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ORIGINAL RESEARCH

Facile microwave assisted flame retardant treatment for cotton fabric using a biobased industrial byproduct: phytic acid

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Abstract A single-step, solvent-free microwave-assisted technique for flame retardant (FR) cotton fabric using a bio-based FR agent, phytic acid is presented. The effects of microwave power and irradiation time on FR characteristics of cotton are investigated. Self-extinguishing cotton fabric with char length of 79 mm and no afterflame is achieved within 4 min of 600 W microwave irradiation whereas a treatment time of as long as 45 min is needed in conventional heating method to achieve the same level of weight add-on or FR performance. The cotton fabric treated with phytic acid in the microwave also exhibits 90% retention of tear strength. Comprehensive characterization of the phytic acid treated cotton fabric using scanning electron microscope (SEM), elemental analysis, thermal gravimetric analysis (TGA), and microscale combustion calorimetry (MCC) correlated with reaction condition allowed the formulation of generalized guidelines applicable for microwave assisted cellulose phosphorylation. The FR mechanism study shows that phytic acid is covalently attached to cellulose and as an acid source, contributes to intumescent char formation during combustion.

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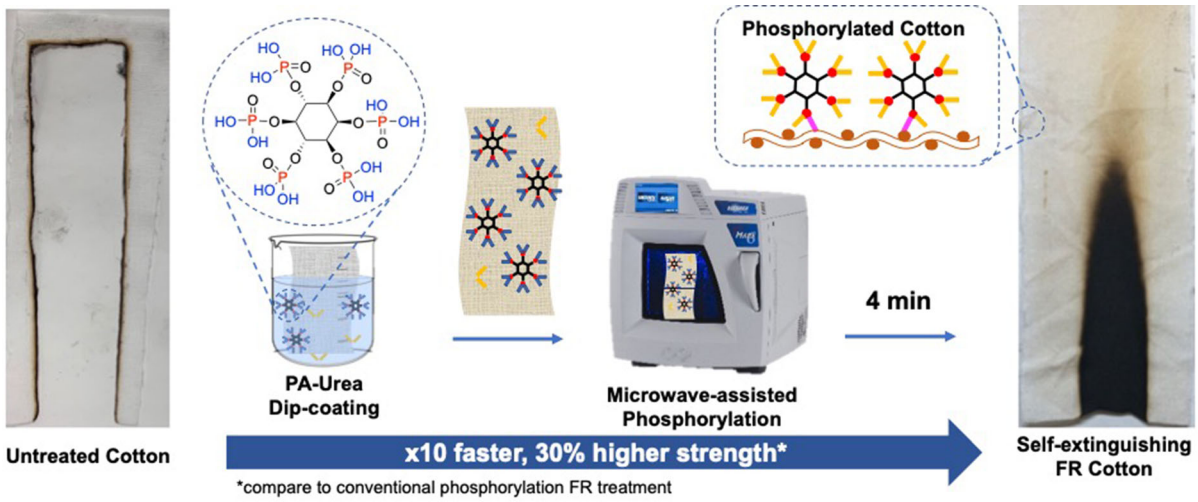
Graphic abstract



Keywords Flame retardant · Natural fiber · Green chemistry · Phytic acid · Microwave assisted treatment

Introduction

Cotton fabric is one of the most widely used biopolymer textiles in the world (Gao et al. 2015). Cotton is extensively utilized in consumer apparel, household upholstery, medical textile and military uniform owing to its excellent biocompatibility, biodegradability, breathability, hydrophilicity and softness. However, it is a flammable material and becomes even a greater fire risk when blended with melt dripping synthetic fibers such as polyamide and polyester because of the wick effect (Lewin 2013). This necessitates the development of cost-effective and eco-friendly flame retardant (FR) solutions and the corresponding treatment method for cotton fabric.

A variety of FR finishing agents based on metal hydroxides, phosphorus, nitrogen or halogen-containing compounds have been developed over the past few decades for cotton fabric. However, due to environmental issues, halogen-containing FR have been banned or limited from commercial use in many countries and territories over the past 30 years (Choudhury 2017). The demand for environmentally friendly FR is stimulating the researchers to explore efficient alternatives to halogen-containing FR. Metal hydroxides such as aluminum and magnesium hydroxide are environmentally friendly but not efficient as the loading required is as high as 45 wt% to make cotton fabric flame resistant (Kilinc 2013). Phosphorous and nitrogen containing FR are now widely used in the industry for cotton fabric as they are effective and environmentally benign. Traditional phosphorus or nitrogen containing FR such as Pyrovatex® and Proban® are efficient and durable since they are grafted onto cellulose through covalent bonds. However, the complexity of the treatment process, incompatibility with certain dyes or the release of toxic degradation products (such as formaldehyde) during combustion is limiting the application of these FR agents (Horrocks 2011; Zhang et al. 2016; Liu et al. 2018). Some of the bio-based phosphorus or nitrogen containing compounds such as deoxyribonucleic acid (DNA) (Carosio et al. 2013; Alongi et al. 2014), chitosan (El-Tahlawy 2008), protein (Bosco et al. 2013; Wang et al. 2014) and banana pseudostem sap (Basak et al. 2015a, b) have been investigated as renewable and environmentally friendly FR for cotton fabrics or cellulosic products. These bio-based FRs are promising solutions to address toxicity of non-renewable phosphorus or nitrogen containing FR although their durability of the FR performance when coated or functionalized on to fabric needs further investigation (Wang et al. 2018).

Phytic acid (PA) is the major storage form of phosphorus in most phosphorus-containing plants and one of the most abundant byproducts in the food industry (Tsao et al. 1997). As low toxicity, biocompatible and renewable organic phosphorus compound, PA has attracted a lot of attention in the field of flame retardant in recent years. Due to its high reactivity and acidic nature, PA and its derivative can easily react with cellulose (Nuessle et al. 1956; Feng et al. 2017; Liu et al. 2018) or bond with cationic polyelectrolytes, such as nitrogen-containing molecules by using sequential layer-by-layer deposition on cotton fabric (Laufer et al. 2012; Xia et al. 2018b). PA has also been studied as FR coating or melt-blended FR additives for other materials such as poly(lactic acid) (Cheng et al. 2016) and poly(propylene) (Zheng et al. 2015). The phosphorylation of cellulose by phytic acid can be carried out at an elevated temperature in the presence of urea. Urea is known to swell the fabric, prevent the cotton from decomposition and also act as a reaction medium. Therefore, an aqueous solution containing a certain amount of PA and urea is used for the functionalization of cotton fabric in the present work.

The pad-dry-cure process is one of the most commonly used methods to produce flame-retardant cotton fabric (Nawab 2016). The conventional phosphorylation heating step in the pad-dry-cure process involves keeping the wet fabric at a temperature greater than 150 °C for up to 45 min (Nuessle et al. 1956; Xia et al. 2017). This temperature results in loss of mechanical properties and discoloration of fabric due to the dehydration and decomposition of cellulose units under hot acidic conditions (Kang et al. 1998; Poon and Kan 2015, p. 2). In addition, this method is not ideal for industrial scale roll-to-roll process due to the heating time. Researchers have made progress on reducing the heating time to about 10 min using the novel FR based on ammonium phytate or chlorine-containing organophosphorus compounds (Liu et al. 2016; Feng et al. 2017). However, these treatment methods are multi-step methods that require synthesis and purification of FR compounds prior to the treatment of fabric.

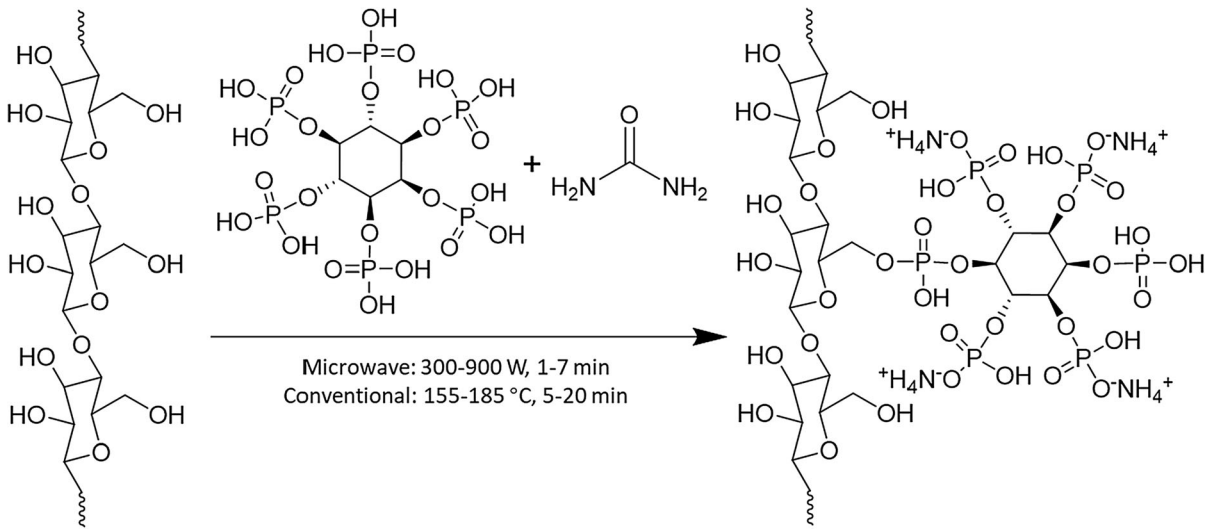
As an alternative to the conventional heating method, microwave irradiation is becoming a popular greener approach to accelerate reactions such as esterification, amidation and phosphorylation. Polar molecules are more susceptible to be activated selectively through microwave irradiation leading to a significant reduction in reaction time and improved yield as compared to conventional heating processes (Caddick 1995; Kuhnert 2002; Nüchter et al. 2004; Ku 2012; Mohd Aris et al. 2017). Many researchers have successfully demonstrated the microwave assisted treatment of cellulose for the application of antibacteria, filtration and hydrophobicity (Gospodinova et al. 2002; Zhong and Netravali 2016; Bhardwaj et al. 2017). However, only a few studies have attempted the microwave assisted FR functionalization of cotton (Chang et al. 2018).

Here we present the use of an industrial byproduct as FR for cotton enabled by microwave assisted phosphorylation. The treatment method was developed under the guidance of principles of green chemistry to prevent the material and energy waste caused by synthesis, separation, purification and solvent consumption. In accordance with the second principle of green chemistry, this process does not use solvents for the phosphorylation reaction thus minimizing waste. This microwave assisted synthesis also allows for a significant reduction in energy consumption and time in line with the fourth principle of green chemistry. The phosphorylation reaction of cotton is shown in Scheme 1. Instead of carrying out microwave-assisted FR treatment in the solution phase, cotton fabric is directly irradiated after being dipped in a solution containing PA and urea. The effects of microwave power and irradiation time on the physical appearance, thermal stability and flammability of cotton fabric are investigated.

Experimental

Materials

Solution of phytic acid (PA) (50% by weight in H_2O) was purchased from Sigma Aldrich. Urea (ACS Reagent Grade) was purchased from Millipore Sigma. Deionized (DI) water produced by EMD Millipore Elix® 3 water filter was used for the preparation of all the aqueous solutions. The 100% woven cotton fabric (122 g/m^2) was purchased from Robert Kaufman Co Inc. All the chemicals were used as received unless specified.



Scheme 1 Flame retardant treatment for cotton using PA and urea

Fabric sample preparation

Cotton fabric was cut into rectangular pieces with a dimension of 5 cm × 13 cm. The fabric was first boiled in a solution containing 5% sodium carbonate for 1 h to remove the impurities. The fabric was then washed in DI water (25 °C) for 15 min and in warm DI water (60 °C) for 15 min. The washing was repeated one more time followed by drying in a hot air oven at 80 °C overnight. The weight of the dried fabric sample was recorded as the weight before any FR treatment.

FR treatment of cotton fabric by microwave irradiation

Urea solution was prepared by adding 8 mL DI water in a beaker containing 3.2 g urea. After the complete dissolution of urea, 2 mL PA solution was added to the beaker. This solution was allowed to equilibrate at room temperature with magnetic stirring for 30 min. Two pieces of fabric were weighed and then dip-coated in the treatment solution. The wet pick-up of the fabric after dip coating treatment was about 300–350%. The two pieces of dip-coated fabric were wrapped around a 400 mL beaker and placed inside a MARS 6 (CEM Corporation) microwave oven. The fabric was then exposed to microwave radiation at designated power for various amounts of time. After the first exposure to microwave radiation, the beaker with the fabric sample is flipped (to avoid overheating of the fabric) and treated again at the same power and time setting. The total time of microwave exposure to both sides of the fabric was taken as the total irradiation time. As a control, two pieces of cotton fabric samples were dip-coated in DI water (without any FR reagents) followed by microwave treatment at 600 W for 4 min.

All treated cotton fabric samples were rinsed in DI (25 °C) with magnetic stirring for 15 min and in warm DI water (60 °C) with magnetic stirring for 15 min. The fabric samples were washed one more time by the same procedure and then dried in an oven at 80 °C overnight.

FR treatment of cotton fabric by conventional heating method

For comparison purposes, the phosphorylation reaction was also carried out using conventional heating in a convection hot air oven. Cotton fabric samples were dip-coated in the treatment solution containing urea and PA (as mentioned in the microwave treatment method). The dip-coated fabric samples were then treated in a convection oven (DN-63, Baxter International Inc.) at various temperatures (155 °C, 170 °C, and 185 °C). The heating time was also varied for 5, 10, 20, and 45 min. All the treated cotton fabric samples were rinsed in DI water (25 °C) with magnetic stirring for 15 min followed by rinsing in warm DI water (60 °C) with magnetic stirring for 15 min.

The fabric samples were washed again by the same procedure and then dried in an oven at 80 °C overnight. The weight add-on (WA) was calculated using the following formula:

$$WA = \frac{W_1 - W_0}{W_0} \times 100\% \quad (1)$$

where W_0 and W_1 represent the weight (after drying) of cotton fabric before and after treatment, respectively.

Structural characterization

Fourier-transform infrared (FTIR) absorption spectra were obtained using an FTIR spectrometer (Nicolet 4700, Thermo Electron Corporation) with a smart orbit attenuated total reflectance (ATR) accessory. The samples were scanned 32 times over a range of 4000–400 cm^{-1} at the resolution of 4 cm^{-1}.

Thermal decomposition study using thermogravimetric analysis

Thermal stability of fabric was studied using thermogravimetric analysis (TGA) carried out on a Discovery TGA 5500 (TA Instruments) under 30 mL/min nitrogen purge. Approximately 5 mg of each material was tested at a heating rate of 20 °C/min from room temperature to 600 °C.

Microscale combustion calorimetry study

Microscale combustion calorimetry (MCC), also known as pyrolysis combustion flow calorimetry (PCFC, Fire Testing Technology Inc.) was used to characterize the heat release characteristics of fabric samples according to ASTM D7309. Approximately 3 mg of sample were loaded into pyrolysis chamber in which the sample was heated from 150 °C to 750 °C at a heating rate of 1 °C/s under the purge of nitrogen at 80 mL/min. The decomposition products were completely oxidized in the combustion chamber at 900 °C under the purge comprising 20 mL/min oxygen and 80 mL/min nitrogen. The oxygen consumption was recorded and used in the calculation of heat release rate (HRR), total heat release (THR) and heat release capacity (HRC).

Cone calorimetry and smoke density analysis

The cone calorimetry analysis was carried out on a dual cone calorimeter (FTT, UK) at heat flux of 50 kW/m^2 with an exhaust flow of 24 L/s according to ASTM E1354-16. Three samples were tested for each type of fabric and the average values of time to ignite (TTI), PHRR, THR, HRC and total smoke release (TSR) were reported.

Flammability test

The flammability of treated cotton fabrics were studied using a modified vertical flame test (Xia et al. 2018a; Yu et al. 2020). A Bunsen burner supplied with in-house natural gas was used as the ignition source. The sample holder for testing fabric had an inside dimension of 38 mm wide and 127 mm long. The flame height was adjusted to 38 mm from the top of the burner to the tip of the flame. The fabric sample was placed 19 mm above the burner. The fabric sample was exposed to ignition flame for 12 s. The burning process was captured by a video camera. The dripping, melting, afterflame time and afterglow time were recorded. The distance from the bottom of the fabric sample to the farthest point of burning was measured after the flame test and noted as char length.

The limiting oxygen index (LOI) of the pristine and treated fabric samples was measured using OI-1 (Govmark, USA) according to ASTM D2863-2000.

Surface morphology and combustion residue analysis

The morphology of the fabric samples was studied using a scanning electron microscope (SEM, JSM-6390, JEOL, Japan) with a 10 kV beam voltage and a 7–9 mm working distance. The pristine fabric and the fabric treated by conventional or microwave assisted technique were imaged in the SEM before and after the vertical flame test. In the SEM, energy-dispersive x-ray spectroscopy (EDX) was also performed on fabric samples before and after the vertical flame test.

Tear strength test

The tear strength of the fabric samples was measured using Elmendorf ProTear Tester (Thwing-Albert Instrument Co., USA) according to ASTM D1424-09

(ASTM International). A pendulum of 1600 g was used in the tear test. The tear strength was measured in both warp (length) direction and the weft (width) direction. The average tear strength of 5 specimens in each direction was reported.

Elemental composition study

The elemental composition of cotton fabric treated by microwave irradiation (600 W, 4 min) was analyzed by Galbraith Laboratories Inc (GLI) using a series of characterization methods. Phosphorus content was analyzed using ICP-OES (Optima 5300, PerkinElmer). Oxygen content was measured using oxygen modified elemental analyzer (FlashEA 1112, Thermo Finnigan LLC, USA). Carbon, hydrogen and nitrogen content was analyzed using elemental analyzer (CHNS/O Analyzer 2400 Series II, PerkinElmer). The P/O/C/N/H compositions are reported in percentage by weight.

Laundry durability study

The microwave treated fabric samples were subjected to laundry cycles according to AATCC test method 135–2003. The durability of the FR performance of the treated fabrics was studied after laundry cycles. The elemental composition of the fabrics (before and after laundry) was evaluated by using a K-Alpha + (Thermo Scientific) X-ray photoelectron spectrometer (XPS).

Results and discussions

In order to validate the efficacy of this greener solvent free microwave assisted phosphorylation of cotton using phytic acid, this reaction is compared with the conventional heating process of modification. A systematic study of both approaches along with results of characterization of the products is described below.

Conventional heating treatment

Reaction temperature and time play vital roles in the phosphorylation of cotton fabric. The phosphorylation reaction is only effective at temperatures higher than 155 °C. But the amount of heat introduced to cotton fabric can cause significant discoloration and loss of mechanical properties of the fabric samples. The phosphorylation using phytic acid and the conventional heating process was carried out at different heating conditions as shown in Table S1. After phosphorylation, all fabric samples treated in the convection hot air oven appeared yellow (Figure S1 in supplementary information). The whiteness indices of conventionally heated fabric are listed in Table S2. Both temperature and time in this treatment exhibited an adverse effect on the whiteness of the cotton fabric. In the case of fabric samples treated at 170 °C and 185 °C for 45 min, the fabric turned grey and dark brown, respectively indicating carbonization caused by heat. The fabric sample treated at 155 °C exhibited the least carbonization as the least discoloration was observed on these fabric samples. It is clear that the conventional heating process caused unfavorable heat induced degradation and carbonization of cotton fabric.

According to the previous literature on phosphorylated cotton, a minimum weight add-on of 9% is normally required to achieve sufficient flame resistance depending on the phosphorus content and composition of the FR treatment agent (Weil and Levchik 2008; Ghanadpour et al. 2015; Horrocks and Anand 2015). As expected, a higher weight add-on of PA was observed on the fabric samples treated at higher reaction temperature or longer reaction time (as shown in Fig. 1a). In this study, a minimum of 6% weight add-on of PA was required to prevent the fabric sample from burning completely to its full length (127 mm) as observed on the sample treated at 185 °C for 5 min (shown in Fig. 1b).

The char length of the fabric sample describes the length of the fabric that was burnt during the vertical flame test. Fabric samples burnt to their full length (127 mm) are considered non-flame resistant in this modified vertical flame test. Samples with shorter char length exhibited better flame resistance. The char lengths of PA treated cotton fabric using the conventional heating process are shown in Fig. 1b and Table S1. The cotton fabric treated at 185 °C exhibited the best flame resistance. It is clear that higher treatment temperature expedited the phosphorylation reaction and led to improved flame resistance of the treated cotton fabric. With longer reaction times the fabric exhibited shorter char lengths with minimum values of 60 mm, 67 mm and 73 mm when samples were treated at a temperature of 185 °C, 170 °C and

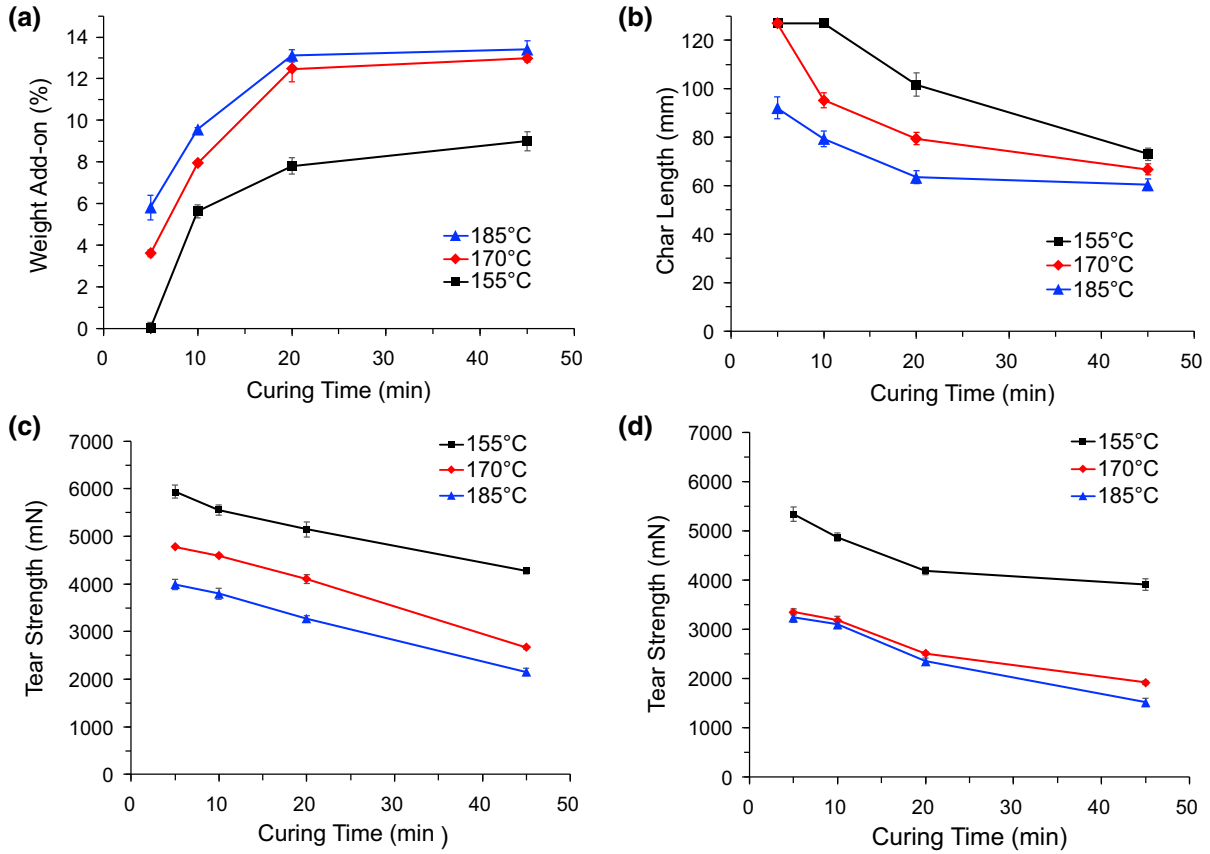


Fig. 1 **a** weight add-on, **b** char length, **c** tear strength in warp direction, **d** tear strength in the weft direction of cotton fabric treated at different conventional heating condition

155 °C respectively. However, the improvement of flame resistance by prolonging the reaction time levelled off after a certain point. This is evident from the minimal difference between the char length of cotton fabric treated at 185 °C for 20 min (64 mm) and that of cotton fabric treated at the same temperature for 45 min (60 mm).

Cellulose based fabrics exhibit loss of mechanical properties under acidic conditions, especially at high temperatures. Excessive heat during the conventional heating process could hydrolyze or carbonize the cellulose and break the hydrogen bonds between cellulose chains and hence cause irreversible loss of mechanical properties, especially tear strength (Kang et al. 1998; Poon and Kan 2015, p. 2). The untreated cotton fabric exhibited a tear strength of 7036 mN in the warp direction and 6272 mN in the weft direction. The tear strength (in both directions) of phosphorylated cotton fabric (treated in a convection oven) decreases gradually as a function of treatment temperature or time as shown in Fig. 1c, d. Although the fabric samples treated at higher temperatures tend to exhibit better flame resistance with similar reaction times, they have shown disproportionally lower tear strength. Considering the minimum char length achieved in the vertical flame test, fabric samples phosphorylated at all temperatures reached a limit at about 60–70 mm, the fabric samples treated at 155 °C for 45 min exhibited a good balance of flame retardant characteristics and retention of mechanical properties. Thus, in the present study, treatment carried in the convection oven at 155 °C for 45 min is noted as the conventional heating method. The cotton fabrics treated by conventional heating method are noted as conventional treated cotton (CTC). The properties of the samples prepared by the conventional heating method are used as a reference for the comparison of phosphorylation carried out using the microwave.

Effect of microwave treatment conditions on weight add-on

The treatment conditions including microwave output and irradiation time were studied to find the optimized weight add-on of the fabric with good FR performance yet high retention of mechanical properties and appearance characteristics. The fabric samples treated by microwave irradiation with a power lower than 750 W or irradiation time of less than 5 min appeared white. Due to the non-uniform distribution of microwave energy hot spots and discoloration were observed on samples treated for 4 min at microwave output of 750 W and 900 W (P4 and P5). Slightly discoloration and hot spots were observed on samples treated at 600 W for 5 min or longer (T5, T6 and T7). Hot spots can be reduced by flipping the sample after exposure at regular intervals or introducing a specialized chamber/microwave guide for fabric treatment (Katovic 2010).

The weight add-on of the cotton fabric treated under different conditions of microwave irradiation is shown in Table 1. The weight add-on increases with higher output or longer duration of microwave irradiation (as shown in Fig. S2). Fabric treated with 600 W of microwave irradiation for 4 min (P3) showed the same weight add-on as the cotton fabric treated in the convection oven at 155 °C for 45 min. It is obvious (in Fig. S3) that microwave treatment is significantly more efficient than the conventional heating method. There are two main reasons for the high efficiency of microwave irradiation. The dielectric heating of microwave is a more efficient heating method that accelerates the phosphorylation reaction by increasing of the diffusion rate of phytic acid/urea into cellulose. And due to the exclusively high absorption of microwave radiation, water (a byproduct of phosphorylation) can be rapidly vaporized and removed from the reaction system resulting in a quicker reaction with a higher yield.

Characterization of treated cotton fabrics

To confirm that the weight add-on was the result of phosphorylation reaction, the fabric samples treated using convection and microwave oven were analyzed by FTIR. Corresponding spectra are presented in Fig. 2a, b. Cotton fabrics subjected to microwave without the reactants (control) exhibit characteristic absorption peaks from C–O–C groups between glucose unit at 1160 cm^{-1} and 1106 cm^{-1} (Suflet et al. 2006). In the spectra of both conventionally heated and microwave treated samples, a new absorption peak at 1704 cm^{-1} attributed to stretching of C=O group was observed. The C=O group resulted from the hydrolysis (depolymerization) of cotton and the formation of D-glucose in open chains forms (formaldehyde) (Feng et al. 2017). The hydrolysis and ring opening process can significantly affect the mechanical properties and appearance of the fabric. When comparing the fabric treated by conventional heating and microwave, all the microwave treated fabric (except P4 and P5) exhibited much lower intensity on the absorption peak at 1704 cm^{-1} which indicated that

Table 1 Weight add-on and char length of microwave treated fabric

Sample	Power (W)	Total time (min)	Weight add-on (%)	Char length (mm)
P1	300	4	0.4	127
P2	450	4	3.3	127
P3	600	4	9.2	79
P4	750	4	9.9	73
P5	900	4	12.8	70
T1	600	1	0.0	127
T2	600	2	2.7	127
T3	600	3	6.0	98
T4 (P3)	600	4	9.2	79
T5	600	5	10.0	70
T6	600	6	12.0	70
T7	600	7	12.2	70
Conventional	N/A	45	9.0	73

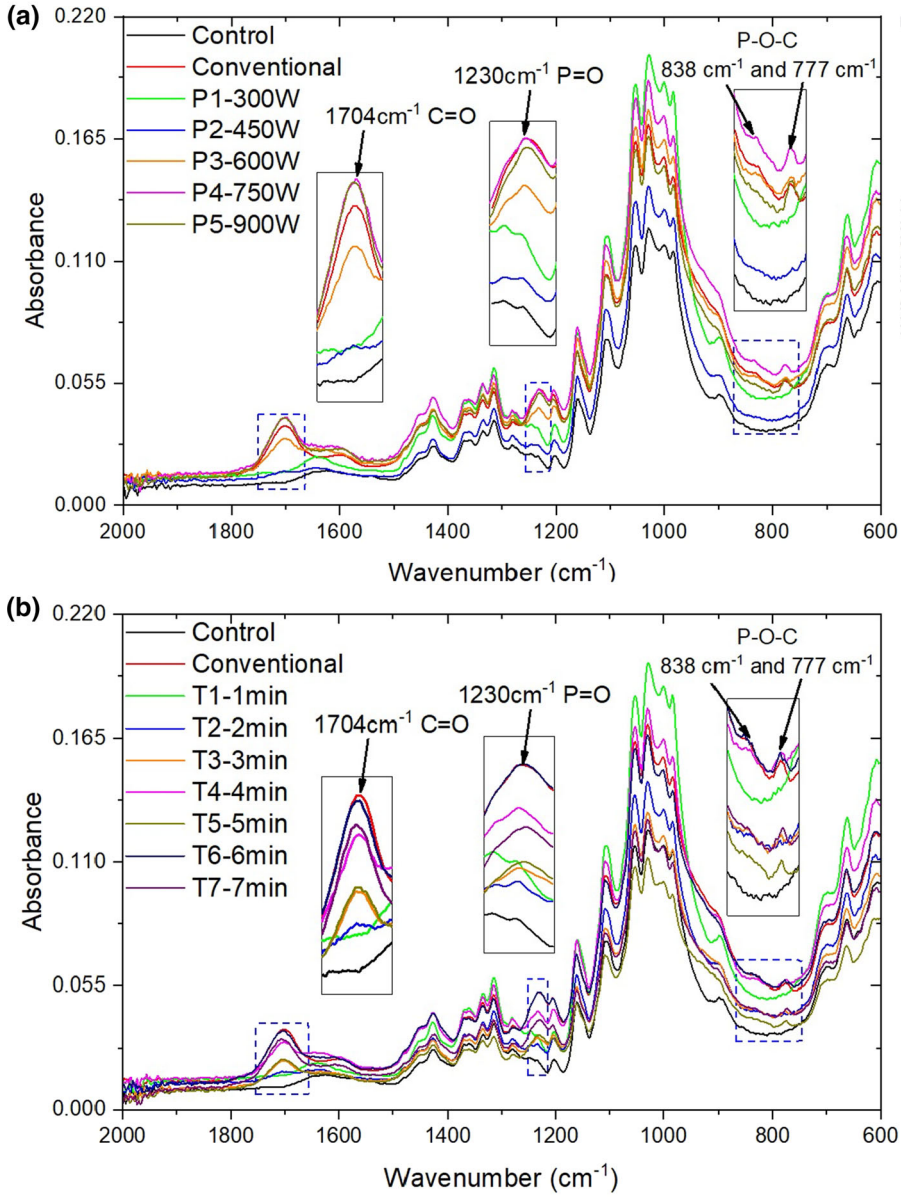


Fig. 2 FTIR spectra of fabric prepared at: **a** different microwave power, **b** different irradiation time

the microwave treatment can prevent hydrolysis at appropriate power settings.

In the case of P4, P5, T6, T7 and conventionally heated fabric, the absorbance at 1704 cm^{-1} is significantly higher than that of the fabrics treated at other conditions indicating extensive hydrolysis and oxidation. The hydrolysis and oxidation resulted in the discoloration and burning spots in the case of P4, P5, T6, T7 and in the case of fabric treated in a convection oven. The phosphorylation of cotton fabric is confirmed by the new absorption peaks at 1230 cm^{-1} and 838 cm^{-1}/777 cm^{-1}, which represent the stretching of P=O and P–O–C groups respectively (Suflet et al. 2006). Although FTIR is a semi-quantitative characterization method, the relative absorbance of the three characteristic bands still indicated that the degree of phosphorylation increases with higher microwave output or longer irradiation time. Only a slight increase in the degree of phosphorylation was observed when the microwave power is

greater than 750 W or when the irradiation time is longer than 4 min. This indicated that the degree of phosphorylation started to level off when microwave power or irradiation time exceed 750 W or 4 min respectively.

To get the elemental composition of the fabric phosphorylated under microwave irradiation, ICP-OES and elemental analysis was carried out on P3 (600 W, 4 min). The elemental composition of microwave phosphorylated cotton, P3 is listed in Table 2. Pure cotton does not exhibit a detectable amount of phosphorus. The sample exhibited a P content of 2.10% by weight and a C content of 38.61% by weight. Based on this ratio the extent of functionalization can be deduced. For every 47 repeating units of cellulose, there are 6 phosphorus atoms (1 phytic acid molecule) attached yielding a degree of functionalization (number of phytic acid attached to each cellulose repeating unit) of 2.15%. As urea decomposes and reacts with phytic acid during phosphorylation reaction, some nitrogen moieties react with phytic acid and remain in the treated fabric after washing and rinsing as evidenced by the 1.67% N content (Nuessle et al. 1956; Gospodinova et al. 2002; Blanchard and Graves 2003). The compounds containing phosphorus and nitrogen have been previously reported to be efficient flame retardant with synergistic effect for cellulosic fibers (Gaan and Sun 2007). There are a few possible structures of nitrogen moieties presented in phosphorylated cotton depending on the reaction temperature (Nuessle et al. 1956). However, the N/P ratio of 1.76 indicates that there are 10.5 nitrogen atoms in each phytic acid molecule. Since substitution of hydroxyl groups in cellulose caused by phosphorylation normally occurs at C-6 position, with the atomic ratio of elements in treated cotton it is possible to point out the two most plausible structures formed during phosphorylation as shown in Fig. 3 (Gospodinova et al. 2002; Liu et al. 2018). Phytic acid could react with multiple primary -OH groups on different cellulosic chains and then form crosslinked structure depending on steric hindrance. A similar crosslinked structure has been reported previously from the phosphorylation reaction of cellulose using phytic acid (Feng et al. 2017; Liu et al. 2018).

Table 2 Elemental composition of microwave treated cotton

Elements	Mass %	Molar %*
C	39.08%	26.65%
H	5.91%	48.04%
O	46.44%	23.78%
P	2.10%	0.56%
N	1.67%	0.98%

*Relative molar percent calculated within C/H/O/P/N. Elements not surveyed are excluded

FR properties

The control cotton fabrics burnt completely in the vertical flame test with no char left (as shown in Fig. S4 in supplementary information). Fabric treated by conventional heating method exhibited an average char length of 73 mm. In the study of the correlation between microwave power and char length, cotton fabrics treated in the microwave oven at a power level lower than 600 W burnt out completely in the vertical flame test with 127 mm ash residue (char length). Samples treated at 600 W or higher were self - extinguishing after the removal of the ignition source. Sample P3, P4 and P5 showed reduced char length (79, 73 and 70 mm respectively) which indicates improved flame resistance due to a higher degree of phosphorylation as shown in Table 1. However, the burn marks and non-uniform phosphorylation on P4 and P5 suggests that hot spots in the microwave treatment become more common at higher power levels.

In the study of correlation of microwave irradiation time and char length, T1 and T2 are the only two samples that burnt out completely (as shown in Fig. S5 in supplementary information) due to insufficient weight add-on. Starting from sample T3, all the fabrics samples treated by 5 min or longer microwave irradiation exhibited self-extinguishing behavior. As shown in Fig. 4b, the char length decreases gradually with increasing irradiation time between 2 and 5 min. The exposure of cotton fabrics to microwave irradiation (600 W) for longer than 5 min is not preferred since no significant improvement of FR performance is observed. A small amount of discoloration caused by non-uniform phosphorylation is also observed on T6 and T7 due to the hydrolysis/oxidation caused by the longer duration of microwave irradiation. However, compared to microwave irradiation time, the output seems to be a more dominating factor on hot spots caused by non-uniform phosphorylation.

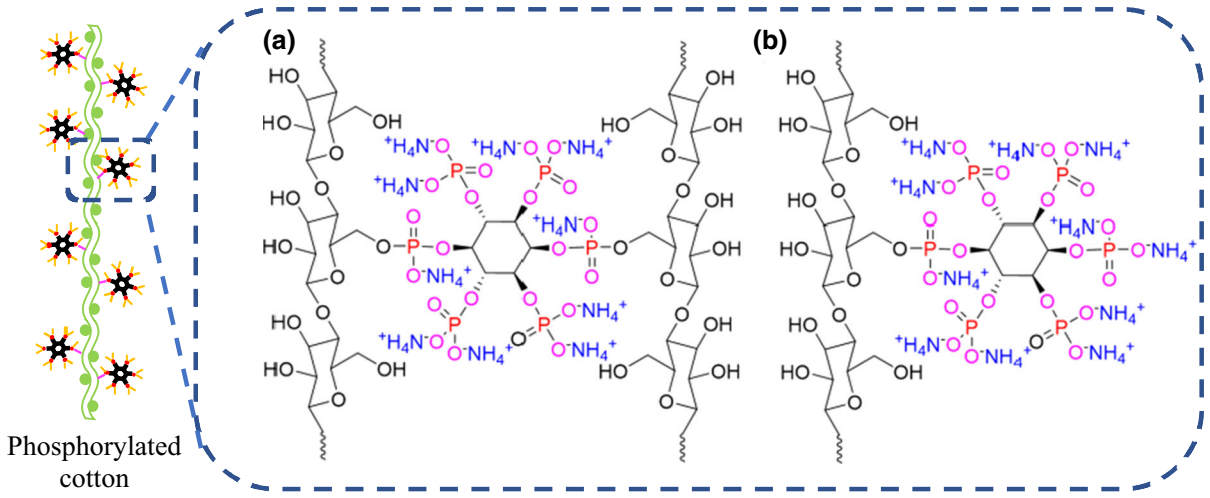


Fig. 3 Possible structure of phytic acid moieties in microwave treated cotton based on elemental composition: **a** $C_6H_{46}O_{22}P_6N_{10}$, **b** $C_6H_{50}O_{23}P_6N_{11}$

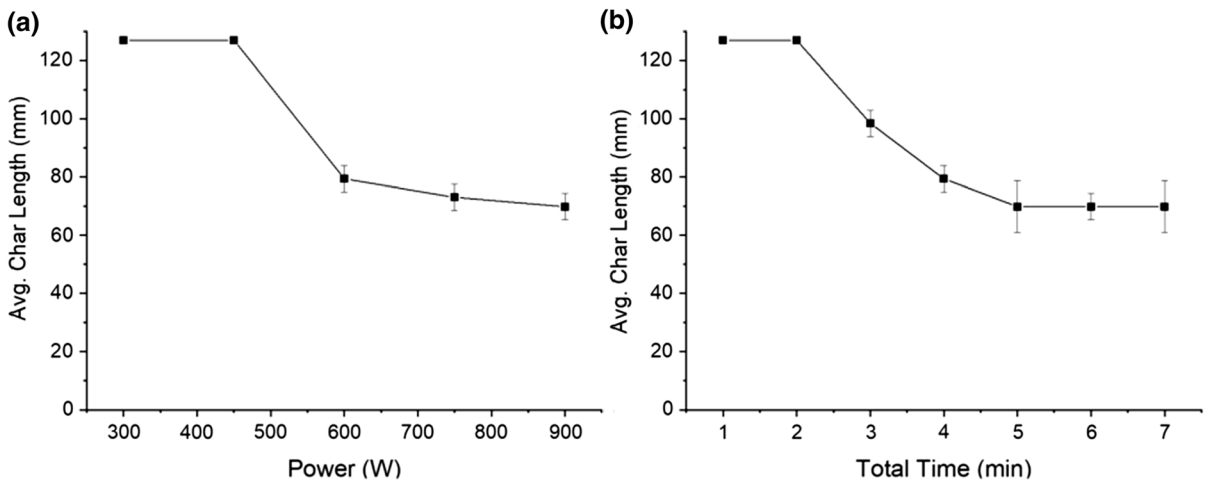


Fig. 4 Effect of **a** microwave power, **b** irradiation time on char length

The flammability of the cotton fabrics was also studied by the LOI test. The LOI refers to the minimum concentration of oxygen that is required to sustain the candle-like burning of polymers. An LOI value of 27–28% is generally required to achieve self-extinguishing behavior (Horrocks et al. 1988). To compare the microwave treatment with the conventional heating method, cotton fabrics treated by 600 W microwave for 4 min (MTC) were tested in comparison to the fabrics treated at 155 °C for 45 min (CTC). The LOI values are shown in Table 3. After grafting with phytic acid, both MTC and CTC exhibit excellent LOI values, increasing from 18.5% to 30.5% and 31.0% respectively. Due to the similar weight add-on and degree of phosphorylation as shown in Fig. 2, the two types of the treated fabric showed almost identical burning behavior in LOI and vertical flame test. Both types of treatment methods imparted flame retardancy to cotton fabric.

Thermal stability

Thermogravimetric analysis was used to evaluate the thermal stability of the control cotton fabric sample. The control cotton fabric sample exhibited a single-stage decomposition with a T_{max} of 386 °C and char

Table 3 LOI and vertical flame test of cotton fabric treated by different methods

Treatment method	WA (%)	LOI	Char length (mm)	Afterflame (s)
Untreated cotton	0	18.5	≥ 127	12
conventional (155 °C, 45 min)	9.0	30.5	73	0
Microwave (600 W, 4 min)	9.2	31.0	79	0

residue of 6.5% at 600 °C as shown in Fig. 5. The decomposition of control cotton fabric is attributed to the depolymerization of cellulose molecules (Davies et al. 2005). For the cotton fabric treated by conventional heating with phytic acid, the maximum weight loss occurred at 279 °C leaving behind 37.5% by weight residue at 600 °C. The reduced T_{max} and improved char residue are associated with the phytic acid catalyzed carbonization of cellulose indicating that the phytic acid can be an excellent flame retardant candidate for cotton fabric (Liu et al. 2018).

Samples P1–P5 were treated with increasing microwave power. The decomposition peaks shifted to a lower temperature region with increasing char yield. This indicates that the flame retardancy of phytic acid treated cotton can be improved by using higher microwave power in the treatment. The detailed data can be found in Table S3. Similar results were observed for the fabric samples treated for increasing microwave irradiation time as shown in Fig. 5b. The improved flame retardancy could be correlated to the phytic acid catalyzed dehydration and carbonization resulting from the higher degree of phosphorylation as confirmed in FTIR analysis.

During the decomposition process, the phosphorylated cellulose forms a significantly higher amount of carbonaceous and polyphosphate residue, serving as a physical barrier insulating the combustible species underneath from oxygen and heat. This insulating barrier results in higher char residue and higher flame resistance (Xia et al. 2017). Upon comparison of the phosphorylation carried using conventional heating method versus microwave assisted phosphorylation, it is evident that the same level of char residue and flame retardant characteristics can be easily achieved by microwave treatment with a much shorter reaction time (as short as 4 min at 600 W).

Microscale combustion and cone calorimetry

MCC is a fast-screening tool that is often employed in evaluating the heat release properties and predicting the flammability of polymeric material in milligram scale. The instrument measures the heat release rate based on oxygen consumption during the combustion of polymeric materials. The heat release characteristics, such as the heat release capacity (HRC), peak heat release rate (pHRR) and total heat release (THR), are derived from heat release rate, which can be correlated to the flammability of polymeric materials (Lyon and Walters 2004). A typical polymeric material with HRC lower than 200 J/g-K usually self-extinguishes

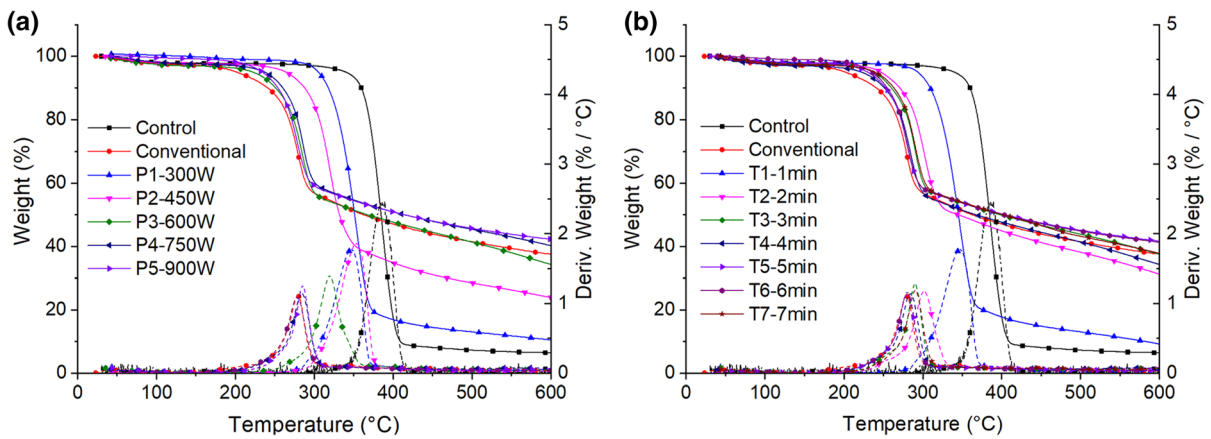


Fig. 5 Thermogravimetric analysis of fabric prepared at: **a** different microwave power, **b** different irradiation time

and is rated as V-0 or higher in UL-94 vertical flammability test. In order to further investigate the flame resistance of treated fabric samples, and to compare the conventional heating and microwave treatment method, MCC was used. The results from cotton samples treated under various microwave power and irradiation time are summarized in Tables S4 and S5, respectively. A typical heat release rate curve with moderate HRC, pHRR and THR that match well with the untreated cotton sample was observed on the control cotton sample which proves that the microwave irradiation does not adversely affect the heat release characteristic of cotton fabric (Yang and He 2012).

In the study of the effect of microwave power on the FR performance, the heat release characteristics of treated cotton fabric samples showed a decreasing trend with increasing microwave power as shown in Fig. 6. The significant reduction of HRC, pHRR and THR occurred at 300–600 W, indicating the transition of cotton from flammable to self-extinguishing. Fabric samples treated at 600 W or higher were self-extinguishing and showed relatively small changes in heat release characteristics with further increase in microwave power. However, the fabric sample prepared at 450 W with 95 J/g-K HRC was not self-extinguishing in the vertical flame test due to the relatively low weight add-on (0.8%) and char residue (23.9%) in TGA.

In the study of irradiation time on the FR performance, reduction of heat release characteristics of treated cotton fabric samples was observed with the increase of irradiation time in the range of 1 – 5 min. The most significant reduction in HRC occurred from T1 (1 min) to T2 (2 min) and T3 (3 min). The significant reduction of HRC, pHRR and THR demonstrated that the flame resistance and phosphorylation of the cotton fabrics are heavily affected by microwave power and reaction time. The change of heat release characteristics was relatively moderate between T5, T6 and T7 (less than 20% compared to T5). The cotton fabric treated at 600 W for 4 min and 5 min showed heat release characteristics comparable to the fabric treated in the convection oven at 155 °C for 45 min. Consequently, they also exhibited similar char yield in TGA and similar char length in the vertical flame test. However, due to an exceptionally shorter treatment time in the microwave treatment process, the discoloration of the cotton fabric caused by the heat induced hydrolysis and oxidation of cellulose has been minimized.

Upon comparison of heat release characteristics and char length of P2 and T3 (Tables S4 and S5), HRC reduced from 95 J/g-K (P2) to 53 J/g-K (T3) while the burning behavior of cotton fabric changed from sustained burning (P2) to self-extinguishing (T3) which indicates a critical transition of burning behavior occurs in this range of HRC. Specifically, the transition to self-extinguishing occurred when HRC reduced from 78 J/g-K (T2) to 53 J/g-K (T3). Therefore, 78 J/g-K to 53 J/g-K can be considered as a critical range of HRC and a predictor of burning

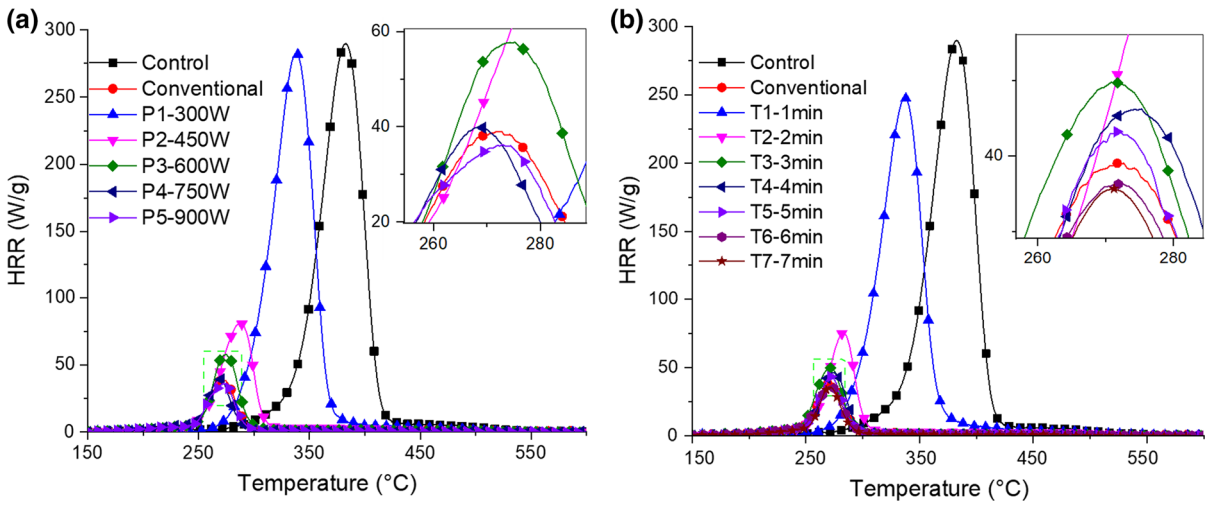


Fig. 6 Micro combustion calorimetry of fabric treated using **a** different microwave power, **b** different irradiation time

behavior in phosphorylated cotton fabric (density: 122 g/m^2).

The combustion behavior of the control cotton fabrics, CTC and MTC were also examined using cone calorimetry. The HRR, THR over time and the pictures of fabric residue are presented in Fig. 7 and the corresponding data are summarized in Table 4. Similar to the MCC result, the control cotton fabric exhibited the highest HRR and THR and burnt completely (for about 40 s) without any char residue as shown in Fig. 7c. The treated fabrics began to char immediately upon exposure to the heater. The PHRR value of CTC and MTC were 19 kW/m^2 and 17 kW/m^2 respectively, which are much lower than that of the control cotton fabrics (96 kW/m^2). The THR values also reduced from 2.1 MJ/m^2 to 1.5 MJ/m^2 and 1.4 MJ/m^2 for CTC and MTC respectively. The significant reduction of heat release characteristics observed in MCC and cone calorimetry test prove that microwave treated fabric exhibits excellent flame retardancy which is very similar to the cotton fabric treated by the conventional heating method. The superior flame resistance can be attributed to the excellent char formation and gas dilution resulting from decomposition of phytic acid and urea.

In addition, the control fabric showed a minimal amount of smoke-release while both types of treated fabric exhibited increased TSR. This phenomenon can be explained by the release of volatile degradation product of PA and urea (NH_3) as an essential part of the FR action. However, MTC showed a TSR of 23 m^2/m^2 which is significantly lower than that of CTC. The reduced value of TSR suggests that the gas dilution action contribute less to the flame retardancy of MTC in comparison to CTC. This observation also coincides with significantly high carbon content in the char residue of MTC as shown in the EDX result in Table S6 in supplementary information. The higher TSR value of CTC might be attributed to the oxidation of the cellulose due to the excessive amount of heat

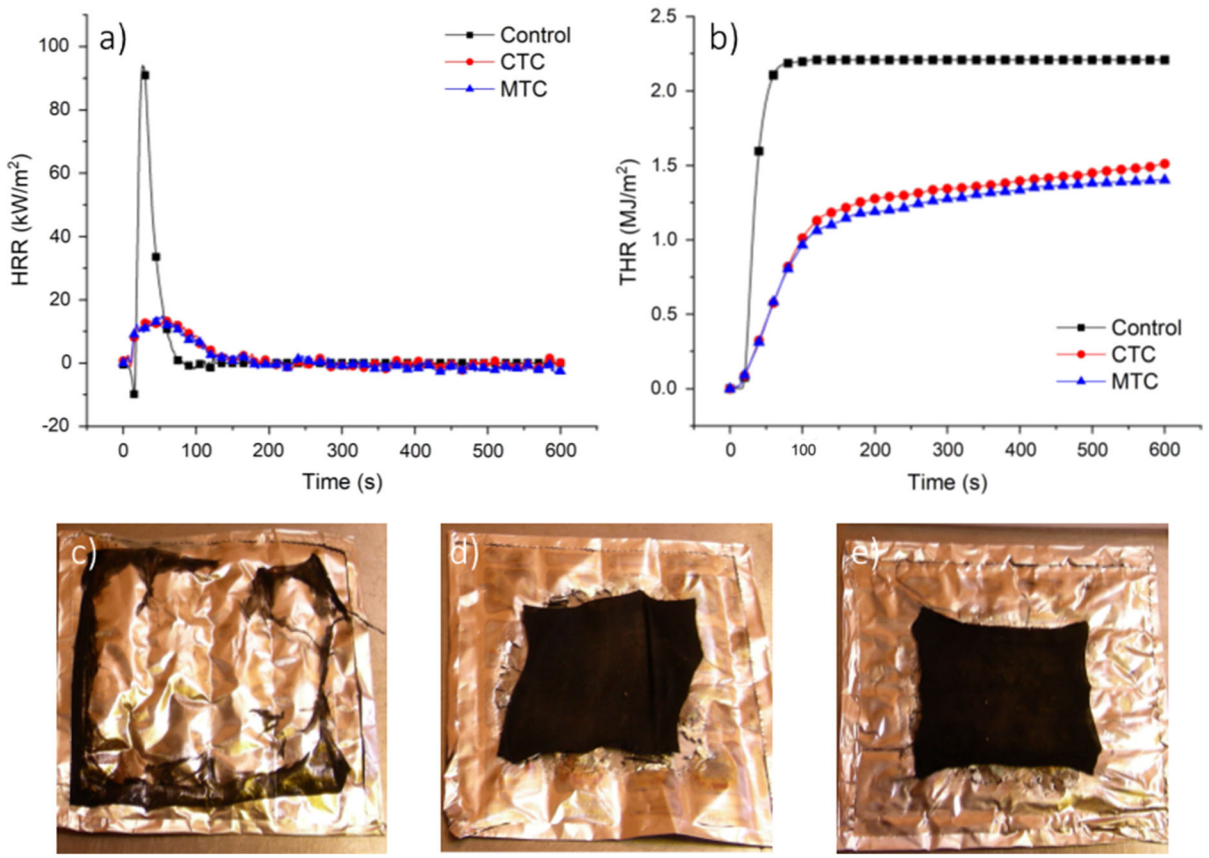


Fig. 7 Cone calorimetry result: **a** HRR curve, **b** THR curve and photo test samples: **c** untreated cotton, **d** CTC and **e** MTC

Table 4 Cone calorimetry date of cotton fabric treated by different methods

Treatment method	TTI (s)	PHRR (kW/m^2)	TPHRR (s)	THR (MJ/m^2)	TSR (m^2/m^2)	FIGRA
Control (untreated)	8	96	27	2.1	1	3.51
CTC	0	19	42	1.5	53	0.62
MTC	0	17	47	1.4	23	0.5

during conventional heating treatment. The partially oxidized cellulose can potentially release degradation products due to the unfavorable incomplete combustion.

Morphology and combustion residue analysis

The surface morphology of the control (untreated) fabric, CTC and MTC (before and after combustion) are shown in Fig. 8. The surface of the untreated cotton fibers is relatively rough as shown in Fig. 8a. Both types of the treated cotton fibers (Fig. 8b, c) exhibit smooth surface morphology which indicates that the phytic acid and urea reacted with the hydroxyl groups of cellulose uniformly rather than just coat the surface of the fibers. The EDX data in Table S6 also prove the presence of P and N on the surface of the fiber. After combustion, a significant amount of intumescent char with hollow structure resulting from volatile gases was observed on both types of treated cotton fabrics as shown in Fig. 8e, f. This phenomenon coincides with the improved char residue observed in thermogravimetric analysis. Polyphosphoric acid formed during combustion induce dehydration and carbonization of cotton fibers which results in the significant reduction of O content and increase of C content as observed in Table S6 (Hendrix et al. 1972; Liu et al. 2018; Xu et al. 2019). The intumescent char serves as physical barrier insulating combustible species from oxygen and heat, therefore resulting in effective protection.

Mechanical properties of microwave treated cotton fabric

As reported previously, exposure to heat in acidic condition adversely affects the tear strength of cotton fabric more than other mechanical properties such as

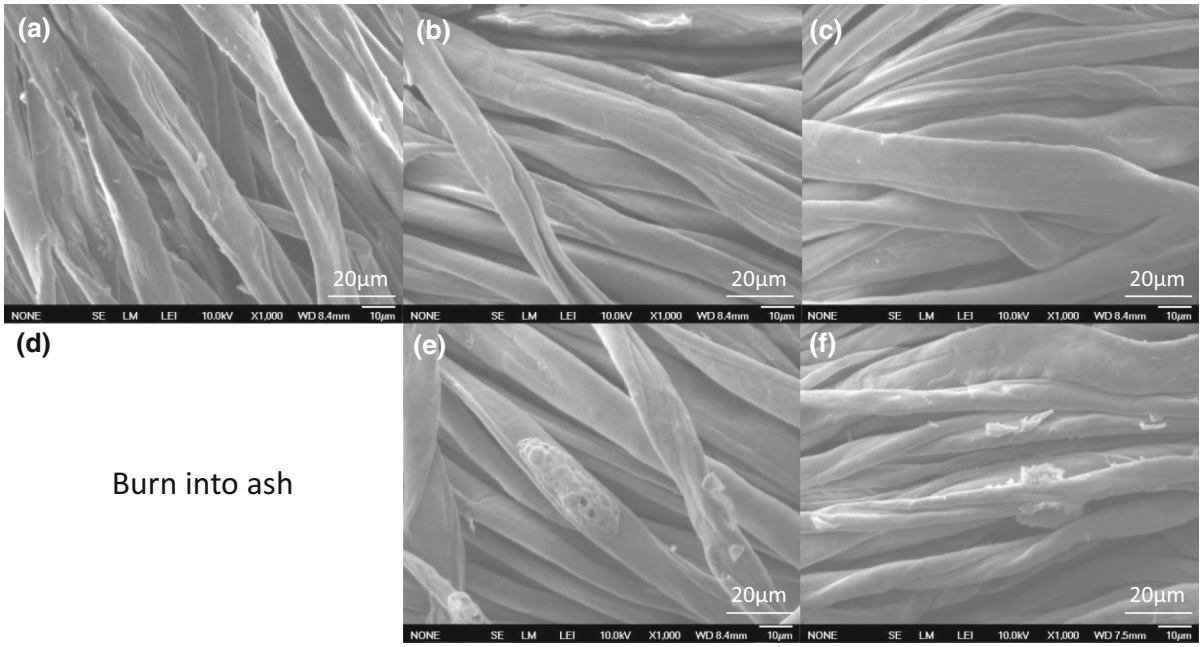


Fig. 8 SEM image of **a** untreated cotton, **b** CTC and **c** MTC before burning, **d** untreated cotton, **e** CTC and **f** MTC after burning

tensile strength (Beninate et al. 1968; Kang et al. 1998). Therefore, it is essential to study the effect of microwave treatment on the tear strength of cotton fabric. As shown in Fig. 9, MTC exhibit 91% and 89% retention of tear strength in warp direction and weft direction respectively. CTC exhibit only 61% retention of tear strength in both directions. It is obvious that cotton fabric prepared by microwave assisted phosphorylation exhibited much higher retention of tear strength than the cotton fabric phosphorylated by convection oven. As discussed earlier, microwave assisted phosphorylation requires a much shorter reaction time to achieve identical FR behaviour compared to the phosphorylation carried out in a convection oven. It is reasonable to conclude that the shorter treatment time in microwave assisted phosphorylation helps retention of tear strength by limiting the hydrolysis reaction of cellulose chain.

Laundry durability of FR performance

The durability of the FR performance through laundry cycles is an important characteristic for most flame retardant fabric used in apparel applications. The laundry durability of the FR fabric obtained from the microwave-assisted phosphorylation was evaluated using vertical flame test after three laundry cycles (as shown in Table 5). Although increased char length was observed after first and second laundry cycle MTC was self-extinguishing only until after the 3rd laundry cycle.

The weight change and the evolution of elemental composition of MTC-L (fabric samples after three laundry cycles) was characterized to better understand the FR mechanism (Table 5 and Fig. 10). After three standard home laundry cycles, MTC-L lost the FR performance and burnt to the full length (127 mm) in vertical flame test. However, the weight loss of MTC-L was only 0.8% compared to neat MTC indicating that the majority of the phytic acid compound was retained after three home laundry cycles indicating covalent attachment to cellulose. The preservation of phytic acid compound was also evidenced by the 2.6% phosphorus content in MTC-L determined using XPS.

However, after three laundry cycles, nitrogen content was reduced to 2.7% as a result of the ion exchange with calcium ions in tap water. Due to the high affinity of phytic acid with divalent metal ions in aqueous solution, the nitrogen containing moieties such as ammonium are rapidly replaced by calcium ions during laundry process (Marolt et al. 2020). The formed calcium salts are not as readily decomposable as the ammonium salts, thus deferring the formation of phytic acid during combustion and reducing the fire resistance of MTC (Nuessle et al. 1956; Sekiguchi et al. 2000; Yang and Wu 2003a,b; Horrocks et al. 2005; Marolt et al. 2020).

For a better understanding of the effect of this ion exchange effect on fire resistance of MTC, additional MTC-L fabrics were placed in acetic acid solution (0.1%) at 60 °C for 15 min. The fabrics were then removed from acid bath and rinsed in deionized water twice. MTC fabrics after 3 laundry cycles and 1 acid washing are noted as MTC-AD. The acid washing successfully unbound the calcium ions and removed the sulfur-based detergent residue as shown in the XPS spectra of MTC-AD (Fig. 10). The acid washing did not affect the nitrogen or phosphorus content significantly. Self-extinguishing behavior with a char length of 83 mm was observed in the vertical flame test of MTC-AD samples which indicates that the fire resistance of MTC was recovered after the acid wash process. It is clear that the loss of fire resistance of MTC after home laundering can be attributed to the

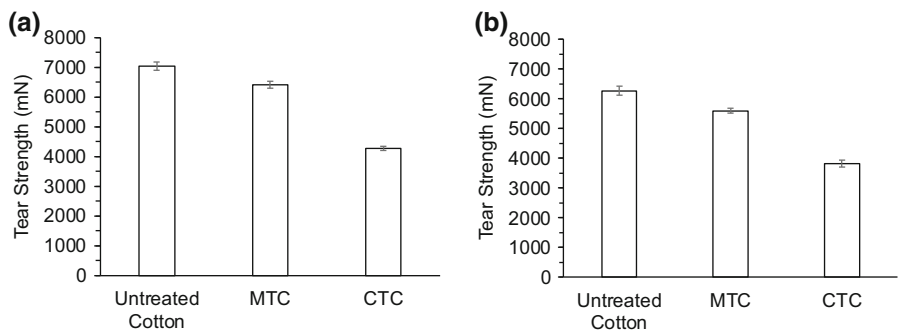


Fig. 9 Tear strength of cotton fabric treated by different method in **a** warp direction and **b** weft direction

Table 5 Weight change, char length and atomic content of MTC after different laundry process

Sample	Weight change (%)	Char length (mm)	Atomic content					
			%C	%O	%N	%P	%Ca	%S
MTC	0	79	64.7 ± 0.1	27.7 ± 0.1	4.8 ± 0.1	2.8 ± 0.1	Negligible	Negligible
MTC-L	− 0.8	≥ 127	64.6 ± 0.1	27.6 ± 0.1	2.7 ± 0.1	2.6 ± 0.1	1.4 ± 0.1	1.0 ± 0.1
MTC-AD	− 1.2	83	64.8 ± 0.1	30.0 ± 0.1	2.5 ± 0.1	2.7 ± 0.1	Negligible	Negligible

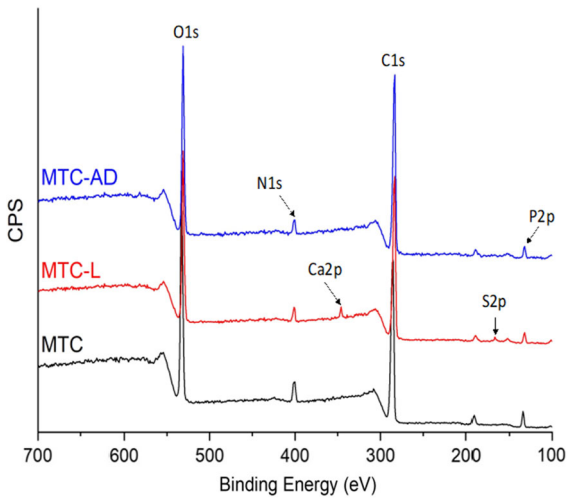


Fig. 10 XPS spectrum of MTC: before laundry (MTC), 3 laundry cycles (MTC-L), 3 laundry cycles and acid dipping (MTC-AD)

ion exchange between ammonium moieties and calcium ions in tap water. Reactions such as esterification or crosslinking of the free acid groups or ammonium moieties using multi-functional amines (TEA) or polyol can be considered as feasible approaches to protect phytic acid compounds from this unfavorable ion exchange effect.

Conclusion

A rapid microwave-assisted FR treatment for cotton fabric using a bio-based industrial by-product, phytic acid is reported in this research. One-step microwave assisted phosphorylation of cotton using phytic acid and a customized setup has been demonstrated. The effects of microwave power and irradiation time on thermal stability, heat release characteristics and flammability have been investigated. Higher weight add-on, higher char yield, lower heat release and better flame resistance were observed with the increase of microwave power and irradiation time. The optimized microwave power and irradiation time were found to be 600 W and 4 min, respectively. Cotton fabric samples treated at these optimal treatment conditions exhibited HRC and THR as low as 49 J/g-K and 1.7 kJ/g, which indicates 84% and 89% reduction compared to the native cotton, respectively. Even with only 2.2% phosphorus content, these fabric samples showed self-extinguishing behavior with char length of 79 mm in the vertical flame test. The cotton fabric phosphorylated for just 4 min using microwave exhibits similar FR characteristics, but significantly better mechanical properties compared to the samples treated for 45 min using convection oven. The microwave-assisted phosphorylation also exhibits good fastness as very little phosphorus content was leached out during standard laundry cycles. Ion exchange, specifically the replacememt of ammonium moieties with calcium ions from hard water is found to cause the loss of fire resistance during laundering. In summary, the reported treatment method using microwave technique have successfully made FR cotton fabric in 4 min with bio-based compound. Efforts to improve uniformity of microwave irradiation in the treatment process are being explored.

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Author contribution All authors contributed to conception and design of this study. Material preparation, data collection and analysis were performed by SY, ZX and WK The manuscript was drafted by SY and all the authors commented on revision of the manuscript. All authors read and approved the final manuscript.

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Declarations

Conflict of interest The authors declare that they have no conflict of interest.

Data availability The authors confirm that the data supporting the findings of this study are available within the article and its supplementary information.

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