Advanced Fiber Materials (2023) 5:731–763
https://doi.org/10.1007/s42765-023-00255-x

REVIEW

A Review of Durable Flame-Retardant Fabrics by Finishing: Fabrication Strategies and Challenges

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Received: 26 October 2022 / Accepted: 1 January 2023 / Published online: 15 February 2023

Abstract

Fabrics with durable flame retardancy are of great importance for preventing potential fire threats in daily life. This review presents a comprehensive discussion of advances in durable flame-retardant fabrics by finishing over the decade. The environmentally sustainable and toxicologically acceptable strategies for improving the durable flame retardancy of fabrics are classified into six types:. (i) the formation of covalent bonds, (ii) the formation of crosslinking networks, (iii) the formation of water-insoluble products, (iv) the use of adhesive layers, (v) the construction of hydrophobic layers, and (vi) the intercalation of flame-retardants into fibres. The design principles, methodologies, and existing problems of different fabrication strategies for imparting durable flame retardancy are summarized and reviewed. The advantages and disadvantages of each strategy are critically discussed. The current challenges and future opportunities are also proposed based on the current market requirements and state-of-the-art technologies. Many recent methodologies have great potential for replacing the conventional durable flame-retardant processes of cellulosic textiles.

Keywords Textile · Finishing · Flammability · Durability

Introduction

The development of textiles plays an important role in the civilization of mankind [1]. Fabrics have historically been essential material in human lives [2]. Unfortunately, the vast majority of fabrics can be easily ignited by small fires, such as those resulting from matches and cigarettes [3]. In addition, flames spread quickly on fabrics due to their large specific surface areas [4]. Fabrics have been the main items that cause civilian deaths and property losses in fire hazards [5, 6]. Figure 1a shows the chemical structures and limiting oxygen index (LOI) values of commonly used natural and synthetic fabrics, including cotton, wool, silk, polyamide (PA), polyethylene terephthalate (PET), and polyacrylonitrile (PAN) fabrics. Wool fabric has the highest LOI value of approximately 25%, cotton fabric has an LOI value of only 18.5%, and most synthetic fabrics have LOI values of less than 21%. The inherent flammability of these fabrics restricts their widespread application. Therefore, it is necessary to endow these fabrics with flame retardancy to meet fire safety requirements.

There are three methods for endowing fabrics with flame retardancy: blends, copolymerization, and finishing methods. Among them, the finishing method is widely used for the modification of fabrics due to its simple process, easy operation, excellent performance, and flexibility. However, the finishing method often involves water as a medium and the treated fabrics easily lose their flame retardancy after washing. From a practical point of view, it is essential to develop flame-retardant fabrics with good washing durability to meet the increasing demands of the market [7]. There is still an increasing concern for health risks caused by formaldehyde released from conventional commercially durable flame-retardant (Pyrovatex CP® and Proban®) treated cotton fabrics. The design and development of durable flame-retardant cotton fabrics with low health and environmental impacts are already popular research topics [8].

Several review papers related to flame-retardant fabrics have been published over the years. These reviews focus on surface treatment methods [9–12], polypropylene fibres

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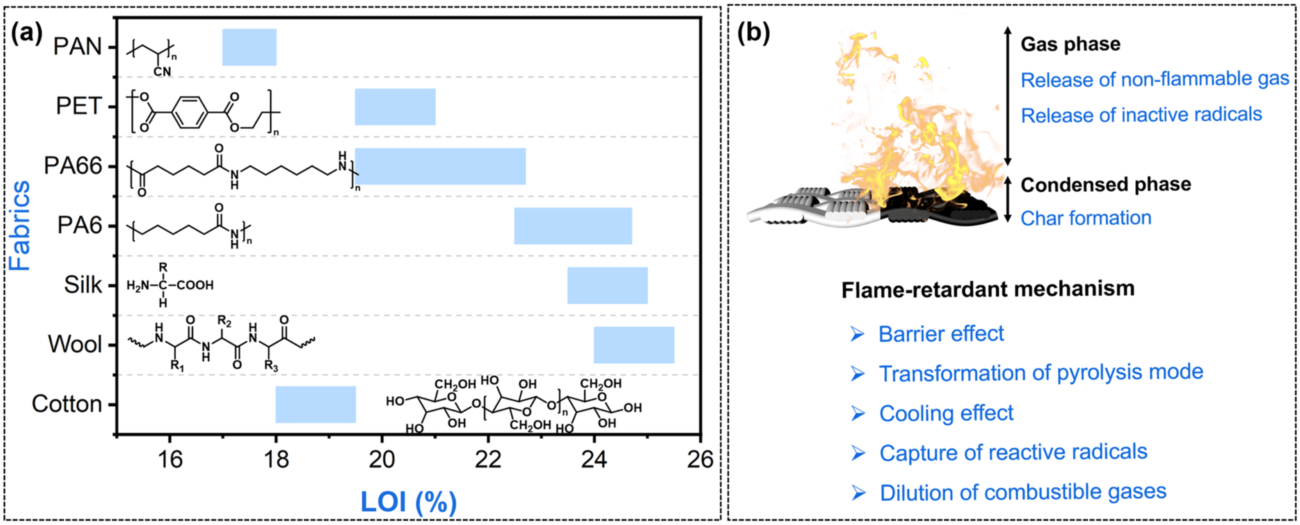


Fig. 1 The chemical structures and LOI values of commonly used fabrics (**a**). Schematic diagram of general flame-retardant mechanism (**b**)

[13], biomacromolecules [14], water-based coatings [15], synthetic textiles [3], phosphorus-based coatings [16, 17], phytic acid-based flame-retardants [18], biosustainable organobromine-containing formulations [19], and polydopamine-assisted coatings [20] respectively. Surprisingly, strategies for endowing fabrics with durable flame retardancy have not been systematically summarized.

This work reviews the state-of-the-art technologies for imparting durable flame retardancy to fabrics over the last decade. The corresponding mechanisms and research progress of each strategy are presented. In addition, the advantages and current chanllenges of each strategy are summarized. Possible future development opportunities of durable flame-retardant fabrics by finishing are also discussed.

Fire Behaviours and Flame-Retardant Mechanisms of Fabrics

The combustion of fabrics involves four components: fuel, oxygen, heat and the chain reactions of free radicals. Once a fabric is heated and decomposed, it releases unstable free radicals and volatile products [21]. The gaseous volatile products can be ignited to generate a large amount of heat in the presence of a sufficient amount of oxygen, which then feeds back to the substrate and leads to further pyrolysis [22, 23]. Due to the large specific surface area of the fabric, it is easier to ignite, and flame spreads quickly through the fabric [24, 25].

Flame-retardant finishing fixes flame-retardant components on the surface of a fabric, which can effectively inhibit combustion [26]. The flame retardancy can be exerted by eliminating the 'four components' of the combustion process, as shown in Fig. 1b. For example, the formation of a dense charcoal layer in the condensed phase prevents oxygen and heat transfer and reduces flammable volatiles [27–29]. The binding of unstable OH· and H· radicals with low reactive radicals in the gas phase can terminate the combustion chain reaction. Diluting combustible gases by releasing non-combustible gases can suffocate the flame [30].

Evaluation Methods of Washing Durability for Flame-Retardant Fabrics

Because the actual manufacturing process of a fabric involves several washing cycles, the evaluation of the durability of flame-retardant fabrics is mainly focused on laundering durability. Currently, the popular method for evaluating the washing durability of flame-retardant fabric is to measure the change of weight gain (W–G) after accelerated washing process according to AATCC 61-2013 No. 1A & No. 2A & No. 3A standards (Table 1). For the No. 1A standard, the fabrics are washed in 200 ml of 40 ℃ water with 0.37% detergent and 10 steel balls. For the No. 2A

Table 1 The standards of laundering and flammability tests

Characterization techniques	Standards
Water laundering test	AATCC 61–2013 No.1A & No.2A & No.3A; ISO 12138–2017
LOI	GB/T 5454-1997, ISO 4589, ASTM D 2863
VBT	GB/T 5455–2014, ASTM D 6413
CCT	ASTM E 1354; ISO 5660
MCC	ASTM D7309

standard, the fabrics are washed in 150 ml of 49 ℃ water with 0.15% detergent and 50 steel balls. For the No. 3A standard, the fabrics are washed in 50 ml of 71℃ water with 0.15% detergent and 100 steel balls. Running the laundering machine at 40 ± 2 rpm for 45 min is regarded as 5 laundering cycles. The laundering liquid is prepared with distilled water, deionized water, or tap water. In addition, there is an ISO 12138:2017 standard of domestic laundering procedures to apply for textile fabrics before flammability testing [31].

The flammability of fabrics before and after washing was also studied to evaluate their durability (Table 1). LOI analysis and vertical burning test (VBT) are small-scale experimental techniques that are often used in the washing durability characterization of flame-retardant fabrics [32, 33]. The LOI refers to the minimal oxygen concentration required to maintain the steady combustion of a sample in a mixture of O_2 and N_2. The VBT refers to igniting the bottom of a piece of fabric for 12 s and recording the after-flame time, after-glow time, damaged length (DL), and melt dripping. The combustion behaviour can be classified according to GB 8624–2012. The cone calorimetry test (CCT) is an effective technique for measuring the combustion properties of fabrics [34]. It enables the measurement of a wide range of fire-related parameters, such as ignition time, heat release rate (HRR), total heat release (THR), mass loss rate, production of CO and CO_2, smoke production rate, and effective heat of combustion [35, 36]. Microscale combustion calorimetry (MCC) requires only milligram quantities of sample and allows the rapid determination of parameters such as the heat release capacity and the heat release rate [37].

Some laboratories use different laundering conditions such as water temperature, type of detergent, washing time, washing machine, and agitation speed. The assessment methods for washing durability from different works are diverse and complex, and the results in individual reports are not suitable for direct comparison. However, the durability of different reports can be compared indirectly based on the change in flame retardancy under similar laundering conditions and laundering cycles (LCs).

Strategy for Washing Durability

In general, the practical application of flame-retardant fabrics requires that their components can withstand repeated washing cycles. Improving durable flame retardancy and increasing the service life of fabric products have attracted much research attention. The strategies for improving the durable flame retardancy of fabrics can be classified into 6 types, which are: covalent bonds, crosslinking networks, water-insoluble products, adhesive layers, hydrophobic layers, and the intercalated flame retardants. The process diagram of each type of strategy is summarized and some representative examples are highlighted in Fig. 2.

Formation of Covalent Bonds

The formation of covalent bonds between fabrics and flame-retardants is an effective way to improve durability. Reactive chemical groups are required to form covalent bonds. Therefore, this method is usually applied to natural fabrics with functional groups, such as cotton fabrics with hydroxyl groups and wool or silk fabrics with amino groups. The formation of covalent bonds can be achieved by the following six methods: esterification by phosphonic acid groups, esterification or condensation by polycarboxylic acids, Kabachnik-Fields reactions, substitution reactions, sol–gel reactions, and UV grafting reactions.

Formation of P–O–C Bonds through Esterification

Flame-retardants with reactive ammonium phosphate groups could react with the hydroxyl groups of cellulosic fabrics (such as cotton fabrics, cotton-containing blend fabrics [45], lyocell fabrics [46–50], and bamboo fabrics [51]), and silk fabrics [52] with the help of dicyandiamide (catalyst) to form P–O–C covalent bonds at high temperature. As shown in Fig. 3a, these kinds of flame-retardants are usually synthesized from raw materials containing hydroxyl or amine groups that act as a skeleton for connecting ammonium phosphate groups. The synthesis process is usually solvent-free or uses only a small amount of water as a solvent, and is considered environmentally friendly. Figure 3b summarizes the development trend of flame-retardants containing ammonium phosphate groups. Figure 3c shows the formation process of covalent bonds [53]. The main results in this section are listed in Table 2. Zhang et al. synthesized an ammonium salt of 1,3-diaminopropane tetra-(methylenephosphonic acid) (ADDTMPA) with 1,3-diaminopropane which has two -NH_2 groups [54]. The ADDTMPA-treated cotton fabric had an LOI value of 41.5%, which was maintained at 26.3% after 50 LCs. The cotton fabric treated with a P/N-containing oligomer with abundant reactive groups (PEI-P) synthesized by Wang et al. had an LOI value of 38.7%, which was maintained at 29.8% after 50 LCs [55]. This result suggested that flame-retardants containing more ammonium phosphate groups provide more covalent bonding sites for cellulose fabrics, leading to better durability. Many researchers have focused on searching for raw materials with more reactive functional groups to improve durable flame retardancy. Ethylene glycol (2-OH groups) [56], hydroxyl-terminated hyperbranched polymers (64-OH groups) [57], 1,3-diaminopropane (2-NH_2 groups) [54], polyethyleneimine (abundant -NH_2 groups) [55], etc., have all been used to prepare durable flame-retardant cotton.

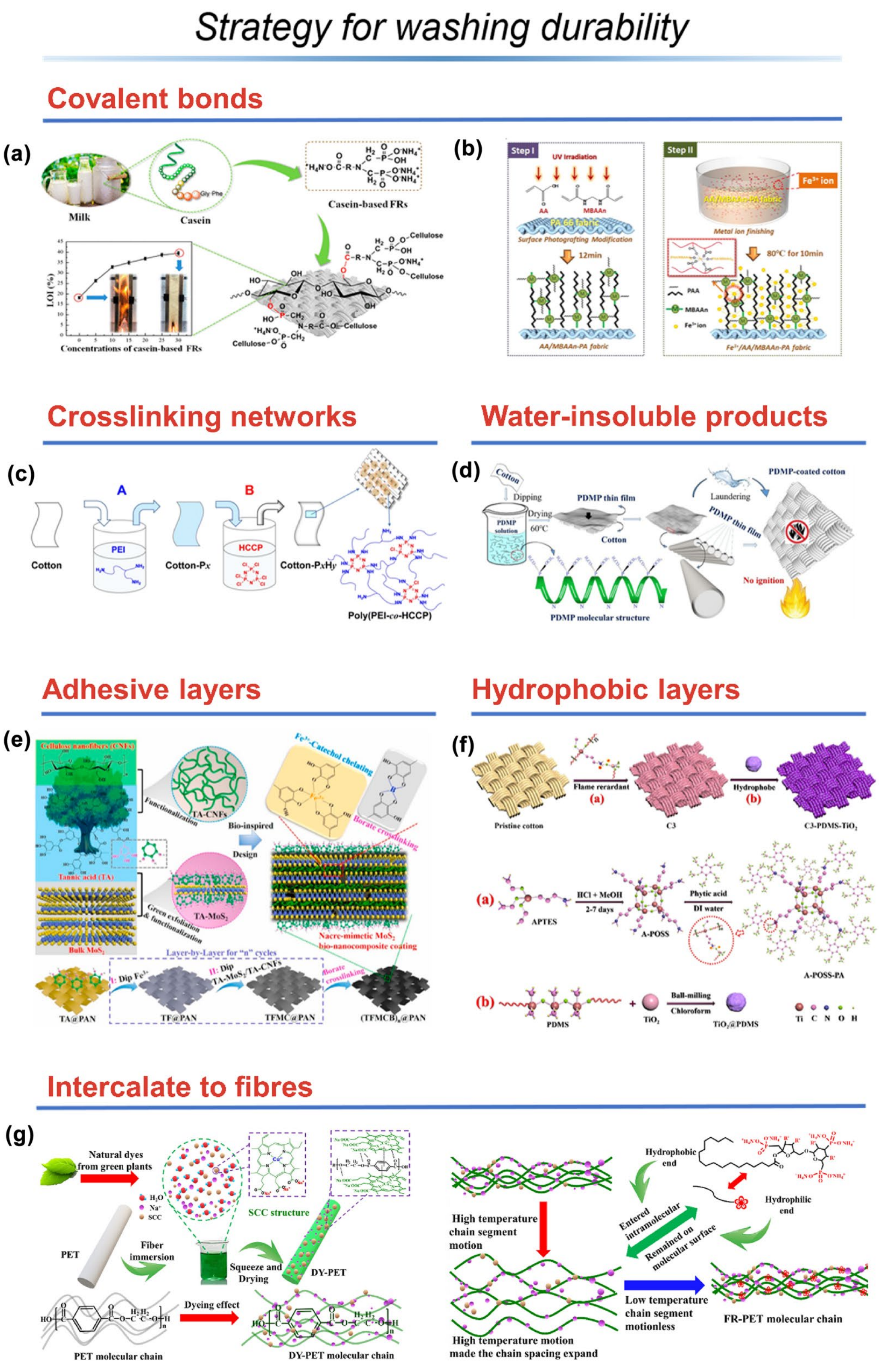


Fig. 2 Typical fabrication strategies for durable flame retardant fabrics: convent bonds. **a**, **b** Reproduced with permission from Ref. [38]. Copyright 2019, American Chemical Society. Reproduced with permission from Ref. [39]. Copyright 2021, American Chemical Society.; crosslinking networks. **c** Reproduced with permission from Ref. [40]. Copyright 2020, Springer Nature; water-insoluble products. **d** Reproduced with permission from ref. [41]. Copyright 2021, American Chemical Society.; adhesive layers. **e** Reproduced with permission from Ref. [42]. Copyright 2021, Elsevier.; hydrophobic layers (**f**). Reproduced with permission from Ref. [43]. Copyright 2020, Elsevier and intercalation of flame retardants into fibres. **g** Reproduced with permission from Ref. [44]. Copyright 2022, Elsevier

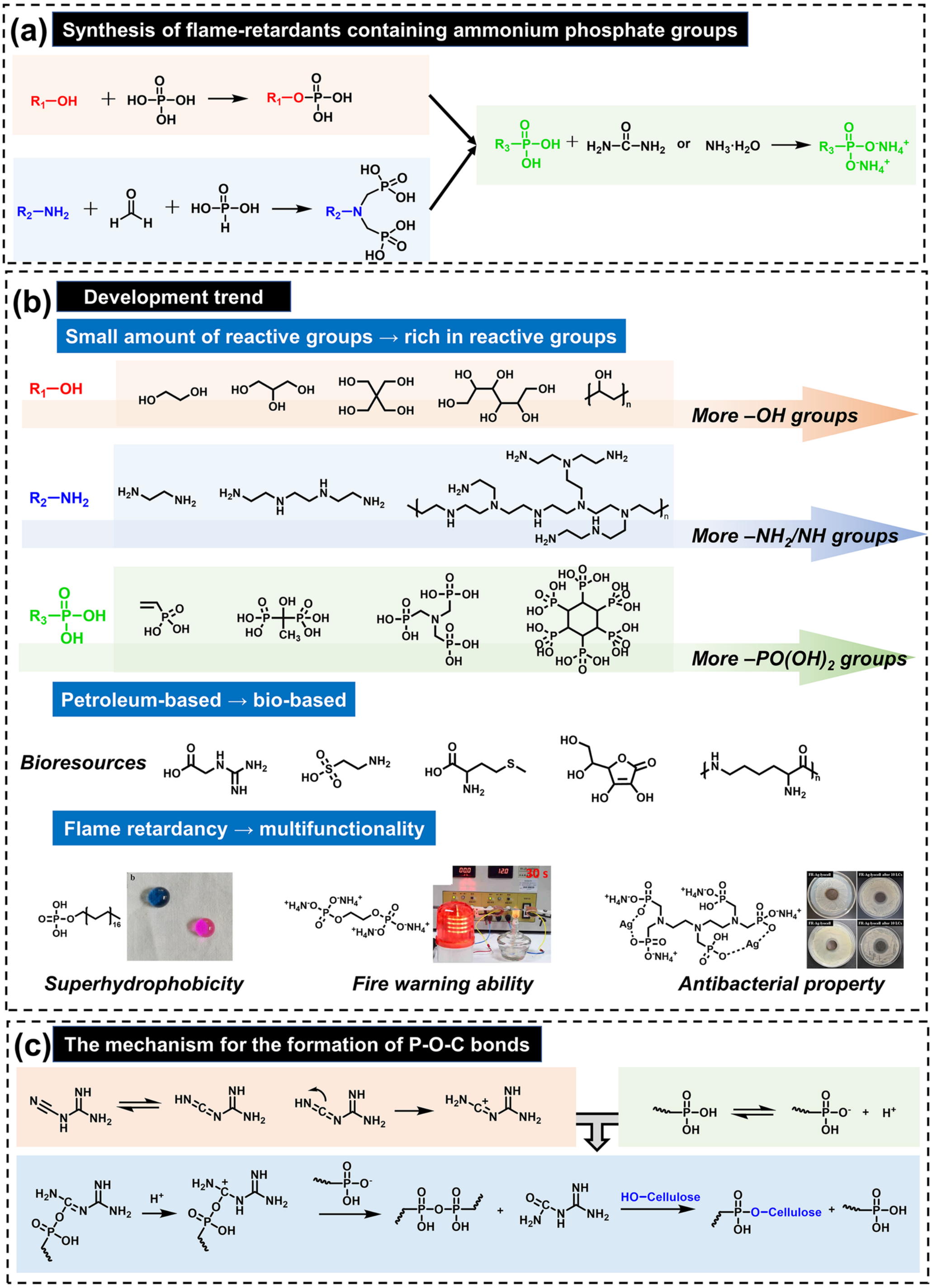


Fig. 3 The synthetic routes (**a**) and development trend (**b**) of flame retardants containing ammonium phosphate groups. Reproduced with permission from Ref. [78]. Copyright 2020, Springer Nature. Reproduced with permission from Ref. [79]. Copyright 2020, Elsevier. Reproduced with permission from Ref. [48]. Copyright 2021, Springer Nature. The mechanism for the formation of P–O–C bonds (**c**)

Due to the shortage of oil resources, the use of renewable resources has attracted much attention. Natural compounds are well suited for textile applications because of their abundance, biocompatibility, and environmental friendliness. The phosphate ammonium salts of phytic acid [52, 58–61], chitosan [62], methionine [63], sodium glutamate [64], sorbitol [65], vitamin C [66], vitamin B5 [67], guanidinoacetic acid [68], ε-polylysine [69], mannitol [70], arginine [50, 51, 71],

Table 2 The flammability and durability of the fabrics treated with flame-retardants containing ammonium phosphate groups

Fabric	Coating	W–G (%)	DL (cm)	LOI (%)	LOI (%) (LCs)	References
Bamboo	ATTPMA	33.8	4.8	50.2	44.5 (50)	[51]
Cotton	AAHMPA	22.4	5.3	45.1	28.6 (50)	[71]
	AASMP	29.0	4.5	45.0	27.5 (50)	[76]
	AATMP	20.3	2.6	44.5	29.5 (50)	[90]
	AATMPEG	17.1	3.5	45.0	33.0 (50)	[91]
	ABTMPA	22.9	5.5	50.2	41.2 (50)	[92]
	ACMPEP	33.4	3.5	42.0	30.0 (50)	[93]
	ACPMPA	24.0	4.8	49.2	34.2 (50)	[72]
	ADBSPA	17.6	6.6	31.7	26.4 (50)	[94]
	ADDTMPA	15.4	4.1	41.5	26.3 (50)	[54]
	ADGP	21.7	3.0	43.7	32.5 (50)	[95]
	ADPTMPA	25.1	3.6	46.5	35.8 (50)	[67]
	ADTPMPA	16.47	3.2	41.5	26.7 (50)	[83]
	AEDTMPA	–	3.0	48.0	31.2 (50)	[96]
	AEGDP	23.7	4.3	41.0	28.4 (50)	[56]
	AGATMPA	24.6	5.8	45.5	29.5 (50)	[68]
	AGPMPA	27.4	2.9	47.9	28.4 (50)	[97]
	AHEDPA	25.2	5.3	42.6	29.5 (50)	[98]
	AHTTPA	23.6	3.3	39.6	29.8 (50)	[99]
	AMHMPA	29.1	4.3	43.0	33.4 (50)	[100]
	AMHPE	20.3	4.9	42.3	27.9 (50)	[70]
	AMVP	13.6	2.6	36.7	27.3 (50)	[101]
	APA	18.8	3.1	43.2	24.7 (50)	[58]
	APEHAP	19.7	2.8	45.2	33.6 (50)	[82]
	APEIAPAP	22.5	4.0	50.5	37.9 (50)	[53]
	APEMPPA	25.0	4.1	44.5	34.7 (50)	[86]
	APGDPE	20.8	5.4	44.5	27.3 (50)	[102]
	APHOMPA	22.1	4.0	40.5	28.8 (50)	[103]
	APP	21.8	4.5	50.1	28.5 (50)	[104]
	APP, PEI, TMC	19.9	3.8	42.0	33.5 (300)	[85]
	APTTP	22.4	3.3	43.8	26.9 (50)	[105]
	ASGTMPA	30.0	3.5	39.5	26.3 (50)	[64]
	ASMPEA	18.4	4.3	40.2	29.4 (50)	[73]
	ASNDP	17.4	5.6	29.5	25.7 (20)	[106]
	ASXPEA	21.2	3.4	45.2	30.2 (50)	[107]
	ATEPAHP	26.0	4.8	40.5	31.8 (50)	[108]
	ATEPEA	23.8	3.9	46.6	27.2 (50)	[109]
	ATPMPA	26.1	2.5	43.6	32.3 (50)	[110]
	CAPD	26.9	6.9	41.6	26.4 (50)	[74]
	Casein-based	16.1	5.0	39.5	26.7 (4)	[38]
	COTP	12.3	6.1	42.5	28.3 (50)	[60]
	DETA-P	20.1	5.2	40.7	29.0 (50)	[81]
	DOPO-AP	21.5	4.0	40.2	26.4 (50)	[111]
	DPG	–	2.4	31.2	24.8 (30	[80]
	FHPOPN	–	5.7	36.4	26.0 (50)	[112]
	FR-CL	18.7	6.3	42.1	27.1 (4)	[113]
	FR-EDTP	23.6	4.2	39.7	28.2 (50)	[72]
	FR–LO	22.7	3.8	43.4	29.7 (50)	[114]
	FR-PA	33.3	5.6	40.5	28.5 (50)	[115]
	HBPOPN	33.5	4.8	46.4	32.8 (50)	[116]

Table 2 (Continued)

Fabric	Coating	W–G (%)	DL (cm)	LOI (%)	LOI (%) (LCs)	References
	HBPOPN	28.2	4.5	43.0	29.6 (50)	[57]
	HBPPN	32.8	5.0	42.8	30.4 (50)	[117]
	Methionine-based	18.6	4.9	43.9	37.7 (50)	[63]
	P/N	33.7	3.3	42.0	33.9 (50)	[118]
	P/N	25.4	8.0	51.1	32.7 (50)	[87]
	PCS	14.1	7.3	28.3	23.0 (10)	[62]
	PEI-P	19.3	3.8	38.7	29.8 (50)	[55]
	PLUEGD	20.1	6.8	42.7	28.6 (50)	[69]
	P-N	35.5	3.6	40.9	32.0 (50)	[119]
	PNH	19.2	3.2	42.7	27.5 (50)	[84]
	P-N-S	35.6	5.5	48.2	32.6 (50)	[120]
	P-N-Si	33.6	3.3	54.5	30.3 (50)	[75]
	PVAAP	24.5	1.8	42.1	26.3 (50)	[121]
	r-GBAP	18.4	5.5	41.6	37.4 (40)	[61]
	TECHPA	25.2	3.7	36.8	31.1 (50)	[122]
	THPO-P	19.9	3.0	45.0	33.4 (50)	[123]
	TPHTDEAT	25.1	3.2	43.3	29.6 (50)	[124]
	UTDDAD	21.0	6.1	42.2	32.0 (50)	[125]
Lyocell	ADTPMPA	13.9	–	44.8	31.3 (20)	[48]
	Arginine-based	11.5	6.3	39.5	37.0 (10)	[50]
	EADP	14.5	6.7	38.0	25.6 (40)	[47]
	P, N	15.6	–	44.2	33.7 (30)	[46]
	PAA	–	~5.9	39.2	30.5 (30)	[59]
	PNPG	–	–	39.3	32.2 (20)	[49]
	SPA	16.0	4.9	40.0	39.1 (20)	[65]
	VCFR	–	–	39.8	26.4 (30)	[66]
Nylon/cotton	PTau	22.5	5.6	36.7	29.2 (40)	[45]
PAN	P-A-PAN	–	–	34.1	29.8 (20)	[126]
Wool	APH	~12.5	9.3	30.6	14.0 (15)	[89]

L-citrulline [72], meglumine [73], taurine [45], and casein [38, 74] have all endowed cellulose fabrics with durable flame-retardancy based on the formation of P–O–C bonds.

Other elements (such as Si, B, S, and Al) were reported to have synergistic effects with ammonium phosphate. Silicon is considered a pollution-free flame-retardant element. During combustion, silicon converts into silicon dioxide on the surface of cotton fabric to impede heat and oxygen transfer [75, 76]. Boron was reported to have a synergistic effect in the phosphorus-nitrogen flame-retardant system [61]. Boron species can decrease the acidity of phosphate, which can delay acid-catalytic degradation and improve thermal stability. In addition, boron can reduce the addition amount of phosphorus-based flame-retardants to achieve environmental protection. Aluminium ions increased flame retardancy and whiteness when combined with ammonium phosphate flame-retardant. Zhang et al. found that the DL of P-Al-N synergistic flame-retardant (PANFR)-treated cotton was reduced by 4 mm compared to that of Al-free flame-retardant-treated cotton, even though the W–G of the former was 2% lower than that of the latter [77]. In addition, the whiteness of the PANFR-treated cotton fabrics was well maintained, compared with that of the Al-free flame-retardant-treated cotton fabrics.

With the increased concern for human health and advancements in flame-retardant technology, endowing fabrics with more functions has attracted increasing attention from researchers. At present, ammonium phosphate flame-retardants have been successfully applied to endow fabrics with multifunctionality, such as superhydrophobic [78], antibacterial properties [48, 80], and fire warning ability [79]. Zhang et al. synthesized a hydrophobic flame-retardant (AMOP) [78]. The cotton fabric treated with 15% AMOP had a water contact angle (WCA) of 142.8° and an LOI value of 27.0%. After 30 LCs, the WCA was increased to 155.1°, and the LOI value was reduced to 19.5%. This was because unreacted AMOP was washed away during the LCs. A multifunctional conductive cotton fabric with high-temperature warning ability was constructed via the layer-by-layer (LbL) method. The LbL components including polyaniline, Ag nanoparticles (NPs), ethylene glycol diphosphoric acid ammonium salt (AEGDP), and 1H,1H,2H,2H-perfluorooctyl trichlorosilane (PFOTS) [79]. Before combustion, Ag NPs were wrapped by PFOTS and formed a poor conductive network. After burning, the waxy layer disappeared, and the dispersed Ag NPs gradually gathered on the fabric surface to form a conductive network and generate a fire warning. Ren et al. synthesized an ammonium salt of diethylene triamine penta methylene phosphonic acid (ADTPMPA) and bonded it to lyocell fabric via P–O–C bonds [48]. The unreacted ammonium phosphate groups provided sufficient binding sites for Ag^+. The LOI for the 30% ADTPMPA-Ag^+-treated lyocell fabric was 44.8%, which was higher than the 42.1% LOI of the ADTPMPA-treated lyocell fabric. In addition, the ADTPMPA-Ag^+-treated lyocell fabric had lower pHRR and THR values, and a higher graphitization degree after burning. After 10 LCs, the ADTPMPA-Ag^+-treated lyocell fabric had an LOI value of 38.8% and maintained its antibacterial properties against *S. aureus* and *E. coli* with inhibition zones of 4.3 mm and 5.8 mm, respectively. Lu et al. synthesized an N,N-di (ethyl phosphate) biguanide (DPG) with both antimicrobial activity and flame retardancy [80]. The DPG was grafted onto cotton fabrics via P–O–C bonds and the double guanidino structure endowed the fabrics with antimicrobial properties. The cotton fabrics treated with 250 g/L DPG had an LOI value of 31.2% and antibacterial ratios of 96.4% and 99.2% against *S. aureus* and *E. coli*, respectively. After 20 LCs, the LOI value was decreased to 26.1%, and the antimicrobial ratio was maintained at 96.0%.

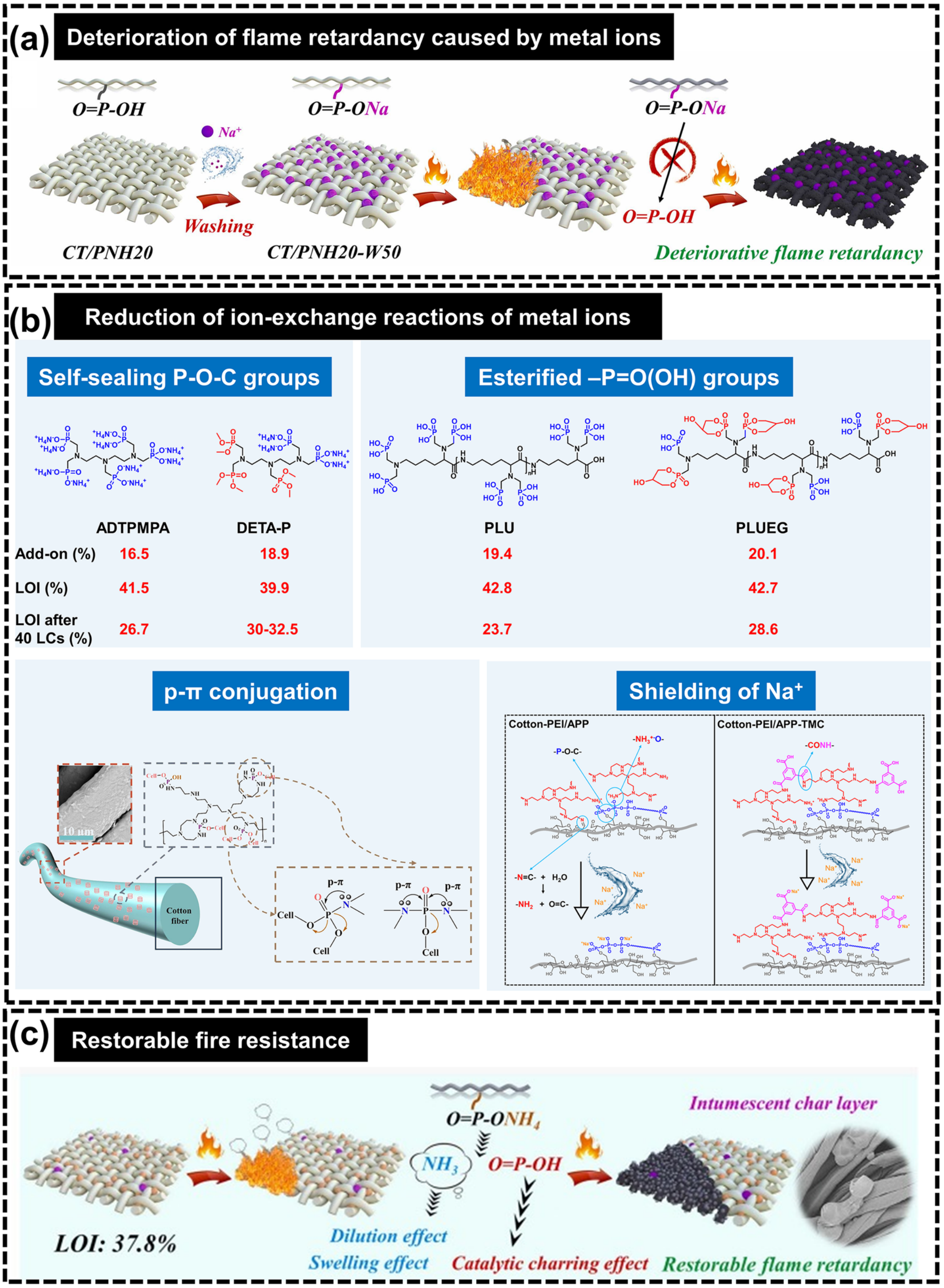
The flame-retardant fabrics with P–O–C bonds showed excellent durability, but their flame retardancy continuously decreased after many LCs, as shown in Fig. 4a. Zhang et al. prepared ε-polylysine-based flame-retardant-treated cotton (PLU-cotton) and decrystallized cotton (PLUD-cotton) fabric samples [69]. The contents of P in the PLU- and PLUD-treated cotton were 2.06% and 2.35% before the LCs, respectively. After 50 LCs, the contents of P in the PLU- and PLUD-treated cotton were slightly reduced to 2.03% and 2.17%, respectively. However, the fabrics were unable to self-extinguish in the VBT after 50 LCs. It was suggested that the ammonium in unreacted ammonium phosphate was replaced by Na^+, Ca^{2+}, and Mg^{2+} in the presence of detergent and tap water during the LCs. Compared with phosphoric acid/ammonium phosphate, phosphoric acid metal salts have weaker catalytic charring ability and cannot fully act as an acid source during combustion, resulting in lower flame retardancy [81]. Much effort has been made to minimize the loss of flame retardancy caused by metal ions during LCs.

Replacing some of the ammonium phosphate groups with ‘self-sealing’ phosphonate groups can improve the durability of flame retardancy as the phosphonate groups do not bind metal ions [74, 81, 82]. The results from Zhang et al. for fabrics with [81] and without [83] phosphonate are compared in Fig. 4b. Before the LCs, diethylenetriamine pentamethyl triphosphonate methyl ester ammonium diphosphonate (DETA-P)-treated cotton fabric showed higher W–G but lower LOI than diethylenetriaminepenta (methylenephosphonic acid) (ADTPMPA)-treated cotton fabric. Compared with the ammonium phosphate group, the phosphonate ester group has a lower flame-retardant efficiency for cotton fabrics. However, after 40 LCs, the LOI of the ADTPMPA-treated cotton fabric was reduced to 26.7%, while the LOI of the DETA-P-treated cotton fabric was maintained at approximately 30.0–32.5%. After 50 LCs, the total Na^+, Ca^{2+}, and Mg^{2+} content of the DETA-P-treated cotton fabric was 1.12%, which was observably lower than the 2.46% of the ADTPMPA-treated cotton fabric. It was indicated that the ion exchange was decreased. The introduction of phosphonate groups into ammonium phosphorus flame-retardants was effective for improving the durability of the flame retardancy of cotton fabrics.

A ‘self-sealing’ phosphonate group-containing flame-retardant (PLUEG) was synthesized by the reaction between glycerol and ammonium phosphate groups containing flame-retardant (PLU) [69], as shown in Fig. 4b. The content of the ammonium phosphate group decreased, while the content of P was maintained. The LOI value of PLUEG-treated cotton fabric was similar to that of the PLU-treated cotton fabric. After 40 LCs, the LOI value of the PLUEG-treated cotton fabric was 28.6%, which was much higher than the 23.7% of the PLU-treated cotton fabric.

Zhang et al. immobilized NH_2-rich polyethyleneimine (PEI) on cotton fabric by interfacial polymerization with trimesoyl chloride (TMC) to protect the underlying ammonium polyphosphate (APP) from metal ions. The cotton fabric was first treated with APP and PEI solution, and then treated with (cotton-PEI/APP-TMC) or without (cotton-PEI/APP) TMC solution. The acyl chloride groups in TMC easily reacted with the amine groups in PEI to form a water-insoluble polyamide layer. After 300 LCs, the contents of Na and N in cotton-PEI/APP were 1.3% and 0.1%, respectively, while the contents of Na and N elements in cotton-PEI/APP-TMC were 0.4% and 3.4%, respectively [85]. This result indicated that PEI was immobilized by the reaction with TMC, which retarded the ion exchange reaction between the underlying APP and metal ions, as shown in Fig. 4b. The cotton-PEI/APP-TMC still showed a self-extinguishing effect in the VBT after 300 LCs.

P_2O_5, the anhydride of H_3PO_4, is highly reactive towards $-NH_2$ and -NH-group-containing PEI. Different from previous studies that introduced phosphorus into PEI by using CH_2O and H_3PO_3 [86], a study introduced phosphorus through the formation of P–N bonds by reacting P_2O_5 with



	ADTPMPA	DETA-P	PLU	PLUEG
Add-on (%)	16.5	18.9	19.4	20.1
LOI (%)	41.5	39.9	42.8	42.7
LOI after 40 LCs (%)	26.7	30-32.5	23.7	28.6

Fig. 4 The deterioration of flame retardancy due to the substitution of ammonium by metal ions (**a**). Reproduced with permission from Ref. [84]. Copyright 2022, Elsevier. Reduction of ion-exchange reactions of metal ions (**b**). Reproduced with permission from Ref. [53]. Copyright 2023, Elsevier. Reproduced with permission from Ref. [85]. Copyright 2023, Elsevier. Restorable fire resistance (**c**). Reproduced with permission from Ref. [84]. Copyright 2022, Elsevier

PEI [53]. The obtained flame-retardant was referred to as the ammonium salt of polyethyleneimine phosphamide phosphoric acid (APEIAPAP). The APEIAPAP-treated cotton had an LOI value of 50.5% and maintained an LOI value of 37.9% after 50 LCs that were classified as more stringent according to AATCC 61–2013 3A. It was proposed that the P element was introduced into PEI through the formation of P-N bonds, which are highly stable against hydrolysis. In addition, the lone pair of N formed a p-π conjugation with the P=O bonds, which reduced the polarity of the

–N–P(=O)–O–C group and improved the bond stability, as shown in Fig. 4b. Moreover, the combination tendency of flame-retardant with metal ions was reduced. Furthermore, APEIAPAP is a polymer flame-retardant, that has the ability to form many covalent bonds with cellulose.

The ion exchange strategy is a facile process for restoring the flame retardancy of fabric which is reduced by the formation of phosphate metal salts. Yao et al. grafted phosphate and melamine (Mel) onto cotton fabric via P–O–C bonds and the Schiff base reaction [87]. The as-prepared cotton fabric had an LOI value of 51.1% and was maintained at 32.7% after 50 LCs. Surprisingly, the cotton fabric showed restorable flame retardancy when immersed in an acetic acid solution. It was suggested that the -NH_2 in Mel combined with the acetic acid, and the Na^+ from the detergent exchanged with the H^+ from acetic acid. Finally, the LOI value was restored from 32.7 to 35.7%. Wang et al. proposed that flame retardancy was restored by immersing the fabric into 0.1 mol/L ammonium sulfate solution at 49 ℃ for 30 min before being thoroughly washed and dried [84]. After the process, the Na content of the fabric decreased from 2.01 to 0.12%, and the N content of the fabric increased from 9.34 to 15.87%. This result indicated that Na^+ was replaced with NH_4^+ in the ammonium sulfate solution by an ion exchange reaction, as shown in Fig. 4c. Nagarajan et al. also found that the flame resistance of washed fabric was recovered after an acid-washing process [88]. Esterification or crosslinking of the unreacted ammonium phosphate groups with polyhydric alcohols or polyamines are considered feasible ways for protecting ammonium phosphate group-containing flame-retardants from the unfavourable effects of ion exchange reactions.

The P–O–C strategy was also used to improve the durable flame retardancy of silk and wool fabrics. These two fabrics have better acid resistance than cotton. The tensile strength of silk fabric with a 22.5% W–G of ammonium phytate was slightly reduced by 13.8% compared with that of the control silk fabric [52]. The tensile strength of wool fabric with a 12.5% W–G of ammonium phytate was slightly increased [89]. It was suggested that the crosslinking between wool molecules and ammonium phytate restricted the relative slippage of wool molecules and hence reinforced the connection between close wool fibres.

These ammonium phosphate flame-retardants are highly designable and show excellent flame retardancy and durability to the cellulose substrate. The flame retardancy is attributed to the powerful condensed-phase flame-retardant mechanism. During combustion, phosphorus-based acids are released from ammonium phosphate-based flame-retardants, which promotes the dehydration and charring of cellulose, contributing to char formation. The char layer acts as a barrier to protect the cotton fabric from the attack of radiant heat and oxygen. However, acidic flame-retardant solutions often

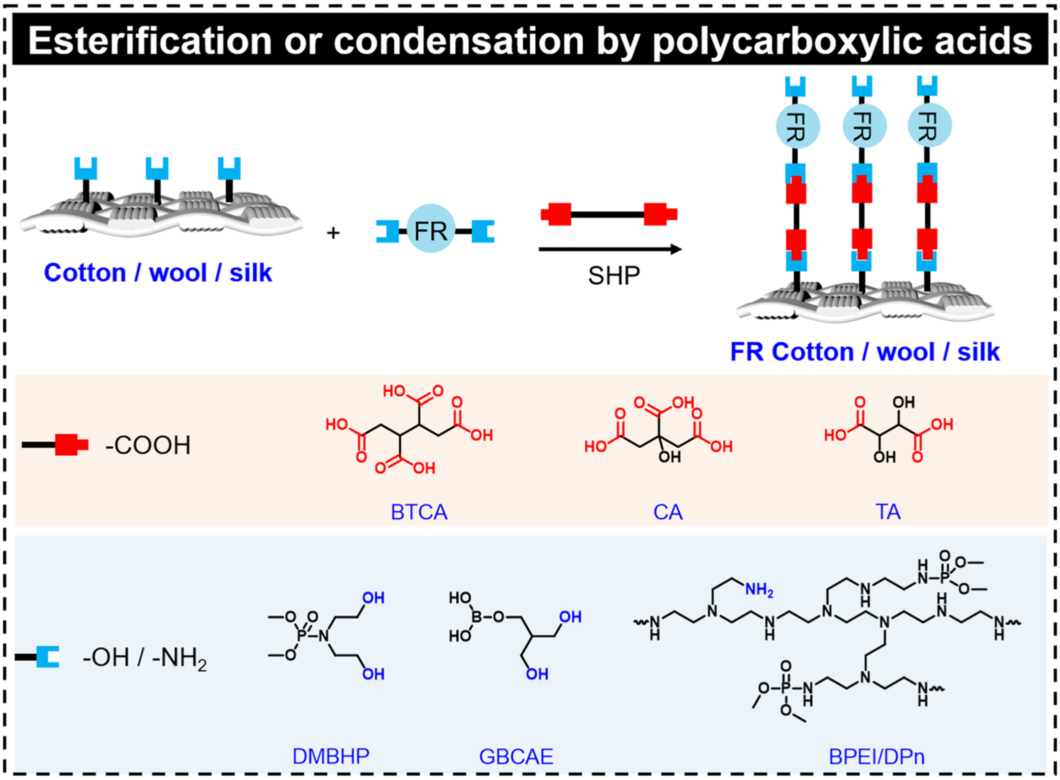


Fig. 5 The fabrication process of durable flame-retardant fabrics with polycarboxylic acids as cross-linking agents

Table 3 The flammability and durability results of fabrics treated with polycarboxylic acids as cross-linking agents

Fabric	Coating	W–G (%)	DL (cm)	LOI (%)	LOI (%) (LCs)	References
Cotton	BPEI/DP4, BTCA	25.1	10.3	28.4	26.7 (5)	[128]
Silk	GBCAE, CA	–	11.0	27.0	26.5 (5)	[131]
	TAPE	16.9	9.5	32.8	26.6 (20)	[132]
Wool	BTCA, PA, TiO_2	13.6	10.2	32.7	27.4 (5)	[129]
	DMBHP, BTCA	22.0	6.5	31.1	26.0 (25)	[130]

DMBHP dimethyl *N*, *N*-bis(2-hydroxyletheylphosphoramidate, *PA* phytic acid, *TAPE* tartaric acid phytate ester

damage the mechanical properties of cellulose fabrics. The ‘P–O–C’ strategy is rarely used for synthetic fabrics due to their lack of active hydroxyl groups. Ren et al. reported the aminoxime modification of PAN fabrics to generate hydroxyl groups on their surface followed by phosphorylation [126], which made it possible to use the ‘P–O–C’ strategy on synthetic fibres.

Formation of C–O–C/C–N Bonds through Esterification or Condensation by Polycarboxylic Acids

Polycarboxylic acids such as citric acid (CA), 1,2,3,4-butanetetracarboxylic acid (BTCA), and tartaric acid (TA) contain several reactive -COOH groups and can react with cotton [127, 128], wool [129, 130], silk [131, 132] fabrics and flame-retardants. Sodium hypophosphite (SHP) is an effective catalyst for polycarboxylic acid crosslinking that significantly reduces the curing temperature of carboxylic acid crosslinkers and reduces the yellowing of fabrics. Therefore, polycarboxylic acids and SHP are widely used when modifying fabrics with flame-retardants. A schematic diagram of the fabrication process based on polycarboxylic acids is shown in Fig. 5 and the results are listed in Table 3. Hasanzadeh et al. grafted fourth generations of poly(amidoamine) (G4-PAMAM) onto cotton fabrics using CA as a crosslinking agent [127]. The burning speed of the G4-PAMAM-treated fabric was 0.16 mm/s and increased to 0.29 mm/s after 5 LCs. However, the breaking strength was greatly reduced from 378 gf/tex for the raw fabric to 274 gf/tex. The strength loss of cotton fabrics may be caused by two reasons. The first is that the crosslinking action of BTCA with cellulose macromolecules hinders the relative slide of cellulose macromolecular chains. The other is that the highly acidic BTCA promotes the hydrolysis of cellulose macromolecules, especially at high temperatures, contributing to a notable decrease in breaking force. Jiang et al. synthesized multi-aminophosphoramide (BPEI/DPn) and applied it to reduce the acidity caused by BTCA [128]. The BPEI/DP4 treated cotton had an LOI value of 29.3% and maintained an LOI value of 27.1% after 5 LCs. It is worth noting that the BTCA-BPEI/DP4 treated fabric maintained approximately 80% of its breaking force.

The durability of boron-based flame-retardants is relatively poor because boron-based flame-retardants have good water solubility and boronic esters are easily hydrolysed [133, 134]. Guan et al. synthesized a reactive borate ester (GBCAE) and then introduced it into silk fabrics with CA as a crosslinking agent [131]. The GBCAE-treated silk fabric had an LOI value of 27.0% and maintained an LOI value of 26.5% after 5 LCs. It was proposed that GBCAE combined with silk fibres by electrostatic attraction and covalent bonding, which is beneficial for improving the durability of treated silk fabric.

Polycarboxylic acids can also be used as a bridge to bond flame-retardants to fabrics. The combination of two or more polycarboxylic acids will help to reduce costs and usage, as well as reduce the degree of yellowing [135].

Formation of P–C–N Bonds via the Kabachnik-Fields Reaction

The Kabachnik-Fields reaction refers to the multicomponent condensation of carbonyl compounds, amines, and phosphonic acid diesters to form alpha-aminoalkyl phosphonates. The Kabachnik-Fields reaction can be divided into two steps: the Schiff base reaction and the Pudovik reaction. The fabrication processes based on the Kabachnik-Fields reaction are shown in Fig. 6a, and the flammability and durability of relevant fabric samples are listed in Table 4. Dimethyl phosphate (DMP) and diethyl phosphite (DEP) have been widely applied in synthesizing flame-retardants because of their reactive P–H units. Guan et al. fabricated flame-retardant silk fabric by covalently cross-linking DEP with glutaraldehyde as a coupling agent [136], as shown in Fig. 6a1. The as-prepared silk fabric had a DL of less than 11.0 cm and maintained self-extinguishing properties over 15 LCs. In addition, Guan et al. synthesized a hybrid silica sol [137] and P/N/S-containing flame-retardant (GASDP) [138], and then bonded them with silk fabrics by Schiff base reaction. The hybrid silica sol (Fig. 6a2) and GASDP (Fig. 6a3) treated silk fabrics reached the B_1 level even after 25 LCs. Li et al. prepared cotton fabric with durable flame

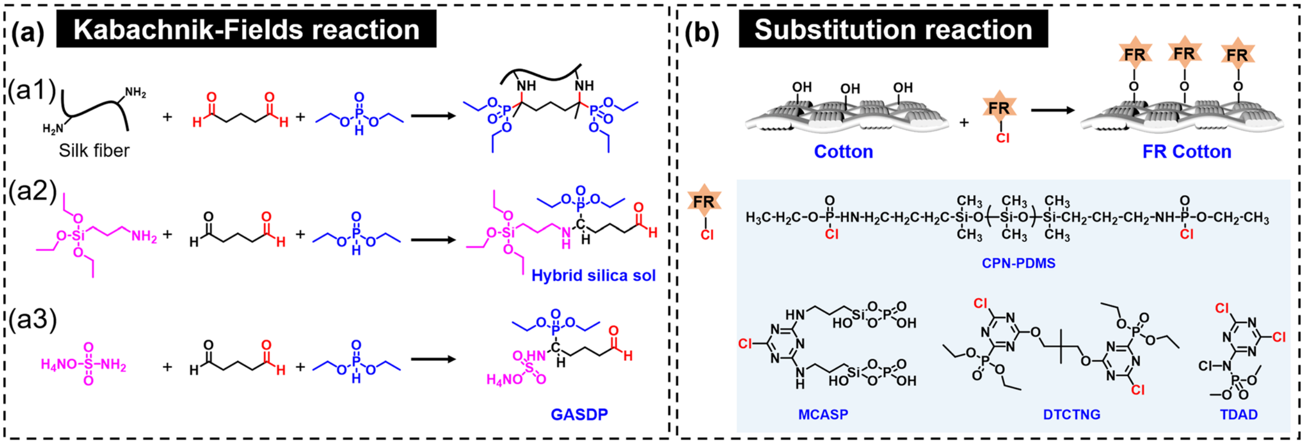


Fig. 6 The fabrication process of durable flame-retardant fabrics by Kabachnik-Fields reaction (**a**) and substitution reaction of reactive Cl atom (**b**)

Table 4 The flammability and durability of samples prepared through the Kabachnik-Fields reaction

Fabric	Coating	W–G (%)	DL (cm)	LOI (%)	Durability (LCs)	References
Cotton	Ethylenediamine /DMP	17.5	–	28.1	LOI: 27.4% (10)	[139]
Silk	DEP	8.1	< 11.0	27.4	DL: 12.5 cm (15)	[136]
	GASDP	~ 12.5	7.5	~ 30.0	DL: 13.2 cm (25)	[138]
	Hybrid silica sol	18.5	8.2	32.7	LOI: 28.0% (25)	[137]

retardancy by using the Kabachnik-Fields reaction [139]. First, the cotton fabric was oxidized by sodium periodate to form -CHO groups. Schiff bases were then obtained by the reaction of -CHO groups with ethylenediamine groups. Finally, DMP reacted with Schiff bases by the P–H addition reaction. The as-prepared cotton fabric had an LOI value of 28.1% that was slightly reduced to 27.4% after 10 LCs.

The Kabachnik-Fields reaction generates products that can be cured in a modest temperature range of only 60–80 °C, which reduces energy consumption in production. However, this strategy is only suitable for fabrics with amino groups, or cellulose fabrics with aldehyde groups after oxidation. In addition, there are fewer flame-retardant monomers with active P–H groups, which shows limited designability.

Formation of C–O–C Bonds via Substitution Reaction

Flame-retardants containing reactive Cl atoms can react with the -OH groups of cotton fabrics by substitution reactions to form ether bonds [140–142]. Figure 6b shows the reactive Cl-containing chemicals used in flame-retardant cotton fabrics, and Table 5 lists the results.

Zhu et al. synthesized a finishing agent (CPN-PDMS) with both flame retardancy and water repellency [143]. CPN-PDMS was loaded onto cotton fabrics through covalent bonding. The CPN-PDMS-treated cotton had an LOI value of 30.6% and maintained an LOI value of 28.5% after 30 LCs. Cyanuric chloride, with three active Cl atoms, is an important chemical in the textile industry and has a strong washing fastness when applied to cotton fabrics. When one or two Cl atoms of cyanuric chloride were replaced by a flame-retardant molecule, the treated cotton showed durable

Table 5 The flammability and durability results of cotton treated with reactive Cl-containing chemicals

Fabric	Coating	W–G (%)	DL (cm)	LOI (%)	LOI (%) (LCs)	References
Cotton	CPN-PDMS	27.1	4.3	30.6	28.5 (30)	[143]
	DTCTNG	30.0	3.7	30.3	20.0 (50)	[140]
	MCASP	–	4.5	31.0	27.2 (25)	[144]
	TDAD-Cl	17.4	14.7	27.5	23.7 (30)	[145]

flame retardancy. For example, monochlorotriazine aminopropyl silanol phosphate (MCASP)-treated cotton had an LOI value of 31.0%, and at still had a remain value of 27.2% after 25 LCs [144]. Similarly, dioxo-(3-triethylphosphite-5-chlorine-1-triazine)-neopentylglycol (DTCTNG)-treated cotton had an LOI value of 30.3% and maintained an LOI value of 20.0% after 50 LCs [140]. Jiang et al. designed a reactive triazine-phosphonate N-halamine precursor (TDAD) and applied it to cotton fabric. After chlorination, the cotton fabric presented a strong bactericidal effect against both positive and negative bacteria. The prepared cotton fabric had an LOI value of 27.5% and maintained an LOI value of 23.7% after 30 LCs [145].

The reactive Cl atom, especially that of acyl chloride, is highly reactive towards the -OH groups of cotton fabrics. However, the synthesis of Cl-containing flame-retardants involves a large amount of organic solvent due to the water sensitivity of the halogen atoms, which is not suitable for large-scale applications.

Formation of Si–O–C bonds by Sol–gel Reactions

Sol–gel flame-retardants are usually obtained from an inorganic or organic−inorganic hybrid coating formed by drying 3D networks through the hydrolysis and condensation of alkoxysilanes. A schematic diagram of the fabrication process of the sol–gel method is shown in Fig. 7a. When applying the sol–gel method to cotton fabrics, condensation occurs between the Si–OH of the colloid and the -OH of the fibres during the drying and curing processes. The condensation process greatly increases the adhesion of the polymer film to the textile. Alongi et al. used various alkoxysilane precursors to create sol–gel coatings on cotton fabrics [146]. Although the burning rate of the fabric treated by these precursors was markedly decreased compared with that of the control cotton fabric, the fabrics did not self-extinguish. To improve the flame retardancy of sol–gel coatings on fabrics, researchers introduced flame-retardants into the sol–gel. Durable flame retardancy was achieved in three ways: (1) the incorporation of P-containing flame-retardants into the silicone sol [147] (Fig. 7b); (2) the design of P- or B-containing reactive monomers [148] (Fig. 7c); and (3) the use of reactive silane coupling agents as bridging units to bond the flame-retardants to fabrics (Fig. 7d). The results of sol–gel-treated fabrics are listed in Table 6.

Tang et al. investigated the durable flame retardancy of PA/silica sol on wool fabric (Wool-3) by performing a nanoparticle adsorption procedure followed by a pad-dry-cure (PDC) process [147]. The flame-retardant wool fabric prepared by the traditional PDC procedure (Wool-3-traditional) was selected for comparison. With the increase in the number of LCs, the flame retardancy of Wool-3-traditional and Wool-3 decreased, while the latter showed a smaller reduction in flame retardancy. After 20 LCs, the DL of the Wool-3-traditional fabric was 15.3 cm and did not reach the B_1 standard. The DL of Wool-3 was lower than 11.0 cm and reached the B_1 standard even after 30 LCs.

The introduction of P- or B-containing alkoxysilane precursors into the sol–gel network can improve durability. The chemical structures of the synthesized reactive P- or B-containing alkoxysilane precursors are shown in Fig. 7c. Lu et al. synthesized a series of alkoxysilane precursors and introduced them into cotton fabrics. After hydrolysis, the Si–OH of the precursor reacted with the -OH groups of the cotton fabrics and the B- or P-containing flame-retardants were covalently bonded to the fabrics. The reaction products of spirocyclic pentaerythritol bisphosphorate disphosphoryl chloride (SPDPC) and 3-aminopropyltrimethoxysilane (APTMS) formed a sol–gel precursor (SPDP-PTMS) [150]. There are two hydrolysable -Si-$(OCH_3)_3$ groups in one SPDP-PTMS molecule. With a 32.2% W–G of SPDP-PTMS, the LOI of the cotton fabric was increased to 29.5% and maintained at 26.2% after 20 LCs. Then, based on potassium cis-tetramethylcyclotetrasiloxanolate (KCTSi), a new sol–gel precursor (SPPTMS) was synthesized by connecting SPDPC and APTMS [151]. There are four hydrolysable -Si-$(OCH_3)_3$ groups in one SPPTMS molecule. Compared with that of SPDP-PTMS, the durability of SPPTMS was slightly improved. With a 30.1% W–G of SPPTMS, the LOI of the cotton fabric was increased to 31.5% and maintained at 26.1% after 20 LCs. A similar durability was achieved with a lower W–G of the flame-retardant. After that, a phosphorus-free B-containing sol–gel precursor (BTDU-PTMS) was synthesized with boric acid, pentaerythritol, cyanuric chloride and 3-aminopropyltrimethoxysilane [152]. With a 30.1% W–G of BTDU-PTMS, the LOI of treated cotton fabric was 32.7% and was maintained at 26.3% after 20 LCs. In addition, the TSP value of the fabric with a 19.9% W–G of BTDU-PTMS was reduced by 43.3%, exhibiting good smoke suppression ability.

Silane coupling agents with reactive functional groups (such as -NH_2, -CH=CH_2, -CH–O–CH_2-, and -SH groups) can be used as bridges to bond flame-retardants to fabrics. Si–OH groups of the hydrolysed silane coupling agent react with -OH groups from cotton fibres and the fibres expose reactive functional groups that can bond with specific flame-retardants. Wu et al. synthesized a -CH=CH_2 group-containing hybrid nanoparticles (SiDP) based on quaternary ammonium salt, inorganic nano SiO_2, and Schiff base [153]. Then, SiDP nanoparticles were grafted to the 3-(trimethoxy silyl) propyl methacrylate (γ-MPS)-modified cotton fabric (Co-SiDP-15%) via radical polymerization, as shown in Fig. 7 (d). After 50 LCs, the pHRR of Co-SiDP-15% was still reduced by 16.3%. Wu et al. also synthesized NH_2-containing nanogels (NG) with flame-retardant and antibacterial properties [149]. Then, the NGs were grafted

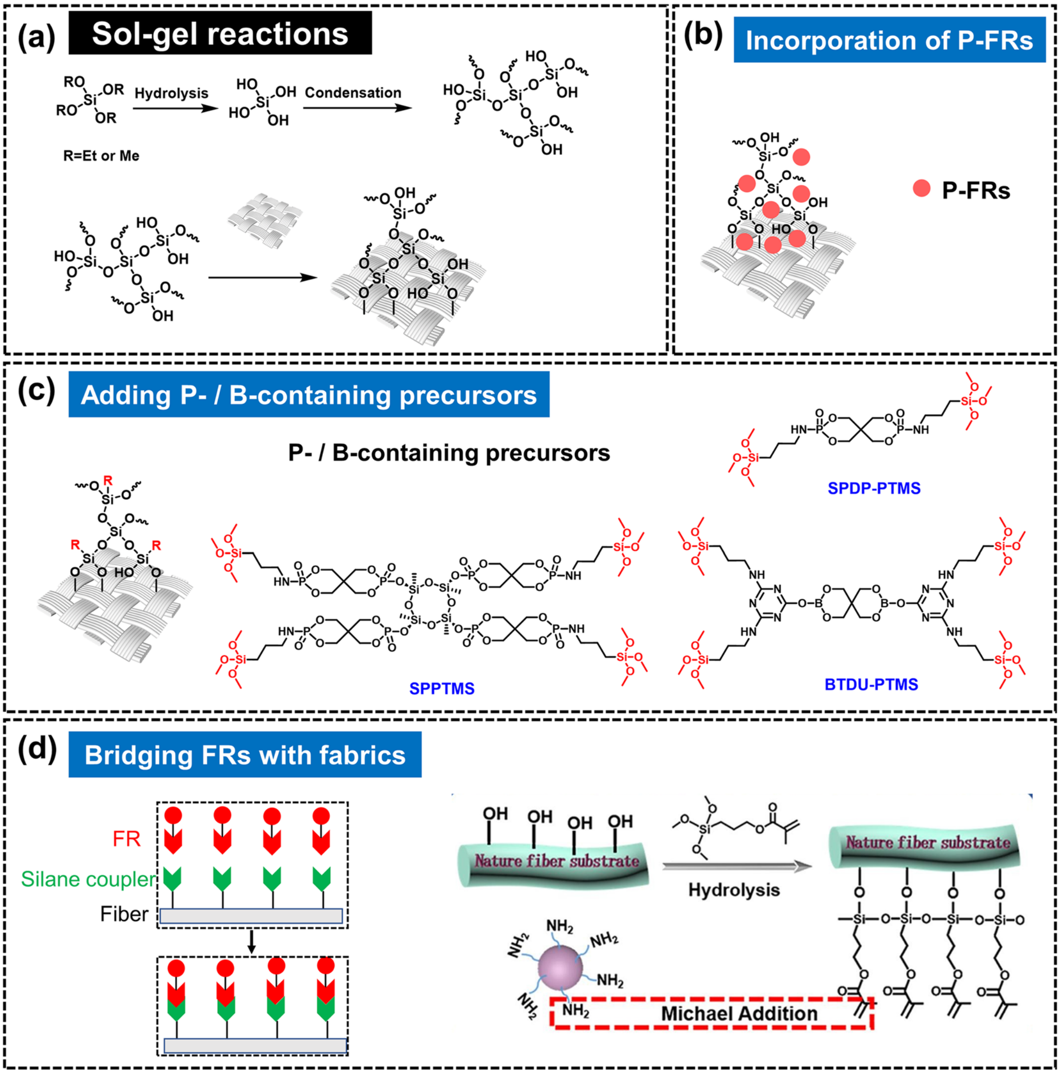


Fig. 7 The fabrication process of sol–gel treated fabrics (**a**); the incorporation of P-FR into silica sol (**b**); the addition of P- or B-containing reactive precursor into silica sol (**c**); the silane coupling agent as the bridge between flame-retardants and fabrics (**d**). Reproduced with permission from Ref. [149]. Copyright 2021, Elsevier

Table 6 The flammability and durability results of fabrics treated with the sol–gel method

Fabric	Coating	W–G (%)	DL (cm)	LOI (%)	LOI (%) (LCs)	References
Cotton	BTDU-PTMS	30.1	8.5	32.7	26.3 (20)	[152]
	DTSP	16.0	11.8	30.3	27.0 (20)	[162]
	FR-0	25.2	7.8	33.2	24.2 (20)	[148]
	MPTES, DHTP	28.1	5.0	26.3	22.4 (5)	[155]
	MPTES, DHTP	60.4	4.6	27.2	25.1 (30)	[154]
	PPDMS	30.4	12.0	29.0	24.7 (20)	[163]
	SPDP-PTMS	32.3	8.8	29.5	26.2 (20)	[150]
	SPPTMS	30.1	8.1	31.5	26.1 (20)	[151]
	TTPBD	17.6	10.7	27.5	24.3 (30)	[164]
Nylon/cotton	GPTMS, PEI, PA	20.1	7.5	29.8	26.7 (15)	[156]
PET	PA; SSP	–	–	31.4	31.0 (45)	[165]
Wool	PA, TEOS	~15.0	~8.0	~38.0	31.0 (20)	[147]

PPDMS poly (oligodimethylsiloxyl spirocyclic pentaerythritol bisphosphorate), *DTSP* dimethyl-3triethoxysilanepropylphosphoramidate, *SSP* sol solution of flexible polysiloxane, *TEOS* tetraethoxysilane to the γ-MPS-modified cotton fabric (Co-NG3) via Michael addition reactions. After 50 LCs, the pHRR and THR of the Co-NG3 sample were still reduced by 22.6% and 16.3%, respectively, compared with those of the control cotton.

Yu et al. bridged cotton fabric and dimethyl-[1,3,5-(3,5-triacryloylhexahydro)triazinyl]-3-oxopropylphosphonate (DHTP) with 3-mercaptopropyltriethoxysilane (MPTES) under the UV-photoinitiated thiolene click reaction [154, 155]. The LOI of 8% DHTP-treated cotton was 27.2%. After 1 LC, the weight loss of DHTP was 7.1%, and the LOI value decreased to 25.7%. However, the weight loss and LOI value (25.1%) of the 8% DHTP-treated cotton fabric remained unchanged after 5 LCs, demonstrating durable flame retardancy.

Zhang et al. fabricated a nylon/cotton blend fabric (G-PEI/PA-NYCO) with durable flame retardancy by a sol–gel process of 3-glycidyloxypropyl trimethoxy silane (GPTMS) followed by a dip-pad process of PEI and PA [156]. The ring-opening reaction occurred between the -NH_2 groups in PEI and epoxide groups in GPTMS. The G-PEI/PA-NYCO fabric maintained self-extinguishing capability even after 20 LCs. The durability was attributed to the formation of linkages between the silicious network and NYCO fabric.

During combustion, the Si-containing composite crosslinked to form Si–O–Si networks and was finally converted into SiO_2 that remained in the char residue, which increased the compactness of the char layer. The sol–gel method results in certain durability, but the resulting flame retardancy is relatively lower, which usually requires a coating with an over 30.0% W–G to achieve an LOI value above 30.0%. The main advantages of the sol–gel process are the mild preparation process, lower degree of chemical utilization, and effective protection of the inherent properties [157]. However, the preparation of sol-gels requires large amounts of organic solvents to slow the hydrolysis rate of the silane coupling agent, which is not environmentally friendly. There are still some sol–gel works that show poor durability [158–161]. It is suggested that the properties of the sol–gel network are related to many factors that influence the hydrolysis and condensation process. The pH value, reaction time and temperature, catalyst, reagent concentration, kind of precursor, molar ratio of water to precursor and organic solvent, ageing temperature and time, and drying process should all be considered in analyzing the properties.

Formation of C–C Bonds by UV Grafting Reactions

In the presence of a photoinitiator, such as benzophenone (BP), polymers are excited and produce free radicals when exposed to ultraviolet (UV) light [166]. Vinyl comonomers can then be grafted onto the fabric surface under UV irradiation. A schematic diagram of UV grafting is shown in Fig. 8a. There are two pathways for utilizing UV grafting to improve the durability of flame-retardant fabrics. First, comonomers containing flame-retardant elements (such as P or N) and vinyl groups are grafted onto the fabric under UV irradiation. Second, UV irradiation can be used to graft reactive groups onto comonomers [such as glycidyl methacrylate (GMA), acrylamide (AM), and acrylic acid (AA)], and then the reactive groups are bonded with flame-retardants. The UV grafting monomers are shown in Fig. 8b. The results of using UV grafting technology in this section are listed in Table 7.

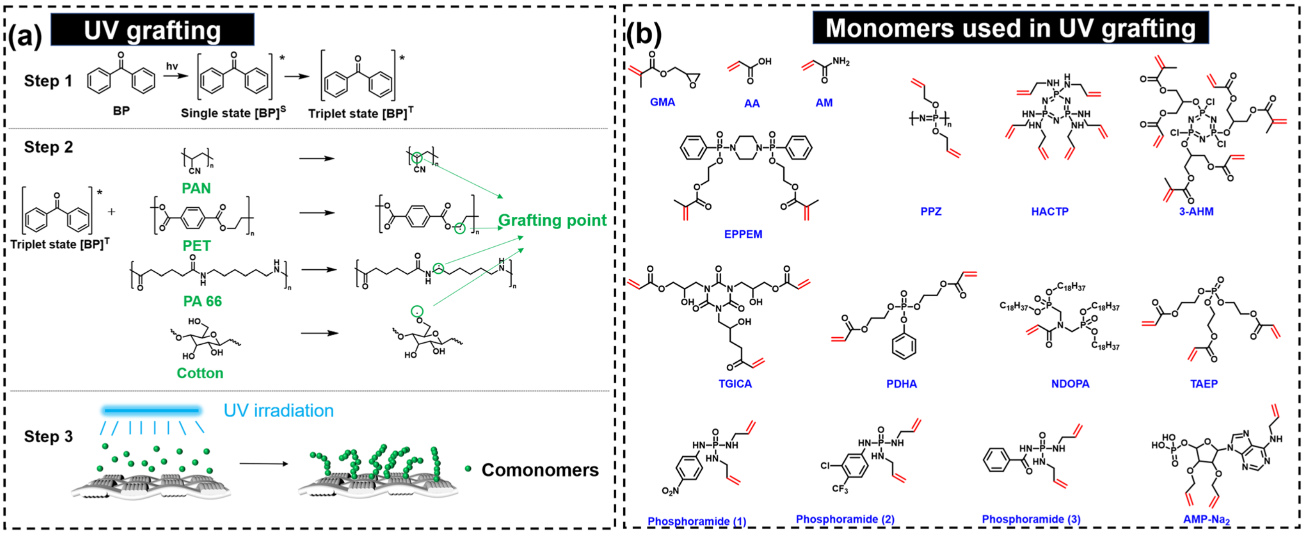


Fig. 8 The fabrication process of UV grafting on fabrics (**a**). The chemical structures of the monomers that have been used in UV grafting (**b**)

Monomers that have unsaturated C=C bonds can bond to cotton fabrics [167]. Researchers have synthesized a series of monomers containing phosphorus atoms and C=C bonds [168–174]. Regarding TAEP- and TGICA-treated cotton, their pHRR and THR values were decreased by 34.6% and 59.1%, respectively [172]. After 10 LCs, their pHRR and THR values still decreased by 22.4% and 54.5% compared with those of the control fabric, indicating that the treated cotton fabric had good washing durability.

However, P-containing comonomers are unfavourable for copolymerization due to steric hindrance. Ren et al. grafted small molecule comonomers such as GMA [175–177] and AA [178] onto PAN fabrics, and then the grafted PAN fabrics underwent acylation, ammonization, or phosphorylation reactions. The UV grafting of PAN fabrics resulted in excellent durability, and most grafted fabrics maintained an LOI value of approximately 30.0% after 30 LCs [175–177].

Zhang et al. grafted PA66 fabric with maleic anhydride (MAn) and then the grafted PA66 fabric was reacted with triethanolamine to improve its durable flame retardancy [179]. The as-prepared PA66 fabric had an LOI value of 29.1%. The LOI value was reduced to 25.7% and 23.6% after washing with water and detergent solution, respectively. In another work, the PA66 fabric (AM-g-nylon-6.6) was grafted with AM in one step [180]. The AM-g-nylon-6.6 with 32.5% AM had a higher LOI value of 24.0% after 10 LCs, indicating that 91.6% of the original LOI was maintained. It was suggested that the C–C bond is more stable than the C–O–C bond in the alkaline condition of being immersed in a detergent solution. N,N′-Methylene bisacrylamide (MBAAm), which has two acrylamide groups, was used as a crosslinker to further improve the durability of AM on PA66 fabric [181]. The fabric treated with 0.05 mass% MBAAm could maintain 91.3% of its LOI value even after 50 LCs. A recent study combined metal ion finishing and UV-photografting (M/P) technology to strengthen the linkages between fabric and metal ions to fabricate an inorganic−organic hybrid coating with durable flame retardancy for PA66 fabric [39]. Specifically, the PA66 fabric was first grafted with AA and MBAAn under UV irradiation and then further reacted with Fe^{3+} by a pad-cure procedure. The W–G of the Fe^{3+}/AA/MBAAn-PA fabric was 39.4% and remained at 34.8% after 45 LCs, which was only an 11.7% reduction in the W–G. The LOI of the Fe^{3+}/AA/MBAAn-PA fabric was maintained at 27.8% after 45 LCs, indicating that flame retardancy was maintained. Similarly, -COOH can improve the combination fastness of Cr^{3+}. Cr^{3+}/AA-PNWF was also prepared by M/P technology [182]. The LOI value of Cr^{3+}/AA-PNWF was reduced to only 25.1% from 27.5% even after 50 LCs, suggesting that the complexation reaction enhanced the washing fastness and durability.

Due to the inherent hydrophobicity and chemical inertness of polyester fabric, the efficacy of the LbL self-assembly method is limited for polyester fabric. Wang et al. reported a surface modification of flame-retardant copolyester fabric achieved by UV grafting and LbL deposition [183]. Polyacrylic acid (PAA) was introduced onto the fabric by UV polymerization, which was then used as the base of the LbL layer. Betadex sulfobutyl ether sodium (SBE-β-CD), γ-aminopropyltriethoxysilane (KH-550), and [(6-oxido-6H-dibenz-[c,e]-oxaphosphorin-6-yl)-methyl] butanedioic acid (DDP) were selected as the LbL components. The reported LbL-coated copolyester fabric maintained its flame retardancy without melt dripping after 10 LCs.

Table 7 The flammability and durability of fabrics prepared by UV grafting strategy

Fabric	Coating	W–G (%)	DL (cm)	LOI (%)	LOI (%) (LCs)	References
Cotton	AMP-Na$_2$, L-cys	8.1	30.0	27.3	25.2 (20)	[173]
	HACTP	23.0	–	–	–	[171]
PA6	AA, Cr^{3+}	–	6.2	27.1	25.1 (50)	[182]
PA66	AA, MBAAn, Fe^{3+}	39.4	17.6	33.4	27.8 (45)	[39]
	AM	32.5	6.8	26.2	22.9 (50)	[180]
	AM, MBAAm	39.9	4.4	25.7	23.5 (50)	[181]
	MAn	6.6	–	29.1	23.6 (10)	[179]
PAN	GMA, Arg, H$_3$PO$_3$	–	–	34.7	29.4 (30) 27.0 (40)	[176]
	GMA, EDA, H$_3$PO$_3$	–	–	34.2	30.7 (30)	[175]
	GMA, H$_3$PO$_3$, NH$_2$NH$_2$·H$_2$O	–	–	32.3	29.3 (30)	[177]
	PAA, EDA, phosphoric acid	–	–	28.1	27.3 (20)	[178]
PET	PAA, KH550, SBE-β-CD, DDP	–	7.5	36.1	29.0 (20)	[183]

Arg L-arginine, *AMP-Na$_2$* adenine nucleotide, *L-cys* L-cysteine, *HACTP* hexa(Allylamino)cyclotriphosphazene

Many flame-retardant fabrics have an LOI value over 27.0 after 20 LCs, which are still indicative of flame-retardant materials. The UV-induced grafting technique has many advantages such as a simple process, low energy consumption, and low damage to the material, and is conducive to continuous processing. However, the homogeneity and copolymerization of monomers on fabrics are two main problems that impede the further development of UV grafting technology in the industry.

Formation of Crosslinking Networks

The formation of crosslinking networks wrapped around the fibres between flame-retardants can effectively improve durability. The formation of crosslinking networks can be categorized into two types. The first type involves the formation of covalent bonds between components of the coating, which does not require a crosslinking agent. The second type involves the addition of crosslinking agents to noncovalently bonded coating components.

Crosslinking Between Components

Figure 9 shows typical crosslinking networks formed by the two components in a coating. The crosslinking network is formed by adding crosslinking agents, UV irradiation [184], plasma treatment, or heating. The crosslinker should be a small molecule, oligomer, or polymer that contains three or more reactive groups, while the flame-retardant should contain multiple reactive groups. The crosslinking reaction takes place by ester exchange (Fig. 9a), Mannich (Fig. 9b), nucleophilic substitution (Fig. 9c), and Michael addition (Fig. 9d) reactions, and so on. The results in this section are listed in Table 8.

Grunlan et al. found that PEI and HCCP precipitated due to the crosslinking reaction between NH_2 and P-Cl in polar organic solvents such as $CHCl_3$ and CH_3CN [40], as shown in Fig. 9 (c). The crosslinking network of PEI and HCCP was formed on the cotton fabric by dipping it successively in PEI and HCCP solution. The as-prepared fabric showed a self-extinguishing effect after 1 LC, but this effect was not observed after 2 LCs. Xin et al. synthesized a formaldehyde-free flame-retardant (Neo-FR) with a phosphonitrilic chloride trimer (HCCP) and acrylamide [185]. The Neo-FR crosslinked with NH_2-rich PEI. Cotton fabrics were first treated with PEI by padding and drying and then treated with Neo-FR. The as-prepared cotton fabric with a 26.5% W–G of the coating had an LOI value of 33.8% and a DL of 7.6 cm. After 30 LCs, the DL was increased to 11.0 cm. The results indicated that Neo-FR is a durable flame-retardant for cotton fabric. Fei et al. synthesized NH_2-containing phenylboronic-grafted PEI (PEIPA), which also formed a crosslinking network with Neo-FR [186], as shown in Fig. 9 (d). The PEIPA- and Neo-FR-treated cotton fabric had an LOI value of 29.65% and maintained an LOI value of 23.2% after 5 LCs, which was still higher than that of the control cotton fabric.

The above crosslinking process requires the use of organic solvents, which raises concerns about the environment. Therefore, researchers are focusing on achieving crosslinking reactions with water-based technologies [187, 188]. Grunlan et al. reported a water-based self-crosslinking network formed by PEI and tetrakis-hydroxymethyl phosphonium chloride (THPC) [188], as shown in Fig. 9b. The PEI aqueous solution was alkaline (pH > 10) due to the basic NH_2 groups. Under alkaline conditions, THPC decomposed and produced tris(hydroxymethyl)phosphine and formaldehyde. Then, PEI reacted with formaldehyde by a Mannich reaction to form a Schiff base. A coupling reaction occurred between the Schiff base and the tris(hydroxymethyl)phosphine. Further condensation converted phosphorus into stable P^{3+} from metastable P^{4+}. After the release of water and formaldehyde at 110 °C, a crosslinking network was formed on the cotton fabric. The as-prepared cotton fabric with a 27.3% W–G of the crosslinking coating had a DL of less than 11.4 cm in the VBT. The twice-washed fabric could also self-extinguish but burned significantly more.

Gaan et al. designed an in-suit Michael addition reaction strategy to form a polymer network within cellulose [189], as shown in Fig. 9d. The cotton fabrics were treated with trivinyl phosphine oxide (TVPO) and piperazine (Pip) or 2,4,6-tri(piperazine1yl)-1,3,5-triazine (TPT) followed by a curing, microwave heating, or steaming process. Finally, the network was formed within the cotton fibres. The steam crosslinked samples exhibited a high P-retention (> 95%) after 50 LCs, demonstrating long-term stability.

P/Si-based flame-retardant nanoparticles (PFR) were synthesized by the radical polymerization of tetramethyl divinyl disiloxane and vinyl phosphoric acid [190]. After a dip-coating process and plasma-induced crosslinking procedure, the cotton fabric showed durable flame retardancy. The as-prepared cotton fabric had an LOI value of 27.0% and still maintained an LOI value of 23.9% after 50 LCs.

Crosslinking by Crosslinkers

Crosslinking networks formed by the addition of crosslinkers are often used in LbL coatings. The LbL method mainly involves an alternate immersion of fabric into positively and negatively charged components such as polyelectrolytes and nanoparticles, that electrostatically interact [193]. The efficiency and functionality of LbL coatings can be achieved by adjusting the number of self-assembled layers and components [194]. However, weak interactions result in poor durability and the active ingredients are lost during LCs.

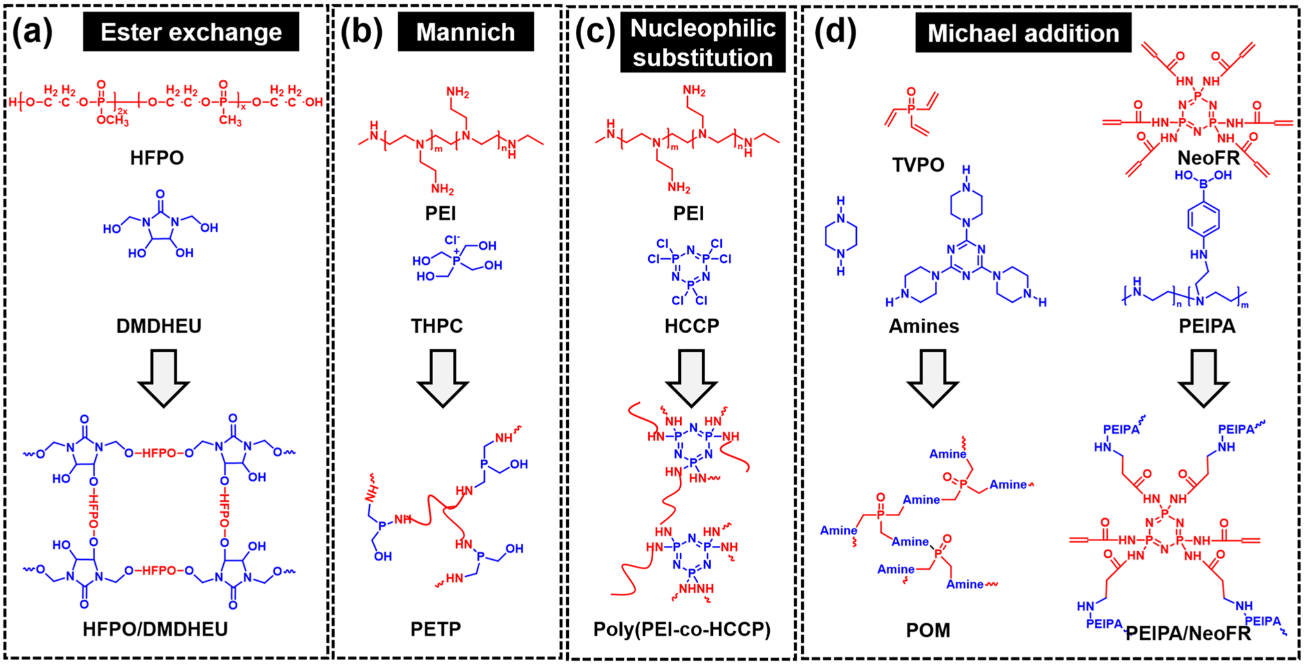


Fig. 9 The formation of the crosslinking networks by ester exchange (**a**), Mannich (**b**), Nucleophilic substitution (**c**), and Michael addition (**d**)

Table 8 The flammability and durability of fabric with crosslinking networks

Fabric	Coating	W–G (%)	DL (cm)	LOI (%)	Durability (LCs)	References
Cotton	PFR	14.0	–	27.0	LOI: 23.9% (50)	[190]
	PEI, HCCP	23	–	33.8	Self-extinguishing (1)	[40]
	PEI, Neo-FR	26.5	7.6	33.8	DL: 11.0 cm (30)	[185]
	PEI, THPC	27.3	~11.4	29.7	Self-extinguishing (2)	[188]
	PEIPA, NeoFR	30	10.0	29.6	LOI: 27.4% (5)	[186]
	Pip, TVPO	–	–	26.9	95% P-retention (50)	[189]
	TPT, TVPO	–	–	27.4	95% P-retention (50)	[189]
Jute	OFR	–	9.3	38.1	LOI: 32.5% (5)	[191]
Nylon/cotton	HFPO, DMDHEU	21.5	9.9	28.1	LOI: 27.4% (40)	[192]
Polyester/cotton	HFPO, DMDHEU	27.3	13.3	28.1	LOI: 26.8% (20)	[192]

HFPO hydroxyl functional organophosphorus oligomer, *DMDHEU* N, N′-dimethyloldihydroxyethyleneurea, *OFR* organophosphorus flame-retardants

Hu et al. made some efforts to improve the durability of LbL coatings [195–205]. The introduction of some small molecules of crosslinkers (such as boric acid, genipin, CA, hypophosphorous acid, and metal ions) into LbL coatings promoted the crosslinking of the polyelectrolyte, and hence improved durability. The results are listed in Table 9. However, the durability of the crosslinked coating was still limited compared to that of other methods. It was suggested that the crosslinker was unable to adequately crosslink each polyelectrolyte and there was a lack of strong bonding between the polyelectrolyte and the substrate.

The formation of crosslinking networks facilitated by flame-retardants with multireactive groups can effectively improve durability. However, the durability of different crosslinking networks varies considerably among different formulations. Among these, the formulations of crosslinking networks that are covalently bonded to the fabric result in better durability.

Introduction of Water-insoluble Products

The washing durability of flame-retardant fabrics can also be improved by introducing weakly water-soluble flame-retardants or reducing the water solubility of the existing flame-retardants on fabrics [206]. Table 10 summarizes the work related to the introduction of water-insoluble products.

Poly(dimethoxy)phosphazene (PDMP) is a water-fast polymer, with a large number of oxymethyl side groups, as shown in Fig. 10a. A single layer of PDMP was coated onto cotton fabric by using a PDMP methanol solution [41]. The affinity between the -OCH_3 in PDMP and the -OH in cellulose improved the durability without the use of an extra binder. The amount of PDMP with a relatively low molecular weight gradually decreased with the number of LCs, while PDMP with a higher molecular weight was considered to be water-fast and was hard to wash off. The cotton fabric with only a 5.3% W–G of PDMP showed a self-extinguishing effect during the VBT. The LOI value of the cotton coated with 9.7% PDMP was 30.3% and was maintained at 28.6% after 50 LCs. In another work, after introducing an adequate amount of unsaturated bonds on the side groups of PDMP, the obtained poly(methoxy/allylphenoxy)phosphazene (PMAP) was coated onto cotton fabrics by applying a photoinduced reaction [184]. The durability of PMAP-treated cotton was further improved compared with that of PDMP-treated cotton. The cotton fabric with a 4.9% W–G of PMAP showed a self-extinguishing effect in the VBT. The cotton fabric with a 9.0% W–G of PMAP had an LOI value of 28.3% and retained more than 95% of its initial mass after 60 LCs. The LOI value of the fabric with 9.0% W–G of cotton was increased to 28.9% from 28.3% after 60 LCs. It was suggested that some unreacted small molecules, such as crosslinking agent and photoinitiator, were washed off during the LCs. In addition, the gas permeability, whiteness, and bending rigidity of the fabric were greatly preserved. In addition, the high flexibility of the "–P=N–"

Table 9 The flammability and durability of fabric with LbL by crosslinking

Fabric	Coating	W–G (%)	DL (cm)	LOI (%)	Durability (LCs)	References
Cotton	PEI, HACA, genipin	15.4	–	–	pHRR: – 57.1% (2)	[198]
PA66	CH, TiO_2, SiO_2, CA	6.6	30.0	21.5	pHRR: – 21% (5)	[195]
	PA, CH, APTES, boron	7.7	30.0	20.6	No dripping (5)	[204]
	PA, CH, borax	14.7	30.0	21.5	UL94-V1 (5)	[205]
	PA, CH, OSA	16.5	30.0	21.8	–	[196]
	PA, CH, GO, CA	4.0	23.0	26.5	pHRR: – 17% (5)	[200]
	PA, CH, SA, MMT, O-Sucrose	15.2	30.0	23.5	UL94-V1 (10)	[203]
	PDP-APTES, boron	8.9	30.0	25.5	LOI: 24.5% (10)	[201]
	PEI, OSA, HA	9.4	–	–	Self-extinguishing (12)	[197]

HACA hypophosphorous acid-modified chitosan, *CH* chitosan, *PDP* phenyl dichlorophosphate, *GO* graphene oxide, *OSA* oxidized sodium alginate, *HA* hypophosphorous acid, *MMT* montmorillonite, *SA* sodium alginate

Table 10 The flammability and durability results of fabrics with water-insoluble products

Fabric	Coating	W–G (%)	DL (cm)	LOI (%)	LOI (%) (LCs)	References
Cotton	PDMP	10.9	3.9	31.5	30.3 (50)	[41]
	PEI, PA	29.2	8.7	40.5	26.3 (20)	[212]
	PEI, PSP	16.5	–	–	–	[209]
	PMAP	9.0	7.7	28.3	28.9 (60)	[184]
	TA, TE, Ca^{2+}	35.2	5.1	27.0	25.0 (50)	[210]
	TA, TE, Ca^{2+}	36.1	5.1	27.0	26.0 (20)	[211]
	TA, TE, Co^{2+}	33.3	30.0	32.5	31.0 (20)	[211]
	TA, TE, Fe^{2+}	29.0	11.2	27.0	27.0 (50)	[207]
	TA, TE, Fe^{2+}	29.0	30.0	27.0	27.0 (20)	[211]
	TA, TE, Ni^{2+}	34.5	30.0	32.0	27.5 (20)	[211]
	TA, TE, Zn^{2+}	32.8	14.6	30.0	29.5 (20)	[211]
PA66	O-IP_6	41.2	11.9	32.3	31.8 (20)	[208]
Wool	PA; CH	19.8	11.6	33.3	28.0 (10)	[213]

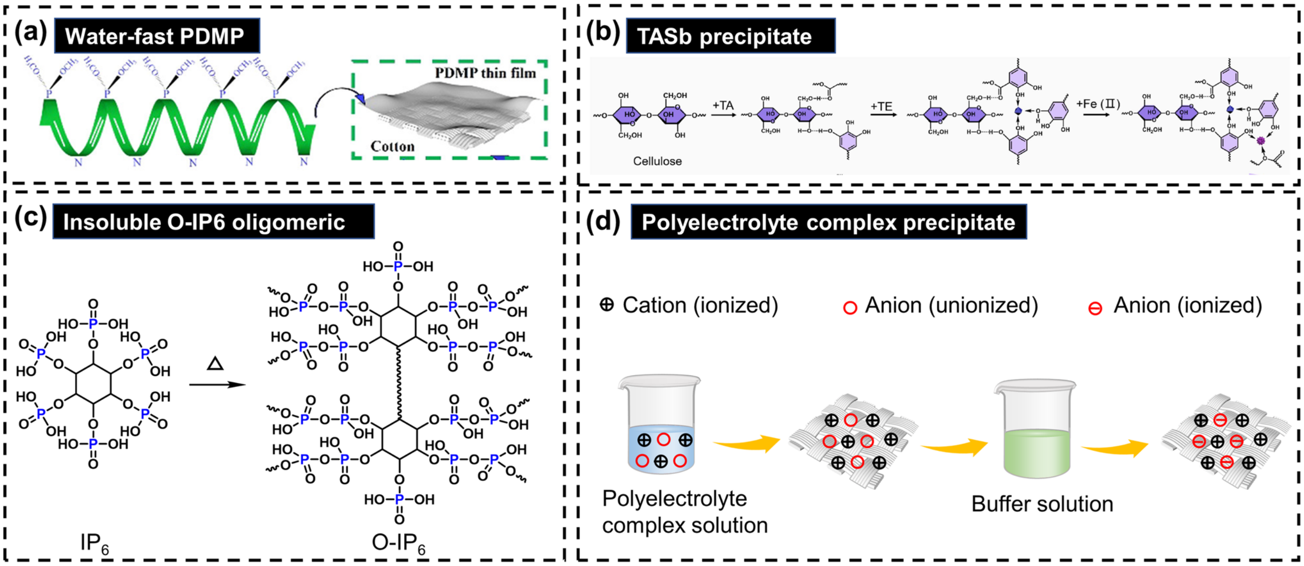


Fig. 10 The introduction of water-insoluble products on fabrics. The application of water-fast PDMP on cotton fabric. Reproduced with permission from Ref. [41] Copyright 2021, American Chemical Society. (**a**) TASb precipitate; Reproduced with permission from ref. [207] Copyright 2021, Elsevier (**b**); insoluble O-IP$_6$ oligomeric [208] (**c**); polyelectrolyte complex precipitate [209] (**d**)

chain in PMAP, an amorphous elastic polymer, did not influence the softness and comfort of the cotton fabric. It was demonstrated that PDMP and PMAP are promising additives for improving the durable flame retardancy of cotton fabrics. However, the involvement of organic solvents such as methanol and tetrahydrofuran in the fabrication process can cause environmental concerns.

Phytic acid (IP$_6$) is a phosphorus-rich, biobased flame-retardant with excellent water solubility. Liu et al. found that IP$_6$ was dehydrated between phosphorus hydroxyl groups to form an oligomer (O-IP$_6$) during the curing process [208], as shown in Fig. 10b. The LOI of the IP$_6$-treated PA fabric reached 31.8% after 20 LCs with water, while the samples lost their flame retardancy after 20 LCs with commercial-grade detergent. It was suggested that the solubility of O-IP$_6$ was decreased and the adhesiveness of O-IP$_6$ was improved, compared with that of IP$_6$. The oligomerization of IP$_6$ improved the durability of O-IP$_6$-treated PA fabric laundered with water only. However, O-IP$_6$ was unstable under alkaline conditions during the heated washing process.

Wang et al. reported a ‘dyestuff fixing’ process to fabricate a biomass-based flame-retardant coating using tannic acid (TA), tartar emetic (TE), and metal ions for cotton fabrics [207, 210, 211], as shown in Fig. 10c. TE reacted with TA to produce antimony tannic acid (TASb), which precipitated on the fabric surface. The hydroxyl groups of TASb coordinated with metal ions. The as-prepared cotton fabrics were referred to as TA20TE10Me10 (Me = Fe, Ca, Co, Ni, and Zn). The combination of electrostatic interactions, hydrogen bonds, and cocoordination enhanced the laundering durability of the treated cotton fabrics. The LOI value of TA20TE10Fe10 was 27.0%, which was higher than the 22.5% for TA/Fe and 24.5% for TA/TE. It was indicated that TA, TE, and Fe^{2+} synergistically improved the flame retardancy of cotton fabric [207]. After 50 LCs, the LOI of TA20TE10Fe10 was maintained at 27.0%. After 100 LCs, the LOI of TA20TE10Fe10 was slightly reduced to 25.0%, and the fabric easily passed the horizontal flammability test. However, the colour of TA20TE10Fe10 turned dark purple, which was attributed to the coordination of TA with Fe^{2+}. In contrast, the coordination of Ca^{2+} did not affect the pristine white colour of the fabric [210]. After 50 LCs, the LOI of TA20TE10Ca10 was reduced to 25.0%. Surprisingly, the TA20TE10Ca10 fabrics had different washing durabilities in deionized water and tap water. After 20 LCs with tap water, the TA20TE10Ca10 sample retained a short DL and passed the VFT, while after 20 LCs with deionized water, the TA20TE10Ca10 sample was completely damaged. The results indicated that the supplementary coordination of Ca^{2+} in tap water was effective in maintaining the flame retardancy of the coating, which was due to the presence of Ca^{2+} in tap water. Wang et al. also compared the flammability and flame-retardant mechanism of different metal ions [211]. The LOI values of the TA20TE10Ni10, TA20TE10Co10, and TA20TE10Zn10 samples were 32.0%, 32.5%, and 30.0%, respectively. The LOI values were only slightly changed even after 20 LCs, suggesting a high durable flame retardancy. The flame-retardant mechanism of TATEMe (Me = Fe, Ca, Co, Ni, and Zn) was different for cotton fabrics. All the Fe^{2+}, Ca^{2+}, Co^{2+}, Ni^{2+}, and Zn^{2+} metal ions in the TATEMe system promoted the char formation of cotton fabric. Among them, the graphitization degrees of the char residues of TATECa and TATEZn were higher, which provided a stronger barrier to inhibit the spread of flames. The TATECa coating also acted in the gas phase to release a large amount of CO_2, which diluted the concentration of combustible gases. The fabrication of the TATEMe coating was eco-friendly because it did not involve the use of Br, Cl, P, or organic solvents. However, the flame retardancy of the TATEMe coating was relatively low and usually required approximately 30% W–G of coating to obtain ideal flame retardancy.

Section "Formation of Crosslinking Networks" summarizes the advances in improving the durability of LbL coatings by cross-linking agents. Another main problem of the LbL method is the repetitive fabrication procedures, which are time-consuming. The one-pot polyelectrolyte-complex method is an ideal alternative solution to the LbL method, which can increase durability and significantly reduce the processing time. The fabrication process is shown in Fig. 10d. The oppositely charged polyelectrolytes are associated with each other to form polyelectrolyte complexes (PEC) in solution. The solubility of the complex was greatly dependent on the pH value, ionic strength, and concentration. For the PEI/poly(phosphate sodium salt) (PSP) complex system, the complex was stable at $pH \geq 9$ [209]. The pH value (9) was higher than the pKa (8.25) of PEI, and most of the $-NH_2$ groups in PEI were unprotonated contributing to the low positive charge of PEI. The electrostatic interaction between PEI and PSP was weakened and a stable water-soluble PEC was formed. After the fabric was treated with PEC solution for 30 s, the fabric was transferred to CA/sodium citrate buffer to ‘cure’ the coating. The PEI/PSP-treated cotton was then treated by soaking in buffer solutions with a pH value of 2–6. More coating remained on the treated fabric after rinsing when the pH value was 2. It was suggested that below a pH of 9, PEI was sufficiently protonated and bound with negatively charged PSP, which formed an insoluble gel on the cotton surface. The as-prepared coating was resistant to vigorous rinsing and reached a W–G similar to that of the coating prepared by the LbL assembly method which usually requires many dipping cycles (> 20). Similarly, PECs systems, such as poly(allylamine hydrochloride) (PAAm)/PSP [214], phytic acid (PA)/PEI [215], PA/CH [213], and (sodium polyborate) SPB/CH [134] systems, were stable at pH values ≥ 12, < 1.5, ≤ 1.3, and < 7, respectively. The PA/CH-treated wool fabric had an LOI value of 33.3% and maintained an LOI value of 28.0% after 10 LCs. However, the durability of other PEC systems was poor. The PEI/PA-treated wool fabric lost its self-extinguishing effect after 15 LCs [215]. After washing, the SPB/CH-treated cotton fabric was not self-extinguished but had a complete char layer [134]. The above results indicated that the PEC methods showed limited enhancements compared to the LbL method.

The formation of water-insoluble products showed high designability, and some strategies resulted in excellent durability. This strategy did not require the formation of covalent bonds with the fabric; hence it can be extended to synthetic fabrics in future studies.

Application of Adhesion Layers

The bioadhesive properties of marine mussels have attracted great interest in recent decades [217, 218]. The polydopamine (PDA) coating can act as a secondary reaction platform, anchoring other chemical components to the surface and thus imparting the desired properties. Similarly, TA and other polyphenols can interact with various substrates through coordination, hydrogen bonding, electrostatic interactions, hydrophobic interactions, and covalent reactions, as shown in Fig. 11 (a). The results for the application of the adhesion layers on fabrics are listed in Table 11.

Wang et al. reported an improvement in the adhesion of self-assembled components to cotton fabric by using PDA as a “molecular glue” [219]. Several bilayers were firmly adhered on the cotton fabric due to π-π stacking between the aromatic structures in phenyl phosphonic acid (PHA) and the benzene rings in PDA. The as-prepared fabric had an LOI value of 31.4% and maintained an LOI value of 24.1% after 50 LCs. It was indicated that the π-π stacking endowed the flame-retardant cotton fabric with laundering fastness over 50 LCs. Mao et al. prepared a hybrid coating constructed by the simultaneous self-polymerization of dopamine and the hydrolysis of $N_3P_3[NH(CH_2)_3Si(OC_2H_5)_3]_6$ [220]. The coating was greatly preserved after 30 LCs, and the surface remained rough. A flame-retardant silk fabric was prepared by the PDA-induced growth of mineralized γ-FeOOH nanorods [221]. The abundant binding sites of PDA were bonded to the silk fabric and coordinated with Fe^{2+}, contributing to the formation of stretched γ-FeOOH nanorods on the surface of the silk fabric. Tang et al. also reported the durable flame retardancy of various polyphenols, such as grape seed proanthocyanidins [222], condensed tannins [223], flavonoids [224], and tannic acid [225] on silk fabrics. After LCs, the LOI of the silk fabrics was well maintained, which was caused by the shrinkage of the fabric during the washing process. However, the coatings prepared by polyphenols usually have a dark appearance. In addition, the growth of the PDA layer is a time-consuming process.

Caramel (Car) polymers are obtained by heating reduced sugars, such as glucose and sucrose, which induces the degradation and polymerization of intermediate reactants. Apart from the sugar and furan units, Car also contains -OH, -COOH, and -CHO groups. The Maillard reaction product (MRP) generated by carbonyl-amino condensation between Car and NH_2-containing chemicals can be firmly adhered to the surface of fabrics because of its strong cohesion and

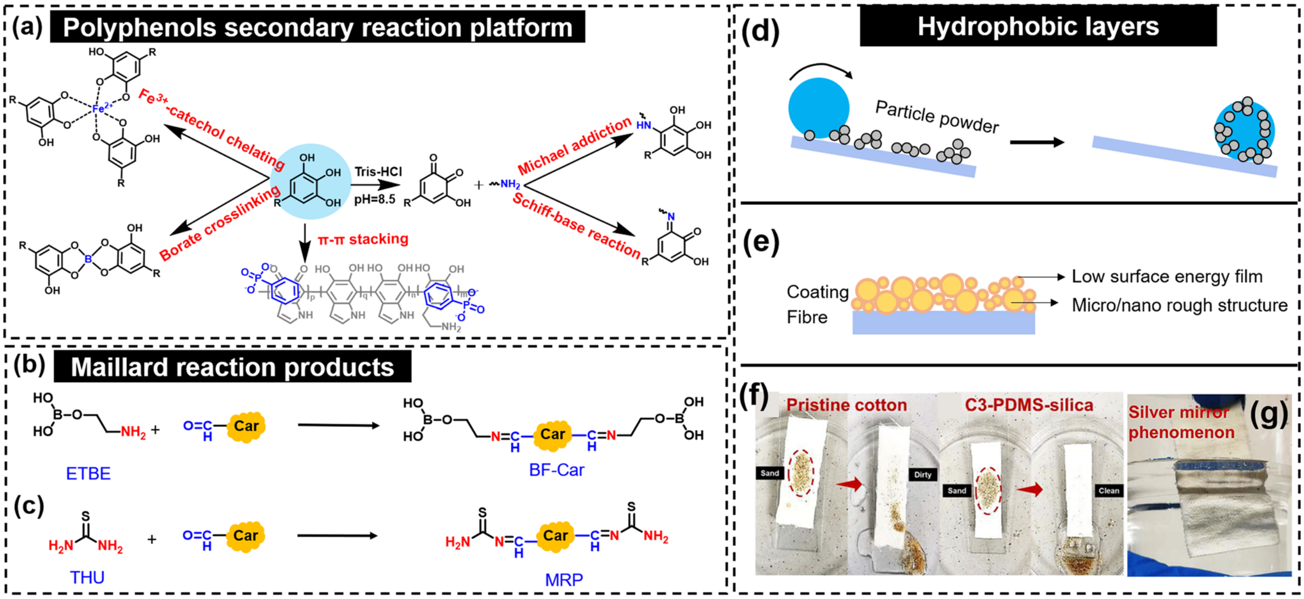


Fig. 11 The polyphenols as a secondary reaction platform (**a**); fabrication of durable flame-retardant fabrics by Maillard reaction (**b, c**). The schematic diagram of the self-cleaning process (**d**) and superhydrophobic coating (**e**); the self-cleaning of C3-PDMS-silica (**f**) and the silver mirror phenomenon (**g**). Reproduced with permission from Ref. [216]. Copyright 2022, Elsevier

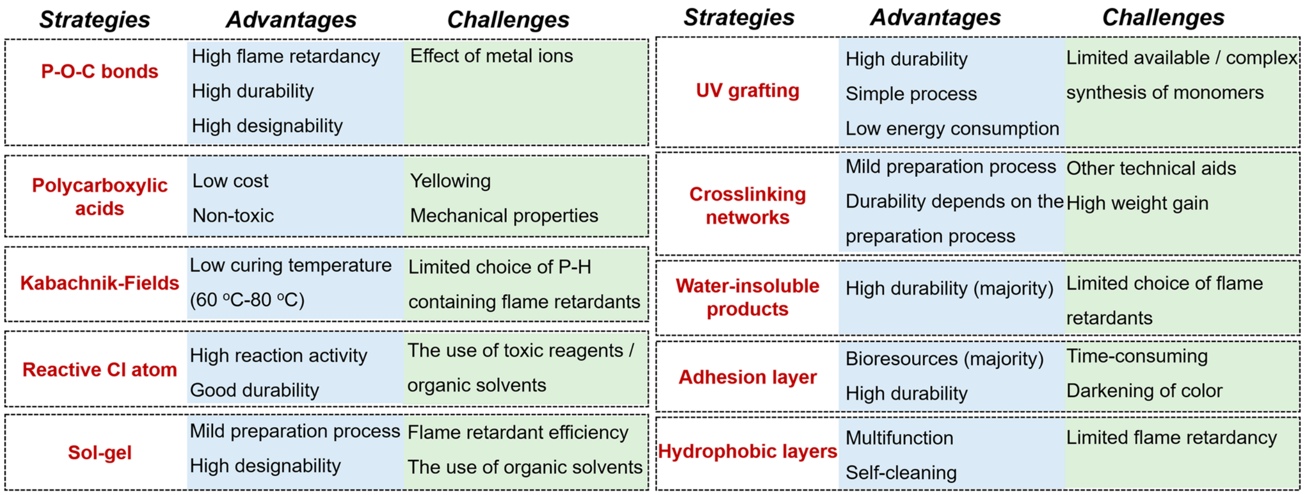
Table 11 The flammability and durability results of fabrics treated with adhesion layers

Fabric	Coating	W–G (%)	DL (cm)	LOI (%)	Durability (LCs)	References
Cotton	PDA; APTES; PHA	33.6	9.5	31.4	LOI: 24.1% (50)	[219]
	RDP	19.7	7.7	34.3	DL: 13.5 cm (10)	[229]
	TA, Borax; PDA	36.7	–	28.5	LOI: 24% (10)	[231]
PA6	MRP	–	11.3	31.6	LOI: 27.4% (45)	[228]
PA66	GAS	8.8	8.0	31.4	LOI: 28.6% (20)	[230]
PAN	TA/Fe^{3+}/TA-MoS_2 /TA-CNFs/Borate	7.3	–	34.8	LOI: 30.1% (80)	[42]
Silk	Dioscorea cirrhosa	–	10.2	28.1	LOI: > 28% (20)	[223]
	Flavonoids; Fe^{2+}; Ti^{4+}	–	< 10.0	27.0	LOI: 27.0% (20)	[224]
	PDA, Fe^{2+}	–	11.2	–	DL: < 12 cm (50)	[232]
	TA; Fe^{2+}	–	~ 12.0	27.5	LOI: 27.5% (20)	[225]
Wool	BF-Car	–	12.5	28.3	DL: 13.5 cm (5)	[226]

Table 12 The flammability and durability of cotton with hydrophobic coatings

Fabric	Coating	W–G (%)	DL (cm)	LOI (%)	Durability (LCs)	References
Aramid	Phosphorus–fluoride emulsion	–	0.7	–	DL: 0.95 cm (10)	[237]
Cotton	AMOP	30	4.8	27.0	LOI: 19.5% (30)	[78]
	DPTES, PDMS, SiO_2	30.3	14.2	26.0	LOI: 24.5% (10)	[216]
	NDOPA	–	35.0	21.0	LOI: 20.1% (30)	[238]
	PA, A-POSS, TiO_2, PDMS	16.2	6.5	29.0	LOI: 28.0% (5)	[43]
	PEI, PA, Fe^{3+}, QAS	28.9	8.0	28.5	DL: 15.0 cm (20)	[242]
	PNCTSi	18.9	4.2	29.8	LOI: 26.2% (20)	[241]
	TA, Borax, PDA	36.7	–	28.5	LOI: 24.0% (10)	[231]
PET	APP, SiO_2, PDA, Ag		5.6	29.0	LOI: 28.4% (10)	[234]
	Carbon microspheres, APP	59.7	4.3	28.8	LOI: 27.7% (10)	[243]
Silk	PA, TEOS, APDTMS or CPTS or MPTS	–	12.0–14.0	33.0–35.0	LOI: 28.0–29.8% (9)	[240]

AMOP ammonium salt of octadecyl phosphate, *APDTMS* 3-aminopropyldimethoxymethylsilane, *CPTS* 3-aminopropyldimethoxymethylsilane, *MPTS* 3methacryloxypropyltrimethoxysilane, *QAS* dimethyloctadecyl [3(trimethoxysilyl) propyl] ammonium chloride



Strategies	Advantages	Challenges
P-O-C bonds	High flame retardancy High durability High designability	Effect of metal ions
Polycarboxylic acids	Low cost Non-toxic	Yellowing Mechanical properties
Kabachnik-Fields	Low curing temperature (60 °C-80 °C)	Limited choice of P-H containing flame retardants
Reactive Cl atom	High reaction activity Good durability	The use of toxic reagents / organic solvents
Sol-gel	Mild preparation process High designability	Flame retardant efficiency The use of organic solvents

Strategies	Advantages	Challenges
UV grafting	High durability Simple process Low energy consumption	Limited available / complex synthesis of monomers
Crosslinking networks	Mild preparation process Durability depends on the preparation process	Other technical aids High weight gain
Water-insoluble products	High durability (majority)	Limited choice of flame retardants
Adhesion layer	Bioresources (majority) High durability	Time-consuming Darkening of color
Hydrophobic layers	Multifunction Self-cleaning	Limited flame retardancy

Fig. 12 The advantage and challenges of different strategies for fabricating durable flame-retardant fabrics

adhesion abilities. Guan et al. synthesized borate-functionalized caramel (BF-Car) and applied it to wool fabrics [226], as shown in Fig. 11b. The treated wool fabric with a W–G of 9.2% had a self-extinguishing effect even after 5 LCs. Thiourea (THU) contains high N (42%) and S (36%) contents and possesses a high ability to capture free radicals. THU acts as an efficient flame-retardant for polyamide fabrics with relatively poor durability [227]. Guan et al. fixed THU on the surface of PA6 fabric through an MRP [228], as shown in Fig. 11c. The treated PA6 fabric had an LOI value of 31.6% and a DL of 11.3 cm without melt dripping. In addition, the fabric achieved a V-0 grade even after 40 LCs.

Some adhesive resins are also used to fix flame-retardants to fabrics. Yu et al. synthesized resorcinol bis(diphenyl phosphate) (RDP) [229]. RDP was firmly bonded to cotton fabric by a crosslinking agent of urea formalin resin (UFR). The N element in UFR had a synergistic effect on improving the flame retardancy of treated cotton fabrics. The DL of the as-prepared cotton fabric was 7.7 cm and was increased to 13.5 cm after 10 LCs. The anionic fixing resin *Sera Fast N-HFG* (NHFG) was also applied to prepare an anionic coating on the surface of fibres [230]. It can protect the inner guanidine sulfamate (GAS) during LCs. The as-prepared fabric was still self-extinguishing after 20 LCs.

The adhesive layer strategy is usually carried out by using biobased materials. The adhesive layer endows good durability to both natural and synthetic fabrics due to the inherent adhesion and cohesion ability of the adhesive layers. The bonding of flame-retardant elements to adhesive layers will further expand its application.

Construction of Hydrophobic Layers

Lotus leaves can grow amidst mud without being stained by the mud, and water drops falling on a lotus leaf carry away the dust on the leaf. Inspired by the lotus leaf, a superhydrophobic coating was constructed to endow fabrics with self-cleaning properties (Fig. 11d) [233]. Moreover, when a superhydrophobic fabric is immersed in water, a portion of air is trapped between the water and the fabric's rough structure, preventing the fabric from being wet. The superhydrophobic coating is achieved by a combination of a micro- and nanoscale rough structure and low surface energy, as shown in Fig. 11e. The construction of a hydrophobic layer on the outer layer of the flame-retardant prevents the loss of the flame-retardant when in water. In flame-retardant and superhydrophobic coatings, a rough structure is usually achieved by components with flame retardancy, such as SiO_2 [216, 234], ammonium polyphosphate (APP) microparticles [234, 235], and phosphate-metal ion complexes [236]. The low-surface-energy components include fluorine-containing [237], silicon-containing, and long-chain alkane-containing chemicals [238]. Among them, long-chain alkanes containing chemicals are highly flammable and are rarely used to improve the water resistance of flame-retardants. For example, N,N-dimethyl-octadecyl phosphate acrylamide (NDOPA)-treated cotton had a WCA of 157.5° and an LOI value of only 21.0% [238]. Polydimethylsiloxane (PDMS) is commonly used to construct low-surface-energy outer layers of flame-retardant superhydrophobic fabrics due to its environmental friendliness, nonflammability, and ability to improve the softness of fabrics [43, 236, 239]. Table 12 lists the flammability and durability of fabrics treated with hydrophobic layers.

Xin et al. prepared a superhydrophobic and flame-retardant cotton fabric (C3-PDMS-silica) by sol–gel treatment with phosphoramidate siloxane flame-retardant (DPTES) combined with the brush-coating process of polydimethylsiloxane@silicon dioxide (PDMS@SiO_2) [216]. The WCA of DPTES-treated cotton was 112° because of the abundant phenyl groups in DPTES. In contrast, the WCA of C3-PDMS-silica was 154°. As shown in Fig. 11 (f), a self-cleaning property was achieved. A stain on the surface of C3-PDMS-silica was easily removed by water. The silver mirror phenomenon was observed when immersing the C3-PDMS-silica under water, indicating that air was trapped between the water and the fabric, as shown in Fig. 11g. The LOI of C3-PDMS-silica was 26.0% and was maintained at 24.5% after 10 LCs. Wang et al. constructed a superhydrophobic and flame-retardant polyester-cotton fabric (DT/Fe-8BL-PDMS) via the self-assembly of a phosphonate-metal complex and the deposition of PDMS [236]. The phosphonate-metal complex formed nanoscale protuberances and covered the fibres completely. After 12 LCs, DT/Fe-8BL-PDMS was still extinguished in the horizontal flammable test without smouldering combustion. Hu et al. reported the step-by-step spraying of alkylammonium functional silsesquioxane (A-POSS), PA, and hierarchical-structured titanium oxide@polydimethylsiloxane (TiO_2@PDMS) on cotton fabric. The surface roughness for the as-prepared cotton fabric was significantly increased to 135.5 nm from 59.2 nm for the control fabric, which was benefitial to obtain a superhydrophobic surface [43]. The as-prepared cotton fabric was self-extinguishing after 5 LCs.

Cheng et al. prepared an organic–inorganic coating for silk fabric with phytic acid as a catalyst for the hydrolysis of tetraethoxysilane [240]. Three kinds of silane coupling agents were added to the hybrid sol as crosslinkers to improve the hydrophobicity of the fabric. After the LCs, the silk fabrics treated with crosslinkers showed a higher LOI value than those without crosslinkers. It was suggested that the introduction of silane crosslinking agents enhanced the hydrophobicity of silk fabrics and promoted the immobilization of the hybrid networks on the silk fabric surface, thus improving the washing resistance of the coatings. Lu et al. synthesized a cyclic-shaped macromolecule (PNCTSi) with both flame retardancy and hydrophobicity properties for cotton fabrics [241]. The PNCTSi-treated cotton had a WCA of 150° and an LOI value of 29.8%. After 20 LCs, the WCA and LOI values were maintained at 125° and 26.2%, respectively, which indicates that the high flame retardancy and hydrophobicity properties were maintained.

The above results demonstrated that hydrophobic coatings could protect flame-retardant coatings. However, the flame retardancy of the superhydrophobic coating was not high enough for many application scenarios. The LOI value of most flame-retardant and superhydrophobic fabrics was less than 30.0%, and a higher W–G of flame-retardant was usually needed. The construction of rough structures or low surface energy with flame-retardant components will be beneficial for reducing the W–G of the coating.

Intercalation of Flame Retardants into Fibres

Some pretreatment processes and technologies are usually adopted to increase the penetration and dispersion of flame-retardants into fibres to improve the durable flame retardancy.

Cotton Fibre

In the cotton fabric, the crystallinity of cellulose is approximately 60%, and the flame-retardants can only penetrate the amorphous region. Zhang et al. pretreated cotton fabrics with concentrated NaOH aqueous solution to break the hydrogen bonds between the cellulosic chains [53, 69]. The mercerized cotton exposed more reactive hydroxyl groups, and some crystalline regions transformed into amorphous regions that were easily permeated by flame-retardants. In addition, urea is usually added to the flame-retardant solution, which facilitates the expansion of cotton fibres [84]. Gaan et al. performed three different crosslinking experiments including steaming, microwave irradiation, and dry heating to induce the faster crosslinking of phosphine oxide macromolecules inside cotton fibres [189]. The prepared fabrics had stable flame retardancy over 50 LCs.

Wool Fibre

In the case of wool fabric, the fibre is covered by cuticle layers [244]. The cuticle layer on the surface is a barrier for nanoparticles to penetrate the wool fibre interior due to its tight structure, which contributes to the surface attachment of nanoparticles [147]. A high immersion temperature (90 °C) can swell the wool fibres and help the flame-retardant diffuse into the wool fibres. In addition, partially removing the cuticle by oxidation reactions can promote the penetration of chemicals into the wool fibres [245].

Synthetic Fibre

It is difficult to endow polyester with durable flame retardancy because of the absence of chemically active groups. The solvent crazing method is stress-induced adsorption which can produce a plasticization effect on a polymer [246]. Plastic deformation results in the formation of dispersed polymer fibrils separated by microvoids [247]. The microvoids with a size of 1–100 nm are filled with the surrounding medium. The nonvolatile additives remain inside the fibres after evaporation of the solvent. During the craze initiation process, additives are incorporated into the bulk of the polymer. Kale et al. fabricated a multifunction polyester fabric by the solvent crazing technique with $ZnCl_2$ dissolved in acetone [246]. Then, the fabric was stretched and dipped in NaOH solution, with nucleated $ZnCl_2$ transforming into ZnO. The LOI value of the treated fabric was improved to 29% from 21% and maintained at 25% after 20 LCs. Ren et al. reported the fabrication of PET fibres with flame retardancy with the ammonium phosphate of sucrose fatty acid ester (APSFA) and sodium copper chlorophyllin (SCC) [44]. The SCC was fixed on the fibres via a dyeing process, and APSFA was inlayed into the PET molecular chains after high-temperature treatment (120 °C). At high temperatures, PET molecular segments showed intensified movement, increasing the intermolecular gaps. The hydrophobic APSFA chains were inlaid into the gaps of the PET molecular chains. When the APSFA solution was cooled down, the thermal motion of the PET molecular chains was greatly reduced. Finally, the hydrophobic part of APSFA securely settled into the PET molecular chains. The LOI of the treated PET fabric slightly decreased to 25.4% from 33.0% after 20 LCs.

For both natural and synthetic fabrics, promoting the penetration of flame-retardants into the fibres is an effective way to improve durability. In future work, this strategy can be used in association with other strategies to improve durability.

Conclusion, Challenges, and Opportunities

This paper summarizes the strategies for imparting durable flame retardancy to common textiles and describes the mechanisms, advantages, and disadvantages of each strategy. Figure 12 shows a summary of the main advantages and challenges of different strategies for fabricating durable flame-retardant fabrics.

Currently, most durable flame-retardants are designed for natural fabrics, especially cotton fabrics, which is due to the existence of a large number of reactive groups in their molecular chains. The formation of P–O–C is regarded as a facile, green, healthy, and environmentally friendly strategy, that can endow cotton fabrics with high flame retardancy and durability with relatively low W–G. In addition, this strategy has also been applied to other fabrics such as wool, silk, PAN, and blended fabrics. Further enhancements in imparting fabrics with multifunction by the P–O–C strategy have attracted increasing attention. The chemical inertness of synthetic fabrics makes it difficult to form chemical bonds between flame-retardants and fibres. Although chemical grafting technology has been developed for over 10 years, commercially available durable synthetic fabric produced from this technology is very rare. For some synthetic fabrics, it is worth considering fixing flame-retardants on the fibres during the dyeing process.

In addition to the conventional methods of improving durability, such as covalent bonding and the formation of crosslinking networks, some new strategies for improving durability are emerging. The formation of water-insoluble products, the use of adhesive layers, the construction of hydrophobic layers, and the intercalation of flame-retardant into the fibres were all applied to improve durability in the last decade. The construction of polyphenol-mediated adhesive layers is time-consuming and results in dark-coloured samples. Further studies should focus on accelerating the formation process of polyphenol coatings and improving their dyeability. The efficiency of flame-retardant superhydrophobic coatings is usually not ideal. Further investigations can consider the use of micro- and nano-scale additives with high flame retardancy to construct the desirable rough structure. Although great breakthroughs have been made in the fabrication of durable flame-retardant coatings, more efforts to improve softness and efficiency and reduce W–G are still needed.

Future studies on the fabrication of durable flame-retardant fabrics will face many tough challenges of stricter legislation regarding human health and environmental protection. Here are a few recommendations for addressing the current concerns.

(i) The combination of two or more durable strategies. This combination is expected to take full advantage of each strategy and produce multifunctional fabric.
(ii) High-energy pretreatment technology for synthetic textiles (high temperature, electron-beam/UV irradiation, and so on). This kind of pretreatment can initiate free radicals, which can guarantee the chemical reactions between the fibres surface and reactive flame-retardants. However, we must pay attention to the reduced mechanical properties. The nonuniformity of the grafting points and the copolymerization of the reactive monomers must be overcome to produce large-scale durable synthetic fabrics by grafting.
(iii) Sustainable and environmentally friendly flame-retardants with low release or that are free of formaldehyde and VOCs. Future legislation will be increasingly strict regarding the amount of toxic compounds released from flame-retardant fabrics. Those employing green manufacturing processes are highly encouraged to reduce the large amounts of energy, water, and chemical solvents consumption in the conventional finishing process. Foam finishing [248] and supercritical CO_2 finishing [249] are

becoming promising methodologies. Biobased and halogen/phosphorus-free flame-retardants can provide an alternative solution to address concerns of health safety and environmental protection.

(iv) Multifunctionality in association with good physical properties. The design of highly efficient flame-retardants with a reduced negative impact on the physical properties of fabrics is still needed. Single-function fabric cannot meet the increased market demand. The demand for fabrics with multifunctionality, such as flame retardancy, antibacterial properties, breathability, soft hand feel, and dyeability, is increasing rapidly. This will become a strong motivating factor for more researchers to explore available technologies and mechanisms.

Acknowledgements This work was supported by the National Natural Science Foundation of China (Grant No. 22075010 and 22175017).

Data availability statement Data available on request from the authors.

Declarations

Conflicts of Interest The authors declare no competing financial interests.

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