

Development and Evaluation of a Water-Based Flame Retardant Spray Coating for Cotton Fabrics

Zope, Indraneel Suhas; Foo, Shini; Seah, Dean Geng Jie; Akunuri, Aswini Tara; Dasari, Aravind

2017

Zope, I. S., Foo, S., Seah, D. G. J., Akunuri, A. T., & Dasari, A. (2017). Development and Evaluation of a Water-Based Flame Retardant Spray Coating for Cotton Fabrics. *ACS Applied Materials and Interfaces*, 9(46), 40782-40791.

<https://hdl.handle.net/10356/89006>

<https://doi.org/10.1021/acsami.7b09863>

© 2017 American Chemical Society (ACS). This is the author created version of a work that has been peer reviewed and accepted for publication by ACS Applied Materials and Interfaces, American Chemical Society (ACS). It incorporates referee's comments but changes resulting from the publishing process, such as copyediting, structural formatting, may not be reflected in this document. The published version is available at: [<http://dx.doi.org/10.1021/acsami.7b09863>].

Downloaded on 27 Aug 2022 02:48:03 SGT

Development and evaluation of a water-based flame retardant spray coating for cotton fabrics

*Indraneel S. Zope, Shini Foo, Dean G. J. Seah, Aswini Tara Akunuri, Aravind Dasari**

School of Materials Science & Engineering (Blk N4.1), Nanyang Technological University,

50 Nanyang Avenue, Singapore 639798

KEYWORDS:

cotton, fabric, flame retardant, vertical flame test, pyrolysis combustion flow calorimetry, wash fastness.

ABSTRACT

In this article, we report on the development of water-based flame retardant coating based on phospho-nitrogen combination for cotton fabrics. A one-step spray-on process was employed to coat the fabrics by taking advantage of the spontaneous reaction between para-phenylene diamine (PDA) and tetrakis(hydroxymethyl)phosphonium chloride (THPC) resulting in an instantaneous precipitation of poly[1,4-diaminophenylene-tris(dimethyl hydroxymethyl)phosphine] (PAP) on the fabric surface. The effectiveness of PAP in improving the flame retardant properties like ignition resistance and lateral flame spread were evaluated in accordance with ASTM D6413 and BS EN ISO 15025 flammability tests. Despite the early (thermal) decomposition onset for coated

fabrics under both oxidative and pyrolytic conditions, remarkably, self-extinguishing behavior (< 3 s) without any lateral flame spread was observed. Possible reaction scheme was also proposed to correlate flame retardant mechanism of the coated fabrics with the observations. Additional analysis via pyrolysis combustion flow calorimetry and vertical flame testing before and after washing showed that flame retardant efficiency did decrease with washing, but the overall performance was still promising.

INTRODUCTION

Flame retardant fabrics are an integral part of protective gear as they are the first line of defense against potential burn injuries. Unsurprisingly, they are used in many applications such as police and military uniforms, firefighters' suits, apparels for motor racing sports, and chemical laboratories (as coats). Even with such high demand, use of 'inherently' flame-resistant fabrics like Nomex® and Kevlar® has been limited to high-risk applications due to their high cost. As a result, continuous efforts have been underway to impart flame-retardancy to fabrics like cotton and polyester, which already have a combined market share of 82 % in textiles¹⁻².

Various coating chemistries and methodologies have been explored to develop flame-retardant cotton and polyester fabrics. Phosphorous³, phospho-nitrogen compounds⁴⁻⁸ and even inorganic compositions⁹⁻¹⁰ have been studied as coatings; while dip coating¹¹, layer-by-layer (or electrostatic) deposition¹²⁻¹³, plasma treatments¹⁴⁻¹⁵, sol-gel¹⁶, dual cure processes¹⁷ apart from traditional pad-dry-cure technique^{8, 18-19} as coating methodologies for their effectiveness.

We have recently used electrostatic self-assembly approach to coat polyester fabrics with polycationic branched polyethylenimine (BPEI) and sodium montmorillonite (smectite clay)²⁰. 10 bilayers on the fabric were required to obtain optimum flame retardancy and combustion properties as well as physiological comfort (in terms of air permeability and moisture management). In

another similar study, layer-by-layer self-assembly technique was used to deposit 100 alternating layers of BPEI/urea/diammonium phosphate mixture and clay platelets on cotton²¹. The heterogeneous coatings showed promising flame retardant properties in terms of peak heat release rate (a reduction of 63 %), char yield (increased from 7.6 % in neat fabric to 33.8 %) and total heat released (75 % reduction) in a micro-scale combustion calorimeter. As expected, the authors have also noted that greater was the amount of phosphorous (diammonium phosphate) and nitrogen (urea), higher was the char yield.

Abrasion resistance during regular use or during washing/tumbling is another parameter that affect the performance and durability of the coatings on fabrics. On this note, Chen et al.²² sequentially deposited BPEI and ammonium polyphosphate (APP) on cotton along with a top layer of fluorinated decyl polyhedral oligomeric silsesquioxane. This produced a durable (wash resistance due to superhydrophobicity of the top layer) and flame retardant fabric. In an alternate approach, Mayer-Gall et al.¹⁹ have demonstrated the effectiveness of polyphosphazene (PPZ) coatings applied via pad-dry-cure method on cotton and cotton/polyester blend fabrics for its durability and abrasion resistance. However, as pointed out by authors, PPZ-based coating requires organic solvents for padding process restricting the opportunities for scale-up. Proban[®], a well-known commercial flame-retardant fabric, claims to withstand 50 laundering cycles²³ without losing the flame-retardant efficiency. It is based on the application of tetrakis(hydroxymethyl) phosphonium chloride (THPC)-urea condensate in an organic solvent on cotton fabrics in a pad-dry-cure processing technique. This is followed by ammonia curing, and finally, oxidation using hydrogen peroxide, resulting in a durable flame-retardant cotton fabric.

Current work focusses on developing a water-based coating utilizing phospho-nitrogen combination using a simple spray-on instead of traditional pad-dry-cure technique or elaborate

layer-by-layer assembly process. The study explores the use of para-phenylene diamine (PDA) and THPC to achieve efficient coating via one-step spray coating. The combination of water soluble APP and THPC is also evaluated. The advantage of spray-on technique includes lower starting material requirement to attain optimum coating thickness while achieving uniform coverage. Consequently, add-on weight would be minimal retaining the “fabric feel” without compromising its flexibility. Coated fabrics will be subjected to standardized tests in accordance with ASTM D6413²⁴ and BS EN ISO 15025²⁵ to assess their effectiveness. Heat release rates will also be determined using pyrolysis combustion flow calorimeter (PCFC) in accordance with ASTM D7309²⁶.

EXPERIMENTAL SECTION

Materials

Commercial white colored cotton fabric (twill 3/1, grammage of 180 g/m²) was locally purchased in Singapore. The fabric was rinsed with deionized water (18.2 Ωcm⁻¹) and dried in convection oven for 10-15 min at 110 °C prior to coating with a flame retardant composition. PDA and 80 % solution of THPC (in water) were obtained from Sigma Aldrich, Singapore; while water soluble grade of APP (approximate number of repeat units of 360) was procured from McKinn International Pte. Ltd., Singapore. Water based (aliphatic) polyurethane (PU) dispersion, with a commercial name of Hauthane L-3192, was procured from C.L. Hauthaway & Sons Corporation, USA.

Synthesis of THPC-PDA coating and spraying conditions

Mixing of water-based solution of PDA (basic) with THPC solution results in a spontaneous precipitation of poly[1,4-diaminophenylene-tris(dimethylhydroxymethyl)phosphine] (PApP) with a yield of 63 wt.%. Utilizing this chemistry, cotton fabrics were alternatively sprayed with 3 wt.%

PDA solution (maintained at pH 11 with the addition of NH_4OH) and 6 wt.% THPC solution. The molar ratio of PDA to THPC was maintained at 1 to 1.13. Spontaneous formation of white colored PApP precipitates was observed on the fabric surface. Uniform coating was achieved by optimizing spraying conditions, i.e., spraying pressure of 3 bar, solution flow rate of 200 ml/h and robot arm speed of 1000 mm/min. Number of steps for robotic arm were optimized to achieve complete coverage of entire area without excessive overlap. It was estimated that the mean droplet size was $\sim 5.7 \mu\text{m}$. To assess the influence of weave pattern on deposition quality, a set of fabric samples were sprayed on rear side (owing to twill 3/1 nature of fabric) had a different surface morphology. All fabrics were coated only on one side. Upon spraying, they were dried in convection oven for 10 min at 110°C and were subsequently used for testing purpose. PApP coated fabrics were further sprayed with a thin layer of water based urethane dispersion (spraying pressure of 3 bar, dispersion flow rate of 50 ml/h and arm speed of 7500 mm/min) to enhance their wash fastness. To evaluate the inherent flammability of urethane coating, urethane coating was also applied on neat fabric. All urethane coated fabrics were dried at 60°C for 30 min in a convection oven.

Surface morphology, chemical analysis and mechanical analysis

Morphology of fabrics was analyzed using JEOL 5410 scanning electron microscope (SEM) with an acceleration voltage of 5 kV. Prior to SEM studies, the samples were sputter coated with a thin layer of gold. Even the charred fabrics were observed in SEM using the same conditions. Structural chemistry of fabric surface was assessed using attenuated total reflectance (ATR) mode of Spectrum GX (Perkin Elmer) Fourier Transform Infrared spectroscopy (FTIR). All spectra were acquired using 16 scans and 4 cm^{-1} resolution. To confirm the structure of PApP, ^{31}P solid state nuclear magnetic resonance (NMR at 242 MHz and 12 kHz spin speed) was carried out using

Bruker 600 MHz with solid state MAS probe. Products were referenced to ammonium dihydrogen phosphate (external reference) with ^1H decoupling and a high-powered decoupling pulse sequence. Mechanical tests were carried out using Instron 5566 universal testing machine. Rectangular fabric strips of dimension 100 mm (l) x 10 mm (w) were tested at 300 mm/min and grip separation of 50 mm. This test was carried out in warp-direction with 3-5 replicates and the reported values are average of samples breaking (ripping) within gauge length.

Thermal stability, flammability, and combustibility of fabrics

Thermo-oxidative stability of coated and uncoated fabric samples was investigated using thermogravimetric analysis (TGA), Q500 (TA Instruments). All samples were pre-dried overnight at 80 °C in a convection oven before testing. Tests were carried out from room temperature to 800 °C employing a heating rate of 20 °C/min under both oxidative and inert atmospheres. Flammability was evaluated in accordance with widely used standards, BS EN ISO 15025:2016 for protective clothing and ASTM D6413 for flame resistance of textiles. Following BS EN ISO 15025, 200 mm x 160 mm of test fabric was subjected to a 25 ± 2 mm of horizontal methane flame for 10 s at a distance of 17 ± 1 mm from front face and 20 mm from bottom edge. According to ASTM D6413, 300 mm x 76 mm of test fabric was subjected to a vertical flame of 38 mm length for 12 s at bottom edge. Combustibility of evolved gases upon thermal decomposition of fabrics was evaluated using pyrolysis combustion flow calorimetry (PCFC) or microscale combustion calorimeter (MCC) from Fire Testing Technology, UK in accordance with Method A of ASTM D7309:2013. Typical PCFC (or MCC) test employs 10-12 mg of test sample that undergoes pyrolysis (in nitrogen) from 150 °C to 750 °C and at a heating rate 60 °C/min. The evolved gases are oxidized in the combustion chamber at a temperature of 900 °C. All tests were carried out in triplicates and an average with % standard deviation are presented.

Wash fastness of the fabrics

To understand the durability of the coatings, coated fabrics were washed in a domestic washing machine (Samsung Wobble Technology 3D, 7.5 kg model). A total of three washing cycles were used. Each washing cycle was 40 min, which included a 34 min of washing / rinsing and 6 min of spin-drying. 20 g of domestic detergent was used for each washing cycle. Fabrics were air dried overnight before subsequent washing cycles. Washed fabrics were further evaluated for changes in their flammability characteristics (using BS EN ISO 15025) and morphological changes, if any.

RESULTS AND DISCUSSION

PApP coating on fabric

PDA reacts spontaneously with THPC under basic conditions leading to the precipitation of the reaction product. To understand this reaction, FTIR spectroscopic technique was utilized. Differences in IR bands between starting materials and PApP product are quite evident (Figure 1A). The presence of IR bands corresponding to secondary aromatic amine i.e. -NH- at 3440, 1610, 1316 and 1230 cm^{-1} (instead of primary amine as seen in PDA) along with IR bands for P–C bond (1413 and 724 cm^{-1}) confirms the successful reaction. These observations concur with an earlier report by Frank et al. concerning the reaction between aniline and THPC²⁷. Elaborate peak assignments concerning PDA, THPC and the reaction product are given in Table 1. Absence of IR band at $\sim 1296 \text{ cm}^{-1}$ (that typically corresponds to $\text{R}_3\text{P=O}$) in PApP suggest that phosphorous in the PApP chain attains a trivalent state. Further, in Figure 1B, the IR spectrum of PApP coated fabric confirms the formation of PApP reaction product on fabric surface. Apart from these, the characteristic signals for C–O–C of the cellulose backbone are also evident in both uncoated and coated fabrics between 1025 and 1170 cm^{-1} .

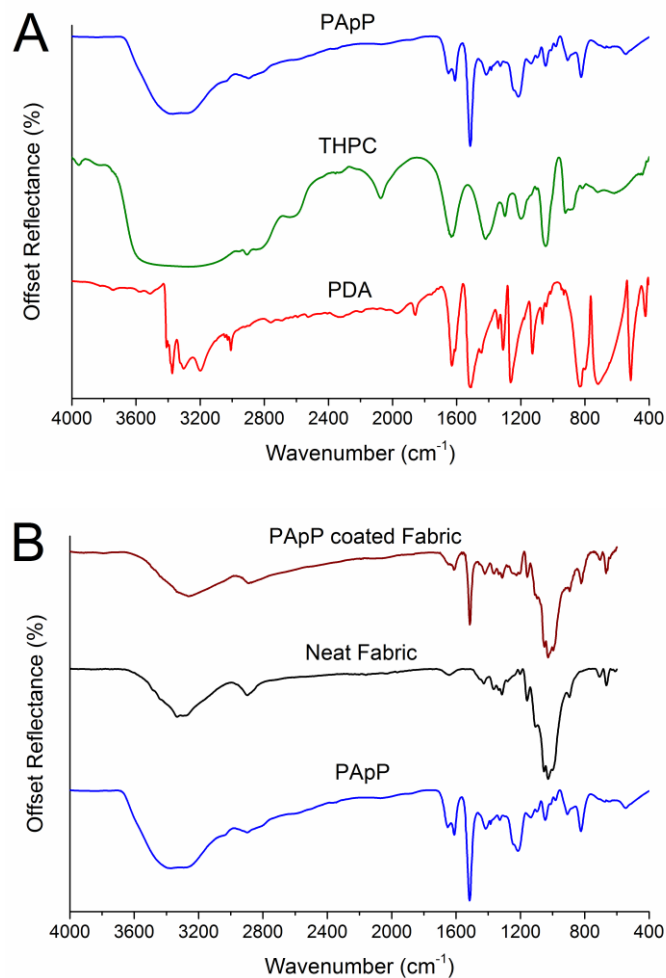


Figure 1. FTIR spectra of (A) THPC, PDA and PApP product; and (B) uncoated and coated fabrics.

Table 1. FTIR band assignments for PDA, THPC and PApP product.

PDA Assignments	THPC Assignments	PApP Assignments
3372 s		3440 s -NH- stretch
3300 s -NH ₂ stretch	3250 br -OH stretch	3263 s -OH stretch
3196 s		
3010 s C-H stretch, Aromatic C=CH	- -	3034 w C-H stretch, Aromatic C=CH

-	-	2959 w 2905 m Aliphatic -CH ₂ - 2825 m	2898 w Aliphatic -CH ₂ -
1630 s	-NH ₂ scissoring	1632 m -OH bend	-
-	-	-	1610 s Sec. -NH bend
1608 s 1511 s 1309 s	Aromatic C-C stretch	-	1610 s CH bend or aromatic C=C stretch 1514 s
-	-	1417 s -CH ₂ bend in P-CH ₂	1413 m -CH ₂ bend in P-CH ₂
1341 s 1260 s	Aromatic =C-NH ₂ stretch	1296 s P=O stretch	1322 m Aromatic =C-NH stretch 1250 m
1064 s	-NH ₂ twist	1044 s C-O stretch	1044 m C-O stretch
826 s	Ring breathing	-	822 m Ring breathing
718 s	-NH ₂ wagging	723 w P-C stretch in P-CH ₂	724 w P-C stretch in P-CH ₂
513 s	Ring deformation	-	545 m Ring deformation

s: strong, m: medium, w: weak, br.: broad

A reaction scheme between THPC and PDA is proposed and is shown in Figure 2. When THPC is deposited on the PDA/NH₄OH layer, THPC reacts with NH₄OH to form an intermediate phosphine and formaldehyde, reaction (a). Formaldehyde, then reacts with PDA to form an intermediate immonium ion via Mannich-type reaction²⁸⁻²⁹, (b). Condensation polymerization between immonium ion and phosphine intermediate results in the polymeric PApP via amine coupling (with formation of phosphonium ion and water)³⁰. Subsequent drying at 110 °C converts phosphorous from metastable P⁴⁺ to stable P³⁺ state with the loss of formaldehyde³¹, yielding PApP

reaction product on the fabric. This reaction was confirmed using ^{31}P solid state NMR (refer Figure S1 in supporting information). The spectrum highlights that phosphonium ion indeed reduces to phosphine upon drying (as both chemical shifts of -35.99 ppm and -41.81 ppm are within P^{3+} range). However, the presence of a small peak at 48.24 ppm in PApP spectra corresponding to P^{5+} range suggests some extent of oxidation of phosphonium ion (to $\text{P}=\text{O}$) upon drying.

Further, the major advantage of the PApP is the presence of rigid benzene ring in backbone that renders solubility resistance in water or organic solvents as opposed to the well reported tetrakis(hydroxymethyl) phosphonium hydroxide (THPOH)- NH_3 polymers, which dissolve after 24-48 h (unless a post-impregnation peroxide oxidation is carried out converting P^{3+} to P^{5+})³². This is also true if aliphatic diamines are used, like THPC-urea system as in Proban® process (prior to NH_3 curing). Limited chemical resistance rendered by aliphatic amine (urea) in THPC-urea polymer (with trivalent phosphorous) makes it susceptible to hydrolytic degradation. Therefore, subsequent ammonia assisted curing is mandatory followed by oxidation to impart durability³³. Hence, the use of PApP coating is promising as it does not need additional curing step along with its resistance to hydrolytic degradation.

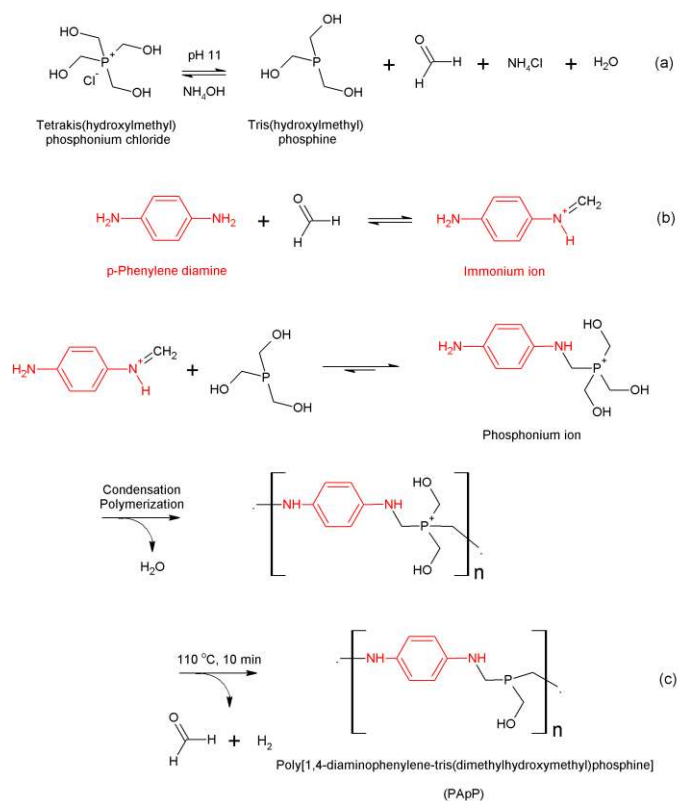


Figure 2. Reaction scheme between PDA and THPC: (a) formation of formaldehyde and phosphine intermediate, (b) formaldehyde-amine reaction to yield an immonium ion in a Mannich-type reaction, and (c) reaction of phosphine intermediate with the immonium ion to complete the amine coupling.

To further identify the extent of deposition and coverage on cotton fabric, SEM observations were carried out on the uncoated and coated fabrics. Low and high magnification micrographs of front and rear of the uncoated fabric show that the fibers are smooth (Figures 3A-3B and 3E-3F). The micrographs of PApP coated fabric show uniform and full coverage of the coating on the weave structure (Figures 3C-3D and 3G-3H) suggesting the effectiveness of spray technique in terms of coating quality. Fine size of PApP particles ensure that the inter-fiber and inter-yarn porosity of the coated fabric remains unaffected as compared to uncoated fabric. This is extremely important as it maintains the physiological comfort for the wearer³⁴. Besides, the coating

uniformity is similar irrespective of the weave pattern, as expected. The weight of the fabric after coating, given in terms of grammage, is $190 \pm 3 \text{ g/m}^2$ for PApP coated fabric as compared to $180 \pm 4 \text{ g/m}^2$ for uncoated fabric. For comparison, grammage of other widely used “inherently” flame resistant woven fabrics like Nomex[®], polybenzimidazole (PBI) fabric and PBI/Kevlar[®] are provided in Table S1 in supplementary information.

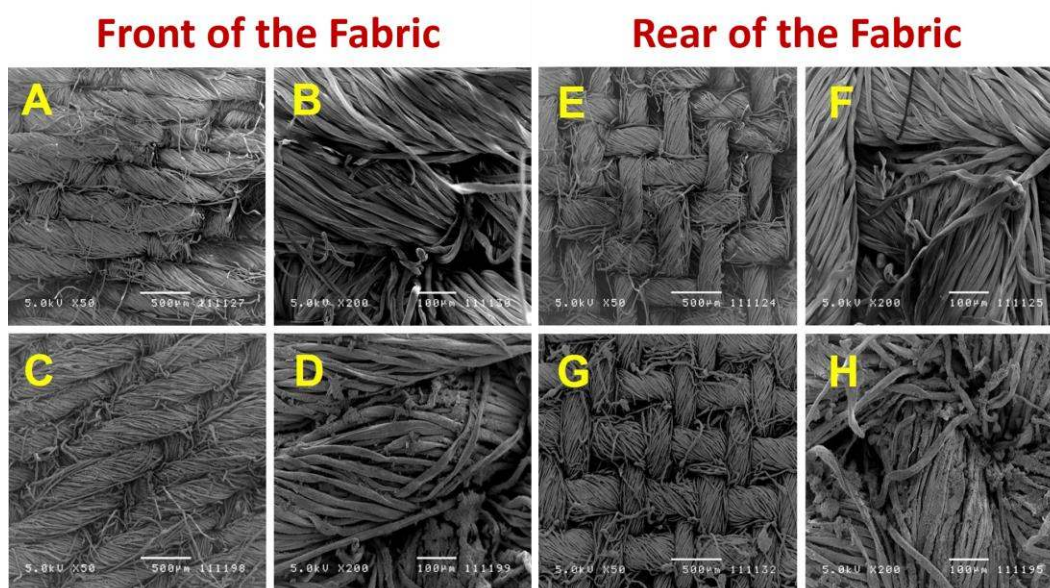


Figure 3. SEM images for cotton fabric, before (A, B, E, F) and after coating of PApP product (C, D, G, H) on both front (A, B, C, D) and rear (E, F, G, H) sides, highlighting the similarity in surface morphology of fabric even after coating.

Thermal stability

The thermal stability of PApP powder along with the uncoated and coated fabrics was evaluated under both oxidative and pyrolytic conditions. Before testing, the PApP powder was filtered out, washed with DI water, dried, and ground to obtain fine powder, which was subsequently used for thermal characterization. Figure 4 shows that the decomposition onset temperature ($T_{10\%}$, where 10% mass loss occurred) of PApP is $\sim 235 \text{ }^\circ\text{C}$ irrespective of the testing atmosphere. This mass

loss corresponds to the loss of formaldehyde and water as a result of crosslinking at methylol site in PApP. Generation of formaldehyde was confirmed by IR peaks (2950 and 2805 cm^{-1} for CH_2 stretch; 1750 cm^{-1} for $\text{C}=\text{O}$ stretch; 1485 , 1250 and 1165 cm^{-1} for CH_2 scissor, rock and wag, respectively) observed in TG-IR patterns for PApP tested under inert atmosphere as shown in Figure S2A. Subtle CO_2 peak at 2358 cm^{-1} in Figure S2B point to complete oxidation of formaldehyde prior to reaching IR cell when PApP was tested with air purge. The possible crosslinked structure shown in Figure 5(I) appears to be stable until $600\text{ }^\circ\text{C}$ resulting in char residues of $\sim 60\text{ wt.}\%$ and $\sim 50\text{ wt.}\%$ under pyrolytic and oxidative conditions, respectively.

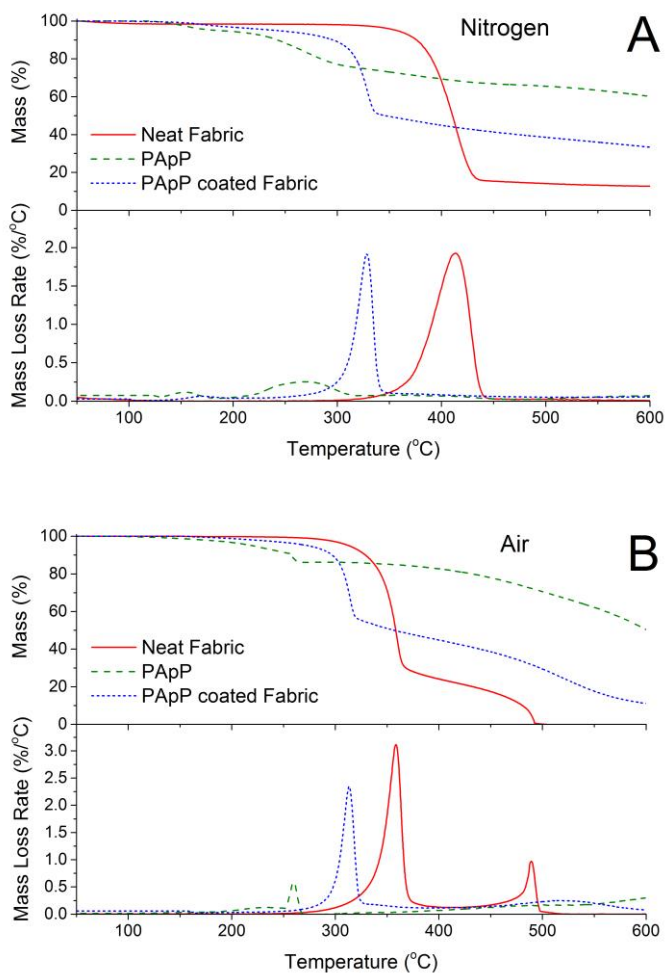


Figure 4. TGA curves for neat fabric, PApP and PApP coated fabric under nitrogen (A) and air (B).

With the coated fabric, the reduction in $T_{10\%}$ when compared to neat fabric as seen from Figure 4 and Table 2 is attributed to two parallel reactions: (1) reaction between formaldehyde (formed during decomposition of PApP) with cellulosic chains leading to chemical crosslinking of cellulose via accelerated dehydroxylation (Figure 5IIa), and (2) crosslinking between methylol group from PApP with methylol (or hydroxyl) groups of cellulose with the elimination of water and the formation of oxymethylene bridge between cellulose and PApP (Figure 5IIb). Reaction shown in Figure 5IIb is a two-step process where first step consists of the formation of hemiacetal, followed by the formation of oxymethylene bridge between cellulosic chains³⁵. Both cases can potentially result in the formation of highly crosslinked and thermally stable matter resulting in higher residues for PApP-coated fabric (Table 2). Similar early onset decomposition temperature has been observed with an electrostatic self-assembled system of chitosan and APP on cotton compared to uncoated cotton³⁶. An observed drop of 29 °C in decomposition onset temperature was attributed to the catalytic dehydration effect of APP (due to the release of phosphoric acid) on cotton³⁷.

Table 2. TGA data obtained under oxidative conditions for neat fabric and coated fabrics.

Condition	Sample	$T_{10\%}$ (°C)	T_{max} (°C)	Residue at 600 °C (%)
	Neat fabric	328	352, 480	0
Air	PApP Product	235	255	50
	Coated fabric	295	305, 517	9.5

	Neat fabric	380	409	12
Nitrogen	PAP Product	238	264	60
	Coated fabric	300	319	30

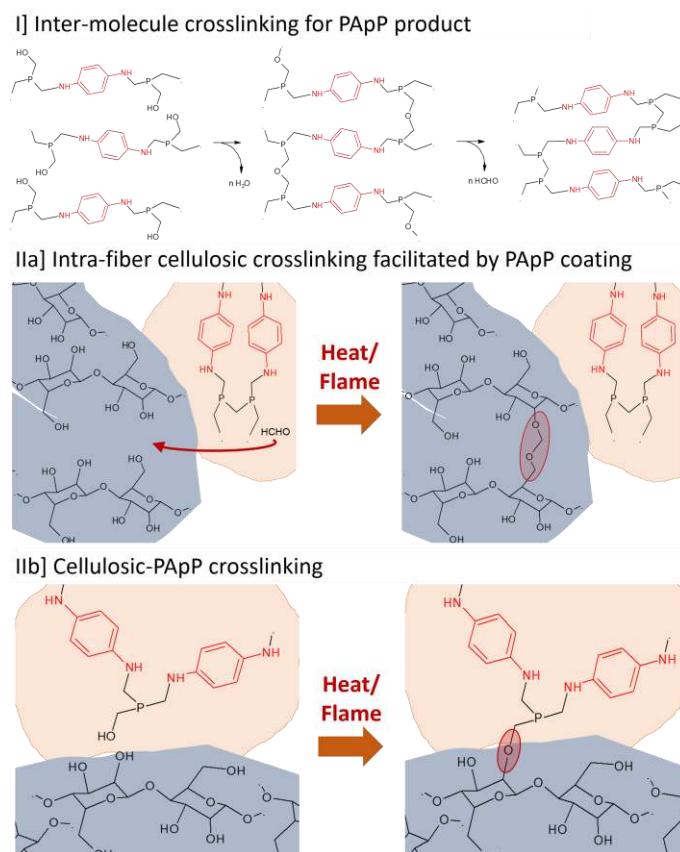


Figure 5. Suggested reactions during decomposition of PAPp (I) and its interaction with cellulose (IIa,b) leading to high char residue content.

Flammability tests

The uncoated and coated cotton fabrics were subjected to vertical flame testing (face-on and edge-on according to BS EN ISO 15025 and ASTM D6413, respectively) to evaluate their flame retardant properties. Upon exposure to direct flame, the uncoated fabric ignites immediately with rapid flame-spread and burn off. Some left over charred strands clearly illustrate the behavior. The PAPp coated fabric displays significant improvement in ignition resistance and flame spread as

seen from Figure 6. Detailed results for ASTM D6413 and BS EN ISO 15025 tests are provided in Tables 3 and 4, respectively. It is interesting to note that even in an edge-on flame test (ASTM D6413) that exposes the uncoated back side of the fabric to flame, the after-flame time is short. This signifies the potential of PApP coating. As expected, in the face test (according to BS EN ISO 15025) there is no lateral/vertical spread of the flame and the after-flame time is extremely short (1 s). That is, the coated fabric self-extinguishes after removing the flame source. Like PApP coatings, excellent flame retardancy behavior has been observed even with APP-THPC coatings (see supplementary information Figure S3-S6, Table S2-S3).

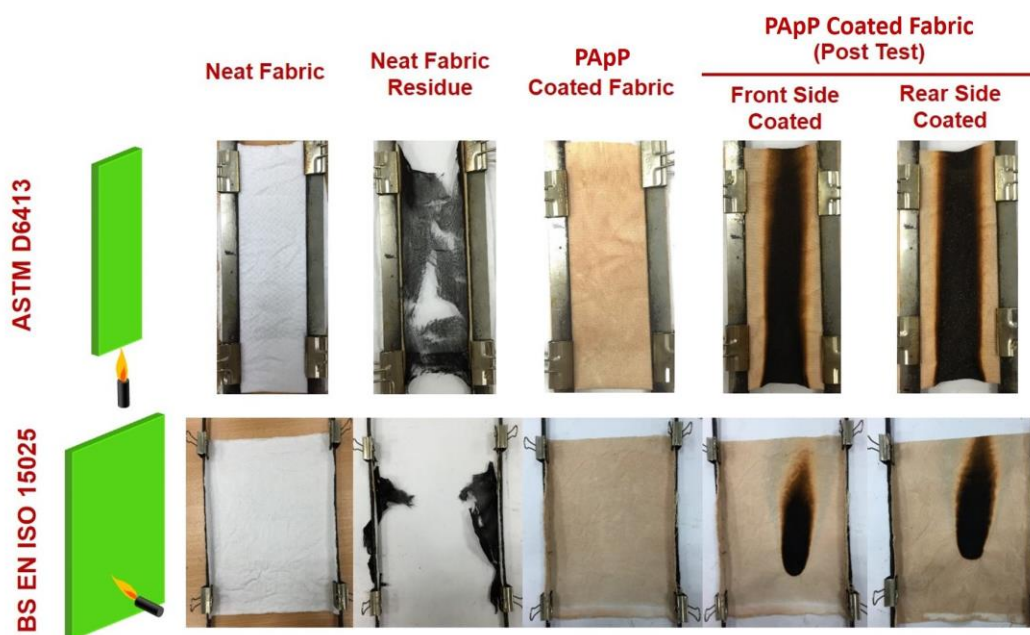


Figure 6. Representative images of neat and PApP coated fabrics before and after flammability tests carried out in accordance with ASTM D6413 (top) and BS EN ISO 15025 (bottom).

Table 3. Results for neat and coated fabric in accordance with ASTM D6413.

ASTM D6413 Results	Neat Fabric	PApP coated fabric	
		Front side	Rear side

After-flame time (s)	21 ± 5	2 ± 2	3 ± 2
After-glow time (s)	49 ± 7	0 ± 0	0 ± 0
Char length (mm)	200	200	200
Occurrence of melting or dripping	No	No	No
Hole formation	Yes	No	No
Comment(s)	Complete burn-off, fragile char	Charred region remains strong	Charred region remains strong
Test passed	No	No*	No*

*because flame reached top edge of the sample.

Table 4. Results for neat and coated fabric in accordance with BS EN ISO 15025.

BS EN ISO 15025 Results	Neat Fabric	PAP coated fabric	
		Front side	Rear side
After-flame time (s)	85 ± 5	1 ± 0	1 ± 0
After-glow time (s)	50 ± 9	0 ± 0	0 ± 0
Flame reaches upper/side edge	Yes	No	No
Afterglow beyond flame area	No	No	No
Appearance of particles	No	No	No
Hole formation	Yes	No	No
Comment(s)	Complete burn-off, fragile char	Extinguishes instantaneously and charred region remains strong	Extinguishes instantaneously and charred region remains strong
Test passed	No	Yes	Yes

To understand the mechanism of flame retardancy achieved with PAP coating, the charred fabrics were characterized by SEM and FTIR. The SEM micrographs in Figure 7A show that the

charred region in the coated fabric retains the original fabric structure / weave morphology and integrity (for front and rear coated fabrics). Also, only minor shrinkage is seen. More interestingly, despite the coating is deposited only on the one side, the charring is uniform throughout. This uniform charring is more evident from the cross-sectional micrograph (Figure 7B) of the fiber strands that illustrate the core-shell morphology like original fibers (lumen-cell walls)³⁸. PApP crosslinks with cellulose or decomposes such that it forms a protective phospho-nitro-carbonaceous shell around the core fiber. Compared to this, the left over (few) strands of untreated fabric exhibited significant shrinkage and lost the weave structure completely. Further, FTIR spectrum (Figure 7C) of the charred residue from the vertical flame test shows the peaks corresponding to C=N, P-C along with carbonyl peaks confirming the above-discussions and even the presence of organic residue. Detailed band assignments are also provided alongside the spectrum.

To further evaluate the flammability of the volatiles generated during pyrolysis of coated and uncoated cotton fabrics, PCFC was carried out. The data of PApP powder by itself is consistent with its TGA data explained earlier. The peak HRR value for the untreated cotton fabric reaches ~187 W/g at ~373 °C, while the coated fabric reaches a peak HRR value of ~102 W/g at ~324 °C (Figure 8 and Table 5). This is a huge reduction of ~45 % in peak HRR value. Lowering of temperature corresponding to the peak HRR is also consistent with previous results of Yang et al.³⁹. They have treated a cotton fabric with 2 wt.% of organo-phosphorous coating (in their case n-methylol dimethylphosphonopropionamide, MDPA) and noted a reduction in temperature of peak HRR by 37 °C (from 376 °C for neat cotton) with a 15 % reduction in peak HRR. Apart from these, in the current work, an increase in char from ~11 % for uncoated fabric to ~28 % PApP

coated fabric (Table 5) is seen that correlates well with the % char obtained from TGA (under nitrogen). Even the THR reduces by ~63 % for the PApP coated fabric illustrating its efficiency.

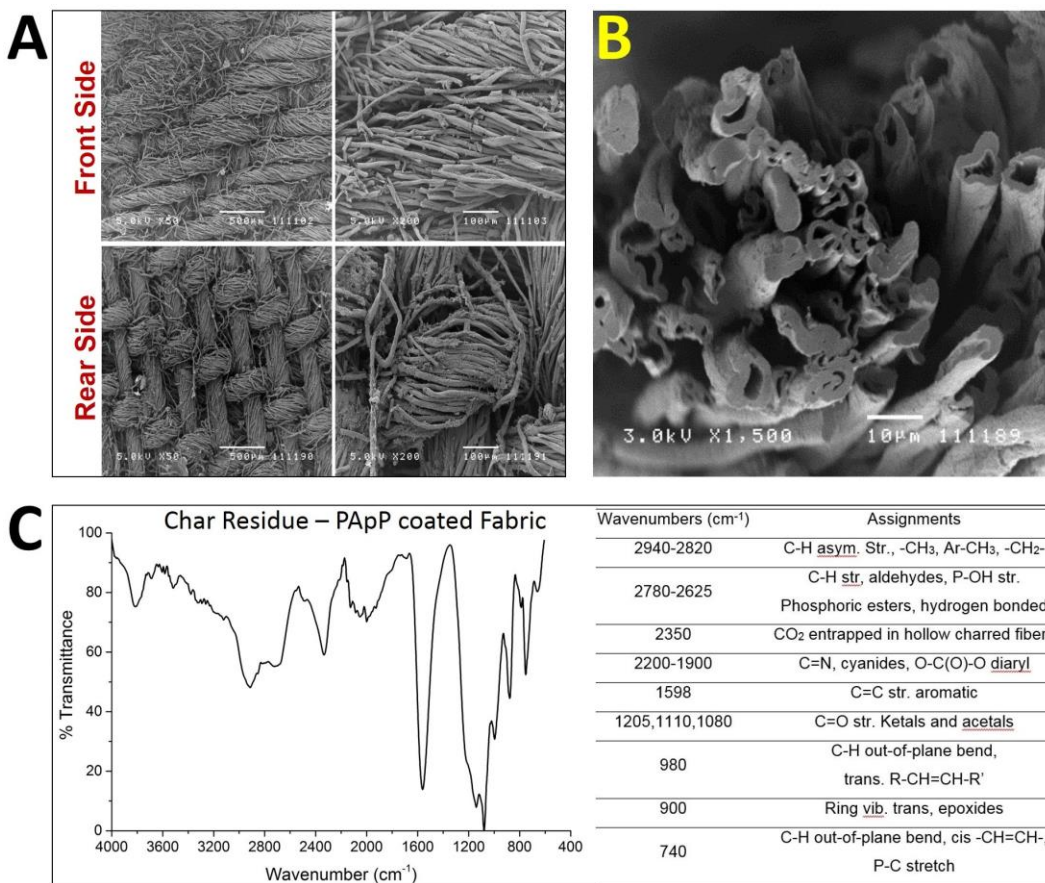


Figure 7. Surface morphology of char residue (A), SEM image of cross-section of charred section of coated fabric, post-test (B) and FTIR spectrum of char and band assignments (C).

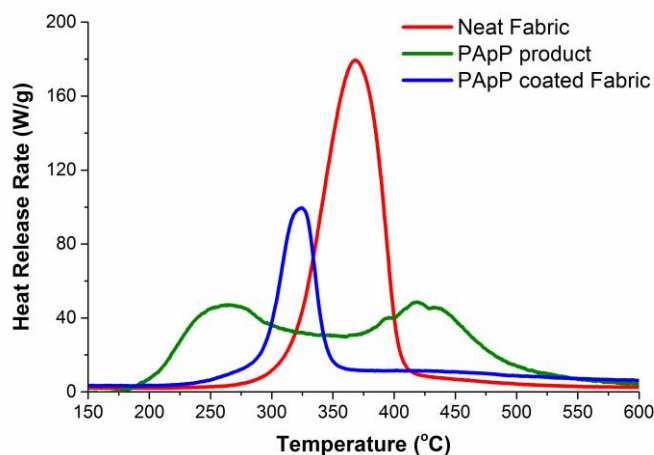


Figure 8. HRR curves for neat fabric, PApP product and PApP coated fabrics.

Table 5. PCFC results for neat fabric, PApP product and coated fabric in accordance with ASTM D7309.

Sample	Peak HRR (W/g)	Peak temperature (°C)	THR (kJ/g)	Char (%)
Neat Fabric	187 ± 11	373 ± 4	11 ± 0.4	11.5 ± 1.1
PApP product	50 ± 3	414 ± 7	10 ± 0.2	42.7 ± 3.3
PApP coated fabric	102 ± 13	324 ± 3	4 ± 0.4	28.6 ± 2.7

Durability

To evaluate the durability (wash-fastness), PApP coated fabric was subjected to a laundering cycle (44 min in a detergent solution) followed by its performance evaluation in accordance with BS EN ISO 15025. After first wash cycle, PApP coated fabric continues to show self-extinguishing behavior while restricting the lateral flame spread. However, an after-flame time of 54 ± 6 s is seen as compared to instantaneous flame extinction in the case of unwashed PApP coated fabric. Despite this, the charred section remained strong without any hole formation similar to unwashed

coated fabric (Figure 9A). The grammage of PApP coated fabric after laundering is reduced to $186 \pm 5 \text{ g/m}^2$ (from the original $190 \pm 3 \text{ g/m}^2$ for unwashed PApP coated fabric). This suggests the loss of excess and/or loosely-bound PApP particles. However, considering the absence of covalent bonding between PApP and cotton, the wash-fastness performance of PApP remains promising.

To further improve the wash-fastness, application of a thin polymeric (water-based PU resin) as a top-coat over PApP-coated fabric was explored. As expected, PU top-coat improves the washing resistance and imparts abrasion resistance without compromising on elasticity of the fabrics (Figure S7). The flame retardant properties, evaluated in accordance with BS EN ISO 15025 for flame spread shows a marginal compromise in the after-flame time after successive washes (zero washes: 13 s; after one wash: 49 s; after two washes: 89 s; and after three washes: 105 s). However, every sample displays self-extinguishing behavior with no lateral flame spread. Images of the fabrics after the flame test are shown in Figure 9B. Efficiency of PApP coating is evident when lateral flame spread behavior is compared between PU-spayed neat fabric and PU-spayed PApP coated fabric.

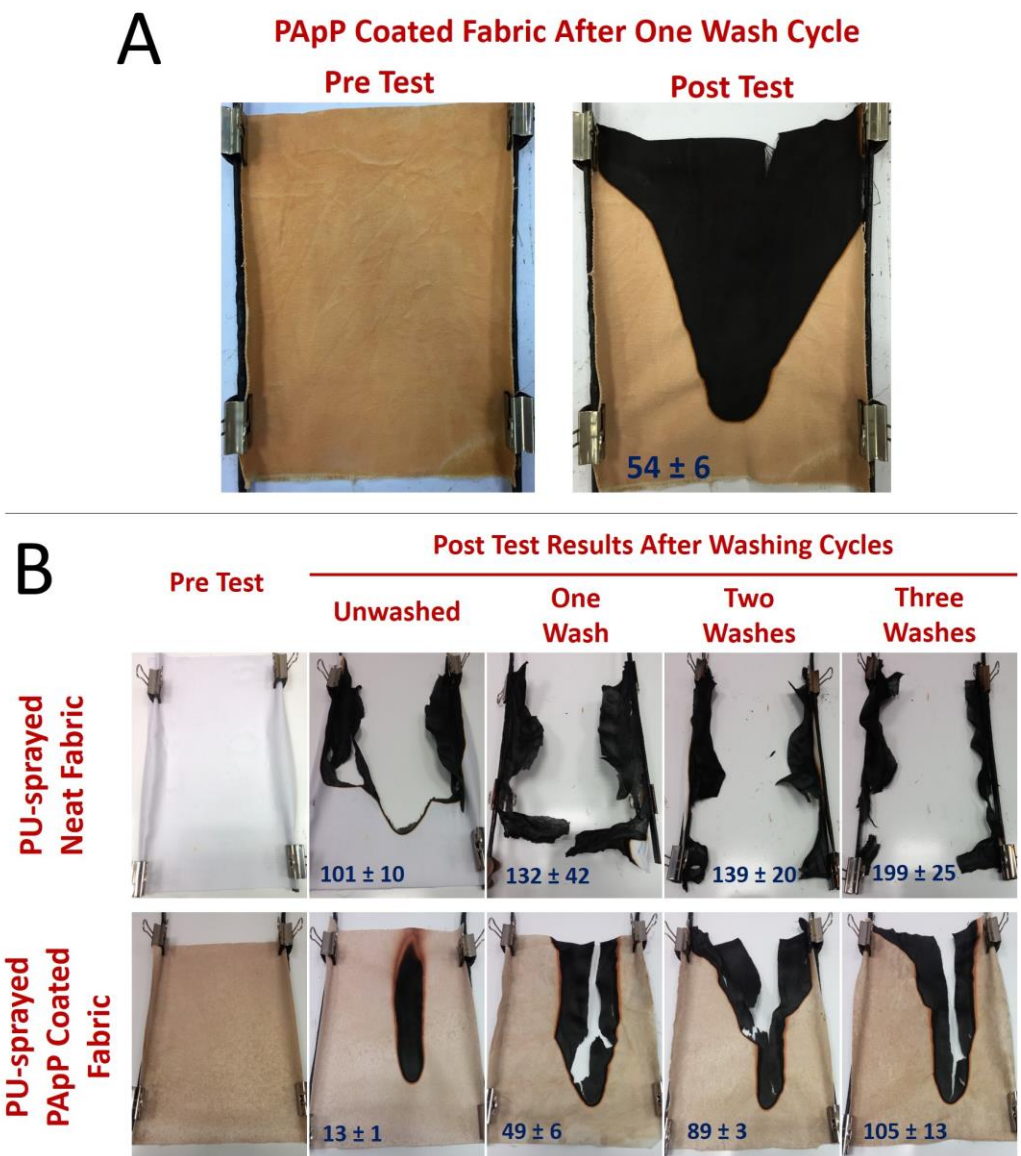


Figure 9. Representative images of PApP coated fabric before and after test (A) and PU-sprayed, neat and PApP-coated fabrics (B) tested in accordance with BS EN ISO 15025 before and after wash cycles. Respective average after-flame times are included for each fabric.

Other than durability, mechanical properties are also important although less critical especially for flame retardant fabrics. PApP coated fabric were (tensile) tested for their breaking stress and elongation-to-break before and after washing cycles. As compared to neat fabric, PApP coated

fabric shows 10 % reduction in breaking stress, but 2.5 times increase in % elongation before failure (Figure S8 and Table S4). It is presumed that coating of (polar) PApP partially replaces inter-chain cellulosic hydrogen bonding at fiber surface with newly developed hydrogen bonds between PApP and cellulosic chains (on fiber surface). This could explain the changes observed in tensile properties. Even an extra top coating of PU does not seem to negatively influence the tensile properties of the fabrics. The slight changes in breaking stress and elongation after different wash cycles are difficult to isolate and explain in the context of this paper as this could be a combination of various factors like the effect of PApP coating on PU, abrasion and changes in properties of PU by itself, and the initiation of hydrolysis of PU.

To sum up, in contrast to the pad-dry-cure technique based flame-retardant treatments, here, a simple water-based spray on technique is employed. Despite coating only on one side of the fabric, excellent flame retardancy is achieved. This gives PApP coated fabrics a functional directionality and so can be used as an integral part of a multi-layered garment. This in fact could do away with the wash fastness and minor changes in tensile properties.

CONCLUSIONS

PApP based flame retardant coating was developed using phospho-nitrogen synergism and applied on cotton fabric using simple water-based spray-on technique. Coated fabrics were subjected to standardized flammability tests in accordance with ASTM D6413 and BS EN ISO 15025 to assess their effectiveness. Heat release rates were also determined using pyrolysis combustion flow calorimeter (PCFC) to evaluate the combustibility of evolved gases. PApP upon exposure to direct flame or intense radiation facilitated intra-fiber crosslinking. The possible crosslinking reactions were proposed with supporting characterization.

The other key advantages of the PApP coating developed in this work include: (i) no requirement of high temperature post-curing, (ii) deposition is only on one side of the fabric (important when grammage of fabrics is an issue), and lastly, (iii) controlled robotic in-line spray and drying set-up can lead to significant cost saving due to spontaneous reaction, uniform coverage on larger surface with lower starting material requirement and no high temperature oxidation requirements.

ASSOCIATED CONTENT

Supporting information include solid state ^{31}P NMR spectra of PApP product and its precursor, details of APP-THPC coated fabric using spray-on technique, and mechanical test results for PApP coated fabrics.

AUTHOR INFORMATION

Corresponding author

*E-mail: aravind@ntu.edu.sg; Fax: +65-6790 9081

ACKNOWLEDGMENT

The authors acknowledge JTC Corporation and Building Construction and Authority (BCA), Singapore, for supporting projects that deal with flame retardancy of polymer coatings through NTU-JTC Industrial Infrastructure Innovation Centre (RCA-16/277) and BCA RID 94.18.2.3, respectively. Authors acknowledge Konstantin Pervushin, Tom Baikie and Dintakurti Sri Harsha Sai for helping with NMR tests and analysis and to Jonathan Jun Yang Siow for helping with mechanical test.

REFERENCES

(1) Textile Exchange's Preferred Fiber Market Report; **Oct 2016**.

- (2) Fire Resistant Fabrics Market by Type (Treated (FR Cotton and FR Viscose), Inherent (Aramid and PBI)), Application (Apparel, Non-Apparel), End Use Industry (Industrial, Defense & Public Safety Services, Transportation) - Global Forecast to 2021 *Markets and Markets*; **Dec 2016**.
- (3) Salmeia, K.; Gaan, S.; Malucelli, G. Recent Advances for Flame Retardancy of Textiles Based on Phosphorus Chemistry. *Polymers* **2016**, *8*, 319.
- (4) Rosace, G.; Colleoni, C.; Trovato, V.; Iacono, G.; Malucelli, G. Vinylphosphonic Acid/Methacrylamide System as a Durable Intumescent Flame Retardant for Cotton Fabric. *Cellulose* **2017**, *24*, 3095-3108.
- (5) Xu, L.; Wang, W.; Yu, D. Preparation of a Reactive Flame Retardant and its Finishing on Cotton Fabrics Based on Click Chemistry. *RSC Adv.* **2017**, *7*, 2044-2050.
- (6) Jimenez, M.; Guin, T.; Bellayer, S.; Dupretz, R.; Bourbigot, S.; Grunlan, J. C. Microintumescent Mechanism of Flame-retardant Water-Based Chitosan–Ammonium Polyphosphate Multilayer Nanocoating on Cotton Fabric. *J. Appl. Polym. Sci.* **2016**, *133*, 43783.
- (7) Fontenot, K. R.; Nguyen, M. M.; Al-Abdul-Wahid, M. S.; Easson, M. W.; Chang, S.; Lorigan, G. A.; Condon, B. D. The Thermal Degradation Pathway Studies of a Phosphazene Derivative on Cotton Fabric. *Polym. Degrad. Stab.* **2015**, *120*, 32-41.
- (8) Horrocks, A. R.; Zhang, S. Enhancing Polymer Flame Retardancy by Reaction with Phosphorylated Polyols. Part 2. Cellulose Treated with a Phosphonium Salt Urea Condensate (Proban CC®) Flame Retardant. *Fire Mater.* **2002**, *26*, 173-182.
- (9) Alongi, J.; Malucelli, G. Cotton Flame Retardancy: State of the Art and Future Perspectives. *RSC Adv.* **2015**, *5*, 24239-24263.
- (10) Carosio, F.; Alongi, J.; Malucelli, G. α -Zirconium Phosphate-Based Nanoarchitectures on Polyester Fabrics Through Layer-by-Layer Assembly. *J. Mater. Chem.* **2011**, *21*, 10370-10376.

- (11) Alongi, J.; Carosio, F.; Frache, A.; Malucelli, G. Layer by Layer Coatings Assembled Through Dipping, Vertical or Horizontal Spray for Cotton Flame Retardancy. *Carbohydr. Polym.* **2013**, *92*, 114-119.
- (12) Carosio, F.; Fontaine, G.; Alongi, J.; Bourbigot, S. Starch-Based Layer by Layer Assembly: Efficient and Sustainable Approach to Cotton Fire Protection. *ACS Appl. Mater. Interfaces* **2015**, *7*, 12158-12167.
- (13) Yang, J.-C.; Liao, W.; Deng, S.-B.; Cao, Z.-J.; Wang, Y.-Z. Flame Retardation of Cellulose-rich Fabrics via a Simplified Layer-by-Layer Assembly. *Carbohydr. Polym.* **2016**, *151*, 434-440.
- (14) Tsafack, M. J.; Levalois-Grützmacher, J. Flame Retardancy of Cotton Textiles by Plasma-Induced Graft-Polymerization (PIGP). *Surf. Coat. Technol.* **2006**, *201*, 2599-2610.
- (15) Caschera, D.; Toro, R. G.; Federici, F.; Riccucci, C.; Ingo, G. M.; Gigli, G.; Cortese, B. Flame Retardant Properties of Plasma Pre-treated/Diamond-like Carbon (DLC) Coated Cotton Fabrics. *Cellulose* **2015**, *22*, 2797-2809.
- (16) Zhang, Q.; Zhang, W.; Huang, J.; Lai, Y.; Xing, T.; Chen, G.; Jin, W.; Liu, H.; Sun, B. Flame Retardance and Thermal Stability of Wool Fabric Treated by Boron Containing Silica Sols. *Mater. Des.* **2015**, *85*, 796-799.
- (17) Alongi, J.; Ciobanu, M.; Malucelli, G. Cotton Fabrics Treated with Hybrid Organic-Inorganic Coatings Obtained Through Dual-Cure Processes. *Cellulose* **2011**, *18*, 1335-1348.
- (18) Wang, S.; Sui, X.; Li, Y.; Li, J.; Xu, H.; Zhong, Y.; Zhang, L.; Mao, Z. Durable Flame Retardant Finishing of Cotton Fabrics with Organosilicon Functionalized Cyclotriphosphazene. *Polym. Degrad. Stab.* **2016**, *128*, 22-28.

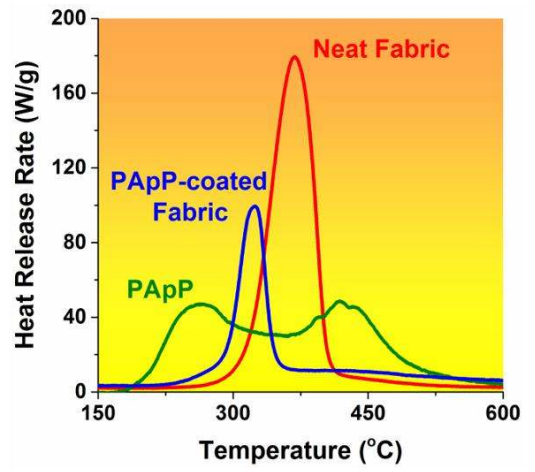
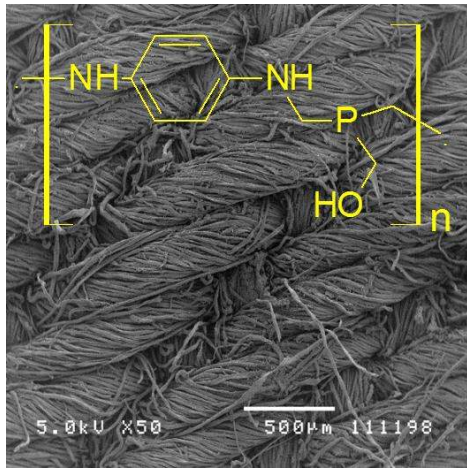
- (19) Mayer-Gall, T.; Knittel, D.; Gutmann, J. S.; Opwis, K. Permanent Flame Retardant Finishing of Textiles by Allyl-Functionalized Polyphosphazenes. *ACS Appl. Mater. Interfaces* **2015**, *7*, 9349-9363.
- (20) New, J.; Zope, I. S.; Abdul Rahman, S. N.; Yap, X. L. W.; Dasari, A. Physiological Comfort and Flame Retardancy of Fabrics with Electrostatic Self-Assembled Coatings. *Mater. Des.* **2016**, *89*, 413-420.
- (21) Chang, S.; Slopek, R. P.; Condon, B.; Grunlan, J. C. Surface Coating for Flame-Retardant Behavior of Cotton Fabric Using a Continuous Layer-by-Layer Process. *Ind. Eng. Chem. Res.* **2014**, *53*, 3805-3812.
- (22) Chen, S.; Li, X.; Li, Y.; Sun, J. Intumescent Flame-Retardant and Self-Healing Superhydrophobic Coatings on Cotton Fabric. *ACS Nano* **2015**, *9*, 4070-4076.
- (23) <http://solvay-proban.com>.
- (24) ASTM D6413 Standard Test Method for Flame Resistance of Textiles (Vertical Test). **Jun 2015**.
- (25) BS EN ISO 15025:2016 Protective Clothing. Protection Against Flame. Method of Test for Limited Flame Spread. **Dec 2016**.
- (26) ASTM D7309 - 13 Standard Test Method for Determining Flammability Characteristics of Plastics and Other Solid Materials Using Microscale Combustion Calorimetry. **2013**.
- (27) Frank, A. W.; Drake, G. L. Aniline Derivatives of Tetrakis(hydromethyl)phosphonium Chloride. *J. Org. Chem.* **1972**, *37*, 2752-2755.
- (28) Manabe, K.; Kobayashi, S. Mannich-Type Reactions of Aldehydes, Amines, and Ketones in a Colloidal Dispersion System Created by a Brønsted Acid–Surfactant-Combined Catalyst in Water. *Org. Lett.* **1999**, *1*, 1965-1967.

- (29) Chung, C.; Lampe, K. J.; Heilshorn, S. C. Tetrakis(hydroxymethyl) Phosphonium Chloride as a Covalent Cross-Linking Agent for Cell Encapsulation within Protein-Based Hydrogels. *Biomacromolecules* **2012**, *13*, 3912-3916.
- (30) Lim, D. W.; Nettles, D. L.; Setton, L. A.; Chilkoti, A. Rapid Cross-Linking of Elastin-like Polypeptides with (Hydroxymethyl)phosphines in Aqueous Solution. *Biomacromolecules* **2007**, *8*, 1463-1470.
- (31) Frank, A. W.; Daigle, D. J.; Vail, S. L. Chemistry of Hydroxymethyl Phosphorus Compounds Part II. Phosphonium Salts. *Text. Res. J.* **1982**, *52*, 678-693.
- (32) Daigle, D. J.; Frank, A. W. Chemistry of Hydroxymethyl Phosphorus Compounds Part IV. Ammonia, Amines, and THPOH: A Chemical Approach to Flame Retardancy. *Text. Res. J.* **1982**, *52*, 751-755.
- (33) Johnson, J. R.; Finley, R. L. Process for Making Flame-Resistant Cellulosic Fabrics, US5238464, **1993**.
- (34) Roy Choudhury, A. K.; Majumdar, P. K.; Datta, C. In *Improving Comfort in Clothing*; Song, G., Ed.; Woodhead Publishing: **2011**; Chapter 1, pp 3-60.
- (35) Meyer, U.; Müller, K.; Zollinger, H. The Mechanism of Catalysis in the Crosslinking of Cotton with Formaldehyde. *Text. Res. J.* **1976**, *46*, 756-762.
- (36) Fang, F.; Zhang, X.; Meng, Y.; Gu, Z.; Bao, C.; Ding, X.; Li, S.; Chen, X.; Tian, X. Intumescent Flame Retardant Coatings on Cotton Fabric of Chitosan and Ammonium Polyphosphate via Layer-by-Layer Assembly. *Surf. Coat. Technol.* **2015**, *262*, 9-14.
- (37) Horrocks, A. R. Flame Retardant Challenges for Textiles and Fibres: New Chemistry versus Innovative Solutions. *Polym. Degrad. Stab.* **2011**, *96*, 377-392.

(38) Wilding, M. A. In *Chemistry of the Textiles Industry*; Carr, C. M., Ed.; Springer Science+Business Media, B.V.: Dordrecht, **1995**; Chapter 1, pp 1-45.

(39) Yang, C. Q.; He, Q.; Lyon, R. E.; Hu, Y. Investigation of the Flammability of Different Textile Fabrics using Micro-Scale Combustion Calorimetry. *Polym. Degrad. Stab.* **2010**, *95*, 108-115.

Table of Contents



Development and evaluation of a water-based flame retardant spray coating for cotton fabrics

*Indraneel S. Zope, Shini Foo, Dean G. J. Seah, Aswini Tara Akunuri, Aravind Dasari**

School of Materials Science & Engineering (Blk N4.1), Nanyang Technological University,

50 Nanyang Avenue, Singapore 639798

*Corresponding author: aravind@ntu.edu.sg

Supporting Information

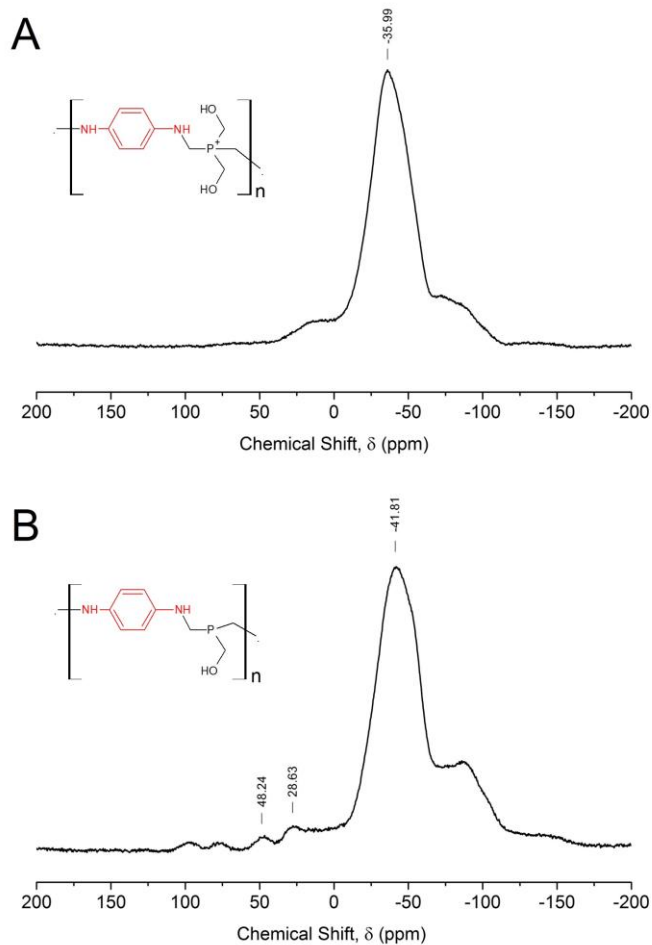


Figure S1. ^{31}P NMR solid state spectra for condensation polymer before (A) and after (B) drying at 110 °C converting phosphonium into phosphine.

Table S1. Estimated grammage of fabrics. Commercial fabrics data is provided as a reference benchmark.

Sample	Grammage (g/m^2)
Neat fabric	180 ± 4
PAP coated fabric	190 ± 3
PU-sprayed neat fabric	211 ± 6
PU-sprayed PAP coated fabric	236 ± 21
Nomex[1]	255
PBI[1]	272
PBI/Kevlar blend[1]	245

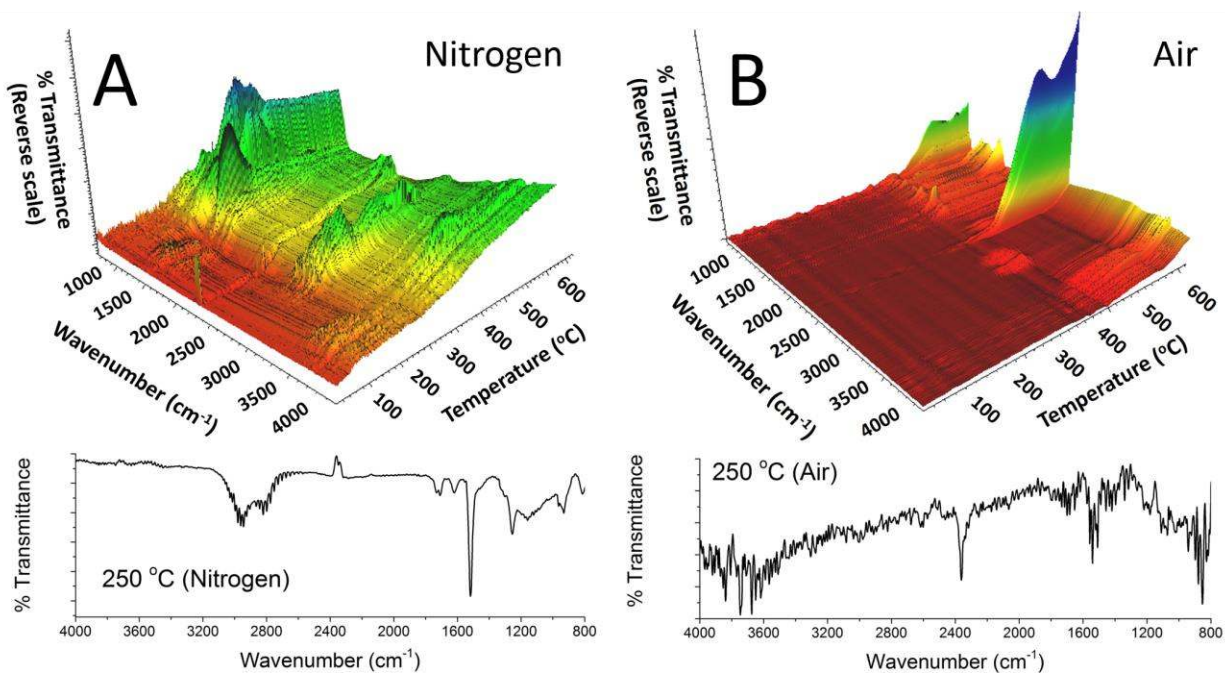


Figure S2. TG-IR curves for PApP product under nitrogen (A) and air (B) highlighting the formation of formaldehyde and its oxidation in respective atmospheres.

System 2

Ammonium polyphosphate (APP)/tetrakis-(hydroxymethyl)phosphonium chloride (THPC) coating.

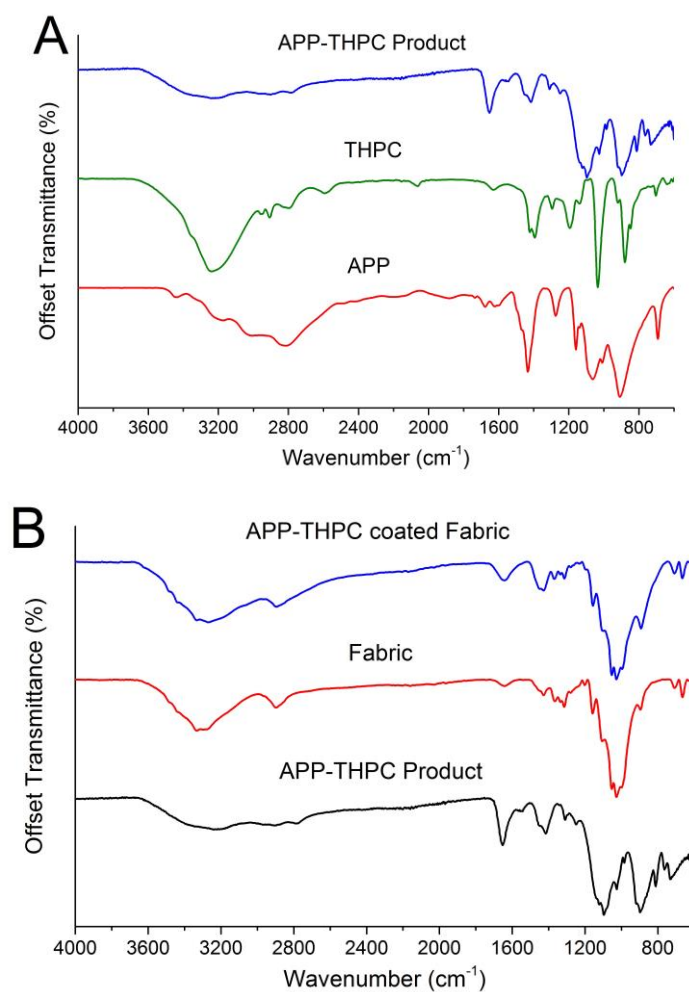


Figure S3. FTIR spectra to confirm successful synthesis of APP-THPC product (A) and its subsequent coating on cotton fabric (B).

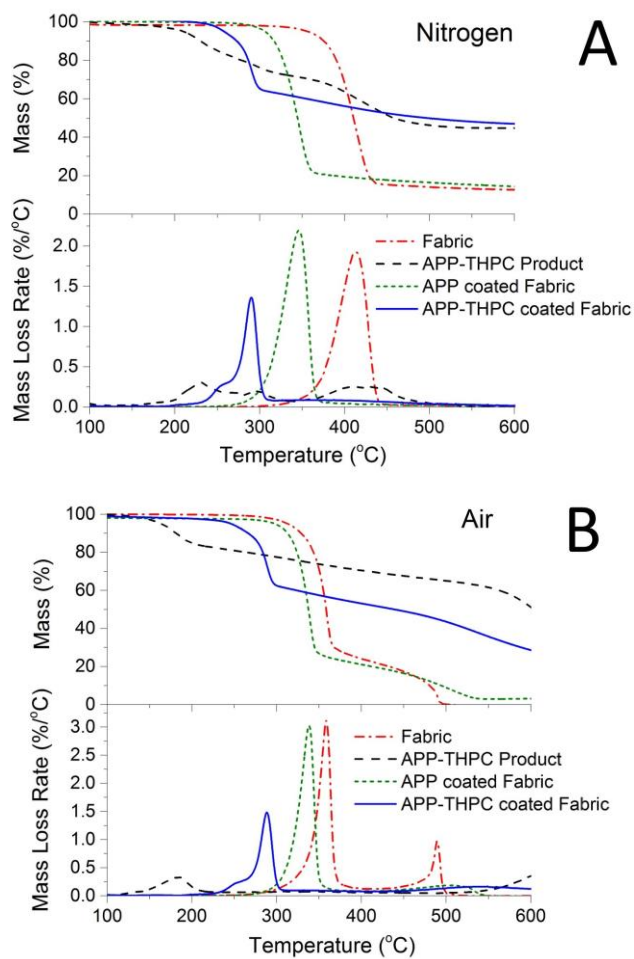


Figure S4. TGA curves for neat fabric, APP-THPC product and coated fabric under nitrogen (A) and air (B).

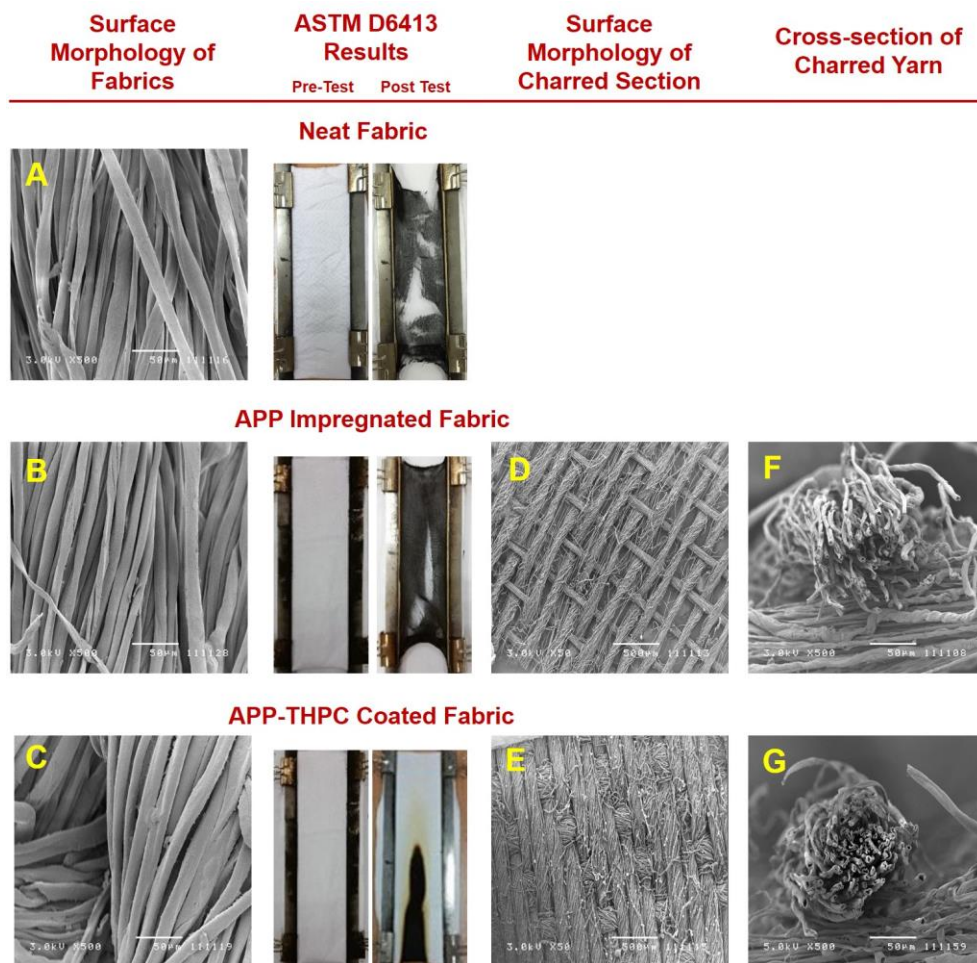


Figure S5. Representative SEM images of untreated fabric (A), APP infused (B) and APP-THPC coated (C) fabrics before test and after flammability test in accordance with ASTM D6413 (D, E). Cross-sectional images of char section of APP infused (F) and APP-THPC coated fabric (G).

Table S2. Results for neat and coated fabric in accordance with ASTM D6413.

ASTM D6413 Results	Neat Fabric	APP impregnated fabric	APP-THPC coated fabric
After-flame time (s)	21 ± 5	15 ± 1	1 ± 1
Afterglow time (s)	49 ± 7	15 ± 3	0
Char length (mm)	200	200	100 ± 10
Occurrence of melting or dripping	No	No	No
Hole formation	Yes	Yes	No
Comment(s)	Complete burn-off, very fragile char	Complete burn-off, very fragile char	Subtle smell
Test passed	No	No	Yes

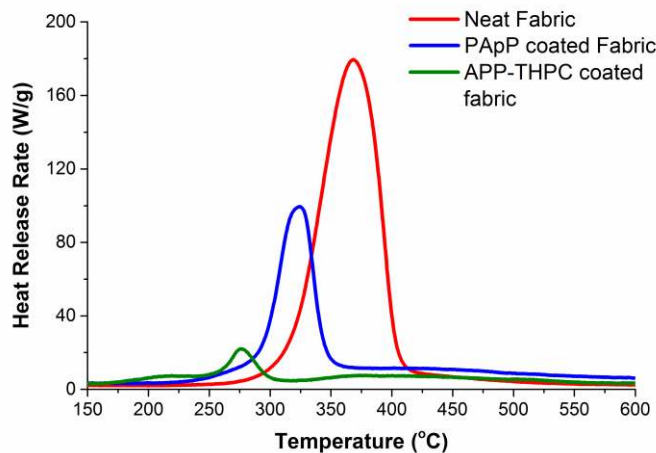


Figure S6. PCFC data for neat fabric, PApP coated and APP-THPC coated fabrics.

Table S3. PCFC data for neat fabric, PDA-THPC product and coated fabrics.

Sample	pHRR [relative % reduction] (W/g)	Peak temperature (°C)	THR (kJ/g)	Char (%)
Neat Fabric	187 ± 11	373 ± 4	11 ± 0.4	13.5 ± 1.1
APP-THPC coated fabric	24 ± 5 [-87 %]	279 ± 7	1.9 ± 0.1	46.1 ± 1.4

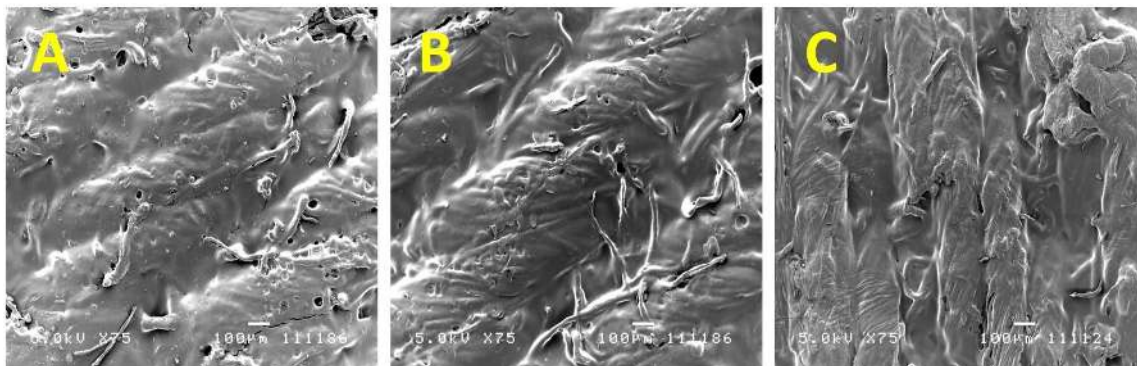


Figure S7. SEM images showing surface morphology of PU-sprayed PApP coated fabric after first (A), second (B) and third (C) washing cycles.

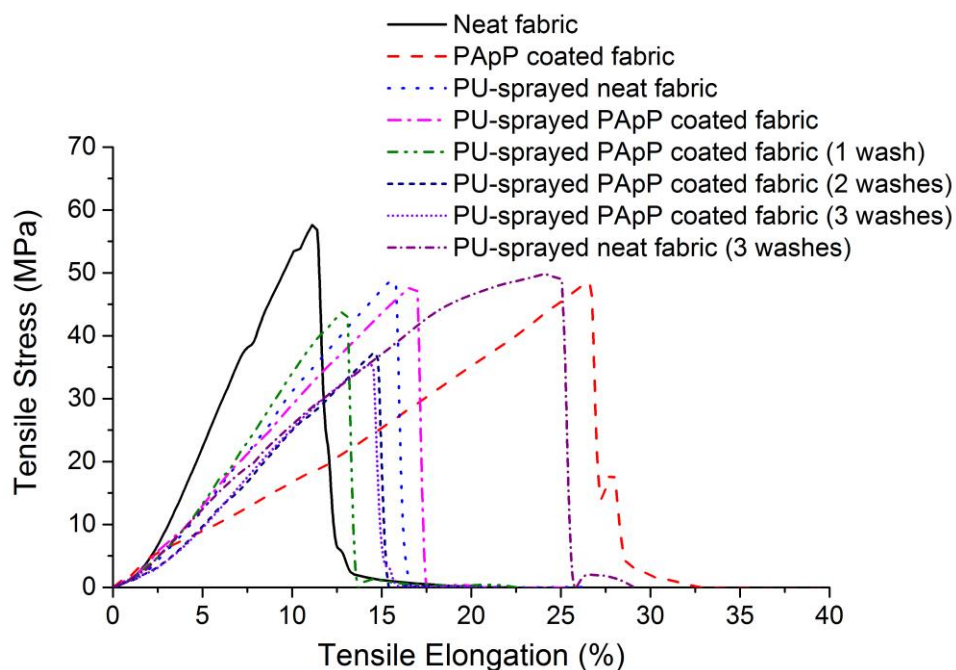


Figure S8. Stress-strain curves for neat and coated fabrics before and after washing cycles.

Table S4. Mechanical test results.

Sample	Load (N)	Breaking Stress (MPa)	Breaking Elongation (%)
Neat fabric	170 ± 5.1	56 ± 1.8	10 ± 2.3
PApP coated fabric	177 ± 8.1	50 ± 3.6	25 ± 3.0
PU-sprayed neat fabric	197 ± 12.9	52 ± 4.6	16 ± 2.2
PU-sprayed PApP coated fabric	183 ± 9.7	49 ± 3.6	14 ± 2.7
PU-sprayed PApP coated fabric (1 wash)	151 ± 5.8	42 ± 1.7	11 ± 1.6
PU-sprayed PApP coated fabric (2 washes)	138 ± 12.7	37 ± 3.1	13 ± 2.5
PU-sprayed PApP coated fabric (3 washes)	138 ± 6.1	36 ± 2.1	15 ± 1.0
PU-sprayed neat fabric (3 washes)	161 ± 8.8	50 ± 5.3	18 ± 5.6

References.

(1) Holmes, D.A.; Horrocks, A.R. In *Handbook of Technical Textiles (Second Edition)*; Woodhead Publishing: **2016**; Chapter 10, pp 287-323.