}]}{[\mathrm{CO_2}] - \mathrm{b}} + \frac{21 - [\mathrm{O_2}]}{(21 - 5.4)} + \frac{[\mathrm{HCN}]}{150} + \frac{[\mathrm{HCl}]}{3700} + \frac{[\mathrm{HBr}]}{3000} \qquad \text{Eq. (2)}$$

Besides Eq. (1,2), Purser model in Eq. (3) was applied also to calculate FED where the concentration of each toxic gas was divided by its lethal concentration and multiply the result by V_{CO_2}. Where, V_{CO_2} is a multiplication factor for CO_2-driven hyperventilation, equal to $\{1 + e[(0.14 \,.\, CO_2) - 1]/2\}$ and A is an acidosis factor, equal to $\{[CO_2] \times 0.05\}$.

$$\mathrm{FED} = \left(\frac{[\mathrm{CO}]}{\mathrm{LC_{50.CO}}} + \frac{[\mathrm{HCN}]}{\mathrm{LC_{50.HCN}}} + \frac{[\mathrm{X}]}{\mathrm{LC_{50.X}}} + \frac{[\mathrm{Y}]}{\mathrm{LC_{50.Y}}} \right) \times \mathrm{V_{CO_2}} + \mathrm{A} + \frac{21 - [\mathrm{O_2}]}{(21 - 5.4)} \qquad \text{Eq. (3)}$$

When FED value is equal to 1, the mixture of the toxic gases is cable of causing death to 50% of the animals that inhaled this mixture (Stec, 2017; Chow et al.2020). The fire toxicity of materials can also be presented by lethal concentration 50 (LC_{50}). It is defined as the concentration of fire effluent which able to cause death in 50% of test animals at a defined exposure time. LC_{50} can be calculated based on FED value, mass loss during combustion (ΔM) and the volume of the combustion chamber (V) following to Eq. (4) (Chow et al. 2020).

$$LC_{50} = \frac{\Delta M}{FED.V} \qquad \text{Eq. (4)}$$

Where, M (in g) is the specific mass loss and V (in m^3) is the total air volume at standard temperature and pressure.

The aims behind this work were to combine TA with melamine and phosphoric acid to form a new multifunction single molecule intumescent flame retardant, MTP, for cotton fabrics. In addition, comparing the efficiency of the new SMIFR with other traditional flame-retardant systems that are based on MP and TA. The thermal stability and flammability properties of the different samples were studied by TGA, UL94, LOI, single flame source and smoke box chamber. The toxic gases evolved during combustion process were determined by FTIR gas analyser and fire toxicity of the samples was evaluated based on FED and LC_{50} data. Tensile strength and antibacterial properties of the treated cotton samples were evaluated.

2. Experimental

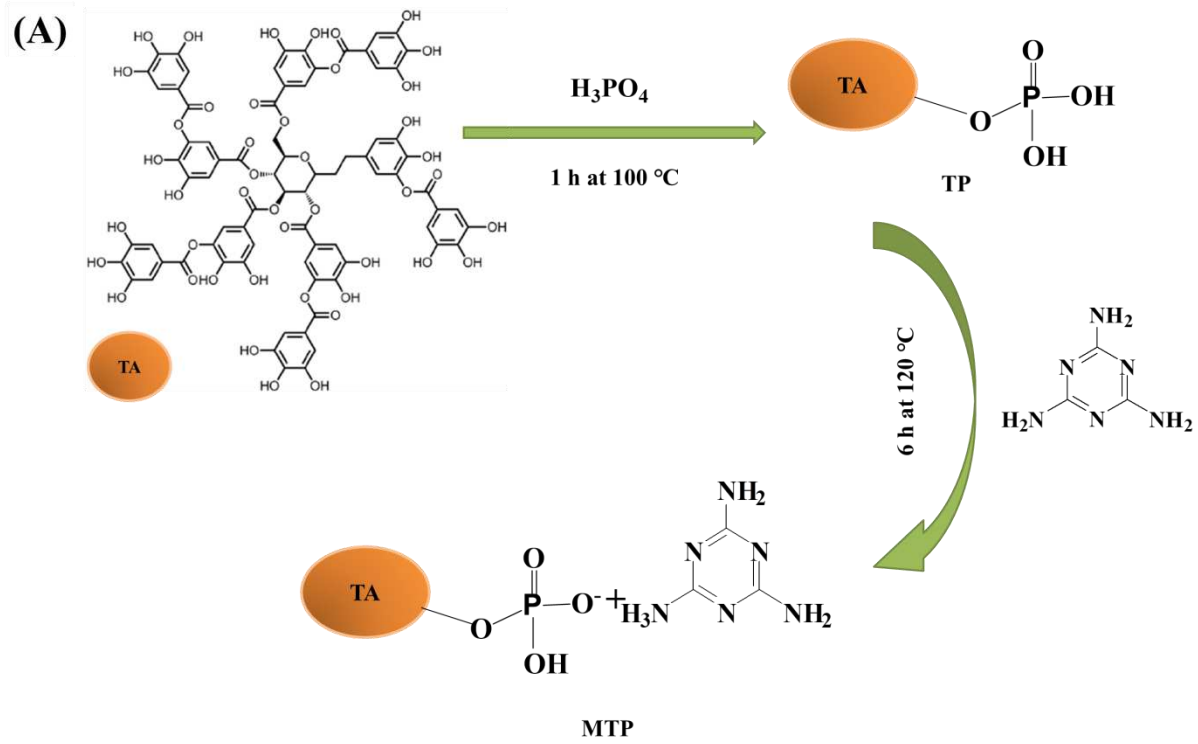
2.1. Materials

Natural cotton fabrics (100%; 120 g/m^2) were supplied by Texmar Company, Egypt. Tannic acid ($C_{76}H_{52}O_{46}$) with M.W 1701.22 g/mol was obtained from S D Fine-Chem Limited, India. Poly (vinyl alcohol) with M.W 115000 g/mol and degree of polymerization 1700 – 1800 was purchased from Oxford Lab Chem, India. Melamine (99%) was purchased from Alfa Aesar Company, Germany. Phosphoric acid (85%) and methanol (99%) were supplied by Sigma-Aldrich Company, Germany. The chemicals were used without further purification. De ionized water was collected from deionized water unit supplied by purite select fusion unit, UK.

2.2. Synthesis of MTP

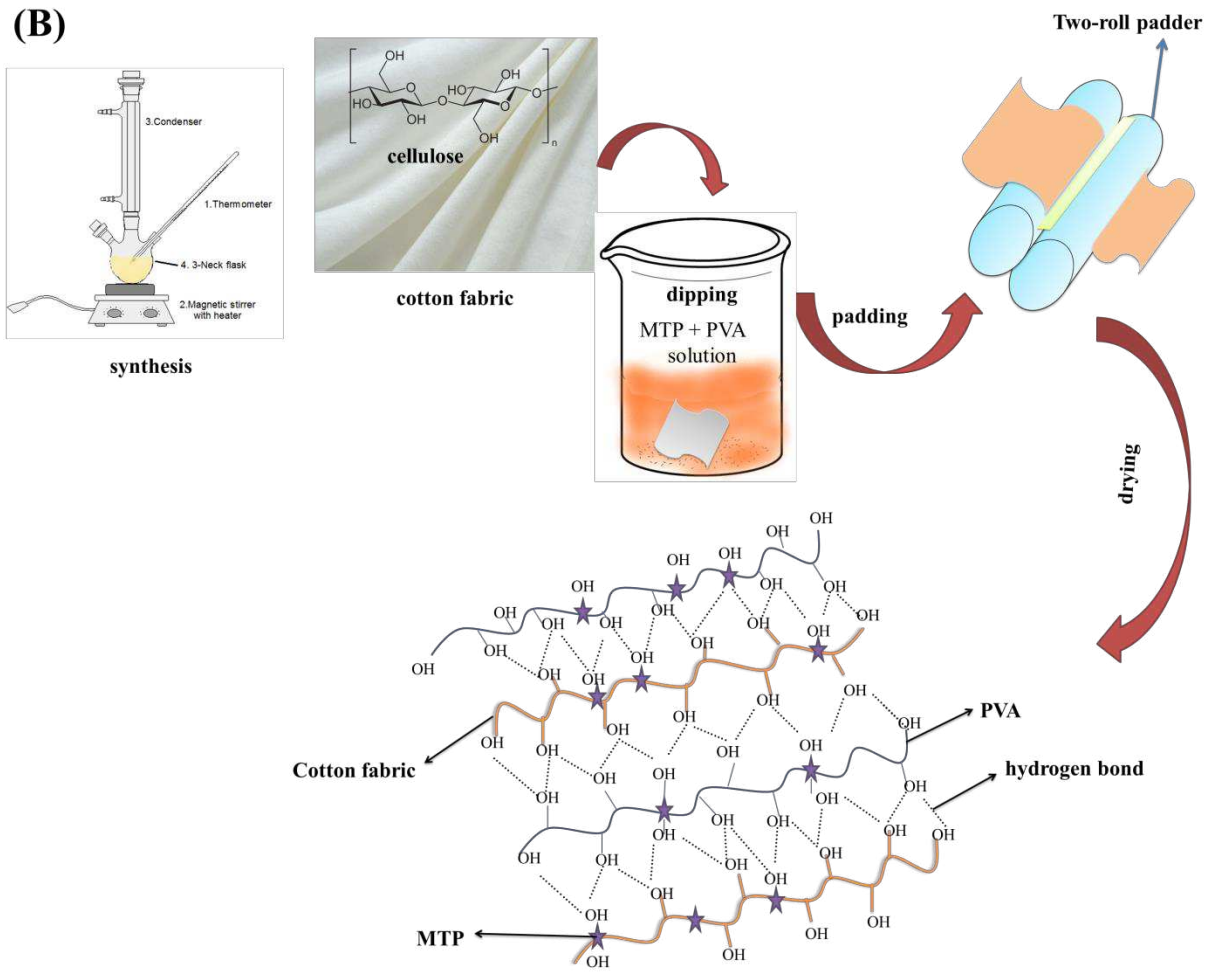
MTP was synthesized by adding 50 g phosphoric acid to 20 g TA to form tannic phosphate (TP) as intermediate. The reactants were stirred on a hot plate with stirrer at 100 ^{O}C and the reaction continued for 1 h till brown solution was obtained. In a round bottom flask with condenser, 30 g of melamine powder was dispersed in 500 mL of methanol. TP solution was added dropwise to melamine (dispersed in methanol) within 30 min, the hotplate temperature

was remained at 120 ^{O}C and the reaction continued for 6 h. The product (MTP) was filtered, washed with methanol, dried at room temperature for 72 h and grinded to fine powder. Fig. 1(A) shows the synthetic route of MTP.


(A)
TA
H_3PO_4
1 h at 100 °C
TP
6 h at 120 °C
MTP

165

166


(B)
3.Condenser
1.Thermometer
4. 3-Neck flask
2.Magnetic stirrer with heater
synthesis
cellulose
cotton fabric
dipping
MTP + PVA solution
padding
Two-roll padder
drying
Cotton fabric
PVA
hydrogen bond
MTP

167

Fig. 1. (A) Schematic illustration of a suggested synthetic route of MTP; (B) the structure of cotton fabric/PVA/MTP prepared by dip-pad-dry method.

2.3. *Preparation of MP*

MP was synthesized according to the procedure in Abdelkhalik et al. (2019). In a round bottom flask linked to condenser, 30 g of melamine was scattered in 250 mL methanol and agitated for 30 min at room temperature using hot plate with stirrer. Then, phosphoric acid (25 g) was added to melamine, the hot plate temperature was regulated at 120 °C and the reaction was kept for 3 h. Finally, MP was obtained, filtered, washed with 500 mL methanol to remove the excess of phosphoric acid and dried for 72 h at room temperature.

2.4. Preparation of flame retardant cotton fabrics

Cotton fabric samples were washed using deionized water and were dried at 60 °C for 1 h before using. Then, the weights of cotton samples with appropriate size were measured and recorded. A beaker containing deionized water and PVA was heated to 150 °C for 30 min using a hot plate with mechanical stirrer at 650 rpm until PVA was dissolved in deionized water. Then, MTP was added into the PVA solution with continuous stirring at 70 °C. PVA/MTP finishing solutions with different MTP concentrations (10%MTP, 20%MTP and 30%MTP) were prepared. The cotton fabric samples were soaked in these solutions at 70 °C for 10 min and 90% pick-up was obtained within three pads. Then, the coated samples were dried at 100 °C for 5 min and cured at 160 °C for 3 min. The other samples which were coated with PVA/MP, PVA/TA and PVA/MP/TA were prepared according to the previous method. For durability study, the coated cotton samples were rinsed several times with tap water, dried at 70 °C for 1 h and weighed. Fig. 1(B) shows the structure of cotton fabric/PVA/MTP prepared by dip-pad-dry method. The weight gain (WG) of MTP-coated cotton fabrics were calculated on the basis of the equation $WG\% = (W_a\text{-}W_b)/W_b \times 100\%$, where, W_a and W_b are the weight of control cotton and MTP coated cotton fabrics, respectively. Table 1 presents the coating composition of cotton fabric samples.

2.5.Characterization and measurements

FTIR spectra were recorded by Nicolet 380 spectrophotometer in the optical range of 4000 – 400 cm^{-1}. Thermogravimetric analysis (TGA) was executed by Shimadzu TGA50 under

nitrogen atmosphere with a flow rate 30 mL/min. TGA measurements were started from ambient temperature to 750 ^{O}C, the heating rate was10 ^{O}C/min and the samples weights were approximately 6 – 7 mg. Vertical and horizontal flammability tests were performed using UL94 flame chamber (purchased from FTT – company, UK). The vertical test was carried out according to ASTM D 6413:(2015) where samples with dimensions 250 mm × 90 mm were subjected to vertical flame with 38 mm height for 12 s. The horizontal burning rate of the samples was evaluated according to ISO 3795:(1989) where samples were exposed horizontally to flame with 38 mm height for 15 s. The ignitability of specimens was determined by single flame source apparatus (manufactured by FTT- Company, UK). In this test a small flame with 20 mm height was directly impinged with a vertically oriented test specimen for 30 s according to ISO 11925-2:(2020). LOI values were determined by oxygen index (supplied by Reohmetric Scientific Ltd, UK) according to standard test method ISO 4589-2:(2017). The samples dimensions were 120 mm length and 50 mm width. Specific optical density was determined by the smoke box chamber (manufactured by FTT - Company, UK) according to standard test method ISO 5659-2:(2017). The specimens' dimensions were 75 mm × 75 mm. Each specimen was wrapped in aluminium foil and subjected horizontally to external heat flux 25 kW/m^2 under non flaming conditions. The smoke box chamber was linked to FTIR gas analyser (supplied by FTT Company, UK) to measure continuously, during smoke density test, the concentrations of the following gases: CO, CO_2, H_2O, NO, NO_2, HCN, NH_3, HCHO, C_3H_8, C_2H_6 and C_6H_{14}. The concentration of O_2 was measured by Testo gas analyser. The recorded concentrations for gases are the average of three tested samples results. SEM images were collected by Quanta 250 FEG (Field Emission Gun) produced by FEI Company, the Netherlands. The assessment of bacteriostatic activity against Gram-positive, Staphylococcus aureus (S. aureus) and Gram-negative, Escherichia coli, (E-Coli) bacteria was assessed using agar diffusion test according to AATCC test method 147-2004 (Parallel Steak Method) and expressed as zone inhibition (mm). Fresh inoculants for antibacterial assessment were prepared on nutrient at 37 °C for 24 h. Any prominent zone of inhibition around the samples was recorded as an inhibitory effect against the above mentioned bacterial species. Tensile strength was measured in the strip method by using universal testing machine (Tinlus Olsen, model H5KT) according to ISO 13934–1:(2013).

Table 1

Coating formulations for cotton fabric samples.

Sample code	Coating composition			
	PVA %	TA %	MP %	MTP %
C0 (control sample)	0	0	0	0
C1	10	0	0	0
C2	10	10	0	0
C3	10	0	10	0
C4	10	5	5	0
C5	10	0	0	10
C6	10	0	0	20
C7	10	0	0	30
C8	10	0	0	30

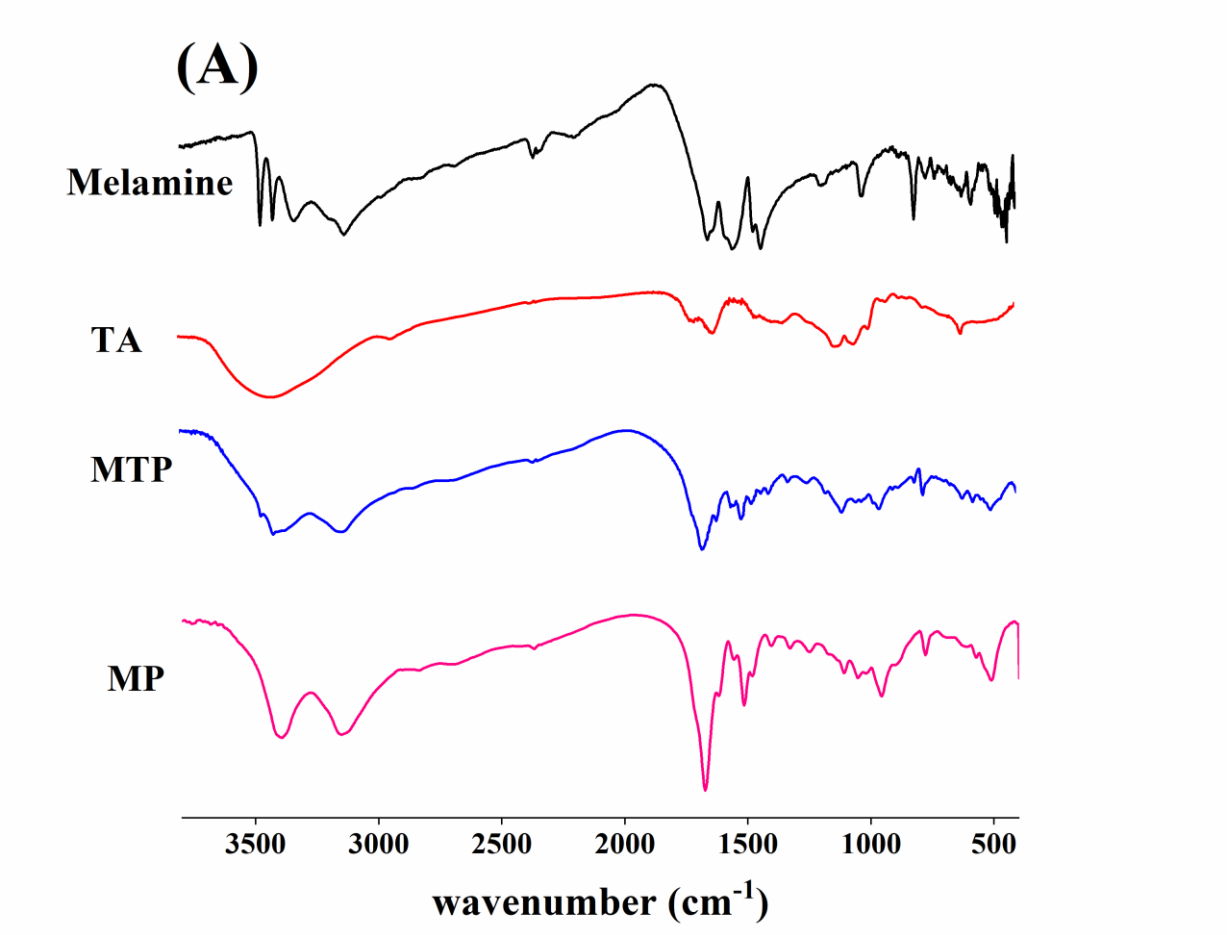
3. Results and discussion

3.1. Characterization of MP, MTP, control and coated samples

3.1.1 FTIR analysis of melamine, TA, MP and MTP

FTIR spectra of melamine, TA, MP and MTP are presented in Fig. 2(A). The main absorption peaks and the corresponding functional groups are presented in Table 2. The data in Table 2 for melamine and TA indicates good consistency with literature data. FTIR absorption peaks of MP agree well with the data recorded in Abdelkhalik et al. (2019) and Chen and Wang, (2007). When comparing FTIR spectra of TA and MTP in Fig. 2(A), it can be seen formation of new peaks in MTP spectrum at 3420 $cm^{-1}$and 3470 cm^{-1} (for NH_2); 3140 $cm^{-1}$and 1406 cm^{-1} (for $^{+}NH_3$); 3370 cm^{-1} (for hydrogen bonded to OH); 2680 cm^{-1} (for OH of O=P-O-H); 1670 cm^{-1}, 1560 cm^{-1} and 817 cm^{-1} (for triazine ring); 1250 cm^{-1}, 1170 cm^{-1} and 1110 cm^{-1} (for P=O, P-O and P-O-C); 499 cm^{-1} and 619 cm^{-1} (for O-P-O stretching). In addition, the absorption peaks of TA at 1620 cm^{-1} and 1425 cm^{-1} (for C – C aromatic); 780 cm^{-1} (for C – H aromatic); 2360 cm^{-1}

(for O-C=O); 1710 cm^{-1} (for C=O) are also found. These data confirm the interaction between phosphoric acid, TA and melamine to form MTP.



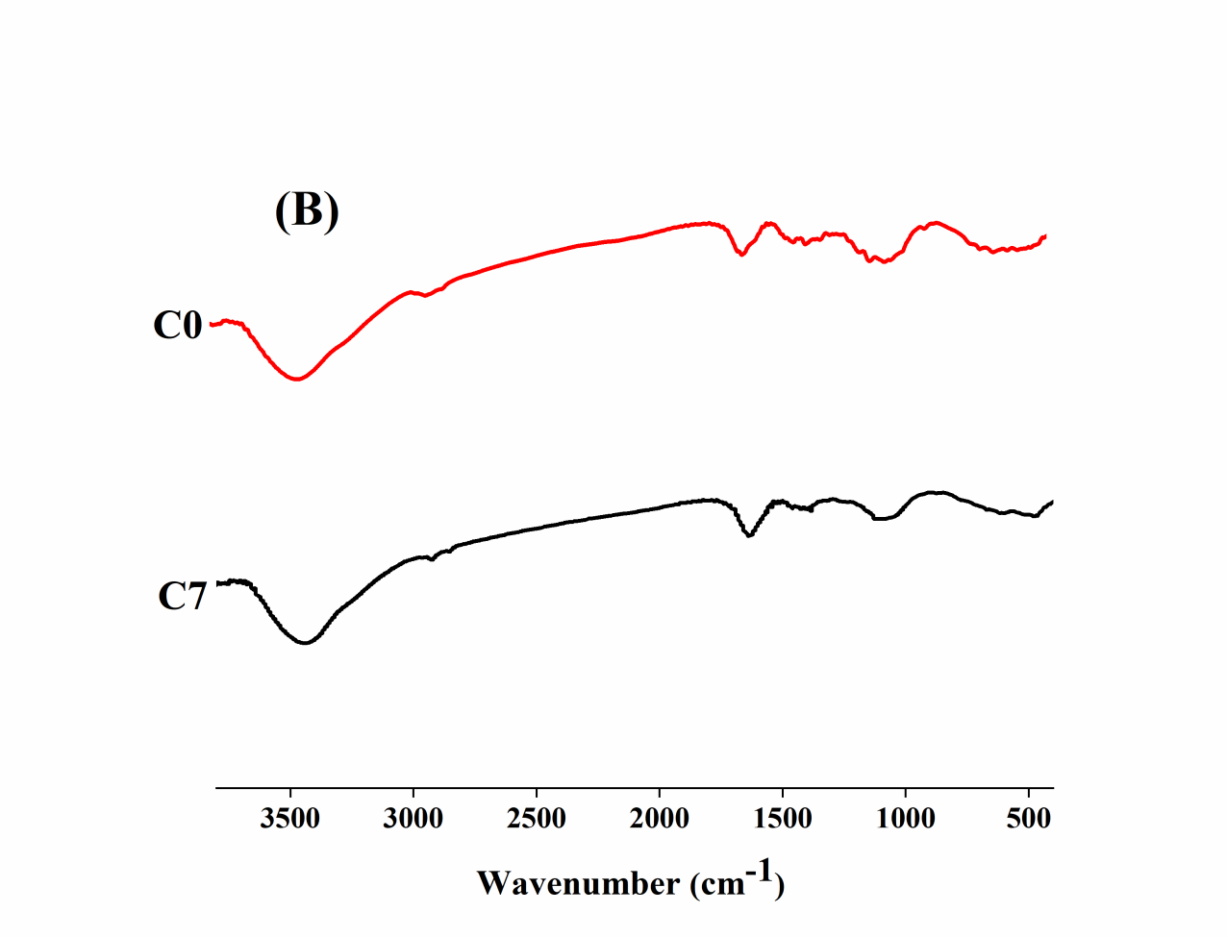


Fig. 2. (A) FTIR spectra of melamine, MP, TA and MTP; (B) FTIR spectra of C0 and C7.

Table 2

FTIR absorption peaks of melamine, TA, MP and MTP.

Compound	Wavenumber (cm^{-1})	Functional group	Reference
Melamine	3469, 3419, 3329, 3128	(-NH_2) primary amine	Makhlouf et al. (2017a,b)
	1652, 1551, 813	Triazine ring	
	1028	(C-N) of primary amine	
TA	3307	OH	Wahyono et al. (2019); Viswanath et al. (2015)
	2833	C-H alkane	
	2860-2920	-C-H- stretching vibrations of CH_2 and CH_3 groups	
	2360	O-C=O	
	1700	C=O	
	1205	C-O	
	1600, 1445	C – C aromatic	
	754	C – H aromatic	
MP	3399	P-O-H, NH_2	Abdelkhalik et al. (2019, 2020); Chen and Wang, (2007)
	3147, 1406	$^{+}NH_3$	
	1670	Triazine ring	
	1050 ,960	P-O	
	1111	P-O-H	
	1254	P=O	
	2680	OH in O=P-O-H	
MTP	3470, 3420	-NH_2	Makhlouf et al. (2017a,b); Abdelkhalik et al. (2019, 2020); Wahyono et al. (2019); Viswanath et al. (2015)
	3370	OH	
	3140, 1406	$^{+}NH_3$	
	2930 , 1320	-C-H- stretching vibrations of CH_2 and CH_3 groups	
	2840	C-H alkane	
	2680	OH in O=P-O-H	
	2360	O-C=O	
	1710	C=O	
	1620 , 1450	C – C aromatic	
	1670,1560, 820	Triazine ring	
	1410	C-N	
	1250 , 1170, 1110	P=O, P – O , P – O – C	
	780	C – H aromatic	
	617 , 499	O-P-O stretching	

3.1.2. FTIR analysis of control and coated samples

FTIR spectra of C0 and C7 samples are presented in Fig.2(B). It is clearly seen in FTIR spectrum of C0 absorption peaks at 3443 cm^{-1} (for H bonded OH groups), 2800 – 3000 cm^{-1} (for C-H stretching), 2920 cm^{-1} (for CH_2 of long alkyl chain), 1630 cm^{-1} (for adsorbed water), 1389 cm^{-1} (for C-H bending), 1120 cm^{-1} (for C-O-C bridge), 1044 cm^{-1} (for C-O stretch) and 894 cm^{-1} (for out-of-phase ring stretch: C1–O–C4; β glucosidic bond) (Chung et al. 2004). FTIR spectrum of C7 shows nearly the same absorption peaks as C0. However, there are some differences where the intensity of the peak 1630 cm^{-1} increased which attributed to the presence of triazine ring in MTP. The peaks at 1160 cm^{-1}, 1120 cm^{-1} and 1044 cm^{-1} are merged in one broad peak in the range 1000 cm^{-1} – 1174 cm^{-1}. Moreover, a new peak appeared at 466 cm^{-1} which refers to O-P-O groups (Dayanand et al. 1996).

3.1.3. SEM images of control and coated samples

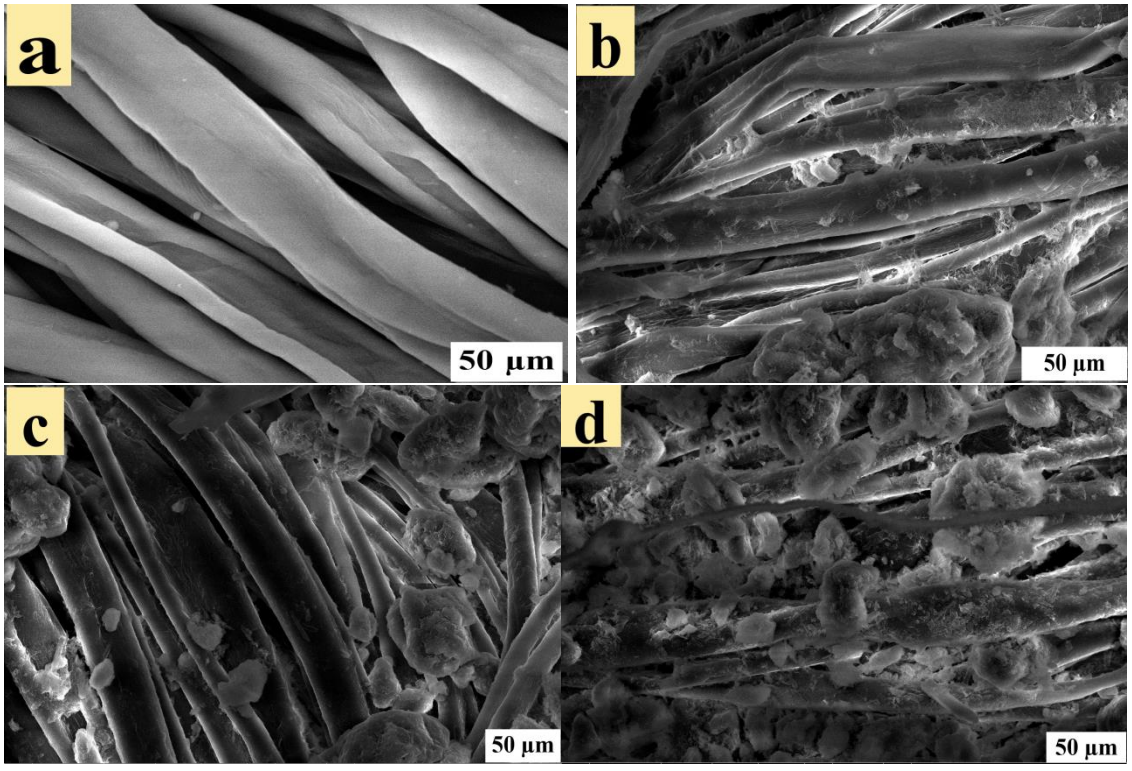


Fig. 3. (a-d) The surface morphology of C0, C5, C7 and C8, respectively.

Fig.3(a-d) shows the surface morphology of control sample and the treated samples (C5, C7 and C8). The surface of control sample is smooth and clear as there is no coating on it (see Fig. 3a). SEM images of treated samples show the presence of flame retardant coating on the surface and the samples are thicker than the control sample. Fig. 3(b,c) shows that the coating particles were able to penetrate into the interior of cotton fibre of C5 and C7 samples. Fig. 3(d)

presents that intensive particles of MTP are found on the surface of C8 sample where the sample is coated with MTP only.

3.2. Flammability properties

3.2.1. Vertical and horizontal flammability tests

The data in Table 3 shows the results of horizontal and vertical burning tests. In horizontal burning rate test, the control sample burnt completely and its rate of burning was 214 mm/min. In vertical flammability test, control sample burnt completely where after flame time (t_{af}) and afterglow time (t_{ag}) were 9 s and 36 s, respectively; and there was no residual char after the test. Addition of PVA to cotton fabric, C1 sample, did not show significant change in horizontal and vertical flammability properties of control sample (see Table 3). C2 sample data indicated that PVA/TA system reduced the rate of burning of control sample by 26.6% and increased its t_{af} to 19 s. C3 sample showed that (PVA/MP) decreased the rate of burning of control sample by 35.5%, while t_{af} raised to 30 s, t_{ag} increased to 40 s and the char length was 250 mm. According to the data in Table 3, C4 failed to achieve better or even the same flammability results of C3. This indicates that addition of TA to PVA/MP decreased the efficiency of PVA/MP as a flame retardant coating for cotton fabrics. The next data for LOI and smoke density for C3 and C4 showed the same behavior also. This may be referred to that MP and TA were decomposing separately at the same time and the presence of TA may be decreased the possibility of interaction between MP and PVA to form a coherent char layer on the sample surface. In contrary, C5, C6, C7 and C8 samples had burning rate 0 mm/min. Moreover, T_{af} and T_{ag} for C5, C6, C7 and C8 samples were 0 s. This confirms that PVA/MTP and MTP alone are highly efficient as flame retardants compared with PVA/TA, PVA/MP and PVA/MP/TA. Fig. 4 shows the different samples after vertical flammability test. It is clearly seen in Fig. 4(a-c) that C0, C1 and C2 burnt completely without leaving char residue. The flame propagated to the end of samples C3 and C4 and the char length values in C3 and C4 were 250 mm (Fig. 4d,e). In contrast, Fig. 4(f-i) shows that the flame did not propagate in samples C5, C6, C7 and C8 and the char length of these samples was 120 mm, 90 mm, 75 mm and 65 mm, respectively. It is expected that the single molecule intumescent flame retardant MTP decomposed to give CO, CO_2, NH_3 and water vapor in the gas phase. In the condensed phase, phosphate groups decomposed to produce phosphoric acid and polyphosphoric acid which interacted with PVA, TA and cotton fabric to form coherent and compact char layer which prevented cotton from the effect of flame. In conclusion, PVA/MTP and MTP alone

presented high efficiency as a flame retardant for cotton fabrics in comparison with PVA/TA, PVA/MP and PVA/TA/MP. The order of different flame retardants based on their efficiency was as follow:

PVA/MTP and MTP > PVA/MP > PVA/MP/TA > PVA/TA > PVA.

Fig. 4. (a-i) Digital photographs for control and treated samples after vertical flammability test.

Table 3

Results of horizontal, vertical flammability and LOI tests before washing process.

Sample code	Horizontal flammability	Vertical flammability			LOI (%)
	Burning rate (mm/min)	t_{af} (s)	t_{ag} (s)	Char length (mm)	
C0	214	9	36	No char*	17.1
C1	211 (1.4%)	14	0	No char*	19.4
C2	157 (26.6%)	19	0	No char*	22.3
C3	138 (35.5%)	30	40	250	28.5
C4	183 (14.4%)	22	0	250	23.2
C5	0	0	0	120	39.4
C6	0	0	0	90	50.6
C7	0	0	0	75	68.4
C8	0	0	0	65	48.1

*No char means that the sample burnt completely without leaving char residue.

3.2.2. LOI data

LOI is defined as the minimum concentration of oxygen, in oxygen and nitrogen mixture, which is able to support flame propagation in a vertical test sample under particular test conditions (ISO 4589-2:(2017)). The higher LOI values of samples relative to blank reflect the increase in flame retardancy of specimens. LOI data are presented in Table 3 and it shows that, in one hand, control sample had LOI value 17.1%. Addition of PVA (C1), PVA/TA (C2) and PVA/MP (C3) increased the LOI value of control sample to 19.4%, 22.3% and 28.5%, respectively. C4 sample showed LOI value 23.2%. This indicates that the coating in C4 sample (PVA/TA/MP) failed to improve LOI value compared to C3 (where PVA/MP was used as a coating). Therefore, adding TA to PVA/MP was not the best choice to improve the flame retardancy of cotton fabrics. On the other hand, C5, C6 and C7 samples showed LOI values 39.4%, 50.6% and 68.4%, respectively. This means that the addition of PVA/MTP to cotton fabric enhanced greatly its flame retardancy. And as the loading level of MTP increased in the

coating formulation, LOI value was increased. It is clearly seen in Table 3 that PVA/MTP system (C5, C6, C7) was highly efficient compared with PVA/MP system (C3). In addition, the coating of C7 was more efficient as a flame retardant than the coating of C8 sample (MTP alone) which had LOI value 48.1%. This means that PVA participated with MTP in improving the flame retardancy of control sample through fixing MTP inside cotton fabric and enhancing formation of thermally stable char layer on samples surface.

3.2.3. Single flame source test

The single flame source test was performed in order to subject the control and coated samples to direct flame for time more than 12 s. This test is a part of fire tests which are used to evaluate the fire performance of building materials. According to ISO 11925-2:(2020), the flame can be applied to sample for 30 s or 15 s. Also the flame can be applied at midpoint of bottom edge of sample or at the sample surface after 40 mm from the bottom edge. In this work, the flame was applied at the midpoint of bottom edge for 30 s and the total test duration was 60 s. The sample is considered pass the test when the flame front doesn't exceed the reference mark at 150 mm within 60 s (30 s as flame application time + 30 s after removing the ignition source away from the sample). It is clearly seen in Table 4 that the samples C0, C1, C2, C3 and C4 failed to pass the test where the flame front reached the reference mark at 150 mm within 60 s. In contrast, the samples C5, C6, C7 and C8 did not ignite and passed the test. This means that addition of PVA/MTP and MTP (alone) to cotton fabrics enhanced greatly its flame retardancy. Moreover, the single molecule intumescent flame retardant, MTP, in PVA/MTP system was more efficient than PVA/TA, PVA/MP and PVA/MP/TA mixtures. According to BS EN 13501-1:(2018), the samples C5, C6, C7 and C8 fulfil the requirements of classes B, C, D, E concerning single flame source test only. But other large scale fire tests such as single burning item test will be necessary to consider the samples achieve completely class B, C and D requirements (BS EN 13501-1:(2018)).

Table 4

Results of single flame source test.

Sample code	Parameters				
	Occurrence of ignition	Whether Flame exceed 150 mm	Time to exceed 150 mm (t_{150} , s)	Ignition of filter paper	Classification
C0	Yes	Yes	35	No	F
C1	Yes	Yes	42	No	F
C2	Yes	Yes	37	No	F
C3	Yes	Yes	55	No	F
C4	Yes	Yes	51	No	F
C5	No	No	0	No	B,C,D,E
C6	No	No	0	No	B,C,D,E
C7	No	No	0	No	B,C,D,E
C8	No	No	0	No	B,C,D,E

3.2.4. Smoke density

The data in Fig. 5 shows the maximum specific optical density (Ds_{max}) for all samples at 25 kW/m^2 and non-flaming conditions. Ds_{max} of control sample was 80.5 and it decreased in C1 and C2 samples by 22.8% and 23.3%. PVA/MP and PVA/MP/TA minimized Ds_{max} of cotton fabrics by 62.7% and 51.4% as it is shown in C3 and C4 results. This indicates that PVA/MP mixture was more efficient as a smoke suppressant than PVA/MP/TA mixture. The samples C5, C6, C7 and C8 showed the maximum reductions in Ds_{max} and the amounts of these reductions were 79.7%, 76.7%, 72.2 and 82.9%, respectively. This is referred to formation of a protective char layer on the cotton fabric surface which saved the underlying polymer from the effect of heat. The digital photographs in Fig. 6 for the samples after smoke density test confirmed this suggestion. It is clearly seen in Fig. 6 that C0, C1 and C2 samples approximately bunt completely. The char residue of C3 sample was coherent and covered the whole sample meanwhile the char residue of C4 was discontinuous and the sample burnt

completely at certain parts. This confirms that PVA/MP mixture was more efficient as flame retardant than PVA/MP/TA. The char residue of samples C5, C6, C7 and C8 in Fig. 6 was continuous, coherent, and compact and were able to protect the underlying cotton samples from the effect of heat and oxygen. This led to higher reductions in Ds_{max} values of C5, C6, C7 and C8 relative to C0. According to smoke density data, the order of the efficiency of different additives as a smoke suppressant is MTP> PVA/MTP >PVA/MP > PVA/MP/TA > PVA/TA > PVA.

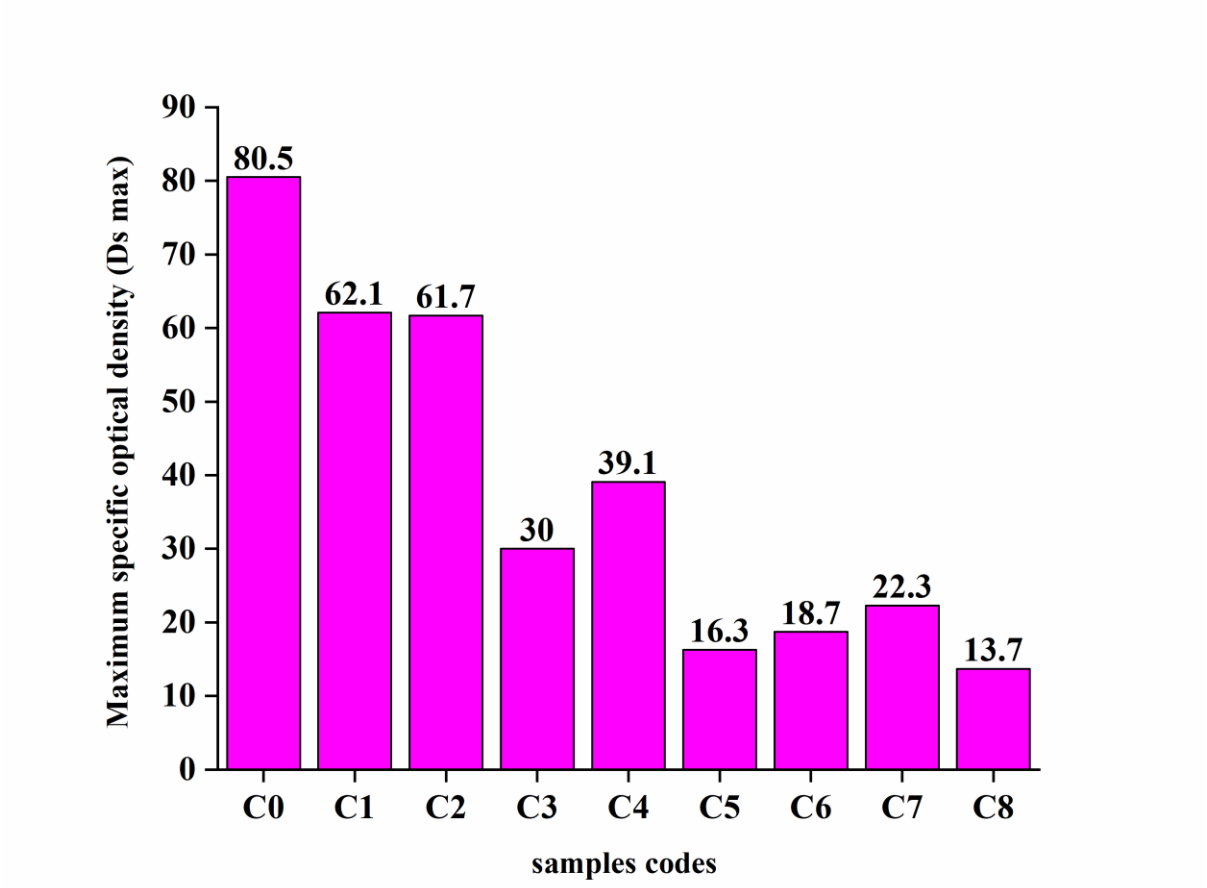


Fig. 5. Values of maximum specific optical density (Ds_{max}) for control and coated samples.

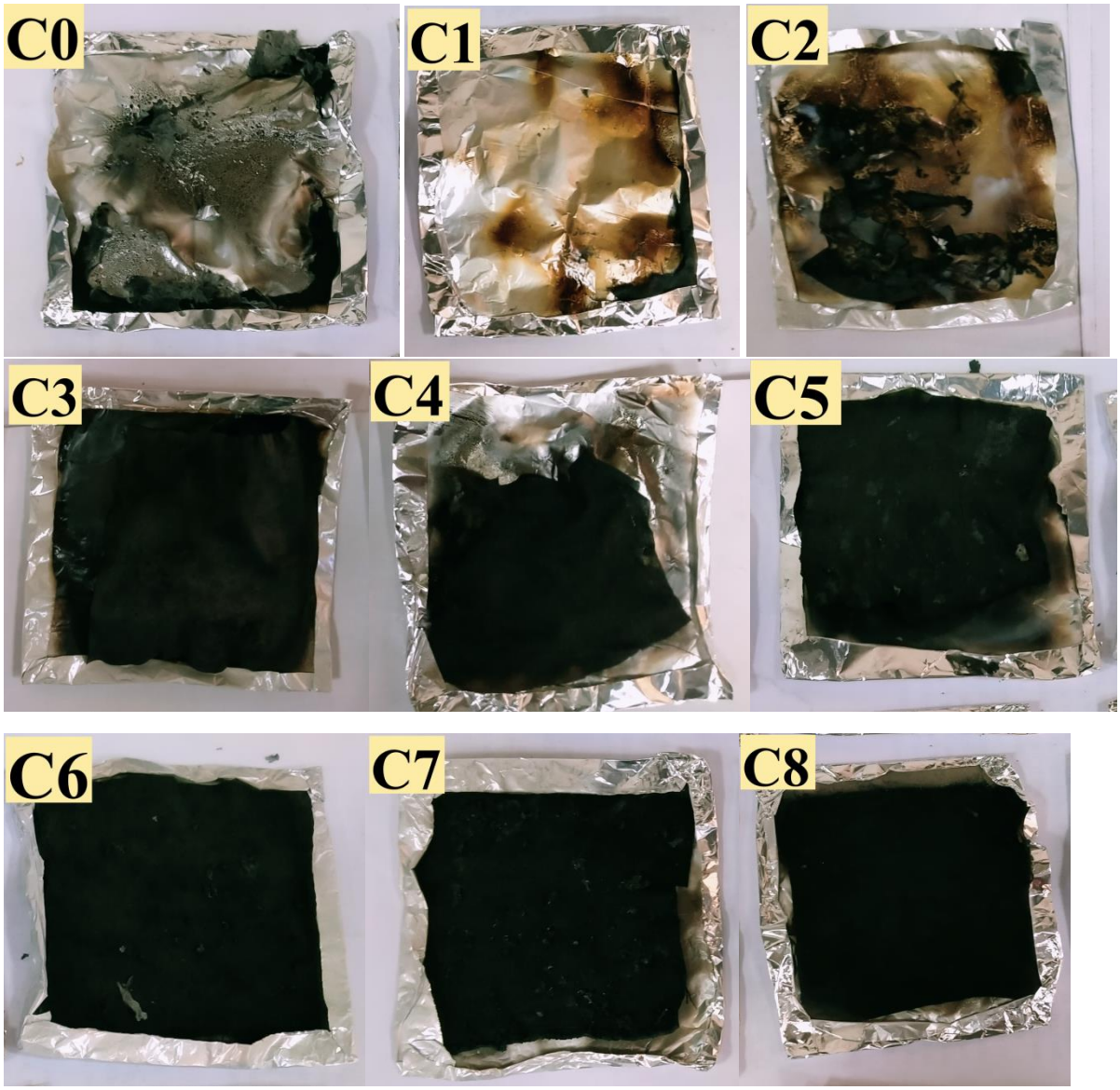
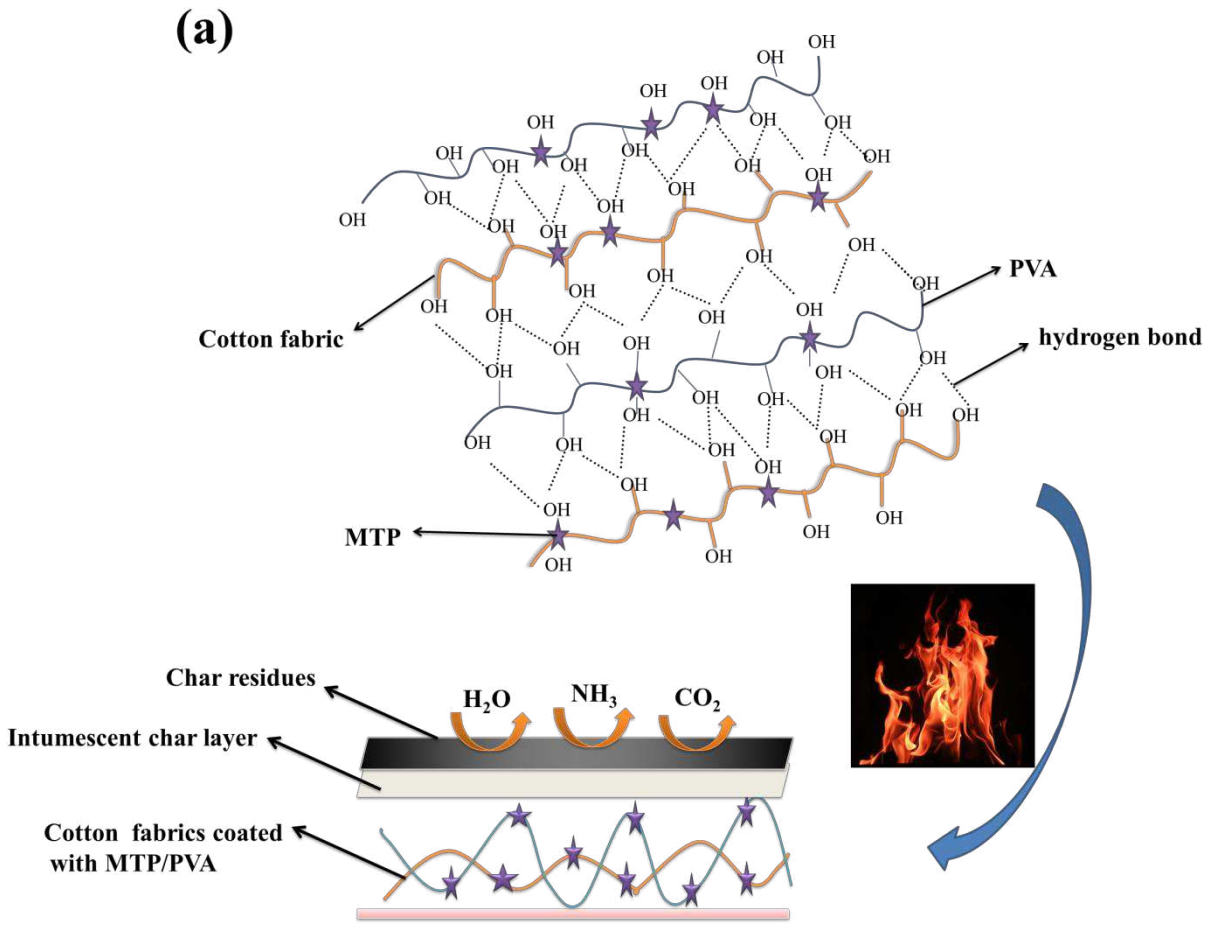


Fig. 6. Digital photographs of control and treated samples after smoke density test.

3.2.5 FTIR gas analyser data and flame retardant mechanism

FTIR gas analyser connected to smoke box chamber was used to identify the combustion products in the gas phase. The data in Table 5 shows the average values for the concentrations of gases which are detected by FTIR gas analyser. According to the data in Table 5, control sample decomposed and gave out mainly CO, CO_2, water vapour, HCHO, C_2H_6 and C_6H_{14}. In addition, NO, HCN, CH_4, C_2H_4 and C_3H_8 were detected at minor concentrations. The presence of NO and HCN in combustion products of C0 sample is referred to the oxidation of nitrogen in the air which was found inside the smoke box chamber. The addition of PVA to cotton fabric, sample C1, increased the concentrations of water vapour, CO, C_3H_8, C_6H_{14} and C_2H_6.

The gases HCHO and CO_2 were also produced, but at lower concentrations compared to control sample. The increase in hydrocarbon gases (C_3H_8, C_6H_{14} and C_2H_6) concentrations is referred to the decomposition of PVA. It was reported that PVA decomposition takes place through dehydration, depolymerization and polyene formation. Then, pyrolysis of polyene formed and producing certain volatile organic compounds (Zaikov and Lomakin, 1998; Gaikwad et al. 2015; Dong et al. 2016). FTIR gas analyser data for C2, C3 and C4 samples showed that addition of PVA/TA, PVA/MP and PVA/MP/TA to cotton fabric succeeded in decreasing its CO and CO_2 production during combustion. Also, the production of hydrocarbon gases (C_3H_8, $C_6H_{14}$and C_2H_6) was also reduced. The maximum reductions were observed in C3 sample where PVA/MP retarded the effect of heat through the formation of a coherent char layer on the cotton sample surface. But the presence of MP in the samples C3 and C4 led to increasing in the concentrations of NH_3 and HCN relative to control sample. This is referred to the decomposition of melamine in MP structure. The data in Table 5 manifested that C5, C6, C7 and C8 samples which contains PVA/MTP and MTP alone as coatings produced the highest concentrations of NH_3 and water vapour relative to the other samples. In addition, the production of CO, HCHO and hydrocarbon gases were decreased relative to C0, C1, C2, C3, and C4 samples. This indicates that degradation of MTP produced water vapour, CO_2 and NH_3 (in the gas phase) which diluted the concentrations of volatile organic compounds and oxygen in the combustion zone. Moreover, the great reduction in the concentrations of HCHO and hydrocarbon gases indicates that PVA and cotton fabrics in C5, C6, C7 and C8 samples maintained most of their main structure during combustion. This is referred to formation of coherent, continuous and compact char layer on cotton fabric, see Fig. 7(a). This char acted as a physical barrier and protected the cotton fabric from the effect heat and flame.



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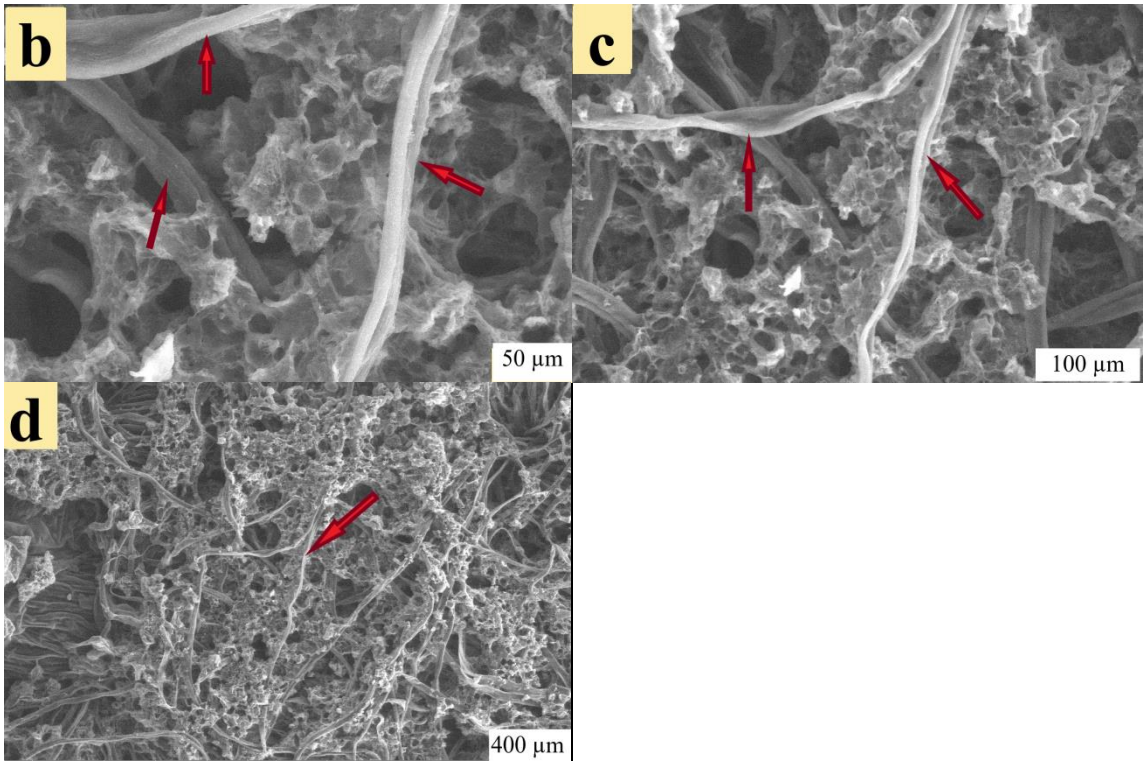

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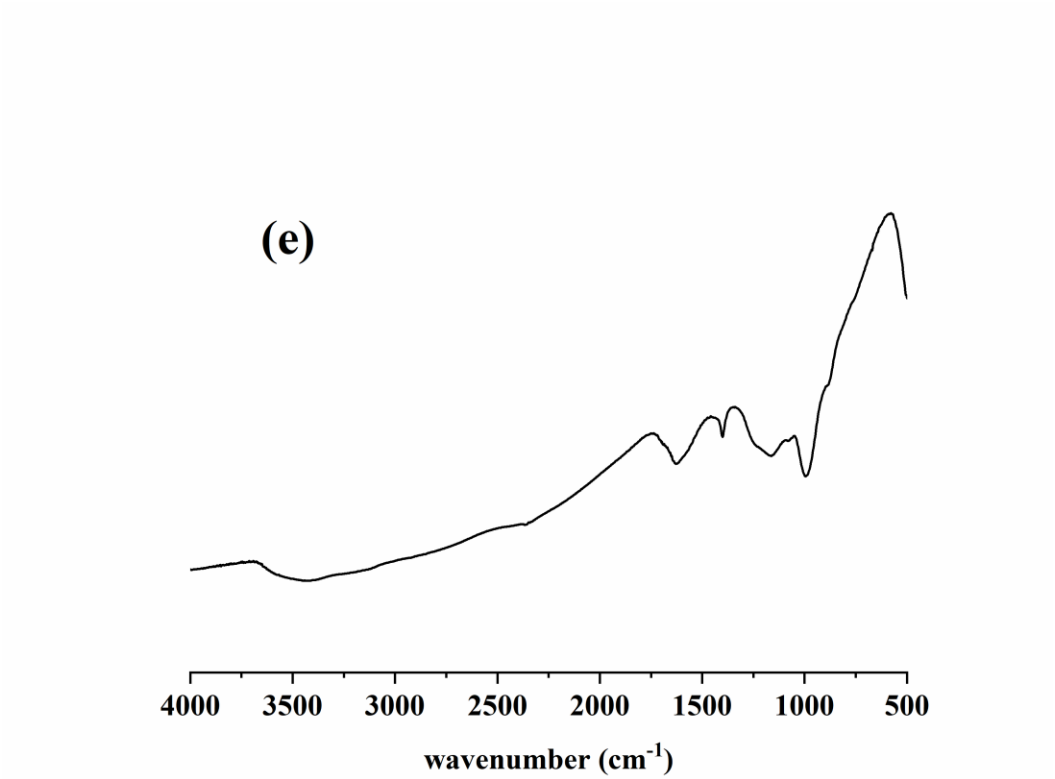

Fig. 7. (a)Schematic illustration of a possible flame retardant mechanism for cotton fabrics treated with PVA/MTP during combustion; (b-d) SEM images for char residue formed after smoke density test of C7; (e) FTIR analysis of char residue of C7 after smoke density test.

Table 5

FTIR gas analyser results for control and treated samples.

Sample codes / Gases	C0	C1	C2	C3	C4	C5	C6	C7	C8
H_2O(v) %	1.05	1.32	1.44	1.28	1.3	1.45	1.73	1.81	1.64
CO Ppm	299	375.5	236.1	115.8	300.4	215.6	49.2	45.8	73.1
CO_2 %	0.040	0.031	0.036	0.028	0.029	0.032	0.095	0.132	0.075
O_2 %	20.6	20.6	20.7	20.7	20.7	20.8	20.8	20.8	20.8
HCHO Ppm	28.7	20.1	11.2	9.5	10.3	6.7	1.8	2.5	4.3
NO Ppm	5.9	8.6	9	9.5	10.6	10.4	11.1	10.6	10
NO_2 Ppm	7.6	2.2	1.4	1.5	1.8	3.9	7.4	8.1	5.5
NH_3 Ppm	1	1.7	2.5	29.8	11.8	22.6	75.3	110.8	130.2
HCN Ppm	2.1	3.4	5.7	10.6	11.2	12.9	11.4	15.2	9.7
C_2H_6 Ppm	16.3	48.1	20.4	6.8	3.2	6.1	5.2	4.7	4.4
C_3H_8 Ppm	8.7	29.5	15.2	2	5.6	2.8	3.6	3.6	3.3
C_6H_{14} Ppm	12.1	35	26.4	13.5	12.7	8.6	7.6	5.7	8

3.2.5.1 SEM image of char residue

Fig. 7(b-d) shows the surface morphology of the char residue of C7 sample after the smoke density test. It is clearly seen that the fibres are grouped together, and the surface was wrapped and protected by a char layer with cellular structure. These properties are referred to that PVA/MTP coating produced during C7 combustion polyphosphoric acid which promoted the dehydration and carbonization of cotton fibre. Moreover, the degradation of PVA/MTP sent out NH_3, CO_2 and water vapour. These gases led to char intumesce. Besides, these gases dilute volatile organic compounds and oxygen in the combustion zone. The intumescent char layer acted as a barrier and protected the cotton from the effect of heat and flame; and reduced the escaping of volatile organic compounds from the substrates to combustion zone, see Fig. 7(a).

3.2.5.2 FTIR analyses of char residue

The char residue after smoke density test for C7 sample was analysed by FTIR. Fig. 7(e) shows broaden peak at 2800 -3600 cm^{-1} due interfering between the peak at 3450 cm^{-1} which is referred to hydrogen bonded OH group and the peak at 2920 cm^{-1}which was attributed to CH_2 group. This confirms the presence of carbon hydrogen chains in the char structure. The peak at 1630 cm^{-1} is for aromatic structure, the peak at 1400 cm^{-1} is for C-N and C=N groups, the peak at 1160 cm^{-1} is for P-O, the peak at 1050 cm^{-1} is for P-O-C, the peak at 984$cm^{-1}$is for polyphosphate and/or pyrophosphate, the peak at 881 $cm^{-1}$is for alkene, the peak at 492cm^{-1} is for O-P-O group (Abdelkhalik et al. 2020, 2019; Wahyono et al. 2019; Makhlouf et al. 2017a,b; Viswanath et al. 2015; Chen and Wang, 2007).

3.2.6 Smoke toxicity

Fire toxicity for all samples was evaluated based on FED and LC_{50} data. FED values were calculated using equations (1,2,3) where the following gases were taken into account: CO, CO_2, NO, NO_2, O_2, HCN, and HCHO. Fig. 8(A) shows that FED values of control and treated samples are lower than 1 regardless the equation used in the calculation. Following to Eq. (1), the samples C4, C5, C6 and C7 have FED values greater than the control sample, but the maximum difference between blank and these samples is very low (0.04) as it is obvious in Fig. 8(A). According to Eq. (2), FED values for treated samples are lower than the control sample which means lower toxicity. Fig. 8(A) presents that calculating FED using Eq. (3) leads to lower FED values for all treated samples relative to cotton fabric. The only exception was C7 which has FED value (0.2) equal to FED value of blank. The data of Eq. (2,3) indicates that the different formulations for coating were able to decrease the fire toxicity of cotton fabrics.

524 LC_{50} values were calculated according to Eq. (4) where FED values were obtained following to
525 Eq. (3). Fig. 8(B) shows that all samples have LC_{50} value greater than the control sample. This
526 indicates that coated samples are less toxic than the control sample. The maximum values for
527 LC_{50} were observed in C5, C6, C7 and C8 which means that PVA/MTP and MTP coatings
528 were able to reduce fire toxicity of cotton fabrics.
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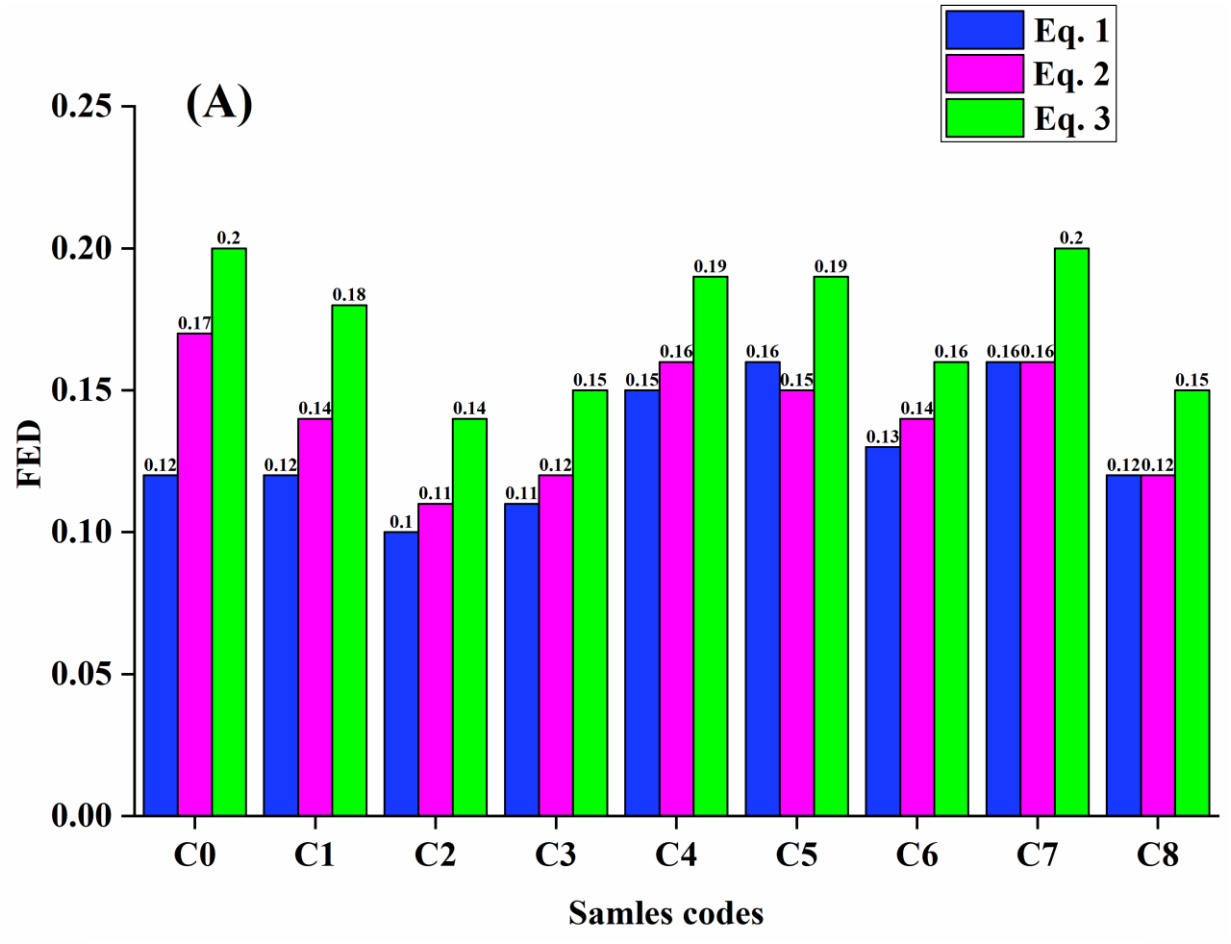

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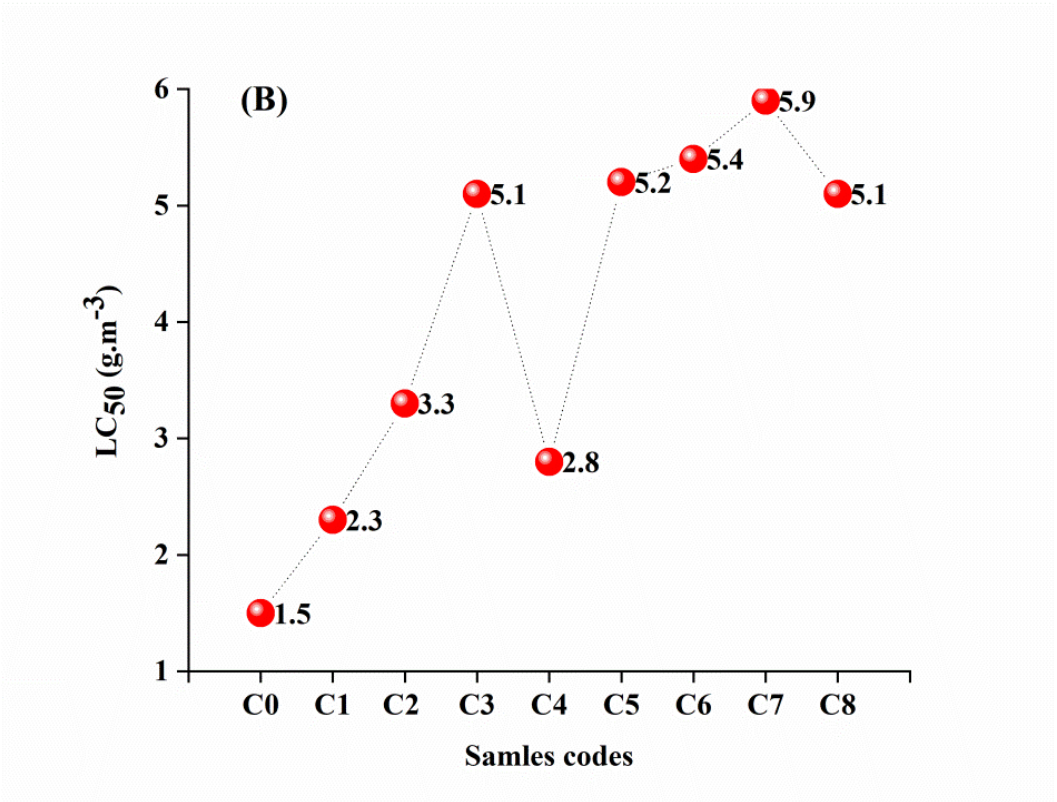

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534 **Fig. 8.** (A) FED and (B) LC_{50} values of control and treated samples.

3.2.7 Antibacterial properties

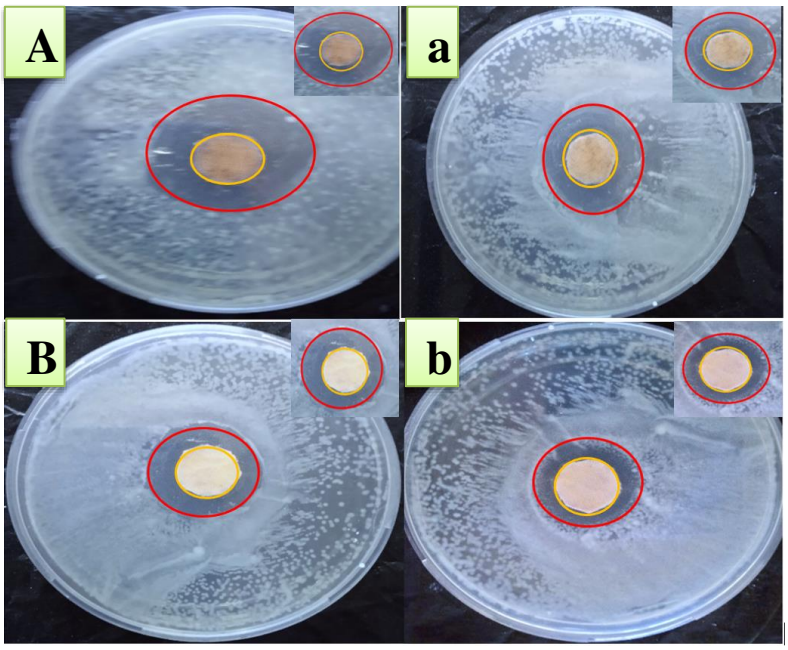

Fig. 9. (A,B) digital photographs for zone of inhibition formed by S.aureus in C7 and C8 respectively; and (a,b) digital photographs for zone of inhibition formed by E. coli in C7 and C8, respectively.

The data in Table 6 show antimicrobial activity inhibition zone in (mm) for C0, C5, C6, C7 and C8. The results prove that there is no zone of inhibition (ZOI) on uncoated cotton (C0), indicating that it has no antibacterial property. However, the antibacterial activity was enhanced when the concentration of MTP increased in the coating formulation. This may be referred to the amine groups in MTP, which are in the form of $^{+}NH_3$ and have positive charges, interacted with the negative charges on the surface of bacteria cells. This interaction led to expanded changes in the cell surface and cell permeability and causes a leakage of thiol of protein. Fig. 9(A,a,B,b) displays the effect of G+ve and G-ve bacteria on the sample treated by MTP in the absence as well as presence of PVA. It is clearly seen that the bacteria die on the surface of coated fabric and inhibition of the growth of bacteria around the coated fabric. According to the data in Table 6, inhibition of S. aureus is more dominant than E-coli. This is attributed to the mode of action of MTP on bacteria includes binding of the cationic MTP with anionic cell surface. The results of antibacterial properties indicated that MTP can be used in home and antimicrobial textile.

557 *3.2.8 Mechanical properties*

558 The data in Table 6 shows tensile strength of control and treated samples. It can be seen that
559 the tensile strength value of control sample decreases with the addition of PVA/MTP and MTP
560 alone. In addition, as the loading level of MTP increases, in PVA/MTP system, the tensile
561 strength value decreases relative to blank. The reductions in tensile strength are 6.5%, 9.1%,
562 18.1% and 3.6% in C5, C6, C7 and C8, respectively which means that PVA/MTP and MTP
563 coatings have a slight negative effect on the tensile strength.

564

565 **Table 6**

566 Tensile strength and antimicrobial activity of control and treated samples.

Sample code	Tensile strength (N)	Antimicrobial activity (Inhibition zone in mm)	
		S.aureus G+ve	E.coli G-ve
C0	320.4	0	0
C5	299.5	12.2	10.6
C6	291.2	15.3	10.4
C7	262.4	22.5	17.6
C8	308.8	20.2	16.4

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576 *3.2.9 TGA of control and treated samples*

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578 **Table 7**

579 TGA data of MTP, PVA, C0, C1 and C7, respectively.

Sample code	$T_{10\%}$ ℃	$T_{50\%}$ ℃	T_{max} ℃	Max. mass loss mg/min	Char at 750 ℃ Wt.%
MTP	285	414	390	0.29	24.6
PVA	224	269	266	0.89	2.5
C0	300	347	348	1.19	0.3
C1	276	346	351	0.9	4.4
C7	251	371	304	0.5	25.5

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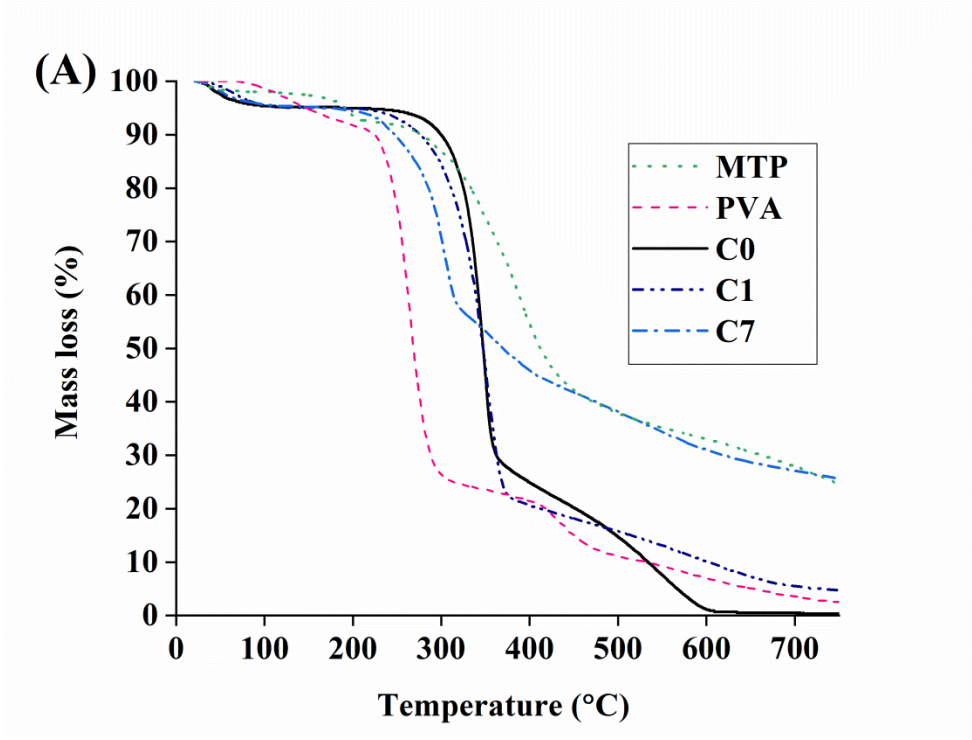

Fig. 10. (A)TGA curves of MTP, PVA, C0, C1 and C7; (B) Digital photographs of C7, C6 and C5 samples after washing and performing vertical flammability test.

TGA was used to study the thermal degradation of MTP, PVA, C0, C1 and C7 samples. The data for thermal analysis are presented in Table 7 and Fig. 10(A). MTP shows, in Fig. 10(A), two decomposition steps. The first degradation step locates between 25 ℃ and 205 ℃ and includes 5.6% weight loss which is signed to losing moisture. The second decomposition step is between 208 ℃ - 493 ℃ and it involves 54.2% weight loss. During this step, $T_{50\%}$ (at 414 ℃) and T_{max} (at 390 ℃) are attained. This step includes dehydration of OH group and abstracting NH_2 group to form non-flammable gases besides evolving of CO and CO_2. In addition, phosphate ester groups decomposed to form polyphosphoric acid which interacted with other elements (C, O, N) to form carbonous char layer. The gradual growing up in temperature after 493 ℃ leads to a gradual increase in weight loss and the residual char at 750 ℃ is 24.6%. PVA sample reaches $T_{10\%}$, $T_{50\%}$ and T_{max} at 224 ℃, 269 ℃ and 266 ℃, respectively, and it leaves 2.5% as char residue at 750 ℃. The thermal degradation of PVA takes place through two steps where the first stage includes dehydration and depolymerization of PVA; and polyene formation. The second decomposition step involves pyrolysis of polyene and it is accompanied by producing certain volatile organic compounds (Zaikov and Lomakin, 1998; Gaikwad et al. 2015; Dong et al. 2016). C0 sample attains $T_{10\%}$, $T_{50\%}$ and T_{max} at 300 ℃, 347 ℃ and 348 ℃, respectively. The main decomposition stage of cotton sample locates between 280℃ - 400 ℃ and it is accompanied with 68.5% weight loss. Thermal degradation of C0 sample takes place either through depolymerization from sugar-based units to form volatile compounds (chiefly including levoglucosan, furan, and furan derivatives) or by glycosyl unit dehydration to form aromatic char layer which is thermally stable compound (Carosio et al. 2015; Wan et al. 2020). Coating cotton fabric with PVA alone decreased its $T_{10\%}$ and $T_{50\%}$ by 24 ℃ and 1 ℃, respectively; and increased T_{max} by 3 ℃. The reduction in $T_{10\%}$ of C1 relative to C0 is referred to dehydration and depolymerization of PVA layer on the cotton fabric surface. TGA data of C7 show that it attains $T_{10\%}$ at 251 ℃. This great reduction in $T_{10\%}$ relative to C0 is attributed to the earlier degradation of PVA/MTP coating which accompanied by evolving of water vapour, ammonia and other volatile compounds. $T_{50\%}$ of C7 is increased by 24 ℃ relative to C0 and by 25 ℃ relative C1. T_{max} of C7 was attained at lower temperature (304 ℃) compared with C1 and C7. This may be referred to decomposition of MTP to form polyphosphoric acid which can accelerate decomposition and interaction with O and C atoms to form an insulating char layer containing polyaromatic structure. The maximum weight loss rate was 1.19 mg/min in C0 and it decreased to 0.5 mg/min in C7. Moreover, the char residue at 750 ℃ increased from 0.3% and 4.4% in C0 and C1 to 25.5% in C7. This indicated that MTP assisted in the formation of an insulating char layer which protected cotton fabric from

the effect of heat, oxygen and slow down the degradation process of C7 sample. Moreover, emission of gases such as NH_3, CO_2 and water vapour expelled degradation heat and decreased the temperature of the treated cotton sample surface (Levchik et al. 1996; Xu et al. 2019; Wan et al. 2020).

3.2.10 Durability study

Table 8

Results of horizontal, vertical flammability and LOI tests after washing process.

Sample code	Horizontal flammability	Vertical flammability			LOI (%)
	Burning rate (mm/min)	t_{af} (s)	t_{ag} (s)	Char length (mm)	
C5	65	7	0	250	24.2
C6	0	0	0	110	33.5
C7	0	0	0	90	49.8
C8	206.1	0	0	No char*	18.5

*No char means that the sample burnt completely without leaving char residue.

The flammability properties of coated samples were studied after washing samples using tap water and drying them at 60 °C for 60 min. The results of horizontal and vertical flammability tests after washing are presented in Table 8. In horizontal flammability test, the flame propagated in samples C5 and C8 and the rate of burning was 65 mm/min and 206.1 mm/min. Meanwhile, flame failed to spread in C6 and C7 and the burning rate was 0 mm/min. In vertical flammability test, C5 results manifested that the flame attained the far end of the sample (char length 250 mm) and T_{af} was 7 s. The flame propagation was decreasing as the concentration of MTP in PVA/MTP coating increased. C6 and C7 showed char length values 110 mm and 90 mm; and T_{af} results were 0 s which meant that C6 and C7 coatings still have high flame retardancy action after washing process. Fig. 10(B) shows C5, C6 and C7 samples after vertical flammability test and it confirms that PVA/20%MTP (C6) and PVA/30%MTP (C7) coatings still have good flame retardancy action after washing the samples using tap water. The data in Table 8 indicated that within flame application time, the flame reached the far end of C8

without leaving char residue. The results of horizontal and vertical flammability tests indicated that C8 samples lost nearly all the flame retardant during washing process. In contrast, PVA in C6 and C7 samples played an important role in fixing the flame retardant (MTP) on the cotton fabric surface during washing process. LOI data in Table 8 confirmed the horizontal and vertical flammability tests results. It can be seen that LOI of C8 after washing is 18.5%, meanwhile LOI values of C5, C6 and C7 are 24.2%, 33.5% and 49.8% respectively.

Single flame source test data in Table 9 are also promoted the previous flammability tests. C8 and C5 failed in single flame source test where the flame front reached the reference mark within 60 s. In contrast, C6 and C7 pass the test and showed a higher degree of flame retardancy compared to C8 and C5 samples. It can be concluded that PVA plays a vital role in fixing MTP on cotton fabric surface and as the concentration of MTP in PVA/MTP mixture increases, the flame retardancy of cotton fabric increases after washing process. Applying MTP alone, as a coating for cotton fabric, is not sufficient to impart flame retardancy to fabric after washing with tap water.

Table 9

Single flame test data after washing process.

Sample code	Parameters				
	Occurrence of ignition	Whether Flame exceed 150 mm	Time to exceed 150 mm (t_{150} , s)	Ignition of filter paper	Classification
C5	Yes	Yes	50	No	Fail
C6	No	No	0	No	B,C,D,E
C7	No	No	0	No	B,C,D,E
C8	Yes	Yes	38	No	Fail

4. Conclusions

1- A novel single molecule intumescent flame retardant (melamine salt of tannic phosphate, MTP) was synthesized and characterized by FTIR.

2- MTP was mixed with PVA solution at 10%, 20% and 30%; and used as a coating for cotton fabrics to improve its flammability properties.

3- Horizontal flammability test data showed that coated samples C5,C6,C7 and C8 had burning rate equal to zero mm/min meanwhile the burning rate of control sample was 214 mm/min

4- Vertical flammability test results indicated that applying MTP/PVA and MTP alone as coatings for cotton fabrics prohibit the flame propagation in cotton fabric samples.

5- LOI of control sample was 17.1% and it increased to 39.4%, 50.6%, 68.4% and 48.1% in C5, C6, C7 and C8 samples, respectively.

6- Single flame source test results showed that samples treated with MTP alone (C8) and PVA/MTP mixture (C5, C6 and C7) was able to pass the test and the flame did not propagate through the samples.

7- Maximum specific optical density (Ds_{max}) of control sample was decreased by 79.7%, 76.7%, 72.2% and 82.9% in C5, C6, C7 and C8 samples, respectively.

8- FTIR gas analyser results indicated that the coatings PVA/MTP and MTP (alone) decreased the emission of CO, CO_2 and HCHO gases from cotton fabrics while NH_3 concentrations increased due to decomposition of melamine part in MTP. The increase in NH_3 and H_2O concentrations in the gas phase dilute the concentration of oxygen and volatile organic compounds in the combustion zone.

9- Digital photos and SEM images for char residue after smoke density test showed that MTP was able to form coherent and insulating char layer on the surface of cotton fabric. This char protected the fabric from the effect of heat and oxygen; and prevented evolving of volatile organic compounds to the combustion zone.

10- The results of LOI, horizontal flammability test, vertical flammability test, single flame source test and smoke density test confirmed that MTP (alone) and PVA/MTP mixture are more efficient as a flame retardants for cotton fabrics than the other flame retardants which consisted of PVA/TA, PVA/MP and PVA/MP/TA. Moreover, addition of TA to PVA/MP led to negative effect where the flame retardancy action of PVA/MP on cotton fabrics was better than PVA/MP/TA system.

11- FED was calculated by different models based on CO, CO_2, O_2, NO, NO_2, HCN and HCHO concentrations. The results indicated that coated samples are less toxic than the cotton fabric sample. LC_{50} calculations led also to the same conclusion.

12- Samples coated with PVA/MTP mixture and MTP (alone) showed antibacterial characteristic against G+ve (S.aureus) and G-ve (E-coli) bacteria. Also, as the concentration of MTP increased in coating formulation, the inhibition zone expressed in (mm) was increased.

13- Thermal analysis data indicated that PVA/MTP mixture enhanced the thermal stability of cotton fabric at high temperature ($T_{50\%}$) and increased the char residue at 750 ℃ from 0.3% in control sample to 25.5% in C7 sample.

14- Durability studies showed that cotton samples coated with PVA/20%MTP (C6) and PVA/30%MTP (C7) can maintain good flame retardancy action after washing them with tap water. In contrast, C8 sample lost its flame retardancy due to losing MTP particles during washing process. This indicated that PVA played an important role in preserving MTP on cotton samples during washing process.

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Figures

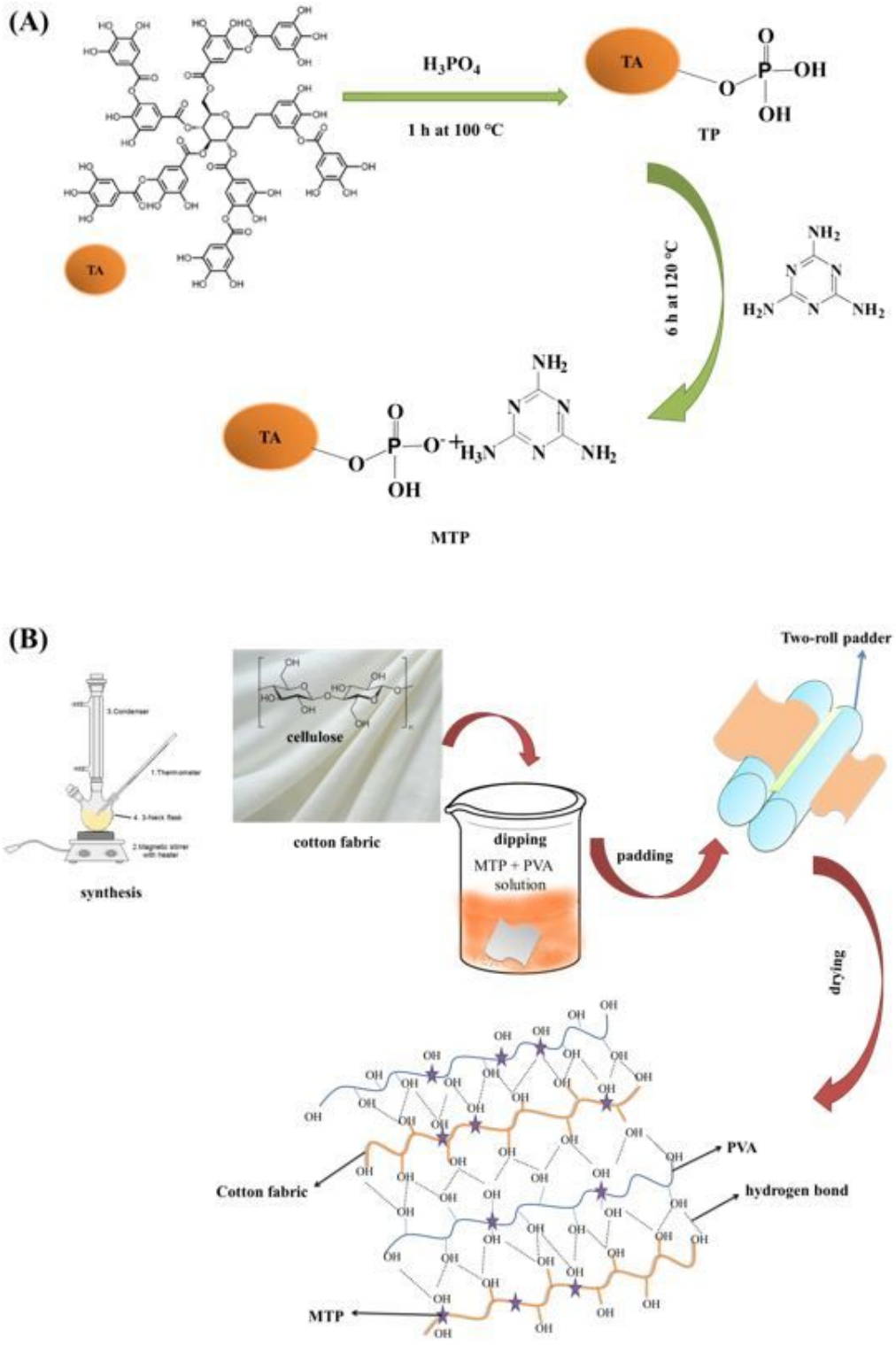

Figure 1

(A) Schematic illustration of a suggested synthetic route of MTP; (B) the structure of cotton fabric/PVA/MTP prepared by dip-pad-dry method.

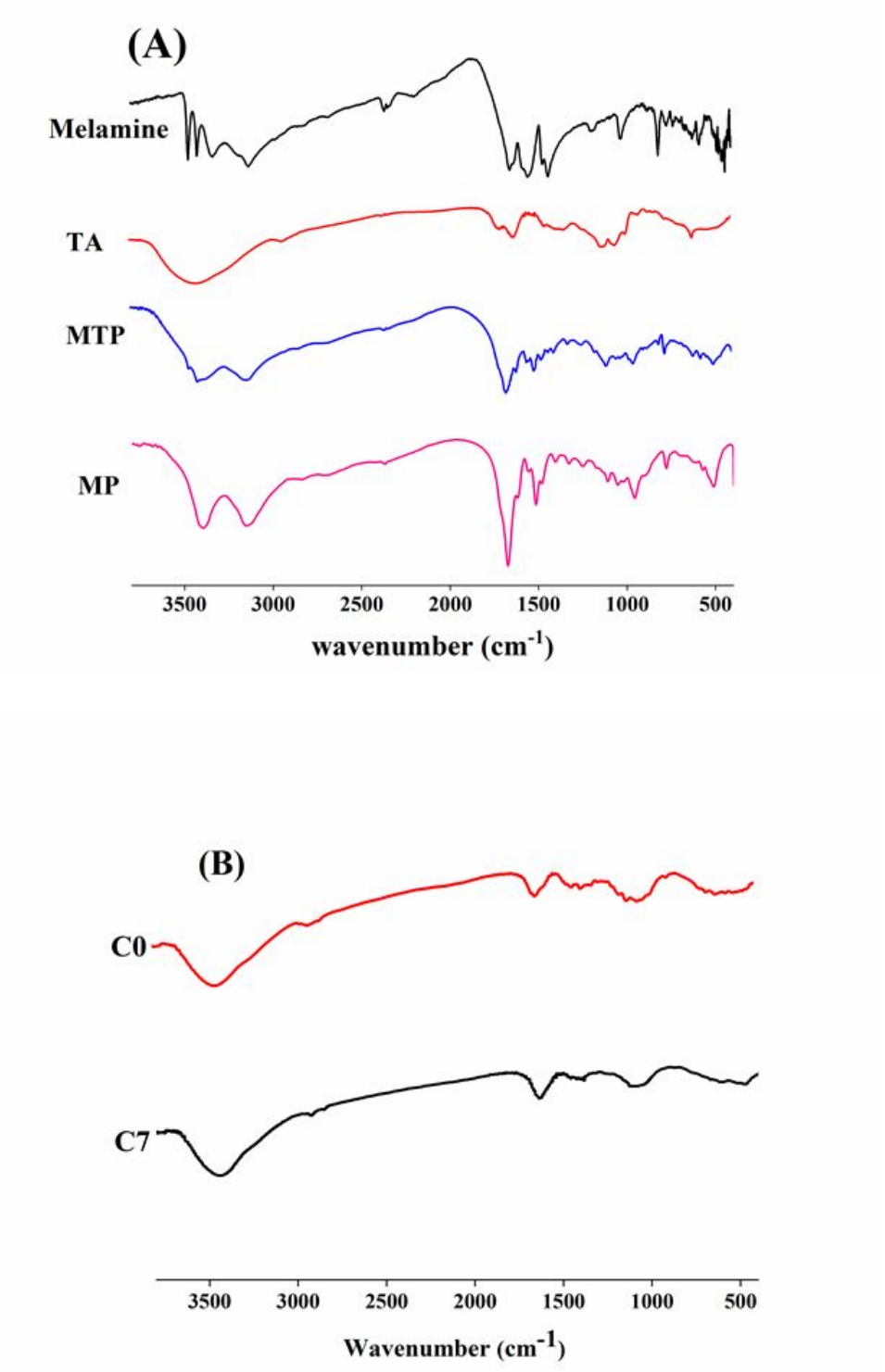

Figure 2

(A) FTIR spectra of melamine, MP, TA and MTP; (B) FTIR spectra of C0 and C7.

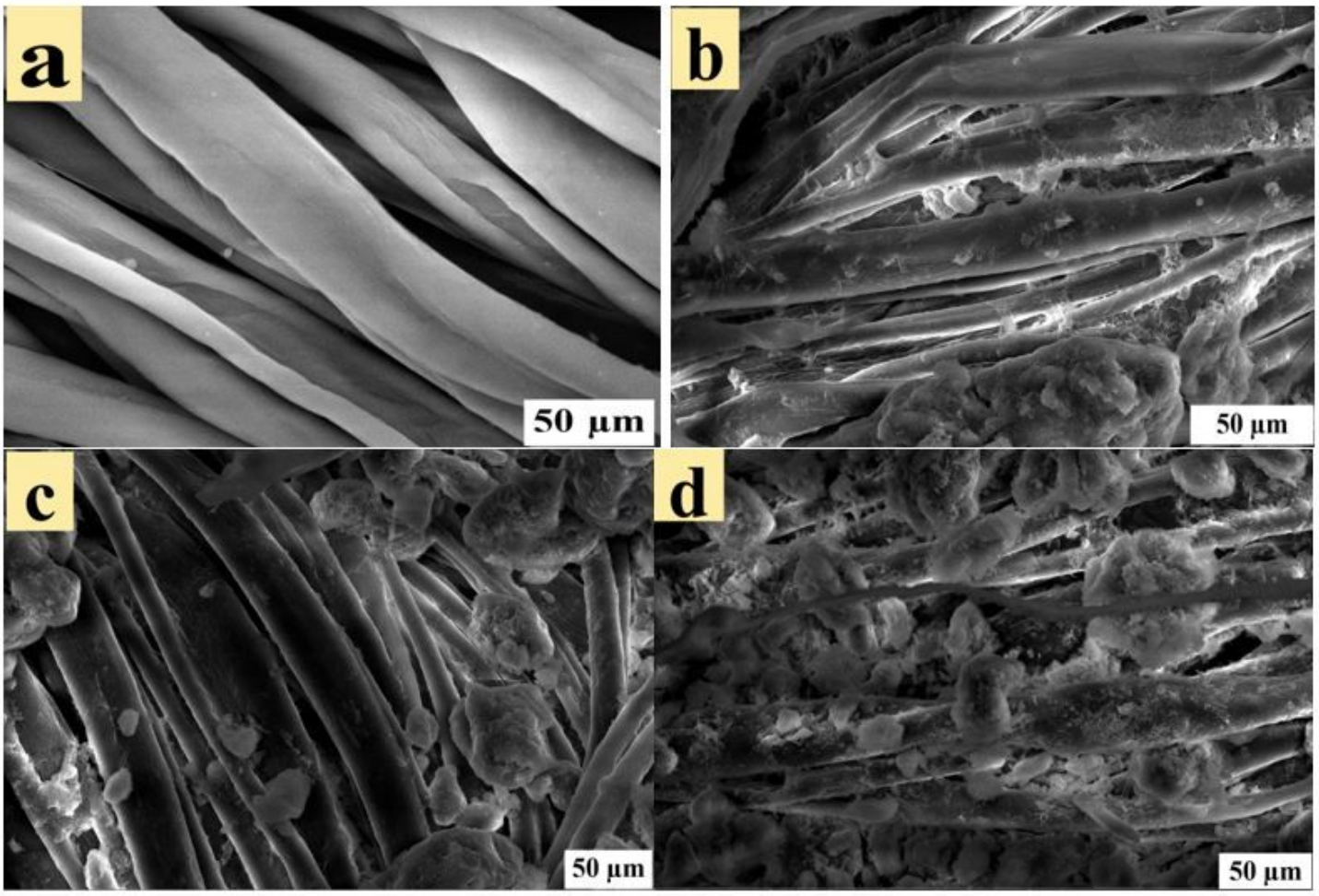

Figure 3

(a-d) The surface morphology of C0, C5, C7 and C8, respectively.

Figure 4

(a-i) Digital photographs for control and treated samples after vertical flammability test.

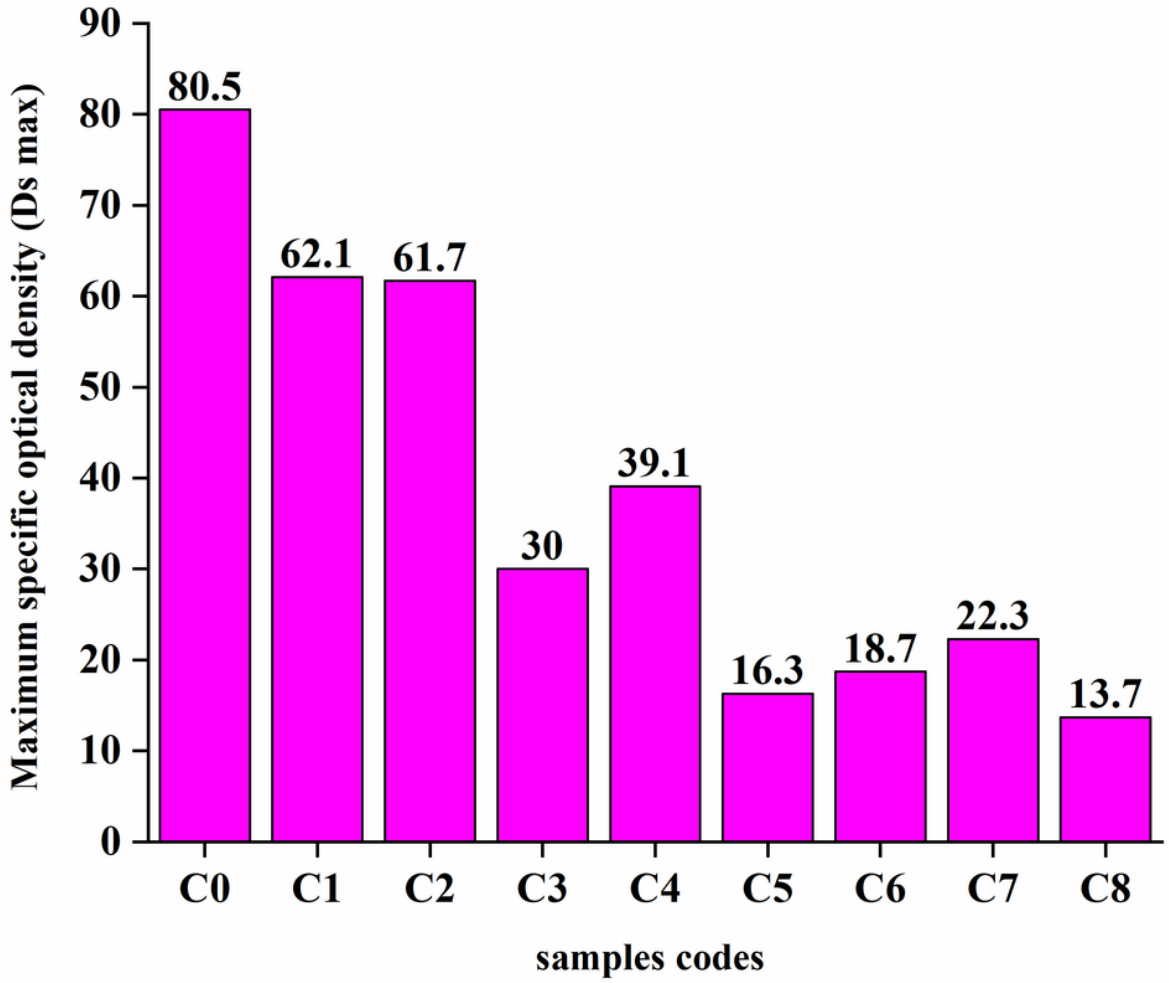

Figure 5

Values of maximum specific optical density (Dsmax) for control and coated samples.

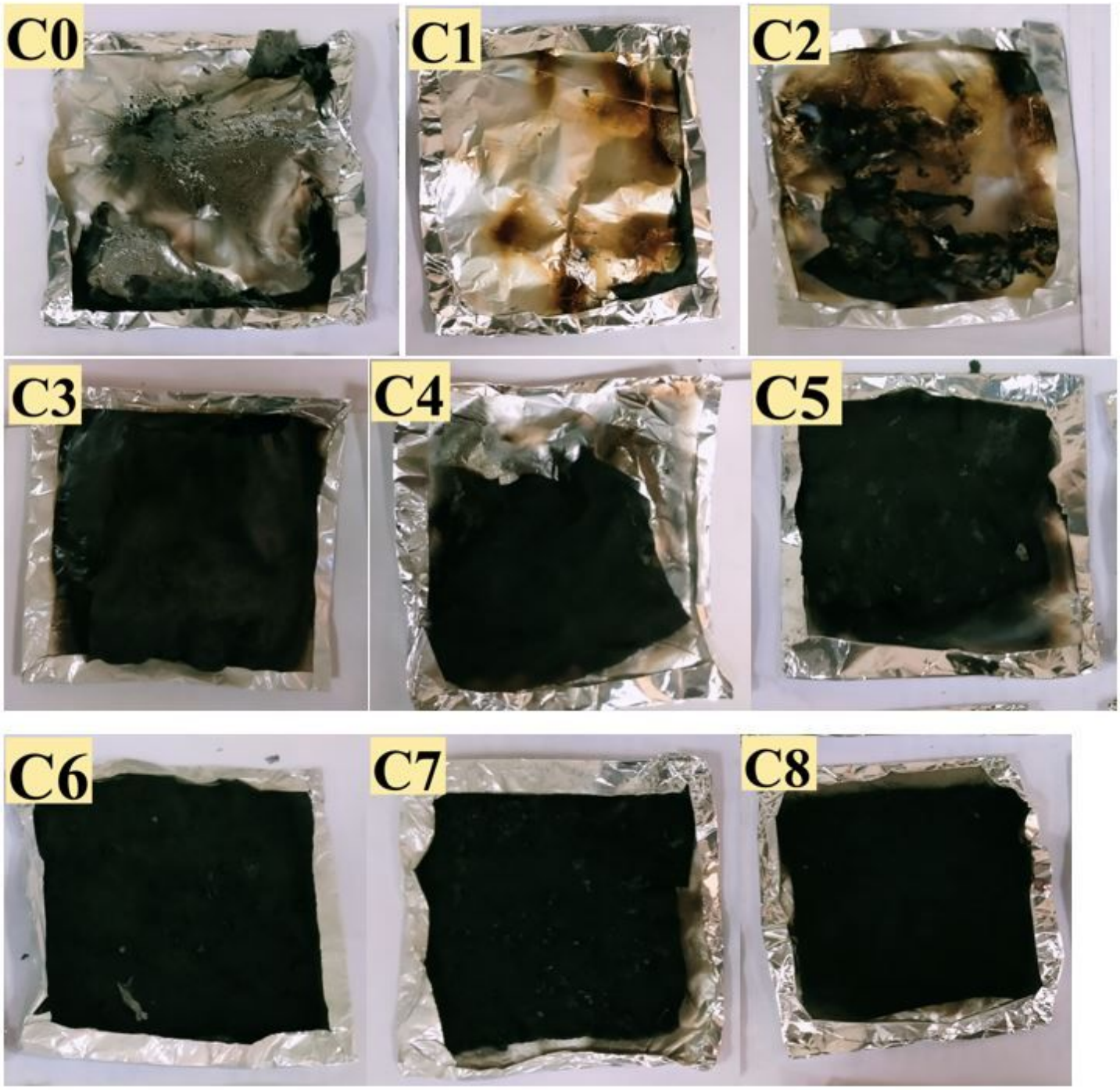

Figure 6

Digital photographs of control and treated samples after smoke density test.

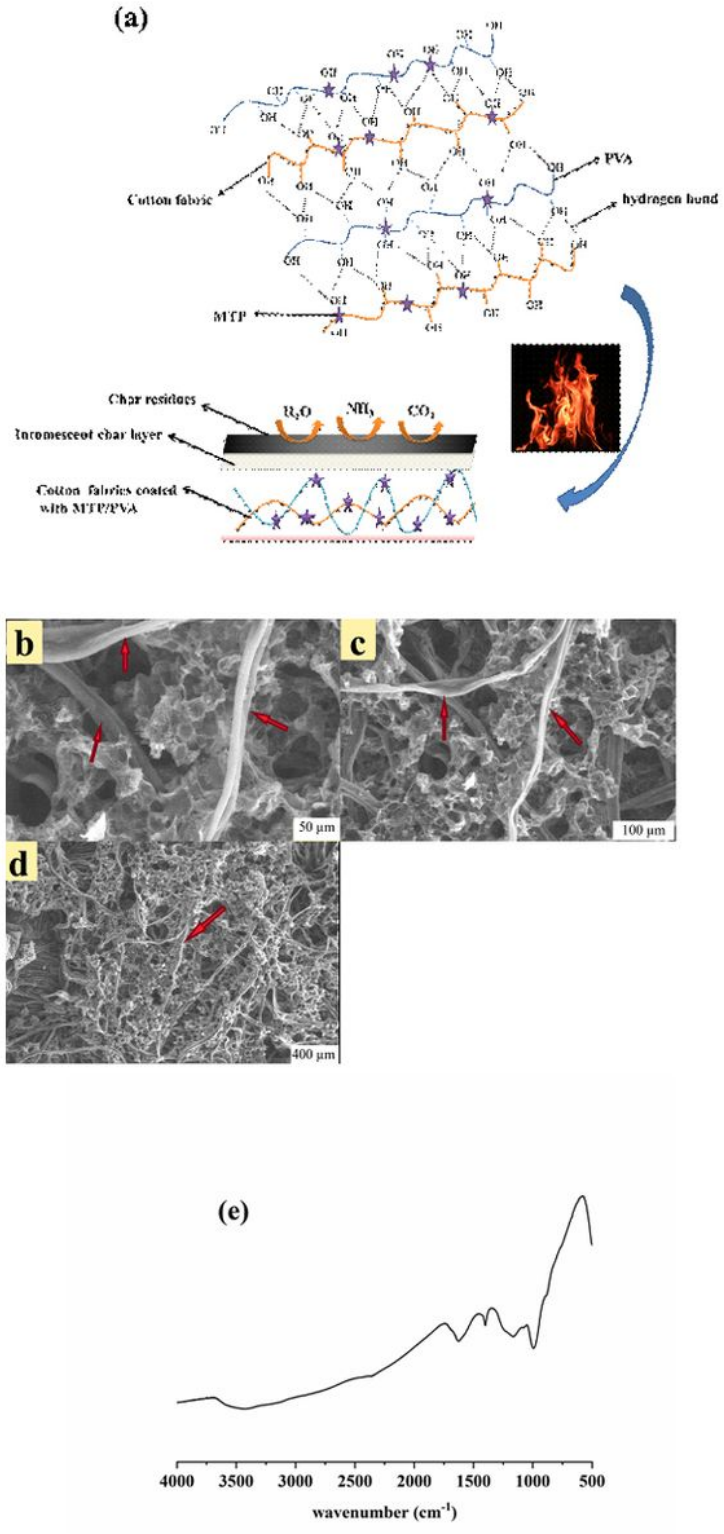

Figure 7

(a)Schematic illustration of a possible flame retardant mechanism for cotton fabrics treated with PVA/MTP during combustion; (b-d) SEM images for char residue formed after smoke density test of C7; (e) FTIR analysis of char residue of C7 after smoke density test.

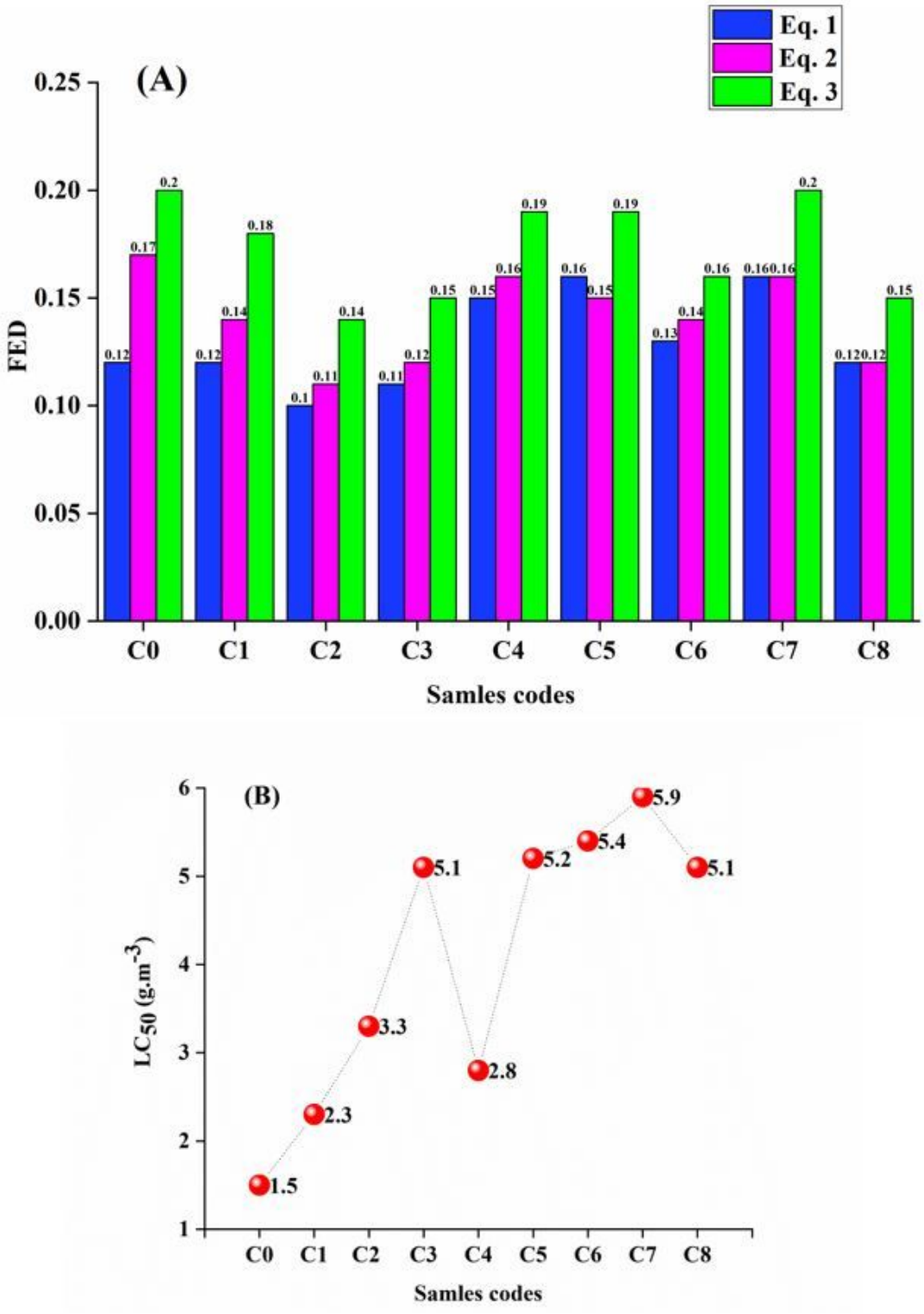

Figure 8

(A) FED and (B) LC50 values of control and treated samples.

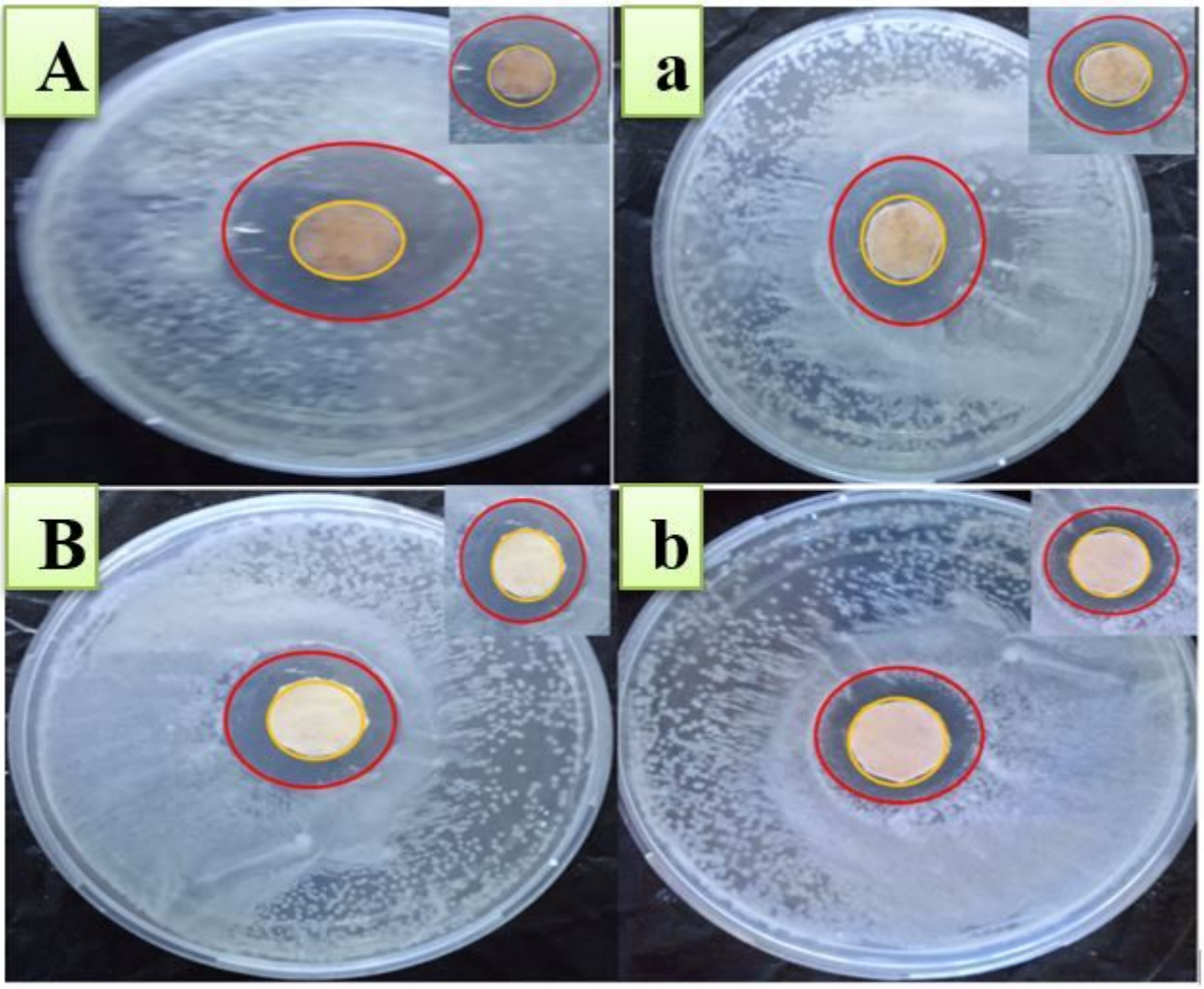

Figure 9

(A,B) digital photographs for zone of inhibition formed by S.aureus in C7 and C8 respectively; and (a,b) digital photographs for zone of inhibition formed by E. coli in C7 and C8, respectively.

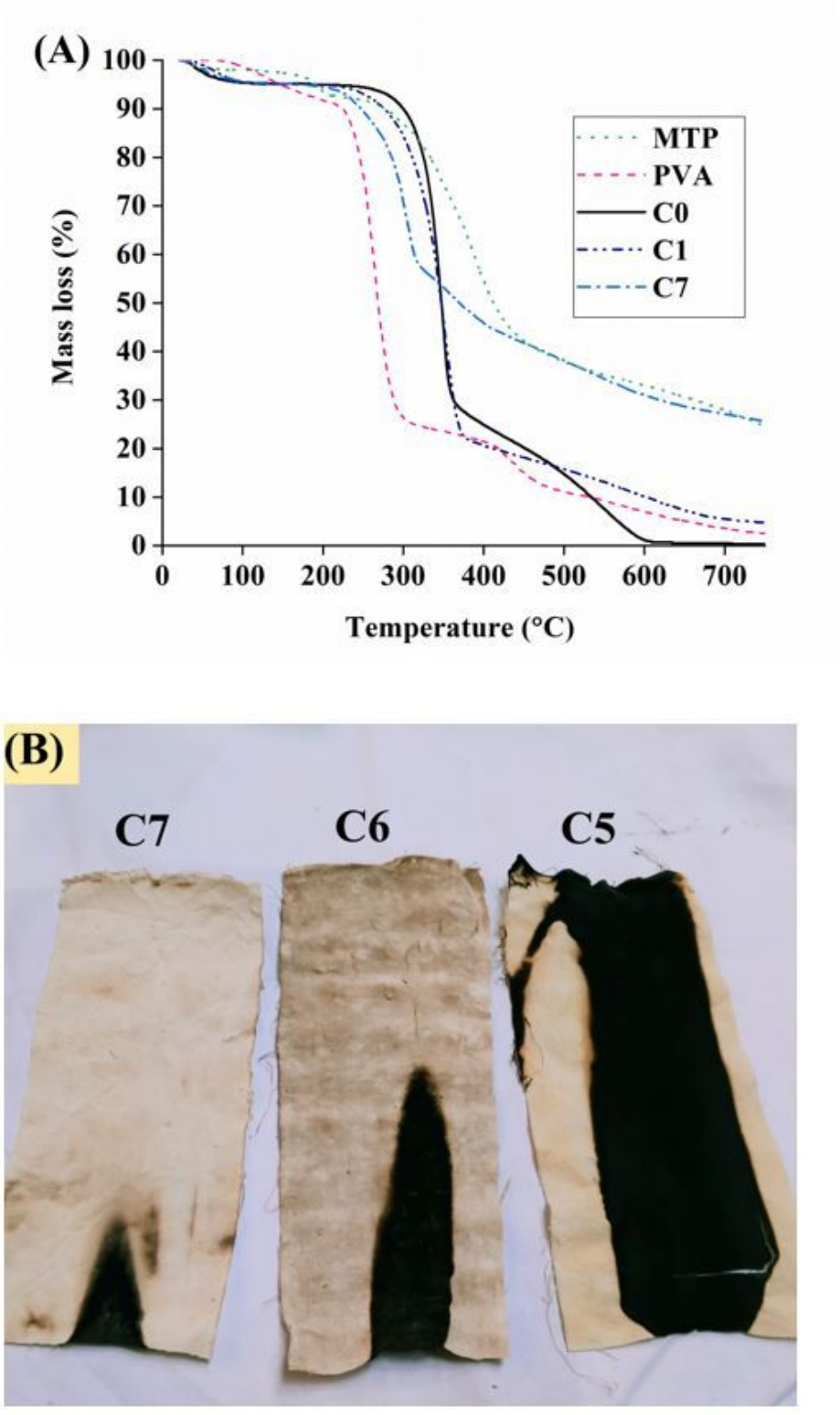

Figure 10

(A)TGA curves of MTP, PVA, C0, C1 and C7; (B) Digital photographs of C7, C6 and C5 samples after washing and performing vertical flammability test.