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Phytic acid: A bio-based flame retardant for cotton and wool fabrics

Kesavarao Sykam [a,*], Michael Försth [b], Gabriel Sas [b], Ágoston Restás [c], Oisik Das [b,*]

[a] Polymers & Functional Materials Division, Indian Institute of Chemical Technology, Uppal Road, Tarnaka, Hyderabad, 500007, Telangana, India
[b] Structural and Fire Engineering Division, Department of Civil, Environmental and Natural Resources Engineering, Luleå University of Technology, 97187, Luleå, Sweden
[c] Department of Fire Protection and Rescue Control, University of Public Service, H-1011, Budapest, Hungary

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ABSTRACT

Phytic acid (PA) is one of the widely used flame retardants (FRs) to treat a variety of fabrics owing to its high phosphorus content of ca. 28 wt% (with respect to its molecular weight), abundance, non-toxicity, and biocompatibility. The current review discusses the state-of-the-art of PA-based FRs for natural fabrics such as cotton and wool. The possibilities of making PA and FR-based multi-functional cotton fabrics having antimicrobial, conductive, hydrophobic properties are reported by virtue of the synergistic benefits associated with chitosan, silicon, nitrogen, and boron-based molecules. The factors influencing the FR behaviour as well as the durability of PA-based cotton and wool fabrics are discussed with respect to the concentration of PA, pH of the coating solution, temperature, and preparation methods. Holistically, PA has been proved to be a potential alternative to halogenated FRs to confer fire retardant property to cotton and wool fabrics.

1. Introduction

Cotton and wool are the most ubiquitous fabrics from natural resources that have been extensively utilised in upholstery, clothing, and industrial applications due to their hygroscopicity, comfort, softness, biocompatibility and breathability properties (Xie et al., 2013; Gao et al., 2015). However, the fire safety of these fabrics is limited due to their inherent low thermal oxidative stabilities when exposed to flame causing financial losses, injuries and deaths (Carosio et al., 2015; Li et al., 2019a). Cotton have low limiting oxygen index (LOI) of 18 % whereas wool fabrics have some extent of inherent flame retardancy owing to their high nitrogen, sulphur and moisture contents of 15–16 %, 3–4 %, and 10–15 %, respectively (Forouharshad et al., 2012; Cardamone, 2013). In spite of wool's reasonable LOI of ~23 % that indicates it's somewhat FR nature, it fails to pass vertical burning tests, which involve direct flame application. To address this issue, FR treatments are performed by impregnating the surface of the fabrics by various methods such as sol-gel process (Barbalini et al., 2019), layer-by-layer (LbL) assembly (Carosio et al., 2013; Chang et al., 2014; Fang et al., 2015, 2016), grafting on to the surface (Liu et al., 2017), and dip-coating technologies.

In light of the aforementioned, the development of FR fabrics is a promising area of research for material chemists (Das et al., 2020b). In this regard, different varieties of FRs have been developed and are classified broadly into two types based on their elemental composition, namely, halogenated, and non-halogenated. Despite the superior performance of halogenated FRs by scavenging active radicals in vapour phase (Das et al., 2020a), there is a ban on them as they produce carcinogenic by-products with unfavourable bio-accumulation capabilities (Rakotomalala et al., 2010; Yoshioka-Tarver et al., 2012; Hobbs, 2019; Mayer-Gall and Derksen, 2019). Non-halogenated FRs are classified into phosphorus-based FRs, nitrogen-based FRs, silicon-based FRs, boron-based FRs, metal hydroxide-based FRs (Morgan and Wilkie, 2014; Rezvani Ghomi et al., 2020) and flavonoid-based FRs such as baicalin, quercetin and rutin (Zhou et al., 2019). Combinations of these non-halogenated FRs are reported to perform better by a synergistic effect compared to the respective individual FRs (Salmeia et al., 2016; Das et al., 2017, 2018a; Sykam et al., 2019; Kim et al., 2020; Zhao et al., 2020). For instance, P—N synergism was reported by Wan et al., wherein tris-(hydroxymethyl)-aminomethane-penta (methylphosphonic acid) was utilised to impart flame retardancy to cotton fabric and the same group has studied P-*N*-S synergism by using thiourea-phosphate polymer (Wan et al., 2019, 2020). In addition, P—N synergism on hemp fibres was reported by Moussa et al., wherein hemp fibres were treated with a solution of phosphonic acid and urea (Moussa et al., 2020).

In the context of fabric with improved FR properties, utilisation of bio-based FRs have attracted interest of chemists because they are

* Corresponding authors.
E-mail addresses: kesavaraosykam@gmail.com (K. Sykam), oisik.das@ltu.se, odas566@aucklamnduni.ac.nz (O. Das).

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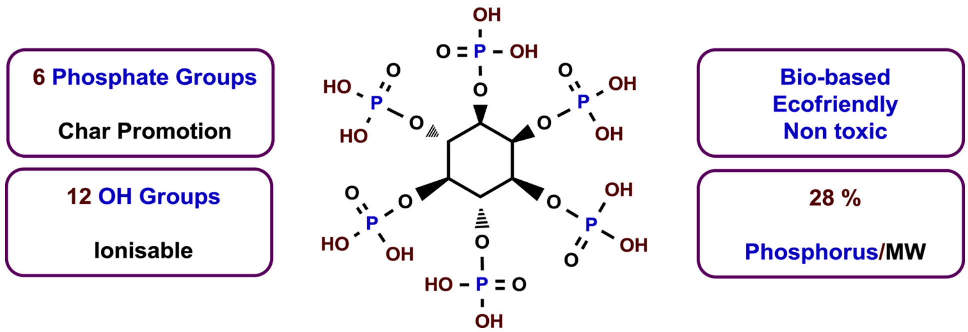

Fig. 1. Structural features of phytic acid.

generally innocuous towards the environment and human health. PA is the one which obeys the aforementioned requirements on account of its biocompatibility, non-toxicity, eco-friendly nature and its availability. It is extracted from beans, legumes, oilseeds, and cereal grains (Duskov et al., 2001). PA is also known as inositol hexakisphosphate. It consists of 6 phosphate groups and 12 hydroxyl groups that can combine with almost all kinds of metal ions and positively charged compounds (Cheng et al., 2019a). Structure of PA and its structural features are depicted in Fig. 1. Owing to its unique structure, high phosphorus content of 28 wt% with respect to its molecular weight (Costes et al., 2017), and its ability to bind cellulose, proteins, and different fabrics such as cotton, wool, nylon, silk and poly (lactic acid) nonwoven fabrics, the demand for PA utilisation as FR has increased (Cheng et al., 2016b; Thota et al., 2020). Moreover, PA and its salts are known to be good partners to positively charged counterparts for involvement in LbL assembly (the technique widely used to make FR fabrics) (Tang et al., 2010). Phosphorus-based FR containing cotton fabrics tend to have lower onset decomposition temperatures compared to the neat substrate. It should be noted that FRs have to catalyse cellulosic degradation below 300 °C in order to promote dense char formation (Aenishänslin et al., 1969). PA is the one that could stimulate the cellulosic degradation below 300 °C when applied to cotton fabrics and catalyses dehydration reaction and supports carbonisation during combustion (Wang et al., 2015). It is also an added advantage for PA-containing FR fabrics that it forms protective layer before the neat fabric decomposes (Gaan and Sun, 2007). On the other hand, PA has the limitation to be used alone in making FR cotton fabrics as it degrades cellulose by the acidic effect. To address this issue amine functionalised molecules or polymers are being used as they ameliorate the acidic nature of PA (Laufer et al., 2012; Li et al., 2019c). On the other hand, owing to PA's large number of negatively charged phosphate groups, its addition to wool fabrics by electrostatic interaction offers effective flame retardancy. (Cheng et al., 2016a). The ability of PA's negatively charged phosphate groups to react with polycationic counterparts creates synergistic FR systems for wool fabric. These polycationic counterparts include chitosan (CH) (Cheng et al., 2019b), and polyethylenimine (PEI) (Cheng et al., 2019c). Contrary to PA's detrimental acidic effect on cotton fabrics, low pH is favourable for wool fabrics as it can ionise –NH_2 groups of wool, thereby, facilitating LbL deposition (Cheng et al., 2016a).

The current review aims to showcase the state-of-the-art of PA as FR component in cotton and wool fabrics. Synergistic effects of PA with CH, silicone-based, nitrogen-based FRs are also discussed. Factors influencing PA deposition on to cotton and wool fabrics such as pH and temperature are mentioned. The problems associated with PA's acid effect on cotton fabric, mould growth on the fabrics, and washing durability of fabrics are discussed in detail. The development of FR multi-functional fabrics associated with PA such as antimicrobial, hydrophobic, and conductive fabrics is also reported. Flammability parameters such as peak heat release rate (pHRR), total heat release (THR), LOI, char yields of neat cotton and wool fabrics with respect to PA-based FR fabrics are summarised in Table 2 & 3 . This review is divided into four parts, where firstly PA-based FR cotton fabrics are detailed, followed by PA-based FR wool fabrics, thirdly, FR mechanism of PA is explained and finally, conclusions and future perspectives are drawn. There are only a few reviews available on FR textiles based on the deposition methods such as sol-gel, LbL assembly and finishing methods, etc. (Wakelyn, 2008; Gaan et al., 2011; Horrocks, 2011; Holder et al., 2017; Trends, 2018; Qiu et al., 2018). Therefore, there is a dearth of reviews regarding the role of PA as an effective FR partner for cotton and wool fabrics. Table 1 summarises the various aspects that have been discussed in the current review.

2. PA-based FR cotton fabrics

2.1. Factors influencing FR performance of PA-based cotton fabrics

The significance of bio-based PA as FR for cotton fabrics was first reported by a study in 2012 (Laufer et al., 2012). The authors prepared PA-based intumescent FR cotton fabric by LbL deposition using PA and CH as anionic and cationic solution, respectively. The effect of pH of the electrolyte medium on PA deposition on to the fabric was studied and it was found that the maximum deposition was attained at pH 4 compared to 5 and 6. The thinnest coating with 30 bilayers, and 66 % PA deposition was observed at pH 4. It was found that the PA/CH-based cotton fabrics with pH 4 had 90 % char residue after vertical flame test and lowered 60 % of pHRR and 76 % of THR compared to the neat fabric. The values of pHRR, THR, LOI, and char yields are summarised in Table 2. The intumescent behaviour was visualised by scanning electron microscope (SEM) of post-burn cotton wherein char bubbles were observed on the top of the sample and in between the fibres. The FR cotton fabrics with pH 6 exhibited weaker intumescent effect by showing less bubbling compared to the one with pH 4 (Laufer et al., 2012). Fig. 2 depicts the LbL deposition method and intumescent char formation of PA/CH-based FR cotton fabric.

Cheng et al., reported an intumescent, bio-based FR for cotton fabric comprising of PA and triethanolamine (TEA) (PA/TEA) that act as an acid source and blowing agent, respectively. Here, TEA was used not only to adjust the pH of the solution but also to provide a synergistic benefit via forming a foaming char during combustion. The influence of FR system's pH on FR behaviour of cotton fabric was studied. A pH of 5 was found to be optimum for the FR's action on the cotton fabric whereas pH of over 5 was deemed unsuitable. Higher loading of TEA was prepared in order to increase the pH, however, it led to ionisation of the cellulose fibre thereby affecting the adsorption of PA onto the cotton, which compromised the FR performance. It is evident from the results that the solution with pH 5 and 100 g/L PA loading had higher LOI value (32 %) than the neat fabric (18 %) (Cheng et al., 2020a). The values of pHRR, THR, LOI and char yields at 700 °C of PA/TEA treated cotton fabrics are provided in Table 2.

The number of bilayers that FR system is involved in to make a FR cotton fabric by LbL assembly is also an important parameter to study. The number of bilayers deposited is directly proportional to the

Table 1
A brief summary of the different aspects covered in the present review.

Author (s)	Research/Novelty	Methodology	Main Result (s)
(Laufer et al., 2012)	Effect of pH on FR performance of PA based cotton fabrics.	• LbL assembly. • CH as cationic solution. • PA as anionic solution.	66 % of PA deposition was observed at pH 4.
(Cheng et al., 2020a)	Effect of pH on FR performance of PA based cotton fabrics.	• PA as acid source. • TEA as blowing agent.	The pH of 5 was found to be optimum for FR action based on the results.
(Zilke et al., 2020)	Effect of deposited bilayers on FR performance of PA based cotton fabrics.	• -LbL assembly. • -PVAm as cationic solution. • -PA as anionic solution.	The 15 bilayered FR coated cotton fabric showed superior FR performance compared to 5 and 10 bilayered FR coated cotton fabric.
(Feng et al., 2017)	Durability of PA-based FR Cotton Fabrics.	Grafting of AP on to the cellulose fibres by using dicyandiamide as catalyst.	Highly durable FR cotton fabric was observed even after 30 laundering cycles with LOI of 31 %.
(Zhu et al., 2020)	Durability of PA-based FR cotton fabrics.	Impregnation of cotton fabrics in PBN solution followed by ultra sonication.	Highly durable FR cotton fabric was observed even after 50 laundering cycles with LOI of 38 %.
(Li et al., 2020)	Development of antimicrobial PA-based FR cotton fabrics.	• LbL assembly. • CH as cationic solution. • AP as anionic solution.	CH/AP-cotton fabrics eliminated bacterial colonies by 83 %.
(Li et al., 2019c)	Development of antimicrobial PA-based FR cotton fabrics.	• LbL assembly. • PCQS as cationic poly-electrolyte solution. • PA as anionic solution.	Eliminated the bacterial colonies of *S. aureus* by 92%.
(Liu et al., 2018a)	Development of hydrophobic PA-based FR cotton fabrics.	• LbL assembly. • -PEI/melamine as cationic solution. • PA as anionic solution. • PDMS was infused to attain hydrophobicity.	Hydrophobic cotton fabrics with a 130° water contact angle was observed.
(Liu et al., 2019)	Development of conductive PA-based FR cotton fabrics.	Polymerising of PPy on to the cotton fabric by using PA as doping agent.	Conductivity of 0.28 S/cm was observed.
(Zhou et al., 2020)	Development of conductive PA-based FR cotton fabrics.	Polymerising PANI on to the cotton fabric by using PA as doping agent.	Switchable conductive FR fabrics were achieved by doping, de-doping and re-doping of PA.
(Li et al., 2017b; Barbalini et al., 2019);	Synergists for PA-based FR cotton fabrics.	Incorporation of Silicon containing molecules.	Condensed phase mechanism by forming dense silicaceous char.
(Barbalini et al., 2020)	Synergists for PA-based FR cotton fabrics.	BC as synergist for PA.	High char residue of 85 % with flame extinguishing property.
(Cheng et al., 2016a, 2019b)	Factors influencing FR performance of PA-based wool fabrics.	The solution's pH, temperature and concentration of PA.	Higher temperatures ca. 90 °C and lower pH of ca. 1 are favourable conditions for high absorption of PA on to the wool fabric.
(Cheng et al., 2020b)	Synergists for PA-based FR wool fabrics.	Silicon containing molecules.	Condensed phase mechanism by forming dense silicaceous char.
(Cheng et al., 2019a)	Durability of PA-based FR wool Fabrics.	Grafting of PA-based reactive FR i.e., HPPHBTCA on to the wool fabric.	HPPHBTCA grafted wool fabrics were self-extinguished even after 20 washing cycles.

concentration of FR deposited onto the fabric (Zilke et al., 2020). PA-based and nitrogen containing FR cotton fabric has been prepared by LbL assembly in which polyvinylamine (PVAm) acted as the cationic layer. A series of bilayers viz. 5, 10, and 15 has been prepared and it was found that the 15 bilayered cotton fabrics showed a superior FR behaviour compared to the neat cotton fabric by virtue of reduction in pHRR by 60 %. The mechanism of flame retardancy of PA/PVAm was well established by thermogravimetric analysis coupled with Fourier transform infrared spectroscopy, FTIR (TGA-FTIR). It was clearly evident from the decreasing peak intensity of C═O stretching (1735 cm^{-1}) frequency of formaldehyde and decreasing transmittance percentage of carbon dioxide (CO_2) (2349 cm^{-1}) and water (bending vibration of water ~1500 cm^{-1}) compared to the neat cotton fabric (Zilke et al., 2020). 2D plots and FTIR-spectra of the neat cotton fabric and PA/PVAm coated cotton fabric are reported in Fig. 3.

2.2. Durability of PA-based FR cotton fabrics

Durability of PA-based FR cotton fabrics is compromised when FRs are physically adsorbed onto the fabrics (Costes et al., 2015; Hernández-Alvarado et al., 2016). This is due to the ionic FRs that are dissolved in water while washing. To address this issue, it is recommended to have a FR that could be covalently linked to the cotton fabric. In this context, ammonium phytate (AP) was used for making a semi-durable FR cotton fabric by a grafting approach via P—O—C linkages to cellulose molecules (Feng et al., 2017). Dicyandiamide was used as the catalyst to promote cross-linking reaction between the cotton fibres. The grafting of AP onto the cotton fabric was confirmed by FTIR spectroscopy through the occurrence of characteristic absorption peaks such as 1238 cm^{-1} and1205 cm^{-1} corresponding to P═O and P—O—C stretching vibrations, respectively. The resultant AP grafted cotton fabrics have shown superior flame retardancy with higher LOI value of 43 % (while LOI of neat cotton was found to be 18 %) and with lower char length of 31 mm, which is ~90 % less compared to the neat cotton fabric (300 mm). Increasing durability of these fabrics was confirmed by LOI of 31 % even after 30 laundering cycles. The values of pHRR, THR, LOI and char yields at 700 °C of AP treated cotton fabrics are summarised in Table 2. In addition, the crosslinking ability of AP on lyocell fibres was successfully demonstrated by Liu et al. (Liu et al., 2018b). On the other hand, the direct utilisation of PA shows adverse effect in mechanical properties of the cotton fabrics. This is due to the acidic effect of PA wherein degradation of cellulosic fibres takes place. This was overcome by using AP instead of PA. The AP treated crosslinked lyocell fabrics were found to have good mechanical properties with a minimum loss of 8% compared to neat fabric's mechanical properties. The LOI of AP cross-linked fabric was 39 %, which is significantly higher than the neat cotton fabric used in the study (17 %) and it is observed that the fabric has met the FR criterion by showing 30 % LOI even after 30 washing cycles. Schematic representation of synthesis and crosslinking reaction of AP with cotton fabric is shown in Fig.4.

As stated before, strong acidic nature of PA limits its direct utilisation

Table 2
Cone calorimetry, LOI, and char yields of neat cotton fabric and PA-treated cotton fabrics.

Sample description	pHRR	% of pHRR decreased w.r.t. neat fabric	THR	% of THR decreased w.r.t. neat fabric	LOI (%)	Char % @ 700 °C		Ref
						N_2	**Air**	
Neat Cotton Fabric	216 ± 5.7[a]	80.18	10.7 ± 0.1[a]	60.74	—	8.7		(Zilke et al., 2020)
PA/PVAm	42.8 ± 5.1		4.2 ± 0.2		—	29.1		
Neat Cotton Fabric	—	—	—	—	18	14		(Liu et al., 2019)
PA/PPy	—	—	—	—	37.6	50		
Neat Cotton Fabric	—	—	—	—	18	12.6		(Zhou et al., 2020)
PA/PANI	—	—	—	—	32	39.2		
Neat Cotton Fabric	223[b]	8.96	19.2[b]	16.66	—	12.8		(Li et al., 2017a)
NaPA/APTES	203		16		—	35.2		
Neat Cotton Fabric	223 ± 15[b]	82.06	19.2 ± 1.6[b]	66.14	18	12.8		(Liu et al., 2018c)
NaPA/APTES/CH	40 ± 6		6.5 ± 0.8		29	37.0		
Neat Cotton Fabric	229.1 ± 6.8[b]	73.67	11.7 ± 0.1[b]	80.34	18		0.0	(Cheng et al., 2020c)
PA/TEOS (0.2/0.6 mol/L)	60.3 ± 1.3		2.3 ± 0.1		29.8		13.8	
Neat Cotton Fabric	106.4[b]	74.71	2.01[b]	39.80	—	3.8		(Barbalini et al., 2019)
PA/TEOS (70/30)	26.9		1.21		—	**41.1**		
Neat Cotton Fabric	195.1[b]	**94.51**	2.804[b]	**57.98**	17.8	0.91		(Feng et al., 2017)
AP	10.7		1.178		**43.2**	**42.46**		
Neat Lyocell Fabric	—	—	—	—	17.0	16.48		(Liu et al., 2018b)
AP	—	—	—	—	39.2	38.89		
Neat Cotton Fabric	259 ± 6.7[a]	61.77	12.0 ± 0.1[a]	76.66	—	5.6 [a]		(Laufer et al., 2012)
PA/CH	99 ± 3.5		2.8 ± 0.1		—	**41.7**		
Neat Cotton Fabric	181 ± 10[b]	55.80	10.6 ± 0.2[b]	64.15	18.0	12.5		(Li et al., 2020)
AP/CH	80 ± 6		3.8 ± 0.1		27.0	34.0		
Neat Cotton Fabric	229.1 ± 6.8[a]	**73.67**	11.7 ± 0.1[a]	**79.48**	17.6	7.9		(Cheng et al., 2020a)
PA/TEA	60.3 ± 0.2		2.4 ± 0.1		**32.4**	**41.2**		
Neat Cotton Fabric	116 ± 7[b]	55.17	3.32 ± 0.11[b]	45.78	—		0.8	(Liu et al., 2018a)
PA-PEI/melamine/ PDMS	52 ± 5		1.80 ± 0.15		—		11.8	
Neat Cotton Fabric	236[b]	75.42	5.94[b]	52.35	18.2	8		(Li et al., 2019b)
PA/PEI/SiO_2	58		2.83		33.7	40.7		
Neat Cotton Fabric	169 ± 0.9[b]	46.15	10.5 ± 1.1[b]	58.09	18	12.5		(Li et al., 2019a)
PA/GP-108	91 ± 0.3		4.4 ± 0.2		29	40.0		
Neat Cotton Fabric	186 ± 2[b]	31.18	10.0 ± 0.11[b]	37.4	—	4.6		(Wang et al., 2015)
PA/SiN	128 ± 7		6.26 ± 0.35		—	**39.9**		
Neat Cotton Fabric	—	—	—	—	18.2	8		(Li et al., 2019c)
$PEI(PA/PCQS)_{30}$	—	—	—	—	29.8	34		
Neat Cotton Fabric	163.072[b]	**78.61**	50.102[b]	**53.91**	19	19.06		(Zhu et al., 2020)
PBN	34.868		23.092		**45**	**36.61**		
Neat Cotton Fabric	105 [b]	46.66	2.1[b]	9.52	—	3.8		(Barbalini et al., 2020)
PA/BC	56		1.9		—	36		

a= MCC (pHRR: W/g) (THR: kJ/g); **b**= CC (pHRR: kW/m^2) (THR: MJ/m^2).

Table 3
Cone calorimetry, LOI, and char yields of neat wool fabric and PA-treated wool fabrics.

Sample description	pHRR	% of pHRR decreased w.r.t. neat fabric	THR	% of THR decreased w.r.t. neat fabric	LOI (%)	Char % @ 700 °C		Ref
						N_2	**Air**	
Neat wool fabric	131.7 ± 3.5[a]		14 ± 0.5[a]		23.6	22.3		(Cheng et al., 2016a)
PA	76.7 ± 1.6	**41.76**	6.7 ± 0.2	**52.14**	**35.2**	**38.0**		
Neat wool fabric	—	—	—	—	23.6		0.2	(Cheng et al., 2020b)
PA/TEOS	—	—	—	—	31.6		25.7	
Neat wool fabric	138.9 ± 3.8[a]		13.3 ± 0.1[a]		23.6	17.3		(Cheng et al., 2019c)
PA/PEI	83.8 ± 0.7	**39.66**	7.4 ± 0.4	**44.36**	**36.8**	**32.4**		
Neat wool fabric	132.8[a]		13.8[a]		23.6	15.9		(Cheng et al., 2019b)
PA/CH-PEC	81.0	38.63	8.1	41.30	33.3	29.0		
Neat wool fabric	—	—	—	—	23.6		2.7	(Cheng et al., 2019a)
HPPHBTCA	—	—	—	—	30.3		23.8	
Neat wool fabric	—	—	—	—	23.6	20.2		(Cheng et al., 2018a)
PA/BTCA/TiO_2	—	—	—	—	34.4	39.0		

[a] MCC (pHRR: W/g) (THR: kJ/g); **b**= CC (pHRR: kW/m^2) (THR: MJ/m^2).

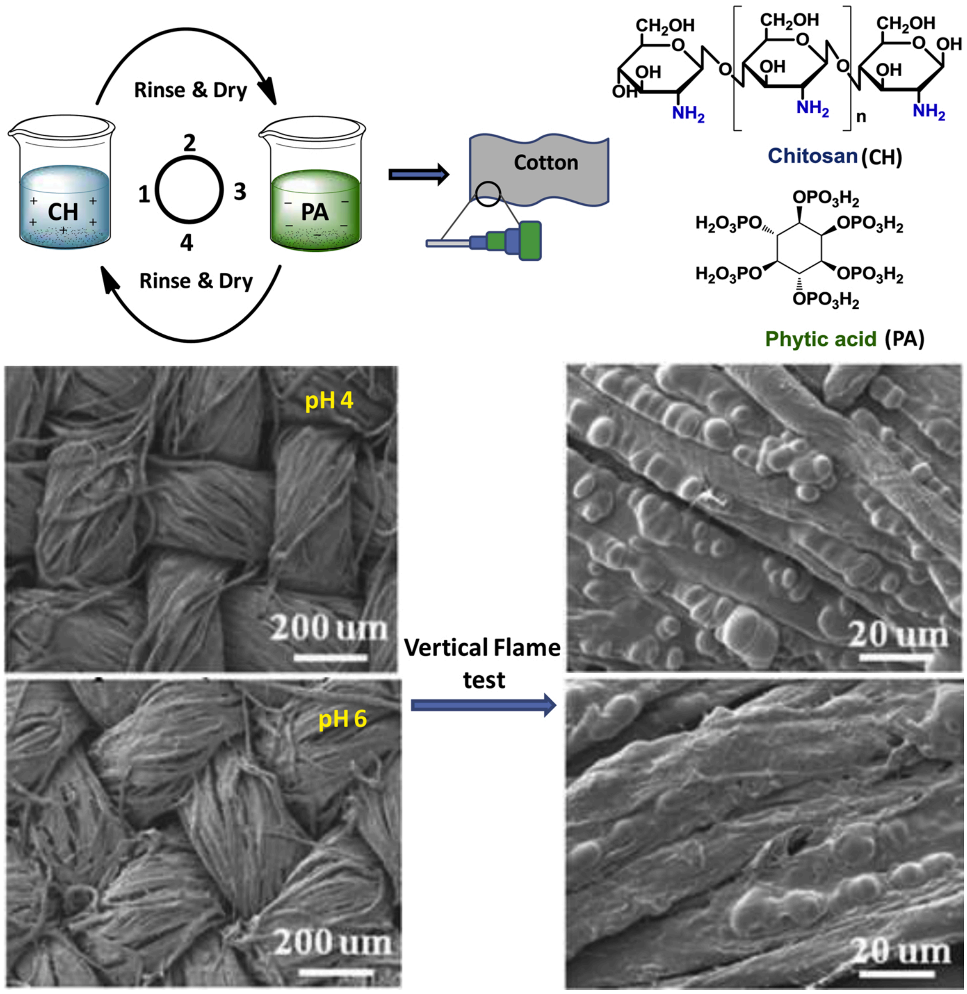

Fig. 2. Schematic representation of Layer-by-Layer assembly of phytic acid/chitosan (PA/CH) system for cotton fabric and scanning electron microscope (SEM) micrographs of cotton fabrics before and after the flame test (intumescent char bubbles can be seen). Adopted and reproduced with permission from the ref (Laufer et al., 2012).

as FR for cotton fabrics. To address this issue, a gel of (3-Piperazinylpropyl)-methyldimethoxysilane (GP-108) was prepared by sol-gel process and it was reacted with PA to produce FR mixture (GPA = GP-108 + PA) with low acidity compared to PA (Li et al., 2019a). FR cotton fabric was prepared with GPA by dip coating method (Fig.5). The resultant GPA-based FR was successfully grafted onto the surface of the fabric and was evident from SEM micrographs and their corresponding energy dispersive X-ray (EDX) analysis. The synergistic effect of GP-108 was studied by varying its concentration with respect to PA while PA concentration remained constant. The synergistic effect was found to be directly proportional to GP-108 loading in terms of increasing char yields, decrease in THR, pHRR, and increasing LOI (Table 2). The mechanism involved the release of a non-flammable NH_3 gas via —NH_2^+— from GP-108 and PA catalysed char formation during combustion. Hence GPA-based FR cotton fabrics have both vapour phase and condensed phase mechanisms.

Boric acid and borax are known to produce eco-friendly, non-toxic FRs for cotton fabrics since many years. However, boron-based FRs are prone to hydrolysation and thereby compromises the washing durability (Lu and Hamerton, 2002; Khalili et al., 2019). PA is found to have the ability to bind boric acid by covalent linkages to tackle the washing durability issue. A chelating, eco-friendly, and bio-based FR cotton fabric was made by a solution of PA in combination with boric acid-urea (PBN) with ultra-sonication at 50 °C with cotton to solution ratio of 1:20 (Zhu et al., 2020). A series of PBN solutions were made by varying PBN concentration from 30 g/L to 120 g/L. It was found that the 30 g/L PBN solution have shown superior FR performance compared to neat fabric as well as the highest loading of PBN i.e. 120 g/L. The successful deposition of PBN was confirmed by X-ray photoelectron spectroscopy (XPS) analysis of coated fabrics with the peaks at 133.87 eV, 400.14 eV and 190.86 eV that correspond to P2p, N1s, and B1s, respectively. The durability of the PBN coatings was well established by LOI values of 30 g/L PBN coated fabric with 45 % and 38 % corresponding to before and after 50 laundry cycles, respectively. The values of pHRR, THR, LOI and char yields at 700 °C of PBN treated cotton fabrics are tabulated in Table 2.

2.3. Antimicrobial and hydrophobic PA-based FR cotton fabrics

Applications of cotton fabrics is not only limited by their inherent flammability but also by their vulnerability to breeding mould when applied in humid environments (Ren et al., 2009; Lin et al., 2018; Wang et al., 2020). This could be overcome by imparting antibacterial property to the cotton fabric. In this context, Li et al. reported, CH and AP-based FR that was prepared by LbL deposition (Li et al., 2020). FR behaviour and antibacterial studies were performed on neat cotton, CH-based cotton, AP-based cotton, and CH/AP-based cotton fabrics. The antibacterial property of cotton fabric with AP was evident from the elimination of bacterial colonies by 83 % whereas cotton fabric with AP/CH has shown outstanding antibacterial property with elimination

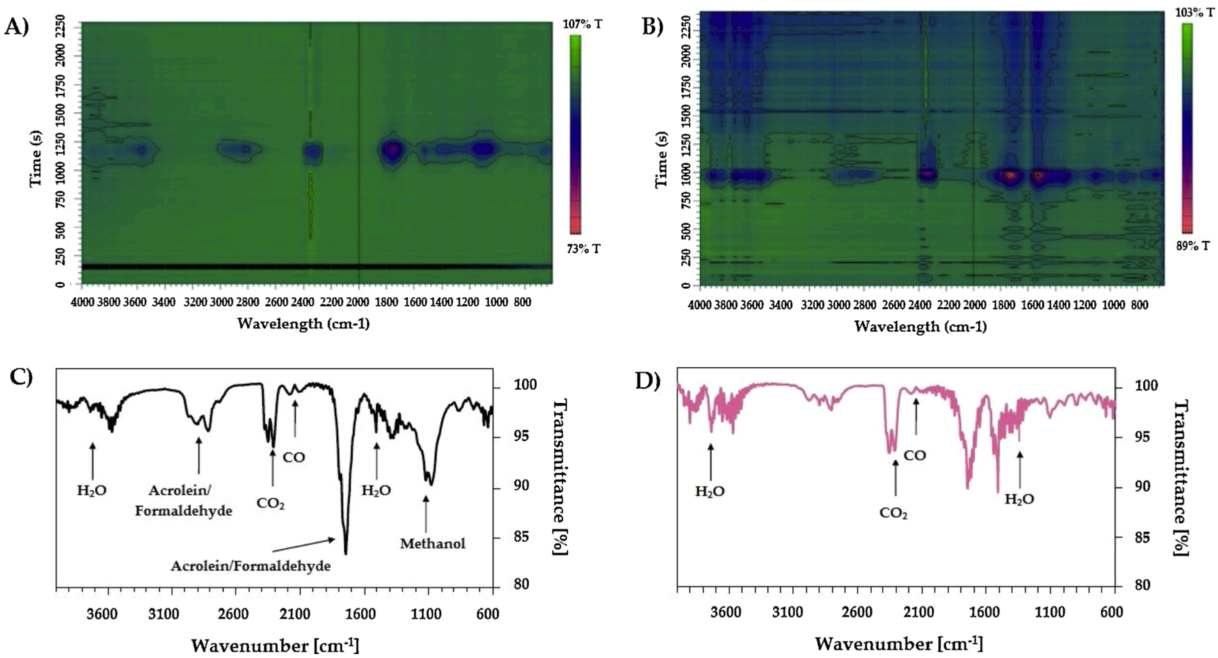

Fig. 3. 2D plots and Fourier transform infrared (FTIR)spectra of neat cotton fabric A) & C) and phytic acid/polyvinylamine (PA/PVAm) 15 bilayers coated cotton fabric B) & D), respectively. Reproduced with permission from the ref (Zilke et al., 2020).

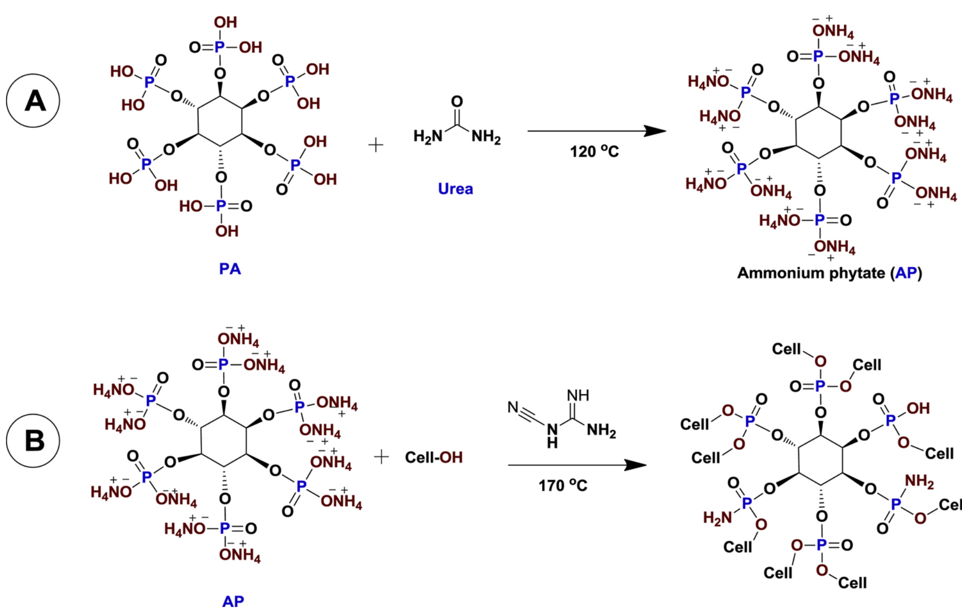

Fig. 4. Schematic representation of A) Synthesis of ammonium phytate (AP), and B) crosslinking reaction between AP and cotton fabric. Adopted with permission from the ref (Feng et al., 2017).

of almost all the bacterial colonies. On the other hand, the neat fabric did not exhibit antibacterial property. This could be due to positively charged —NH_3^+ present in CH that destroy the cell wall of bacteria (Kritchenkov et al., 2019). Hence, the CH/AP-cotton fabrics showed synergistic effect in FR property as well as antibacterial behaviour through the reduction in heat and smoke production and reduction in *E. coli* colonies, respectively. AP showed significant FR mechanism in both condensed and vapour phases through phosphoric acid catalysed char formation and ammonium ions released ammonia and nitrogen gases. Li et al. developed a FR and antimicrobial cotton fabric by PA-based nitrogen and silicon containing poly-electrolyte system (Li et al., 2019c). Initially, cationic poly-electrolyte i.e. poly[3-(5,5-cyanuricacidpropyl)-siloxane-co-trimethyl ammoniumpropyl siloxane chloride] (PCQS) was prepared. The FR and antimicrobial cotton fabrics were made by LbL assembly wherein PA was used as the anionic electrolyte. In order to improve adhesion to cotton fabric, 1 wt% of PEI was used as primer coating. A series of bilayers were prepared viz. 10, 20, and 30 and it was found that the cotton with $PEI(PA/PCQS)_{30}$ have shown superior FR behaviour, which is evident from higher LOI of30 %, lower char length of 8.1 cm in vertical burning test compared to the neat cotton (LOI of 18 %) as well as $PEI(PA/PCQS)_{10}$ whose char length was found to be more than 30 cm. The values of pHRR, THR, LOI and char yields at 700 °C of PEI(PA/PCQS) treated cotton fabrics are provided in Table 2. It was also noted that cotton fabrics with PEI(PA/PCQS) were successfully able to extinguish flame when they reached to 20 and 30 bilayers (Fig. 6). The synergistic effect of PCQS with PA was well

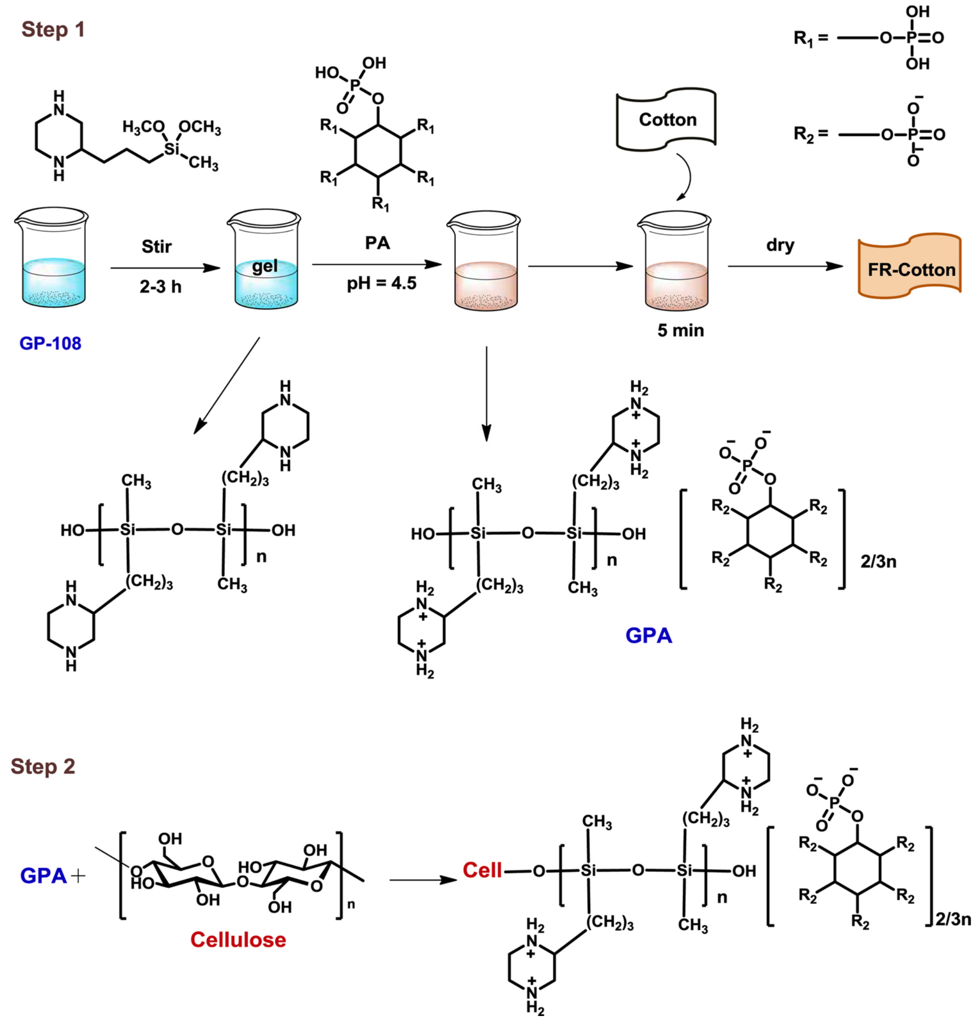

Fig. 5. Schematic representation of (3-Piperazinylpropyl)-methyldimethoxysilane (GP-108) and phytic acid (GPA)-based FR cotton fabrics. Reproduced with permission from the ref (Li et al., 2019a).

established and was directly proportional to the PCQS loading. Antibacterial efficiency of PEI(PA/PCQS)$_{30}$ was found to be greater compared to the other combinations and control fabric by reducing bacterial colonies, 92 % of *S. aureus* and 48 % of *E.coli.* The antibacterial property was credited to the quaternary ammonium salts present in it (Murugan et al., 2010; Huang et al., 2012). However, The efficiency of PEI(PA/PCQS)$_{30}$ was limited for *E.coli* colonies as it depends on degree of adherence of bacteria to the fabric. In order to achieve higher efficiency, PEI(PA/PCQS)$_{30}$ was chlorinated with 0.8 % Cl^{+} ions and found 100 % efficiency towards *S. aureus* as well as *E.coli.*

It is also known that PA and silicon containing FRs tend to improve cotton fabric's washing stability (Liu et al., 2018a). The washing stability of these fabrics are improved either by covalently linking FR to cellulose fibres or by improving the hydrophobicity of the fabric. In addition, imparting hydrophobicity to the cotton fabric by silicon-containing nano particles or by its precursors can also address the issue of breeding mould in moist environments. PA-based bi-functional cotton fabric with flame retardancy and hydrophobicity was prepared by LbL assembly using PEI/melamine as the cationic polyelectrolyte solution and sodium hydroxide treated PA as the anionic electrolyte (Liu et al., 2018a). Hydrophobic nature of the resultant FR cotton was attained by infusing poly(dimethylsiloxane) (PDMS). 4 bilayered coatings were made with PA-PEI/melamine and with PDMS (PA-PEI/melamine/PDMS) for studying both the FR and water repellent behaviours. It was observed that PA-PEI/melamine with PDMS has shown significant synergistic effect in FR behaviour by reducing pHRR by 50 % compared to the neat fabric. The mechanism involved the catalytic effect of PA-PEI/melamine to promote char formation followed by stabilising the resultant char by PDMS. A 130° water contact angle was observed for coated fabrics with PDMS, which is considered as non-wetting (Das et al., 2018b). Synergistic effect of silica with PA was well established and visualised by vertical burning test wherein a 4 bilayered PA coated cotton fabric had char length of 141 mm whereas 4 bilayered PA/PDMS coated one had 81 mm char length (Fig. 7). Similarly, an intumescent hybrid FR cotton fabric containing nanosilica (SiO_2), PEI and PA was made by LbL assembly and was reported by Li et al.(Li et al., 2019b). SiO_2 could easily be absorbed by the cotton fabrics as it has large surface area and it has the additional advantage of improving flame retardancy even at less numbers of LbL assembly cycles. The resultant PA/PEI/SiO_2 coated cotton fabrics exhibited significantly high LOI value of 34 % and lowered pHRR, and THR values compared to neat cotton (LOI of 18 %) fabric by 75 % and 52 %, respectively (Table 2).

2.4. Conductive PA-based FR cotton fabrics

A bi-functional cotton fabric with electrical conductivity and flame retardancy was reported by Liu et al. (Liu et al., 2019) and such fabrics could be useful in sensors, anti-static packaging, wearable displays, and electromagnetic shielding (Cherenack and Van Pieterson, 2012). In this context, a polypyrrole (PPy) was deposited onto the surface of cotton

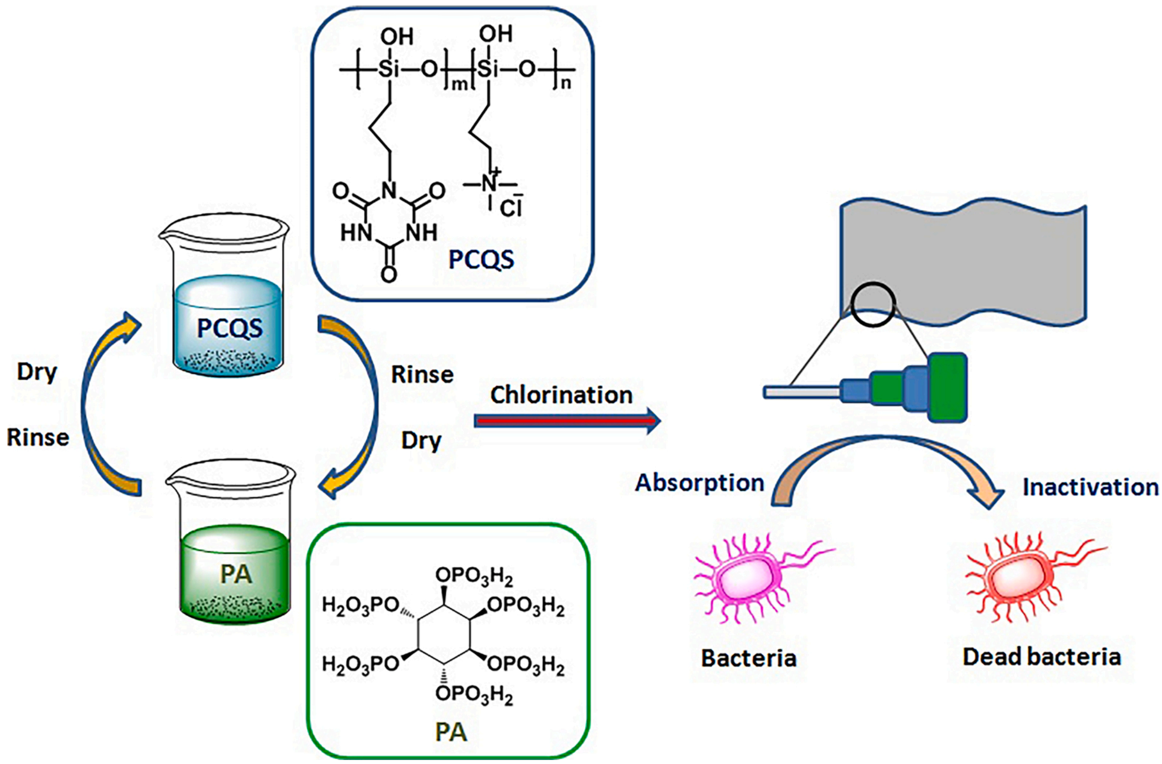

Fig. 6. Illustration of phytic acid/poly[3-(5,5-cyanuricacidpropyl)-siloxane-co-trimethyl ammoniumpropyl siloxane chloride (PA/PCQS)-based flame retardant, and antibacterial cotton fabric. Adopted from the ref (Li et al., 2019c).

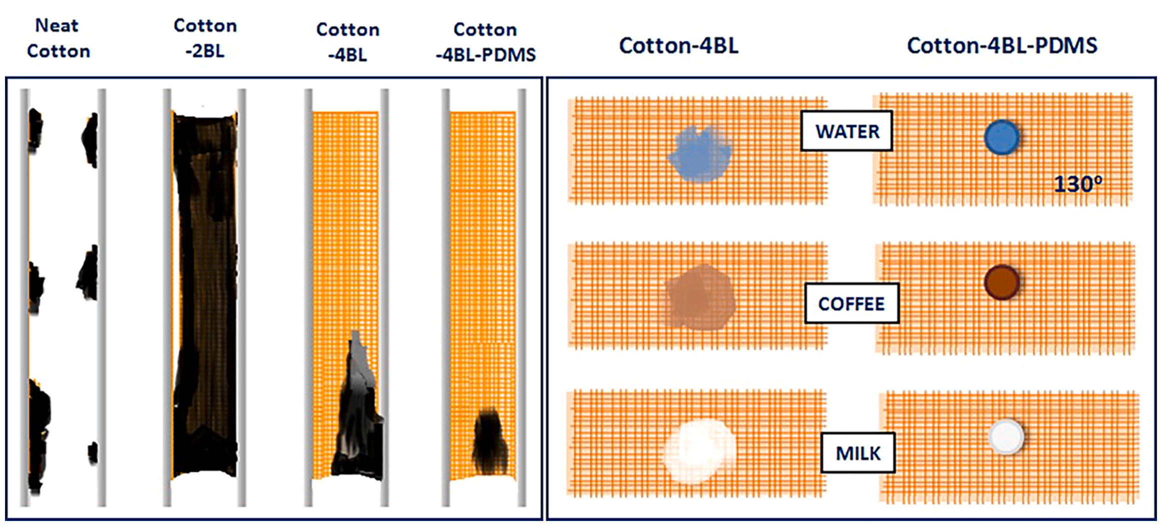

Fig. 7. Graphical representation of the result of neat cotton fabric, 2 bilayered (2 BL), 4 bilayered phytic acid/ polyethylenimine /melamine/cotton (Cotton-4BL), and 4 bilayered phytic acid/ polyethylenimine/melamine /PDMS/cotton (Cotton-4BL-PDMS) after vertical flame test and contact angle of different liquids. Adopted from the ref (Liu et al., 2018a).

fabric wherein PA has been used as the doping acid as well as the FR. It was found that the conductivity of the resulting fabrics (PA/PPy) was purely dependent on PPy loading and was directly proportional to the PPy concentration. However, FR performance was significantly improved by changing the concentration of PA as dopant in terms of higher LOI (38 %), higher char yields at 700 °C (50 wt %) and lower char length (2.3 mm/cm) in vertical flame test compared to neat cotton fabric (LOI of 18 %, char yields at 700 °C of 14 wt %) as well as PPy loaded cotton fabrics (LOI of 20 %, char yields at 700 °C of 32 wt % and char length of 30 mm/cm) (Liu et al., 2019). In addition, cotton fabric with switchable FR and conductive behaviour was developed by *in-situ* polymerisation of polyaniline (PANI) with PA doping and reported by Zhou et al. (Zhou et al., 2020). The FR and conductivity switching was carried out by doping (incorporation of PA during the polymerisation of aniline), de-doping (removal of PA from doped cotton fabric by immersing the fabric in a soap solution for 30 min followed by washing with tap water and drying), and re-doping (immersion of de-doped cotton fabric in PA solution for 30 min) of PA and this was confirmed by EDX elemental analysis of the cotton fabrics in which phosphorus content was less in de-doped and higher for doped and re-doped cotton fabrics. FTIR analysis was also used to distinguish between successful de-doping and re-doping by the disappearance and the appearance of characteristic stretching frequency at 1253 cm^{-1} that corresponds to P═O stretching. It was found that under de-doped state, the fabrics have shown no flame retardancy as well as no conductivity. However, flame retardancy and conductivity was regained after re-doping and were almost equal to the initially doped fabrics (Zhou et al., 2020).

2.5. Synergists for PA-based FR cotton fabrics

It is reported that phosphorus containing FR cotton fabrics show synergistic effect when combined with silicon containing molecules (Alongi et al., 2012, 2013; Wang et al., 2018). Polysiloxanes and its precursors are considered to be the best choice for combining P-based FR to impart synergism as they possess high thermal stabilities and ability to form dense silicaceous char layers during combustion (Dong et al., 2015). Li et al. developed sodium phytate (NaPA) and 3-aminopropyl triethoxysilane (APTES) containing FR cotton fabric (NaPA/APTES) by LbL assembly (Li et al., 2017a). Aqueous solution of APTES at acidic pH was used as the positive electrolyte whereas NaPA was used as the negative electrolyte. APTES was hydrolysed during the coating process. The uniform deposition of APTES and NaPA was confirmed by SEM morphologies wherein surface roughness was gradually increased by increasing concentration APTES. The synergistic effect of CH on NaPA/APTES-based cotton fabrics (NaPA/APTES/CH) was also studied by the same group. It is evident from the results that the FR system has successfully shown the synergistic effect in resisting fire by increasing the char yields (37 % at 700 °C) and LOI (29 %), while decreasing the THR and pHRR compared to the neat fabric by 50 % and 80 %, respectively (Liu et al., 2018a,b,c). A hybrid intumescent coating comprising of PA and nitrogen-based silane hybrid (SiN) (PA/SiN) was reported by Wang et al. in which PA acted as the anionic solution and SiN acted as the cationic solution (Wang et al., 2015). The coating was successfully attached to the cotton fabric by LbL deposition method. SiN was prepared by sol-gel method by using TES-IC (product of urethane reaction between 1,3,5-tris(2-hydroxyethyl) isocyanurate (THEIC) and 3-triethoxysilyl propyl isocyanate (TESPI) and APTES. A series of SiN-based FR cotton fabrics were made by varying the number of bilayers deposited on to the cotton fabric viz. 5, 10, and 15. It was observed that the 15 bilayered PA/SiN-based coated fabric has shown superior FR performance by extinguishing flame immediately after ignition and by reducing the THR and pHRR by 38 % and 31 %, respectively compared to the neat cotton fabric. The values of pHRR, THR, LOI and char yields at 700 °C of PA/SiN treated cotton fabrics are given in Table 2. The intumescent behaviour was evident from SEM micrographs of post-burnt samples wherein the swelling of char can be visualised.

An attempt was made to study the optimum concentration of sol consisting TEOS and PA to impart flame retardancy to cotton fabric by sol-gel method by Barbalini et al. (Barbalini et al., 2019). Such sol-gel processes containing silicon precursors are known to combine with hydroxyl groups of PA as well as cellulose fibres by their partially hydrolysed alkoxy groups. Moreover, making a sol with PA has an additional advantage of avoiding acid catalyst such as HCl to hydrolyse the alkoxy groups of TEOS as PA itself is an acid. The synergistic effect of TEOS with PA was studied by varying the percentages of deposition of PA and TEOS in sol (PA/TEOS) and comparing them with cotton/TEOS and cotton/PA-based fabrics. Itis found that cotton fabric with sol (PA/TEOS (40/60)) has shown higher char yields at 700 °C (49 %) compared to the one with sol (PA/TEOS (70/30)) that had 41 % char residue. Hence, the synergism of TEOS on PA was confirmed by char formation and was directly proportional to TEOS concentration (Barbalini et al., 2019). It should be noted that char yields of cotton/PA and cotton/TEOS have been lowered compared to cotton/PA/TEOS fabrics irrespective of the PA/TEOS ratio. It was observed from vertical flame test and cone calorimeter tests that the cotton fabric with PA:TEOS ratio 70:30 have shown good FR property in terms of lower heat release rate (1.2 MJ/m^2), and lower pHRR with 75 % less compared to the neat cotton fabric (Table 2).

Cheng et al. reported PA and Si-based FR cotton fabric with a hybrid sol consisting of PA, TEOS (PA/TEOS (0.2/0.6 mol/L)), citric acid, sodium alginate along with ethanol (Cheng et al., 2020c). The cumulative effect of silica with PA was established by the self-extinguishing behaviour of cotton fabric by forming a protective char during combustion and it was confirmed by the increasing concentrations of P and Si present in char layer of burnt samples. The successful deposition of hybrid PA-silica sol with spherical silica particles was clearly evident from the SEM micrographs.

On the other hand, bio-molecules such as nucleic acids, banana pseudostem sap, extracts of pomegranate rind and proteins have also been utilised to confer flame retardancy to natural and synthetic textiles (Malucelli et al., 2014; Basak et al., 2015; Basak and Ali, 2017; Malucelli, 2019). In addition, a carbon-rich product (biochar, BC) that is obtained by thermo-oxidative chemical conversion of biomasses (Das et al., 2019; Babu et al., 2020) have gained much attention in the field of FR fabrics. It was found that the BC could be applied synergistically with PA to confer FR property to cotton fabric (Barbalini et al., 2020). Barbalini et al. reported a mixture of bio-based FR dispersion comprising PA and BC in equal weight ratio. To evaluate the synergism, a comparative study between neat cotton fabrics, PA coated cotton (PA/COT), BC coated cotton (BC/COT), and PA/BC/COT has been done through flame spread and cone calorimetry tests. It was found that BC/COT could not self-extinguish the flame during vertical flame test, however, the synergistic effect of BC with PA was confirmed by extinguishing the flame with high char residue (85 %) for PA/BC/COT sample compared to PA/COT (53 %) and the neat fabric. The values of pHRR, THR, LOI and char yields at 700 °C of PA/BC treated cotton fabrics are tabulated in Table 2. It was also noted that PA/BC/COT with 8% (add-on wt%) have successfully resisted ignition during cone calorimetry tests when a radiant heat flux of 35 kW/m^2 was applied (Barbalini et al., 2020).

In summary, PA has been proved to be a potent alternative to halogenated FRs to bestow FR property to cotton fabrics. From the studies, it can be concluded that at pH of 4–5, PA could act as an effective FR without compromising the fabric's mechanical properties. At low pH (~1), PA degrades cotton fibres by cellulosic degradation (Patra et al., 2020). In order to achieve the aforementioned pH range (4–5), electrolyte solutions are made by combining PA with amine functionalised molecules or polymers such as CH, TEA, GP-108, PVAm, and urea and also combining PA with a strong base like sodium hydroxide. It should be noted that the combination of PA with these amine functionalised partners imparts synergism in FR behaviour by achieving intumescent char formation upon combustion. Limitation of washing durability of physically adsorbed PA-based FR cotton fabrics were treated by covalently linkable derivatives of PA such as AP, GPA, and PBN. To address the mould growth on cotton fabrics, PA was combined with the molecules, which can offer antibacterial as well as hydrophobic properties to the cotton fabric. In this regard, bio-based amine functionalised polymer i.e., CH, cationic polyelectrolyte with quaternary ammonium salt i.e. PCQS and silicon functionalised molecules and polymers viz. APTES, TEOS, and PDMS were employed.

To determine the most suitable combinations of PA with other molecules or polymers for rendering cotton fabric fire retardant, the values of LOI, % of reduction of pHRR and THR with respect to neat cotton fabric was taken into account. It is evident from the literature cited in this review that AP treated and crosslinked FR cotton fabric have shown superior FR property and was supplemented by LOI of 43 %, reduction of 95 % pHRR, 58 % THR with reference to neat fabric and by higher char yields of 43 wt% at 700 °C (Feng et al., 2017). PBN treated cotton fabric had one of the best combinations of PA owing to its highest LOI of 45 % and reduction of 79 % pHRR, 55 % THR with respect to neat cotton fabric and char residue of 37 wt% at 700 °C (Zhu et al., 2020). In addition, PA/TEA treated cotton fabrics have shown good char yields (41 wt %), LOI (32 %), reduction in pHRR (74 %), and THR (80 %). On the other hand, PA/CH, PA/TEOS and PA/SiN combinations are found to have good char yields at 700 °C viz. 42, 41 and 40 wt %, respectively.

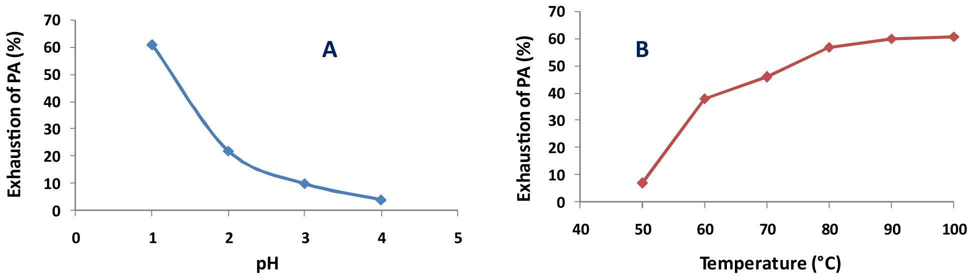

Fig. 8. Effect of pH (A), and temperature (B) on uptake of phytic acid by wool fabric. Adopted and reproduced with permission from the ref (Cheng et al., 2016a).

Hence, boron, nitrogen, and silicon-containing molecules or polymers could be the best partners for PA in cotton fabrics to resist flame spread. Cone calorimetry (CC), microscale combustion calorimetry (MCC), LOI, and char yields at 700 °C data of reviewed articles of PA-based cotton fabrics are summarised in Table 2.

3. PA-based FR wool fabrics

3.1. Factors influencing FR performance of PA-based wool fabrics

The FR efficiency of PA on wool fabrics was studied on the basis of adsorption of PA on to the fabric by Cheng et al. (Cheng et al., 2016a). The solution's pH, temperature and concentration of PA in electrolyte solution greatly influence the FR performance. The uptake of PA by the wool fabric was gradually increased when temperature increased from 30 °C to 90 °C. It is because of the tendency of wool fibres to swell by greater extent at higher temperatures (90 °C) leading to the maximum uptake of PA. The adsorption of PA on to the wool fabric is purely by electrostatic interactions between wool fibres containing positively charged amino groups and negatively charged phosphate groups in the case of PA. Hence, a lower pH of 1.2 was found to facilitate greater adsorption of PA whereas pH of 4.1 had lower adsorption and this was due to the reducing quantity of positively charged amino groups at that pH. In addition, PA adsorption, weight gain, and flame retardancy of wool fabric were significantly increased upon increasing of PA concentration. The flame retardancy of PA-based wool fabric was established by LOI of 35 % with a weight gain of 17 % and by forming an intumescent char, which was clearly visualised in SEM micrographs. The effect of pH and temperature on the uptake of PA by the wool fabric is shown in Fig.8. The values of pHRR, THR, LOI and char yields at 700 °C of PA treated wool fabrics are provided in Table 3.

Similarly, water soluble CH and PA containing polyelectrolyte complex (PA/CH-PEC) was prepared at pH of 1.3 for making FR wool fabric by the coating method (Cheng et al., 2019b). Citric acid was used as solvent for making CH solution that acted as the crosslinking agent. The water soluble PA/CH-PEC was precipitated while coating on wool fabrics by adding a buffer solution of pH 4. The coating with 2% CH and 10 % PA deposition has shown considerably higher FR performance compared to the neat wool fabric. The values of pHRR, THR, LOI and char yields at 700 °C of PA/CH-PEC treated wool fabrics are tabulated in Table 3. The authors suggested not using more than 2% concentration of CH as it becomes too viscous to apply as coating. The mechanism of this FR fabric (PA/CH-PEC) involved a formation of a foaming char that acted as a barrier between oxygen and combustible radicals generated from the substrate during combustion. The foaming char was illustrated in SEM micrographs of char residues after the flame tests (Cheng et al.,

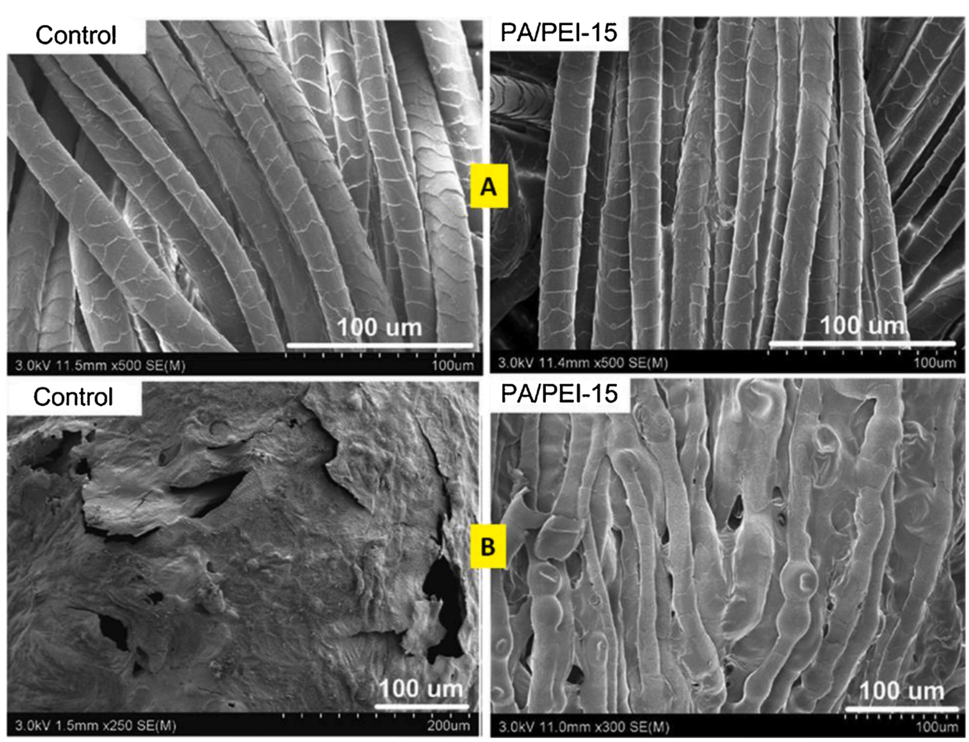

Fig. 9. SEM micrographs of neat and phytic acid/ polyethyleneimine (PA/PEI) coated wool fabrics A) before B) after flame test. Reproduced with permission from the ref (Cheng et al., 2019c).

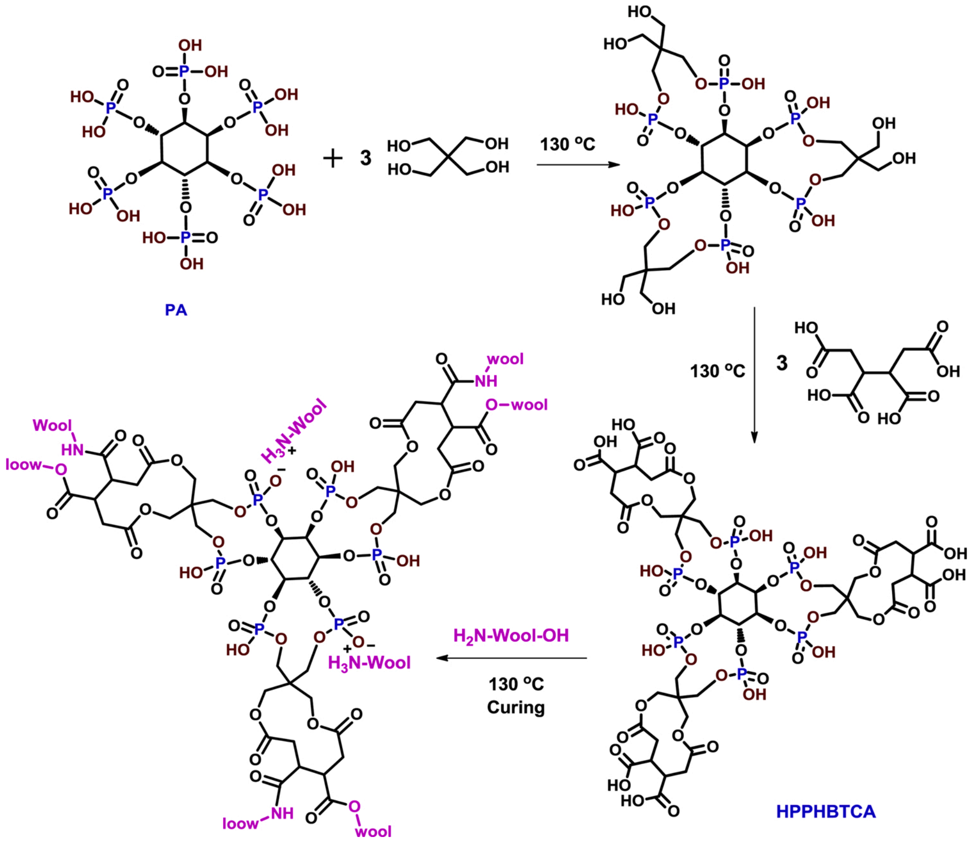

Fig. 10. Schematic representation of synthesis and the cross-linking reaction of hexapentaerythritol phytate hexabutane tetracarboxylic acid ester (HPPHBTCA) with wool fabric. Adopted and reproduced with permission from the ref (Cheng et al., 2019a).

2019b).

PA-based organic-inorganic hybrid FRs have been developed for wool fabrics to impart synergistic benefits of inorganic filler for char formation and PA for catalysing the charring process. In this regard, silicone-based precursors are widely used. However, these inorganic precursors form a cuticle layer on the surface of the fabric leading to a lower surface smoothness of the fabric and also leach out during washing cycles (Cheng et al., 2018b). To address this issue, high temperatures are recommended for treating wool fabrics by FR liquids as they swell up and allow inorganic nanoparticles to bind the fibres (King and Pierlot, 2009). Cheng et al. reported PA/TEOS-based organic-inorganic hybrid sol with constant concentration of PA (0.1 mol/L) with varying concentrations of TEOS (0.1, 0.2, and 0.3 mol/L) for wool fabrics made by pad-dry-cure method (PDC) (Cheng et al., 2020b). PDC method involved three stages viz. padding, drying and curing. Initially, sol treated fabrics were passed through a padder. Then the padded fabrics were dried at 80 °C for 3 min and cured at 160 °C for 3 min. The resultant wool fabric (PA/TEOS ratio 0.1/0.6 mol/L) have shown immense flame retardancy by showing less smoke density, which was 80 % less compared to the neat wool and with 32 % LOI. A water soluble polyelectrolyte complex comprising of PA and PEI has been reported by the same research group (Cheng et al., 2019c). The resulting FR wool fabrics showed good flame retardancy and self-extinguishing property even after 10 washing cycles. The values of pHRR, THR, LOI and char yields at 700 °C of PA/PEI treated wool fabrics are summarised in Table 3. These fabrics have shown intumescent mechanism of flame retardancy. The durability of these wool fabrics was found to be adequate and was attributed to the crosslinking ability of PA/PEI system both ionically and covalently with the wool fibres. SEM micrographs of the neat and PA/PEI coated wool fabrics before and after flame test are depicted in Fig.9.

3.2. Durability of PA-based FR wool fabrics

Despite its significant FR competence, physically adsorbed PA-based wool fabrics have limited washing durability as PA leaches out during washing. This could be overcome by covalently linking PA to the fibres of the fabrics. In this context, PA-based reactive FR namely hexapentaerythritol phytate hexabutane tetracarboxylic acid ester (HPPHBTCA) was reported by Cheng et al. (Cheng et al., 2019a). HPPHBTCA was synthesised by using PA, pentaerythritol and 1,2,3, 4-butanetetracarboxylic acid (BTCA). The reaction involved phosphate ester formation by PA and pentaerythritol and the resultant polyol aided in esterification reaction with butanetetracarboxylic acid. Wool fabric was treated with different concentrations (0.07, and 0.14 mol/L) of HPPHBTCA solutions at room temperature and the HPPHBTCA grafted wool fabrics were cured at 160 °C. Thermal stabilities and FR efficiency of these wool fabrics increased compared to the neat fabric and are directly proportional to the concentration of HPPHBTCA. It was evident from the appearance of expanded circular char bubbles from SEM micrographs of high loading HPPHBTCA compared to the low loading counterparts. Increasing P content in burnt samples of HPPHBTCA wool fabrics compared to un-burnt samples was an evidence of condensed phase FR mechanism. Schematic representation of synthesis and cross-linking reaction of HPPHBTCA with wool fabric are shown in Fig. 10.

FR behaviour and washing durability of the organic-inorganic FR containing wool fabrics are greatly influenced by the methods of manufacturing. For instance, PA, BTCA, and titanium dioxide (TiO_2) nanoparticles containing FR system was developed for wool fabric and applied by different methods such as PDC and exhaustion assisted pad-dry-cure method (EPDC). In both the methods, the concentrations of components (PA, BTCA, and TiO_2), drying temperature (80 °C), and curing temperature (160 °C) remained same except for the temperature

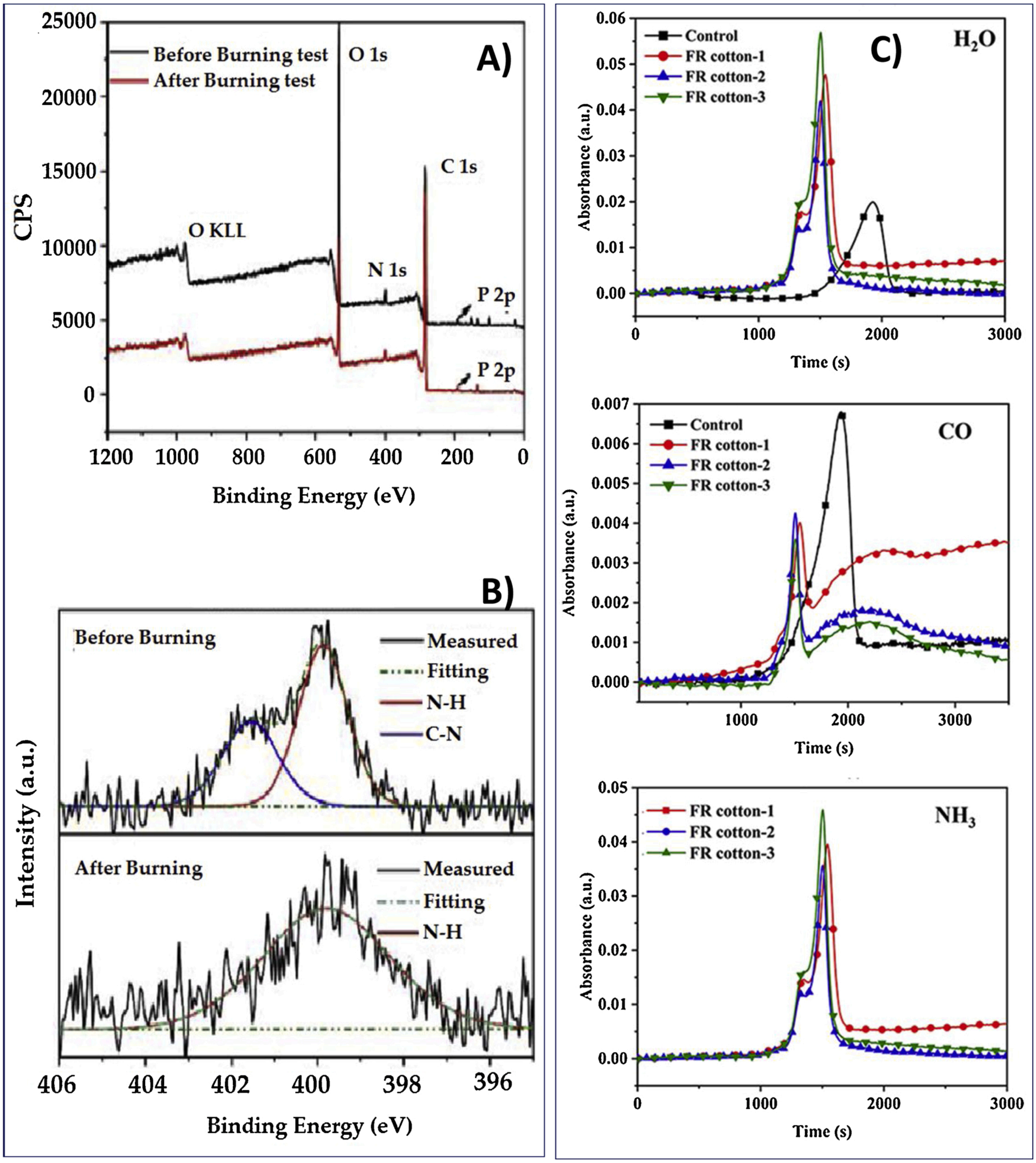

Fig. 11. A) XPS spectra of ammonium phytate/chitosan treated cotton fabrics, B) N1s elements of the same fabric. Reproduced with permission from the ref (Li et al., 2020) C) absorption intensities of water, CO, NH_3 at their corresponding degradation temperatures from TGA-FTIR of cotton samples. Reproduced with permission from the ref (Li et al., 2019a).

of FR system at which wool fabrics were immersed. In PDC method, wool fabrics were immersed in FR system at room temperature whereas in EPDC method, the fabrics were immersed at 90 °C. FR property and washing durability of the wool fabric developed by EPDC have shown better performance compared to the wool fabric with PDC. It was evident from high LOI (34 %) of wool fabric by EPDC, which reduced a little (30 %) even after 5 washing cycles. On the other hand, LOI of wool fabric by PDC lowered to 27 % after the washing cycles (Cheng et al., 2018a).

In summary, adsorption of PA on wool fabrics was reported to be maximum at low pH (~1). This is because the adsorption of PA is governed by electrostatic interactions between phosphate groups and intrinsic —NH_2 groups of wool fibres. Limitation of washing durability of PA-based wool fabrics was addressed by incorporating covalently linkable reactions such as esterification and amidation. In addition, incorporation of TEOS along with PA to the wool fabric successfully addressed the issue of washing durability. Inorganic fillers such as TiO_2, and TEOS containing PA-based FR wool fabrics have shown synergism in FR performance. Higher temperatures (~90 °C) are favourable to treat wool fabrics with PA/inorganic fillers containing sols. At the high temperatures, wool fibres tend to swell and adsorb PA at greater extent. In the case of FR-wool fabric, utilisation of 70 % aqueous solution of PA (120 % of the weight of wool fibre) was found to be the best in imparting flame retardancy compared to PA's combinations. This is because of its highest LOI of 35 % and reduction of 42 % pHRR, 52 % THR with respect to neat cotton fabric and char residue of 38. wt% at 700 °C (Cheng et al., 2016a). On the other hand, PA/PEI combinations have achieved similar performance even at low concentration of PA (PA=15 wt%; PEI=15 wt

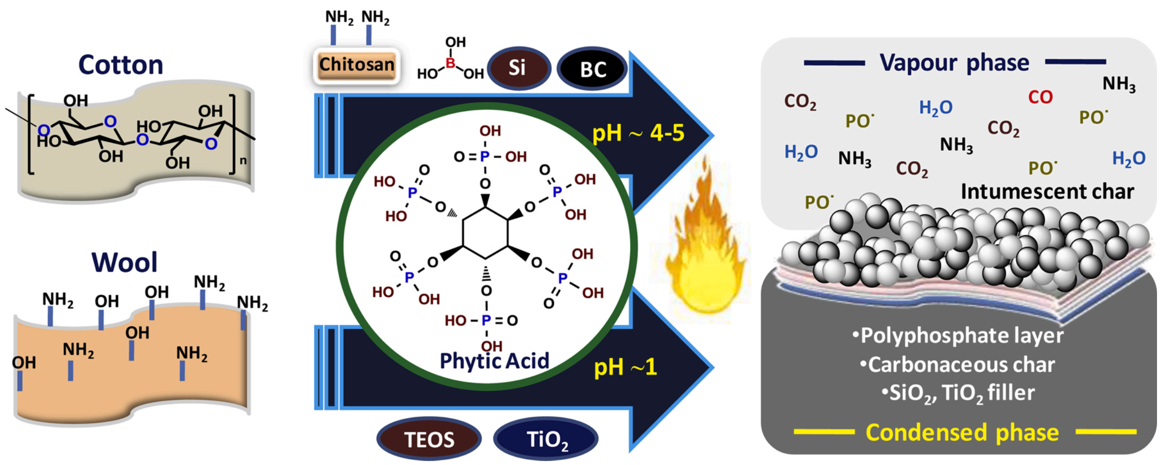

Fig. 12. Schematic representation of phytic acid-based FR cotton and wool fabrics towards their FR mechanism.

%) where 50 % PA solution was used (Table 3). CC, MCC, LOI, and char yields at 700 °C data of reviewed articles of PA-based wool fabrics are mentioned in Table 3.

4. FR mechanism by PA

Combustion of any polymer substrate is a cyclic process that needs an adequate ignition either by a spark or by a flame. During the combustion, the polymer decomposes and releases CO_2, water, combustible gases such as CH_4 and H_2 along with formaldehyde, heat, and smoke. These combustible gases further release heat by reacting with air/oxygen. The resultant heat loops back to the polymer to decompose it further (Wilkie and Morgan, 2009). FRs are used to disrupt the combustion cycle either by forming protective dense char on the substrate that act as a barrier between combustible gases and oxygen/air, and heat (condensed phase mechanism) or by producing radical scavengers that could quench the chain propagation (vapour phase mechanism).Thermo oxidative decomposition of cotton fabric was first reported by Bradbury et al. and the decomposition happens through cellulosic degradation via the formation of levoglucosan that further decomposes to yield flammable volatiles and char (Bradbury et al., 1979). Jimenez et al. reported the gaseous products that are released from cotton fabric during combustion through a coupled FTIR-mass loss calorimeter and identified formaldehyde, water, CO, and CO_2 as the primary decomposition products (Jimenez et al., 2016). PA, polyphosphates and its salts are involved in condensed phase mechanism by promoting char (Basak et al., 2015) as well as vapour phase mechanism through scavenging combustible radicals by PO radicals (Liu et al., 2020). During the combustion, these phosphates are decomposed and produce phosphoric acid. The resultant phosphoric acid reacts with hydroxyl groups of cellulose (a process called phosphorylation) to initiate dehydration reaction and subsequently catalyses carbonisation (Fang et al., 2016; Holder et al., 2017). The phosphorylation of cellulose is catalysed by nitrogen containing molecules via P–N intermediates (ED Weil - Fire retardancy of polymeric materials and, 2000). Li et al. have found enhanced release of water (3593 cm^{-1}), CO_2 (2361 cm^{-1}), and NH_3 (3583 cm^{-1}) from AP/CH/cottons compared to neat cotton fabric and was confirmed by their increasing absorption intensities in the corresponding FTIR peaks (Li et al., 2020). Similar patterns were observed by Li et al. in their work on GPA treated cotton fabrics and absorption intensities of water, CO, and NH_3 are depicted in Fig.11 (Li et al., 2019a). The release of NH_3 was further corroborated by XPS analysis, wherein AP/CH/cotton before burning showed two peaks at 399.8 eV and 401.6 eV corresponding to N–H and C–N, respectively, whereas its char showed only one peak at 399.8 eV (N–H) (Fig.11). This is due to the elimination of NH_3 from CH. Hence, the synergism of AP and CH was confirmed by intumescent char formation and the FR mechanism involved exclusion of ammonia (NH_3) gas (Li et al., 2020). Similar pattern of exclusion of NH_3 gas under combustion was also found in PA/CH treated wool fabrics (Cheng et al., 2019b).

The condensed phase mechanism of PA-based cotton fabrics were confirmed by the formation of dense phosphorus char upon burning and was demonstrated by EDX elemental analysis of char wherein increasing phosphorus content was observed compared to the un-burnt sample (Cheng et al., 2020a). The condensed phase mechanism of PA was further synergised by the inclusion of boric acid, silica-containing polymers/molecules, TiO_2 and BC in FR system (Cheng et al., 2018a; Barbalini et al., 2020; Zhu et al., 2020). Since boric acid has the tendency to dehydrate the cellulose, it therefore catalyses carbonisation reaction. Whereas, silica-containing polymers/molecules (TEOS, SiN and PDMS) could produce dense silica residue in their char upon combustion by depolymerisation of polysiloxanes (Liu et al., 2018a). This silica residue acts as a blanket of insulation that delays the heat transfer as well as volatilisation of combustible gases from the underlying virgin fabric (Li et al., 2013).

In addition to PA's role on wool fabric to catalyse the formation of an insulating char layer, it also catalyses SiO_2 formation from its precursor (TEOS) (Cheng et al., 2020b). The synergistic FR mechanism of PA with silica was evidenced by forming dense protective char (comprising of silica and phosphorus) that acts as a physical barrier for heat and oxygen. This mechanism is revealed by FTIR spectra wherein the appearance of Si-O-Si (1081 cm^{-1}), P—O (890 cm^{-1}), O—P—C (984 cm^{-1}) stretching vibrations are observed for char residues of burnt wool samples. Similar effect was observed for PA/TiO_2-based FR wool systems wherein the char residue was found to have phosphorus as well as titanium (Cheng et al., 2018a). The gas phase and intumescent flame retardant mechanism was observed in PA-based wool fabrics (wherein PA is combined with amine functionalised counterparts such as CH and PEI) by expulsion of NH_3 gas during combustion (Cheng et al., 2019c). In a nutshell, PA-based FR cotton and wool fabrics involve in condensed phase as well as gas phase mechanisms. Schematic representation of PA-based FR cotton and wool fabrics towards their FR mechanism is depicted in Fig.12.

5. Conclusions and future perspectives

The review and analysis of past literature reveal that PA and its derivatives as bio-based and eco-friendly substances have successfully proven to be potential FRs for cotton and wool fabrics. The aforementioned substances are also effective alternatives for both halogenated and conventional FRs. Up on application in fabrics, the PA-based FRs tend to catalyse the carbonisation of cellulose fibres forming dense protective char layer on the fabric surface that hinders heat transfer between the un-burnt virgin layer and the surrounding environment. Additionally, the blanketing char layer impedes oxygen reaction with active radicals. Hence, PA-based FRs can efficiently facilitate condensed phase mechanism akin to other conventional FRs such as ammonium polyphosphate. However, it is to be noted that PA can also be involved in gas phase reactions. The intumescent char formation is also observed for cotton fabrics when PA is combined with ammonium ions and amine functionalised partners such as CH, TEA, SMF, and PEI. However, PA-based wool fabrics have shown intumescent char formation even without the aforementioned synergists. This could be due to its inherent amine functionality and wool's intrinsic flame retardancy properties bestowed by high nitrogen, sulphur and moisture contents in the fibre. The beneficial intumescent char formation on the fabrics' surfaces can be clearly visualised in SEM micrographs of cotton as well as wool after flame tests. For cotton, the optimum pH for adding PA is higher than that for wool fabrics. There is an issue with the washing durability for PA-based wool fabrics but that is usually remedied by employing covalently linkable reactions namely, esterification and amidation. PA-based FR fabrics are particularly beneficial for partially or completely immobile older adults who are vulnerable to burn-related fatalities induced by smoking and/or cooking. Therefore, PA-based FR fabrics can play a vital role in eliminating this public health problem by providing fire prevention, protection and safety for older adults, who have enhanced possibilities for igniting a fire and lowered changes of surviving it. Moreover, PA has been used as doping agent in developing conductive fabrics. These fabrics have applications in sensors, anti-static packaging, wearable displays, and electromagnetic shielding. The flexibility of PA to be applied on to fabrics by LbL assembly, sol-gel method, dip-coating method, and PDC methods enhances its potential to be used in industrial scale. Furthermore, its biocompatibility, non-toxicity, high percentage of phosphorus, and a broad range of synergies with other classes of FRs make PA a strong candidate for developing an array of FR fabrics in an industrial scale.

Declaration of Competing Interest

The authors declare no conflict of interest.

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