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Review Article

Flame retardant finishing of textiles – A comprehensive review

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Flame retardant (FR) finishing is one of the most vital finishes required to develop flame retardant textiles for human protection. Traditional flame retardants are based on halogen, phosphorus and phosphorus-nitrogen chemistry. However, some of these compounds have limitations, such as formaldehyde release, toxicity, effluent generation, reduction in strength, stiffening of fabric, shade change and liberation of toxic gases. New innovative routes to develop flame retardant textiles like nanotechnology, plasma, and layer-by-layer techniques and intumescent flame retardant coating are explored by the researchers. To achieve sustainable FR finishing, finishes based on natural resources are also explored. Hydrogel-based FR finishing is an innovative area with a great prospect of exploration in flame retardant textiles. This paper reports a comprehensive information on FR finishing of textiles. The advanced methods for producing flame retardant coatings, including UV curing, microencapsulation, spray coatings, and sol-gel coating, are also reviewed.

Keywords: Flame retardant finishing, Hydrogel-based finishing, Intumescent flame retardant coating, Sustainable finishes

1 Introduction

Among all the functional finishes for textile substrates, flame retardant (FR) finishing is the most vital, as it is linked to human protection. When ignited by a source, the textile material catches fire quickly, burns, and can cause hazards. If the same textile material is finished with efficient flame retardant, the propagation of flame is stopped, and the fire gets extinguished once the ignition source is removed. The limiting oxygen index (LOI), indicating the minimum oxygen concentration in the oxygen-nitrogen mixture required to support candle-like burning, is an important indicator of flammability. Also, textiles with LOI of less than 21 can catch fire readily and burn in an ambient atmosphere. Textiles with LOI between 21 and 27 can also catch fire, but they burn slowly in the ambient air. Textiles with LOI greater than 27 are generally considered flame retardant materials. Apart from LOI, the peak heat release and burning rates are crucial for flame retardant textiles. The burning behaviour of textiles will also depend on the type of textile structure directly related to the availability of oxygen passing through the textile structure.

Fire accidents can occur anywhere at any time; hence, flame retardancy became essential for providing absolute protection to prevent such accidents. Fire fighters, military as well as emergency personnel also need flame retardant textiles. Textile fibres, both natural and synthetic, are used in apparel, home furnishing, hotels, hospitals, architecture, and transportation (railways, aeroplanes). Natural fibres, like cotton, wool, silk, and flax, are prone to burning. The situation in the case of synthetic fibres is more complicated as they shrink, melt, and burn at a faster rate when in contact with flame. Shrinking of the fibre and dripping of the molten backbone of synthetic fibre (polymer) can cause a high degree of skin burning. The lower LOI value of textile fibres makes flame retardant finishing a requirement for most of them. Hence, it becomes an indispensable aspect of producing textiles finished with flame retardants[1–4]. The thermal transition temperatures of different fibres and their LOI are depicted in Table 1.

1.1 Mechanisms of Flame Retardant Finishing of Textile Materials

The mechanism for imparting flame retardancy to a textile material can be easily understood by first studying the fibre combustion process in the presence of the ignition source. Combustion is an exothermic process which needs three components for burning, i.e. heat, oxygen, and fuel. The combustion process is self-catalytic and proceeds until the heat, oxygen, and fuel are depleted. When a heat source is applied to any textile material, its temperature rises, and the

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Table 1 — Thermal transition temperatures and limiting oxygen index of different fibres

Fibre	Glass transition temp. (T_g),°C	Pyrolysis temp. (T_p), °C	Melting temp. (T_m), °C	Combustion temp. (T_c), °C	LOI, %	Ref.
Cotton	-	350	-	350	18-18.5	4-6
Viscose	-	350	-	420	18.9	4
Wool	-	245	-	600	23.6-25	4,7,8
Polyester	70-90	420-450	255	480	20-21	4,9
Nylon 6	47-50	431	215	460	20-21.5	4
Acrylic	100	250	>220	290	18.2	4
Polypropylene	-20	469	165	550	18.6	4

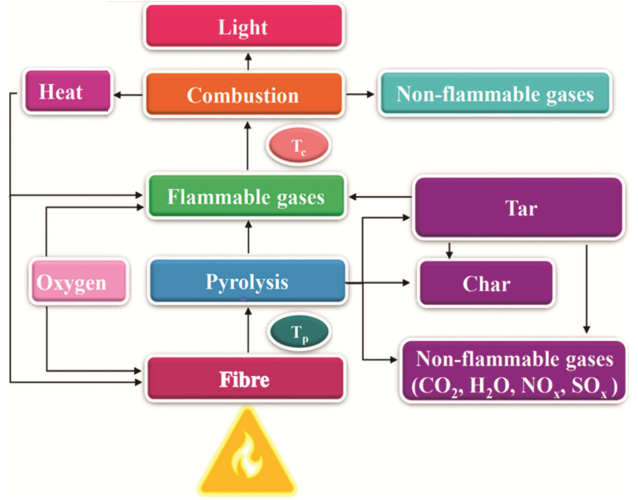

Fig. 1 — Combustion cycle of a fibre[2]

pyrolysis temperature (T_p) is reached. Formation of various non-flammable gases, such as water vapour, carbon dioxide, higher oxides of sulphur and nitrogen, carbon char and tar (liquid condensates); and flammable gases like hydrogen, carbon monoxide, and other oxidizable organic volatiles occursduring pyrolysis. These flammable gases rapidly burn when in contact with oxygen, leading to heat energy liberation. Thus, a further rise in temperature leads the fibre to reach its combustion temperature (T_c). The generated heat energy accelerates the pyrolysis of polymer again, which consecutively generates more flammable gases, leading to intense combustion[1,2]. The illustration of the combustion cycle of fibre is depicted in Fig. 1.

The various mechanisms for preparing an effective flame retardant textile material are further discussed.

One such approach could be absorbing the heat from the strong endothermic reaction caused by fire-retardant material. This will prevent the attainment of pyrolysis temperature, suppress the combustion, and reduce the burning surface temperature. It will also limit the production of combustible gases, which prevent flame propagation. Examples of such an approach are using calcium carbonate or aluminium trihydrate coatings onto the textile substrate, as depicted in Figs 2 (A) and (B). Such inorganic materials do not have chemical bonding potential with textile fibre. Hence, this finish lacks wash-durability.

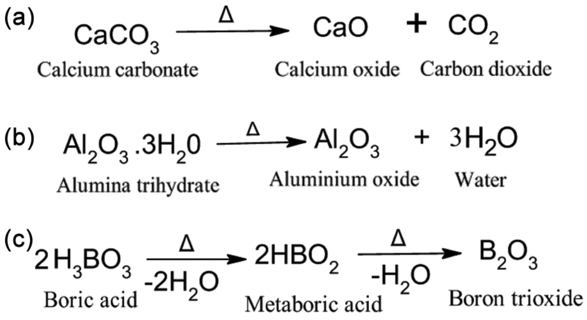

Fig. 2 — Decomposition reaction of (A) calcium carbonate, (B) aluminium trihydrate and (C) boric acid

Another approach could be, forming a glassy or foamy insulating layer onto the fibre surface at a temperature below the pyrolysis temperature. A glassy layer insulates the textiles and further prevents combustion. Boric acid and its various hydrated salts work on this approach, as depicted in Fig. 2(C). When heated, it produces a foamed glassy surface and releases water vapour.

However, another approach involves altering the pyrolysis temperature of the fibre. Due to this, the formation of non-flammable gases occurs, which prevents the fibre from further burning. The dilution of oxygen and flammable gases is another approach for reducing the flammability of the textile substrate. Either the replacement or dilution of the surrounding oxygen and flammable gases can be done by using inert and non-flammable gases to either diminish or end the combustion process.

Another approach involves stopping the combustion via interference with the help of free radical reactions, which further prevents the continuous burning[1,2]. Figure 3 indicates the

$$MX \xrightarrow[\Delta]{} HX + M^+$$

$$H^+ + HX \rightleftharpoons H_2 + X^\bullet$$

$$HO^\bullet + HX \rightleftharpoons H_2O + X^\bullet$$

$$RH + X^\bullet \rightleftharpoons R^\bullet + HX$$

$$R^\bullet + X^\bullet \longrightarrow RX \text{ (not flammable)}$$

Fig. 3 — Competing free radical reactions during combustion of halogen-containing material

mechanism of halogen-based compounds through the quenching of free radicals to provide the flame retardancy totextiles.

Intumescence is another approach that could be used to suppress the flammability of textiles. For impartingintumescentflame retardant behaviour, it must consist of three main components, namelyan acid source (phosphoric acid-based source), a carbon/char source, and a blowing agent (nitrogen-containing systems). On exposure to a flame source, the intumescent material degrades and forms an insulating char that can entrap the gaseous species and prevent the burning[10]. A lesser amount of any of the threecomponents will not give the desired outcomes.

1.2 Durability of Flame-Retardants on Textiles

One major issue with the flame retardant finishes is the limited durability against washing treatments. Alkaline washing treatments using anionic surfactants can also affect durability because such surfactants can make complexes with cationic flame retardants. Even if the textile is exposed to sunlight and weathering conditions, durability gets hampered. The combined action of sunlight and laundering can significantly lower the durability[11]. The effectiveness of durability can be improved using fibre-reactive flame retardants.

As per the retention of flame-retardancy after repeated launderings, flame retardant textiles can be classified as non-durable (washed off immediately after being laundered but are unaffected by dry cleaning), semi-durable (unaffected by water soaking and a few wash cycles), and durable (can withstand 50 -100 washcycles)[10].

Halogen, phosphorus, and nitrogen-based compounds are quite effective. Still,some havevarious associated issues like formaldehyde release, toxicity, effluent generation, reduction in tear and tensile strength, stiffening, shade change, and the liberation of toxic and corrosive gases. Even in certain countries, some of these toxic formulations are banned.Various flame retardants available for textile finishing are discussed in further sections.

2 Traditional Flame Retardants and Related Issues

2.1 Inorganic Flame Retardants

Inorganic flame retardants include compounds like aluminium hydroxide, aluminium trioxide, and magnesium hydroxide. When heated by a source, aluminium hydroxide releases water vapour, which cools the textile material to a temperature below that, which is required for sustaining the combustion process. Even the water vapour liberated helps in the dilution of gases, and the oxide layer formed on the textile material helps to form an insulating protective char layer[12]. Generally, aluminium hydroxide is required in large amounts to impart flame retardancy[13]. These flame retardants can be applied to textiles using exhaust and padding methods. The mechanical properties of textiles will change by using a higher amount of flame retardants.

2.2 Halogen-based Flame Retardants

Halogen-based flame retardants are generally based on chlorine and bromine chemistry. These compounds work on the radical chain mechanism, which occurs in the gas phase during combustion. Compounds like decabromodiphenyl or pentabromodiphenyl ethers, and polychlorinated biphenyls are effective, but these are banned due to their toxicity. These compounds are proven to be persistent and bio-accumulative. Also, the finish is not durable and can be removed easily by washing. Chlorine and bromine compounds, along with antimony, have also shown synergistic results in flame retardancy, but due to adverse environmental impacts, halogen-based compounds are not recommended[1,12,14,15].

2.3 Phosphorus-based Flame Retardants

Halogen-based formulations show negative environmental impacts and are replaced by phosphorus-based flame retardants. Under the effect of flame, these phosphorus compounds form phosphoric acid, which acts in a condensed phase by forming char. Phosphorus-based flame retardants are divided into inorganic, organic, and halogen-containing categories. These compounds are easy to apply and could be used to finish a wide range of textile fibres. Ammonium polyphosphate and red phosphorus are the flame retardants with the least issues, but certain health effects could not be ignored. Phosphorus-based flame retardants are found to be less toxic as compared to the halogen-based ones[12,14]. The decomposition and combustion behaviour of fibres are changed by phosphorus-based compounds, which promotes char formation. Some phosphorus compounds release free radicals, which react with H and OH radicals to prevent further decomposition. The mechanism of flame retardation is related to the interaction of flame retardant with textiles, the chemical structure of flame retardant, and the textile substrate.

During the application of finish and usage of finished textile, small molecules of organophosphorus FR agents are released into the water bodies. These compounds are also environment-persistent, bio-accumulative, and possess various ecological risks[16]. Further, formaldehyde is released from the phosphorus-containing compounds having N-methylol groups[3]. These organophosphorus FR agents are also responsible for eutrophication and pollution[17].

2.4 Phosphorus and Nitrogen-based Flame Retardants

Phosphorus and nitrogen showa synergistic effect for flame retardancy on textile substrates.At higher temperatures, phosphorus-containing flame retardants form phosphoric acid that crosslinks with the hydroxyl group of cotton. Nitrogen acts in synergism with phosphorus-containing flame retardants and increases efficiency. These compounds produce more char compared to that obtained with the halogen-based ones. Pyrovatex (N-methylol phosphono propionamide derivatives) and Proban (hydroxy methylphosphonium salts) are used on cellulosic fabrics. Tetrakis (hydroxymethyl) phosphonium chloride (THPC) and urea formulations can affect dye classes like direct, reactive, and acid dyes. In the case of Pyrovatex, after the first wash of the finished textile, 50% of the flame retardant gets removed[1,18].

Proban and Pyrovatex require adverse acidic conditions and higher add-on (%)for their application on the textile substrate to impart effective flame retardancy. These flame retardants are applied through padding, drying and curing; however, such treatments could also impartstiffness to the fabric. This might cause a reduction in its tensile strength. Besides, these treatments are expensive, non-eco-friendly, and require a high curing temperature[19]. Nitrogen-containing fibres such as wool and silk can make a synergistic combination with phosphorus-based flame retardants.

2.5 Borax and Boric Acid-Based Flame Retardants

Borax and boric acid formulations are also known to impartflame-retardancy totextiles. Boric acid’s melting temperature is lowered by borax, releasing water vapour. A thick layer of boron trioxide is formed, which insulates and prevents the textile substrate from burning. As no chemical bond is formed with the textiles, the finished textile loses its efficacy after the first wash[1]. Cross-linkers can provide a strong bonding between textiles and flame retardants. Most of the available traditional flame retardants are not reported to be eco-friendly and possess various drawbacks, such as:

- Reduction in tear and tensile strengths and an increase in the fabric's stiffening, especially in cases where the acidic catalyst is used along with the flame retardant formulations.
- High drying and curing temperatures are required to apply such commercial and traditional flame-retardants, which makes the process quite a time and energy consuming, consequently increasing the cost.
- Bromine and chlorine-based halogenated flame retardants are toxic, hazardous, and bio-accumulative.
- Certain formulations are even sensitive to various dyestuffs.
- Release of formaldehyde from the flame retardant treated fabrics, which contains methylolated cellulose cross linking groups. Formaldehyde release is reported as carcinogenic and poses health hazards to industrial workers and to the environment.
- The complex curing process can cause issues related to health and well-being.
- Discharge of harmful compounds into the effluent after finishing of the fabric could affect the environment[1,20].

3 Flame Retardancy Using Nanotechnology

Nanotechnology-based finishes are efficient alternatives to traditional flame retardants. Nanotechnology deals with the phenomenon that occurs at atomic and molecular levels using a 1-100 nm length scale in any dimension, which can be used to control or manipulate matter at the atomic scale[21].

3.1 Montmorillonite

Montmorillonite, a nano clay particle, is a chemically hydrated sodium calcium aluminium magnesium silicate hydroxide, known for its application in the coating to impart flame retardancy to cotton and polyester fabrics. However, the exact mechanism of action is not known. It is assumed that the nano clay gets deposited on the fabric surface and forms an oxygen barrier, thus retarding the burning process and forming a char layer. Nano clayalone is insufficient to impart flame retardancy and, hence, can be combined with conventional compounds. As nano clays are biodegradable and obtained from purely natural sources, they are regarded as eco-friendly[21]. Various approaches, such as incorporating nano clay particles during the manufacturing of fibres and coating of nano clay particles to textiles, can be utilised. The first one can give an efficient wash-durable effect due to the entrapment of particles inside the fibre.

3.2 Zinc Oxide Nanoparticles

Zinc oxide nanoparticles were also utilised in the flame retardant coating of cellulosic textiles. Zinc oxide nanoparticles were applied to various substrates (100% cotton and 65/35% cotton/polyester blend) using polycarboxylic acids, such as butane tetracarboxylic acid (BTCA), succinic acid,and sodium hypophosphite (SHP) via the pad-dry-cure method. The combination of malic acid (MA), SHP, and hydroxyalkyl functional organophosphorus compound, along with BTCA,is also reported for imparting flame retardancy. The finished cotton fabric shows some yellowness. Additionally, zinc oxide works as a catalyst to increase the char formation when used along with polycarboxylic acid and SHP. With the use of SHP, phosphorus is deposited on the fabric, which results in a higher quantity of char, there by decreasing the flammability of the treated fabric. To reduce the flammability of fabric, BTCA showed better results than succinic acid[22].

3.3 TiO_2 and SiO_2 Nanoparticles along with Chitosan and Phytic Acid

Applying TiO_2 and SiO_2 nanoparticles along with chitosan and phytic acidshow reduced flammability of treated polyamide 66 (PA66) fabric. When phytic acid and TiO_2/SiO_2 nanoparticles are used together, the LOI (24.5) of fabric and char yield increase. Further, the application of chitosan in combination with phytic acid and TiO_2/SiO_2 nanoparticles as the active components and BTCA as a cross-linker on PA66 fabric through pad-dry-cure technique shows an intumescent and thermal shielding effect, which results in the reduction in peak heat release rate (-25%). Along with flame retardancy, the hydrophilicity and tensile strength of the fabric arealso enhanced. Hence, combining nanoparticles and bio-based compounds could be better than traditional flame retardant chemicals. Its disadvantages, like hampering the elastic properties of the treated PA66 fabric due to the cross-linking are observed. Since there is no improvement in the anti-dripping properties of treated PA66 fabric, further optimisation is required[23].

3.4 TiO_2 Nanoparticles along with Proteins

Combining $TiO_2$and protein systems applied using a dip-pad-dry-cure method impart flame retardancy to the cotton fabric. It is observed that the nanoparticles and protein-based system decrease the burning rate with an increase in burning timeinthe horizontal flammability test[24].

Nanoparticles show promising flame retardant outcomes. However, toxicity associated with nanoparticles is a significant concern, preventing the commercialization of such molecules.

4 Flame Retardancy Using Layer-by-Layer Assembly Technique

Layer-by-layer (LbL) technique is hailedas an evolution of nanoparticle adsorption process. Based on electrostatic interactions, step-by-step films are built. The LbL was first described in 1966 but re-discovered several years later[25]. It is a water-based method to form multilayer films, by alternate deposition of positively and negatively charged polyelectrolyte onto the textile fabric. Flame retardancy can be imparted using the LbL assembly technique with hybrid organic-inorganic, all-inorganic, and all-polymer in tumescent systems[26]. Each positive and negative pair of films deposited onto the fabric is termed abilayer (BL)[27].

4.1 Cationic Chitosan along with Anionic Ammonium Polyphosphate

Researchers also utilised cationic chitosan and anionic ammonium polyphosphateto prepare cotton fabric with an excellent intumescent flame-retardancy using the LbL technique. Chitosan works as a carbon donor and blowing agent, whereas ammonium polyphosphate is an acid donor. After evaluating coated fabric, increased residual char production decreased peak heat release rate, and total heat release rate due to accelerated charring and inhibition of volatile gases is observed. The coating with 20 BL could lead to effective fire retardancy with the treated fabric's self-extinguishing behaviour. However, an increase in the number of bilayers on the fabric results in a stiff handle of treated fabric[26].

4.2 Cationic Chitosan and Anionic Phytic Acid

A combination of cationic chitosan and anionic phytic acid is considered as a green and completely bio-renewable source for imparting flame retardancy to the cotton fabric using the LbL assembly technique. Phytic acid is a source of phosphorus, while chitosan consists of nitrogen. When both these components are combined, it results in a renewable intumescent coating on cotton fabric. The thinnest films (30 BL~10nm thick) are obtained at a *p*H 4. It is observed that coated fabric completely extinguishes the flame, reducing the peak heat release rate (-60%) and total heat release rate (-76%). It is believed that such behaviour is ascribed to the presence of high phosphorus content, which enhances the intumescent behaviour of the coated fabric[27].

4.3 DNA and Chitosan

DNA and chitosan are also reported in the literature for their application viathe LbL technique on the cotton fabric as a green coating for imparting fire resistance. Due to its chemical structure, DNA imparts intumescence to the cotton fabric. DNA is a precursor of phosphoric acid the deoxyribose acts as a char source, and the bases containing nitrogen might release ammonia. When combined with chitosan, DNA helps in the easy formation of a thermally stable char, making this system highly efficient. After 5 BL deposition of DNA and chitosan, smooth coatings are observed as compared to the untreated cotton fabric. 20 BL assemblies of DNA and chitosan impartes the self-extinguishing behaviour of cotton fabric, increasesthe LOI (up to 24), and reducesthe heat release rate by 40%. Although the DNA used is expensive as compared to other chemicals, the required degree of purity for the flame retardant application is much lower than that needed for biological use and could be compensated; hence, it could lead to a reduction in cost[28].

4.4 Cationic Starch along with Polyphosphoric Acid

Cationic starch, along with polyphosphoric acid, are coated on the cotton fabric using the LbL technique. Starch is also used as a sustainable, bio-based efficient coating, protecting the cotton from catching fire and causing the associated hazards. Starch, upon heating,can form a thermally stable char layer. The dehydration ability of polyphosphoric acid has further improved the effect. It is also observed that after the coating application, the char-forming ability is further enhanced. After applying only 2 BL with less than 5% weight deposition on cotton fabric, the self-extinction of flame is observed. A significant reduction in the total heat release rate (-40%) is also observed in cone calorimetry[29].

4.5 Potassium Alginate (PA) and Polyhexamethylene Guanidine Phosphate (PHMGP)

The environment-friendly antimicrobial PHMGP is combined with potassium alginate, a green polymeric material extracted from seaweed, for coating cotton fabric using the LbL technique to impart antimicrobial and flame retardant properties. The coated fabric shows more char residue as compared to the uncoated one. Vertical flammability results for the coated fabric have shown the elimination of the after-glow phenomenon at 2s after extinguishing. Also, there is a reduction in the peak heat release rate and the total heat release rate of the coated cotton fabric. The peak heat release rate decreases with increased BL for the coated cotton fabric. The intumescent coating is formed, which shows excellent flame retardant and antimicrobial properties[30].

The main issue encountered in the LbL assembly technique for obtaining flame retardancy is the requirement of more bilayers to achievea significant effect. However, applying morebilayers might result in a stiff handle of treated fabric[26]. Thus, higher number of bilayers should be avoided.

5 Plasma-Assisted Flame Retardant Finishing of Textiles

Permanent fireproofing on fabric such as cotton is a challenging aspect. Moreover, the coating formed must be resistant to washing and remain attached to the fabric's surface. Hence, experiments are carried out to form durable flame retardant coatings using plasma technology[31]. This section mainly discusses the use of plasma to fixor cureflame retardant chemicals on the textile materials.

PAN fabric is treated using argon plasma, with four acrylate monomers (containing phosphorus) such as dimethyl(acryloyloxymethyl)phosphate (DMAMP), diethyl(acryloyloxyethyl)phosphate (DEAEP), diethyl(acryloyloxymethyl)phosphate (DEAMP), and diethy-2-(methacryloyloxyethyl)phosphate (DEMEP). Also, new phosphoramidate monomers (such as diethyl (acryloyloxyethyl) phosphoramidate (DEAEPN) and acryloyloxy-1,3-bis(diethylphosphoramidate) propan (BisDEAEPN))are synthesised, and their plasma-induced graft polymerisation on the cotton fabric is reported. It is detected that using DEAEPN, the LOI value of cotton fabric reached 28.5, while treatment with

BisDEAEPN enhanced the LOI value of cotton to 29.5. This could be further explained by the presence of phosphoramide monomers, consisting of nitrogen, which synergistically enhanced the performance of phosphorus-based flame retardants. Even after laundering, an LOI of 25 is maintained for the fabric treated with acrylate phosphoramide monomers and DEAEP[31].

Atmospheric pressure dielectric barrier discharge plasma has also been experimented with by researchers. The plasma-treated fabric is further treated with flame retardants through the conventional pad-dry-cure method. It is reported that to achieve LOI value of 25 using plasma, the time and temperature for curing are 90s and 160°C, as compared to 114s and 180°C respectively, achieved in the absence of plasma treatment. Though the reductions in time and curing temperature are achieved, a substantial loss in the treated fabric's mechanical strength is seen. It is also stated that plasma itself is responsible for reducing the mechanical strength of the fabric. It is suggested that the time for plasma pre-treatment must be further reduced so that the chemical bond between cotton and treatment chemical could be formed with the retention of mechanical strength of fabric[32].

Researchers also reported atmospheric pressure plasma as a pre-treatment on the cotton fabric to enhance post-finishing (flame retardant properties). Plasma pre-treatment is reported to improve the flame retardancy of cotton fabric treated with an organic phosphoric acid (fire retardant) with melamine resin (cross-linker), phosphoric acid (catalyst), and zinc oxide(co-catalyst).The treated cotton sample with the prepared formulation showed a reduction in mechanical properties, which were further compensated by the plasma pre-treatment[33].

The technology of plasma is known as waterless and eco-friendly, but still, it is a costlier process for producing flame retardant textiles[32]. Poor result reproducibility is another undesirable aspect associated with plasma technology.

6 Natural Resources-based Sustainable Green Flame Retardants for Textile Finishing

In an era where sustainability and growing environmental awareness are evident, producing eco-friendly flame retardant fabrics has become essential. These environment-friendly flame retardant finishes will not only protect from major human health hazards, associated toxic effects, and negative environmental impacts but also help in reducing the carbon footprint. In the last 5-10 years, studies have essentially been carried out to obtain eco-friendly biomolecules, either extracted from plants (grains and sap-based) or animal (polysaccharides or protein-based) natural sources for producing flame retardant textile material. Instead of throwing it into the landfill, the agro-food industry waste could be utilized as a flame retardant finish for textiles. Even the process of application of biomolecules on textiles is simple, and the application can be done using already existing systems of the textile industry. Also, biomolecules are dissolved or suspended in lower concentrations in an aqueous medium such that no volatile organic carbon (VOC) species are generated.

Most plant extracts and waste animal products contain phosphorus, nitrogen, other inorganic compounds, and metal oxides, which could be utilised to impart flame retardancy to cellulosic, protein-based, and lignocellulosic textile materials[34–36].

6.1 Animal-based Natural Resources for Flame Retardant Finishing of Textiles

Various animal-based natural resources are already reported in the literature for imparting flame retardancy to the textile substrate. The animal-based natural resources with potential applications in flame retardant finishing of textiles are depicted in Fig. 4.

6.1.1 Chitosan

Chitosan, an amino polysaccharide obtained via alkaline deacetylation of chitin, is an eco-friendly

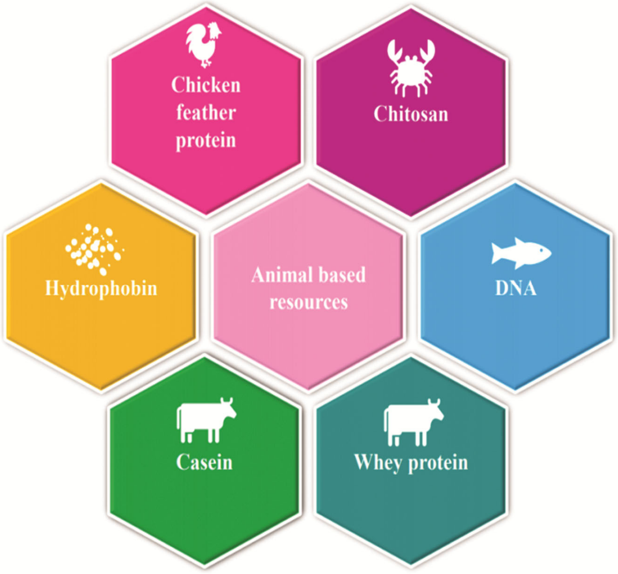

Fig. 4 — Animal-based natural resources for flame retardant finishing of textiles

natural source to impart flame retardancy to cotton fabric. Researchers[37] dissolved chitosan in the citric acid solution, added it to a phosphorylation bath consisting of butane tetracarboxylic acid (BTCA), diammonium hydrogen phosphate (DAHP), and sodium hypophosphite (SHP), and then applied it to cotton fabric. Chitosan, when added, acted as a nitrogen source in synergy with phosphorus during the phosphorylation process. It is also reported that when the chitosan concentration is increased from 1% to 2%, enhancement in flame retardancyis observed. Increasing the concentration above 2% showed a limited impact on the treated fabric's thermal degradation. DAHP (concentration varying from 0% to 10%) is added to the bath to obtain durability against washing. The optimum concentration of chemicals for reduced flame retardancy is 1% chitosan, 10% DAHP, 4% BTCA, and 6% SHP[37].

6.1.2 Deoxyribonucleic Acid (DNA)

DNA obtained from the herring sperm isalso utilised to impart enhanced flame retardant properties and thermal stability to the cotton fabric. DNA is considered as an intumescent flame retardant, as it comprises all three components needed to show intumescent behaviour. It contains phosphate groups, which could form phosphoric acid; the deoxyribose unit, which acts as a carbon source and a blowing agent (which, upon heating, form char and release water); and the nitrogen-containing bases (adenine A, cytosine C, guanine G, and thymine T), which might release ammonia. It is observed during the flammability testing in a horizontal configuration that the the fabric did not burn even after applying flame for 3 s. The LOI value of 28 is reported for DNA-treated fabricas compared to LOI of 18 for the untreated one. However, the main issues with DNA include its high cost and poor durability in washing[5].

In another experiment, DNA in various concentrations (5, 10, 19 wt %) is coated on the cotton fabric, considering percentage weight increase of fabric sample after finishing relative to the original weight of the fabric sample (wt.%). It is detected that 10 wt.% DNA is the least amount that must be applied to the cotton fabric to achieve self-extinction when subjected to a methane flame. Also, in the case of 19wt. % DNA, the treated fabric can resist the irradiative heat flux of 35 kW/m^2. The DNA-treated cotton fabric did not burn in cone calorimeter testing. Due to the protective coating done by DNA, the treated cotton fabric ispyrolyzed instead of burning. The protective coating absorbed heat, formed char and released inert gases[38].

6.1.3 Whey Proteins

Whey proteins, the by-product of cheese, could also be used to form coatings onto the cotton fabric, which can potentially impart flame retardancy. Whey protein isolate (WPI) shows better mechanical and excellent oxygen barrier properties despitehaving water adsorption capabilities. It forms transparent, colourless, odourless, and flexible films onto the cotton fabrics. In some cases, plasticizerscan be applied within the protein mixture to form films and decrease the film brittleness. These films reduce the intermolecular forces between adjacent protein chains, thereby imparting more extensibility and flexibility. Researchers utilized whey proteins (folded and unfolded) and proved them to be the potential sources for enhancing flame retardancyin cotton fabric. An increased burning time and reduced burning rate are observed for the treated cotton fabric[39].

6.1.4 Caseins and Hydrophobins

Caseins and hydrophobins are other finishes for reducing the flammability of cotton fabric. Caseins consist of phosphorus-rich proteins, while hydrophobins consist of sulphur-rich proteins. The proteins obtained from animal or microbial sources can also be utilised for imparting flame retardancy to cotton fabric. Casein is a milk protein (80%) obtained during skimmed milk production, while hydrophobins are obtained from filamentous fungi. These proteins induce dehydration of cellulose in place of depolymerization, thereby producing a thermally stable char. Also, it is reported that the fabrics coated with caseins and hydrophobins show higher burning time (40% higher), reduce the total burning rate (lower by 35%), and form a consistent residue[40].

Caseins (from bovine milk), due to their high phosphorus content, are also used to improve the flame retardancy and thermal stability of polyester and polyester-cotton fabrics via impregnation methods. This biomacromolecule could produce char and inhibit the formation of volatile species. The thermal stability of the casein-treated fabric increases along with resistance to an irradiative flux, in the case of both nitrogen and air atmosphere. A reduction in the burning rate (-70%) and an increase in LOI value (21 from 26) are observed in the case of polyester fabric. The burning rate is slowed down (-40%), and even resistance to irradiative flux, is reported for the polyester-cotton blend treated with caseins. However, the issue of melt dripping for the polyester fabric still needs to be solved[9].

The application of casein phosphopeptide (CPP) along with ferrous and titanium sulphates is also reported in preparing durable flame retardant silk fabric. The silk fabric treated with 10 g/L CPP and mordanting with ferrous and titanium sulphates show LOI values of 27.8 and 28 respectively, along with smoke-suppressant effects. A residual char length of less than 15 cm is observed even after 20 wash cycles. A condensed phase mechanism is proposed in which the complex of CPP and metal ions work. The good charring ability of treated fabric and the enhanced thermal stability, even at high temperatures, are the factors responsible for increasing flame retardancy. Bright yellow colour with good wash and rub fastness properties is also imparted[41].

6.1.5 Chicken-Feather Protein

Chicken-feather protein, another eco-friendly, protein-based, nitrogen-containing flame retardant, isutilised to treat cotton fabric. Chicken feather protein, along with nitrogen and phosphorus-containing monomers (melamine and sodium pyrophosphate), and a crosslinker (glyoxal) are used. The P-N based chicken-feather protein FR, along with borax and boric acid, are applied to the woven cotton fabric. An enhanced flame retardancy along with thermal stability of the treated fabric, due to the formation of a compact and homogenous in tumescent char layer, is reported. LOI values obtained are also higher than the control fabric. It is also stated that chicken feather protein acted synergistically with borax and boric acid[42].

Results in terms of LOI, add-on percentage on cotton fabric, burning rate, burning time, and residue of a few natural-based animal resources already discussed in the previous paragraphs are depicted in Table 2.

6.2 Plant-based Natural Resources for Flame Retardant Finishing of Textiles

The various plant-based natural resources reported in the literature for imparting flame retardancy to the textile substrate are depicted in Fig. 5.

6.2.1 Spinach Leaves Juice

Spinach leaves juice, a vegetable extract, is used to reduce cotton fabric’s flammability. Flame retardancy in the spinach juice-treated textile can be ascribed to proteinous nitrogen, metal salts, and silicates. The extracted juice is applied to the bleached and mercerized cotton fabric in alkaline conditions. Compared to the untreated fabric, the treated fabric shows good flame retardancy. After applying spinach juice extract, the LOI value of the treated cotton fabric is increased. The total burning time also increased, which can help to provide extra time for escaping the fire hazard zone to extinguish the fire. The total heat generation for the treated fabric is further reduced. Another advantage in terms of good weathering fastness propertiesis claimed. The natural green colour is imparted to textile, which makes it suitable for application in colouration and imparting flame retardant finish for home furnishing products. In alkaline conditions, it is observed that without any dilution for the spinach juice extract, i.e. (1:0) is the best for imparting flame retardancy[43].

6.2.2 Banana Pseudostem Sap (BPS)

BPS, a green plant extract from a renewable source, also showed promising results in imparting flame retardant properties to cellulosic fabrics. The sap extracted from the plant is made alkaline and then applied on the pre-mordanted, bleached, and mercerized cotton fabric. The non-diluted BPS application on cotton textiles under alkaline conditions showed the best results, as the increased LOI values were obtained. In the vertical flammability test, the flame is observed for the first 10 s, and then it got extinguished. In the case of the horizontal flammability test, no flame is observed, but burning with afterglow is seen. The flame retardant properties shown by the BPS-treated cotton fabric are ascribed to the presence of phosphate, nitrogen, metal

Table 2 — Summary of natural animal-based resources for FR finishing of cotton

Natural animal-based resource	LOI, %	Add-on, %	Burning rate, mm/s	Burning time, s	Residue, %	Ref.
Control cotton fabric	18	-	1.5	78	-	39
DNA	28	19	-	-	-	5
Whey protein (unfolded)	-	20	1.1	133	5	39
Whey protein (folded)	-	25	1	126	30	39
Caseins	-	20	1	100	34	40
Hydrophobins	-	20	1.1	104	19	40

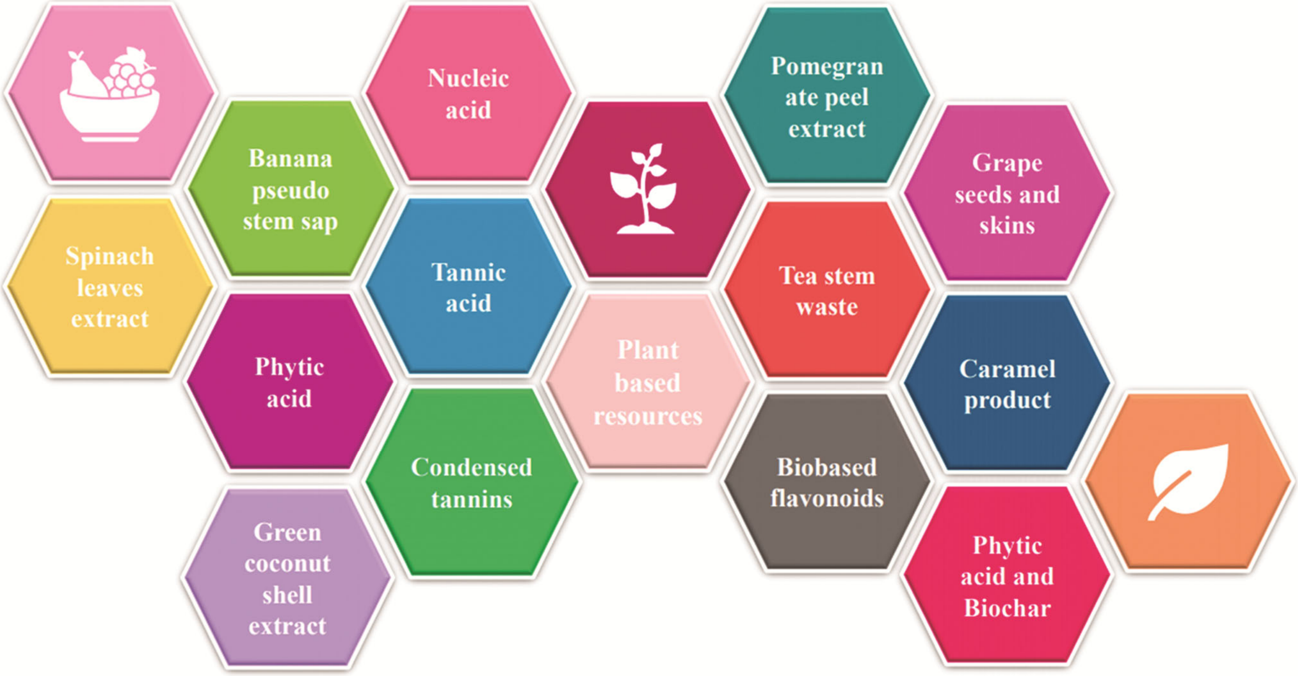

Fig. 5 — Plant-based natural resources for flame retardant finishing of textiles

salts (potassium chloride and sodium chloride), and inorganic materials. These compounds assisted in the formation of char and non-flammable gases during the burning of treated cotton. Also, BPS showed inherent dyeing properties as a natural khaki colour is produced after the application on cotton fabric, which is stable to sunlight exposure. The simple and cost-effective process can be used to provide both colouration and functionalization[44].

An eco-friendly agricultural waste product is also used on proteinous wool fabric to impart flame retardancy. An acid dye (CI Acid Blue 25) dyeswool fabric using water and BPS asthe medium. Dyeing, with the help of BPS at a *p*H of 5.5, showed more colour strength, colour exhaustion, and thermal stability than untreated wool fabric. The treated wool fabric exhibits self-extinguishing behaviour at a specific char length with increased LOI values. It is also stated that instead of water, BPS could be used as a dyeing medium[7].

6.2.3 Phytic Acid (PA)

PA, a bio-based, naturally occurring compound, has also shown promising results for imparting flame retardant properties to wool fabric. It is identified as inositol hexakisphosphate acid or phytate in salt form and is considered an eco-friendly biomolecule, as it can be obtained from plant tissues such as cereal grains, beans, and oilseeds. Phytic acid comprises 28% phosphorus (based on its molecular weight), which can be used as a phosphorus source in the flame retardant finishing of textiles. Researchers applied PA on wool fabric using the exhaustion method. A good flame retardancy is observed for treated wool. Due to its high char-forming ability, it works through a condensed phase mechanism. However, PA has shown slight adverse effects on the strength and whiteness of the treated wool fabric. Also, the washing resistance of treated wool fabric could be better and needs to be improved[8].

In another study, it is reported that PA can enhance the flame retardancy of silk/wool blend fabric. The PA-treated blend exhibited inferior FR properties compared to the conventional agents (K_2TiF_6 and K_2ZrF_6). However, the treated blend showed better FR properties after washing. Compared to the conventional systems, PA acted as the best smoke suppressant, reduced the heat release capacity, and gave the best catalytic char-forming effect. However, the whiteness of the blend is reduced due to the action of PA[45].

6.2.4 Green Coconut Shell Extract (CSE)

Green coconut (*Cocos nucifera* Linn.) shell extract, a waste bio-resource, is also used to impart flame retardant properties to textiles. Green coconut mesocarp is cut into pieces, and sap is extracted.

Researchers applied CSE on the cotton fabric under different *p*H conditions, i.e. acidic, alkaline, and neutral. The dimensions of the CSE obtained were in nanoscale and were applied by using the exhaustion method. After the application of CSE on the fabric in alkaline conditions, it is observed that the LOI increased by 72.2%. This increase could be attributed to the presence of different inorganic and organic compounds; the formation of char layers at a lower temperature, which act as a protective barrier against flame and heat; and reduced volatilization, which further reduced the formation of combustible gases. CSE also formed a coating layer onto the fabric, which acted as a fire barrier. A condensed phase in tumescent mechanism is proposed. A natural brown colour is obtained, which could change to red with increased *p*H. The treated fabric even exhibited antibacterial properties against Gram-positive and Gram-negative bacteria[46].

CSE is also applied on the jute fabric. The extract is acidic; and hence, it is made alkaline and neutral before applying to the jute fabric. Good flame retardant properties and an increase in thermal stability are observed, along with an increase in LOI by 48% under alkaline conditions and 81% in concentrated conditions. The reduced flammability is ascribed to the presence of phosphate compounds and inorganic metals, which are responsible for producing more char and non-flammable gases. Apart from flame retardancy, the jute fabric also showed natural colour, UV protection, and antibacterial properties. Comfort and strength are retained even after the application of CSE[47].

CSE is also utilised to impart multifunctional properties, such as flame retardancy, UV protection, and colouration on the proteinous wool fabric. The concentrated CSE is applied to the wool fabric at a *p*H of 4.5. CSE-treated wool fabric shows more exhaustion, good colour strength, and enhancement in thermal stability than the treated wool with synthetic acid dyes. An increment in the LOI value of the treated wool fabric is observed along with the fabric's self-extinguishing behaviour. The reduced flammability is ascribed to the presence of sulphate, phosphate, metal salts, silicates, etc.[48].

6.2.5 Nucleic Acid

Nucleic acidextracted from spent brewer’s yeast, and vegetable scraps (agro-industrial biological wastes)is also reported to impart flame retardancy to cotton fabric. This green extraction method is simpler, cheaper, and more reliable than that of the purified fish DNA. For both purified DNA and brewer's yeast nucleic acid, the add-on values (8 wt. %) on the fabric were equal. Self-extinguishing and similar behaviour are observed for both purified DNA and the spent brewer’s yeast. However, the nucleic acids obtained from vegetable scraps were not as effective, which might be due to the lower final dry add-on values (about 5 wt. %). Hence, the nucleic acid obtained from agro-food waste is found to be a good alternative to expensive purified DNA[49].

6.2.6 Tannic Acid

Tannic acid, a natural polyphenolic compound along with sodium ions, is also reported to produce an intumescent flame retardant cotton fabric. A low thermal conductivity, along with low flammability, is exhibited by the treated cotton fabric. It is reported that tannic acid alone is sufficient to change the thermal pattern of pyrolysis and combustion of cotton, along with an increment in char length; however, the LOI value is not enhanced. Hence, alow concentration of sodium hydroxide is added to enhance flame retardancy. Sodium ions led to increased adsorption of tannic acid on the cotton fabric, and catalyzed the decarboxylation of tannic acid, and dehydration of cellulose. The intumescent char layer obtained resulted in a reduction of heat release capacity by 82% and increased LOI to 30.2[50].

Condensed tannins obtained from *Dioscorea cirrhosa* (DC) tuber, a natural plant source, also impart flame retardant properties to silk fabric. The aromatic structure of tannins is the suitable reason for its application in thermal insulations and FR fabrics. Eco-friendly, nontoxic condensed tannins, when applied in a weakly acidic condition using the impregnation method, provided excellent and durable flame retardant properties to silk fabric. It had been reported that condensed tannins on silk fabric worked through a condensed phase mechanism. Also, 300 g/L DC extract gave the highest LOI (28.1), while with the application of 37.5 g/L DC extract, good flame retardancy is attained, as represented by the LOI value of 27.2.A shorter char length is observed for the treated silk fabric compared to the untreated silk fabric. Apart from flame retardancy, good antioxidant, antibacterial, and UV protection properties are imparted to the silk fabric. It is also reported that the treated fabric exhibits good durability to repeated washing. When treated with DC extract, the silk fabric gives a reddish-brown appearance, which could be used as a natural dye source. With an increase in DC extract concentration, the treated silk fabric's colour depth is found to be increased. This negatively impacted the colour appearance of silk fabric, as white FR silk fabric could not be produced using condensed tannins[51].

Two coloured silk fabrics (*Gambiered Gauangdong* silk) with shiny black on the face side and reddish-brown on the backside are produced using condensed DC extract. A coating with condensed DC extract followed by mordanting with iron salt consisting of mud is done to obtain flame retardancy. The coating formed char during combustion,thus enhancing the flame retardant properties of the treated silk fabric. Multifunctional properties such as waterproof, flame retardancy, antioxidant, and antibacterial properties are imparted to the treated silk fabric[52].

Tannic acid TA (hydrolyzable tannin form), naturally occurring polyphenols found in plants in the presence of ferrous ion mordant, also imparted durable green antibacterial and flame retardant properties to the silk fabric. It is reported that tannic acid (20 wt. %) and 2 g/L ferrous sulphate are used in combination with silk fabric to increase LOI value from 23.6 to 27.5, an increase in antibacterial activity from 22% to 95%, and a decrease in damaged length. The treated silk fabric showed enhanced thermal stability in both nitrogen and air and retained its properties even after 20 washes. The ternary TA-ferrous ion-silk complex works through a condensed phase mechanism and is responsible for the excellent wash durability of the functional properties of the treated silk fabric. Enhanced flame retardancy obtained could be explained by the charring layer formed onto the treated fabric[17].

6.2.7 Pomegranate Peel Extract

Pomegranate peel extract has also been reported to impart flame retardancy to the cotton knitted fabric. In an experiment, zinc sulphate is used as a mordant for dyeing with pomegranate peel extract. The flame retardant activity of the fabric treated with pomegranate extract is stated due to nitrogen, potassium, chlorine, and certain traces of other elements, along with aromatic phenolic rings. The treated cotton exhibited multifunctional properties like antibacterial, UV protection, antioxidant properties, and enhanced thermal stability. Yellow-brown shades were shown by the treated cotton knitted fabric with excellent wash fastness properties[53].

In yet another study, pomegranate rind extract is also used to reduce the flammability of the lignocellulosic jute fabric. An increase in LOI value for the treated fabric to 38 is reported. A self-extinguishing behaviour for char length of 60 mm isalso reported by researchers[54].

6.2.8 Tea Stem Waste

A tea stem waste extracted after tea processing could also be used forsimultaneous colouration and flame retardancy to the silk fabric. The extract is obtained in alkaline conditions. During the alkaline extraction, the oxidative polymerization of polyphenols led to the development of macromolecular polyphenols responsible for imparting flame retardant properties to the silk fabric. The highest uptake by silk fabric is reported at a *p*H of 3 and a temperature of 30°C. The dyed silk showed good wash fastness properties; however, the perspiration and wet rubfastness properties were poor. Researchers further performed post-mordanting with metal salts to improve the poor fastness properties. The treated silk fabric also exhibited good flame retardant, antibacterial, and antioxidant properties. After post-mordanting, the flame retardancy is further enhanced, but a negative impact is observed on antibacterial and antioxidant properties. The improved flame retardant properties are ascribed to the increased charring behaviour of silk fabric after the application of tea stem waste extract[55].

6.2.9 Bio-based Flavonoids Combined with Metal Salts

Bio-based flavonoids, combined with metal salts, are also known to impart flame-resistant properties. Three kinds of bio-based flavonoids, namely baicalin, quercetin, and rutin, are applied onto the silk fabric using post-mordanting with metal salts. The smoke suppression, thermal behaviour, and charred structures of silk fabric are studied. The treatment of flavonoids followed by metal salt onto the silk fabricled to a good char formation, increased LOI, flame suppression, and enhanced flame-resistant properties. A good flame retardant, antibacterial, and moderate antioxidant properties are reported even after 20 washing cycles. So, this eco-friendly approach could not only provide the silk fabric with multifunctional properties but also impart colour[56].

6.2.10 Grape Skins and Seeds

Grape skins and seeds, a low-value by-product from the wine industry, are rich in polyphenolic compounds. Grape seed proanthocyanidins (GSP) are also utilized to impart colouration, antibacterial and flame retardant properties to silk fabric. The treated silk fabric is yellowish-brown and displayed acceptable colourfastness to washing, perspiration, and rubbing, but poor light fastness. To improve the light fastness, post-mordanting is suggested as an option. An improved flame retardancy along with increased thermal stability and the charring ability of silk are also reported by researchers. The treated silk fabric showeda condensed phase mechanism of flame retardancy. It is also reported that with an increase in GSP dosage, the LOI is improved, while damage length is decreased[57].

6.2.11 Phytic Acid along with Biochar

Phytic acid and biochar were also applied on cotton fabric to reduce its flammability. Phytic acid is a phosphorus-based compound obtained from a natural plant source, while biochar consists of carbon and is obtained from biomass. An aqueous mixture of phytic acid and biochar (1:1 weight ratio) is applied to the cotton fabric. This bio-sourced system enhanced the flame retardancy, and the final add-on on the fabric is just 8 wt. %. A self-extinguishing behaviour is attained by the treated fabric, and even under the exposure of 35 kW/m^2,the fabric did not ignite. The treated fabric exhibited poor wash fastness, but the washed fabric showed better fire-resistant properties[58].

6.2.12 Caramel product

Caramel product obtained after heating glucose in alkaline conditions (sodium hydroxide) imparts flame retardant properties to silk fabric. The caramel product is applied to silk fabric using the exhaustion technique in acidic conditions (*p*H 3 at 90°C). Brown colour, along with good flame retardant properties, is imparted. Caramelized solution (1%) imparts self-extinguish functionality, and if taken in an adequate amount, it could provide a semi-durable flame-resistant finish to the silk fabric. The property of bubbling upon heating the caramel is responsible for theflame retardant properties of the treated silk. Also, the intumescent char layer is formed onto the treated fabric, revealing a condensed charring mechanism. However, a slight adverse effect on tensile strength and handle of treated silk fabric is also observed[59].

Results in terms of add-on percentage and LOI of some research works reported for flame retardant finishing of various textile materials using plant-based extracts are summarised in Table 3.

7 Flame Retardant Finishing Using Intumescent Systems

The intumescent-based flame retardants are special cases of the solid (condensed phase) mechanism. A thermally stable char layer is generally formed, which acts as a barrier when a heat source irradiates an intumescent material and reduces flammability. An intumescent system/material consists of three major components: an acid source, a carbon source, and a blowing agent. However, the limited durability of the coated textiles and enhanced stiffening are the major issues being encountered with such formulations[60].As reported in the literature, some intumescent flame retardant formulationsfor different textile materials are summarised in Table 4.

8 Prospective Flame Retardant Coatings by Hydrogels

The already prevailing flame retardant polymer fabrics such as aramids are not widely used as these

Table 3 — Summary of application of plant-based resources for FR finishing of textiles

Natural plant-based resources	Fabric	Addon, %	LOI, %	Ref.
Spinach leaves extract	Cotton	3.5-8	26-30	43
Banana pseudostem sap	Cotton	2-4.5	26-30	44
	Wool	3-5	29-35	7
Phytic acid	Wool	-	28-35.2	8
	Silk/wool blend	-	29	45
Green coconut shell extract	Cotton	4.12-5.97	23-31	46
	Jute	4.92-9.18	25-38	47
	Wool	6.89-10.9	30-36	48
Nucleic acid	Cotton	8	-	49
Pomegranate peel extract	Cotton	-	-	53
Tea stem waste	Silk	-	26.3-26.75	55
Phytic acid and biochar	Cotton	4-10	-	58

Table 4 — Some intumescent flame retardant formulations on different textile materials

Intumescent flame retardant formulation	Textile material	Flame retardant properties	Additional property	Ref.
Modified I-type ammonium polyphosphate (APP) +dicyandiamide (catalyst) using P-O-C covalent bond	Cotton	• LOI 50.1 (30% APP) • LOI 28.5 after 50 washes • No after-flame or afterglow during vertical burning • Reduced peak heat and total heat release rate • Good flame retardancy	• Excellent durability against washing • Physical properties retained after treatment	61
Poly hexamethylene guanidine phosphate + ammonium polyphosphate using layer-by-layer assembly	Cotton	• Increase in residue • No afterglow • Intact weave structure in the vertical burning test	Antimicrobial effect against *E. coli* and *S. aureus*	62
Positively charged chitosan (CH) + negatively charged ammonium polyphosphate (APP) using layer-by-layer technology	Polyester	• After 10 BL, the anti-dripping property improved • LOI value improved (25.5) • Even char production	-	63
Vinylphosphonic acid (VPA) + methacrylamide (MAA) + potassium persulphate as a radical initiator	Cotton	• Stable char layer formed after burning • Self-extinguishing effect observed in the horizontal flammability test • Weight loss after the first wash but later not observed	The Durability of the treated fabricob served after 5 wash cycles	64
Polyethyleneimine (PEI) wrapped nano-silica + polyphosphoric acid (PPA) using layer-by-layer technique followed by dip pad cure coating with water-repellent chemical	Cotton	• Good fire-retardant properties • LOI 28.2 • Increase in thermal stability attained with 41% of char yield at 600°C, 9.2 cm char length, • No after-flame and after-glow detected	• Excellent hydrophobic properties with a contact angle of 142° ±1°, • Reduction in breaking strength moderate	65
Polyelectrolyte polyethyleneimine (PEI) + ammonium polyphosphate (APP) using layer-by-layer technology	Ramie	• Self-extinguishing behaviour of fabric when tested for vertical flammability • Fire retardant properties and thermal properties obtained • Higher char residue at 400°C - 600°C as compared to the control fabric	-	66
Phenylboronic acid (PA) and branched polyethyleneimine in acetone chemical using the dipping process followed by crosslinking	Cotton	• Add-on of 33.8 % provided self-extinguishing behaviour; • LOI got enhanced • Total heat release rate reduced compared to that of the control fabric	Semi-durable coatings obtained	67
Negatively charged ammonium polyphosphate + positively charged chitosan using layer-by-layer assembly with ultrasonication rinsing after each layer deposition	Cotton	• 20 BL of formulation sonicated and non-sonicated imparted flame retardant properties to treated fabric	-	68
Ammonium polyphosphate, pentaerythritol and melamine	Nylon-6.6	• Prevented melt dripping for treated fabric • Above 13% char residue, which could even reach 24% at 750°C • LOI of 27.9	The formulation could be used for curtains and carpets where wash durability is not needed	69

(*contd.*)

Table 4 — Some intumescent flame retardant formulations on different textile materials (*contd.*)

Intumescent flame retardant formulation	Textile material	Flame retardant properties	Additional property	Ref.
Phosphorylated sodium alginate, dipentaerythritol, and ammonium polyphosphate by melt blending into fibre	Isotactic polypropylene	• Flame retardant properties and thermal stability achieved • Heat release rate and total heat release reduced drastically along with smoke suppression (-76%)	-	70
Sodium polyphosphate, poly(allylamine) (PAH), and TiO_2 nanoparticles using layer-by-layer technology	Polyester and polyamide	• Reduction in peak heat release rate observed for polyamide fabric (-26%), while for polyester fabric, alimited effect reported	-	71
Cationic branched polyethylenimine with urea + anionic clay nanoparticles using layer-by-layertechnique	Cotton	• Enhancement in thermal stability • Decreased heat release rate and increased burning time	-	72
Chitosan, ammonium polyphosphate, and silica using layer-by-layer technique (quad-layer formed)	Polyester -cotton blends	• Reduction in flammability • Afterglow suppression along with an increase in char residue	-	73
Ammonium polyphosphate, branched poly (ethylenimine), and fluorinated-decyl polyhedral oligomeric silsesquioxane	Cotton	Tri-layer coating produced a char layer, along with self-extinguishing behaviour	Superhydrophilicity, along with self-healing property	74
Cationic polyallylamine along with anionic sodium polyphosphate using layer-by-layertechnique	Polyamide 6.6	40 BL coated sample showed a reduction in peak heat release rate (-36%)	-	75
Sodium polyborate along with poly hexamethylene guanidine phosphate using layer-by-layer assembly	Cotton	• 10 BL coating completely extinguished flame along with a decrease in peak heat release rate, total heat release rate, • LOI increased	-	6
Phytic acid, chitosan, and silicon dioxide modified with hexamethyldisilylamine	Cotton	Flame retardant, and water repellent properties, retained even after 50 abrasion cycles using sandpaper	Superhydrophobicity imparted	76
Cationic casein, anionic ammonium polyphosphate	Cotton	With an increase in casein, char residue enhanced, but comfort properties were improper after 5 wt. % casein	-	77
Banana pseudostem sap (BPS) + boric acid	Cotton	• Banana pseudostem sap, along with 3% boric acid, imparted flame retardancy • LOI 42	-	78
Ammonium polyphosphate + phosphorus	Polyester	• Melt dripping after treatment for the polyester fabric prevented	-	79

are quite costly, have low decomposition temperatures, and can cause burns to fire-fighting personnel. Hence, it becomes important to manufacture such fabrics, which are fire retardant and anti-burn in nature[80]. Due to its high specific heat capacity and latent heat of vaporization, water makes it an excellent fire extinguisher. However, water cannot be used as it exists at room temperature in a liquid state with no fixed shape. Hence, for resisting fire, hydrogels have been discovered that are quite effective and can be used to prepare fire fighter's protective clothes[81,82].

Hydrogels are hydrophilic having cross linked polymeric networks, where water is the dispersing medium. These are water-swollen and formed by the reaction of either a single monomer or between two monomers. These have a special ability to swell and retain water but do not dissolve in water. The hydrophilic functional groups linked to the polymeric chains are the reason that hydrogels absorb water, whereas they resist the dissolution in water due to the crosslinks that are formed between the chains[83].

The hydrogel can function as a fire-retardant coating due to its very high water content. It can absorb a huge amount of heat energy and release it when evaporation occurs. The combustibles, when coming in contact with the water vapour, instantly form an oxygen barrier layer, and further stop the combustion process by reducing the temperature[81,82].Various hydrogels, found to be flame retardants, are discussed in this section.

The physically crosslinked hydrogels of Li-alginate/ poly(acrylamide-co-stearyl methacrylate) are reported to behave as an excellent and tough flame-resistant material. The obtained flame-resistant hydrogel can sustain the flame at even 1300°C for 50 s. It is also reported that even if the prepared hydrogel is scratched, it can recover back and show self-healing properties. As hydrogels possess the property to retain water, they could last for around 6 months or even more. So, the Li-alginate/ poly(acrylamide-co-stearyl methacrylate) hydrogels could be used for making flame-resistant coatings for fireproof fabrics, and for protection to trees and the buildings structures[81].

Poly (N-isopropylacrylamide), sodium alginate (SA), and silver nanoparticles are also reported to form a physical interpenetrating polymer network (IPN) on cotton fabric. It is observed that prepared IPN hydrogel could hold water up to 2186% at 20°C, thus exhibiting an excellent ability to absorb the heat when the water got evaporated. It is also revealed that the prepared IPN hydrogel shows good elastic and strength properties. When tested by vertical flammability, hydrogel fabric laminate cannot burn when ignited by a flame source for 12 s, while the control cotton fabric is burnt out. Due to the presence of silver nanoparticles along with SA reducing agent, it is also observed that the hydrogel fabric laminate displays antibacterial properties (around 96%) against *E. coli* and *S. aureus* bacteria. Hence, it is concluded that the prepared hydrogel laminate could be used to produce the firefighter protective clothes[82].

Starch grafted with butyl acrylate (BA) to form starch-g-poly (butyl acrylate) (PBA) is reported to form a hydrogel structure that can hold a huge amount of water. This prepared hydrogel, along with mica (layered aluminium silicate),are reported to impart flame retardancy. The obtained bio-nano composite is found to be biodegradable, along with the added benefits of thermal stability and water absorbency. The prepared bio-nano composite on wood could delay the ignition time, reducing the peak heat release rate[84].

Polyisocyanate, a water-soluble prepolymer when dissolved in either a solution of an intumescent or a flameretardant material or an aqueous slurry, had been reported to produce flame retardant protective coatings. The gel prepared can impart a coating that could save it from a flame source. The crosslinked polyurethane coating can produce solid content on the material[85].

In another study, the xanthan gum (XG) is used to prepare a green hydrogel, which functions as a flame retardant solution and is sprayed to prevent forest fires. It was also detected that to increase the effect, intumescent formulation with resorcinol diphenyl phosphate (RDP) (acid source) and starch (charring agent) was used along with xanthan gum as a coating. It is reported that the formulation can stop the self-combustion of the grass[86].

Poly (N-isopropylacrylamide), SA, and poly (vinyl alcohol) are reported to form a triple network hydrogel onto the cotton fabric. The prepared hydrogel-fabric laminate can impart excellent flame retardancy. When exposed to a flame source, the hydrogel-fabric laminate is intact for 12 s. The obtained hydrogel displayed excellent swelling ratio, swelling and deswelling behaviour, and antibacterial properties. SAis even able to enhance the water retention properties of the hydrogel. The thermal stability of the prepared hydrogel is best when SA and poly (vinyl alcohol) are in a ratio 2:1[87].

Water-soluble chitosan, acrylic acid, polyvinyl alcohol-based macromonomer, and copper (Cu (II)) ion together are reported to form a flame retardant self-healable hydrogel. The prepared hydrogel is coated onto polyester fabric. The hydrogel-coated fabric's thermal stability is found much higher than that of the original fabric. A decrease in the peak heat release rate for the hydrogel-coated fabric isobserved. The hydrogel-coated fabric can self-extinguish when tested for vertical burning[88].

Chitosan-grafted poly (acrylic acid-co-methacrylamide) hydrogel is also prepared for the mine-fire fighters. The water absorbance capability of the prepared hydrogel is enhanced due to the grafting of chitosan in an acidic solution as well as in deionized water. Water retention is enhanced for the prepared hydrogel. The prepared hydrogel prohibited the initial oxidation of coal. So, it is an excellent mine-fire retardant material[89].

Table 5 — Flame retardant coatings on different textile materials produced by other processes

Flame retardant formulation	Method	Textile material	Flame retardant properties	Ref.
Tri(acryloyloxyethyl) phosphate (TAEP) and triglycidyl isocyanurate acrylate (TGICA)	UV curing	Cotton	Decrease in peak heat release rate, heat release rate, and total heat of combustion observed, an increase in LOI value for coated fabric	90
Vinylphosphonic acid and acrylamide comonomers	UV curing	Cotton	With an increase in acrylamide concentration, the flammability further reduced, enhancement in LOI (32) , with self-extinguishing behaviour even at 5 laundering cycles	91
Positively charged alumina coated silica with negative charged unmodified silica	Spray-assisted (horizontal) layer by layer	Polyester	Anti-dripping observed, with an increase in time of ignition, reduction in heat and smoke produced and incorporation of more uniform coating	92
Para-phenylene diamine (PDA) along with tetrakis(hydroxymethyl) phosphonium chloride (THPC)	One-step spray process	Cotton	Water-based coating of phosphorus nitrogen combined formulation showed reduced flammability along with self-extinction within 3 s	93
Silica-based layer-by-layer assemblies	Dipping, horizontal, vertical, and spray coating	Cotton	Horizontal spraying systems gave better homogenous coating layer, provide best flame retardant properties compared to vertical and dip method	94
Diammonium hydrogen phosphate (DAHP) microcapsules on polyurethane shell	Micro-encapsulation	Cotton	Durable flame retardant coatings, intumescent	95
(3-Glycidyloxypropyl triethoxysilane modified N-(phosphonomethyl) iminodiacetic acid (PGPTES) + tetraethylorthosilicate (TEOS)	Sol-gel technique	Cotton	Coating self-extinguishing in nature, imparts flame retardant properties, reduction in heat release rate	96
Phytic acid and urea + tetraethoxysilane (TEOS)	Sol-gel technique	Polyacrylonitrile (PAN.)	Flame retardant properties with thermal stability, self-extinguishing behaviour for treated fabric, enhanced LOI (42.1)	97
Nitrogen-modified silane hybrid + phytic acid	Sol-gel along with layer-by-layer technique	Cotton	Reduced thermal stability, enhancedchar formation, 15 BL extinguish flame completely with a reduction in peak heat (-31%) and total heat release rate (-38%)	98
Succinic acid, malic acid, and tartaric acid (TTA)	Pad-dry-cure	Cotton	Succinic acid more efficient flame retardant than malic and tartaric acid	99
Zirconium oxychloride optimized	Exhaustion procedure	Wool	Treated wool shows higher LOI than untreated	100

9 Other Flame Retardants

Various coatings for imparting flame retardancy to different textile materials have been reported to be produced by UV curing, microencapsulation, spray coatings, and sol-gel methods. Some of them are summarised in Table 5.

10 Conclusion

In order to protect textile materials and their users from fire hazards, a flame retardant finishing is an ideal approach. Variety of attempts have been reported in the literature which are reviewed and reported in this paper. Although traditionally used compounds based on halogen, phosphorus, phosphorus-nitrogen, borax, and boric acid chemistry are efficient flame-retardants, some are known to have adverse effects on the environment, health and safety. Various innovative techniques like nanotechnology, plasma, LbL, and intumescence have been explored. However, due to current trends in greener methods and environmentally safe products, it has become essential to explore sustainable and green coatings to produce flame retardant textiles. Although hydrogel is found to be an efficient flame retardant, it is explored to a limited extent in the flame retardant finishing of textiles. The exploration of sustainable flame retardants for imparting efficient and durable flame retardant textiles at low add-on levels will remain the quest to research this vital area of material science.

References

1 Samanta KK, Basak S & Chattopadhyay SK, Sustainable flame-retardant finishing of textiles: advancement in technology, in *Handbook of Sustainable Apparel Production*, edited by SS Muthu (CRC Press,Boca Raton), 2015, 51.

2 Schindler WD & Hauser PJ, *Chemical Finishing of Textiles* (Woodhead Publishing Limited, Boston, New York), 2004, 98.

3 Horrocks AR, *Polym Degrad Stab,* 96 (2011) 377.

4 Pandit P, Singha K, Kumar V & Maity S, Advanced flame-retardant agents for protective textiles and clothing, in *Advances in Functional and Protective Textiles*, edited by S Ul-Islam and BS Butola (Woodhead Publishing Limited), 2020, 397.

5 Alongi J, Carletto R A, Di Blasio A, Carosio F, Bosco F & Malucelli G, *J Mater Chem A,* 1 (2013) 4779.

6 Fang F, Zhang X, Meng Y, Ding X, Bhao C, Li S, Zhang H & Tian X, *Cellulose,* 23 (2016) 2161.

7 Basak S, Samanta KK, Chattopadhyay S K, Pandit P & Maiti S, *Color Technol,* 132 (2016) 135.

8 Cheng XW, Guan JP, Chen G, Yang XH & Tang RC, *Polymers,* 8 (2016) 122.

9 Carosio F, Di Blasio A, Cuttica F, Alongi J & Malucelli G, *Ind Eng Chem Res,* 53 (2014) 3917.

10 Malucelli G, Textile finishing with biomacromolecules: A low environmental impact approach in flame retardancy, in *The Impact and Prospects of Green Chemistry for Textile Technology*, edited by S Ul-Islam and BS Butola (Woodhead Publishing Limited 2018), 251.

11 Calamari TA & Harper RJ, Flame retardants for textiles, in *Kirk-Othmer Encyclopedia of Chemical Technology*, edited by K Othmer (John Wiley & Sons Inc.), 1980.

12 Zaikov GE & Lomakin SM, *J Appl Polym Sci,* 86 (2002) 2449.

13 Costes L, Laoutid F, Brohez S & Dubois P, *Mater Sci Eng R Reports,* 117 (2017) 1.

14 Van der Veen I & de Boer J, *Chemosphere,* 88 (2012) 1119.

15 Inagaki N, Hamajima K & Katsuura K, *J Appl Polym Sci,* 22 (1978) 3283.

16 Tang B, Poma G, Bastiaensen M, Yin SS, Luo X J, Mai B X & Covaci A, *Environ Int*, 126 (2019) 512.

17 Zhang W, Yang ZY, Tang RC, Guan JP & Qiao YF, *J Clean Prod,* 250 (2020) 119545.

18 Salmeia KA, Gaan S & Malucelli G, *Polymers,* 8 (2016) 319.

19 Levchik SV &Weil E D, Developments in phosphorus flame retardants, in *Advances in Fire Retardant Materials*, edited by AR Horrocks , D Price (Woodhead Publishing Limited, Boston, New York), 2008, 41.

20 Horrocks AR, Flame Retardant Textile Finishes, in *Textile Finishing: Recent Developments and Future Trends*, edited by K L Mittal and T Bahners (Scrivener Publishing LLC), 2017, 69.

21 Ghosh A, *Int J Eng Technol,* 11 (2011) 34.

22 El-Hady MMA, Farouk A & Sharaf S, *Carbohydr Polym,* 92 (2013) 400.

23 Kundu C K, Song L & Hu Y, *J Taiwan Inst Chem Eng,* 112 (2020) 15.

24 Ortelli S, Malucelli G, Cuttica F, Biosi M, Zanoni I & Costa A L, *Cellulose,* 25 (2018) 2755.

25 Alongi J, Carosio F & Malucelli G, *Polym Degrad Stab,* 106 (2014) 138.

26 Fang F, Zhang X, Meng Y, Gu Z, Bao C, Ding X, Li S, Chen X X & Tian X Y, *Surf Coatings Technol,* 262 (2015) 9.

27 Laufer G, Kirkland C, Morgan AB & Grunlan JC, *Biomacromolecules,* 13 (2012) 2843.

28 Carosio F, Di Blasio A, Alongi J & Malucelli G, *Polymer,* 54 (2013) 5148.

29 Carosio F, Fontaine G, Alongi J & Bourbigot S, *ACS Appl Mater Interfaces,* 7 (2015) 12158.

30 Fang F, Chen X, Zhang X, Cheng C, Xiao D, Meng Y, Ding X, Zhang H & Tian X, *Prog Org Coatings,* 90 (2016) 258.

31 Tsafack M J & Levalois-Grützmacher J, *Surf Coatings Technol,* 201 (2006) 2599.

32 Thi H N, Hong KVT, Ha TN & Phan DN, *Polymers,* 12 (2020) 1.

33 Lam YL, Kan CW & Yuen CWM, *Cellulose,* 18 (2011) 151.

34 Pandit P, Nadathur GT & Maiti S. Green and Sustainable Textile Materials using Natural Resources, in *Green and Sustainable Advanced Materials Vol 1: Processing and Characterization*, edited by S Ahmed and C M Hussain (Scrivener Publishing), 2018, 213.

35 Malucelli G, *Molecules,* 24 (2019) 3774.

36 Malucelli G, Bosco F, Alongi J, Carosio F, Di Blasio A, Mollea C, Cuttica F & Casale A, *RSC Adv,* 4 (2014) 46024.

37 El-Tahlawy K, *J Text Inst,* 99 (2008) 185.

38 Alongi J, Carletto R A, Di Blasio A, Cuttica F, Carosio F, Bosco F & Malucelli G *Carbohydr Polym,* 96 (2013) 296.

39 Bosco F, Carletto R A, Alongi J, Marmo L, Di Blasio A & Malucelli G, *Carbohydr Polym,* 94 (2013) 372.

40 Alongi J, Carletto R A, Bosco F, Carosio F, Di Blasio A , Cuttica F, Antonucci V, Giordano M & Malucelli G, *Polym Degrad Stab,* 99 (2014) 111.

41 Zhang W, Wang M, Guan J P, Tang RC & Qiao YF, *J Taiwan Inst Chem Eng,* 101 (2019) 1.

42 Wang X, Lu C & Chen C, *J Appl Polym Sci,* 131 (2014) 1.

43 Basak S, Samanta KK & Chattopadhyay S K, *J Text Inst,* 106 (2015) 1338.

44 Basak S, Samanta KK, Saxena S, Chattopadhyay S K, Narkar R, Mahangade R & Hadge GB, *Polish J Chem Technol,* 17 (2015) 123.

45 Zhang X, Zhou X Y, Cheng XW & Tang RC, *J Clean Prod,* 198 (2018) 1044.

46 Teli M D & Pandit P, *J Ind Text,* 48 (2018) 87.

47 Teli MD, Pandit P & Basak S, *J Ind Text,* 47 (2018) 1261.

48 Teli MD & Pandit P, *ACS Sustain Chem Eng,* 5 (2017) 8323.

49 Bosco F, Casale A, Gribaudo G, Mollea C & Malucelli G, *Ind Crops Prod,* 108 (2017) 208.

50 Nam S, Condon BD, Xia Z, Nagarajan R, Hinchliffe DJ & Madison C A, *J Anal Appl Pyrolysis,* 126 (2017) 239.

51 Yang TT, Guan JP, Tang RC & Chern G, *Ind Crops Prod,* 115 (2018) 16.

52 Yang T T, Guan JP, Chen G & Tang RC, *Ind Crops Prod,* 111 (2018) 117.

53 Meena V & Sheikh J, *Cellul Chem Technol,* 52 (2018) 883.

54 Basak S & Ali S W, *Polym Degrad Stab,* 144 (2017) 83.

55 Cheng TH, Liu ZJ, Yang JY, Huang YZ, Tang RC & Qiao Y F, *ACS Sustain Chem Eng,* 7 (2019) 18405.

56 Zhou Y, Tang RC, Xing T, Guan JP, Shen ZH & Zhai AD, *Ind Crops Prod,* 130 (2019) 580.

57 Guo L, Yang ZY, Tang RC & Yaun HB, *ACS Sustain Chem Eng,* 8 (2020) 5966.

58 Barbalini M, Bartoli M, Tagliaferro A & Malucelli G, *Polymers*, 12 (2020) 811.

59 Cheng XW, Huang Y T, Zhang C, Gu WW, Ma YD, Shi FY & Guam J P, *J Clean Prod,* 266 (2020) 121977.

60 Kozlowski R, Wesolek D, Wladyka-Przybylak M, Duquesne S, Vannier A, Bourbigot S & Delobel R, Intumescent Flame-Retardant Treatment for Flexible Barriers, in *Multifunctional Barriers for Flexible Structure*, edited by S Duquesne, C Magniez and G Camino (Springer Series in Material Science), 2007, 36.

61 Lu Y, Jia Y, Zhang G & Zhang F, *Cellulose,* 25 (2018)5389.

62 Fang F, Xiao D, Zhang X, Meng Y, Cheng C, Bao C, Ding X, Cao H & Tian X, *Surf Coatings Technol,* 276 (2015) 726.

63 Fang Y, Liu X & Tao X, *Prog Org Coatings,* 134 (2019) 162.

64 Rosace G, Colleoni C, Trovato V, Iacono G & Malucelli G, *Cellulose*, 24 (2017) 3095.

65 Li S, Lin X, Li Z & Ren Z, *Compos Commun,* 14 (2019) 15.

66 Zhang T, Yan H, Wang L & Fang Z, *Ind Eng Chem Res,* 52 (2013) 6138.

67 Chan SY, Si L, Lee KI, Ng PF, Chen L, Yu B, Hu Y, Yen R K K, Xin J H & Fei B, *Cellulose,* 25 (2018) 843.

68 Jimenez M, Guin T, Bellayer S, Dupretz R, Bourbigot S & Grunlan J C, *J Appl Polym Sci,* 133 (2016) 1.

69 Li L, Chen G, Liu W, Li J & Zhang S, *Polym Degrad Stab,* 94 (2009) 996.

70 Pallmann J, Ren YL, Mahltig B & Huo TG, *J Appl Polym Sci,* 136 (2019) 1.

71 Apaydin K, Laachachi A, Ball V, Jimenez M, Bourbigot S & Ruch D, *Colloids Surfaces A Physicochem Eng Asp,* 469 (2015) 1.

72 Chang S, Slopek RP, Condon B & Grunlan JC, *Ind Eng Chem Res,* 53 (2014) 3805.

73 Alongi J, Carosio F & Malucelli G, *Cellulose,* 19 (2012) 1041.

74 Chen S, Li X, Li Y & Sun J, *ACS Nano,* 9 (2015) 4070.

75 Apaydin K, Laachachi A, Ball V, Jimenez M, Bourbigot S, Toniazzo V & Ruch D, *Polym Degrad Stab,* 106 (2014) 158.

76 Fu J, Yang F, Chen G, Zhang G, Huang C & Guo Z, *New J Chem,* 43 (2019) 10183.

77 Faheem S, Baheti V, Tunak M, Wiener J & Militky J, *Cellulose,* 26 (2019) 3557.

78 Basak S, Samanta KK, Chattopadhyay SK, Saxena S & Narkar R, *Indian J Fibre Text Res,* 43 (2018) 36.

79 Zhou Y, Cui YZ, Liu GJ & Lv LH, *Adv Mater Res,* 785(2013) 714.

80 Illeperuma W R K, Rothemund P, Suo Z & Vlassak JJ, *ACS Appl Mater Interfaces,* 8 (2016) 2071.

81 Cui XF, Zheng WJ, Zou W, Liu XY, Yang H, Yan J & Gao Y, *Polym Chem,* 10 (2019) 5151.

82 Yu Z, Suryawanshi A, He H, Liu J, Li Y, Lin X & Sun Z, *Cellulose,* 27 (2020) 5391.

83 Ahmed E M, *J Adv Res,* 6 (2015) 105.

84 Mallick BN, Rana PK & Sahoo PK, *Adv Polym Technol,* 34 (2015) 1.

85 Wood LL & Fulmer GE, *US Pat* 19, 18974, 9 March 1979.

86 Cai J R, Cui A & Cheng K, Development of a hydrogel-based intumescent flame retardant system for limiting wildfire propagation in *ACS Spring 2020 National Meeting & Expo*, 2020, 1.

87 Yu Z, Liu J, He H, Ma S & Yao J, *Carbohydr Polym,* 255 (2021) 117485.

88 Liu X & Xiao C, *Environ Technol Inno,* 20 (2020) 101087.

89 Jiang Z & Dou G, *ACS Omega,* 5 (2020) 2303.

90 Xing W, Jie G, Song L, Hu S, Lv X, Wang X & Hu Y, *Thermochim Acta,* 5123 (2011) 75.

91 Kim S J & Jang J, *Fibers Polym,* 18 (2017) 2328.

92 Carosio F, Di Blasio A, Cuttica F, Alongi J, Frache A & Malucelli G, *Ind Eng Chem Res,* 52 (2013) 9544.

93 Zope I S, Foo S, Seah D, Akunuri A & Dasari A, *ACS Appl Mater Interfaces,* 9 (2017) 40782.

94 Alongi J, Carosio F, Frache A & Malucelli G, *Carbohydr Polym,* 92 (2013) 114.

95 Giraud S, Bourbigot S, Rochery M, Vroman I, Tighzert L & Delobel R, *Polym Degrad Stab,* 77 (2002) 285.

96 Castellano A, Colleoni C, Iacono G, Mezzi A, Plutino M R, Malucelli G & Rosace G, *Polym Degrad Stab,* 162 (2019) 148.

97 Ren Y, Zhang Y, Gu Y & Zeng Q, *Prog Org Coatings,* 112 (2017) 225.

98 Wang X, Romero MQ, Zhang XQ, Wang R & Wang DY, *RSC Adv,* 5 (2015) 10647.

99 Wu X & Yang C Q, *J Fire Sci,* 27 (2009) 431.

100 Forouharshad M, Montazer M, Bameni Moghadam M & Saligheh O, *J Fire Sci,* 28 (2010) 561.