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DOCTORAL DISSERTATION

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Zagreb, 2023

Sveučilište u Zagrebu

Tekstilno-tehnološki fakultet

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POVRŠINSKA MODIFIKACIJA PAMUČNIH TEKSTILIJA USPORIVAČIMA GORENJA METODOM NANOSA SLOJ-PO-SLOJ

Doktorski rad

Mentori:
Prof. dr. sc. Sandra Bischof & Prof. dr. sc. Bojana Vončina

Zagreb, 2023.

To my son Jura

Disertacija je pisana kao skup objavljenih znanstvenih radova popraćen kritičkim preglednim poglavljem (tzv. Skandinavski model) temeljem članka 14. Pravilnika o doktorskim studijima na Sveučilištu u Zagrebu (pročišćen tekst) od 7. rujna 2016. koji obuhvaća Pravilnik o doktorskim studijima na Sveučilištu u Zagrebu kojega je Senat donio na 11. sjednici održanoj 20. travnja 2010. te Pravilnik o izmjenama i dopunama Pravilnika o doktorskim studijima Sveučilišta u Zagrebu kojega je Senat donio na 10. sjednici održanoj 19. svibnja 2016.

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Tema doktorskog rada „Površinska modifikacija pamučnih tekstilija usporivačima gorenja metodom nanosa sloj-po-sloj“ prihvaćena je na 10. redovitoj sjednici u akademskoj godini 2015./2016. Fakultetskog vijeća Sveučilišta u Zagrebu Tekstilno-tehnološkog fakulteta, održanoj 19. rujna 2016., te odobrena od Senata Sveučilišta u Zagrebu na 5. redovnoj sjednici Senata održanoj 15. studenog 2016., u akademskoj godini 2016./2017. Odluka o pisanju doktorskog rada prema skandinavskom modelu donešena je na 5. redovitoj sjednici Senata Sveučilišta u Zagrebu održanoj 25. siječnja 2022. (KLASA : 643-03/21-11/135, Urbroj 380-130/134-22-4)

The dissertation was written as a set of published scientific papers accompanied by a critical review chapter (Scandinavian model) based on article 14 of the Doctoral studies regulations at the University of Zagreb (consolidated text) from 7th September 2016, which includes the Doctoral studies regulations at the University of Zagreb adopted by the Senate at its 11th session, held on 20th April 2010 and the Rulebook on amendments to Doctoral studies regulations at the University of Zagreb, adopted by the Senate at its 10th session, held on 19th May 2016.

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The topic of the dissertation "Flame Retardant Surface Modification of Cotton Textiles Using Layer-by-Layer Deposition" was accepted at the 10th regular session of the Faculty Council of the University of Zagreb Faculty of Textile Technology in the academic year 2015/2016, held on 19th September 2016, and approved by the Senate of the University of Zagreb at the 5th regular Senate session held on 15th November 2016, in the academic year 2016/2017. The decision to write the topic of the dissertation according to the Scandinavian model was approved by the Senate of the University of Zagreb at the 5th regular Senate session held on 25th January 2022 (KLASA: 643-03/21-11/135, Urbroj: 380-130/134-22-4).

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SUMMARY

The main goal of this thesis was to develop sustainable and biodegradable flame retardant (FR), as well as multifunctional FR/antimicrobial (AM), finishing of cotton by means of an emerging technique called layer-by-layer (LbL) deposition as a response to technological drawbacks of current commercial FR and multifunctional wet finishing processes. Those are high amounts of conventionally applied chemicals, emission of toxic and cancerogenic formaldehyde during production or product life cycle, loss of tensile strength of FR-treated cotton fabrics, and a large number of process steps at high temperatures, which require high water and energy consumption. Additionally, the current Pyrovatex® process is less compatible with antibacterial finishes, so it is challenging to fulfill commercial requirements for FR/AM cotton, such as limiting oxygen index (LOI) values of ≥ 28%, self-extinguishing in vertical flammability test (VFT) and 100% bacteria reduction at the same time. In this thesis, a conventional treatment that usually requires the addition of very high amounts of different FR compounds has been replaced with an environmentally friendlier treatment. LbL deposition uses the ability of polyelectrolyte aqueous solutions to build charged layered assemblies attracted by weak electrostatic forces on the surface of chemically bleached cotton, with slight influence on mechanical properties of treated cotton fabric and at temperatures below 100 °C. Additionally, by means of LbL deposition, cotton was successfully functionalized with FR and AM agents by using only chemicals from renewable sources such as cereals, legumes, and crustaceans waste or minerals.

In this thesis, several environmentally friendly and low-cost agents from renewable sources have been used for LbL: cationic branched polyethyleneimine solution (BPEI, 5 wt%), anionic phytic acid salts solution (PA, 2 wt%, pH 4), cationic chitosan solution (CH, 0.5 wt%, pH 4), and copper (II) sulfate pentahydrate ($CuSO_4$ x $5H_2O$, 2 wt%) to reduce the flammability of cotton and achieve additional antimicrobial properties. BPEI has been used as a prime layer for better adhesion to cotton. Cotton has been alternately immersed into anionic PA and cationic CH-urea (U) solutions until the desired number of bilayers (BL) has been reached. Each deposition step was followed by rinsing in deionized water (DI) to remove all unbound polyelectrolytes. The final step was the immersion into $CuSO_4$ x $5H_2O$ solution to increase AM properties.

The LbL deposited cotton fabric self–extinguished in VFT with the LOI values ranging from 24.5 to 28.0% with 17.3–19.0% of add-ons compared to a conventional process, where the add-on ranges from 20.0–25.0%. For comparison, add-on of non-durable FR finishes such as boric acid/borax, is ~ 10%, and diammonium phosphate/ammonium sulfamate is ~ 15%.

Furthermore, the Pyrovatex® process, which requires about 350 g/l of different agents, was replaced by a more environmentally friendly treatment using agents in a concentration usually ≤ 100 g/l with a slight influence on the mechanical properties of the treated cotton fabric (up to ± 14 % change in break strength) at temperatures below 100 °C. In comparison, the Pyrovatex® process reduces the breaking strength by 20-25%, while non-durable FR agents generally reduce the breaking strength.

The microscale combustion calorimeter (MCC) values showed a peak heat release rate (pHRR) reduction of 50.9–61.8% and a total heat release rate (THR) reduction of 54.3–70.3%, compared with untreated cotton.

Thermogravimetric (TGA) analysis showed the reduction of the first decomposition temperature peak (T_1) of 57–66 °C relative to untreated cotton and an increase of char yield (%) at T_1 from ~ 43–46% for untreated to ~ 56–63% for FR treated cotton fabric.

The post-burn char mainly contains carbon, oxygen, phosphorus, nitrogen (and copper) as measured by energy-dispersive X-ray spectroscopy (EDS) analysis.

SEM analyses confirmed N-P intermediates, produced by PA and CH-U upon heating, which phosphorylate cellulose at a temperature below 350–400 °C by producing intumescent char, which acts as a physical barrier that blocks heat and oxygen to the polymer surface. The addition of Cu^{2+} metal ions further catalyzes cellulose phosphorylation. At the same time, generated non-flammable gases dilute the concentration of the combustible gases and absorb heat, causing the bubbling effect.

The FR/AM nanocoating also reduced Gram-negative *K. pneumoniae* and Gram-positive *S. aureus* bacteria by almost 100%.

Using LbL deposition proved to be an alternative and efficient FR and AM treatment applying environmentally benign compounds from renewable sources in very low concentrations for non durable purposes only. With the wider availability of biodegradable chemicals from renewable sources at lower costs and improving wash durability, LbL deposition has the potential to become an industrially feasible solution for FR or multifunctional FR/AM functionalization of cotton. Future research will be expanded to the improvement of wash durability as well as dye compatibility with conventional dyeing/printing processes.

KEYWORDS: layer-by-layer, cotton, flame retardant finishing, antimicrobial finishing, phytic acid, environmentally friendly finishing

SAŽETAK

Tekstilna industrija jedna je od vodećih svjetskih industrija čiji proizvodi obuhvaćaju gotovo svaki aspekt svakodnevnog života s različitim proizvodima jer se mogu koristiti u modi, zabavi, medicini, transportu, sportu i wellnessu, kućanstvu, poljoprivredi i vojsci. Najveći tržišni udio od 52 % ukupne svjetske proizvodnje vlakanaje je u 2020. imao poliester (PES). Drugo najprodavanije vlakno u svijetu bio je pamuk s udjelom od 24 %, treće mjesto je pripalo poliamidu (PA 66) s udjelom od 5 %, dok na sva ostala vlakna otpada 19 %. Tekstilna industrija je jedan od najvećih zagađivača okoliša počevši od uzgoja biljke, preko procesa proizvodnje vlakana, predenja, bojanja, tiska i završne obrade tkanina u kojima se koristi ogromna količina fosilnih goriva, toksičnih kemikalija, vode i električne energije. Europska komisija je 2020. izdala novi akcijski plan kružnog gospodarstva za čišću i konkurentniju Europu sa naglaskom na razvoj mjera kojima se s jedne strane potiču potrošači da upotrebljavaju održive tekstilne materijale proizvedene iz sekundarnih sirovina ili nastale recikliranjem, a s druge se strane potiču proizvođači da smanjuju upotrebu toksičnih kemikalija u proizvodnim procesima upotrebom ekološki prihvatljivijih kemikalija ili uvođenjem novih zelenih tehnologija. Ovaj doktorski rad bavi se problematikom upotrebe velikih količina kemikalija u postupcima mokre obrade pamučnih tekstilija obrađenih usporivačima gorenja (*engl. flame retardant* – FR) i multifunkcionalnim FR/antimikrobnim (AM) obradama primjenom inovativne tehnike visoko učinkovite obrade pod nazivom „sloj-po- sloj (*engl. layer-by-layer* – LbL) naslojavanje uz primjenu alternativnih kemikalija iz biljnih/životinjskih i mineralnih izvora.

Pamuk pripada skupini biljnih celuloznih vlakana, te se sastoji od celuloze (~ 94,0 %), proteina (~ 1,3 %), anorganskog pepela (~ 1,2 %), pektina (~ 0,9 %), jabučne, limunske i drugih organskih kiselina (~ 0,8 %), voska (~ 0,6 %), ukupnog šećera (~ 0,3 %) i ostalog (~ 0,9 %). Celuloza $(C_6H_{10}O_5)_n$ je polimer nastao polikondenzacijom anhidro–d–glukopiranoznih jedinica u konfiguraciji $4C_1$ lanca povezanih β–1,4–glukozidnim vezama u kristalnoj strukturi sa stupnjem polimerizacije (DP) od 1.000–30.000. U svakoj jedinici anhidroglukoze unutar molekule celuloze postoje tri reaktivne hidroksilne skupine (primarna skupina na C6 i dvije sekundarne grupe na C2 i C3 grupama) smještene u ravnini prstena. Ove hidroksilne skupine (-OH), atomi kisika d-glukopiranoznog prstena (-O-) i glikozidna veza (-O-) međusobno djeluju unutar lanca ili s drugim celuloznim lancem tvoreći intramolekularne i intermolekularne vodikove veze (H-veze), koje su odgovorne za snažnu interakciju između celuloznih lanaca. U amorfnim dijelovima celuloze, kao i na površini vlakana, ove negativno nabijene -OH i -O- funkcionalne skupine odgovorne su za H-vezivanje molekula vode, kao i za adsorpciju

pozitivno nabijenih molekula koje privlače slabe elektrostatske sile. Zbog visoke reaktivnosti funkcionalnih skupina -OH i -O- u molekuli celuloze, može doći i do nekoliko kemijskih reakcija kao što su: supstitucija (esterifikacija, eterifikacija), deoksihalogenacija, oksidacija, kisela hidroliza, oksidativno cijepanje, oksidacija u karboksilne skupine, redukcija u alkohol i/ili formiranja radikala. Funkcionalne skupine su odgovorne za visoku propusnost vlage i vode, kao i za visoku zapaljivost. S jedne strane pamuk je ugodan za nošenje, ali je sklon rastu bakterija. Zbog toga je pamučne tkanine namijenjene za radnu i zaštitnu odjeću potrebno obraditi usporivačima gorenja, a one koje se upotrebljavaju u domaćinstvima, ugostiteljskim objektima ili ustanovama za medicinsku skrb i njegu, poželjno je i dodatno obraditi antimikrobnim sredstvima. Na tržištu postoje postojane i nepostojane obrade protiv gorenja. Postojane se temelje na organo-fosfornim spojevima kod kojih je prisutan sinergizam dušika i fosfora, s minimalnim udjelom fosfora od 1 – 3%. To su N-metiloldialkilfosfonopropionamidi (tzv. Pyrovatex® postupak) i (hidroksimetil)fosfonijev klorid (THPC)/urea (tzv. Proban® postupak). Tipična Pyrovatex® receptura sastoji se od oko 350 g/l različitih kemikalija (N-metiloldialkilfosfonopropionamida, melaminske smole, omekšivača, kiselog katalizatora i sredstva za kvašenje). Pyrovatex® postupak se sastoji od nekoliko proizvodnih koraka: impregnacija tkanine, sušenje, umrežavanje na 170 °C, neutralizacija u lužnatom mediju, nekoliko ciklusa pranja u vodi i ponovno sušenje, što zahtijeva velike količine vode i električne energije. Slobodni formaldehid se oslobađa za vrijeme umrežavanja na temperaturama većim od 140 °C. Izloženost formaldehidu udisanjem, dermalnim kontaktom i kontaktom očima dovodi do oštećenja organa, a može uzrokovati karcinom nazofarinksa, plućnu fibrozu, teratogenost, neurotoksičnost itd. Pamučna tkanina obrađena Pyrovatexom® dobiva na masi 20 – 25 %, dok istovremeno gubi na vlačnoj čvrstoći 20 – 25 % i na prekidnoj sili do 50 %. Kod Pyrovatex® postupka moguće je istovremeno pamučnu tkaninu obraditi i FR i vodoodbojnim/uljeodbojnim obradama, no vrlo je teško istovremeno postići FR i AM obradu zbog različite prirode vezivanja, odnosno mehanizma djelovanja usporivača gorenja i antimikrobnih sredstava. Tzv. Proban® postupak se uglavnom koristi na američkom tržištu, te se sastoji od nekoliko koraka: impregnacija pamučne tkanine otopinom ili pjenom THPC/uree kompleksa u prisutnosti sredstva za kvašenje i omekšavanje, sušenje, umrežavanje amonijakom, oksidacija polimera u poli(fosfinoksid) u razrijeđenoj kupelji hidrogen peroksida, nekoliko ciklusa pranja u vodi i sušenje na kraju postupka. Za razliku od Pyrovatex® postupka, u potonjem se umreženi polimer ne veže na molekulu celuloze, već se umreženi polimer međusobno prožima unutar strukture mikrofibrilarne celuloze. Za Proban® postupak je potrebna specijalizirana jedinica za umrežavanje amonijakom. Izloženost amonijaku udisanjem, dermalnim kontaktom i kontaktom očima dovodi do ozljeda rožnice i opeklina na koži, kronične plućne bolesti, a može izazvati i neurotoksičnost. Postojani usporivači gorenja su vezani za celulozu čvrstim kovalentnim vezama (Pyrovatex®) ili su umreženi unutar mikrofibrilarnih struktura celuloze (Proban®) kako se ne bi otpuštali tijekom životnog ciklusa proizvoda. U komercijalne nepostojane obrade protiv gorenja spadaju dinatrijev tetraborat ili boraks ($Na_2B_4O_7$ x $10H_2O$), amonijev polifosfat ($(NH_4)_3PO_4$), diamonijev fosfat ($(NH_4)SO_3NH_2$), amonijev sulfamat ($(NH_4)SO_3NH_2$) i amonijev bromid (NH_4Br).

Antimikrobni spojevi namijenjeni pamuku ne bi smjeli biti vezani za celulozu čvrstim kovalentnim vezama jer se na taj način ne mogu kontrolirano otpuštati u prisutnosti vlage, te time usporavati rast bakterija. Antimikrobna sredstva koja se koriste u postupcima mokre obrade pamuka najčešće su kvaternarni amonijevi spojevi, limunska kiselina, metalne (nano)čestice (i soli), prirodni polimeri (npr. kitozan), ekstrakti različitih biljnih eteričnih ulja itd.

Kako bi se prevladali gore navedeni tehnološki nedostaci obrada protiv gorenja kao i multifunkcionalnih FR/AM obrada pamučnih tkanina, javila se potreba za uvođenjem novih ekološki povoljnijih sredstava, ali i metoda kao što su npr. sol-gel, UV obrade, obrade plazmom, te LbL naslojavanje.

LbL naslojavanje je postupak uranjanja pamučne tkanine naizmjenično u otopine pozitivno i negativno nabijenih polielektrolita do postizanje željenog broja dvoslojeva (BL), troslojeva (TL) ili četveroslojeva (QL) različitih funkcionalnosti. Između svakog uranjanja u suprotno nabijene polielektrolite tkanina se ispire u deioniziranoj vodi (DI). Interakcija između slojeva suprotnih naboja prvenstveno je uzrokovana slabim elektrostatičkim silama, ali i na interakcijama donor/akceptor, donor/akceptor H-vezi, kovalentnim vezama, π-π interakcijama i stereo kompleksnim formacijama. Kod konvencionalnog LbL naslojavanja, slojeve suprotnog naboja privlače slabe elektrostatske sile polielektrolita topivih u vodi, polianiona i polikationa s jednom nabijenom grupom po monomernoj jedinici, ali i polimeri koji mogu tvoriti H-veze. Ove veze su osjetljive na uvjete okoliša i formirani slojevi se iz tog razloga lako razbijaju. Za formiranje trajnih slojeva koriste se koordinacijski polimeri koji mogu formirati organsko-anorganske hibridne višeslojne strukture. Ove složene strukture mogu se dalje podvrgnuti postkemijskim reakcijama, kao što su UV ili toplinsko umrežavanje. Nekonvencionalne metode LbL naslojavanja obično uključuju dva koraka. Prvi korak je formiranje supramolekularnog kompleksa na temelju različitih interakcija (elektrostatskih, vodikovih ili π-π kompleksa, blok kopolimernih micela) u rasutom stanju. U drugom koraku, supramolekularni kompleks se koristi kao građevni blok za sastavljanje LbL struktura. Kemijski bijeljeni pamuk posjeduje negativno nabijene skupine sposobne za interakciju s pozitivno nabijenim (makro)molekulama slabim elektrostatskim silama i H-vezama, što ga čini odličnim supstratom za LbL naslojavanje. Zbog visoke reaktivnosti -OH skupine također mogu formirati organsko-anorganske hibridne višeslojne strukture, kao i supramolekularne komplekse kovalentnim vezanjem, π-π interakcijama i stereokompleksnim formacijama.

Glavni cilj ove doktorske dizertacije bio je razviti alternativnu vatrootpornu i/ili multifunkcionalnu FR/AM obradu namijenjenu pamučnim tkaninama uz pomoć nove tehnike koja se naziva sloj-po-sloj (LbL) naslojavanje uz korištenje sredstava iz obnovljivih izvora (biljni i životnijski otpad), te minerala od kojih su neki poznati od davnina.

U ovom radu korištena su ekološki prihvatljiva sredstava za LbL naslojavanje pamuka: fitinska kiselina (PA) i kitozan (CH). Dodatno su korišteni razgranati polietilenimin (*engl. branched polyethylenimine* - BPEI), urea (U) i bakrov (II) sulfat pentahidrat ($CuSO_4$ x $5H_2O$) kako bi se smanjila zapaljivost pamuka i postigla višenamjenska FR/AM svojstva. PA soli kelatirajuća su sredstva bogata fosforom (P ~ 28 % Mw) koje se dobivaju iz biljnih/sjemenskih izvora (mahunarke, žitarice, uljarice, pelud i orašasti plodovi). Lako apsorbiraju viševalentne metale stvarajući netopive komplekse. PA soli se koriste kao dodatak prehrani, pa je njihova upotreba sigurna za zdravlje. CH je prirodni linearni polisaharid koji se sastoji od nasumično raspoređenog β-(1-4)-vezanog D-glukozamina (deacetilirana jedinica) i N-acetil-D-glukozamina (acetilirana jedinica). CH je izabran zbog široke dostupnosti jer se nalazi u egzoskeletu škampa, rakova, kukaca i stijenkama gljiva. Može se otopiti samo u kiselom mediju (pH ~ 4), zbog pKa vrijednosti amino skupine od 6,5. Stupanj deacetilacije hitina kao i protoniranje amino skupina smještenih na C-2 poziciji D-glukozamina daju molekuli CH pozitivan naboj, što je čini dobrim sredstvom za LbL naslojavanje. Budući da je bogat ugljikom (C) i dušikom (N), CH je potencijalno sredstvo za pjenjenje u bubrećim obradama protiv gorenja, ako je vezan na fosforne (P) spojeve koji generiraju fosfonsku kiselinu kod zagrijavanja. S druge strane CH je dobro poznato sredstvo za kelatiranje, kao i antimikrobno sredstvo, pa se u svrhu LbL naslojavanja pamuka, pozitivno nabijena otopina CH može pomiješati sa spojevima male molekularne mase kao npr. urea (U) ili solima bakra (Cu^{2+}) kako bi se poboljšala FR svojstva pamuka, te istovremeno postigla i antibakterijska svojstva. BPEI je viskozan kationski polimer topiv u vodi i bogat dušikom (N) koji osim primarnih i sekundarnih posjeduje i tercijarne amino skupine. Kationski naboj BPEI-a omogućuju protonirane amino skupiname (NH^+, NH^{2+}, NH^{3+}), koje snažno stupaju u interakciju s negativno nabijenim polimerima. Kao kationski polimer bogat dušikom, BPEI se koristi u LbL naslojavanju pamuka kao temeljni sloj za bolje prianjanje na pamuk ili kao alternativa za komercijalne organofosforne usporivače gorenja ukoliko se kombinira sa sredstvima na bazi fosfora (P) s kojim djeluje sinergistički. Urea (U) je bezbojna netoksična molekula topiva u vodi i bogata dušikom. Bakrov (II) sulfat pentahidrat ($CuSO_4$ x $5H_2O$) odnosno modra galica je među najstarijim korištenim antimikrobnim sredstvima, ali zbog svoje karakteristične plave boje nije široko korišten za obrade tekstilnih materijala. Bakar se i danas koristi u dermatologiji kao sredstvo za njegu kože protiv iritacije zbog visoke osjetljivost mikroorganizama na bakar.

U ovoj doktorskoj dizertaciji pamuk je prvo uronjen u kationsku otopinu BPEI (5 wt%) koji je temeljni sloj za bolje prianjanje sredstava na pamuk. Pamučna tkanina je zatim naizmjenično uronjena u anionsku PA (2 wt%, pH 4) i kationsku otopinu CH-U (u 0,5 wt% CH otopinu dodano je 10 wt% U, pH 4) dok se ne postigne željeni broj dislojeva (BL). Nakon svakog koraka naslojavanja slijedilo je ispiranje u DI kako bi se uklonili svi nevezani polielektroliti. Na kraju LbL naslojavanja pamučna tkanina je uronjena u otopinu $CuSO_4$ x $5H_2O$ (2 wt%).

Masa svih uzoraka izmjerena je nakon sušenja na 80 °C tijekom 24 sata, prije i nakon LbL naslojavanja, kako bi se izračunao maseni prirast (%).

Zapaljivost uzoraka je izmjerena ispitivanjem gorivosti vertikalnim testom prema ASTM D6413/D6413M-15 normi i u uređaju za ispitivanje graničnog indeksa kisika (LOI, %) prema ISO 4589-2:2017 normi.

Toplinska svojstva kao što su brzina oslobađanja topline (pHRR, W/g) i ukupna brzina oslobađanja topline (THR, J/g) ispitana su na mikrokalorimetru za sagorijevanje (*engl. microscale combustion calorimeter* - MCC) zagrijavanjem od 75-650 °C (brzina zagrijavanja od 1 ° C/min) u smjesi plinova koja se sastoji od 20 % O_2 i 80 % N_2 prema ASTM D7309-19a normi A.

Termogravimetrijskom analizom (*engl. thermogravimetric analysis* - TGA) je mjeren gubitak mase (%) tijekom kontroliranog zagrijavanja od 50 do 850 °C pri 30 °C/min u zraku. Iz osnovnih podataka su dalje izvedene derivativne termogravimetrijske krivulje (*engl. derivative thermogravimetric DTG curves*).

Analiza razvijenih plinova (*engl. evolved gas analysis* - EGA) nastalih tijekom zagrijavanja uzoraka ispitana je primjenom FT-IR spektrometra (*engl. Fourier-transform infrared* – FT-IR) s TG-IR sučeljem (engl. *thermogravimetric – infrared* – TG-IR*)* u apsorbanciji, u rasponu valnih duljina 4000–450 cm^{-1}, razlučivosti 4,0 cm^{-1} i s intervalom zagrijavanja od 27 minuta. Spektri su analizirani putem softvera PerkinElmer Spectrum 100 v 6.3.5 uz automatsku korekciju bazne linije i normalizaciju prema sljedećim parametrima maksimuma apsorpcijskih vrpca: granica ordinate 1.5 A, početak valne duljine 4000 cm^{-1}, kraj 450 cm^{-1}, automatska nulta točka 2318 cm^{-1}.

Morfologija uzoraka, prije i nakon ispitivanja gorivosti, analizirana je skenirajućim elektronskim mikroskopom SEM pomoću detektora sekundarnih elektrona (*engl. secondary electron detector* – SE) na 5 kV. Svi uzorci su prethodno napareni slojem od 5 nm kroma zbog elektrovodljivosti.

Kemijska analiza pepela nakon gorenja provedena je pomoću SEM-EDS detektora na 10 i 20 kV.

Antimikrobna ispitivanja provedena su prema normi AATCC 100-2019 primjenom gram-negativne bakterije *K. pneumoniae* i gram-pozitivne *S. aureus*.

Pamučna tkanina obrađena LbL naslojavanjem se sama ugasila tijekom VFT ispitivanja, a vrijednosti LOI-a kretale su se u rasponu od 24,5 – 28,0 % sa 17,3 – 19,0 % prinosa mase u usporedbi s tipičnim Pyrovatex® postupkom, gdje je prinos 20 – 25 %, a vrijednosti LOI-a su oko 28 %. Za usporedbu prinos mase nepostojanih sredstava protiv gorenja npr. borne kiseline/boraks je oko 10 %, a diamonijevog fosfata/amonijevog sulfamata je oko 15 %.

Nadalje u ovoj doktorskoj dizertaciji Pyrovatex® postupak koji zahtijeva oko 350 g/l različitih sredstava zamijenjen je ekološki prihvatljivijim obradom (LbL naslojavenjem) korištenjem sredstava u koncentraciji obično ≤ 100 g/l s neznatnim utjecajem na mehanička svojstva obrađene pamučne tkanine (do ± 14 % prekidne sile) na temperaturama ispod 100 °C. Za usporedbu, Pyrovatex® postupak smanjuje prekidnu silu za 20 – 25 %, dok nepostojana sredstva općenito smanjuju prekidnu silu.

MCC kalorimetrijske vrijednosti pokazale su smanjenje najveće brzine otpuštanja topline (pHRR) za 50,9 – 61,8 % u odnosu na neobrađeni pamuk i smanjenje ukupne brzine oslobađanja topline (THR) za 54,3 – 70,3 % u odnosu na neobrađeni pamuk.

TG analiza je pokazala smanjenje maksimalne temperature dekompozicije (T_1) obrađene pamučne tkanine za 57 – 66 °C u odnosu na neobrađenu i povećanje pougljenjenog ostatka (%) na T_1 u rasponu 43 – 46 % za neobrađenu na 56 – 63 % za obrađenu pamučnu tkaninu.

Na T_1 FT-IR spektri hlapljivih plinova nastali zagrijavanjem pamučne tkanine obrađene LbL naslojavanjem (CH/PA-U) sadrže vodu (H_2O); metan (CH_4)/metanol (CH_3OH); ugljikov dioksid (CO_2); ugljikovog monoksid (CO); formaldehid, eter/ester mravlje kiseline, cikloalkane; N-H, kao i PH i NH spojeve. Levoglukozan koji je odgovoran za visoku zapaljivost celuloze nije pronađen. Naknadnom obradom u otopini $CuSO_4$ x $5H_2O$ hlapljivi plinove nastali zagrijavanjem obrađene pamučne tkanine još dodatno sadrže spojeve sumpora (S-S), bakrov monosulfid (CuS) i bakrov (II) oksid (CuO). N-P plinski međuprodukti mogu djelovati u plinskoj fazi kao hvatači slobodnih radikala.

EDS analiza pokazala je da ostatak nakon gorenja obrađenih tkanina uglavnom sadrži ugljik, kisik, fosfor, dušik u slučaju PA/CH-U obrade, a u slučaju naknadne obrade sa $CuSO_4$ x $5H_2O$ ostatak nakon gorenja dodatno sadržava i bakar. PA i CH-U kod zagrijavanja proizvode N-P međuprodukte, koji fosforiliraju celulozu na temperaturi ispod 350 – 400 °C proizvodeći pougljenjeni ostatak, koji djeluje kao fizička barijera blokirajući dovod topline i kisika na površinu polimera djelujući isto tako i u kondenzirajućoj fazi. Cu^{2+} ioni dodatno kataliziraju fosforilaciju celuloze djelujući u kondenzirajućoj fazi, no istovremeno nanočestice CuO ili CuS prisutne u hlapljivim plinovima mogu djelovati kao inertna prašina koja apsorbira i raspršuje toplinu uzrokujući snižavanje temperature.

FR/antimikrobni nanosloj pokazao je smanjenje Gram-negativne *K. pneumoniae* i Gram-pozitivne *S. aureus* za gotovo 100 % zahvaljujući Cu^{2+} ionima i kitozanu.

U radu je dokazano je da je LbL naslojavanjem pamuka moguće postići učinkovitu kombiniranu FR i AM obradu korištenjem alternativnih sredstava u koncentracijama ≤ 100 g/l, što je znatno manje u odnosu na klasične komercijalne obrade protiv gorenja primjenom tzv. Pyrovatex® postupka, no obrada nije postojana. Također je dokazano da je moguće proizvesti multifunkcionalnu pamučnu tkaninu koja zadovoljava komercijalne zahtjeve FR/AM obrada: zahtjev negorivosti (LOI ≥ 28 %) i smanjenje razvoja gram-negativnih i gram-pozitivnih bakterija za 100 %. Uz veću dostupnost biorazgradivih kemikalija iz obnovljivih izvora po nižim troškovima i poboljšanjem postojanosti na pranje, LbL naslojavanje ima potencijal postati industrijski izvodljivo rješenje za FR ili višenamjensku FR/AM funkcionalizaciju pamuka. Buduća istraživanja proširit će se na poboljšanje postojanosti na pranje kao i kompatibilnost s konvencionalnim procesima bojenja/tiskanja.

KLJUČNE RIJEČI: sloj-po-sloj, pamuk, pirofobna obrada, antimikrobna obrada, fitinska kiselina, ekološki prihvatljiva obrada

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LIST OF PUBLISHED PAPERS

This work is based on the following scientific papers:

1. Magovac, E.; Vončina, B.; Jordanov, I.; Grunlan, J. C.; Bischof, S. Layer-by-Layer Deposition: A Promising Environmentally Benign Flame-Retardant Treatment for Cotton, Polyester, Polyamide and Blended Textiles. *Materials (Basel).* **2022**, *2*, 1–30, doi:10.3390/ma15020432.

Abstract:

A detailed review of recent developments of layer-by-layer (LbL) deposition as a promising approach to reduce flammability of the most widely used fibers (cotton, polyester, polyamide, and their blends) is presented. LbL deposition is an emerging green technology, showing numerous advantages over current commercially available finishing processes due to the use of water as a solvent for a variety of active substances. For flame-retardant (FR) purposes, different ingredients are able to build oppositely charged layers at very low concentrations in water (e.g., small organic molecules and macromolecules from renewable sources, inorganic compounds, metallic or oxide colloids, etc.). Since the layers on a textile substrate are bonded with pH and ion-sensitive electrostatic forces, the greatest technological drawback of LbL deposition for FR finishing is its non-resistance to washing cycles. Several possibilities of laundering durability improvements by different pretreatments, as well as post-treatments to form covalent bonds between the layers, are presented in this review.

2. Magovac, E.; Vončina, B.; Budimir, A.; Jordanov, I.; Grunlan, J. C.; Bischof, S. Environmentally Benign Phytic Acid-Based Nanocoating for Multifunctional Flame-Retardant/Antibacterial Cotton. *Fibers*. **2021**, *13*, 1-13 doi:10.3390/fib9110069.

Abstract:

Environmentally benign layer-by-layer (LbL) deposition was used to obtain flame-retardant and antimicrobial cotton. Cotton was coated with 8, 10, and 12 phytic acid (PA) and chitosan (CH)-urea bilayers (BL) and then immersed into copper (II) sulfate ($CuSO_4$) solution. Our findings were that 12 BL of PA/CH-urea + Cu^{2+} were able to stop flame on cotton during vertical flammability testing (VFT) with a limiting oxygen index (LOI) value of 26%. Microscale combustion calorimeter (MCC) data showed a reduction of peak heat release rates (pHRR) of more than 61%, while the reduction of total heat release (THR) was more than 54%, relative to untreated cotton. TG-IR analysis of 12 BL-treated cotton showed the release of water, methane, carbon dioxide, carbon monoxide, and aldehydes, while by adding Cu^{2+} ions, the treated cotton produces a lower amount of methane.Treated cotton also showed no levoglucosan. The intumescent behavior of the treatment was indicated by the bubbled structure of the post-burn char. Antibacterial testing showed a 100% reduction of *Klebsiella pneumoniae* and *Staphylococcus aureus*. In this study, cotton was successfully functionalized with a multifunctional ecologically benign flame-retardant and antibacterial nanocoating, by means of LbL deposition.

3. Magovac, E.; Budimir, A.; Jordanov, I.; Bischof, S.; Grunlan, J. C. Antibacterial cotton from novel phytic acid-based multilayer nanocoating. *Green Materials.* **2021**, *2000050,* doi:10.1680/jgrma.20.00050.

Abstract:

In an effort to impart antimicrobial behavior to cotton using renewable and environmentally benign components, fabric was treated using layer-by-layer (LbL) assembly. Alternating layers of phytic acid (PA) and chitosan (CH) were deposited from water. Cotton coated with four and eight bilayers (BLs) of anionic PA and cationic CH, with and without adding copper (II) sulfate ($CuSO_4$) into the CH solution, was evaluated in accordance with the American Association of Textile Chemists and Colorists (AATCC) TM 100-2019 test method. Gram positive *Staphylococcus aureus* and gram-negative *Klebsiella pneumoniae* were used to determine whether the addition of copper salt into a CH network improves antibacterial efficacy. The copper ions were successfully incorporated into the CH network formed using LbL assembly onto cotton fibers. The location of deposited copper ions was determined with electron microscopy. Just four BLs of PA/ CH–copper (II) sulfate kill 100% of gram-positive and gram-negative bacteria and add only 5.2 wt% to the fabric. This nanocoating provides a unique opportunity to impart antibacterial behavior to textiles without harming the environment.

4. Magovac, E.; Jordanov, I.; Grunlan, J.C.; Bischof, S. Environmentally-Benign Phytic Acid-Based Multilayer Coating for Flame Retardant Cotton. *Materials (Basel).* **2020**, *13*, 5492, doi:10.3390/MA13235492.

Abstract:

Chemically bleached cotton fabric was treated with phytic acid (PA), chitosan (CH) and urea by means of layer-by-layer (LbL) deposition to impart flame retardant (FR) behavior using only benign and renewable molecules. Samples were treated with 8, 10, 12 and 15 bilayers (BL) of anionic PA and cationic CH, with urea mixed into the aqueous CH solution. Flammability was evaluated by measuring limiting oxygen index (LOI) and through vertical flame testing. LOI values are comparable to those obtained with commercial flame-retardant finishes, and applying 10 or more bilayers renders cotton self-extinguishing and able to pass the vertical flame test. Microscale combustion calorimeter (MCC) measurements show the average reduction of peak heat release rate (pHRR) of all treated fabrics of ~61% and the reduction of total heat release (THR) of ~74%, in comparison to untreated cotton. Decomposition temperature peaks (T1max) measured by thermogravimetric analyzer (TG) decreased by approximately 62 °C, while an average residue at 650 °C is ~21% for 10 and more bilayers. Images of post-burn char indicate that PA/CH-urea treatment is intumescent. The ability to deposit such a safe and effective FR treatment, with relatively few layers, makes LbL an alternative to current commercial treatments.

5. Magovac, E.; Bischof, S. Non-halogen FR treatment of cellulosic textiles. *Tekstil.* **2015**, *64*, 298-309.

Abstract:

A historical overview of the most commonly used textile flame retardants (FR) is given, with an emphasis on halogen-free FRs acting through their mechanism to slow down or prevent burning. Since a large number of halogen FRs are toxic, or potentially toxic, to the organisms and the environment, there is a need for them to be replaced by eco-friendly agents. The paper presents new alternative FRs that are trying to be put into practice, as well as different methods of their application onto textiles in comparison to one another. One of the possible ways of developing alternative FRs could be the application of bio-macromolecules such as chitosan, phytic acid, casein, whey, hydrophobins or DNA.

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ABBREVIATIONS AND SYMBOLS

ALG	alginate
AMM	p-aminobenzene sulfonic acid modified melamine
AP	ammonium phytate
APP	ammonium polyphosphate
APTES	3-aminopropyl triethoxysilane
BaCl2	barium chloride
BL	bilayer
BPEI	branched polyethyleneimine
BSE	back-scatter electron detector
C	carbon
CC	cone calorimeter
$(C_6H_{10}O_5)_n$	cellulose
$C_4H_6O_4Co$ x $4H_2O$	cobalt acetate tetrahydrate
$C_4H_6O_4Ni$ x $4H_2O$	nickel acetate tetrahydrate
CH	chitosan
CH_2O	formaldehyde
CH_4	methane
CH_3OH	methanol
CO	carbon monoxide
CO_2	carbon dioxide
CS	cationic starch
Cu^{2+}	copper (II) ion
CuO	copper (II) oxide
CuS	copper sulfide
$CuSO_4$ x $5H_2O$	copper (II) sulfate pentahydrate, blue vitriol
DI	deionized water
DNA	deoxyribonucleic acid
DTG	derivative thermogravimetry
EDS	energy-dispersive X-ray spectroscopy
EGA	evolved gas analysis
FR	flame retardant
FT-IR	Fourier transform infrared spectroscopy
GNP	graphene nanoplatelets

HA	hypophosphorous acid
HACH	hypophosphorous acid-modified chitosan
$HCOOCH_3$	ester of formic acid
HCN	hydrogen cyanide
HFT	horizontal flammability test
HT	hydrotalcite
H_2O	water
LbL	layer-by-layer
LOI	limiting oxygen index
MCC	microscale combustion calorimeter
ME	melamine
MMT	sodium montmorillonite
N	nitrogen
NaClO	sodium hypochlorite
$Na_2B_4O_7$ x $10H_2O$	disodium tetraborate or borax
NH_3	ammonia
NH_4Br	ammonium bromide
$(NH_4)_2HPO_4$	ammonium polyphosphate
$(NH_4)_3PO_4$	diammonium phosphate
$(NH_4)SO_3NH_2$	ammonium sulfamate
N-MDMPA	N-methylol dimethylphosphonopropionamide
NO_x	nitrogen oxide
NO_2	nitrogen dioxide
O	oxygen
P	phosphorus
PA	phytic acid
PCH	phosphorylated chitosan
PCQS	poly[3-(5,5-cyanuric acid propyl)- siloxane-co-trimethylammonium propyl siloxane chloride]
PDAC	poly (diallyl dimethylammonium chloride)
PDDA	poly dimethyl diallyl ammonium chloride
PDMS	polydimethylsiloxane
PEI	polyethyleneimine
pHRR	peak heat release rate

PPA	polyphosphoric acid
PSP	sodium polyphosphate
PSS	poly (4-styrene sulfonic acid)
PVA	polyvinyl alcohol
PVAm	polyvinyl amine
QL	quadlayer
SA	sodium alginate
SE	secondary electron detector
SEM	scanning electron microscope
Si	silicon
SiO_2	alumina-coated silica nanoparticles
SMF	sulfonated melamine-formaldehyde
SO_2	sulfur dioxide
SO_3	sulfur trioxide
TGA	thermogravimetric analysis
TG-IR	thermogravimetric-infrared interface
THAM	tris(hydroxymethyl) aminomethane
THPX	tetrakis(hydroxymethyl) phosphonium salt
THR	total heat release rate
TL	trilayer
U	urea
VFT	vertical flammability test

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1. INTRODUCTION

The textile industry is one of the leading industries worldwide, covering almost every aspect of life with various products used in fashion, entertainment, medical, transportation, sports and fitness, home, agriculture, and military. The global textile market is expected to grow from $594.61 billion in 2020 to $821.87 billion in 2025, with Asia-Pacific as the most significant region accounting for 51 percent of the market in 2020 [1]. In 2020, polyester had the largest market share of around 52% of total global fiber production among all textile fibers. The second most globally produced fiber was cotton, with around 24%, whereas the third place was polyamide, with around 5% [2]. From that point of view, the textile industry is one of the most significant environmental pollutants ranging from plant harvesting (e.g., cotton as one of the most chemically dependent crops consuming vast amounts of water, pesticides, and insecticides), where the accumulated chemicals destroy the soil and water, to textile manufacturing processes, such as the production of virgin synthetic fibers, spinning, dyeing, printing, and finishing of fabrics, where a huge amount of fossil fuels, toxic chemicals, water, and electrical energy are used [3].

In 2020 European Commission issued a new Circular Economy Action Plan for a cleaner and more competitive Europe by "developing ecodesign measures to ensure that textile products are fit for circularity, ensuring the uptake of secondary raw materials, tackling the presence of hazardous chemicals, and empowering business and private consumers to choose sustainable textiles and have easy access to re-use and repair services" as well as "methodologies to minimise the presence of substances that pose problems to heatlh or the environment in recycled materials and articles made thereof" [4].

This doctoral thesis deals with the problem of tackling the presence of hazardous chemicals in wet finishing processes for flame retardant and multifunctional flame retardant/antibacterial cotton by using chemicals from renewable sources as well as a new emerging technique of polyelectrolyte layering called layer-by-layer (LbL) deposition.

1.1. Surface functionalization of cotton

Cotton belongs to a group of plant cellulosic fibers consisting of cellulose (~ 94.0%); protein (~ 1.3%); inorganic ash (~ 1.2%); pectic substances (~ 0.9%); malic, citric, and other organic acids (~ 0.8%); wax (~ 0.6%); total sugars (~ 0.3%) and other (~ 0.9%) [5]. Cellulose $(C_6H_{10}O_5)_n$ is a polycondensation-formed polymer of anhydro-d-glucopyranose units in the $^4C_1$-

chair configuration linked by β–1,4–glucosidic links in a crystalline structure with the degree of polymerization (DP) of 1,000–30,000. In each anhydroglucose unit within the cellulose molecule, there are three reactive hydroxyl groups (a primary group at C_6 and two secondary groups at C_2 and C_3 groups) positioned in the plane of the ring (Figure 1) [6].

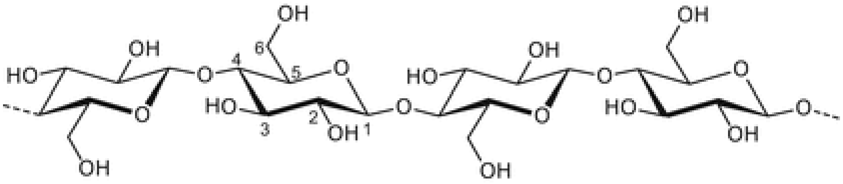

***Figure 1:** Cellulose molecule [6]*

These hydroxyl groups (-OH), the oxygen atoms of the d-glucopyranose ring (-O-), and the glycosidic linkage (-O-) interact with each other within the chain or with another cellulose chain by forming intramolecular and intermolecular hydrogen bonds (H-bonds), which are responsible for the strong interaction between cellulose chains. In native cellulose or cellulose I (e.g., cotton), H-bonds are formed mainly between the oxygen atom in C_3 and the OH at C_6 (Figure 2a). The irreversible transition to cellulose II occurs by treating cellulose I with alkali, and an intermolecular hydrogen bond of OH–C_2 to OH–C_2 of the next chain is formed (Figure 2b) [6]. Figure 2 shows a scheme of the H bonding system in cellulose I (a) and II (b) [7].

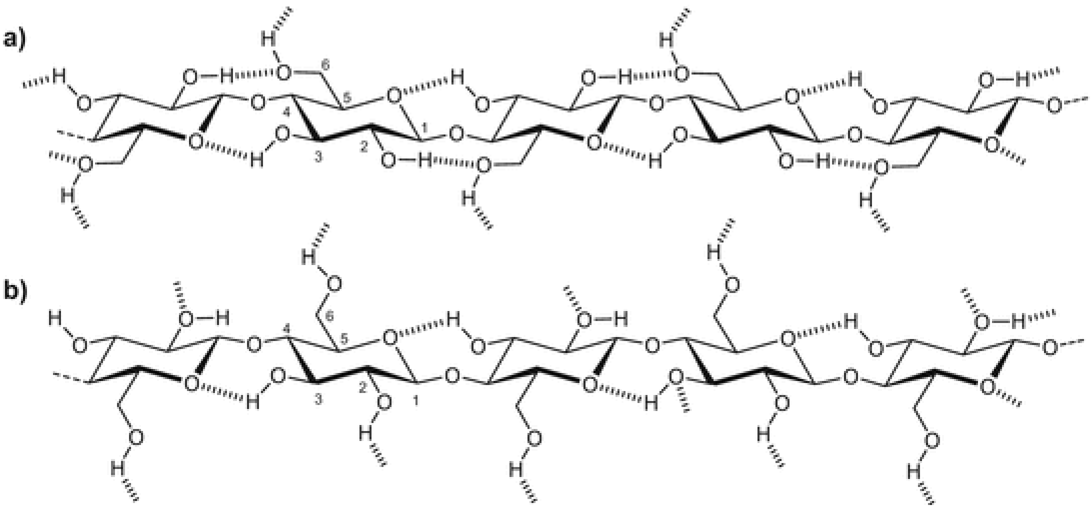

***Figure 2:** A scheme of the H bonding in (a) cellulose I and (b) II [7]*

In addition to the crystalline domains, there are amorphous or noncrystalline regions in cellulose domains or at the surface of cellulose crystals, where the interactions between solid cellulose and water, enzymes, and reactive or adsorptive substances occur first. Negatively charged -OH and -O- functional groups are responsible for the H-bonding of water molecules and the adsorption of positively charged species attracted by weak electrostatic forces. Due to the high reactivity of -OH and -O- functional groups in cellulose molecules, cellulose can undergo several chemical reactions such as substitution reactions (esterification, etherification), deoxyhalogenation, oxidation, acid hydrolysis, oxidative cleavage, oxidation to carboxyl, reduction to alcohol and formation of radical by abstraction of $H^{\cdot}$ as shown in Figure 3 [8]. These functional groups are responsible for the high moisture and water uptake of cellulose and high flammability. The ability of cellulose to absorb moisture and release it on the surface of the fabric is the main reason why cotton is comfortable to wear. However, the negative side of moisture absorption is bacterial growth.

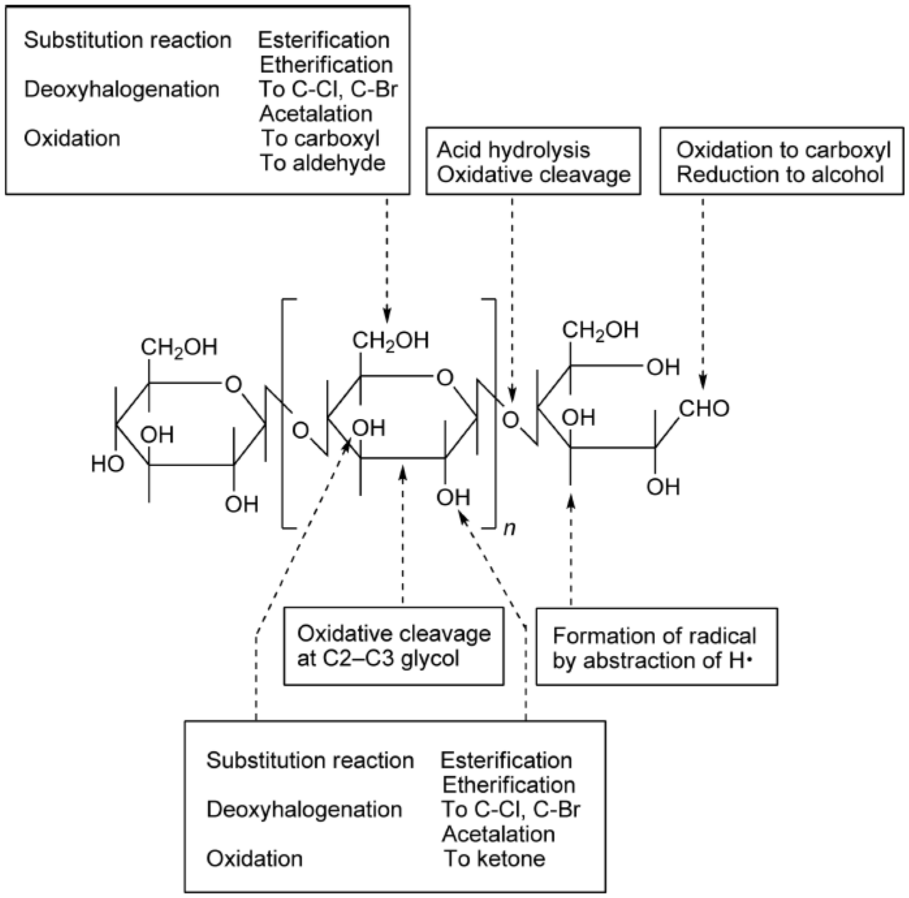

Figure 3: *Positions in cellulose structure for chemical reactions [8]*

To overcome these drawbacks of cellulose, cotton and its blends (with ≥ 50 wt% of cellulose) are commercially treated with various durable or semidurable flame retardant (FR) or/and antimicrobial finishes depending on the end use in wet finishing processes or as backcoating.

1.1.1. Flame retardant (FR) functionalization of cotton

In 2021, over 19,000 deaths worldwide caused by a fire in buildings (91%), vehicles (8%), and other places (4%) have been reported by the International Association of Fire and Rescue Services, which highlights the need for flame retardancy of fabrics [9]. In 2018, the flame retardants (FR) market reached 2.8 million tons, and producing non-halogenated FRs took about 31% of this total [10]. Cotton is a highly flammable fiber due to -OH and -O- functional groups in cellulose molecules [8]. In order to burn the polymer, an external ignition (heat) source should be present to initiate degradation of the polymer (fuel), which starts by free radical chain elimination evolving non-combustible gases, liquid condensates, and tars. Free radicals react with oxygen in the air (the oxidizing agent), evolving flammable gases and visible flame, further heating the polymer and encouraging burning [11]. The schematic of polymer burning is presented in Figure 4 [12].

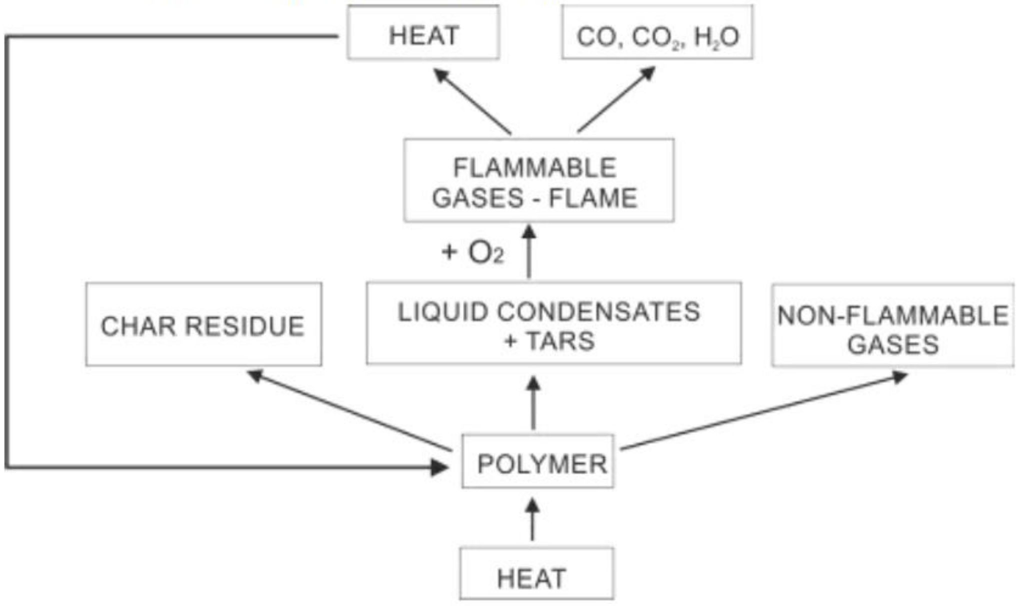

Figure 4: *Schematic of polymer burning [12]*

Adding FRs with different modes of action into this chain removes one or more components of the polymer burning. Adding FR finishes to cotton removes heat, fuel and/or oxidizing agents from the polymer acting in vapor (gas) and/or condensed phase. Pyrolytic products of cellulose react with atmospheric oxygen generating free radicals, which further propagates the cellulose combustion by the branching reaction:

$H\bullet + O_2 = OH\bullet + O\bullet$ (1)

$O\bullet + H_2 = OH\bullet + H\bullet$ (2)

$OH\bullet + CO = CO_2 + H\bullet$ (3)

By adding halogen derivates into the polymer system, chainbranching reactions are hindered by the following reactions:

$MX = M\bullet + X\bullet$ (4)

$MHX = HX + M\bullet$ (5)

$RH + X\bullet = HX + R\bullet$ (6)

$H\bullet + HX = H_2 + X\bullet$ (7)

$OH\bullet + HX = H_2O + X\bullet$ (8)

where MX and MHX are FR molecules containing halogen atom (X), H is hydrogen, M• is the residue of the flame-retardant molecule, and RH is a molecule (such as cellulose) containing hydrogen [13]. It is believed that halogen-based FRs compete act in the gas-phase by competing in the reactions for the free radicals (H•, O•, OH•) essential for flame propagation (so-called radical trap theory of flame inhibition). However, halogens can also act physically by reducing the oxygen (O) concentration of the surrounding atmosphere, thus suppressing the flame [14].

Phosphorus (P) based FRs can act in the gas and condensed phase. In the gas phase, their mechanism of action is similar to hydrogen halides where PO• radical plays the major role. The proposed chainbranching reactions are as follows [15]:

$PO\bullet + H\bullet \rightarrow HPO$ (9)

$PO\bullet + OH\bullet \rightarrow HPO_2\ HPO + H\bullet \rightarrow H_2 + PO\bullet$ (10)

$OH\bullet + H_2 + PO\bullet \rightarrow H_2O + HPO$ (11)

$HPO_2\bullet + H\bullet \rightarrow H_2O + PO$ (12)

$HPO_2\bullet + H\bullet \rightarrow H_2 + PO_2$ (13)

$HPO_2\bullet + OH\bullet \rightarrow H_2O + PO_2$ (14)

However, in the condensed phase, it enhances char formation by chemical interaction between FR and the polymer at temperatures lower than those of the pyrolytic decomposition. These chemical reactions include dehydration of the polymeric with the release of water (H_2O), cyclization, cross-linking with P compounds or their decomposition products such as phosphoric acid/acid-forming agents, aromatization/graphitization, and the formation of char, which acts as a shield protecting the fabrics from flame, while H_2O cools down the system by removing heat from the fire [13].

The mode of action of sulfur (S) based FRs is similar to that of P-based FRs, which means they act in gas and condensed phase. S species can inhibit H• and OH• radicals in the flame [16]. The proposed chainbranching reactions are as follows [17]:

$$SO_2 + H\bullet \rightarrow \bullet HOSO \tag{15}$$

$$\bullet HOSO + H\bullet \rightarrow SO_2 + H_2 \tag{16}$$

$$\bullet HOSO + OH\bullet \rightarrow SO_2 + H_2O \tag{17}$$

S-based FRs that form sulfonic acid entities upon decomposition may also act in a condensed phase by cationic crosslinking with polymers (carbonium ion disproportionation) while forming the char at the surface of the degrading polymer and releasing H_2O. The char acts as a shield protecting the fabrics from flame, while H_2O cools down the system by removing heat from the fire [18]. The proposed chainbranching reactions are as follows [13]:

$$R_2CH\text{–}CHR'OH \rightarrow R_2CH\text{–}CHR'OH_2^+ \rightarrow H_2O + R_2CH\text{–}C^+HR' \tag{18}$$

The efficiency of P-based FRs can be enhanced by adding nitrogen (N) compounds into the FR system. Two theories about N-P synergism include gas/condensed phase:

1. N compounds generate inert gases such as nitrogen monoxide (NO), and nitrogen dioxide (NO_2), which trap free radicals and reduce the O concentration of the surrounding atmosphere, thus suppressing the flame acting in the gas phase [13,19–21],
2. N and P compounds react to form N-P bonds with better thermal stability than O-P bonds. In this way, the retention of N and P in the char increases. These intermediates contain N-P bonds formed during pyrolysis and effectively act on the phosphorylation of cellulose and the catalysis of the dehydration reaction in the condensed phase [22–24].

Metal-based FRs act in the gas/condensed phase depending upon the form of the transition metal compound and the polymer [25]. Gas-phase transitional metal species react with the free radicals in the flame, thus reducing the availability of these species for initiating the second stage of the combustion, reducing the heat release rate and slowing the temperature rise [26]. This gas-phase mechanism involves a reaction of metal oxide (M) or hydroxide (M) with H or

OH radical with the release of H_2O (or H_2), which cools down the system and removes heat [27]:

$$H + MO + (X) = HMO + (X) \tag{19}$$

$$HMO + OH \text{ (or H)} = MO + H_2O \text{ (or } H_2\text{)} \tag{20}$$

Another theory states that dispersed inert dust of metal nanoparticles works as a distributed heat sink in the premixed flame and retards the propagation of the flame in the premixture [28].

In the condensed phase, metal compounds interact with functional groups and catalyze crosslinking of the polymer and dehydration, which leads to the release of H_2O and char formation. Formed char acts as a shield [29].

Ideal FRs for textiles should fulfill the following requirements:

- cost-effective and easy to apply in the industry;
- durable for at least 50 laundry cycles (Pyrovatex®, Proban®);
- wear resistant;
- high air/moisture permeability (comfortable and pleasant to wear),
- should not change the appearance of fabric (color, shade); and
- should be non-toxic to humans or the environment during industrial production, usage, disposal, or fire [12].

Two types of durable FR finishes for cellulose fabrics have been dominating the market, both based on organo-phosphorus compounds (nitrogen-phosphorus synergism, with phosphorus content minimal 1–3 wt%): N-methylol dialkyl phosphonopropionamides (Pyrovatex®) and tetrakis (hydroxymethyl) phosphonium chloride (THPC)/urea (Proban®).

N-methylol dialkyl phosphonopropionamides-based FR finishes are used for cotton and cotton blends containing ≥ 70% cotton. A typical Pyrovatex® standard recipe consists of N-methylol dialkyl phosphonopropionamides, melamine resin, softener, acid catalyst and wetting agent. The Pyrovatex finishing process consists of several production steps: application of recipe formulation by padding, drying, curing at 170 °C, neutralising in caustic soda, and several cycles of washing in water and drying. The covalent binding between FRs and cellulose occurs during curing at 170 °C, as shown in Figure 5. The ecological drawback of the process is the release of free formaldehyde during production and the product life cycle. Additionally, the process requires high water and energy consumption [30]. Formaldehyde exposure through inhalation, dermal, and eye contact leads to site-specific and dose-dependent health impairments in many organs, such as nasopharynx carcinoma, pulmonary fibrosis, teratogenicity, neurotoxicity etc. [31].

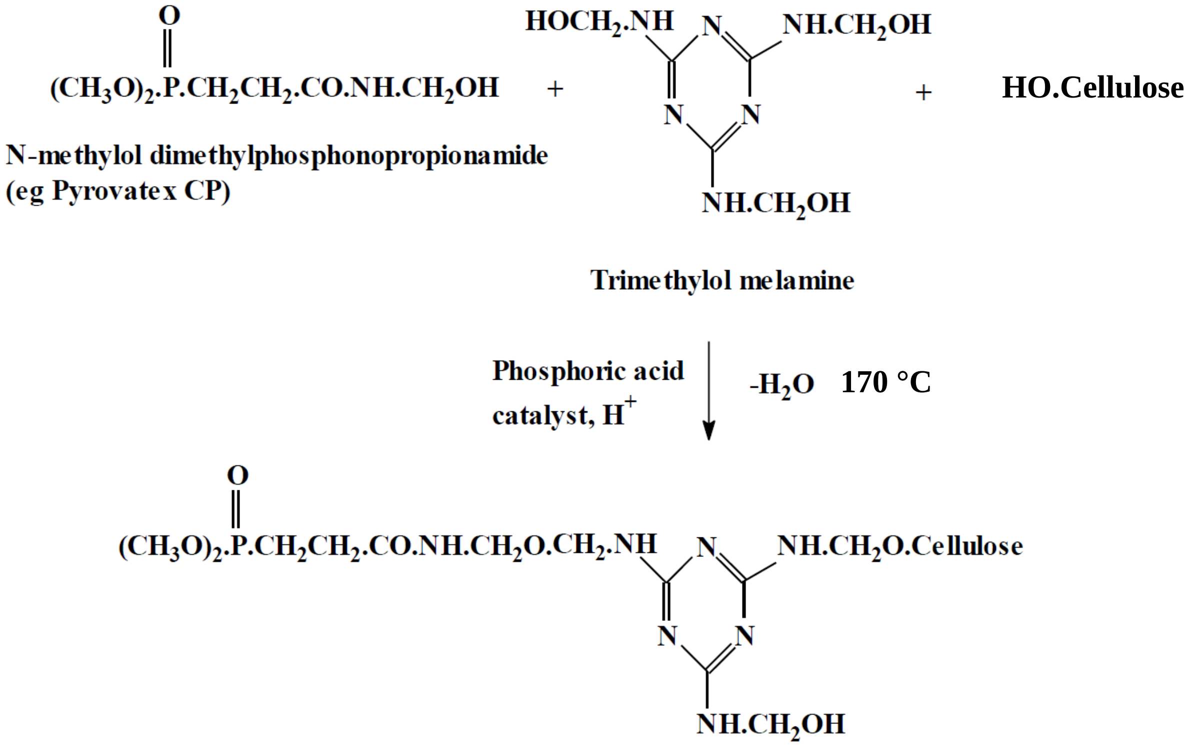

Figure 5: *Chemistry of Pyrovatex® [30]*

Tetrakis (hydroxymethyl) phosphonium chloride (THPC)/urea-based FR finishes are used for cotton and cotton blends containing ≥ 55% cotton. A typical Proban® process consists of several steps: applying the THPC/urea complex solution in the presence of wetting and softening agent by padding or foaming onto the fabric, drying, ammonia curing, oxidizing the polymer to a poly(phosphine oxide) in a dilute hydrogen peroxide bath, several cycles of washing in water and drying at the end. Unlike the Pyrovatex® process, the cross-linked polymer is not grafted onto the cellulose molecular in the latter. However, the network of cross-linked polymer interpenetrates within a microfibrillar cotton cellulose structure. The chemistry of the Proban process is shown in Figure 6. The process requires a specialist ammonia gas cure unit [30]. Ammonia exposure through inhalation, dermal, and eye contact leads to corneal injury and burns on the skin, chronic lung disease, perforation of the hollow viscera and neurotoxicity [32].

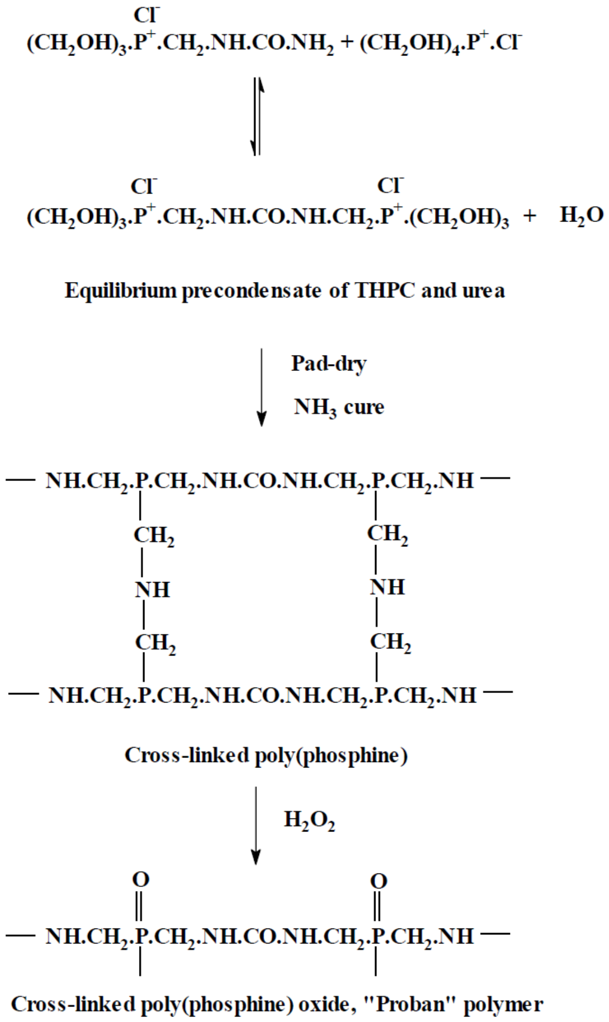

Figure 6: *Chemistry of the Proban® [30]*

Healthier formaldehyde-free alternatives of cross-linking agents on industrial scale processes are butyl tetracarboxylic acid (BTCA), mainly used for cotton fleece and children’s nightwear. However, the resulting finish is semi-durable [33].

Other commercial FR finishes for cotton are non-durable ones, which include inorganic salts such as disodium tetraborate or borax ($Na_2B_4O_7$ x $10H_2O$), ammonium polyphosphate ($(NH_4)_3PO_4$), diammonium phosphate $(NH_4)_2HPO_4$) and ammonium sulfamate ($(NH_4)SO_3NH_2$) and ammonium bromide (NH_4Br) [34].

Backcoating is typically applied for carpets made of all types of fibers and cotton and cellulose-based fabrics. In backcoating treatments, decabromodiphenyl ether (Deca BDE, bromine content minimal 5 wt%) /antimony trioxide (ATO, Sb_2O_3) based formulations are applied in an acrylic co-polymer resin matrix (as solvent base systems, chemically cured systems, hot melt process), which is then applied to fabric surface [30]. European Commission banned deca BDE in 2019, confirming that “the persistent and bioaccumulative properties of decaBDE give rise to specific concerns about its widespread distribution and potential to cause irreversible long-term harm to the environment, even after emissions have ceased. In addition, exposure to deca BDE may result in neurotoxicity in mammals, including humans” [35]. Halogen-based FRs have been replaced with ammonium polyphosphate (APP) [36].

To conclude, the disadvantages of current commercially available FR finishing processes for textiles are:

- toxic formaldehyde emission in Pyrovatex® finishing;
- loss in tensile properties and abrasion resistance in Pyrovatex® finishing (where phosphoric acid is the cross-linking catalyst);
- requirement for toxic ammonia curing in Proban® finishing;
- dyestuffs interaction (e.g., Proban® process);
- ecotoxicological and bioaccumulative properties of Deca BDE/ATO-based FRs in backcoating;
- high water and energy consumption.

New environmentally-benign chemicals and technologies such as sol-gel, UV, and plasma grafting treatments or layer-by-layer (LbL) deposition are needed to overcome these technological drawbacks. Before considering any of above mention alternative treatments, however, one should be aware of the following:

- thickness of fabrics;
- the minimal wt% of active compounds such as phosphorus (P), nitrogen (N), bromine (Br), or antimony trioxide (ATO) levels required for an acceptable level of FR effect;
- required durability of FR treatment;
- influences of surface treatment on fabric properties.

In the sol-gel surface treatments (semi)metal alkoxides such as tetramethoxysilane (TMOS), tetraethoxysilane (TEOS), aluminum isopropoxide, and titanium tetraisopropoxide are used as reactive precursors in hydrolysis and successive condensation reactions. The precursors are first partly hydrolyzed by water molecules forming (semi)metal (M)-OH groups, which then undergo condensation reactions with other alkoxy groups (forming alcohols as by-products), or other hydroxyls groups (forming water as a by-product). The schematic of sol-gel chemistry is shown in Figure 7 [37].

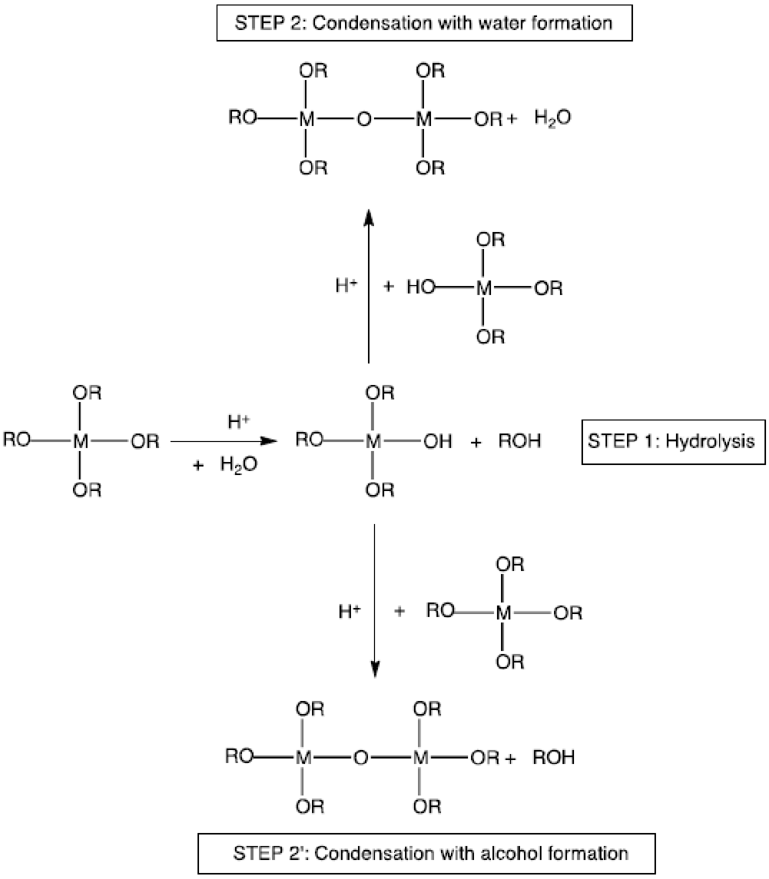

Figure 7: *Chemistry of sol-gel [37]*

The main advantages of the sol-gel method on textiles are the following:

- the reactions occur near the ambient temperature at mild conditions (~ pH 5.5);
- apart from (semi)metal alkoxides, organic compounds can be employed as well;
- by-products are low molecular weight molecules such as alcohols and water;
- wash durability of sol-gel treatment on cellulose textile;
- the treatment can be carried out using traditional wet-finishing production plants;
- depending on the chemicals used, the multifunctionality of the textile coating can be achieved [37].

UV and plasma grafting treatments are eco-friendly processes that modificate the fiber surface without influencing bulk properties. Plasma can be a mixture of inert gas molecules, ions, free radicals, electrons, and photons, filled in a plasma environment with a net of electric charge of zero and a low degree of ionization. Plasma surface modification of textile includes cleaning, activation, grafting, etching, and polymerization, achieved mainly by cold flame low-pressure atmospheric argon plasma, dielectric barrier discharge plasma, and cold oxygen plasma. Using plasma, many useful functional properties can be created on textiles, such as increased surface softness and dyeability, antistatic, antimicrobial, hydrophilic, hydrophobic, and FR properties in laboratory conditions etc. [38]. There is only one fully commercial process using atmospheric plasma/UV Laser (Multiplexed Laser Surface Enhancement System, MTIX Ltd., Huddersfield, UK) in the market claiming that flame retardancy may be introduced either by pre-impregnating/coating prior to plasma/UV or by the introduction of volatile/aerosol flame retardant precursors into the plasma zone. The system eliminates a number of wet processing cycles in textile finishing [39].

Layer-by-layer (LbL) deposition dates back to the 1960s, to the invention of Iler and Kirkland, who discovered that cationic boehmite fibrils and anionic silica particles built inorganic layered structures in the form of films [40,41]. In 1992, Decher et al. built an LbL assembly using a cationic solution of poly[diethylmethyl(4-vinyl benzyl)ammonium iodide] and poly(allylamine hydrochloride) and anionic solutions of sodium poly(styrene sulfonate) and potassium poly(vinyl sulfate) [42]. In 2013, Ariga et al. published a review on the potential industrial application of LbL deposition for (bio)sensors, bioreactors, enzyme devices, drug delivery/release, cell coatings, solar cells, lithium batteries, photovoltaic devices, supercapacitors, transistors, color displays, and gas barriers [43]. The LbL deposition of textiles involves immersing fabric into the solutions of oppositely-charged polyelectrolytes or spraying the fabrics with charged solutions. The fabric is washed up with deionized water (DI) between two polyelectrolyte immersion steps. By repeating these steps, it is possible to build LbL structures with the desired number of bilayers (BL), trilayers (TL), or quadlayers (QL) with different functionality depending on the chemical used [44]. Figure 8 represents typical 2 BL LbL deposition steps on fabric.

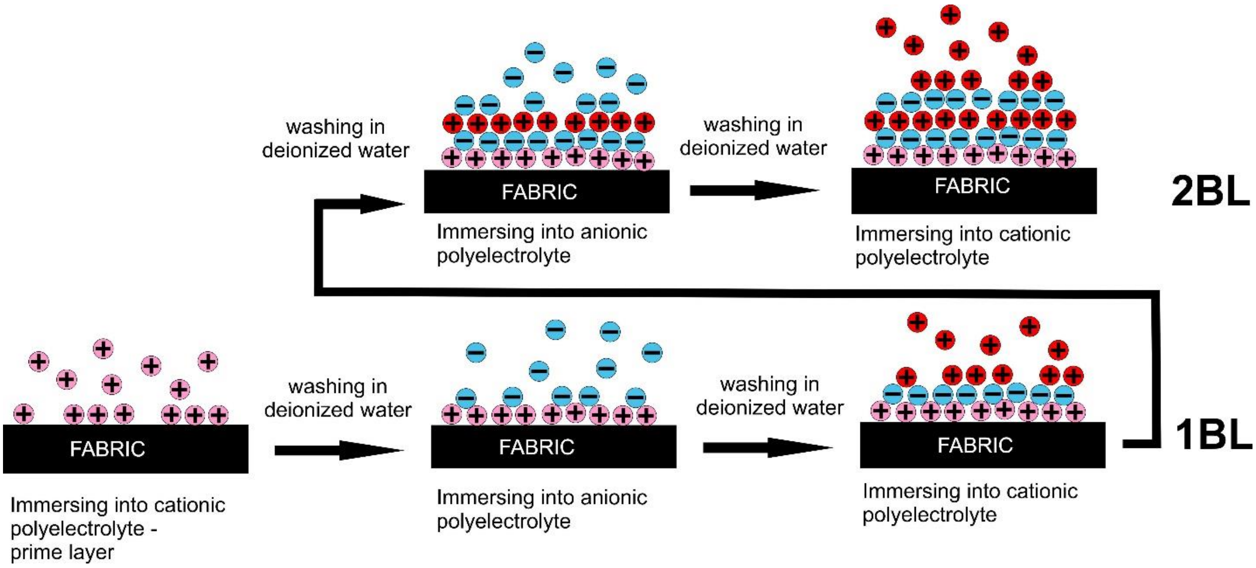

Figure 8: *Schematic of typical layer-by-layer deposition of fabrics*

The interaction between opposite charges layers is primarily by weak electrostatic forces. However, today the emphasis is also on donor/acceptor interactions, hydrogen bond donors/acceptors, covalent bonds, π-π interactions, and stereo-complex formations [45]. In conventional LbL deposition, layers are attracted by weak electrostatic forces of polyelectrolytes soluble in water, polyanions, and polycations with one charged group per monomer unit. However, polymers bearing hydrogen bond donors and acceptors can also form assemblies. These weak bonds are sensitive to environmental conditions, and formed layers are easy to break. Coordination polymers (inorganic or organometallic polymer structures containing metal cation centers linked by ligands) have been employed to form organic-inorganic hybrid multilayer assemblies to form durable coatings. These complex structures can be subjected to post-chemical reactions, such as UV or thermal curing. Unconventional methods of LbL deposition usually include two steps. The first step is forming a supramolecular complex based on various interactions (electrostatic, hydrogen-bonded, or π-π complexes, block copolymer micelles) in bulk solution. In the second step, the supramolecular complex is subsequently used as a building block for LbL assembly [46].

Chemically bleached and mercerized cotton has negatively charged hydroxyl groups (-OH), the oxygen atoms of the d-glucopyranose ring (-O-), and the glycosidic linkage (-O-), able to interact with positively charged (macro)molecules (water, salts, charged nanoparticles, organic compounds, complexes) by weak electrostatic forces and hydrogen bonds (H-bonds) [6,7]. Due to high reactivity, these groups can also form organic-inorganic hybrid multilayer assemblies and supramolecular complexes by covalent binding, π-π interactions, and stereo-complex formations [8].

1.1.2. Antimicrobial surface functionalization of cotton

Negatively charged hydrophilic functional groups responsible for the flammability of cellulose, such as hydroxyl groups (-OH), the oxygen atoms of the d-glucopyranose ring (-O-), and the glycosidic linkage (-O-) are also responsible for high moisture and water uptake. Raw cotton or sized cotton yarns/fabrics are primarily treated with different antimicrobial/antifungal agents during storage or shipment of fabrics with sized warp under conditions of temperature above 40 °C and humidity. The second reason for antimicrobial fabric treatment is to reduce or eliminate bacteria growth on fabrics used in home care patients by using antimicrobial textiles that release antimicrobial agents from the fabric in the presence of moisture. Most hospitalized patients face a high risk of nosocomial infections in hospitals and home care. In 2020, two pathogens were reported responsible for bloodstream infections in hospital patients: Gram-negative *Escherichia coli* and Gram-positive methicillin-resistant *Staphylococcus aureus* [47]. Surface antimicrobial functionalization of cotton textiles is intended for home use, such as face masks, linings, bedding, covers, curtains, pillows, towels, underwear, and sportswear. Factors influencing the antimicrobial effectiveness of antimicrobial agents are the type of microorganisms, the chemical structure and concentration of the antibacterial agent, the mode of action, and environmental conditions (temperature, pH, and moisture) [48].

Bacteria are generally divided into two main categories depending on the outer membrane cell structure responsible for interacting with the environment. Gram-positive and Gram-negative bacteria possess cell wall peptidoglycans conferring the characteristic cell shape, thus providing the cell with mechanical protection. Peptidoglycans comprise a glycan backbone of N-acetylated muramic acid and glucosamine, and peptide chains cross-linked with bridges in Gram-positive or partially cross-linked in Gram-negative bacteria. Peptidoglycans are covalently bound to teichoic acids, negatively charged polyol phosphate polymers in Gram-positive bacteria but absent in Gram-negative bacteria. As membrane teichoic acids, there are lipoteichoic acids, polymers of amphiphilic glycophosphates with the lipophilic glycolipid, anchored in the cytoplasmic membrane. On the other hand, the major component of the outer membrane of Gram-negative bacteria is lipopolysaccharide (LPS), a complex molecule consisting of a lipid A anchor, a polysaccharide core, and chains of carbohydrates. Due to the presence of the teichoic acid and polysaccharides of Gram-positive bacteria and the lipopolysaccharide of Gram-negative bacteria, the surface of bacterial cells stabilized by divalent cations such as Mg^{2+} and Ca^{2+} is negatively charged. Differences in cell structure between Gram-negative and Gram-positive bacteria are shown in Figure 9 [49]**.**

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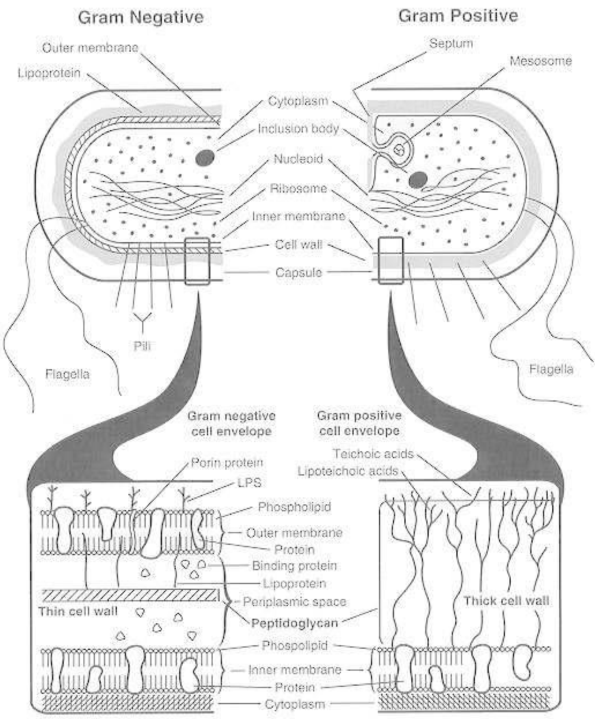


Figure 9: *Schematic of cell structures of Gram-negative and Gram-positive bacteria [49]*

Antimicrobial agents can be divided into groups based on the mechanism of antimicrobial activity. The main groups are: agents that inhibit cell wall synthesis, depolarize the cell membrane, inhibit protein synthesis, inhibit nucleic acid synthesis, and inhibit metabolic pathways in bacteria [50]. The first antimicrobial agents used for the surface functionalization of cotton were bisphenol compounds (e.g., triclosan) and triclocarban.

The mode of action of triclosan and triclocarban (Figures 10a-b) involves blocking lipid biosynthesis by binding with enoyl-acyl carrier protein reductase enzyme, which prevents the fatty acid synthesis required for lipid production in the bacteria and building and reproducing cell membranes, thus acting as a bacteriostatic [51].

a) b)

Figure 10: *Structural formula of a) triclosan and b) triclocarban [51]*

In 2016 the U.S. Food and Drug Administration (FDA) banned the use of triclosan and triclocarban, stating them as “environmentally persistent endocrine disruptors that bioaccumulate in and are toxic to aquatic and other organisms” [52]. Due to the high toxicity of bisphenol and triclocarban, other more ecological compounds such as quaternary ammonium compounds, citric acid, natural polymers (e.g., chitosan), metal (nano)particles (and its salts), extracts of plant essential oils such as peppermint, tea tree, eucalyptus etc. have been used since then [53–57].

Cationic antimicrobials such as quaternary ammonium (QAC) compounds are hydrophobic with having negatively (ammonium groups) and positively charged (halogenated) parts of the molecule. The halogenated part of the molecule interacts initially with the wall and membrane by displacing Ca^{2+} and Mg^{2+} divalent cations. The next step is the interaction between the positively charged ammonium group and the negatively charged cell membrane of the bacteria compounds resulting in a surfactant–microbe complex. This process interrupts the function of the cell membrane and the protein activity, causing death. QACs also interact with intracellular targets and bind to DNA, which means that QAC act as bacteriostatics at low concentrations (0.5–5 mg/l) and as biocides at higher concentrations (10–50 mg/l). The antimicrobial activity depends on the length of the alkyl chain, the presence of the halogenated group, and the number of ammonium groups in the molecule [58,59]. Different types of QAC compounds are shown in Figure 11.

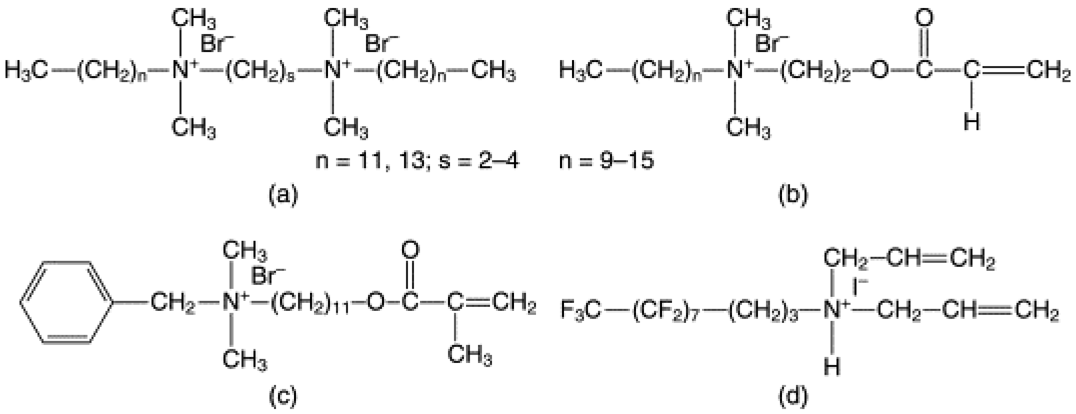


Figure 11: *Structural formula of different QACs: (a) diquaternary ammonium salt (alkanediyl- α, ω -bis(dimethylalkyl ammonium bromide)), (b) alkyl(2- (acryloyloxy)ethyl)dimethyl ammonium bromide, (c) benzyl(11-(acryloyloxy)undecyl) dimethyl ammonium bromide; (d) N -(4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11-heptadecafluoroundecyl)- N, N -diallylmethyl ammonium iodide [58]*

The citric acid (CA) acts as a biocide, and its mode of action is pH dependent. At pH 9.5, the antimicrobial activity of CA is increased due to increased chelation of Mg^{2+} and Ca^{2+} ions, as well as the increase in the less stable negatively charged groups of the bacterial membrane, which at the end causes a disruption of membrane and leaching the cytoplasm [60].

Another eco-friendly antimicrobial agent is chitosan (CH). A generally accepted opinion about its antibacterial mode of action is that positively charged $-NH_2$ groups bind to the negatively charged bacterial cell membrane and cause membrane disruption and leakage of the cytoplasm, thus acting as a biostatic [61]. Its mode of action will be discussed in detail in the Discussion.

Surface antimicrobial functionalization of cotton textiles is intended for home use, such as face masks, linings, beddings, covers, curtains, pillows, towels, underwear, and sportswear, but also for storage or shipment of fabrics with sized warp, under conditions of temperature above 40 °C and humidity. An ideal antimicrobial agent should fulfill the following properties:

- efficiency against pathogenic microorganisms without influencing the growth of normal non-pathogenic skin flora;
- hypoallergenic, non-irritating and non-cytotoxic;
- effectiveness at low concentrations and low contact time;
- colorlessness and odorlessness;
- preservation of the mechanical and physical properties of textiles, such as strength and comfort;
- resistance to UV radiation;
- washing durability;

- compatible with textile chemical processes;
- application with the use of standard equipment;
- cost-effective and
- eco-friendly [48].

Depending on the stability of antimicrobial compounds on textiles, cotton antimicrobial finishes are mostly semi-durable (at least 15 laundry cycles), which means the antimicrobial agent is washed up throughout laundering. Antimicrobial compounds intended for cotton are integrated into the fabrics in the wet finishing process and are not usually chemically bonded to cellulose, which is very important for their leaching. If they were covalently bound, the antimicrobial finish would be more wash resistant but less effective against microorganisms. The finished fabric moderates the bacteria growth by controlled release of antimicrobial agents from the fabric in the presence of moisture [58,62].

On a laboratory scale, antimicrobial compounds could be added to cotton surfaces by sol-gel, UV, and plasma grafting treatments, microencapsulation, or layer-by-layer (LbL) deposition [58,63,64]. Factors influencing the antimicrobial effectiveness of antimicrobial agents are their chemical structure and concentration, mode of action, type of microorganisms, and environmental conditions (temperature, pH, and moisture) [48]. Antimicrobial agents used for the surface functionalization of cotton are triclosan, triclocarban, phenyl derivates, quaternary ammonium compounds, citric acid, metal (nano)particles (and salts), natural polymers (e.g., chitosan), extracts of plant essential oils such as peppermint, tea tree, eucalyptus etc. [53–57].

To conclude, the disadvantages of the current antimicrobial functionalization of cotton are:

- toxic formaldehyde emission in wet finishing if melamine resin as a binder is used;
- loss in tensile properties and abrasion resistance;
- poor wash durability;
- ecotoxicological and bioaccumulative properties of some antimicrobial agents
- high water and energy consumption in case of wet finishing.

Multifunctional FR/antimicrobial finishing of cotton is a challenging issue due to demands on wash durability of FR finish (at least 50 laundry cycles), which is possible to achieve by covalent binding of FR agents to -OH groups (Pyrovatex® process) and demands on leaching of antimicrobial agents in the presence of moisture, which is effective if the antimicrobial agent is not bond covalently to cellulose [30,62].

In the laboratory scale, the following surface functionalization approaches were used to achieve FR/antimicrobial properties of cotton: wet finishing [65], sol-gel [66], microencapsulation[67], atmospheric plasma [68], polymerization grafting [69] and layer-by-layer deposition [70].

2. HYPOTHESES CONFIRMATION

2.1. Myo-inositol hexaphosphate (PA) is an effective alternative flame retardant (FR) since it is a natural source of phosphorus (P) in plants, easily binds metal ions, and as a polyelectrolyte can be layered on cotton by means of LbL deposition.

Myo-inositol hexaphosphate, also known as phytic acid (PA), is an effective agent due to its natural source of phosphorus and can be used as an alternative flame retardant. PA is an anionic electrolyte successfully layered with cationic polyelectrolytes such as branched polyethylenimine (BPEI) and chitosan using the LbL method. Since PA is a compound rich in phosphorus, it effectively reduces the flammability of cotton material. This effect is enhanced by layering nitrogen-containing compounds (BPEI, CH, and urea - U). PA easily binds copper salts of strong electrolytes. By increasing the number of PA/CH bilayers on the cotton fabric from 4 to 8, the mass of the treated fabric increases from 8.3% to 14.5%, compared to the untreated fabric, which simultaneously increases the reduction of *Staphylococcus aureus* bacteria from 76.8% to 97.9% according to the AATCC TM 100-2019 standard. However, the increase in the number of bilayers did not affect the reduction of *Klebsiella pneumoniae* bacteria, which was about 70%, regardless of the increase in bilayers. With the addition of copper salts to chitosan, the mass increase is only 5.2% for 4 bilayers or 5.6% for 8 bilayers, which means that the addition of copper (II) sulfate pentahydrate, as a strong electrolyte, decreased the mass of the material, but this did not negatively affect the efficiency of processing for antimicrobial protection. When copper (II) sulfate pentahydrate was added as a top layer after 12 bilayers of PA/CH+U, excellent FR results of reduced flammability were achieved, as proven by vertical flammability testing according to ASTM D6413/D6413M-15 standards.

2.2. Branched polyethyleneimine (BPEI) is a biocompatible polyelectrolyte rich in nitrogen and, in synergy with PA, provides effective FR treatment.

BPEI is a biocompatible cationic polyelectrolyte rich in nitrogen that acts synergistically with phosphorus from the anionic PA layer, and in this work it was used exclusively as a primary layer for better adhesion of PA/CH or PA/CH+U bilayers to cotton. CH and U molecules contain nitrogen and act synergistically with phosphorus from PA. The cotton fabric deposited with 30 bilayers of PA/CH was tested according to the ASTM D6413/D6413M-15 vertical flammability test (VFT), and the following results were obtained: afterglow time 0 s and afterflame time 0 s, which means that the treated fabric shows very good FR results of reduced flammability. Testing in a microscale combustion calorimeter according to the ASTM D7309−21a method showed a reduction in the peak heat release rate (pHRR) by 62% and the total heat release (THR) by 77%, compared to untreated cotton, with a high char yield of 41.7%. By adding U, it is possible to additionally reduce the number of bilayers from 30 to 10 with the same FR efficiency.

2.3. Kaolin is an aluminosilicate effective in FR treatments even in low concentrations and is suitable for LbL deposition of cotton.

Although the effectiveness of aluminosilicate was proven in the previous work by using impregnation procedures and in composite materials for functionalization of fibers reinforcement, its effectiveness via the LbL method is not presented within the dissertation because numerous literature references indicated that it could not fulfill the high commercial requirements posed on FR agents for cotton [71,72].

2.4. Blue vitriol, as a natural source of copper salts, enhances the effect of an alternative organophosphorus FRs of cotton while achieving fungicidal protection.

Blue vitriol, i.e., copper (II) sulfate pentahydrate, enhanced the effect of reduced flammability of cotton layered with PA/CH-U with simultaneous antimicrobial protection in the case when it was added as a top layer on 12 bilayers of PA/CH-U. In this case, the pHRR value was reduced by ~ 62% compared to untreated cotton, which is 11% better than the pHRR value of cotton treated without adding copper (II) sulfate pentahydrate. At the same time, the LOI value increased from 21.5% (untreated cotton) to 26.0%, which is the minimum requirement for the material to be characterized as self-extinguishing. The PA/CH-U sample, after adding copper (II) sulfate pentahydrate in the final treatment, shows 100% antimicrobial efficiency against the tested bacteria (*Klebsiella pneumoniae* and *Staphylococcus aureus*). Further antifungal testing of cotton was not carried out since it had already been proved in the papers of other authors that copper salts have excellent antimycotic effectiveness, in addition to antibacterial ones [73–75].

2.5. By optimizing the parameters of LbL deposition (type of polyelectrolyte, number of layers, and order of polyelectrolytes in layers, pH, and concentration of solution), it is possible to achieve the same efficiency as using commercial FRs.

Cotton treated with 30 bilayers of PA anionic solution (2%, pH 4) and CH cationic solution (0.5%, pH 4) met the reduced flammability requirement per the ASTM D6413/D6413M-15 standard. In order to reduce the number of bilayers while maintaining good efficiency, 10% U was added to the chitosan solution at the same pH, which reduced the number of bilayers needed to meet the non-flammability requirements from 30 to 10. The sample treated in this way shows a high limit value of the oxygen index (LOI = 28%), which meets the commercial requirements for cotton with reduced flammability (LOI ≥ 26%).

3. MATERIALS AND METHODS

Materials

- Cotton fabric, chemically bleached, desized, 119 g/m^2, USDA Southern Regional Research Center (New Orleans, LA, USA) [70,76,77];
- Branched polyethyleneimine (BPEI, M ~ 25,000 g/mol, ≤ 1% water), Sigma Aldrich (Milwaukee, WI, USA) [70,76,77];
- Phytic acid (PA)
    - Phytic acid sodium salt hydrate (M ~ 660 g/mol), Sigma Aldrich (Milwaukee, WI, USA) [76,77];
    - Phytic acid dodecasodium salt hydrate (M ~ 924 g/mol, purity ≥ 75%), Biosynth Carbosynth Ltd. (Compton, UK) [70];
- Urea (U), Sigma Aldrich (Milwaukee, WI, USA) [70,76];
- Hydrochloric acid (HCl), Sigma Aldrich (Milwaukee, WI, USA) [70,76,77];
- Sodium hydroxide (NaOH), Sigma Aldrich (Milwaukee, WI, USA) [70,76,77];
- Chitosan (CH)
    - Chitosan powder (M ~ 60,000 g/mol 75–85% deacetylated), G.T.C. Bio Corporation (Qingdao, China) [76,77];
    - Chitosan powder (M ~ 190,000–310,000 g/mol, 75–85% deacetylated) [70];
- Copper (II) sulfate pentahydrate ($CuSO_4$ x $5H_2O$), Sigma Aldrich (Milwaukee, WI, USA) [70,77];
- Deionized (DI) water, 18.2 mW [70,76,77].

All polyelectrolyte solutions were prepared as follows:

- cationic BPEI solution (5 wt%) in DI;
- anionic PA solution (2 wt%, pH 4) in DI;
- cationic CH solution (0.5 wt%, pH 4) in DI;
- U (10 wt%) in cationic CH (0.5 wt%, pH 4);
- $CuSO_4$ x $5H_2O$ (2 wt%) in DI;
- $CuSO_4$ x $5H_2O$ (2 wt%) in cationic 0.5 wt% CH, pH 4.

The pH of the solutions was adjusted with 0.1 M HCl and 0.1 M NaOH.

LbL deposition

Cotton fabric was first washed in a standard detergent solution and dried in an oven for 24 h at 80 °C before LbL deposition. Cotton fabrics were deposited via LbL deposition according to the following three schemes (the immersing time was 5 min for the first layer and 1min for each additional layer; each immersion step was followed by rinsing in DI water):

- 8, 10, 12, 15 BL of $PA^-/(CH\text{-}U)^+$, BPEI as a primer for better adhesion to cotton [76];

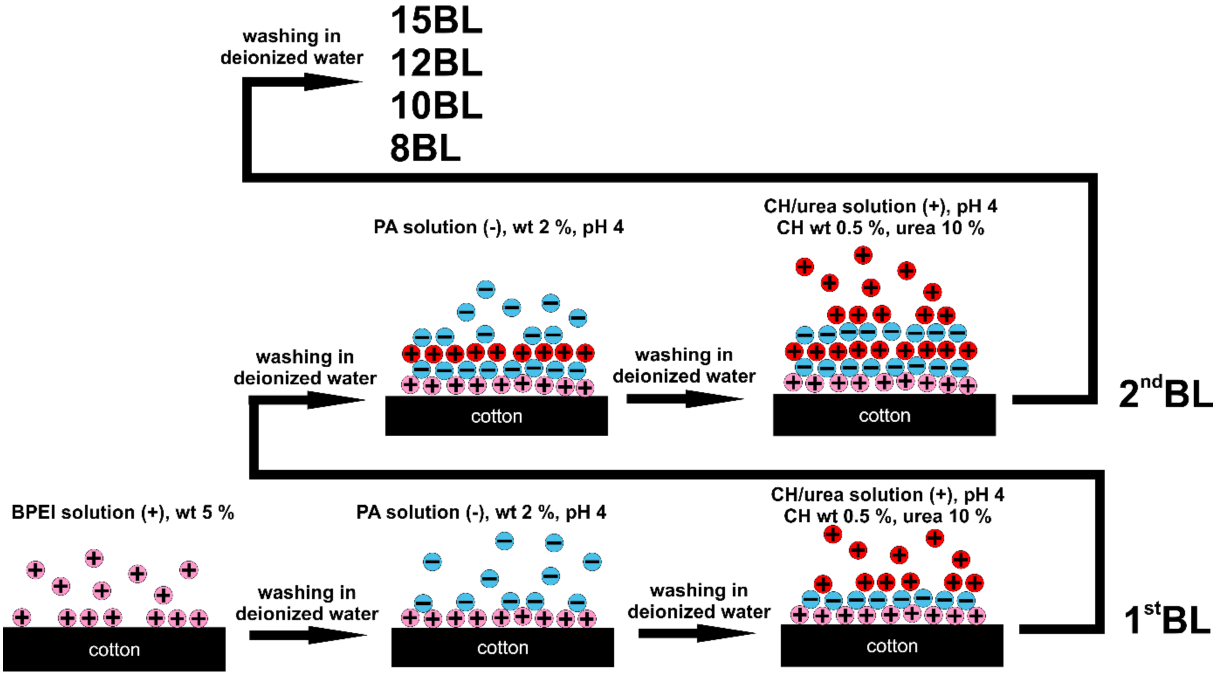


Figure 12: *LbL deposition of cotton with 8, 10, 12, and 15 BL of PA/CH-U [76]*

- 4, 8 BL of PA^-/CH^+ and $PA^-/(CH\text{-}CuSO_4 \text{ x } 5H_2O)^+$, BPEI as a primer for better adhesion to cotton [77];

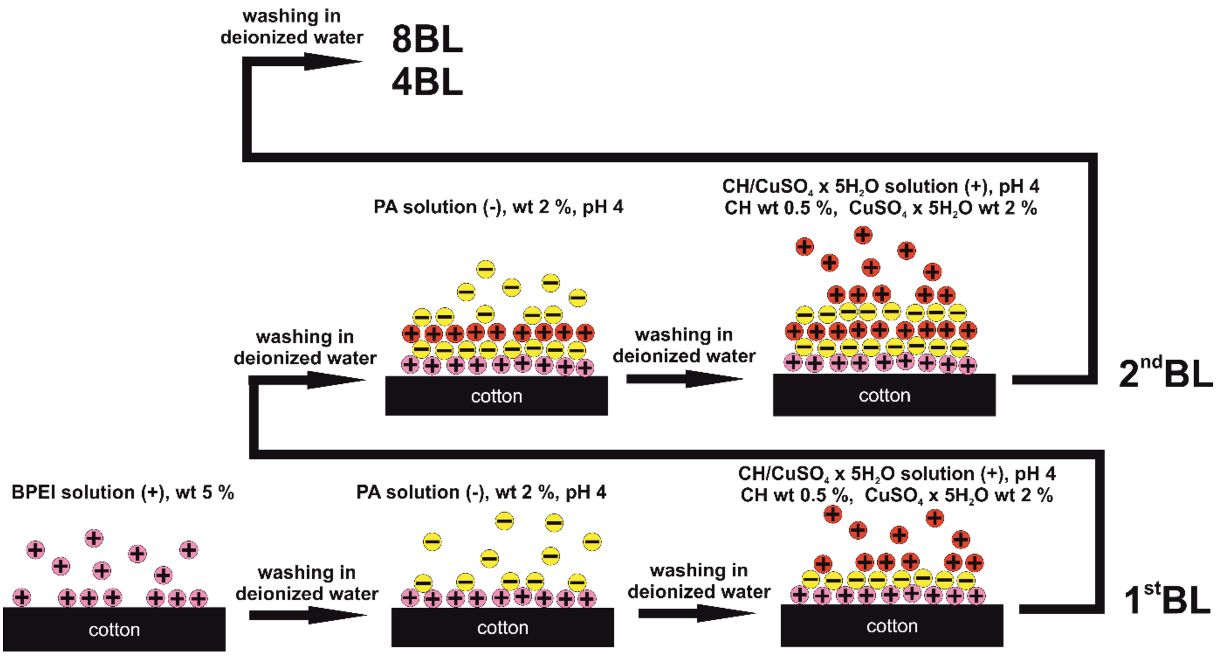


Figure 13: *LbL deposition of cotton with 4, 8 BL of PA^-/CH^+ and $PA^-/(CH\text{-}CuSO4 \text{ x } 5H_2O)^+$ [77]*

- 8, 10, 12 BL of $PA^-/(CH\text{-}U)^+$ + immersion into $CuSO_4$ x $5H_2O$ solution, BPEI as a primer for better adhesion to cotton [70].

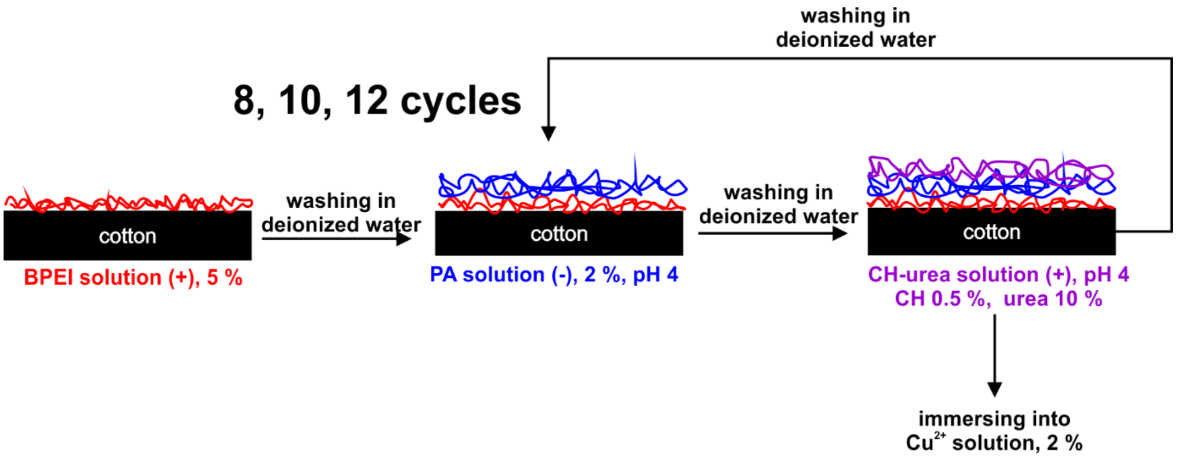


Figure 14: *LbL deposition of cotton with 8, 10, 12 BL of $PA^-/(CH\text{-}U)^+$ with immersion into $CuSO_4$ x $5H_2O$ solution [70]*

All samples are dried in the oven at 80 °C for 24 h after the treatment.

Characterization

The weights of all samples were measured after drying in the oven at 80 °C for 24 h, before and after LbL treatment, to calculate weight gain (%) and the following equation:

$$Weight\ gain\ (\%) = \frac{m\ (treated)}{m\ (untreated)}\ x\ 100 \tag{21}$$

Limiting Oxygen Index (LOI) was measured according to ISO 4589-2:2017 Plastics – Determination of burning behavior by oxygen index – Part 2: Ambient-temperature test [78] using LOI module (Dynisco, Heilbronn, Germany [76] and Concept Equipment, Poling, UK [70]). Using LOI, it is possible to determine the minimum volume fraction of oxygen in admixture with nitrogen that will support the combustion of small vertical test specimens under specified test conditions (23 °C ± 2 °C). The results are defined as oxygen index (OI) values. The method is provided for self-supporting testing materials in vertical bars or sheets up to 10.5 mm thick. It is suitable for solid, laminated, or cellular materials with an apparent 100 kg/m3 or greater density. The methods might also apply to some cellular materials with an apparent density of less than 100 kg/m^3. A method is provided for testing flexible sheets or film materials while supported vertically. The method has been developed for plastics but validated by the University of Zagreb Faculty of Textile Technology for textile fabrics. In the case of textile testing, form V has been used: 52 mm x 140 mm with ignition procedure B (propagating ignition). It is also possible to use a short procedure. Applied model of LOI device, produced by Concept Equipment is shown in Figure 15.

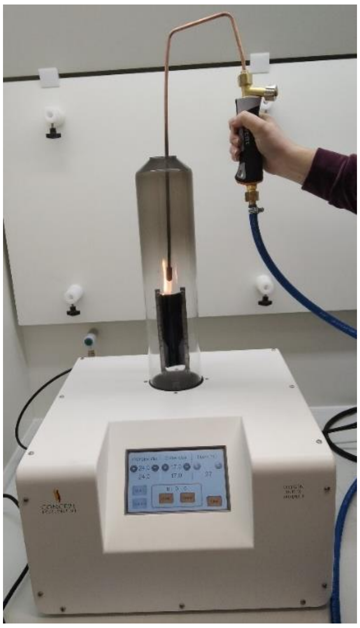


Figure 15: *LOI device, Concept Equipment*

Vertical flammability test (VFT) was carried out in a standard Govmark chamber (Farmingdale, NY, USA) according to ASTM D6413/D6413M-15 Standard Test Method for Flame Resistance of Textiles (Vertical Test) [79]. Specimen of dimensions 76 mm x 300 mm are ignited with a burner to measure the vertical flame resistance of textiles. Immediately after the flame is removed (after 12 s), the afterflame and afterglow time are measured. At the end of the combustion, the char length is measured (mm). The char length (mm) is measured at the end of testing. According to test results, the fabric can be labeled as non-combustible – the fabric passed or did not pass VFT, which means the fabric: 1. did not ignite (passed VFT), 2. the fabric ignited, but self-extinguished after some time (passed VFT) or 3. the fabric burned out completely (did not pass VFT). The VFT chamber used for the experiment is shown in Figure 16.

Figure 16: *VFT chamber, Govmark*

A Govmark MCC-2 (Heilbronn, Germany) microscale combustion calorimeter (MCC) was used to measure the heat release of cotton samples according to ASTM D7309-19a Standard Test Method for Determining Flammability Characteristics of Plastics and Other Solid Materials Using Microscale Combustion Calorimetry, Method A [80]. In this procedure, the specimen is subjected to controlled heating in an oxygen-free/anaerobic environment (N_2) for thermal decomposition. The gases released by the specimen during controlled thermal decomposition are swept from the specimen chamber by a non-oxidizing/inert purge gas (typically N_2), subsequently mixed with excess oxygen, and completely oxidized in a high-temperature combustion furnace (the mixture of gases consists of 20% O_2 and 80% N_2). The volumetric flow rate and volumetric oxygen concentration of the gas stream exiting the combustion furnace are continuously measured during the test to calculate the heat release rate using oxygen consumption. In Method A, the heat of combustion of the volatile component of the specimen (specimen gases) is measured but not the heat of combustion of any solid residue. The temperature range used for the research was 75–650 °C with the mixture of gases consisting of 20% O_2 and 80% N_2 at 100 mL/min gas flow rate and heating rate of 1 °C/min. The mass of samples was ~ 5 mm, and three measurements per sample were performed to calculate the standard deviation. At the end of the measurement, the following parameters were recorded:

heat release rate (HRR, W/g), peak heat release rate (pHRR, W/g), the temperature at pHRR (T_{pHRR}, °C), total heat release (THR, J/g) and char yield (%). HRR is the heat generation rate during controlled heating from 75 to 650 °C at 1 °C/min. PHRR is the maximum heat release rate during the heating at T_{pHRR}. THR is the heat released by the combustion of one gram of any substance. The MCC data are recorded as plot curves with temperature (T, °C) at X-axis and heat release rate (HRR, W/g) at Y-axis. The repeatability of the MCC measurement was determined by 3 replicated samples for each treatment to calculate standard deviations. The MCC chamber used for the experiment is shown in Figure 17.

Figure 17: *MCC, Govmark*

Thermogravimetric analysis (TGA) was performed with a PerkinElmer Pyris 1 (Shelton, CT, USA) device. All samples were heated from 50 to 850 °C with a heating rate of 30 °C/min in the air (flow rate: 30 mL/min). In TGA, the mass of a sample (5-10 mg) is measured over time (min) or temperature (°C) changes under controlled heating rates in different atmospheres such as N_2, O_2, and air. The data are recorded as plot TG curves with temperature (T, °C) or time (t, min) X-axis and weight loss (mg or%) Y-axis. These basic data can be further derived (first derivate) to obtain DTG curves, which are helpful for precise determination of inflection points such as the beginning of decomposition (at T_{onset}), the highest weight loss rate in mg or %/min (at T_{peak}) and the end of the decomposition (at T_{end}). TG analyzer can be coupled with different evolved gas analysis systems (EGA) such as Fourier Transform Infrared spectrometers (FT-IR), mass spectrometers (MS), or gas chromatograph – mass spectrometers (GC/MS) [81].

This research performed evolved gas analysis (EG) via a PerkinElmer Spectrum 100 FT-IR spectrometer with TL 8000 TG-IR interface (Shelton, CT, USA) in absorbance, wavelength range 4000–450 cm^{-1}, resolution 4.0 cm^{-1}, and with a 27-minute heating interval. The spectra were analyzed via a PerkinElmer Spectrum 100 v 6.3.5. software (Shelton, CT, USA). The applied baseline correction of all spectra was automatic, and all spectra were then normalized according to the following peak/abscissa parameters: ordinate limit 1.5 A, start 4000 cm^{-1}, end 450 cm^{-1}, auto zero point 2318 cm^{-1}. The applied TG-IR unit is shown in Figure 18.

Figure 18: *TG-IR, PerkinElmer*

Before and after performing VFT, the morphology of the samples was analyzed with a Tescan MIRA LMU FE-SEM (SE detector, 5 kV, Brno, Czech Republic). Except for the char, all samples were coated with 5 nm of chromium (Q150T ES Sputter Coater, Quorum Technologies, Laughton, UK).

The chemical analysis of post-burn char was studied using a Tescan Mira LMU FE SEM (backscattered electron BSE detector, 10 and 20 kV) equipped with an energy dispersive X-ray spectroscopy (EDS) detector (Oxford Instruments, Oxford, UK). The applied SEM-EDS unit is shown in Figure 19.

Figure 19: *SEM-EDS, Tescan – Oxford Instruments*

Antimicrobial testing was performed according to AATCC Test Method 100-2019 Test Method for Antibacterial Finishes on Textile Materials: Assessment of antibacterial activity finishes on textile material [82] against Gram-negative *Klebsiella pneumoniae* and Gram-positive *Staphylococcus aureus*.

The percentage of reduction of the bacteria was calculated according to the following equation:

$$R\ (\%) = \frac{C-A}{C}\ x\ 100 \tag{22}$$

where R (%) is the reduction of bacteria, C is the number of bacteria recovered from the inoculated untreated control specimen swatches in the jar at “zero” contact time, and A is the number of bacteria recovered from the inoculated treated test specimen swatches in the jar, incubated over the contact period of 24 h.

4. DISCUSSION

4.1. Advantages of LbL deposition of cotton with FRs

The idea of employing layer-by-layer deposition as a potential textile finishing technique for cotton dates back to 2005, when Hyde et al. deposited an anionic solution of poly(sodium 4-styrene sulfonate) (PSS) and cationic solution of poly(allylamine hydrochloride) (PAH) to build 20 BL on the cationized cotton surface [83]. In 2010 Li et al. deposited 20 BL of positively charged solution of branched polyethylenimine (BPEI) and negatively charged suspension of sodium montmorillonite (MMT) to achieve cotton of reduced flammability by means of LbL deposition [71]. Officially, that was the first attempt at employing LbL deposition for FR functionalization of cotton. Despite reduced peak heat release rates (pHRR) and total heat release rates (THR), none of the coated samples passed the vertical flammability test (VFT).

The first multifunctional (FR/antimicrobial) functionalization of cotton by means of LbL deposition was performed by Fang et al. in 2015. Cotton was deposited with a cationic solution of poly hexamethylene guanidine phosphate (PHMGP) and an anionic solution of ammonium polyphosphate (APP), forming 5–20 BL. The results indicated increased thermal properties of coated cotton, such as increased char residue after performing TG analysis in the air (2.8% for 20 BL) and increased antimicrobial activity against Gram-positive and Gram-negative bacteria. However, none of the samples showed self-extinguishing behavior in VFT as well as the horizontal flammability test (HFT) [84].

The reason for the growing interest in this topic is an attempt to replace current commercial FR (and antibacterial) wet finishing technologies of cotton functionalization due to the implementation of new EU directives for product/production sustainability with the aim of reduction of waste, waste water and toxicity of chemical by using more ecological approaches and green chemistry from renewable sources. As mentioned in Table 1, the current commercial finishing process to reduce the flammability of cotton has many technological and ecological drawbacks.

Durable Pyrovatex® treatment requires desized, scoured, and chemically bleached cotton fabric free of hydrophobic waxes, pectins, and proteins to render cotton hydrophilicity by exposing more negatively charged functional groups of cotton such as hydroxyl groups (-OH), the oxygen atoms of the d-glucopyranose ring (-O-), and the glycosidic linkage (-O-) [8]. A typical Pirovatex CP® standard recipe requires ~ 361 g/l of different chemical compounds (Table 1). Among FR active ingredients such as N-methylol dialkyl phosphonopropionamides, melamine resin, and phosphoric acid, there are also other excipients such as softeners and wetting agents. Pyrovatex® treatment includes at least 10 process steps such as padding, drying, curing, neutralization in caustic soda, at least five water washing cycles, and end drying to remove all water. The process consumes a lot of water and energy due to the high temperatures used during two steps: drying at 130 and 110 °C, curing at 150 or 170 °C, and washing at temperatures from 60 to 90 °C. Another problem is free formaldehyde emission after curing during the production and product life cycles. Cotton fabric treated with Pyrovatex® loses tensile (20–25%) and tear (up to 50%) strengths [30]. By applying the Pyrovatex® process, dry add-ons of cotton fabric are between 20 and 25% [85].

When the results are compared with non-durable commercial FR cotton treatment, e.g., boric acid/borax, it can be noticed that similar quantities are required ~ 10% add-on, while diammonium phosphate/ammonium sulfamate requires ~ 15% add-on and include two (pad-dry) or four (pad-heat cure-wash off-dry) process steps [34,86].

Furthermore, the current Pyrovatex® process is compatible with water/oil repellent finishes to achieve multifunctionality of cotton while simultaneously satisfying all commercial FR requirements such as LOI ≥ 28% and self-extinguishing in VFT and wash durability for at least 50 laundry cycles [30]. However, with the Pyrovatex® process, it is challenging to satisfy multifunctional FR and 100% bacteria reduction because antimicrobial compounds should leach the fabric to be effective against bacteria, which means they should not be covalently bonded to cellulose [58,62]. It means that satisfying flame retardancy of cotton achieved by the Pyrovatex® process diminishes or nullifies satisfying antimicrobial properties.

LbL deposition as an alternative, until now lab scale technique, has shown many advantages over the current Pyrovatex® process in terms of reducing chemicals, reducing energy used for the process, minimal influence on mechanical properties, and the possibility to use eco-friendly chemicals. First, the LbL process requires only charged FR compounds in quantity lower than 10 wt% and optionally charged primer polyelectrolyte for better adhesion of FR compounds (typically 1 wt%). Magovac et al. reported that 5 wt% BPEI as a primer, 2 wt% of phytic acid (PA), 0.5 wt% of chitosan (CH), and 10 wt% of urea (U) were sufficient to self-extinguish cotton fabric in VFT [70,76]. FR compounds used for LbL deposition are long-chain organic polymers, short-chain organic molecules, colloid dispersion of inorganic nanoparticles based on existing commercial organophosphorus FRs (and antimicrobial compounds) such as urea, melamines and their derivates, and ammonium polyphosphate (APP), silica, but also alternative green compounds from renewable sources such as chitosan and its derivates, phytic acid salts, DNA, eggs/white proteins, alginates, clay, silica nanoparticles, and silica compounds. LbL deposition and the Pyrovatex® process require desized, scoured, and chemically bleached cotton of negative charge. The number of steps required for LbL deposition depends on the type of chemicals used in the process, the number of layers, the required functionality of cotton fabric (FR, antibacterial etc.), additional sonication, additional drying, or curing, but the process itself is performed at room temperature. Formaldehyde emission during the process or product life cycle is unknown, but there is expected to be no emission due to low-temperature process steps and no curing. Data on break strength and elongation of cotton treated with FR (and antibacterial agents) by means of LbL deposition are very limited, but authors reported no influence on the break strength or the break strength was in the range ± 10% [71]; the break strength increased up to 10% [87], the elongation break increased for 71.6% [88], the break strength decreased for 12% [89], the break strength decreased for 14% [90]. Dry add-ons of fabric depend on the chemical used, but it is reported to be 5.4–39.1% for LbL-coated cotton (Tables 6 and 9). Magovac et al. reported that only ~ 18% add-ons of cotton fabric (consisting of phytic acid, chitosan, urea, and deposited by LbL deposition) were sufficient to self-extinguish in VFT, which is 2–7% lower than Pyrovatex® add-on [70,76]. Furthermore, by means of LbL deposition, it is possible to achieve multifunctionality of cotton such as FR, water/oil repellents, antistatic-, UV- protective-, wrinkle-resistant-, conductive- and antibacterial properties. For organophosphorus FRs to be effective, phosphorus content should be between 1.9 and 2.0% for cotton treated by means of the Pyrovatex® process and LbL deposition [30,91]. Table 1 presents a brief comparison of Pyrovatex® treatment and LbL deposition.

Table 1: *Comparison of novel LbL deposition with commercial Pyrovatex CP® treatment*

LbL deposition (lab scale)* [70,76]	**Pyrovatex CP® treatment (industrial scale, standard recipe)**
Pre-treatment: desizing, scouring, bleaching	Pre-treatment: desizing, scouring, bleaching
A typical recipe of chemical compounds: • primer (BPEI) – 50 g/l • chitosan (CH) – 5 g/l • urea (U) – 100 g/l • phytic acid sodium salt hydrate (PA) – 20 g/l • $CuSO_4$ x $5H_2O$ (optional), 20 g/l • deionized water (DI) as a solvent	A typical recipe of chemical compounds**: • N-methylol dialkyl phosphonopropionamides – 280 g/l • melamine resin – 35 g/l • acid catalyst – 20 g/l • wetting agent – 1.25 g/l • softener – 25 g/l • distilled water as a solvent [30,92]
Series of process steps:	Series of process steps:

1. immersing into bath 0 with BPEI at room temperature 2. rinsing in bath 1 with DI (to remove any physically entangled or loosely bound polyelectrolyte) at room temperature 3. immersing into bath 2 with PA at room temperature 4. rinsing in bath 3 with DI (to remove any physically entangled or loosely bound polyelectrolyte) at room temperature 5. immersing into bath 4 with CH-U at room temperature 6. rinsing in bath 5 with DI at room temperature 7. repeating steps 3–6 until the desired number of bilayers (10 to 12) 8. drying in the oven at 80 °C for 24 h	1. immersing into a bath with chemical compounds/padding 2. drying in stenter owen at 130 °C 3. curing in baker at 150 °C, 4.5 min; or stenter 170 °C, 1 min 4. neutralizing in caustic soda and soda ash at 30–45 ºC to remove all residual phosphoric acid catalyst, uncross-linked phosphonamide, and some surface cross-linked polymer 5. at least 5 cycles of washing in water at 60–90 °C 6. drying in stenter at 110 °C [30]
No wash durability	Wash durability: over 50 wash cycles at 75 °C in the absence of bleach [30]
Compatibility with antibacterial compounds to achieve multifunctionality ($CuSO_4$ x $5H_2O$)	Compatibility with water/oil repellent finishes achieving multifunctionality [30,92]
Possibility to achieve commercial FR (and antimicrobial) cotton requirements such as LOI ≥ 28%, self-extinguishing in VFT, 100% bacteria reduction	Difficult to achieve multifunctional FR and antibacterial requirements at the same time at an industrial scale [58,62]
Add-ons of fabric ~ 17.3–19.0%	Add-ons of fabric: 20–25% [85]

*all values are expressed as g/l instead of wt% for easier comparison

**for home textiles, LOI=28%

Despite many advantages of LbL deposition as alternative functionalization of FR cotton, there have been many technological drawbacks to improving the full commercialization of the process, as shown in Table 2.

The first drawback is poor durability, as reported in only a few studies. Zhang et al. reported only electromagnetic interference shielding ability after performing home laundering cycles according to GB/T 17595-1998. No results of HFT of washed-treated cotton fabrics were reported [88]. Pan et al. subjected LbL-treated genipin crosslinked FR cotton fabric to home laundering cycles according to GB/T 17595-1998, but washed samples did not pass HFT [93]. Lin et al. immersed LbL-treated FR/superhydrophobic cotton into an aqueous HCl solution with a pH of 2 or an aqueous NaOH solution with a pH of 12 at 25 °C for 12 h to measure acid/alkali resistance. The treated cotton retained hydrophobic properties, but there is no report on flammability [94]. Xue at al. subjected FR, superhydrophobic, and conductive LbL-treated cotton fabrics to home laundering according to AATCC Test Method 61–2003. Again, the treated cotton retained hydrophobic properties, but there is no report on flammability [95]. However, Grunlan et al. managed to achieve laundering durability of polyester-cotton fabric after five home launderings with detergent with a stable polyelectrolyte complex of poly(allylamine) and polyphosphate LbL coating in buffer solution [96].

The second negative drawback to overcome is the high number of immersion steps (dipping – rinsing) to build the number of layers required for a commercial level of flame retardancy. For 30 BL of chitosan (CH, 0.5 wt%, pH 4) and phytic acid (PA, 2 wt%, pH 4), the LbL deposition process took around 10 hours in lab scale by hand immersing, squeezing, rinsing in water, squeezing and around one night for drying at 80 °C in the oven [97]. The third problem was how to control the degree of contamination of polyelectrolytes due to the large number of immersing/rinsing steps of the same material in the same baths. To reduce the number of steps, the original recipe should be optimized by adding other chemicals, such as urea [76], or rinsing in appropriate polyelectrolyte solutions instead of deionized water [98]. The sixth problem of biobased chemicals such as PA solution is its tendency to be spoiled by microorganisms after 2–3 days. To make LbL deposition feasible at the industrial level, new large-scale robotic production lines should be constructed, which require high investments. The potential producer integrating the LbL process should also be aware of difficulties in purchasing highly purified and standardized eco-friendly chemicals from different suppliers. The more purified the chemicals, the more expensive they are. SWOT analysis of LbL deposition is shown in Table 2.

Table 2: *SWOT analysis of LbL deposition*

Internal origin	**Strengths**	**Weaknesses**
	Pre-treatment of cotton fabric is the same as for Pyrovatex® treatment (desizing, scouring, bleaching) Low concentrations of FR (and antibacterial) compounds (polyelectrolytes) ≤ 100 g/l*	Poor or no wash durability – additional curing at higher temperatures or post-treatment in citric buffer solution to form an insoluble complex is required to achieve wash durability High water consumption (series of water baths for electrolyte solutions and rinsing)

	Temperature range: from ambient temperature – to 100 °C Use of deionized water as a solvent for polyelectrolyte or for rinsing the fabrics Minimal influence on mechanical properties Possibility to achieve required (FR and antimicrobial) effectiveness on the cotton substrate prior to washing	Time-consuming due to the high number of immersing/rinsing steps Difficulties in controlling parameters influencing layers growth (pH) Construction of new large-scale robotic production lines requires high initial costs
External origin	**Opportunities**	**Threats**
	Possibility to use eco-friendly chemicals from renewable and mineral sources such as chitosan and its derivates, phytic acid salts, DNA, eggs/white proteins, alginates, clay, silica compounds	Difficulties in purchasing highly purified and standardized eco-friendly chemicals from different suppliers; Chemicals from animal/plant-based sources are easily spoiled and could be expensive for large-scale industrial production, causing possible high costs for the end product

* all values are expressed as g/l instead of wt% for easier comparison

4.2. Flame retardant (FR) cotton materials

The first part of the discussion deals with the technological advantages and disadvantages of LbL deposition as FR functionalization of cotton, emphasizing the ability to pass the VFT, possess satisfying mechanical properties, and wash durability of LbL FR nanocoating. In the second part of the discussion, the emphasis is on chemicals used for LbL deposition and their influence on the thermal behavior of LbL FR coated cotton fabrics measured by limiting oxygen index (LOI), microscale combustion calorimeter (MCC), cone calorimeter (CC), thermogravimetric analyzer (TGA) and evolved gas analysis by TG-IR. According to Table 6, chemicals and their combination used to reduce the flammability of cotton by means of LbL deposition can be divided into six groups:

1. organic polyelectrolytes such as polyethyleneimines (PEIs) and poly(vinylamine) (PVAm), poly(acrylic acid) (PAA);
2. urea (U) and urea-based compounds such as melamine (ME), sulfonated melamine-formaldehyde (SMF), p-aminobenzene sulphonic acid-modified melamine (AMM);
3. inorganic salts based on polyphosphoric acids (PPA), such as ammonium polyphosphate (APP) and sodium hexametaphosphate (PSP);

4. metal salts such as barium chloride ($BaCl_2$), cobalt acetate tetrahydrate ($C_4H_6O_4Co$ x $4H_2O$), nickel acetate tetrahydrate ($C_4H_6O_4Ni$ x $4H_2O$);
5. quaternary ammonium salts such as polydiallyldimethylammonium chloride (PDAC);
6. colloidal suspensions of nanoparticles: silanes for sol-gel reactions such as 3-aminopropyl triethoxysilane (APTES), nanoclays such as hydrotalcite (HT), sodium montmorillonite (MMT) and graphene nanoplatelets (GNP);
7. biopolymers and biomolecules such as poly(vinyl alcohol) (PVA); poly(4-styrenesulfonic acid) (PSS); chitosan (CH) and its derivates such as hypophosphorous acid-modified chitosan (HACH); alginates (ALG) such as sodium and potassium alginates; biobased cationic starch (CS); phytates such as myo-inositol hexaphosphate (PA); deoxyribonucleic acid (DNA) and eggs white protein;
8. other excipients such as organic tris(hydroxymethyl)aminomethane (THAM).

Polyethyleneimine (PEI)

Polyethyleneimine (PEI) is a viscous, highly charged, water-soluble cationic polymer rich in nitrogen in linear and branched shapes. Linear PEI (Figure 20) possesses primary and secondary amino groups, whereas branched PEI (Figure 21) additionally possesses tertiary amino groups [99]. The cationic charge of PEI is enabled by protonated amino groups (NH^+, NH_2^+, NH_3^+), which strongly interact with negatively charged species [100]. The protonation degree of PEI varies with different environmental pH [101]. Due to its positive charge, PEI is used as a carrier for gene delivery treatment since it interferes with negatively charged cell membranes and reacts with the DNA [99]. The ability of PEI to enter cell membranes easily is also used to prepare bioactive coatings that kill bacteria upon contact [102]. As a nitrogen-rich and positively charged polymer, PEI is used for LbL deposition as a primer layer for better adhesion of oppositely charged layer on cotton [76], but also as an alternative for commercial organophosphorus flame retardants if combined with phosphorus species [88]. Despite the safety data sheet statement that PEI "contains no components considered to be either persistent, bioaccumulative and toxic (PBT), or very persistent and very bioaccumulative (vPvB) at levels of 0.1% or higher and does not contain components considered to have endocrine disrupting properties according to REACH Article 57(f) or Commission Delegated regulation (EU) 2017/2100 or Commission Regulation (EU) 2018/605 at levels of 0.1% or higher" [103], PEI could, however, induce acute brane toxicity, especially PEI with larger molecular weight and more branching of the macromolecule [99]. PEI is unfortunately not considered biodegradable [103].

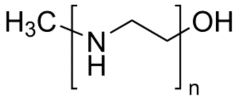


Figure 20: *Structural formula of linear PEI [104]*

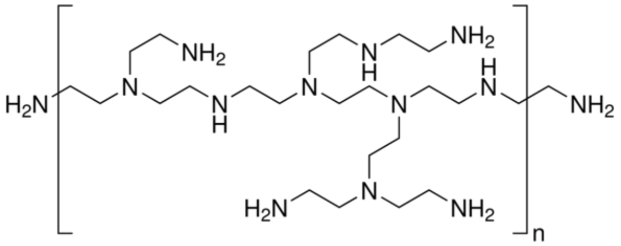


Figure 21: *Structural formula of branched PEI [103]*

If (B)PEI is used as a primer layer for LbL coating of cotton, it acts as a positively charged bridge between negatively charged functional groups of cotton cellulose and negatively charged second layer of other polyelectrolytes [70,76,90,91,98]. In that context, their nitrogen functional groups do not influence the overall reduced flammability of cotton, and it is not expected to influence antibacterial activity.

As a primer polyelectrolyte, BPEI is prepared in a concentration of ≤ 5 wt% and at pH neutral environment, where N, NH, and NH_2 groups become protonated and highly attracted by negatively charged functional groups of cellulose as well as other anionic polyelectrolytes [101]. It is believed that nitrogen functional groups in BPEI interact with -OH functional groups in cellulose by weak electrostatic H-bonds in LbL assemblies [105].

BPEI, however, can also act synergistically with phosphorus (P) rich compounds in cotton FR systems due to high nitrogen content (N), so it can also be used as a cation counterpart of bilayering. BPEI (0.1 wt%, pH 10) has been used as a cation counterpart of anionic nanoclay montmorillonite (MMT) dispersion (1 wt%, pH 10) to deposit 5 and 10 BL of cotton. Even though none of the coated cotton samples passed VFT, the study revealed that LbL coating neither significantly improves nor harms the mechanical strength of the fabric. The study also showed that as the number of layers increase (so as the amount of FR compounds), the flammability of cotton decreases. Reduced flammability means more char left after performing

TG and MCC measurements and reduced pHRR and THR rates. More layers also means more FR add-ons on cotton fabric [71].

PEI has been used for preparing 1 wt% cationic sol with silica nanoparticles (SiO_2) at pH 5 and combined with 2 wt% anionic phytic acid (PA) solution at pH 6 to reduce the flammability of cotton. The resulting 2-bilayer (BL) LbL coated fabric (add-on 11.3%) self-extinguished in VFT with a limiting oxygen index (LOI) value of 26%. Unfortunately, the authors did not present a cone calorimeter or TGA data of 2 BL coatings. However, they mentioned that pHRR rates (kW/m2) of 7 BL were 75% lower and THR values 52% lower than untreated cotton. The author also stated that the char residue at 600 °C was 40.7% after heating in TG under a nitrogen atmosphere.

LbL coating consisting of PEI-SiO_2/PA generates intumescent (bubbling) char (SEM images) consisting of carbon (C), nitrogen (N), oxygen (O), silicon (Si), and phosphorus (P) according to EDS analysis [106]. To reduce the number of BL required to achieve the same VFT performance, PA was replaced with polyphosphoric acid (PPA), and the concentrations of polyelectrolytes solution were doubled (2% PEI-SiO_2 and 4 wt% PPA) under the same pH. The results showed that only 1 BL with the add-on of 23.4% of PEI – SiO_2/PPA self-extinguished the cotton flame in VFT with LOI values of 29.6%. TG data in nitrogen showed 44% of char left at 600 °C under nitrogen [89]. However, it is unclear whether the reduction of the number of BL (from 2 to 1 BL) with the same FR performance came from different types of phosphorus-rich chemicals (PA vs. PAA), from the double increase in polyelectrolyte concentrations or from the increased immersion time (from 1 min to 20 min) in each electrolyte, or the combination of both.

PEI (0.5 wt%) can be combined with melamine (ME, 2 wt%) in a cationic solution at pH 4 and anionic PA solution (3 wt%, pH 4) to form 4 BL deposited cotton able to pass VFT. The cone calorimeter data showed a pHRR reduction of 59% and a THR reduction of 24% compared to untreated cotton with only 5.1% of an add-on. The percent of char left after heating in TG in the air was 7.8% at 600 °C [107].

Zhang et al. successfully reduced the flammability of cotton by combining solely PEI (0.5 wt%, pH 9.2) and PA (2 wt%, pH 4) in 8 BL (add-on 24.2%). Coated cotton passed VFT with the exceptional LOI value of 37% and reduced cone calorimeter values (pHRR reduced by 38% and THR reduced by 22%). That was the only study dealing with evolved gas products generated by heating in the air in TGA, which showed that FR coating reduced the release of a toxic gas for cotton during the initial thermal degradation process (CO_2, CO, aliphatic esters) relative to untreated cotton [88]. If 0.5 wt% PEI is combined with 0.3 wt% of hypophosphorous acid-modified chitosan (HACH) to form 10 BL, it forms a very efficient FR able to pass horizontal flammability test (HFT) with only 12.1% add-on. The coating reduced the pHRR by 73% and the THR value by 80%. Unfortunately, the coating was non-wash durable even after the crosslinking [93]. The structural formula of HACH is shown in Figure 22 [108].

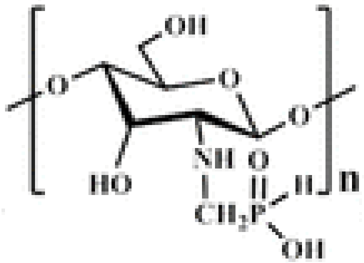


***Figure 22:** Structural formula of HACH [108]*

If PEI is not used in synergy with P compounds, it is useless in the sense of flame retardancy, even if combined with metal salts and sodium alginate as a natural metal chelating agent [109]. Another synthetic, highly charged water-soluble cationic polymer rich in N with the highest content of primary amine functional groups of any polymer is poly(vinylamine) (PVAm). Depending on pH, it strongly interacts with negatively charged species due to protonated amino groups (NH3+). The structural formula of PVAm is shown in Figure 23 [110]. The PVAm properties and applications as an interfacial agent are compared to those of linear PEI, polyallylamine (PAAm), and chitosan (CH) [111].

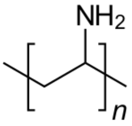


***Figure 23:** Structural formula of PVAm [110]*

The properties of PVAm as an N-P FR agent were investigated by Zilke et al., who successfully LbL deposited cotton with 15 BL (add-on 18.8%) of anionic PA solution (5 wt%, ph 0.7) and cationic PVAm solution (5 wt%, pH 8.7). The resulting fabric passed VFT with reduced MCC values (pHRR for 80% and THR for 61%) and the amount of char after performing MCC of 32.3%. The gases generated by heating in TG (nitrogen atmosphere) were toxic acrolein (1735 cm^{-1} and 1710 cm^{-1}), formaldehyde (1735 cm^{-1} and 2800 cm^{-1}), CO_2 (2349 cm^{-1}), water (1500 cm^{-1}), carbon monoxide (2171 cm^{-1}) and methanol (1070 cm^{-1}). The study also revealed that the molar ratio of P/N for effective FR should be 3:5 or 2.0 wt% of P and 1.4 wt% of N [91].

To conclude, (B)PEI and PVAm proved to be very efficient nitrogen-rich polyelectrolytes that easily bind negatively charged -OH functional groups of cellulose (H-bonds) and, combined with phosphorous-rich compounds, form an efficient FR system. As can be seen from Table 3, (B)PEI/PVA has been used with SiO_2 nanoparticles or ME to form cationic sol for further hybrid LbL deposition with phosphorus-rich anionic polyelectrolytes such as PA and PPA [89,106,107], but also alone with anionic polyelectrolyte such as nano clays (MMT) [71] and biomolecules (PA, SA, HACH) [88,91,93,109]. Despite being declared biocompatible and used mainly as a carrier for gene-drug, they are not considered biodegradable. For safety reasons, they should be used as little as possible. It should be mainly used as a primer (or a bridge) between negatively charged cotton surfaces and other negatively charged compounds for better adhesion. The (B)PEI and PVAm properties and applications as interfacial agents are compared to those of chitosan (CH) so that wherever it is possible, CH should be used instead of (B)PEI and PVAm [111].

Sodium montmorillonite

Sodium montmorillonite (MMT) belongs to a smectite group of naturally occurring cationic nano clays insoluble in water with the structural formula shown in Figure 24 [112]. Its layered structure (ca. 1 nm in thickness) consists of stacked layers, and each layer is composed of two O-Si-O tetrahedral sheets sandwiching one O-Al (Mg)-O octahedral sheet (ca. 100 nm × 100 nm in width and length). Due to the isomorphous substitution, the layer is positively charged, and then cations are positioned in the interlayered space of metal (M) cations. Neighboring layers are held together by van der Waals force and electrostatic force to form the primary metal particles of M [113]. As MMT is a hydrophilic material, its compatibility with most organic polymers is very poor [114].

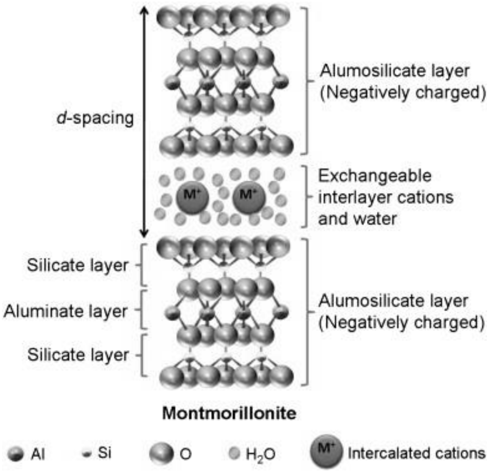


Figure 24: *Layered structure of MMT [112]*

The potential of MMT as an efficient FR for LbL deposition of cotton has been used in several studies, where MMT was coupled with positively charged polyelectrolytes such as BPEI [71] and bio-based cationic starch (CS) [72] in a simple LbL assembly. The results are, however, unsatisfactory. Anionic MMT dispersion (1 wt%, pH 10) and BPEI solution (0.1 wt%, pH 10) have been used to deposit 10 BL of cotton, but the coated sample did not pass VFT despite reduced THR values for 20% compared to untreated cotton [71]. Another study combined 1 wt% dispersion of anionic MMT with 1 wt% bio-based cationic starch (CS) solution. Even 20 BL of CS/MMT coating on cotton did not pass VFT with a reduced pHRR value of 21.3% and a THR value of 14.7% [72]. CS is obtained by attaching positively charged groups to the carbohydrate backbone, such as ammonium from quaternary ammonium salt, and it is mainly used in the paper industry or as a warp-sizing agent in the textile industry [115]. To achieve appropriate flame retardancy of cotton, MMT should be combined with P-N-rich compounds such as ammonium polyphosphate (APP) and acrylate polyurethane (PU) in very complex nanocomposites, which then can serve to form anionic dispersions for layering with cationic polyelectrolytes such as BPEI [116]. As can be seen from previous studies, PEI was combined with metal salts [109] as well as nano clays such as MMT [71] to reduce the flammability of cotton, but the studies also confirm that PEI is not efficient if not combined with phosphorus-rich compounds such as PA [88,106,107], PPA [89] and HACH [93].

Phytic acid salts

Phytic acid (PA) salts are easily obtained phosphorus-rich (~ 28% Mw) chelating agents from plant/seed sources (e.g., legumes, cereals, oilseeds, pollens, and nuts) with high absorption of multivalent metals such as Fe^{3+}, Zn^{2+}, and Ca^{2+} forming insoluble complexes [117]. Salts are also used as food additives, so their use is safe [118]. Since PA easily interacts with minerals and trace elements in the gastro-intestinal chyme, it inhibits the absorption of essential trace elements and minerals, which may lead to Fe^{3+}, Zn^{2+}, and Ca^{2+} deficiencies due to the fact that humans lack the enzyme needed to break down PA to obtain phosphorus [119]. The structural formula of sodium phytate is shown in Figure 25 [120].

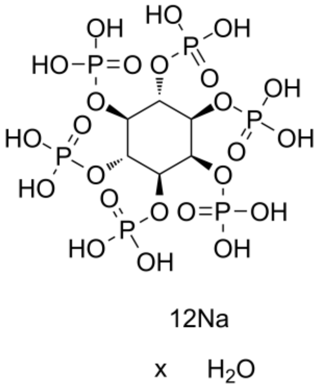


Figure 25: *Structural formula of PA [120]*

It consists of six phosphate groups and twelve -OH groups that can promote charing during the combustion of carbon-rich polymers such as cellulose, so it can be used as an alternative phosphorus-rich FR with a known mode of action. By adding PA and its derivates into FR finishes for cotton, PA forms acidic intermediates by phosphorylation of cellulose acting as a catalyzer, which further dehydrates forming char and releases water at the same time [121]. As an anionic compound, PA has been used as a polyelectrolyte for LbL deposition. In fact, the majority of studies regarding cotton flame retardancy by means of LbL deposition use PA, as presented in Table 3. Laufer et al. were the first to study the potential of PA in cotton flame retardancy obtained by LbL assembly. They study the influence of different pH of PA and chitosan (CH) solutions on film growth and overall flame retardancy. PA (2 wt%) and CH (0.5 wt%) were coupled as an anionic and a cationic counterpart and BPEI as a primer (1 wt%). As a result, 30 bilayers (BL) of PA-CH created at pH 6 were thicker and had 48 wt% PA in the coating, while the thinnest films with a PA content of 66 wt% were created at pH 4. Cotton fabric treated at pH 4 passed VFT with an add-on of 16%. MCC data showed the pHRR and THR reduction of 62% and 77% and char of 41.7% [122]. The influence of pH, the concentration of polyelectrolytes, ionic strength, temperature, macromolecular structure, and charge density on layers growth has been studied intensively, but the behavior of polymers deposited depends rather on the type of polymers used. There is no general rule that could be applied to all types and combinations of polyelectrolytes. The increase in multilayer thickness can be either linear or exponential [123]. In an effort to reduce the number of necessary steps in the LbL process with the same or enhanced FR performance of Laufer et al. was a starting point [122], Magovac et al. introduced urea, a nitrogen-rich compound into cationic CH solution to form LbL assembly with anionic PA [76]. Urea (U) is a colorless, non-toxic, and naturally occurring nitrogen-containing molecule soluble in water produced by the protein metabolism of mammals but has been synthetized from ammonia and carbon dioxide for over a century [124]. It is a raw material used mostly for the production of agricultural fertilizers as well as for urea-melamine-formaldehyde resins and flame retardants. Its structural formula is shown in Figure 26 [125].

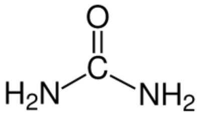


Figure 26: *Structural formula of U [125]*

Adding U (10 wt%) to cationic CH solution (0.5 wt%) at pH 4 makes it possible to reduce the number of BL in PA/CH assembly from 30 to 10 with the add-on of only 17.3%. Coated cotton fabric passed VFT with an LOI value of 28%. The MCC data showed pHRR and THR reductions of 59.5 and 70.3% relative to untreated cotton and char of 32.6%. According to TG analysis performed in the air from 50 to 650 °C (30 °C/min, flow rate: 30 ml/min), there are two major weight losses at 334 °C (T_1) and 604 °C (T_2), where 10 BL sample loses 37 and 79% of its original weight. At 650 °C, char yield is ~ 15% [76]. Figure 27 compares TGA curves of 30 BL of PA/CH and 10 BL of PA/CH-U coated samples compared to untreated cotton (control).

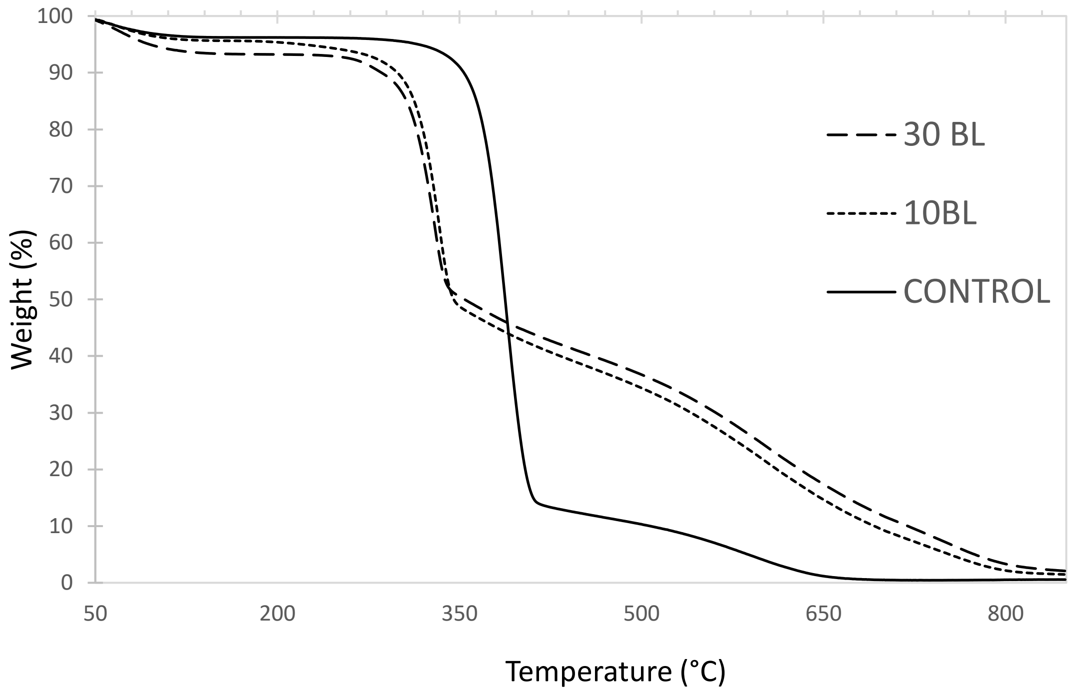


Figure 27: *TG curves of untreated cotton and cotton samples treated with 10 BL of PA/CH-U and 30 BL of PA/CH*

Usually, the decomposition of cellulose is a two-step process. The first weight loss starts between 50 and 100 °C due to the evaporation of moisture. The first decomposition stage begins between 250 and 400 °C, with dehydration and depolymerization of polymer chains of cellulose. At this stage (T_1), cellulose loses 95% of its weight, generating non-flammable gases such as carbon dioxide (CO_2) and water (H_2O) and flammable gases such as carbon monoxide (CO), methane (CH_4), aldehydes (C=O), carboxylic acid esters (C-O-C), levoglucosane and primary char [126]. The second decomposition stage starts between 500 and 650 °C with its maximum at T_2, where levoglucosane produces flammable gases such as CO and secondary char [127]. Above 800 °C, all organic compounds burn out, leaving only inorganic char [128]. Shafizadeh et al. stated that the type of gas products generated by heating cellulose is not atmosphere (N_2 or air) dependent [126]. Benítez-Guerrero et al. [129], however, did not find CH_4 in IR gas spectra of cellulose heated in the air, which differs from Horrocks et. [130], who found CH_4. According to the literature, TG-IR gas analysis of cellulose performed in an N_2 atmosphere (flow rate 40 ml/min) at 30 °C to 750 °C at different heating rates at ~ 400 °C showed mainly the presence of H_2O, CH_4, CO_2, CO, and other compounds with the functional groups such as C=O, C=C, C-O-C/C-C as presented in Figure 28 [131].

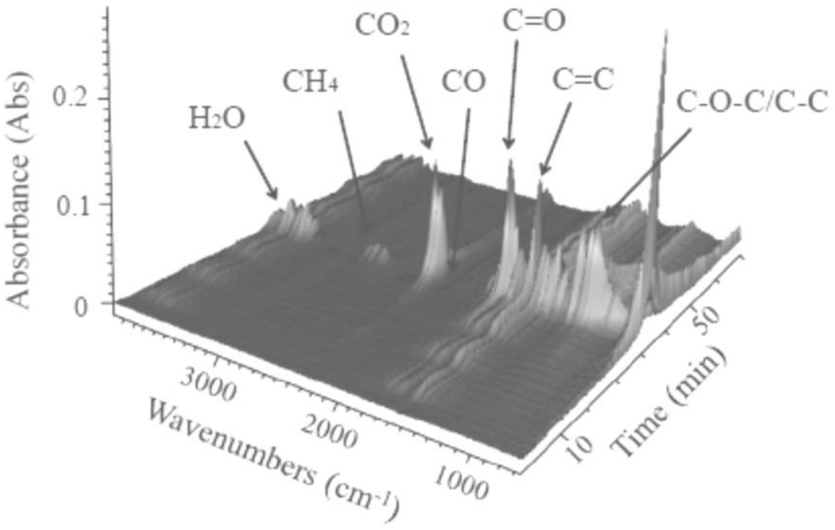


Figure 28: *TG-IR evolved gas analysis of cellulose in* N_2 *[131]*

Magovac et al. [70] showed that by heating cellulose from 50 to 850 °C at rate of 30 °C/min in the air (flow rate 20 ml/min) the main gas products at ~ 396 °C are H_2O, CH_4/CH_3OH, CO_2, CO, formaldehydes and highly flammable levoglucosan, which is in accordance with Horrocks et. [130]. However, the peak of ethen at 950 cm^{-1} and acetylene at 720 cm^{-1} is not found, not because they do not exist, but because they might be overlapped with other spectra such as H_2O. As seen in Figure 29, between 3800 cm^{-1} and 3500 cm^{-1} lie characteristic peaks of medium stretching vibrations of O-H bonds in a molecule of H_2O or alcohol [132]. C-H stretching of CH_4 or CH_3OH lies between 3000 cm^{-1} and 2750 cm^{-1} [133]. The strong antisymmetric stretching and rotational bands from the R branch of the C=O bonds in CO_2 lie between 2450 cm^{-1} and 2300 cm^{-1} [134]. Double peaks at 2172 cm^{-1} and 2112 cm^{-1} represent the stretching vibrations of C=O molecules of CO [133]. The C=O stretching vibration of aliphatic aldehyde (formaldehyde) lies at 1744 cm^{-1}. At 1182 cm^{-1} lies strong C-O-C stretching of formic acid ester [135]. A very sharp peak at 1062 cm^{-1} can be assigned to levoglucosan (C-O-C), which is the compound responsible for the high flammability of cellulose [130]. At 668 cm^{-1}, there is a very sharp peak of weak bending vibrations from the Q branch of the C=O bonds from CO_2 [134].

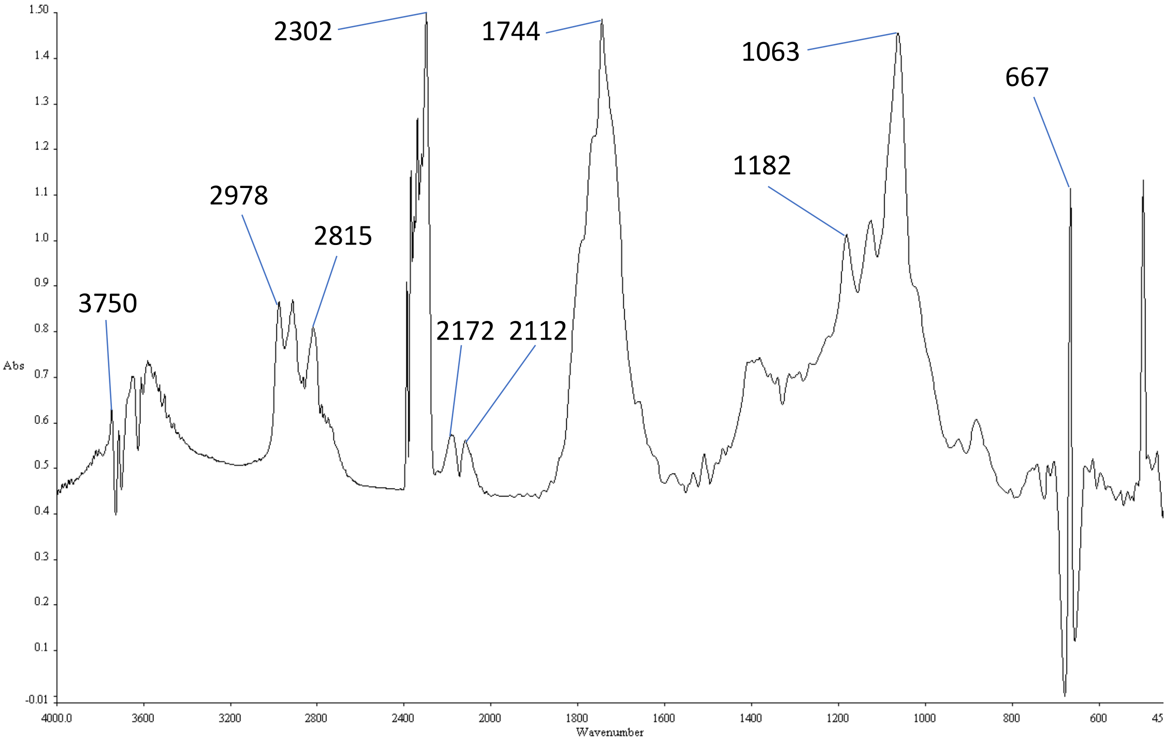


Figure 29: *TG-IR spectra of evolved gases of cellulose at the first decomposition stage ~ 396 °C [70]*

At ~ 578 °C, TG-IR spectra of cellulose consist of H_2O or CH_3OH (between 3800 cm^{-1} and 3500 cm^{-1}), CO_2 (between 2450 cm^{-1} and 2300 cm^{-1}, and a peak at 668 cm^{-1}), CO (double peaks at 2181 cm^{-1} and 2107 cm^{-1}), and levoglucosan (at 1062 cm^{-1}) as shown in Figure 30 [70]. Peaks between 3800 cm^{-1} and 3500 cm^{-1} at 578 °C are more likely part of the background noise of the TG-IR interface than H_2O generated from cellulose.

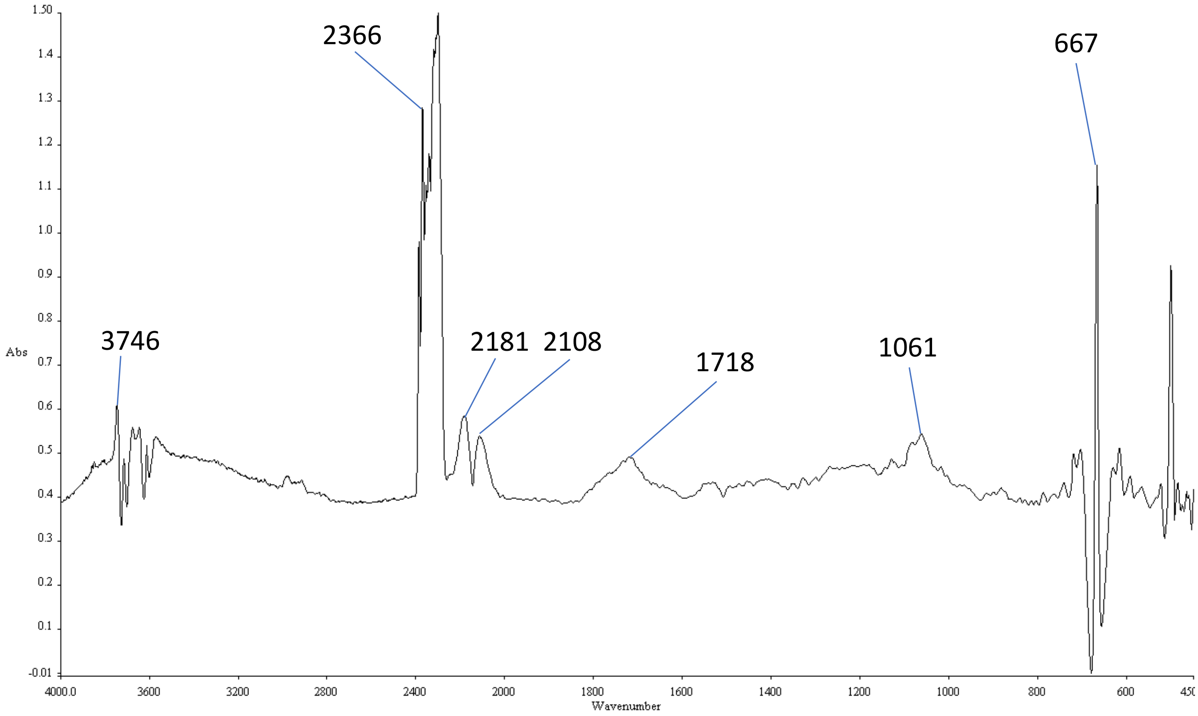


Figure 30: *TG-IR spectra of evolved gases of cellulose at the second decomposition stage ~ 578 °C [70]*

Absorbance peak values with corresponding wavelengths (cm^{-1}) of evolved gases of untreated cotton at the first and the second decomposition stages are presented in a separate table (Table 3) due to better visibility.

Table 3: *Summary of TG-IR analysis of untreated cotton at 396 and 578 °C*

			Temperature (°C)			
			396		578	
Functional groups	Covalent bonds vibrations	Wavelength range (cm^{-1})	cm^{-1}	Abs	cm^{-1}	Abs
R-OH	st O-H	3800–3500	3750	0.62	3746	0.60
-CH$_3$	st C-H	3000–2750	2978	0.86		
			2815	0.80		
CO$_2$	st C=O	2450–2300			2366	1.20
			2302	1.40		
CO	st C≡O	2300–2100	2172	0.57	2181	0.58
			2112	0.55	2108	0.53
CH$_2$O formaldehyde	st C=O	1740–1720	1744	1.48	1718	0.49
Ester of formic acid HCOOCH$_3$	st C-O-C	1210–1160	1182	1.01	/	/

R-O-R, levoglucosan	st C-O-C (asym)	1310–1000	1063	1.45	1061	0.54
CO_2	d C=O	668	667	1.10	667	1.14

Chemical interaction between the FR agent and cellulose molecules occurs by adding phosphorus (P) based FR on the cellulose surface at temperatures lower than those of the pyrolytic decomposition of cellulose. P species phosphorylate the cellulose with the release of H_2O, which further leads to dehydration, cross-linking, and char formation, as presented in Figure 31. Thermally stable char coats the polymer surface, acting as a shield, which prevents further burning and smoldering of the polymer. At temperatures above 600 °C, char undergoes oxidation, but a phosphorus compound in char inhibits the complete oxidation of carbon to CO_2 [136].

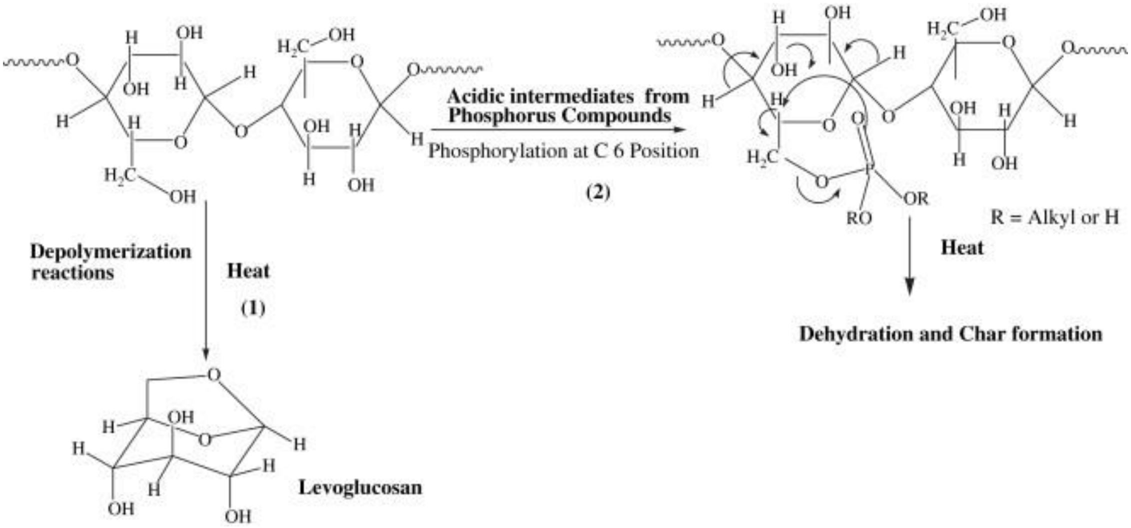


Figure 31: *Mode of action of phosphorus flame retardants [136]*

Phosphorus-based FRs reach their maximum efficiency if combined with nitrogen (N) compounds, forming so-called N-P synergism [137]. Compounds rich in N release nitrogen, which binds to high energy free radicals in oxidation, generating non-flammable gases such as NO and NO_2, which suppress the flame, but covalent bonds between N and P in organophosphorus FRs are thermally much more stable than those between P and oxygen in phosphorus-based FRs, which makes the reaction of phosphorylation easier [19,20,138]. The reaction is accompanied by bubbling structures (the intumescent char) formed on the charring surface of treated polymers during combustion. This bubbling effect is caused by the release of non-flammable gases [13]. The intumescent char protects fabrics from flame, while H_2O cools down the system by removing heat from the fire. By adding N-based compounds into PA based FR system, such as urea (U) at 120 °C, N-P intermediates are generated with the release of CO_2, as shown in Figure 32a. At ~ 170 °C, these N-P intermediates react with cellulose, as shown in Figure 32b [139].

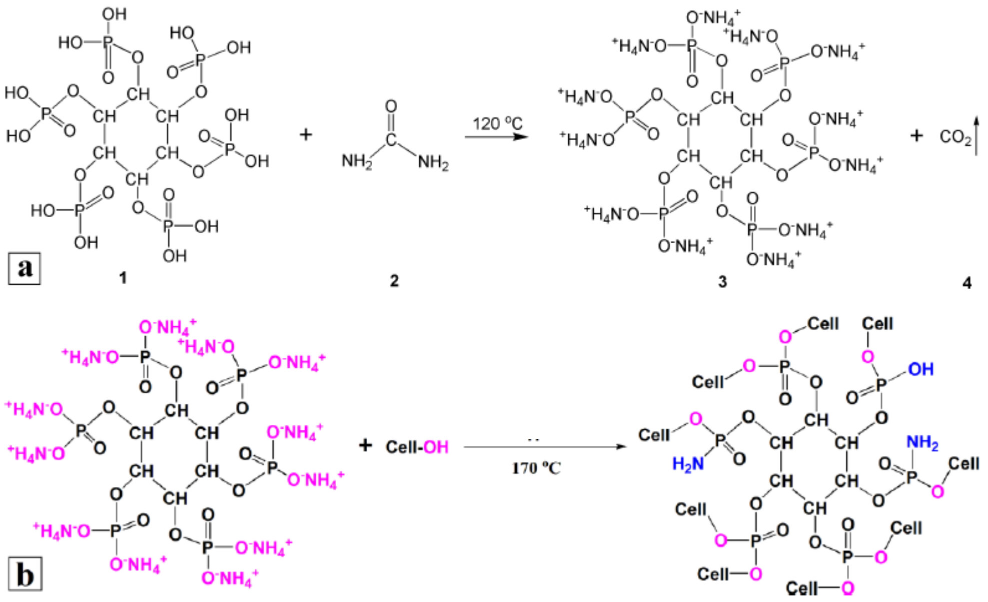


__Figure 32:__ A possible reaction between a) PA and U b) PA-U intermediate and cellulose [139]

By further heating at temperatures below the decomposition temperature of untreated cellulose (350–400 °C), N-P cellulose derivates undergo the phosphorylation reaction with acidic intermediates from P-N compounds, which further dehydratize into char with the release of non-flammable gases such as H_2O, NO, and NO_2, which dilute oxygen in the air, thus suppressing the flame.

Magovac et al. research [70] shows that by applying 12 BL of PA/CH-U FR finishes onto cotton, the decomposition temperature starts at ~ 300 °C, which is ~ 50 °C lower than untreated cotton and reaches its maximum at ~ 327 °C. TG-IR spectra of evolved gases of 12 PA/CH-U treated cotton at the first decomposition stage show several characteristic groups of peaks (Figure 33), while the absorbance values at the first decomposition stages of untreated and 12 BL PA/CH-U treated cotton are given in Table 4.

Between 3800 cm^{-1} and 3500 cm^{-1} lie the medium stretching vibrations of O-H bonds in a molecule of H_2O or alcohol [132]. Between 3000 cm^{-1} and 2750 cm^{-1} lies the C-H stretching of

CH_4 or CH_3OH [133]. Characteristic peaks between 2450 cm^{-1} and 2300 cm^{-1} belong to the strong antisymmetric stretching and rotational bands from the R branch of the C=O bonds in CO_2 [134]. Double peaks at 2172 cm^{-1} and 2112 cm^{-1} represent the stretching vibrations of C=O molecules of CO [133]. A peak at 1744 cm^{-1} matches the C=O stretching vibration of formaldehyde [135].

At 1510 cm^{-1}, a peak matches the deformation vibrations of CNH bonds in 5-ring imides (the region between 1510–1500 cm^{-1}) [140]. The peak at 1182 cm^{-1} represents stretching vibrations of C-O-C of ester of formic acid, while the peak at 1106 cm^{-1} belongs to asymmetric stretching of C-O-C bonds in ether [141]. No levoglucosan is found at 1063 cm^{-1}.

At 902 cm^{-1}, a peak matches the stretching vibrations of CH in cycloalkanes (the region between 920 and 880 cm^{-1}) [142]. PH_2 wagging of the R-PH compound has been found in the region between 840 and 810 cm^{-1} (peak at 828 cm^{-1}) [143]. Treated cotton shows two peaks at 742 cm^{-1} and 702 cm^{-1}, probably due to NH bond wagging [144]. A very sharp peak at 668 cm^{-1} belongs to weak bending vibrations from the Q branch of the C=O bonds from CO_2. Other compounds may exist, but their spectra are overlapped with H_2O and CO_2 [145]. Other compounds, such as hydrogen cyanide (HCN) at the spectral range between 706 and 716 cm^{-1} and nitrogen dioxide (NO_2) at the spectra range between 1545 and 1659 cm$^{-1,}$ may exist, but they are overlapped with spectra of other compounds [146,147].

Comparing the results in Table 3, untreated cotton produces more flammable gases such as CH_4/CH_3OH while heating relative to PA/CH-U cotton. This is visible through reduced absorbance values of st C-H vibrations of 0.86 and 0.80 for untreated cotton and 0.60 and 0.68 for cotton treated with 12 BL PA/CH-U. Treated cotton generates fewer aliphatic aldehydes (Abs of st C=O vibrations is 1.23) compared to untreated cotton (1.48) and shows no levoglucosan at 1063 cm^{-1}, a compound responsible for the high flammability of cellulose [70]. However, gas products of treated cotton contain R-NH and R-PH compounds, which may oxidize to NO_X and PO_X state acting in the gas phase. However, Magovac et al. research [65] shows that by applying 12 BL of PA/CH-U FR finishes onto cotton, the char increases at the first decomposition stage from 43.6% for untreated cotton to 57.8% for treated cotton, which means that even small fraction of FR N-P compounds might be trapped in char acting in the condensed phase. For comparison IR spectra of gases generated by heating Pyrovatex® treated cotton in the air show characteristic peaks of H_2O (3728 and 3625 cm^{-1}), CH_4 (3017 and 1305 cm^{-1}), CO_2 (2359, 2342 and 670 cm^{-1}), CO (2173 and 2118 cm^{-1}), aldehydes (1700 and 1724 cm^{-1}), levoglucosan (1050 cm^{-1}), ethen (950 cm^{-1}) and acetylene (720 cm-^{1}) [130]. Other authors found HCN (between 706 and 716 cm^{-1}) and NO_2 (between 1545 and 1659 cm^{-1}) [146,147].

According to the literature, cotton treated with different FRs generates similar gas products, so it is expected that durable/non-durable N-P organophosphorus FRs such as ammonium polyphosphate, diammonium phosphate or Pyrovatex® generate similar gas products with an identical mode of action previously explained in the introduction part of thesis [148].

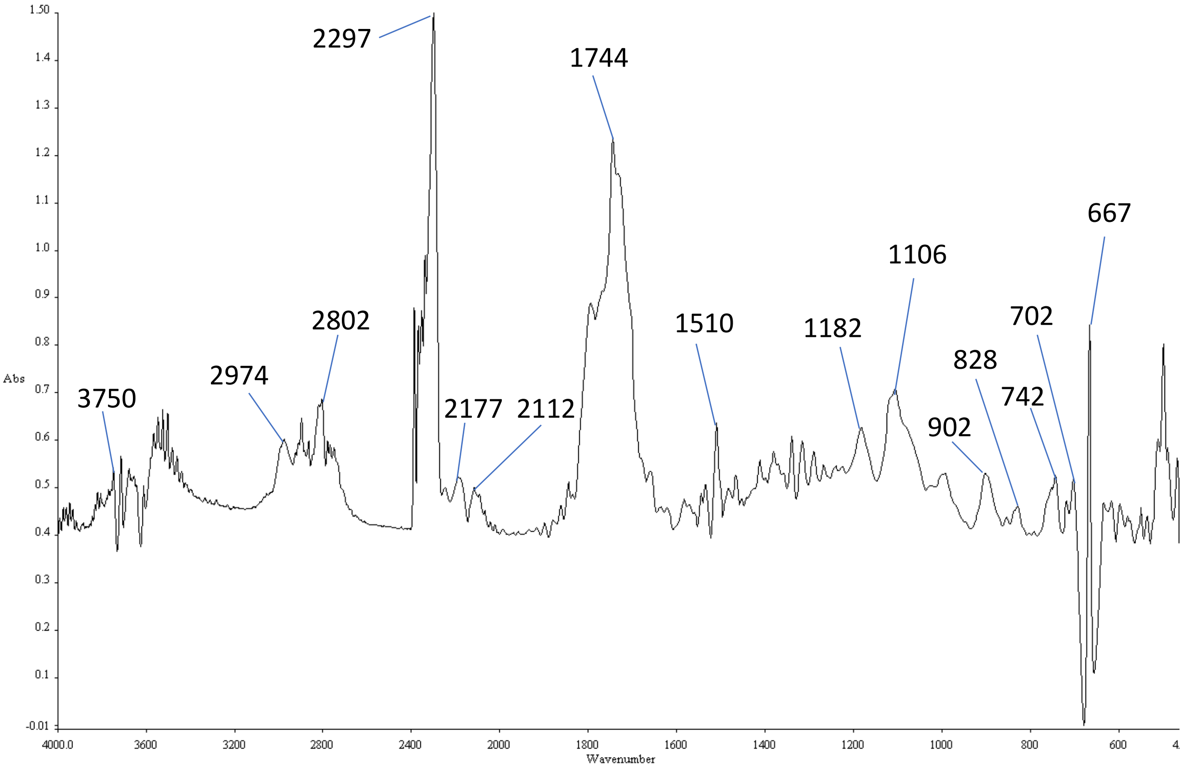


Figure 33: *TG-IR spectra of evolved gases of 12 BL PA/CH-U treated cotton at ~ 339 °C*

Table 4: *Summary of TG-IR analysis of untreated cotton (control) at 396 and 12 BL PA/CH-U treated cotton at 339 °C*

			Temperature (°C)			
			Control		12 BL PA/CH-U	
			396		339	
Functional groups	Covalent bonds vibrations	Wavelength range (cm^{-1})	cm^{-1}	Abs	cm^{-1}	Abs
R-OH, H_2O	st O-H	3800–3500	3750	0.62	3750	0.53
-CH_3	st C-H	3000–2750	2978	0.86	2974	0.60
			2815	0.80	2802	0.68
CO_2	st C=O	2450–2300	2302	1.40	2297	1.49
CO	st C≡O	2300–2100	2172	0.57	2177	0.51
			2112	0.55	2112	0.49

CH_2O formaldehyde	st C=O	1740–1720	1744	1.48	1744	1.23
Imides, 5-ring	d CNH	1510–1500	/	/	1510	0.64
Ester of formic acid $HCOOCH_3$	st C-O-C	1210–1160	1182	1.01	1182	0.63
R-O-R, ether	st C-O-C (asym)	1175–1038	/	/	1106	0.71
R-O-R, Levoglucosan		1310–1000	1063	1.45	/	/
Cycloalkanes	st CH	920–880	/	/	902	0.53
R-PH compound	wagging PH_2	840–810	/	/	828	0.46
Amines, R-NH_2, R_2NH	d N-H	850–700	/	/	742	0.52
			/	/	702	0.50
CO_2	d C=O	668	667	1.10	667	0.83

TG-IR spectra of evolved gases of 12 PA/CH-U treated cotton at ~ 636 °C show several characteristic groups of peaks (Figure 34), while the absorbance values at the second decomposition stages of untreated and 12 BL PA/CH-U treated cotton are given in Table 5. At ~ 636 °C, the IR spectra of gas products of 12 BL PA/CH-U treated cotton consists of H_2O (3800–3500 cm^{-1}), CO_2 (2450–2300 cm^{-1}, sharp peak at ~ 668 cm^{-1}), CO (2181 cm^{-1} and 2108 cm^{-1}) as seen in Figure 34 and Table 5. It is unlikely that H_2O is still generated at temperatures above 600 °C, so the possible explanation could be the background noise.

Comparing the results in Table 5, untreated cotton produces more H_2O while heating relative to PA/CH-U cotton. This is visible through reduced absorbance values of st O-H vibrations of 0,60 for untreated cotton and 0.14 for cotton treated with 12 BL PA/CH-U. Secondly, treated cotton generates more CO_2 while heating (Abs of st C=O vibrations 1.46) compared to untreated cotton (1.20) and less CO (Abs of st C≡O vibrations 0.53 and 0.12) compared to untreated cotton (0.58 and 0.15). Treated cotton shows no levoglucosan at 1063 cm^{-1}, a compound responsible for the high flammability of cellulose. As expected, there is no levoglucosan at 1062 cm^{-1}, which means that even a small fraction of FR compounds decreases the amount of levoglucosan responsible for the high flammability of cellulose, thus producing more post-burn char [70].

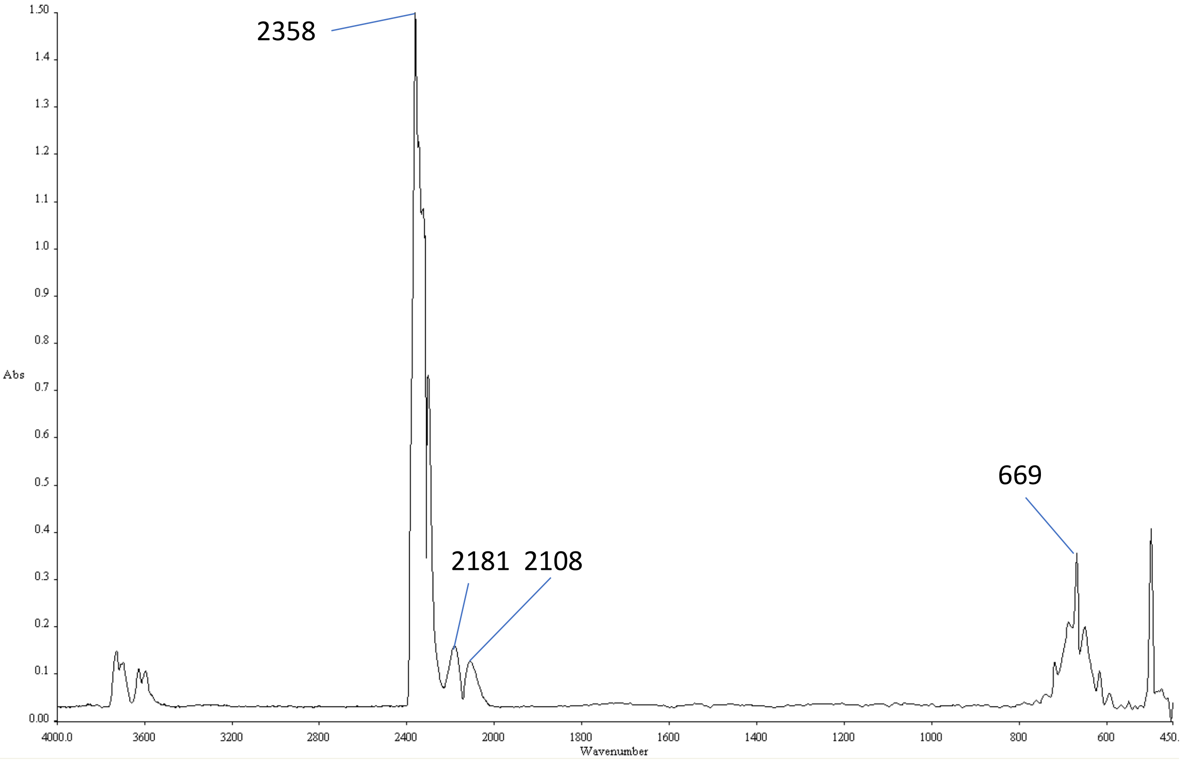


Figure 34: *TG-IR spectra of evolved gases of PA/CH-U treated cotton at ~ 636 °C*

Table 5: *Summary of TG-IR analysis of untreated cotton (control) at 578 and 12 BL PA/CH-U treated cotton at 636 °C*

			Temperatures (°C)			
			Control		12 BL PA/CH-U	
			578		636	
Functional groups	Covalent bonds vibrations	Wavelength range (cm^{-1})	cm^{-1}	Abs	cm^{-1}	Abs
-OH, H_2O	st O-H	3800–3500	3746	0.60	/	/
CO_2	st C=O	2450–2300	2366	1.20	2358	1.46
CO	st C≡O	2300–2100	2181	0.58	2181	0.15
			2108	0.53	2108	0.12
R-O-R, levoglucosan	st C-O-C (asym)	1000–1310	1061	0.54	/	/
CO_2	d C=O	668	667	1.14	669	0.

Zhang et al. treated cotton with 8 BL of PEI/PA and found reduced emission of flammable gases such as CH_4/CH_3OH, CO, and aliphatic esters, as well as reduced emission of CO_2 relative to untreated cotton. Additionally, they found PO_2 and PO_3 compounds at 1020 cm^{-1}, but it seems that FR coating did not influence the amount of H_2O emitted from the sample [88]. Zilke at al.

[91] analyzed IR spectra of volatile products of cotton treated with 15 BL of PA and polyvinylamine (PVA) and found cis and trans C=O stretching vibrations of a flammable and toxic acrolein at 1735 cm^{-1} and 1710 cm^{-1}, the C=O stretching vibrations of formaldehyde at 1735 cm^{-1}, CH_2 stretching vibrations of formaldehyde at 2800 cm^{-1}, CO_2 (2349 cm^{-1}), H_2O (~ 1500 cm^{-1}) and the stretching vibrations of CO at 2171 cm^{-1}. FR cotton generally produced less flammable gases such as acrolein, formaldehyde, and CO but produced more CH_3OH relative to untreated cotton. At the same time, coated cotton generated more inflammable gases such as CO_2 and H_2O.

All N-P LbL FR cellulose systems seem to generate more or less identical gas compounds at the first decomposition stage (T1), regardless of FR agents used [130]. Li et al. [149] and Liu et al. [150] stated less inflammable gases (functional groups C-H, CO, C=O, C-O-C) and more inflammable gases (H_2O, CO_2). Pan et al. stated less flammable gases (CO, carbonyl compounds), no CH_3OH, and more CO_2 [151]. Chen at al. reported more flammable gases (C-H, CO), less flammable gases (C=O, C-O-C), and the same amount of inflammable gases (H_2O, CO_2), but they also reported inflammable gases (-N-H, -P-O-H) relative to untreated cotton [152]. Due to the detection limits of evolved gas analysis (EGA) by FTIR, other organic compounds and P or N gas compounds generated during the combustion of FR cotton are detectable only by use of the PY-GC-MS technique [153,154]. Zhu et al. found that pyrolysis products of untreated cotton and cotton treated with organophosphorus FRs differ slightly in type and the percentages of pyrolyzed products. While untreated cotton releases H_2O and CO_2 (CO), alcohols, aldehydes, ketones, furans, benzene, esters, ethers, levoglucosan and other unidentified substances, FR-treated cotton does not release aldehydes and benzene and the percentage of H_2O and CO_2 (CO), furans, esters and other unknown substances is slightly increased, while the percentage of ketons and ethers decreases. N compounds can also be detected [155,156].

The post-burn char of 12 BL PA/CH-U treated cotton contains C, O, P, and N, along with impurities in traces according to EDS analysis (Figure 35), which means that P and N trapped C and block it from complete oxidation by generating charing shield on polymer surface in the form of bubbling typical for intumescent FR (Figure 36b) [76]. TG-IR analysis of volatile products (Table 4) and EDS analysis of post-burn char (Figure 35) prove that N-P-based FRs act in a gas and condensed phase. SEM images of cotton surface layered with 12 BL PA/CH-U show a paste-like coating structure, which means that LbL coating cannot give the coating uniformity and equality (Figure 36a).

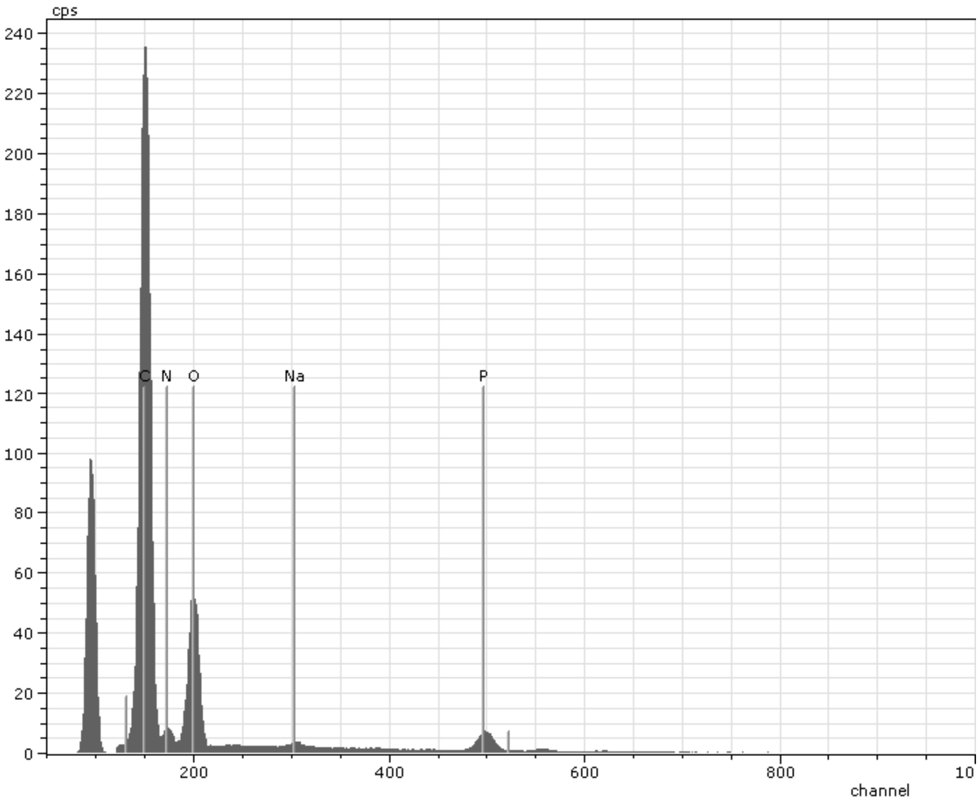
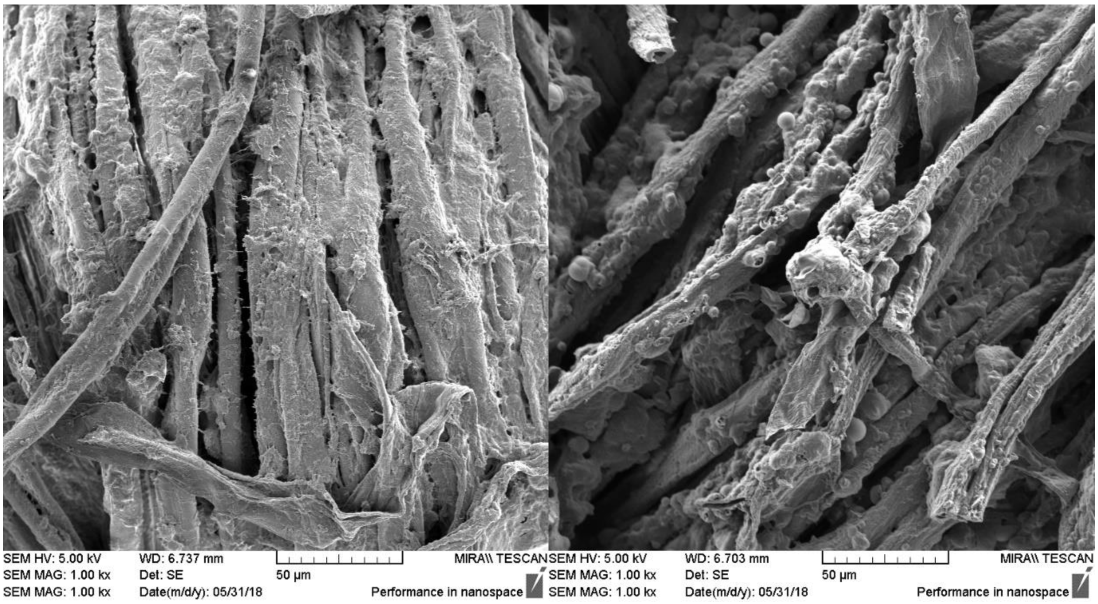


Figure 35: *EDS analysis of post-burn char of 12 BL PA/CH-U treated cotton*



a) b)

Figure 36*: SEM images of a) 12 BL PA/CH-U coated cotton b) post-burn char of 12 BL PA/CH-U coated cotton*

Other authors also used PA. Liu et al. [157] coated cotton fabric with fully biobased compounds, eggs white protein (cationic solution), and anionic PA. 2BL coated cotton passed VFT with a 39.1% add-on. The cone calorimeter (CC) data showed pHRR and THR reduction of 23% and 63% relative to untreated cotton and 52.2% of char.

PA has also been used with 3-aminopropyl triethoxysilane (APTES), a cationic coupling agent rich in N and silicon (Si), mainly used as a sol-gel precursor in the preparation of sol-gel materials and coatings [158]. The chemical is not biodegradable [159]. The structural formula of APTES is shown in Figure 37 [160].

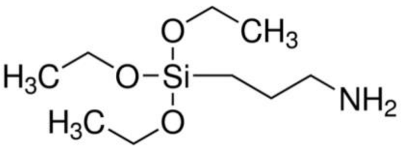


Figure 37: *Structural formula of APTES [160]*

Silanes generally generate high add-on coating (~ 33%) with PA at only 5 wt% colloidal suspension at pH 3.4. 15 BL of APTES/PA coating on cotton reduced pHRR and THR values by 9% and 17% with only 27.3% of char, according to CC data. Coated sample passed VFT with an LOI value of 37%. Adding CH (1wt%, pH 3.5) into the system as 15 QL (APTES/PA/CH/PA) on cotton, pHRR, and THR values were reduced for 82 and 66% with the char yield of 37%.

Among the lowest add-ons sufficient for cotton to pass VFT were achieved using ME or sulfonated melamine formaldehyde (SMF), which are all urea-based derivates. Sulfonated melamine formaldehyde (SMF) is a water-miscible anionic polymer used as a plasticizer in concrete admixtures to increase the fluidity, mechanical strength, and resistance to environments with the structural formula shown in Figure 38 [161]. According to the safety data sheet, due to formaldehyde content, SMF may cause eye and skin irritation and is considered carcinogenic [161,162].

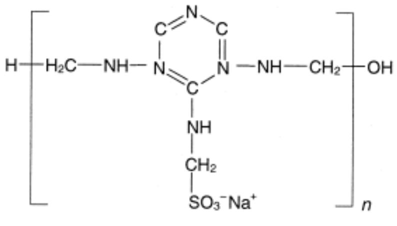


Figure 38: *Structural formula of SMF [161]*

If anionic PA solution (3 wt%, pH 4) is combined with cationic PEI (0.5 wt%) and ME (2 wt%) solution at pH 4 to form 4 BL deposited cotton, the add-on of only 5.1% was sufficient to self-extinguish the flame in VFT. The cone calorimeter data showed a pHRR reduction of 59% and the THR reduction of 24% relative to untreated. The percent of char left after heating in TG in the air was 7.8% at 600 °C [107]. By adding SMF (1 wt%) to anionic PA solution (2 wt%) and combining it with cationic CH solution (0.5 wt%, pH 5), it is possible to build 10 BL coating sufficient to self-extinguish the flame in VFT with only 5.9% add-on [151].

Chitosan

Chitosan (CH) is a natural linear polysaccharide composed of randomly distributed β-(1-4)-linked D-glucosamine (deacetylated unit) and N-acetyl-D-glucosamine (acetylated unit) and obtained by deacetylation of chitin found in the exoskeleton of shrimp, crustaceans, insects and fungus wall. It can only be dissolved in acid conditions due to the amino group's pKa value of 6.5 or pH ~ 4 [163]. It has been widely used for sensing, textile, tissue engineering scaffolds, wastewater treatment, the food industry, and drug delivery [164]. Chitosan is also an efficient antimicrobial compound, which will be discussed in detail in Section 3 [77,165]. Figure 39 represents the structural formula of CH [166].

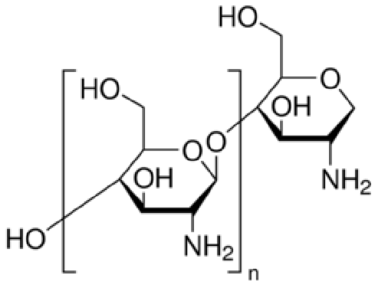


Figure 39: *Structural formula of CH [166]*

The degree of deacetylation of chitin and the protonation of the amino groups located at the C-2 position of the D-glucosamine give the CH molecule a positive charge, making it a good candidate for LbL deposition. As a naturally occurring carbohydrate rich in carbon (C) and nitrogen (N), CH is a potential intumescent FR if coupled with P compounds that generate phosphonic acids upon heating. Besides, reactive -OH and -NH_2 functional groups in molecules make CH ideal for modifying with phosphorus-containing species in the form of hypophosphorous acid-modified chitosan (HACH) [93]. On the other side, CH is a well-known chelating agent, so to build an efficient FR nanocoating on cotton using LbL deposition, positively charged CH solution can be mixed with low-molecular-weight compounds to enhance flame retardancy such as U [76], P-aminobenzene sulphonic acid-modified melamine (AMM) [167] or metal salts (Cu^{2+}) [70]. The flame retarding effect of CH as a cationic counterpart in building LbL assembly with negatively charged PA has been discussed in detail in the previous section while discussing PA in effective N-P flame retardant LbL coating for cotton [76,122,150,151]. Even a shallow concentration of CH (0.5–1.0 wt%) in solution at low pH (~ 4) can be effective in reducing the flammability of cotton if combined with anionic phosphorus-rich polyelectrolytes such as ammonium polyphosphate (APP) [152,167] and sodium hexametaphosphate (PSP) [98]. Ammonium polyphosphate (APP) is used as a food additive, emulsifier. As a fertilizer, but mainly as a flame retardant (APP form II, degree of polymerization ≥ 1000), for thermoplastics, polyurethane foams, textile backcoatings (instead of banned Deca BDE/ATO flame retardant), paints, adhesives, thermosets, wood, paper etc. [168] According to safety data sheet (SDS), APP is non-persistent, non-bioaccumulative and non-toxic [169]. Figure 40 represents the structural formula of APP, form II [170].

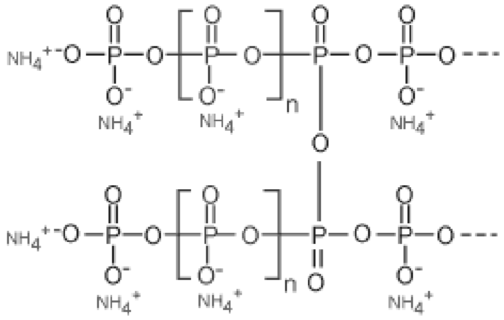


Figure 40: *Structural formula of APP (Form II)* [170]

Only 1 wt% of APP is sufficient to build 3 BL of APP/CH to pass VFT with only a 10.1% add-on. The cone calorimeter data showed 56% and 37% of pHRR and THR reduction, with 33.2% of char left after the combustion [152]. In another study, only 3.3 wt% of anionic APP solution and 1 wt% of cationic CH-AMM were sufficient for 15 BL-coated cotton that passed VFT with only 18.5% of the add-on. The LOI value was 31.5%, and cone calorimeter data showed 40% and 60% of pHRR and THR reduction [167]. Unfortunately, p-aminobenzene sulphonic acid-modified melamine (AMM) is due to the content of phenylazoaniline considered carcinogenic [171].

Another phosphorus-rich, non-persistent, non-bioaccumulative, non-toxic, and water-soluble compound used as a food additive, water softener, and chelating agent in cosmetic formulations is hexametaphosphate (PSP) with the structural formula shown in Figure 41 [172,173].

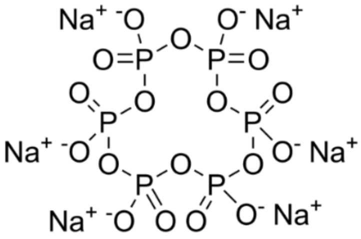


Figure 41: *Structural formula of PSP [174]*

Lazar et al. combined CH (1 wt%, pH 4) with PSP (2%, pH 4) in 15 BL coating according to the usual textile procedure, including rinsing with DI between two dips in polyelectrolyte. The coating cotton fabric self-extinguished in VFT, showing a pHRR reduction of 66% and a THR reduction of 76% with only 14.8 add-on of coating. The fabric was rinsed in tris(hydroxymethyl)aminomethane (THAM) to reduce the number of necessary steps instead of rinsing in DI. The result showed almost identical thermal performance with 10 BL [98]. THAM is used in biochemistry and molecular biology to prepare buffers at a physiological range of 7.3 to 7.5, so it is compatible with biological fluids [175]. The structural formula of THAM is shown in Figure 42 [176].

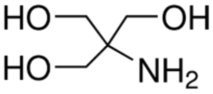


Figure 42: *Structural formula of THAM [176]*

Other chemicals used to reduce the flammability of cotton by means of LbL deposition are briefly shown in Table 6 and include polydiallyldimethylammonium chloride (PDAC) [177,178], poly(acrylic acid) (PAA) [177], deoxyribonucleic acid (DNA) [178], hydrotalcite (HT) [178], poly(vinyl alcohol) (PVA) [179], graphene nanoplatelets (GNPs) [179] and poly(4-styrene sulfonic acid) (PSS) [179]. All of the chemicals mentioned above have been considered safe [180–182] except PAA [183] and GNP, which chemical, physical, and toxicological properties have not been thoroughly investigated [184]. Those chemicals increased the thermal properties of cotton after a certain number of layers, such as reduced cone calorimeter values and with increased char content, but insufficient to pass VFT.

Table 6: *Chemicals used for FR LbL deposition of cotton*

Primer	Recipe	Number of layers	FR properties results	Literature
	BPEI$^+$ 0.1%, pH 10 / MMT$^-$ 1%, pH 10	20 BL	VFT result: did not pass Add-on: 4.06% MCC results: THR reduction 20%, char 10.49%, TG in the air at 600 °C: char 2.82% Mechanical strength: same as untreated cotton	[71]
	(PEI+SiO$_2$)$^+$ 1%, pH 5 / PA$^-$ 2%, pH 6	2 BL	VFT result: passed LOI: 26% Add-on: 11.3% Minor loss of breaking strength	[106]
	(PEI+SiO$_2$)$^+$ 2%, pH 5 / PPA$^-$ 4%, pH 6	1 BL	VFT result: passed LOI: 29.6%, Add-on 23.4% TG in N$_2$ at 600 °C: char 44% Minor loss of breaking strength: 11.9% (warp), 7.4% (weft)	[89]
	(PEI+ME)$^+$ PEI 0.5%, ME 2%, pH 4 / PA$^-$ 3%, pH 4	4 BL	VFT result: passed Add-on: 5.1% CC results: pHRR reduction 59%, THR reduction 24% TG in the air at 600 °C: char 7.8%	[107]
	PEI$^+$ 0.5%, pH 9 /PA$^-$ 2%, pH 4	8 BL	VFT result: passed LOI: 37% Add-on: 24.2% CC results: pHRR reduction 38%, THR reduction 22% TG in the air at 800 °C: char 5.81% TG-IR in N$_2$: reduced emission of CO$_2$, CO, aliphatic esters, PO$_2$ and PO$_3$ compounds Increased elongation break for 71.6%.	[88]
	PEI$^+$ 0.5%, pH 9	10 BL	HFT results: the samples did not pass	[109]

	/SA^- 0.3%, pH 7 + post immersion into: $BaCl_2$ $C_4H_6O_4Ni \times 4H_2O$ $C_4H_6O_4Co \times 4H_2O$)			
	PEI^+ 0.5% /$HACH^-$ 0.3% + crosslinking with genipin 1%	10 BL	HFT results: both samples passed Add-ons: • Without crosslinking 12.1% • With crosslinking 15.4% MCC results: • Without crosslinking – pHRR reduction 73%, THR reduction 80% • Crosslinking – pHRR reduction 65%, THR reduction 73% TG in the air at 700 °C: • char 18.7% (without crosslinking) • char 21.9% with crosslinking Enhanced the tensile strength and elongation at the break of the cotton fabric Non-durable to laundering	[93]
$BPEI^+$ 1%, pH 11.7	PA^- 5%, pH 0.7 / $PVAm^+$ 5%, pH 8.7	15 BL	VFT result: passed Add-on: 18.8% MCC results: pHRR reduction 80%, THR reduction 61%, char 32.3% TG in the air at 700 °C: char 3.1% TG-IR in N_2: less acrolein, less formaldehyde, more CO_2, more H_2O, less CO, more CH_3OH P/N molar ratio: 3:5 P: 2.0%, N: 1.4%	[91]
	CS^+ 1% / MMT^- 1%	20 BL	VFT result: did not pass CC results: pHRR reduction 21.3%, THR reduction 14.7%, char 9.9% TG in N_2 at 800 °C: char 8.5%	[72]
	$APTES^+$	15 BL	VFT result: passed	[149]

	5%, pH 3.4 / PA$^-$ 2%, pH 3.5		LOI: 37% Add-on: 33.4% CC results: pHRR reduction 9%, THR reduction 17%, char 27.3% TG in N_2 at 700 °C: char 35.2% TG-IR in N_2: fewer flammable gases (C-H, CO, C=O, C-O-C), more inflammable gases (H_2O, CO_2)	
	APTES$^+$ 5%, pH 3.4 / PA$^-$ 2%, pH 3.5 / CH$^+$ 1%, pH 3.5 /PA$^-$	15 QL	VFT result: passed LOI: 29% Add-on: 32.5% CC results: pHRR reduction 82%, THR reduction 66%, char 27.3% TG in N_2 at 700 °C: char 37% TG-IR in N_2: fewer flammable gases (C-H, CO, C=O, C-O-C), more inflammable gases (H_2O, CO_2)	[150]
	CH$^+$ 0.5%, pH 5 / (SMF+PA)$^-$ SMF 1% PA 2%	10 BL	VFT result: passed Add-on: 5.9% TG in the air at 700 °C: char 41% TG-IR in N_2: more CO_2, less CO, less carbonyl compounds, no CH_3OH	[151]
BPEI+ 1%	PA$^-$ 2%, pH 4 / CH$^+$ 0.5%, pH 4	30 BL	VFT result: passed Add-on: 16% MCC results: pHRR reduction 62%, THR reduction 77%, char 41.7%	[122]
BPEI$^+$ 5%	PA$^-$ 2%, pH 4 / (CH+U)$^+$ pH 4 CH 0.5% U 10%	10 BL	VFT result: passed LOI: 28% Add-on: 17.3% MCC results: pHRR reduction 59.5%, THR reduction 70.3% TG in the air at 650 °C: char 14.6%	[76]
	Egg white protein$^+$ pH 8.5 / PA$^-$ 70%, pH 1.5	2 BL	VFT result: passed Add-on: 39.1% CC results: pHRR reduction 23%, THR reduction 63%, char 52.2% TG in the air at 600 °C: char 32.9%	[157]

			Py-GC/MC: less alcohols, phenols, aldehydes, ketones, esters, ethers, aromatic rings, and other flammable substances, non-flammable H_2O, CO_2, NH_3	
APTES$^+$ 1%	APP$^-$ 1% / CH$^+$ 0.5%	3 BL	VFT result: passed Add-on: 10.1% CC results: pHRR reduction 56%, THR reduction 37%, char 33.2% TG in N_2 at 700 °C: char 34.3% TG-IR in N_2: more inflammable gases (H_2O, CO_2), found inflammable gases (-N-H, -P-O-H), more flammable gases (C-H, CO), less flammable gases (C=O, C-O-C)	[152]
	(CH+AMM)$^+$ CH 1% AMM 3.3% / APP$^-$ 3.3%	15 BL	VFT result: passed LOI: 31.5% Add-on: 18.5% CC results: pHRR reduction 40%, THR reduction 60%, char 24.1% TG in N_2 at 600 °C: char 32.8% Little negative impact on the mechanical property (maximum force, tensile elongation break)	[167]
PEI$^+$ 1%	PSP$^-$ 2%, pH 4 / CH$^+$ 1%, pH 4 + rinsing in DI or rinsing in THAM (pH 4)	15 BL (rinsing in DI) 10 BL (rinsing in THAM)	15 BL rinsed in DI: VFT result: passed Add-on: 14.8% MCC results: pHRR reduction 66%, THR reduction 76%, char 36.7% 10 BL rinsed in THAM: VFT result: passed Add-on: 14.6% MCC results: pHRR reduction 73%, THR reduction 78%, char 37.9%	[98]
	PDAC$^+$ 1% / PAA$^-$ 1% / PDAC$^+$ /	5 QL	VFT result: did not pass Add-on: 20% HFT result: passed CC results: pHRR reduction 4%, THR reduction 30%, char 20%	[177]

	APP$^-$ 1%			
BPEI 0.1%	PDAC$^+$ 1% / DNA$^-$ 1% + immersion into HT (0.1%)	10 BL 5 BL (immersion into HT)	10 BL: HFT result: passed Add-on: 13% CC results: pHRR reduction 20%, THR reduction 21%, char 6% 5 BL immersion into HT: HFT result: passed Add-on: 6% CC results: pHRR reduction 25%, THR reduction 16%, char 8%	[178]
	PVA$^+$ 0.25% / (GNP+PSS)$^-$ GNP 0.1% PSS 0.1%	10 BL	VFT result: did not pass CC results: pHRR reduction 34%, THR reduction 47%, char 47.8% TG in the air at 600 °C: char 1.06%	[179]

4.3. Multifunctional FR and antimicrobial (AM) cotton materials

The technological aspects of LbL deposition have been discussed in the first part of the discussion. The second part emphasizes the thermal efficiency and ecological aspects of FR chemicals used for LbL deposition. This part of the discussion deals with the multifunctional properties of cotton fabrics, e.g., flame retardancy and antimicrobial properties. According to Table 9, chemicals and their combination used to reduce the flammability and antimicrobial activity of cotton by means of LbL deposition can be divided into six groups:

1. organic polyelectrolytes such as polyethyleneimines (PEIs);
2. urea (U);
3. inorganic salts such as ammonium polyphosphate (APP), polyhexamethylene guanidine phosphate (PHMGP);
4. metal salts such as copper(II) sulfate pentahydrate ($CuSO_4$ x $5H_2O$), sodium hypochlorite (NaClO);
5. colloidal suspensions of nanoparticles: compounds based on silanes for sol-gel reactions such as quaternary ammonium salts poly[3-(5,5-cyanuricacidpropyl)- siloxane-co-trimethylammonium propyl siloxane chloride] (PCQS);

6. biopolymers and biomolecules such as chitosan (CH); alginates (ALG) such as potassium alginates; phytates such as myo-inositol hexaphosphate (PA) and ammonium phytate (AP); deoxyribonucleic acid (DNA).

Among chemicals mentioned above, some of them can act both as FR and antimicrobial agents, such as polyethyleneimines (PEIs), polyhexamethylene guanidine phosphate (PHMGP), metal salts, poly[3-(5,5-cyanuricacidpropyl)- siloxane-co-trimethylammonium propyl siloxane chloride] (PCQS), chitosan (CH). Any highly positively charged compound can potentially act as an antimicrobial agent.

The efficiency of chitosan (CH) to act synergically with P-rich compounds acting as a source of carbon (C) and nitrogen (N) to form intumescent char has been discussed in the previous section. The reason why CH is used as a new-age antimicrobial agent is enabled by protonated highly charged -NH_2 groups that act against bacteria in a very complex way depending on many factors such as concentration, types of bacteria, molecular weight (MW), positive charge density, pH, physical state, temperature and time, chelating capacity and ionic strength [165]. The minimum CH inhibitory concentration (MIC) required to completely inhibit bacterial growth after incubation at 37 °C for 72 is between 0.005 and 0.1%, depending on bacteria species and MWs of CH. Below these concentrations, it promotes some bacteria's growth in acid environments. Generally spoken CH shows a stronger antimicrobial effect against Gram-positive bacteria than Gram-negative bacteria, which is probably caused by the difference in their cell membrane structure, which in the case of Gram-positive bacteria consists of several layers, whereas Gram-negative bacteria form a single thin layer internal to the outer membrane layer, a capsule [185]. Magovac et al. [77] treated cotton fabric with 4 and 8 BL of anionic PA solution (2 wt%, pH 4) and cationic CH (0.5%, pH 4). The study confirmed that despite a different number of layers (different concentrations), CH was less effective against Gram-negative *K. Pneumoniae* than Gram-positive *S. aureus.* By increasing the number of bilayers (PA/CH) from 4 to 8 with increasing the add-ons from 8.3 to 14.5%, the reduction of Gram-negative *K. Pneumoniae* remains ~ 71%. However, the reduction of Gram-positive *S. aureus* increases from ~ 77 to 97% with increasing the number of bilayers (CH concentration) at the same MW, as shown in Figure 43 [77].

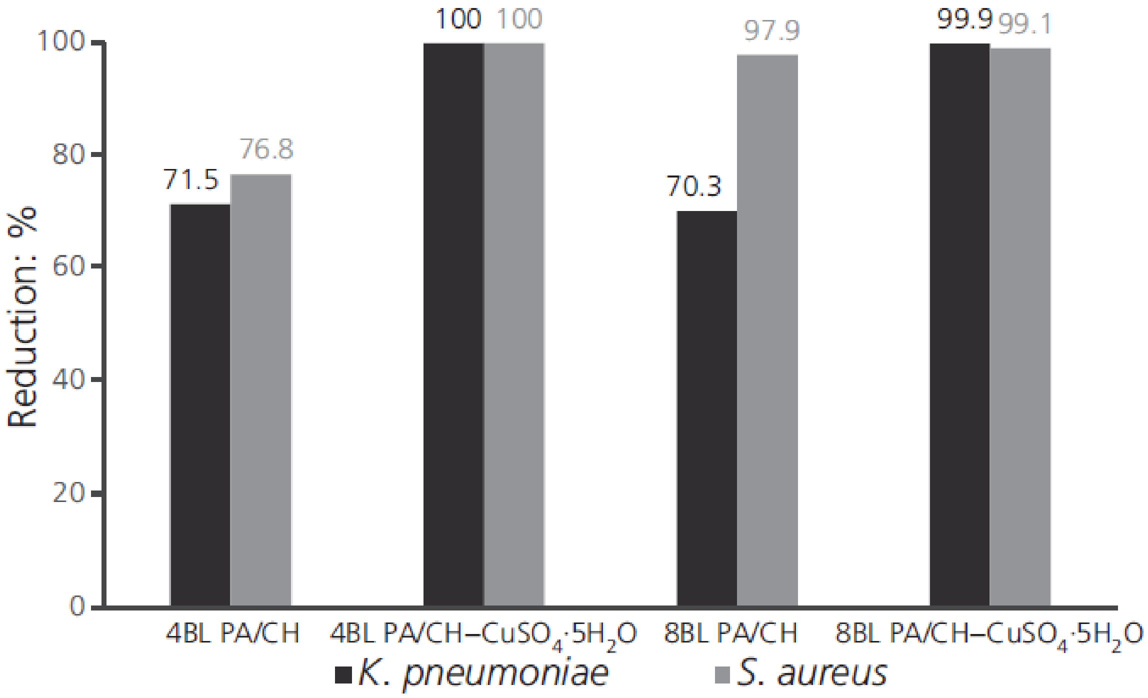


Figure 43: *Influence of treatment on reduction of K. Pneumoniae and S. aureus after 24 h of incubation (%) [77]*

The antibacterial activity of low MW chitosan is higher than that of the high MW samples for some bacteria [186]. Positive charge density is associated with the deacetylation degree (DD) of CH. The higher the number of amino groups linked to C-2 in chitosan, the more enhanced the antibacterial activity is. CH with higher DD shows a stronger inhibitory effect on bacteria than CH with a lower DD [187]. One of the most critical factors influencing the antimicrobial activity of CH as a weak base is its solubility in water obtained by dilution in an aqueous acidic solution (pH <6.5) [188]. Chitosan has a strong affinity capacity for transitional metal ions such as Ni^{2+}, Zn^{2+}, Co^{2+}, $Fe^{2+,}$ and Cu^{2+} in acid conditions by forming complexes but weak capacity for alkali and alkali-earth metals such as Ca^{2+} and Mg^{2+} [189]. The –OH and $-NH_2$ groups of chitosan are suitable ligands to coordinate with transition metal ions to get the chitosan-metal complex [190]. Copper ions can be adsorbed by chelation on amino groups and hydroxyl groups (especially in the C-3 position) of CH, forming $Cu[NH_2(OH)_2]$ complex below pH 6.1. Copper bonds to one nitrogen atom and three oxygen atoms in two different ways depending on pH, metal concentration, and metal/ligand ratio, as shown in Figure 44 [191].

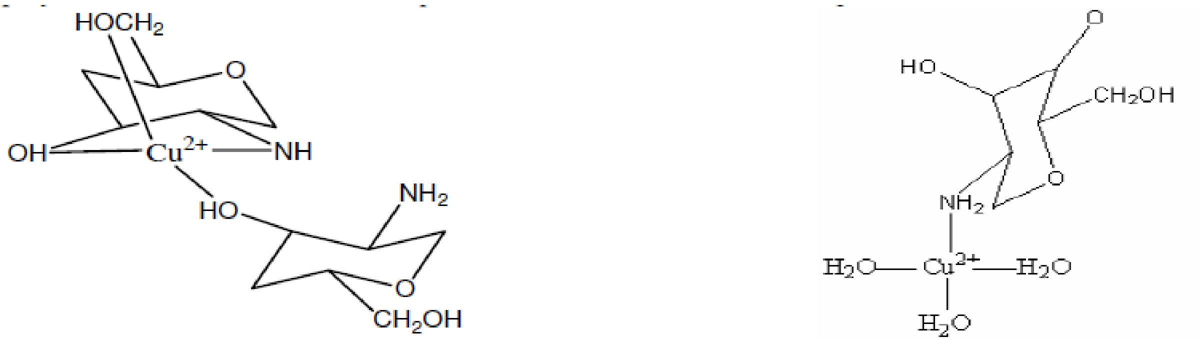


***Figure 44:** Possible Cu^{2+}-CH complex structures [191]*

Adding metal ions into the CH solution increases the antimicrobial activity of CH [192]. This is in line with Magovac et al. [77] research showing that adding Cu^{2+} ions into CH solution increases the reduction of Gram-negative *K. pneumoniae* from ~ 71% to ~ 100% according to AATCC TM 100-2019 test method at the same CH concentration, the same pH and the same MW. This study also showed that adding strong electrolytes such as $CuSO_4$ x $5H_2O$ in cationic CH solution, even in small quantities (2 wt%), reduces the ability of polyelectrolytes to build LbL assembly. The add-ons are only 5.2 and 5.6% for 4 BL and 8 BL. It is more likely that strong electrolytes form stereo complex formations of much stronger binding strenght than weak electrostatic force between two layers of PA/CH-Cu^{2+}.

The potential of metal ions as antimicrobial agents has been growing due to the spread of microbial resistance to classical antibiotics. Some trace metals in the form of metal complexes play a crucial role in biological processes as catalytic or structural cofactors. At high concentrations, however, they appear to be very toxic. Metal complexes possess several modes of action: exchange or release of metal ligands, redox activation, and catalytic generation of toxic reactive oxygen species (ROS), acting as enzyme deactivators and disrupting bacteria membrane function or damaging DNA. The most promising metal-based complexes of antimicrobials are silver, copper, zinc, iron, ruthenium, gallium, bismuth, vanadium, gold, iridium, cobalt, nickel, manganese, and their mixtures [193]. Among all transition metals, only copper and iron complexes react with reactive oxygen species (ROS) such as superoxide anion ($O_2^{\bullet -}$) and hydrogen peroxide (H_2O_2) generated in living organisms, which results in apoptosis or programmed cell death of bacteria or cells attacked by pathogenic microorganisms or carcinogenic cell [194]. $O_2^{\bullet -}$ is a byproduct of respiration and a crucial component of the immune defense system. The concentrations of $O_2^{\bullet -}$ in a cell controls superoxide dismutase (SOD), a copper-containing enzyme that catalyze $O_2^{\bullet -}$ into O_2 or H_2O_2 [195]. The level of H_2O_2

should be in the optimal range to maintain cell homeostasis; otherwise, it causes apoptosis of a cell [196]. The presence of cuprous ions is essential for many biological processes, so the bacteria, depending on environmental conditions, allow uptake of Cu^{2+} by the outer membrane protein binding sites, but in very small quantities and controlled manner [197]. If the concentration of cuprous ions exceeds the optimal levels, copper ions react with $O_2^{\bullet -}$ and H_2O_2 in a process called the Fenton reaction [198]:

$$Cu^{2+} + O_2^{\bullet -} = Cu^{+} + O_2 \tag{23}$$

$$Cu^{+} + H_2O_2 = O_2 + OH^{\bullet} + OH^{-} \tag{24}$$

$OH^{\bullet}$ radicals are highly reactive and enzymatically independent, so they cannot be neutralized through enzymatic reactions, leading to oxidative damage to proteins, DNA, and lipids and, consequently, death [195].

In an effort to reduce the flammability of cotton with enhanced antimicrobial properties, cotton has been treated with different compounds, as shown in Table 9. The results of antimicrobial activity cannot be compared to one another due to the usage of different test methods such as AATCC 100-2019 [82], ASTM E2149-20 [199], GB/T 20944.3-2008 [200] and Kirby-Bauer Disk Diffusion Susceptibility Test Protocol [201] that express the test results differently.

Li et al. treated cotton with 30 BL of anionic PA solution (2 wt%, pH 4) and 1 wt% colloidal suspension of a cyanuric acid copolymer of poly[3-(5,5-cyanuricacidpropyl)- siloxane-co-trimethylammonium propyl siloxane chloride] (PCQS). Cyanuric acid is mainly used for the disinfection of swimming pools, spas, and other waters for which it is important to maintain chlorine disinfection that might otherwise decline rapidly due to sunlight [202], while quaternary ammonium salt siloxane acts as an antibacterial agent. The structural formula of PCQS is shown in Figure 45 [203].

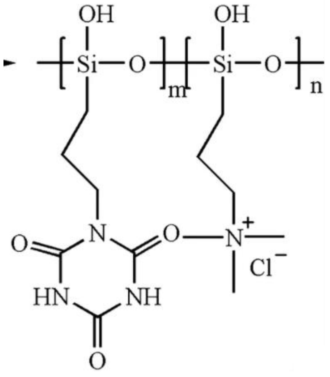


Figure 45: *Structural formula of PCQS [203]*

30 BL of coating passed the VFT with an LOI value of 29.8%. 21.2% of add-on reduced 92.2% of Gram-positive *S. aureus,* while only 47.7% of Gram-negative *E. coli*. according to AATCC 100-2020. The author of this study subsequently immersed 30 BL coated cotton into sodium hypochlorite (0.5%, pH 7) to enhance the antimicrobial efficiency without disturbing thermal properties. The resulting fabric passed VFT with a 28.5% LOI value and an increased overall bacteria reduction of 100%. Char left after heating in TG in N_2 atmosphere at was ~ 36% for both samples [90].

Metal compounds (M) can act as antimicrobial agents and/or as FRs. Because strong electrolytes in the form of metal salts may interrupt LbL growth [77], they have been chiefly added as a top layer. The studies have namely shown that the top layer, which comes in contact with the bacterium, is the most important for bacteria-killing [204,205]. M added into the intumescent organophosphorus FR system catalyzes phosphorylated cellulose crosslinking and promotes char formation [206]. The combustion of these metal ions cross-link intermediates probably generates metal oxides or metal carbonates acting as a barrier between the flame and the condensed phase of the polymer surface, which stops oxygen penetration and prevents the spread of flammable gases and flame penetration to inner layers of the polymer [207]. This explains why the intumescent M-N-P FR systems are more efficient than N-P systems alone.

Magovac et al. [70] treated cotton fabric with 2 wt% anionic PA solution (pH 4) and cationic 0.5 wt% CH and 10% U solution (pH 4) forming 8, 10, 12 BL. 12 BL coating (add-on 18.5%) self-extinguished in VFT according to Figure 46. 12 BL coated fabric were subsequently immersed into 2 wt% $CuSO_4 \times 5H_2O$ solution to impart antimicrobial properties additionally. The resulting add-on on fabric was 19%; the fabric passed VFT with a char length of 6.5 cm (Figure 46). The LOI value was 26%. The commercial requirements of LOI for durable FR cotton are 28% or above [208].

	Control	PA/CH-Urea			PA/CH-Urea + Cu^{2+}		
Number of BL	n/a	8	10	12	8	10	12
Image							
Char length (cm)	n/a	n/a	n/a	6.7	n/a	n/a	6.5

Figure 46: *The results of the VFT of cotton coated with different recipes [70]*

The influence of metal ions such as copper (II) ions (Cu^{2+}) from $CuSO_4$ x $5H_2O$ on the FR intumescent system (12 BL PA/CH-U) is briefly shown in Figure 47. The pHRR of cotton at ~ 389 °C is ~ 271 W/g. By treating cotton with PA/CH-U the pHRR decreases up to 40% at ~ 319 °C, while by adding $CuSO_4$ x $5H_2O$ into the FR system, the pHRR decreases up to 56% at ~ 311 °C.

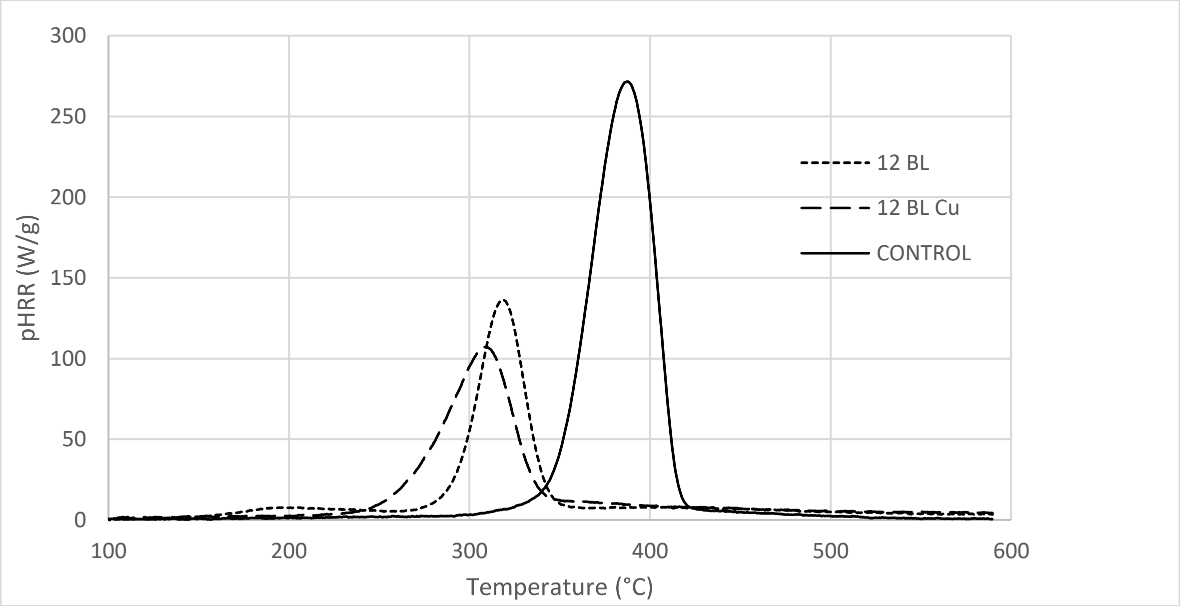


Figure 47: *MCC curves of untreated and 12 BL PA/CH-U and 12 BL PA/CH-U+$CuSO_4$ x $5H_2O$ treated cotton*

Cu^{2+} salts added into the intumescent 12 BL PA/CH-U system also catalyze the phosphorylated cellulose crosslinking and promote char formation, reducing flammable, volatile compounds.

It is also possible that $CuSO_4$ x $5H_2O$ forms sulfonic acid intermediates upon decomposition, acting in a condensed phase while forming the char at the surface of the degrading polymer and releasing H_2O. The char acts as a shield protecting the fabrics from flame, while H_2O cools down the system by removing heat from the fire [18]. S species can inhibit H• and OH• radicals in the flame [16]. Described mode of action is identical to commercial non-durable FRs based on ammonium sulfamate and borax [34,209].

The influence of Cu^{2+} in PA/CH-U system on thermal stability by heating from 50 to 850 °C in the air is presented in a group comparison of DTG curves of untreated and 12 BL PA/CH-U and 12 BL PA/CH-U+$CuSO_4$ x $5H_2O$ treated cotton in Figure 48 and group TG data comparison in Table 7. The IR spectra of gases generated by heating cotton treated with 12 BL PA/CH-U+ $CuSO_4$ x $5H_2O$ at the first decomposition stage at 330 °C are shown in Figure 49. The group comparison of IR spectra of evolved gases generated by heating from 50 to 850 °C in the air of untreated (control), 12 BL PA/CH-U, and 12 BL PA/CH-U+ $CuSO_4$ x $5H_2O$ treated cotton with the absorbance values is presented in Table 8 and Figure 50.

As presented in Table 7 and Table 8, the first decomposition stage of cotton occurs between 360-421 °C with volatile products such as H_2O, CH_4/CH_3OH, CO_2, CO, formaldehyde, levoglucosan, and other compounds. At 396 °C, the char yield is 43.6%. The second decomposition stage occurs between 496–607 °C, releasing H_2O, CO_2, CO, formaldehyde, and other compounds. At 650 °C, the char yield is 0.4%. By adding 12 BL PA/CH-U treatment, cotton decomposes earlier at 312 °C. At 339 °C, the char yield is 57.8%, and volatile gases do not contain levoglucosan, as presented in Table 7 and Table 8. At 650 °C, the char yield is 14.9%.

By adding $CuSO_4$ x $5H_2O$ into intumescent PA/CH-U system, the first decomposition stage starts even earlier at 261 °C (Table 7) with the release of H_2O (3750 cm^{-1}) [132], CH_4/CH_3OH (2978 and 2810 cm^{-1}) [133], CO_2 (2358 and 667 cm^{-1}) [134], CO (2172 and 2112 cm^{-1}) [133], formaldehyde (1744 cm^{-1}) and ethers (1106 cm^{-1}) [135], CuO or CuS compounds (500 cm^{-1}) or other sulfur compounds with S-S bonds (452 cm^{-1}) [210,211] as presented in Figure 49. Levoglucosan is not found. Other compounds such as HCN (between 706 and 716 cm^{-1}), NO_2 (between 1545 and 1659 cm^{-1}), and sulfur dioxide (SO_2) in the spectral range between 1321 and 1396 cm^{-1} may exist, but they are overlapped with spectra of other compounds [146,147]. Other N or P compounds may also exist but are not visible in the IR spectrum. At 650 °C, the char yield is 13.3% (Table 7). From Figure 48, it is visible that FR treatment strongly reduces the weight loss rate. Previous research concluded that $CuSO_4$ x $5H_2O$ acts as a wall/shield for absorption and dissipation of heat at the combustion zone of the cellulose, thus protecting the polymer from burning because $CuSO_4$ x $5H_2O$ loses H_2O above 800 °C and decomposes into copper (II) oxide (CuO) and sulfur trioxide (SO_3), which is far above the decomposition temperature of cellulose (~ 350 °C) [212]. Magovac et al. [70] found out that CuO or CuS nanoparticles are present in volatile gaseous products generated by heating of 12 BL PA/CH-U+$CuSO_4$ x $5H_2O$ treated cotton at 339 °C, which explains the fact that there is almost no difference in amount of char left at 650 °C between 12 BL PA/CH-U (14.9%) and 12 BL PA/CH-U+$CuSO_4$ x $5H_2O$ treated cotton (13.3%). These nanoparticles may act as the inert dust that absorbs and dissipates the heat, causing a lowering of temperature.

Table 7: *Summary of thermogravimetric analysis of untreated and FR-treated cotton* [70]

Sample	Onset 1/°C	T_1/°C	End 1/°C	Char at T_1 (%)	Onset 2/°C	T_2/°C	End 2/°C	Char at 650 °C (%)
Untreated cotton	360	396	421	43.6	496	578	607	0.4
12 BL PA/CH-U	312	339	354	57.8	512	636	711	14.9
12 BL PA/CH-U+Cu^{2+}	261	330	354	56.2	464	636	700	13.3

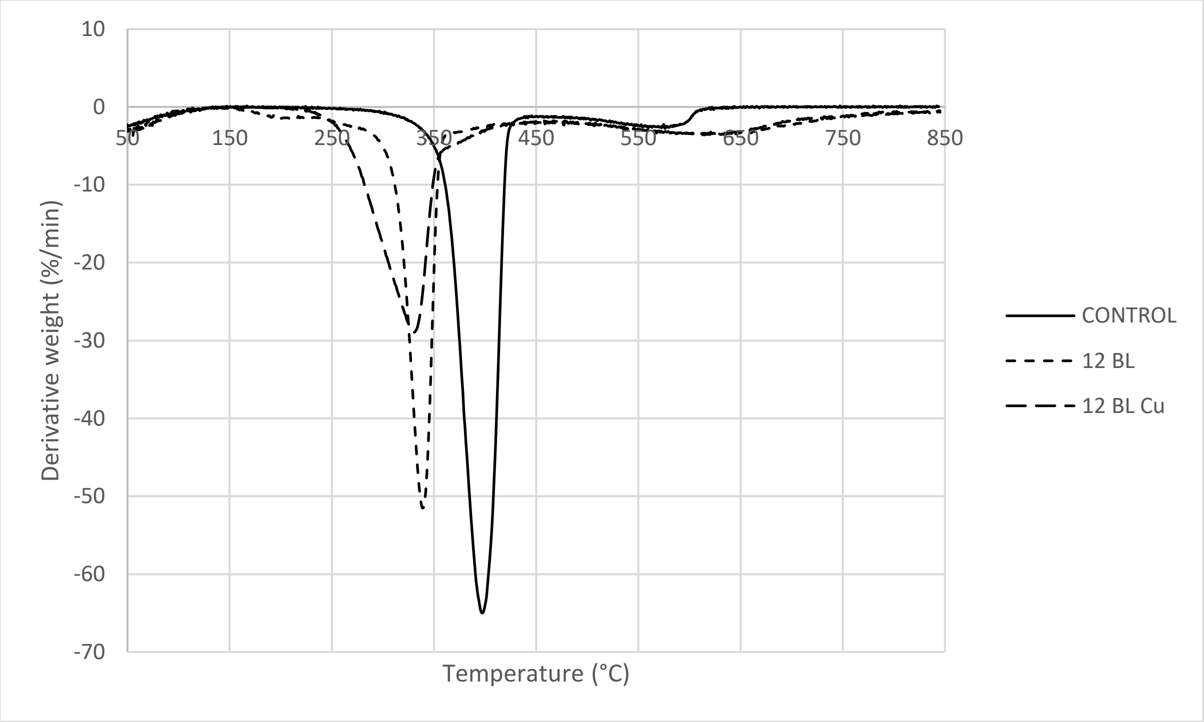


Figure 48: *DTG curves of untreated and 12 BL PA/CH-U and 12 BL PA/CH-U+$CuSO_4$ x $5H_2O$ treated cotton*

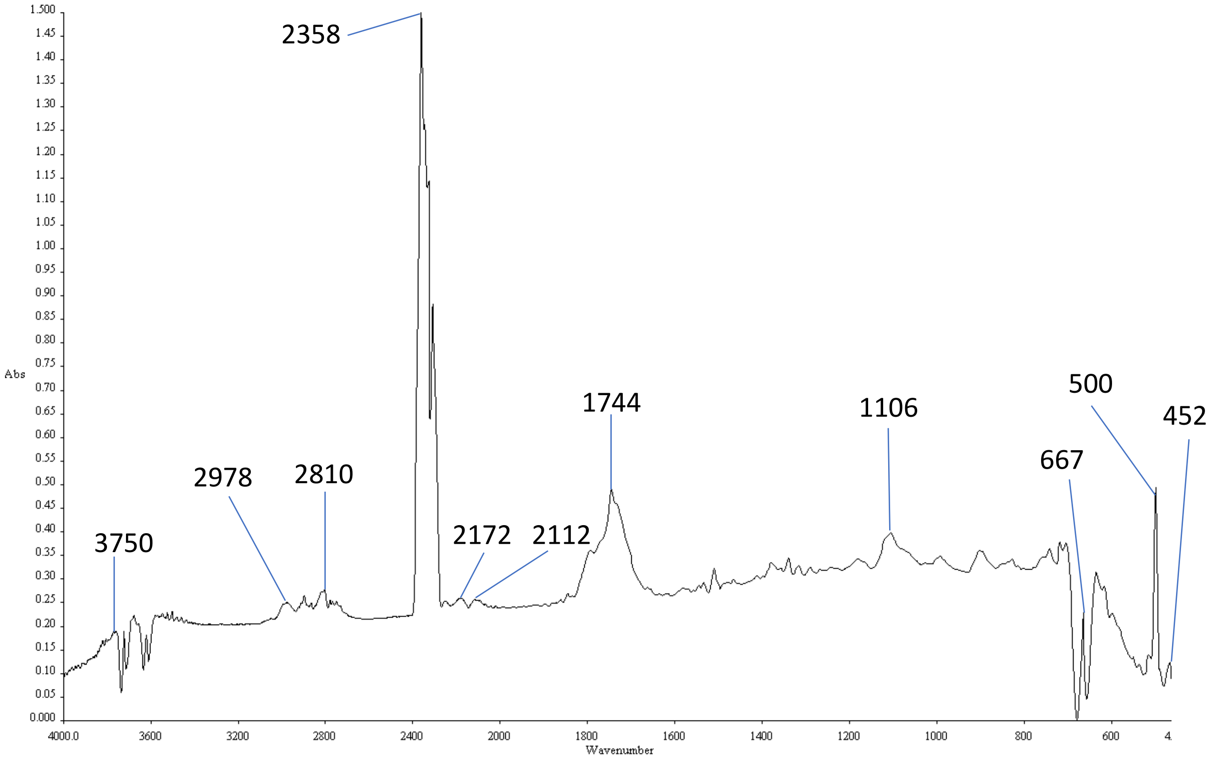


__Figure 49:__ TG-IR spectra of evolved gases of 12 BL PA/CH-U+$CuSO_4$ x $5H_2O$ *treated cotton at ~ 330 °C*

The critical differences between cotton treated with 12 BL PA/CH-U and 12 BL PA/CH-U+Cu at the first decomposition stage are the lower release of flammable gases such as CH_4/CH_3OH and aldehyde during combustion of PA/CH-U+$CuSO_4$ x $5H_2O$ treated cotton relative to PA/CH-U treated cotton as seen in Table 8 from the absorbance values. The overall levels of flammable gases of treated cotton samples are reduced (CH_4/CH_3OH, CO, aldehyde), and highly flammable levoglucosan is not found IR spectra of treated cotton (Figure 50).

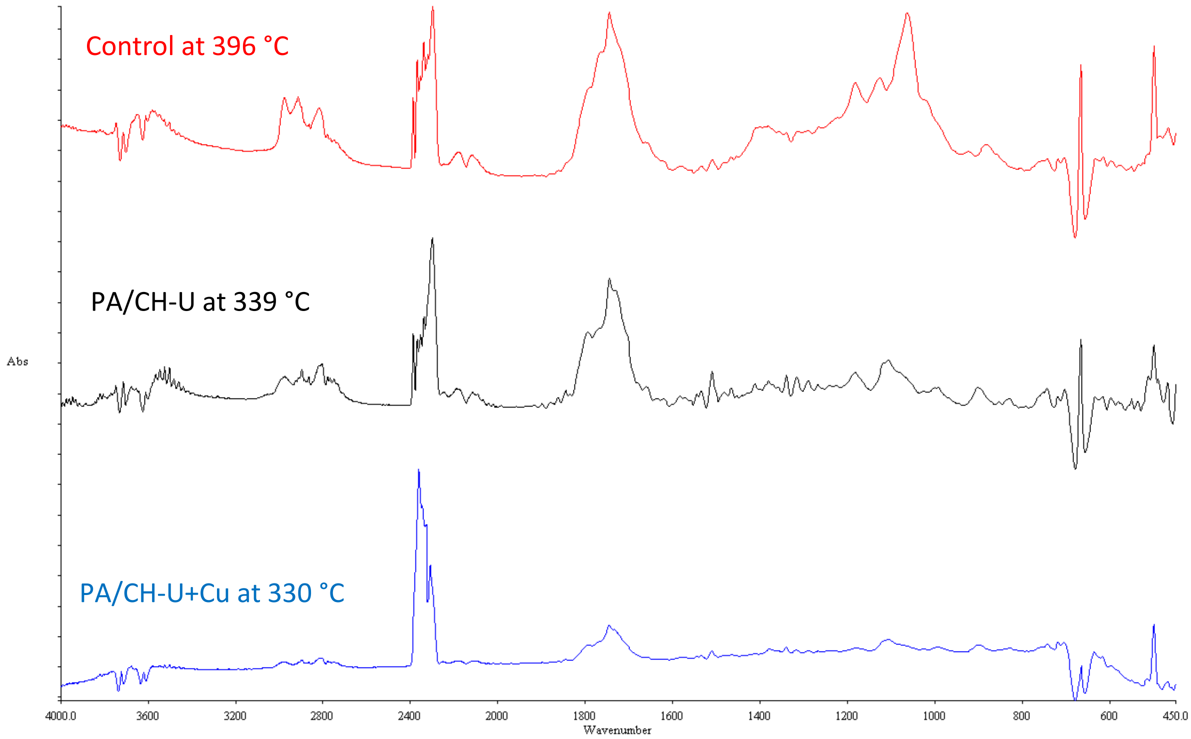


Figure 50: *TG-IR spectra of untreated (control), 12 BL PA/CH-U, and 12 BL PA/CH-U+$CuSO_4$ x $5H_2O$ treated cotton at the first decomposition stage (T_1) [70]*

Table 8: *Summary of TG-IR analysis of untreated cotton (control), 12 BL PA/CH-U, and 12 BL PA/CH-U+ $CuSO_4$ x $5H_2O$ treated cotton at the first decomposition stages*

			Temperature (°C)					
			Control		12 BL PA/CH-U		12 BL PA/CH-U + Cu	
			396		339		330	
Functional groups	Covalent bonds vibrations	Wavelength range (cm^{-1})	cm^{-1}	Abs	cm^{-1}	Abs	cm^{-1}	Abs
R-OH, H_2O	st O-H	3800–3500	3750	0.62	3750	0.53	3750	0.17
$-CH_3$	st C-H	3000–2750	2978	0.86	2974	0.60	2978	0.25
			2815	0.80	2802	0.68	2810	0.27
CO_2	st C=O	2450–2300					2358	1.47
			2302	1.40	2297	1.49		
CO	st C≡O	2300–2100	2172	0.57	2177	0.51	2172	0.25
			2112	0.55	2112	0.49	2112	0.25
CH_2O formaldehyde	st C=O	1740–1720	1744	1.48	1744	1.23	1744	0.49
Imides, 5-ring	d CNH	1510–1500	/	/	1510	0.64	/	/
Ester of formic acid $HCOOCH_3$	st C-O-C	1210–1160	1182	1.01	1182	0.63	/	/

R-O-R, ether	st C-O-C (asym)	1175–1038	/	/	1106	0.71	1106	0.40
R-O-R, Levoglucosan		1310–1000	1063	1.45	/	/	/	/
Cycloalkanes	st CH	920–880	/	/	902	0.53	/	/
R-PH compound	PH_2 (wagging)	840–810	/	/	828	0.46	/	/
Amines, R-NH_2, R_2NH	d N-H	850–700	/	/	742	0.52	/	/
			/	/	702	0.50	/	/
CO_2	d C=O	668	667	1.10	667	0.83	667	0.22
CuO, CuS		580–440	/	/	/	/	500	0.49
Sulfur compound	S-S variable-weak stretching	500–400	/	/	/	/	452	0.08

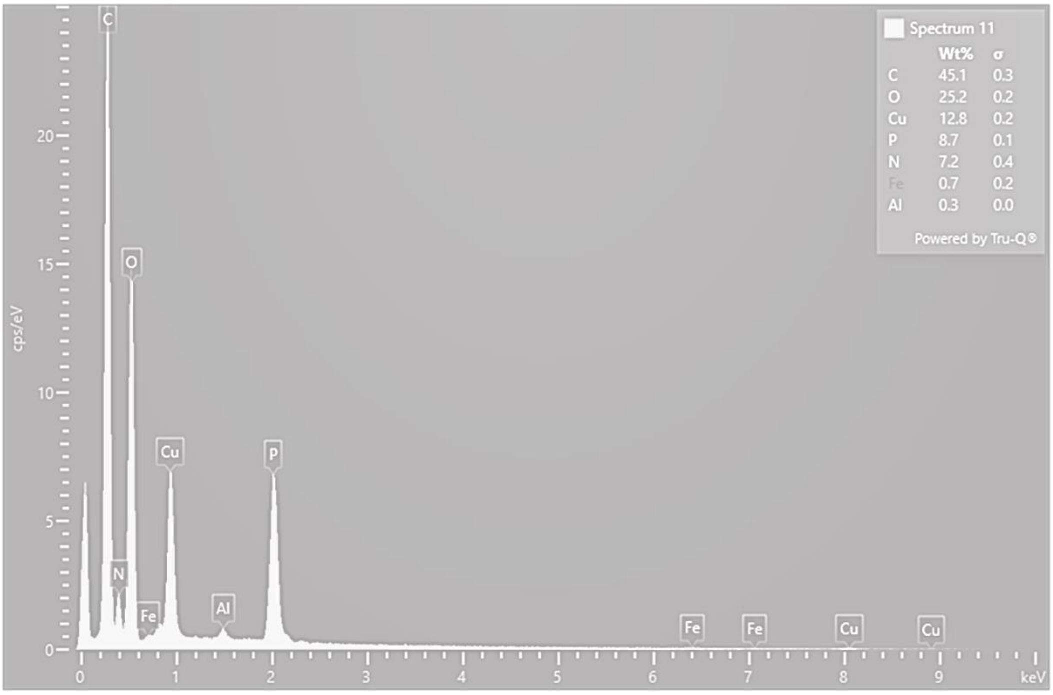
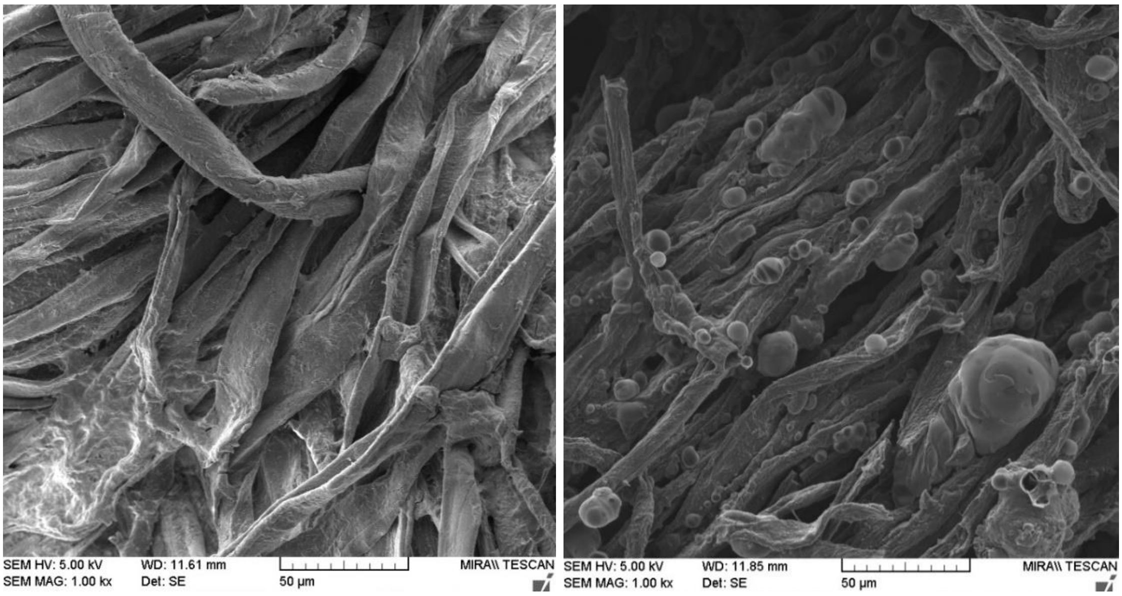


Figure 51: *EDS analysis of post-burn char of 12 BL PA/CH-U+Cu treated cotton*

The post-burn char of 12 BL PA/CH-U+$CuSO_4$ x $5H_2O$ treated cotton contains C, O, P, N, and Cu along with impurities in traces according to EDS analysis (Figure 51), which means that N, P, and Cu trapped C and block it from full oxidation by generating charing shield on polymer surface in the form of bubbling typical for intumescent FR (Figure 36b) [73].

TG-IR analysis of volatile products (Table 8) and EDS analysis of post-burn char (Figure 51) prove that N-P-Cu-based FRs act in a gas and condensed phase.

The post-burn char of 12 BL PA/CH-U+$CuSO_4$ x $5H_2O$ shows a bubbling structure typical for intumescent FR (Figure 52b), while the cotton surface shows a paste-like structure of coating without uniformity fo the layers (Figure 52a).



a) b)

Figure 52: *SEM images of a) 12 BL PA/CH-U+$CuSO_4$ x $5H_2O$ coated cotton b) post-burn char of 12 BL PA/CH-U+$CuSO_4$ x $5H_2O$ coated cotton*

Additionally, antibacterial testing according to AATCC 100-2004 against Gram-positive *S. aureus* and Gram-negative *K. Pneumonie* showed 100% reduction, meaning adding Cu^{2+} ions into the P-N system enhanced flame retardancy as well as antimicrobial property could be achieved.

Li et al. deposited 1 BL of cationic CH (pH 3) and anionic AP solution (3 wt%, pH 7) to reduce the flammability of cotton as well as add antibacterial properties [87]. The resulting fabric achieved excellent flame retardancy with only an 8% add-on passing the VFT with the LOI value of 27%. The cone calorimeter data showed reduced pHRR and THR values of 59 and 64% and char of 34%. TG-IR spectra of evolved gases generated during heating in N_2 showed increased levels of flammable gases such as H_2O, CO_2, and N-H and decreased levels of flammable gases (C-H, C=O, C-O-C) as expected. The antibacterial activity according to GB/T 20944.3-2008 tested against Gram-negative *E. Coli* showed a reduction of 99.3%.

Ammonium phytate (AP) is a salt of phytic acid rich in nitrogen with the structural formula shown in Figure 53 [213]. AP is considered as safe.

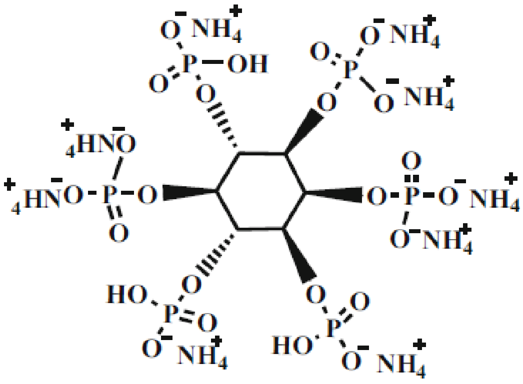


Figure 53: *Structural formula of AP [213]*

Fully biobased FR and antimicrobial coating of cotton by means of LbL deposition was prepared by Casale et al. [214] consisting of cationic CH (0.5 wt%, pH 3.5) and anionic DNA (0.5 wt%, pH 7) solution. In an effort to achieve wash resistance, a photoinitiator was added to CH solution (4 wt%) for UV radiation as a post-treatment of 30 BL deposited cotton. The resulting fabric passed HFT with only 4.8% of an add-on. According to the Kirby-Bauer test, the inhibited ratio of *S. aureus* and *E. coli* was ~ 0.03 and ~ 0.04, and the bacteria reduction of *S. aureus* according to ASTM E 2149-01 was 57%. UV radiation, however, did not have a significant influence on the wash durability of the coating. Fang et al., in their two studies [84,215], used polyhexamethylene guanidine phosphate (PHMGP), an extremely toxic antibacterial agent with the structural formula shown in Figure 54 [216].

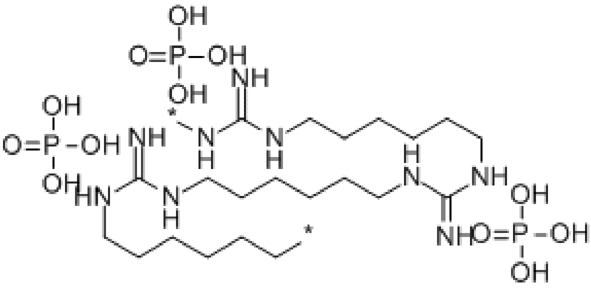


Figure 54: *Structural formula of PHMGP* [216]

In the first study [84], 0.1 wt% of positively charged PHMGP solution was combined with anionic APP (0.1 wt%, pH 11) to form 20 BL coating on cotton. In the second study [215], APP was replaced with an anionic 0.1 wt% solution of alginate (ALG). Both coatings showed inhibited ratios of *S. aureus* and *E. Coli* of ~ 0.03 and ~ 0.04 with bacteria reduction of 100% for both bacteria according to AATCC 100-2004, but with poor flammability results. The samples did not pass VFT as well as HFT. Chemicals used for FR LbL deposition of cotton are shown in Table 9.

Table 9: *Chemicals used for FR-antimicrobial LbL deposition of cotton*

Primer	**Recipe**	**Number of layers**	**FR / antibacterial results**	**Literature**
PEI^+ 1%	PA^- 2%, pH 4 / $PCQS^+$ 1% + immersion into NaClO 0.5%, pH 7	30 BL 30 BL + NaClO	30 BL VFT result: passed LOI: 29.8% Add-on: 21.2% TG in N_2 at 600 °C: char 37% Bacteria reduction AATCC 100-2004: *S. aureus* – 92.2% *E. coli* – 47.7% 30 BL immersed into NaClO VFT result: passed LOI: 28.5% Add-on: unknown TG in N_2 at 600 °C: char 34% Bacteria reduction AATCC 100-2004: *S. aureus* – 100% *E. coli* – 100% Minimal influence on the break strength	[90]
$BPEI^+$ 5%	PA^- 2%, pH 4 /$(CH+U)^+$ pH 4 CH 0.5% U 10% + immersion into $CuSO_4$ x $5H_2O$	12 BL	VFT result: passed LOI: 26% Add-on: 19% MCC data: pHRR reduction 61.8%, THR reduction 54.3% TG in the air at 650 °C: char 13.3% TG-IR in air: less H_2O, almost no CH_4/CH_3OH, more CO_2, almost no CO, less C=O (aldehyde)	[70]

	2%		Bacteria reduction AATCC 100-2004: *S. aureus* – 100% *K. pneumoniae* – 100%	
	CH^+ pH 3 / AP^- 3%, pH 7	1 BL	VFT result: passed LOI: 27% Add-on: 8% CC data: pHRR reduction 59%, THR reduction 64%, char 20.1% TG in N_2 at 700 °C: char 34% TG-IR in N_2: more H_2O, more CO_2, N-H, less C-H, less C=O, less C-O-C Antibacterial rate GB/T 20944.3-2008: *E. coli* – 99.3% Tensile strength improved by 10%	[87]
	$(CH+photoinitiator)^+$ pH 3.5 CH 0.5% Photoinitiator 4% / DNA- 0.5%, pH 7 + post-treatment (UV radiation) Last layer CH^+	30 BL	HFT result: passed Add-on: 4.8% CC data: pHRR reduction 36%, THR reduction 45%, char 15% TG in the air at 600 °C: char 7.4% Kirby-Bauer test: Inhibited ratio – *S. aureus* ~ 0.03 Inhibited ratio – *E. Coli* ~ 0.04 Bacteria reduction ASTM E 2149-01: *S. aureus* – 57%	[214]
	PHMGP+ 0.1% / APP- 0.1%, pH 11	20 BL	VFT result: did not pass HFT result: did not pass LOI: 19.5% Add-on: 2.8% TG in the air at 600 °C: char 7.1% Kirby-Bauer test: Inhibited ratio – *S. aureus* ~ 0.03 Inhibited ratio – *E. Coli* ~ 0.04	[84]
	$PHMGP^+$ 0.1% / ALG^- 0.1%	20 BL	VFT result: did not pass HFT result: did not pass Add-on: 4.8% MCC data: pHRR reduction of 29%, THR reduction of 24% TG in the air at 600 °C: char 12.7% Kirby-Bauer test:	[215]

			Inhibited ratio – S. aureus ~ 0.03 Inhibited ratio – E. Coli ~ 0.04 Bacteria reduction AATCC 100-2004: *S. aureus* – 100% *E. coli* – 100%	

5. CONCLUSION

This thesis gives an insight into the research of the possible use of LbL deposition as a response to technological and ecological drawbacks of the current commercial finishing process. The aim was to keep cotton FR effective while reducing the quantity of chemicals and, if possible, to replace them with chemicals from renewable sources while reducing the energy consumption of the process. The results of the thesis confirmed that by means of LbL deposition is possible to reduce the amount of chemicals to only 100 g/l using DI as a solvent of eco-friendly chemicals (BPEI, PA, CH, U) at temperatures below 100 °C. The add-on of commercial organophosphorus flame retarding treatment for cotton is between 20 and 25%, whereas the add-on of 10 BL of PA/CH-U coating is 17.3%, which means that LbL deposition consumes less chemicals for similar FR efficiency. Obtained results are compared with commercial non-durable FR cotton treatment, and what can be noticed is that a similar add-on range is present on typical non-durable systems, e.g., boric acid/borax (~ 10% add-on) and diammonium phosphate/ammonium sulfamate (~ 15% add-on) [34]. Data on break strength and elongation break of cotton treated with FR/AM by means of LbL deposition are limited. Up to now, it is reported that break strength after LbL treatments decreased by 10% [71], 12% [89], or 14% [90]. Few papers mention an increase of breaking strength up to 10% [87] and an elongation break increase of 71.6% [88]. For comparison, Pyrovatex ® treatment leads to a significant loss in tensile strength (20–25%) and tear strength (up to 50%) of treated cotton [30], while other non-durable FR finishes for cotton generally decrease the breaking strength of cotton fabrics [217–219]. The thesis confirmed the FR effectiveness of phytic acid (PA) in the form of an anionic solution in low quantities (20 g/l) if combined with a cationic N-rich solution of CH (5 g/l) and U (100 g/l). Only 10 BL of PA/CH-U coating was sufficient to self-extinguish flame in VFT with the LOI value of 28.0% for FR cotton. The MCC data showed a pHRR reduction of 59.5% and the THR reduction of 70.3% compared to untreated cotton. TGA analysis showed a reduced weight loss rate, reduced first decomposition temperature (by 55 °C) compared to untreated cotton (~ 400 °C), and more char yield at 650 °C (~ 15%) compared to untreated cotton (~ 0.4%). PA as a P-rich polymer and CH-U as N-rich polymers chemically interact with each other forming acidic N-P intermediates, which further phosphorylate and dehydrate cellulose at temperatures lower than those of the thermal decomposition of cellulose [139]. These reactions are accompanied by an increase in char content and a decrease in temperature of the first decomposition stage compared to untreated cotton. Thermally stable cross-linked char coats the polymer surface, acting as a shield, which prevents further burning and smouldering of the polymer. At temperatures above 600 °C, the char undergoes oxidation, but the presence of a P compound in char inhibits complete oxidation of the carbon to CO_2. FT-IR analysis of gases generated by heating PA/CH-U treated cotton in the air at the first decomposition stage shows the generation of H_2O, CH_4/CH_3OH, CO, formaldehydes, ethers/esters of formic acids, 5-ring imides, cycloalkanes, as well as PH and NH compounds. No levoglucosan is found, which confirms that acidic N-P intermediates from PA/CH-U successfully phosphorylated the cellulose and inhibited the generation of highly flammable levoglucosan. Since the PH and NH compounds are found in IR spectra of gas products, they may act in the gas phase as free radicals scavengers, which are essential for flame propagation, but it is also possible that their intermediates act physically by reducing the O concentration of the surrounding atmosphere thus suppressing the flame [14]. The post-burn char of PA/CH-U treated cotton after performing VFT consists mainly of C, O, P, and N, which means that P and N trapped C and blocked it from full oxidation by generating charing shield on the polymer surface in the form of bubbling typical for intumescent FR and condensed phase [76]. TG-IR analysis of volatile products and EDS analysis of post-burn char prove that PA/CH-U based FRs act in a gas as well as condensed phase, where CH and cellulose act as carbon donors, PA as an acid donor and U as a blowing agent that generates gas [220]. Another advantage of LbL deposition over commercial FR finishes for cotton is compatibility with antimicrobial treatments (for the comparison, commercial FR finishes for cotton are compatible with water/oil repellent finishes [30], but are incompatible with antimicrobial treatments [58,62]). Cu^{2+} salts (in form of $CuSO_4$ x $5H_2O$) added as the top layer enhanced the FR effect of 12 PA/CH-U BLs on cotton while achieving antimicrobial properties at the same time. Additionally, the pHRR value was reduced to ~ 62% (compared to untreated cotton), which is 11% more compared to pHRR value of samples without the additional Cu^{2+} layer. At the same time it increased the LOI value from 21.5 (untreated cotton) to 26.0%. For comparison 12 BL PA/CH-U treatment increased the LOI value to 24.5%. By adding $CuSO_4$ x $5H_2O$ into intumescent 12 PA/CH-U system, the first decomposition stage of treated cotton starts at 261 °C with release of H_2O, CH_4/CH_3OH, CO_2, CO, formaldehyde, ethers, CuO or CuS compounds or other S compounds with S-S bonds according to FT-IR gas spectra. For comparison the first decomposition stage of samples without the additional Cu^{2+} layer starts at 312 °C with release of H_2O, CH_4/CH_3OH, CO, formaldehydes, ethers/esters of formic acids, 5-ring imides, cycloalkanes, as well as PH and NH compounds. CuO or CuS nanoparticles present in volatile gasous product generated by heating may act as the inert dust that absorps and dissipates the heat causing a lowering of temperature and also explains the fact that there is almost no difference in amount of char left at 650 °C between 12 BL PA/CH-U (14.9%) and 12 BL PA/CH-U+$CuSO_4$ x $5H_2O$ treated cotton (13.3%). No levoglucosan is found, which means that acidic N-P-Cu intermediates dehydrate the cellulose by cross-linking and inhibited the generation of highly flammable levoglucosan. The post-burn char of 12 BL PA/CH-U+$CuSO_4$ x $5H_2O$ treated cotton contains mainly C, O, P, N and Cu according to EDS analysis, which means that N, P and Cu trapped C and block it from full oxidation by generating charing shield on polymer surface in a form of bubbling typical for intumescent FR. However, S is not found, either due to detection limits of EDS or due to all S gas compounds evolved while heating. TG-IR analysis of volatile products and EDS analysis of post-burn char prove that N-P-Cu based FRs act in a gas as well as condensed phase. 12 BL PA/CH-U+$CuSO_4$ x $5H_2O$ coating not only reduces the flammability of cotton to level of commercial FRs, but also kills 100% of gram-positive *S. aureus* and Gram-negative *K. Pneumonie* bacteria at the same time. In spite of the fact that CH itself is efficient environmentally-friendly antimicrobial agent for Gram-positive bacteria (the bacteria reduction ~ 100%), it is less efficient for Gram-negative bacteria (the bacteria reduction ~ 71%). By immersing 12 BL PA/CH-U treated cotton into Cu^{2+} solution (20 g/l), the bacteria reduction of Gram-negative *K. Pneumonie* increases to 100%. The reason why FR treated cotton is immersed just once at the end of LbL deposition is because it has been proven that strong electrolytes such as $CuSO_4$ x $5H_2O$ solution may disturb the growth of LbL assembly. From the ecological point of view, the gases generated by combustion of waste made of PA/CH-U and PA/CH-U+$CuSO_4$ x $5H_2O$ treated cotton are not environmentally-friendly, neither is the post-burn char left after combustion. Inhalation of toxic gases generated by combustion can lead to death and FR compounds have been found in the atmosphere, soil, water and in biological samples with no data on their influence on environment [221]. From that point of view it is very difficult to solve all environmental issues arising in production, usage or waste disposal of FR or multifunctional FR/AM treated cotton, but when developed novel treatments solves even a small part of it, it is already a big step forward. With the wider availability of biodegradable chemicals from renewable sources at lower costs and improving wash durability, LbL deposition has the potential to become an industrially feasible solution for FR or multifunctional FR/AM functionalization of cotton. Future research will be expanded to the improvement of wash durability as well as dye compatibility with conventional dyeing/printing processes.

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7. ANNEX

7.1. Magovac, E.; Vončina, B.; Jordanov, I.; Grunlan, J.C.; Bischof, S. Layer-by-Layer Deposition: A Promising Environmentally Benign Flame-Retardant Treatment for Cotton, Polyester, Polyamide and Blended Textiles. *Materials (Basel).* **2022**, *2*, 1–30, doi:10.3390/ma15020432.

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Review

Layer-by-Layer Deposition: A Promising Environmentally Benign Flame-Retardant Treatment for Cotton, Polyester, Polyamide and Blended Textiles

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Abstract: A detailed review of recent developments of layer-by-layer (LbL) deposition as a promising approach to reduce flammability of the most widely used fibers (cotton, polyester, polyamide and their blends) is presented. LbL deposition is an emerging green technology, showing numerous advantages over current commercially available finishing processes due to the use of water as a solvent for a variety of active substances. For flame-retardant (FR) purposes, different ingredients are able to build oppositely charged layers at very low concentrations in water (e.g., small organic molecules and macromolecules from renewable sources, inorganic compounds, metallic or oxide colloids, etc.). Since the layers on a textile substrate are bonded with pH and ion-sensitive electrostatic forces, the greatest technological drawback of LbL deposition for FR finishing is its non-resistance to washing cycles. Several possibilities of laundering durability improvements by different pre-treatments, as well as post-treatments to form covalent bonds between the layers, are presented in this review.

Keywords: layer-by-layer; flame retardancy; cotton; polyamide; polyester

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1. Introduction

Textiles make up one of the world's largest industrial sectors, covering a wide range of industrial applications, such as apparel, footwear, automotive/aircraft/shipbuilding industry, civil engineering, agriculture, medicine, etc. Different industrial applications need functional properties such as flame retardancy, conductivity, magnetic shielding, antistatic and antimicrobial properties achieved by using chemicals and processes that, quite often, result in environmental pollution [1]. To reduce the consumption of water, energy and chemicals in the textile industry, the European Commission is emphasizing new industrial treatments, sustainable chemicals from renewable sources, recycling and reuse of textiles without negative impacts on fiber/fabric mechanical properties, visual appearance, wash durability or loss of any other specific property through the product life cycle [2]. In 2021, the International Association of Fire and Rescue Services reported over 19,000 deaths in the world caused by fire in buildings (91%), vehicles (8%) and other places (4%), which highlights the need for flame retardancy of fabrics [3]. In 2018, the flame-retardant (FR) market reached 2.8 million tons worldwide and the non-halogenated sector took about 31% of this total [4].

Effective FRs for textiles should fulfill the following requirements:

- Cost-effective and easy to apply in industry;
- Durable for at least 50 laundry cycles;
- Wear-resistant;
- High air/moisture permeability (comfortable and pleasant to wear),
- Should not change the appearance of fabric (color, shade);
- Should be non-toxic to humans or environment during the industrial production, usage, disposal, or fire [5].

Three types of approaches have been commonly used for obtaining flame-retardant textiles, i.e., mechanical incorporation of retardants into the filaments during extrusion, binding FR co-monomers in the process of polymerization and surface modification by FR coatings, which has become one of the most convenient, cost effective and most efficient ways to protect against fire [6]. Current commercially available FRs for finishing of the fabrics are mostly based on halogen (organo-halogen, halogen-antimony and halogen-phosphorus), phosphorus (organo-phosphorus and antimony-phosphorus), boron or metal hydroxides systems, as well as inorganic additives [7]. There are several techniques to add FR compounds onto a fabric depending on the end use, type of fabric, or material composition. Cotton and cotton blends require adding commercially available durable FRs based on tetrakis(hydroxymethyl) phosphonium salt (THPX) in a precondensate ammonia cure process and N-methylol dimethylphosphonopropionamide (N-MDMPA) derivatives in the pad–dry–cure process [8]. The drawbacks of these processes are the use of toxic ammonia in the case of the cure process and the release of formaldehyde during the production and product life-cycle in the pad–dry–cure process [9]. Where it is not possible to use THPX or MDMPA in the production process due to the environmental concerns, formaldehyde-free crosslinking agents such as butyl tetracarboxylic acid (BTCA) are used, but the resulting finish is usually only semi-durable [10]. Durable FR finishes for cotton and cotton blends are particularly important for safety clothes, while semi-durable FRs can be used for certain textile applications such as cotton fleece. FRs intended for man-made fibers, such as polyester (PES) and polyamide, can be applied to the textile by a thermosol treatment involving aqueous padding, drying and heating of the fabric. Dopents or co-reactant FRs can be added directly in melt spinning, but these additives alter the mechanical properties of polyester and polyamide fibers, thus limiting their use [11,12]. Durable intumescent FRs based on toxic halo–organic–antimony compounds can be added to all textiles by back-coating with appropriate resin [10,13].

Due to the very high demands on energy and water consumption, as well as the amount of chemicals used, some of them being toxic, there is a need to overcome these drawbacks by introducing new environmentally benign chemicals from renewable sources, such as chitosan, phytic acid, alginates, deoxyribonucleic acid, hydrophobins, caseins, whey proteins, etc. The traditional finishing of textile materials imparts a thick coating (~1 µm thickness) onto the fabric that results in altered properties of the coated fabrics, such as lower stiffness, significant loss of strength and poor abrasion resistance [10]. In an effort to minimize thickness of deposition and weight of textiles, several techniques, such as nanoparticle adsorption, sol–gel and dual-cure processes and layer-by-layer (LbL) deposition, are used [11,14–16].

2. LbL Deposition

LbL deposition dates back to the 1960s, to the invention of Iler and Kirkland, who discovered the buildup of inorganic films based on cationic boehmite fibrils and anionic silica particles [17,18]. In 1992, Decher et al. performed LbL assembly using cationic poly-[diethylmethyl(4-vinylbenzyl)ammonium iodide] and poly(allylamine hydrochloride) (PAH), as well as anionic solutions of sodium poly(styrenesulfonate) and potassium poly(vinyl sulfate) [19]. In 2013, Ariga et al. published a review on the possible application of LbL deposition in various industrial fields, including (bio)sensors, bioreactors, enzyme devices, drug delivery/release, cell coatings, solar cells, lithium batteries, photovoltaic devices, supercapacitors, transistors, color displays and gas barriers. Compounds used for LbL deposition include polyelectrolytes, inorganic nanoparticles, small derivatives based on nitrogen and phosphorus, small organic molecules, macromolecules (including biomacromolecules, such as proteins or deoxyribonucleic acid (DNA)), inorganic compounds, metallic or oxide colloids [20]. The LbL deposition process includes immersing the substrate into the solutions of oppositely charged polyelectrolytes or spraying the substrate with charged solutions [21]. In this way, it is possible to build LbL structures with the desired number of bilayers (BLs), trilayers (TLs), or quadlayers (QLs) with different functionality [22]. The interaction between opposite charges in multilayer film build-up is primarily electrostatic forces, but, today, researchers have explored donor/acceptor interactions, hydrogen bond donors/acceptors, covalent bonds, π–π interactions and stereo complex formations [23]. In conventional LbL deposition, layers are attracted by weak electrostatic forces of polyelectrolytes soluble in water, polyanions and polycations with one charged group per monomer unit, but polymers bearing hydrogen bond donors and acceptors are also able to form assemblies. These weak bonds are sensitive to environmental conditions and formed layers are easy to break. To form durable coatings, coordination polymers (inorganic or organometallic polymer structure containing metal cation centers linked by ligands) have been employed to form organic–inorganic hybrid multilayer assemblies. These complex structures can further be subjected to post-chemical reaction, such as UV or thermal curing. Unconventional methods of LbL deposition usually include two steps. The first step is forming a supramolecular complex based on various interactions (electrostatic, hydrogen-bonded, or π–π complexes, block copolymer micelles) in bulk solution. In the second step, the supramolecular complex is subsequently used as a building block for LbL assembly [24].

LbL assembly has been used to functionalize textiles with different properties, such as flame retardancy [25], conductivity [26], electromagnetic interference shielding [27], antimicrobial properties [28] and hydrophobicity [29]. These coatings can be applied on fabrics by dipping and by vertical or horizontal spraying [21]. Mateos et al. constructed a proof-of-concept automatic coating system capable of producing reproducible and precise layering with the possible industrial, large-scale application of LbL deposition by dipping [30]. Krogman et al. developed an automated system capable of depositing polymer films from atomized polyelectrolyte mists by spraying [31]. Jang et al. developed a robotic dipping system for layer-by-layer deposition of thin films [32]. Factors influencing the reproducible results are longer adsorption time and rinsing volume to avoid the cross-contamination of deposition solutions (dilution factor should be at least 1:106), as well as surface coverage of functional groups [22]. Parameters influencing the growth kinetics of LbL assembly include the type of polyelectrolytes, their molecular weights and concentrations in solutions, the pH of solutions, addition of low-molecular-weight additives or salts, additional sonication of the solutions, adsorption time and rinsing solutions [33–36]. Larger polyelectrolytes form slightly thicker coatings and require longer deposition times, while smaller molecules show strong dip time-dependent thickness of the LbL assembly [37]. Gamboa et al. investigated the influence of rinsing and drying on the growth of layers by means of an automated deposition system. In terms of thickness up to 40 BLs, the thickest films could be achieved by rinsing upward and drying upward the substrate as an intermediate step between dipping into or spraying with oppositely charged polyelectrolytes, which completely eliminated electrolyte contamination [38]. LbL deposition is a promising technique for textile finishing due to a very low concentration of active substances in polyelectrolyte solutions. Only several milligrams per milliliter are needed to obtain desired properties [39]. The purpose of this review is to present the current state of the art and future perspectives of LbL deposition applied to reduce the flammability of the most widely used textiles—cotton, polyesters, polyamides (PA6, PA 6.6) and their blends.

3. Thermal Degradation of Polymers

In order to burn a polymeric material, thermal energy from an external source must be present to raise its temperature and initiate degradation. How much energy a given polymer absorbs depends on several factors, such as surface reflectance and absorption characteristics, and the level and the spectral characteristic of the radiant flux in the IR region. Generally, if the absorption coefficient of the polymer with respect to the external radiation is large, the temperature of the polymer surface becomes high and thermal decomposition occurs by free radical chain elimination, evolving non-combustible as well as combustible gases, which further encourage burning. These elimination reactions include random or chain end-initiated scissoring of the weakest bonds in the bridging groups connecting the aromatic rings or heterocycles, propagation and termination reactions, ending up with the formation of char in the condensed phase [40,41]. In general, the burning of polymers can be characterized by four components: heat, the oxidizing agent, the fuel (polymer) and an uninhibited chemical chain reaction. The schematic overview of polymer burning is represented in Figure 1 [5].

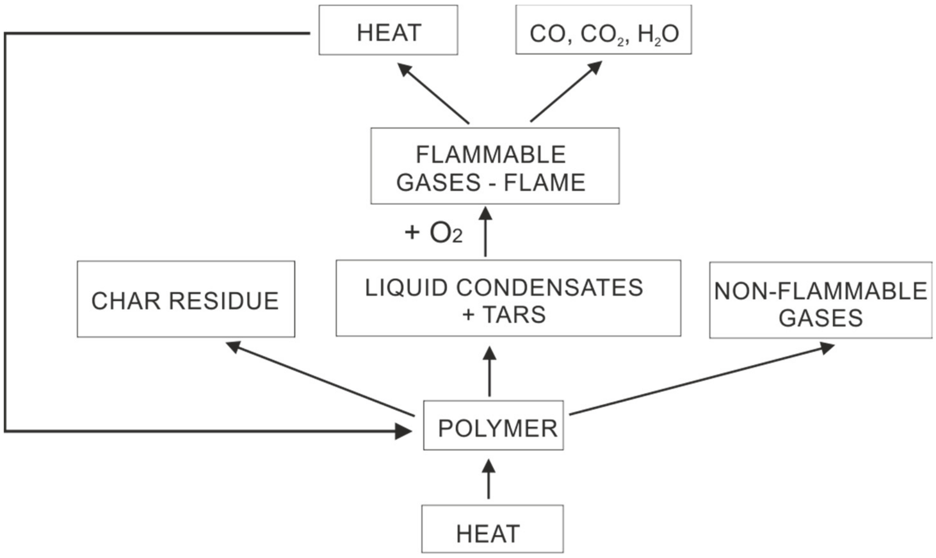


Figure 1. Schematic of polymer burning [5] Reproduced with permission from Magovac, E.; Bischof, S., Tekstil; published by Hrvatski inzenjerski savez tekstilaca, 2015.

To prevent or to stop the fire, one or more contributors of the fire have to be removed. This is achieved by adding flame retardants with different modes of action into polymers acting chemically and/or physically in the condensed phase and/or in the gas phase [7]. Halogen-based flame retardants act chemically in the gas phase by hindering the chain-branching reactions with atmospheric oxygen, thus producing hydrogen and hydroxyl free radicals, which further propagate polymer combustion. They also dilute the flame and decrease the mass concentration of combustible gases, reducing the heat release evolved in the combustion of the gases and acting physically in the condensed phase [42]. Organophosphorus flame retardants act in the condensed phase by dehydration of polymers and char formation that acts as an insulating shield on the surface of the unburnt polymer, preventing further thermal decomposition as well as lowering the rate of transport of the combustible pyrolysis products to the flame. The process is accompanied by the endothermic release of water [43]. Flame retardants based on metal hydroxides, such as aluminum trihydroxide, release water endothermically during the decomposition to aluminum oxide acting in the condensed phase. The resulting aluminum oxide forms a shield layer, which protects unburnt polymer from burning gases in the flame [44].

3.1. Cotton

Among all natural fibers, cotton ranks second in textiles, with a market share of around 23% of the global fiber production in 2019 [45]. Cotton fabrics are pleasant to wear due to moisture up-take, enabled by the highly hydrophilic and reactive hydroxyl groups of glucose in cellulose [46]. Fabrics made of cotton and its blends are used for medical applications, apparel, sportwear, fashionwear and for safety clothes. However, due to its chemical composition, cotton is very flammable. The oxidative thermal decomposition of cellulose fibers starts with water desorption at ~25 °C and ends at 150 °C; it continues with cellulose dehydration between 150 and 240 °C. Above 240 °C, two parallel chemical reactions start. One is cellulose dehydration, resulting in the generation of primary char as well non-flammable gases such as water, carbon monoxide and carbon dioxide. A second chemical reaction is the depolymerization of primary char between ~240 °C and 400 °C, resulting in the generation of highly flammable levoglucosan, which, at temperatures between ~400 °C and 700 °C, yields flammable gases and initiates the generation of secondary char residue, stable at temperatures above 700 °C [47].

3.2. Polyester Fibers

Polyester fibers are the most widely used fibers worldwide, with a share of around 52% of the global fiber production in 2019 [45]. The production of polyester is low cost and the polymer is obtained by the esterification of ethylene glycol and purified terephthalic acid (TA) or dimethylterephthalate (DMT) in the presence of a catalyst. The fibers are strong and durable, dyeable, chemically and wrinkle-resistant. Fabrics made of polyester and its blends are used for apparel, sportswear, footwear, household, furniture and technical textiles, such as tire cords, car seat belts, etc. The undesirable property of polyester fibers is high flammability, with the formation of molten droplets that can easily spread the fire to other materials. Structural intermolecular changes caused by heating start near the glass transition temperature (T_g~80 °C) and continue through melting (T_m) between 250 and 300 °C. Above 380 °C, the thermal decomposition temperature (T_p) of polyester occurs regardless of the type of atmosphere (vacuum, nitrogen, or air). Temperature deviations of T_g, Tm and T_p are caused by deviations in molar mass, chemical composition, different catalysts used during the polyester production and the presence of additives [48]. At lower heating rates, pyrolysis takes place through four stages. In the first stage, free radical chain elimination occurs, generating methyl vinyl terephthalate and terephthalic acid. At ~280 °C, the vinyl polymerization of methyl vinyl terephthalate occurs. At ~300 °C, methyl vinyl terephthalate separates from the linear polymer chain, while forming double bonds in the linear polymer. At ~400 °C, linear polymer chain cyclization occurs [49].

3.3. Polyamide Fibers

Polyamide fibers had a market share of around 5% of the global fiber production market in 2019 [45]. The production is low cost and the polymer is obtained by the polycondensation reaction of ε-caprolactam (PA6) or the polycondensation reaction of a diamine and dicarboxylic acid (e.g., hexamethyldiamine and adipic acid—PA6.6), containing at least 85% by weight of diamine and dicarboxylic acid. Their unique properties, such as elasticity, strength, heat-, cold- and chemical resistance, makes polyamides ideal for making technical textiles such as ropes for boats, car seat belts, life vests, luggage as well as apparel such as combat uniforms, socks and swimwear [50,51]. However, PA6.6 and PA6 fibers are very flammable, with the formation of molten droplets.

The glass transition temperature of PA6 and PA6.6 fibers is between 45 and 60 °C and the melting point is between 172 and 260 °C. The range in these temperatures are also caused by deviations in molar mass, chemical composition, various catalysts used during production and the presence of additives and copolymers [52]. The decomposition temperature of polyamide also varies, but it starts, generally, between 310 and 400 °C, with a primary scission reaction of $-NH–CH_2-$ bonds and free radicals' formation, followed by a complex series of secondary reactions [53]. Polyamide decomposition reactions are divided into two processes, i.e., cyclization of a part of the polymer chain of adipic acid and subsequent reactions and cleavage of the polymer chain, as well as subsequent condensation reactions (i.e., crosslinking of amine groups) [54]. The FR properties of polyamides are achieved by various organo-halogen compounds, such as trialkylphosphates and phosphonates in the form of copolymers and melamine salts [12,55,56].

3.4. Fiber Blends

While the behavior of cotton, polyester and polyamide is predictable during combustion, their blends react unpredictably depending on the blend ratio. During the thermal degradation of the cotton/polyester blend, cotton decomposes at ~320 °C, which is below the temperature of thermal degradation of polyester (~380 °C), thus making cotton the initial source of ignition in cotton/polyester blends. At temperatures between 250 and 260 °C, polyester melts, tending to wick on the cotton char, which results in the so-called scaffolding phenomenon [57]. Molten polyester furnishes additional fuel to the gas phase and, as the polymer temperature is raised, heat is produced from the combustion of cotton decomposition products. Additional fuel increases the vigor of gas phase oxidation [58,59]. By reducing the ratio of cotton in cotton/polyester blends, the total heat release (THR) values, as well as the char yield, increase [60,61]. Oppositely to cotton/polyester blends, by reducing the ratio of cotton in cotton/PA 6 blends, THR increases and char yield decreases [60]. This is likely due to fact that polyamide melts below the temperature of decomposition of cotton at ~256 °C, protecting the cotton until the temperature of the cotton's decomposition reaches ~320 °C [62,63].

The gaseous products of the combustion of textiles are mostly toxic and consist, mainly, of ammonia (NH_3), carbon dioxide (CO_2), carbon monoxide (CO), various aliphatic and aromatic hydrocarbons, various aldehydes and acetates, hydrogen cyanide (HCN), hydrogen halides, sulfides, nitriles, nitrogen oxides (NO_x) and nitrogen acid [64–67]. Gases found in the blood of fire victims are usually HCN and CO. Other toxic compounds generated in fires, such as hydrogen chloride (HCl), hydrogen fluoride (HF) and hydrogen bromide (HBr), belong to the category of inorganic irritants, acting as immediate corrosive agents of the surface of the respiratory tract [68].

4. Layer-by-Layer Deposition on Textiles

Layer-by-layer deposition is a simple technique, able to effectively deposit active compounds on textiles. The major drawback of this technique is the poor interfacial adhesion between the textile material and polyelectrolyte solution, which depends, generally, on the hydrophilicity and surface charge of the substrate, the polyelectrolyte charge, pH and ionic strength of the solution. The general process of LbL deposition on textiles is shown in Figure 2. Before LbL deposition, the surface of textile materials should be charged enough, either positively or negatively, depending on the charge of polyelectrolytes used in the process.

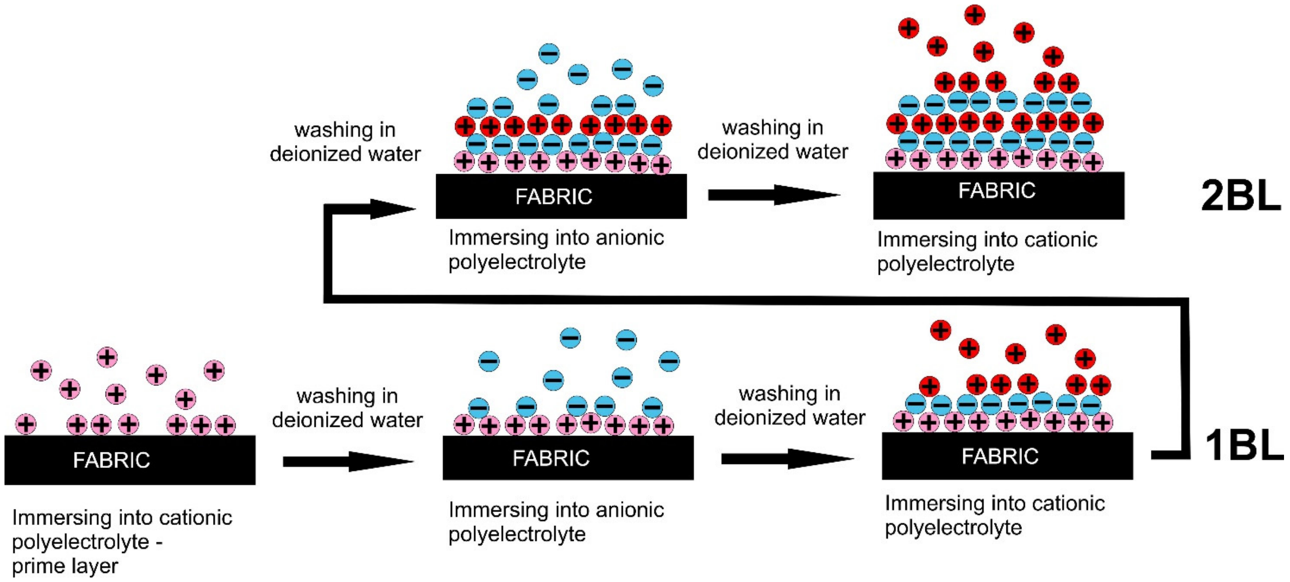


Figure 2. Schematic of typical layer-by-layer deposition process of immersing fabrics into oppositely charged polyelectrolytes with a primer layer.

Cellulose fibers are highly reactive due to the presence of surface hydroxyl groups, which enable them to react with FR compounds forming semi-durable or durable FR finishes. Polyester and polyamide fibers have a limited number of functional groups (such as -OH, -COOH, -O-CH_2-CH_2-, -NH_2, etc.) on the fiber surface, which reduces the FR processability of the fabrics [69–71]. Even though cotton is composed of more than 90% cellulose, a negligible amount of surface-located hydrophobic waxes, pectins and proteins make raw cotton quite hydrophobic. Therefore, commercial wet processing, such as desizing to remove size, scouring to clean hydrophobic waxes, pectins and proteins and bleaching to increase the whiteness of cotton, is conducted to render cotton hydrophilic and able to accept aqueous treatment. Since wet processing of cotton is economically unfavorable due to production of effluents with high chemical oxygen demand (COD) and biochemical oxygen demand (BOD), enzymatic scouring is an excellent method to overcome these negative issues by treating the cotton at lower temperatures, for less than one hour, in near-neutral pH conditions [72,73].

Polyamide and polyester fibers are mainly hydrophobic due to insufficient functional groups on their surfaces [74]. Several processes have been reported to functionalize them by chemical and physical methods [75]. Chemical methods include alkaline or acid hydrolysis, having a negative environmental impact and causing damage to fabrics [76]. UV radiation and plasma activation are less harmful, but functionalization is uneven and requires complex and very expensive machinery [77–80]. Enzymatic modification of the polyamide and polyester surface is another biochemical treatment performed under environmentally benign and energy-saving conditions by using enzymes [81–83]. Another method for increasing the surface charge of the textiles and achieving better adhesion is applying a primer polyelectrolyte layer with an opposite charge than the substrate surface, such as branched polyethyleneimine (BPEI) or 3-aminopropyl triethoxysilane (APTES) [84].

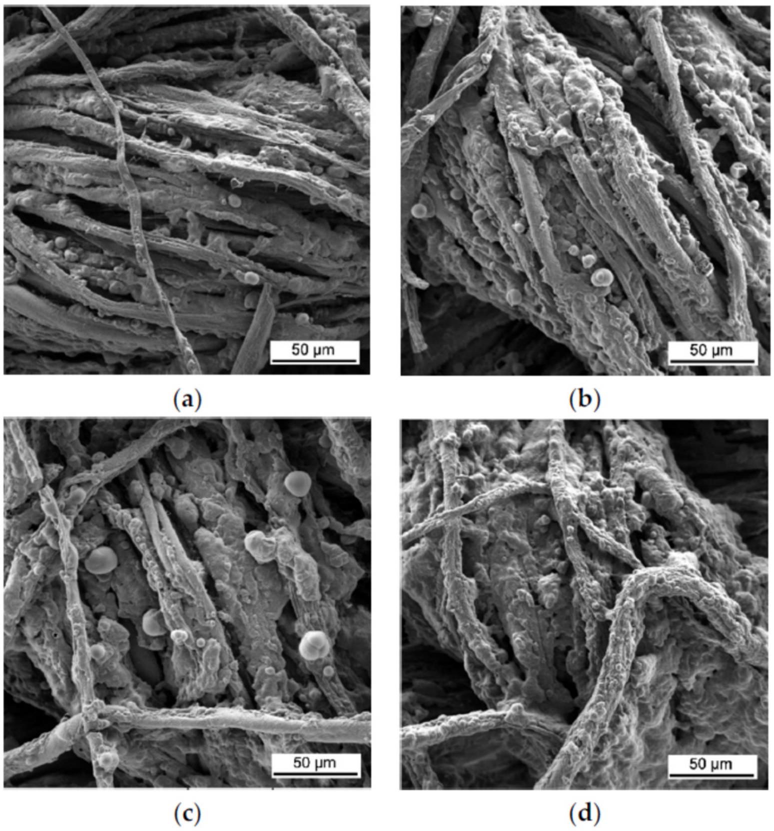
4.1. Layer-by-Layer Deposition to Reduce Flammability of Cotton

The majority of scientific papers on the application of LbL deposition to reduce the flammability of fabrics has been devoted to cotton. The compounds used for the deposition of cotton are long-chain organic polymers [85–89] and short-chain organic molecules [90–92], as well as suspensions of inorganic nanoparticles [93–95].

One of the first studies regarding the LbL deposition of cotton with FRs was performed in 2010 by Li et al. They treated cotton fabrics with 5–20 BLs of cationic branched polyethyleneimine (BPEI) of different pH and anionic sodium montmorillonite (MMT) clay of different concentration. The study revealed that the layers became thicker by increasing the pH of the BPEI solution or the concentration of MMT clay. Cotton treated with 20 BLs of BPEI at pH 7 and 1 wt% MMT showed reduced afterglow time in vertical flame tests [85].

Polyethyleneimine (PEI) is a highly charged cationic polymer, rich in nitrogen, that exists in linear and branched states. The difference between these two polymers is in the type of amino group; linear PEI possesses primary and secondary amino groups, whereas branched PEI also possesses tertiary amino groups [96]. As a nitrogen rich and positively charged polymer, PEI is an excellent candidate for LbL deposition on a negatively charged, chemically bleached cotton surface. MMT is nanoclay consisting of an aluminum oxide/hydroxide layer stuck between silicate layers. Most of the clay minerals tend to have a negative charge resulting from the substitution of the silica cation (Si^{4+}) by the aluminum cation (Al^{3+}) in the clay sheet structure [97]. Choi et al. used 1 wt% bio-based cationic starch (CS) and anionic MMT, forming 5, 10 and 20 BLs. The LbL-coated cotton samples reduced afterglow time in vertical flame tests (VFTs) but burned completely [93]. In the majority of studies dedicated to cotton flame retardancy by means of LbL, BPEI is used either as a primer layer for better adhesion of chemical compounds to the cotton surface or as one of the oppositely charged pairs for a bilayer recipe.

Another chemical compound used either as a primer layer or as one of the oppositely charged polyelectrolyte is a positively charged coupling agent rich in nitrogen and silicon 3-aminopropyl triethoxysilane (APTES), which is mostly used as a sol–gel precursor in the preparation of sol–gel materials and coatings [98]. Li et al. coated cotton fabric with 5, 10 and 15 BLs of 5 wt% cationic APTES and 2 wt% anionic phytic acid (PA), with drying at 100 °C after each dipping step. The 15 BL treatment was able to stop fire immediately after removing the ignition source [99]. PA is an inexpensive and easily obtained phosphorus-rich chelating agent from plant/seed sources, with high absorption of polycationic compounds [100]. In 2019, the same group of authors used a 1 wt% cationic suspension of PEI with alumina-coated silica nanoparticles (SiO_2) at pH 5 (instead of APTES) and anionic 2 wt% PA at pH 6 forming two, four and seven BL. The minimum number of BLs passing VFTs was 2, with the limiting oxygen index (LOI) value of 26.0%. The study also showed a minor loss in breaking strength in the warp and weft directions (~15%) relative to untreated cotton, likely caused by the formation of hydrogen bonds between SiO_2–PEI/PA and cotton fibers and the breaking of intermolecular and intramolecular hydrogen bonds in cellulose. The minor reduction in the loss of breaking strength after LbL treatment is an advantage over the commercial processes, which exhibit higher loss in mechanical strength [94]. The same authors used 4 wt% anionic polyphosphoric acid (PPA) instead of PA, thus reducing the number of BLs from two to one with the same FR and mechanical performance [101]. Anionic PA, as a green alternative to commercial phosphorus-based FR for cotton, has been used by several authors. Liu et al. coated cotton with a cationic solution of 0.5 wt% PEI, with added low-molecular-weight 2.0 wt% melamine (ME) at pH 4 in combination with 3.0 wt% PA at pH 4, forming two and four BLs. Only the samples coated with four BLs passed VFTs [90]. In another study 5, 10 and 15 QLs of cationic 5.0 wt% APTES, 2 wt% anionic PA, 1 wt% cationic chitosan (CH) and again anionic PA (the pH of all solutions was 3.5) were deposited with subsequent dipping and drying at 100 °C. The LOI value fabric coated with 15 BLs was 29.0% and it passed VFTs [86]. CH is another positively charged polymer from renewable sources (shells of shrimp and other sea crustaceans) widely used for LbL deposition due to its pKa value of 6.5 from amino group in a linear polysaccharide molecule composed of β-(1-4)-linked d-glucosamine (deacetylated unit) and N-acetyl-d-glucosamine (acetylated unit) [102]. Chen et al. pre-treated cotton by immersing it into positively charged APTES to improve the adhesion of two, three and six BLs consisting of polyanionic ammonium polyphosphate (APP, 1 wt%) and polycationic CH (0.5 wt%). Each immersion step was followed by drying at 100 °C. Only three and six BLs passed VFTs [87]. Anionic PA (2 wt%), with added sulfonated melamine-formaldehyde (SMF, 1 wt%), was used in the study of Pan and Zhao in 2018. Cotton fabric was coated with 5 and 10 BLs of cationic CH (0.5 wt%, pH 5) and anionic PA–SMF (pH 5). Only fabric treated with 10 BLs passed VFTs [91]. Zhang et al. successfully coated cotton with eight BLs of positively charged PEI (0.5 wt%, pH 9) and negatively charged PA (2.0 wt%, pH 4) by dipping in deionized water (DI) and drying after each dip. The coated fabrics passed VFTs [88]. Zilke et al. pre-treated cotton fabric with BPEI (1 wt%) to add a positive charge on the fabric surface and then dipped it into anionic PA (5 wt%, pH 0.7) and cationic 5 wt% polyvinyl amine (PVAm), forming 5, 10 and 15 BLs. The lowest number of BLs passing horizontal flame spreading test was 10 [89]. PVAm is a linear polymer with the highest content of primary amine functional groups of any polymers [103]. Magovac et al. used 8, 10 and 12 BLs of anionic PA (2 wt%, pH 4) and cationic CH (0.5 wt%) with added urea (U, 10 wt%), where 10 BLs passed VFTs and the char left after performing the test showed characteristic intumescent bubbling, as shown in Figure 3 [92].



(**a**) (**b**) (**c**) (**d**)

Figure 3. SEM images of the char of cotton samples treated with (**a**) 8, (**b**) 10, (**c**) 12 and (**d**) 15 BLs of PA/CH-U after performing vertical flame testing [92].

The thermogravimetric analysis (TGA) showed an increase in char with the increase in bilayers at 650 °C (from 1.2% for untreated cotton to 7.0% for 8 BLs and 14.1% for 10, 12 and 15 BLs), as well as the reduction in degradation temperatures, as shown in Figure 4 [92]. CH-U/PA decreased the decomposition rate of cotton by generating more non-flammable gases (e.g., CO, CO_2, NO_x) instead of highly flammable levoglucosane, which diluted the concentration of the combustible gases and absorbs heat, causing bubbling. At the same time, urea catalyzed the reaction of PA, as well as the decomposition of cellulose at lower temperature, thus forming intumescent char, which acted as a physical barrier that blocked heat and oxygen [104].

In 2020, Liu et al. studied the reduction in the flammability of cotton by using fully environmentally benign compounds—egg white protein and PA. Egg white protein is rich in amino acids, phosphorus, sulfur and metal complexes, such as calcium, iron, etc. Due to its complex nature, the protein attracts negatively charged PA. The study showed that even one BL of egg white protein and PA (70 wt%) gave excellent FR performance. TGA in air demonstrated a char yield of almost 33% at 600 °C and microscale combustion calorimeter (MCC) data revealed a 23% reduction in pHRR and a 67% reduction in THR [105].

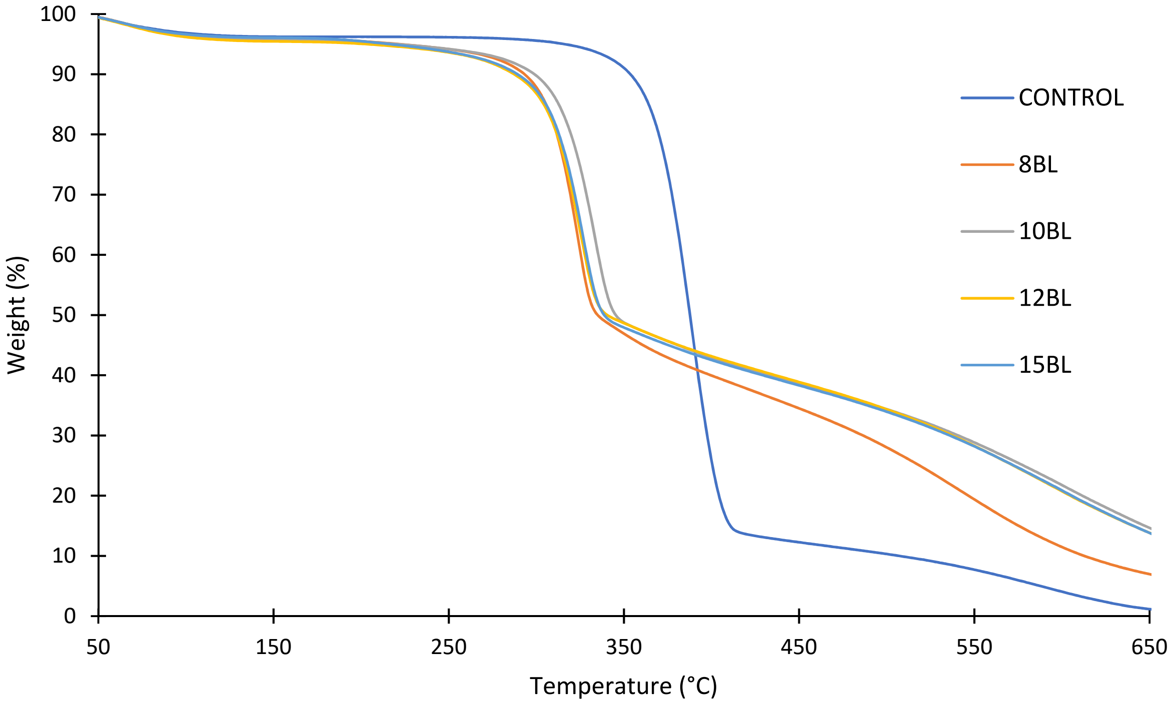


Figure 4. TGA of untreated and treated cotton fabrics with 8, 10, 12 and 15 BLs of PA/CH-U [92].

Another high charge density cationic nitrogen-rich polymer used in LbL polyelectrolyte pairs is polydiallyldimethylammonium chloride (PDAC), widely used for coagulating and removing negatively charged particles and dissolved organic matter from drinking water [106]. Carosio et al. used a 1 wt% cationic solution of PDAC, 1 wt% anionic poly (acrylic acid) (PAA) and anionic 1 wt% suspension of APP. Cotton treated with a combination of PDAC/PAA/PDAC/APP in 1, 5 and 10 quadlayers (QLs), passed the horizontal flame test (HFT) [107]. In their second study, instead of APP, they used nitrogen and phosphorus-rich anionic 1 wt% DNA, forming 5 and 10 BLs. Such treated cotton was then immersed into 0.1 wt% and 1 wt% hydrotalcite (HT) nanoparticle suspensions. HT is a zeolite that is used as an antacid in medicine. The 0.1 wt% HT concentration lowered the minimum number of BLs required for obtaining cotton self-extinguishment. All samples passed the HFT, but the 0.1 wt% HT concentration showed the best performance in terms of pHRR (33%) and THR reductions (27%), relative to untreated cotton [108]. Jang et al. used 0.25 wt% cationic polyvinyl alcohol (PVA) and a 0.1 wt% anionic suspension of graphene nanoplatelets (GNP) and poly (4-styrenesulfonic acid) (PSS) to build 10 BLs on cotton. It resulted in a reduction in pHRR by 34.4% and in THR by 47.4%, respectively, but did not pass VFTs [95].

Another interesting study made by Pan et al. was to investigate the effect of barium, nickel and cobalt ions crosslinked with alginate on the thermal stability and flammability of cotton fabric. Cotton was coated with PEI (0.5 wt%, pH 9) and anionic sodium alginate (SA; 0.3 wt%, pH 7), forming 10 BLs. The samples were then immersed into 5 mol/L solutions of metal salts, such as barium chloride ($BaCl_2$), cobalt acetate tetrahydrate ($C_4H_6O_4Co$ x $4H_2O$), or nickel acetate tetrahydrate ($C_4H_6O_4Ni$ x $4H_2O$), for crosslinking. Adding metal ions led to improved char residue and reduced DTG peak compared to untreated cotton, as well as the reduction in HFT burning rate. In terms of durability of treatment, the metal crosslinked LbL coating was durable even up to 6 h of washing in a detergent solution [109]. Alginate is a linear polysaccharide consisting of a-l-guluronic acid and β-d-mannuronic acid residues produced by brown algae and bacteria. It is used in the food industry as a thickening agent, gelling agent, emulsifier, stabilizer and texture-improver, as well as in medicine for wound dressing [110]. Pan et al. continued their studies on reducing the flammability of cotton and, instead of anionic alginate, they used a 2 wt%

anionic hypophosphorous acid-modified chitosan (HACH) solution, forming 5 and 10 BLs of PEI/HACH. The cotton fabric was then immersed into a 1 wt% solution of genipin, a natural cross-linker for chitosan, proteins, collagen, etc. Ten bilayer coatings extinguished the fire of cotton during the horizontal burning test. PHRR and THR of 10 BL fabrics were reduced by 73% and 80%, comparing with those of pure cotton. Cotton coated with 10 BLs and cross-linked with genipin exhibited FR properties up to two washing cycles [111].

Wang et al. coated cotton fabrics with a 1 wt% cationic solution of CH with added p-aminobenzene sulfonic acid-modified melamine (AMM, 3.3 wt%) and 3.3 wt% anionic APP to build 5, 10 and 15 BLs. The resulting 15 BLs on cotton fabric exhibited excellent FR properties (LOI 31.5%, 40% decrease in pHRR, 60% THR reduction with 24.1 wt% char residue and passed VFTs), as well as showing low cytotoxicity in a cell culture [112]. In 2020, Lazar et al. pre-treated cotton fabric with a 1 wt% solution of PEI to generate a positive charge on a cotton surface and then coated it with 5, 10 and 15 BLs of 2 wt% anionic PSP (pH 4) and 0.1 wt% cationic CH (pH 4). Each dipping step was followed by rinsing in deionized water. The resulting FR cotton fabric passed VFTs. By adding a 100 mM solution of tris(hydroxymethyl)aminomethane (THAM, pH 4) to the rinsing steps, the number of bilayers needed to achieve the same FR properties of treated cotton fabrics passing VFTs was reduced to 10 [113]. Table 1 gives a review of polyelectrolytes used to achieve FR of cotton fabrics.

Table 1. Polyelectrolytes used to achieve FR of cotton.

Pre-Treatment	Recipe	Number of Layers	Literature
	$BPEI^+/MMT^-$	5, 20 BLs	[85]
	CS^+/MMT^-	5, 10, 20 BLs	[93]
	$APTES^+/PA^-$	5, 10, 15 BLs	[99]
	$(PEI+SiO_2)^+/PA^-$	2, 4, 7 BLs	[94]
	$(PEI+SiO_2)^+/PPA^-$	1 BLs	[101]
	$(PEI+ME)^+/PA^-$	2, 4 BLs	[90]
	$APTES^+/PA^-/CH^+/PA^-$	5, 10, 15 QLs	[86]
Primer layer $APTES^+$	APP^-/CH^+	2, 3, 6 BLs	[87]
	$CH^+/(SMF+PA)^-$	5, 10 BLs	[91]
	PEI^+/PA^-	8 BLs	[88]
Primer layer $BPEI^+$	$PA^-/PVAm^+$	5, 10, 15 BLs	[89]
Primer layer $BPEI^+$	$PA^-/(CH+U)^+$	8, 10, 12, 15 BLs	[92]
	Egg white $protein^+/PA^-$	1 BLs	[105]
	$PDAC^+/PAA^-/PDAC^+/APP^-$	1, 5, 10 QLs	[107]
	$PDAC^+/DNA^-$	5, 10 BLs	[108]
	$PVA^+/(GNP+PSS)^-$	10 BLs	[95]
	PEI^+/SA^-	10 BLs	[109]
	$PEI^+/HACH^-$	5, 10 BLs	[111]
	$CH^+/APP^-(CH+AMM)^+/APP^-$	5, 10, 15 BLs	[112]
Primer layer PEI^+	PSP^-/CH^+	5, 10, 15 BLs	[113]

Most of the studies dedicated to cotton flame retardancy by means of LbL deposition show that compounds consisting of nitrogen, phosphorus, sulfur or inorganic particles reduced the pHRR values from 23% to 73% and the THR values from 27% to 80%, relative to untreated cotton. There is no general rule regarding how to obtain an optimal combination of FR ingredients to achieve a self-extinguishing behavior of cotton comparable to commercial flame-retardant finishing. The FR properties of LbL-treated cotton depended on the ionic strength of charged layers, number of layers, chemicals used, concentration of polyelectrolytes in solution, pH of solution, dipping time, pre-treatment of cotton fabrics and post-treatment of treated fabrics. By increasing the number of layers, as well as the concentration of chemical compounds in charged solutions (up to 10 wt%), the thermal stability of cotton increased. In terms of durability of LbL treatments, only a few studies show that the durability of FR on cotton was poor and the chemicals were washed away. The durability of FR treatment up to two laundry cycles in water or detergent solution was improved by post-curing with a crosslinking agent [111].

4.2. Multifunctional Finishing of Cotton

Besides excellent flame retardancy, cotton fabrics should very often satisfy many other properties, such as antistatic, antibacterial properties, hydrophobicity, self-cleaning and antifouling properties, wrinkle resistance, UV protection, electromagnetic interference shielding and conductivity [114]. The multifunctionality of cotton is possible to achieve via LbL deposition of commercially available compounds or simply by immersion of LbL-treated cotton into an active substance as a post-treatment. The wash durability of such multifunctional properties could be much better with crosslinking performed during thermal curing. An et al. coated cotton first with PEI (0.01 M) as a primer and then with 5 mg/mL of a graphene oxide (GO) anionic suspension and 3 wt% cationic caprolactam modified casein emulsion (CA), forming 1, 5 and 10 BLs. The final step was immersion into a sodium borohydride ($NaBH_4$) solution, followed by APP (7 wt%) solution. The obtained LOI of this treated cotton fabric (10 BLs) was 23.6%, passing VFTs, whereas pHRR was reduced by 64% and THR was reduced by 38%, relative to untreated cotton. These fabrics also obtained excellent antistatic properties [115]. Zang et al. coated cotton fabrics with 10 QLs (two-sided) of cationic APTES (5 wt%, pH 4), anionic SA (3 mg/mL, pH 7), anionic APP (1 wt%, pH 9) and different concentrations of anionic GO (0.5; 1; 1.5 mg/mL) by spraying, which resulted in a fabric with improved FR, antistatic and antibacterial properties. Among all the treated fabrics, cotton treated with a 1 mg/mL concentration of anionic GO had the best self-extinguishing performance, with a pHRR value of about 3.2% of uncoated cotton (the reduction in pHRR was ~96.8% and that in THR was ~93%) [116].

Another interesting study dealing with FR and the antimicrobial properties of LbL-coated cotton comes from Li et al. Cotton fabrics were first pre-treated with 1 wt% cationic PEI as a primer and then coated with 10, 20 and 30 BLs of an anionic PA solution (2 wt%, pH 4) and a 1 wt% cationic poly[3-(5,5-cyanuricacidpropyl)-siloxane-co-trimethylammoniumpropylsiloxane chloride (PCQS) solution. At 30 BLs, the break strength of the treated cotton decreased by 14% in the warp and by 6% in the weft direction. The fabric that passed VFTs (30 BLs), with an LOI value of 29.8%, was then immersed into a 0.5 wt% antibacterial sodium hypochlorite solution (NaClO) at pH 7. The strength of cotton slightly decreased after chlorination [117]. In 2020, the same researchers treated cotton with one BL of a cationic CH solution and a 3 wt% anionic ammonium phytate (AP) solution (pH 7) to reduce the number of BLs, thus obtaining fabric with efficient FR as well as antimicrobial properties. The LOI value of this treated cotton was 27%, with a char length of 78 mm after performing VFTs [118]. In 2021, Magovac et al. used a 2 wt% anionic PA solution (pH 4) and 0.5 wt% cationic CH solution (pH 4) with added U (10 wt%) to form 8, 10 and 12 BLs. At the end of the layering, the FR-treated cotton fabric was immersed into a 2% $CuSO_4$ solution to achieve additional antibacterial property. The results showed that cotton treated with 12 BLs self-extinguished the flame in VFTs (char length, 6.5 cm), with an LOI value of 26% and a reduction in pHRR by 62% and in THR by 54%. The resulting cotton killed almost 100% of bacteria [104].

Li et al. coated cotton fabric with cationic PEI with added SiO_2 and anionic PPA (1 BL), as mentioned in Section 4.1. This fabric was finally treated with a commercially available water-repellent finish (6 wt%, pH 6) by a dip–pad–dry process. The resulting fabrics passed VFTs and exhibited excellent hydrophobic properties [101]. Excellent FR, as well as hydrophobic properties, could be achieved by coating cotton with four BLs of cationic PEI with added melamine (ME) and anionic PA, then immersing into chloroform solution and curing [90].

Another interesting study was conducted by Lin et al. by coating cotton fabric with only one BL of cationic BPEI (2 mg/mL) and anionic APP (80 mg/mL) and immersing it into polydimethyl siloxane (PDMS) with fluorinated silica (F-SiO_2), followed by crosslinking in an oven at 130 °C for 30 min. This fabric exhibited excellent FR (the sample passed VFTs; pHRR and THR values were reduced by 86% and 39%), hydrophobic, self-cleaning, self-healing and antifouling properties with acid/alkali resistance [119]. The same properties could be achieved by coating cotton fabric with 16 BLs of cationic poly (dimethyldiallyl) ammonium chloride (PDDA) and anionic boron nitride nanosheets (BNNS) [120]. To obtain FR, wrinkle-resistant, antibacterial and UV-protective properties of cotton fabric, Safi et al. dipped fabrics first into a cationic solution consisting of 1 wt% CH, 5 wt% citric acid and 2 wt% sodium hypophosphite (SHP), followed by drying at 110 °C; then, they dipped them into a solution of 5 wt% sodium lignin sulphonate (SLS) and 4 wt% boric acid (BA), followed by drying at 80 °C for each dip. At the end, the fabrics were cured at 150 °C for 4 min. Three bilayers passed VFTs with an LOI of 30.5, while the pHRR was reduced by 50% relative to untreated cotton [121].

In a recent study by Xue et al., cotton fabric was coated with 10 BLs of cationic BPEI and anionic carbon nanotubes (CNT). Ten bilayers were then immersed into BPEI and APP, forming one BL. Each dipping was followed by drying at 60 °C. The resulting multilayered fabrics exhibited excellent FR (char length after combustion in VFTs was 7 cm) as well as conductive properties. By immersing the same fabric into one trilayer (TL) consisting of BPEI/APP/PDMS instead of BPEI/APP and subsequent drying and curing at 60 °C, the resulting fabric became superhydrophobic, acid/alkali/organic solvent-resistant, UV-protective and wash-resistant after long-time laundering [122]. To obtain excellent FR properties, conductivity and electromagnetic interference shielding durable under continuous external forces or washing tests, Zhang et al. treated fabrics with eight BLs of PEI and PA followed by drying after each dip (already mentioned in Section 4.1). The coated fabric was then immersed into a 0.8 wt% ethanol suspension of silver nanowires (AgNWs) from one to four times, followed by drying at 50 °C after each immersion step. Only four-time-immersed treated cotton suppressed flames, passing VFTs with an LOI value of 37% and a reduction in pHRR and THR by 41.4% and 27.1%, respectively [88]. Table 2 reviews polyelectrolytes used to combine FR with other functional properties and achieve the multifunctionality of cotton fabrics.

Studies dedicated to LbL deposition for multifunctional finishing of cotton show an unlimited choice of chemicals at a very low concentration (up to 10 wt%) applied either as layers or by immersing treated cotton into a charged solution at the end of the deposition. This multifunctional finishing reduced the pHRR values by 41–97% and the THR values by 27–93%. By combining different chemicals and varying their concentrations as well as number of layers, it was possible to achieve multifunctional cotton with LOI values greater than 29% [117,121]. A few studies show that LbL deposition had minimal influence on the break strength of treated cotton (at a certain number of layers, the break strength decreased by 14% in the warp and by 6% in the weft direction) [117]. The major problem of LbL multifunctional finishing is wash durability, which could be improved by post-curing with an appropriate crosslinking agent [88,119,122].

Table 2. Polyelectrolytes used to achieve FR and other multifunctional properties of cotton.

Pre-Treatments	Recipe	Number of Layers	Properties	Literature
Primer layer PEI^+	GO^-/CA^+	1, 5, 10 BLs	FR, antistatic	[115]
Primer layer GO^-	$APTES^+/SA^-/APP^-/GO^-$	10 QLs on 2 sides of fabric	FR, antistatic, antibacterial	[116]
Primer layer PEI^+	$PA^-/PCQS^+$, immersion into NaClO	10, 20, 30 BLs	FR, antibacterial	[117]
	CH^+/AP^-	1 BL	FR, antibacterial	[118]
Primer layer $BPEI^+$	$PA^-/(CH + U)^+$, immersion into $CuSO_4$	8, 10, 12 BLs	FR, antibacterial	[104]
	$(PEI + SiO_2)^+/PPA^-$, immersion into repellent finish	1 BL	FR, hydrophobic	[101]
	$(PEI + ME)^+/PA^-$, immersion into chloroform solution	4 BLs	FR, hydrophobic	[90]
	$BPEI^+/APP^-$	1BL	FR, hydrophobic	[119]
	$PDDA^+/BNNS^-$	16 BLs	FR, hydrophobic	[120]
	(CH + citric acid + SHP)/(SLS + BA)	1, 2, 3 BLs	FR, antibacterial, UV-protective, wrinkle resistant	[121]
	$(BPEI^+/CNTs)_{10}/BPEI^+/APP^-$ $(BPEI^+/CNTs)_{10}/BPEI^+/APP^-/PDMS$	10 BLs+1 BL 10 BLs+1 TL	FR, conductive FR, conductive, hydrophobic	[122]
	PEI^+/PA^-	8 BLs	FR, electromagnetic interference shielding	[88]

4.3. Layer-by-Layer Deposition to Reduce Flammability of Polyester

There are relatively few studies regarding the use of layer-by-layer deposition to reduce the flammability of polyester [107,123–131]. The compounds used for the treatment of polyester are long-chain organic water-soluble polymers (polyelectrolytes), short-chain organic molecules and suspensions of inorganic nanoparticles. For a better adhesion of these compounds to polyester, or as one of the oppositely charged pair of a BL, long-chain organic water-soluble charged polymers, such as PDAC, PAH, CH and PEI/BPEI, have been used [107,123,125–128]. Another option to increase the charge of polyester fabric is surface functionalization, such as alkali hydrolysis and UV-grafting [130].

Carosio et al. used a 1 wt% positively charged PDAC solution, widely utilized for building LbL assemblies in combination with 1 wt% negatively charged PAA, capable of crosslinking at temperatures above 200 °C, as well as a 1 wt% negatively charged APP suspension. Polyester fabrics treated with a combination of PDAC/PAA/PDAC/APP in 1, 5 and 10 quadlayers (QLs), limited the flammability of the fabrics by suppressing the afterglow and melt dripping, as well as lowering heat release during combustion [107]. In another study, three different 0.2 wt% cationic suspensions compounds—PDAC, SiO_2 and polyhedral oligomeric silsesquioxane cage molecules carrying eight n-propylammonium chloride groups (POSS®)—with a 0.2% anionic suspension of α-zirconium phosphate (ZrP) were deposited as 5 and 10 BLs. The treated fabric showed an overall improvement in thermal stability by increasing the time to ignition (up to 86% for PDAC) and decreasing the pHRR (up to 26% for POSS). Alumina-coated silica nanoparticles reduced the production of smoke (up to 25%), but no VFT was performed [123]. The same group of authors studied the influence of LbL spraying vs. dipping on the flammability of fabric. Polyester was coated with five BLs of a cationic 0.2 wt% suspension of alumina-coated silica colloidal nanoparticles and a 0.2 wt% suspension of anionic silica colloidal nanoparticles. This study demonstrated that building layers by spraying is more efficient for achieving a homogeneous coverage, as well as suppressing the dripping of the polyester fabric [124].

Apaydin et al. combined cationic PAH, anionic sodium polyphosphate PSP, a flame retardant and a negatively charged suspension of titanium dioxide (TiO_2) in 5, 10 and 15 QLs of PAH/PSP/PAH/TiO_2. However, even at 15 QLs, the pHRR decreased only by 14%, which means that the treatment had little influence on flammability [125]. PAH has been used as a cationic polyelectrolyte rich in nitrogen for the preparation of hollow microcapsules for biomedical drug delivery [132]. Jordanov et al. showed that, by adding low-molecular-weight FR compounds into a 1 wt% cationic CH network, in combination with a 1 wt% anionic APP suspension, it was possible to reduce the number of bilayers needed to pass the VFT (from 30 BLs to 10 BLs). As low-molecular-weight FR additives, nitrogen and nitrogen/sulfur-based derivatives such as 13 wt% guanidine sulfamate (GSM), 13 wt% U, or 13 wt% thiourea (THU) were used in the cationic CH solution. The sample coated with 10 BLs of CH–GSM/APP showed the same self-extinguishing properties as polyester coated with 30 BLs of CH/APP. Moreover, the 10 BLs CH–GSM/APP coating reduced the pHRR by 61.7% relative to uncoated polyester, as shown in Figure 5 [126].

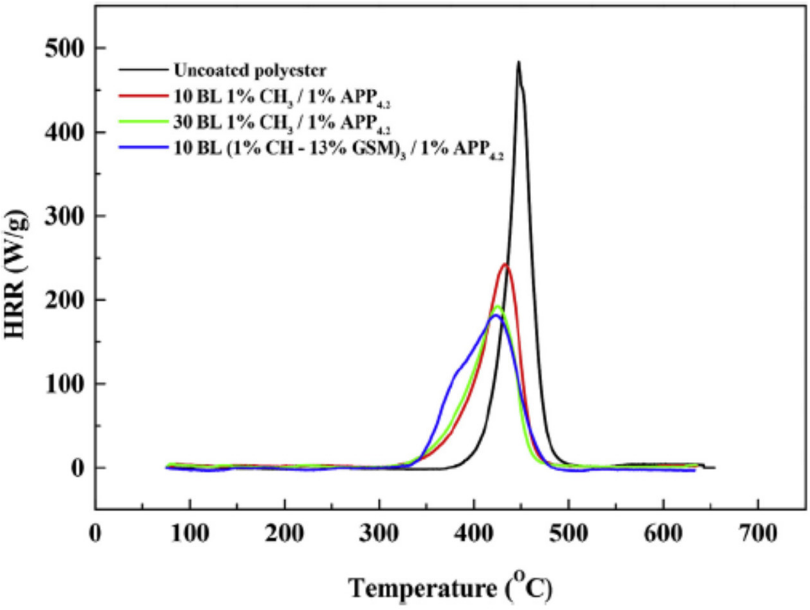


Figure 5. MCC curves of heat release rates as a function of temperature for uncoated and coated polyester [126] Reproduced with permission from Jordanov, I.; Magovac, E.; Fahami, A.; Lazar, S.; Kolibaba, T.; Smith, R.J.; Bischof, S.; Grunlan, J.C. Flame, Polym. Degrad. Stab.; published by Elsevier Ltd., 2019.

Other authors used nitrogen-rich high-molecular-weight cationic PEI or BPEI for coating polyester. Wattanatanom et al. studied the influence of polyelectrolyte concentrations, as well as the number of layers, on the flammability, break strength and stiffness of LbL treated polyester fabric, including wash resistance of FR coating. Another study used a 0.5 wt% cationic BPEI solution and a 5, 7 and 10 wt% anionic APP suspension to reduce flammability and anti-dripping properties. The fabric was first padded in BPEI solution, dried at 80 °C and then padded in APP solution and dried at 110 °C to deposit three, five and seven BLs. Increasing the number of bilayers (three, five and seven BLs) or the concentration of the solution (5, 7 and 10 wt%) improves flame retardancy and anti-dripping of polyester by decreasing after-flame time of coated fabric and self-extinguishing the flame [127]. In a second study with the same formulations, they showed that increasing the concentration of APP, as well as the number of layers, led to an increase in the break strength and stiffness of the fabric, indicating that FR finishing via LBL deposition did not degrade the strength. The formulation of 10 wt% APP at seven BLs showed wash durability of the FR coating for one washing cycle [128]. Carosio et al. investigated how adding salt into solutions influenced the layers, improving the FR properties with the same number of BLs. The authors used 0.1 wt% cationic BPEI as a primer layer to functionalize polyester. The fabric was then immersed into a 0.7 wt% anionic MMT suspension, rinsed in deionized water and then immersed into cationic 1 wt% octapropylammonium polyhedral oligomeric silsesquioxane (OAPOSS) to deposit five BLs. Adding 0.10 M sodium chloride (NaCl) into both the cationic and anionic solutions modified the ionic strength of the systems, which resulted in thicker and more homogeneous coatings. A thicker coating decreased flame spread rate in horizontal flammability tests relative to fabric with the same number of BLs without added NaCl and the fabric showed no melt-dripping. The FR coating showed the same performance after a 1 h washing at 70 °C [129]. Pan et al. alkali hydrolyzed polyester (PET) fabric, UV-grafted it with commercial thickening agent acrylamide (AM) and benzophenone and coated this pre-treated fabric with 5, 10 and 15 BLs of a 0.5 wt% cationic PEI solution and a 0.3 wt% anionic oxide sodium alginate (OSA) solution, a natural polysaccharide found in brown algae. After LbL treatment, the fabrics were immersed into 10 wt% hypophosphorus acid for crosslinking, as shown in Figure 6. Fabric treated with 15 BLs did not show any melt-dripping in horizontal flammability tests and the fire self-extinguished. The pHRR and THR values decreased by 44% and 29.4% relative to untreated fabric and the FR treatment was durable for 12 laundering cycles [130].

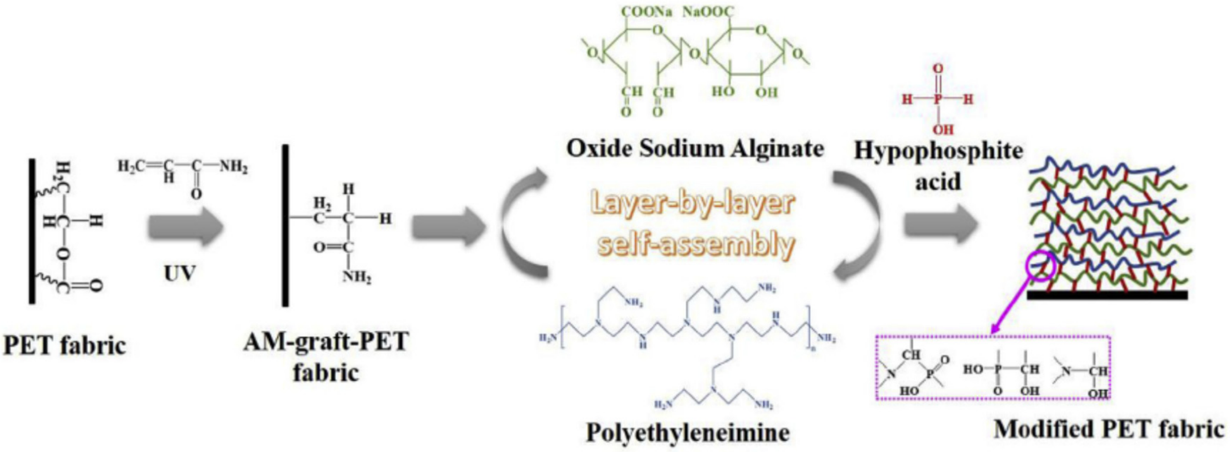


Figure 6. Schematic of LbL deposition of pre-treated MA-graft-polyester (PET) fabric coated with 15 BLs of OSA/PEI and post-treated with HA cross-linking [130] Reproduced with permission from Pan, Y.; Liu, L.; Song, L.; Hu, Y.; Wang, W.; Zhao, H., Polym. Degrad. Stab.; published by Elsevier Ltd., 2019.

The influence of dipping time in polyelectrolyte solution on the flammability of polyester fabric was investigated by Jiang et al. One trilayer (TL) was built by immersing the fabric into a 5 wt% cationic sol solution of flexible polysiloxane (SSP) prepared by sol–gel from methyltriethoxysilane (MTES), isopropanol (IPA) and hydroxy-terminated polydimethylsiloxane (PDMSOH) and a 10 wt% anionic PA solution. One TL consisted of SSP/PA/SSP. The dipping time was set to 0, 5, 10, 15 and 20 min. The study showed that the FR properties of the fabric improved with soaking time, so 20 min of soaking exhibited self-extinguishing properties of polyester fabrics during VFTs, with a 65% reduction in pHRR in comparison with untreated polyester. The FR effect of this fabric was durable up to 45 washing cycles [131]. A summation of the polyelectrolytes used to achieve FR of polyester fabrics is provided in Table 3.

Table 3. Cationic/anionic compounds used to achieve FR of polyester fabrics.

Pre-Treatment	Recipe	Number of Layers	Literature
	$PDAC^+$/PAA^-/$PDAC^+$/APP^-	1, 5, 10 QLs	[107]
	$PDAC^+$/ZrP^- $SiO_2{}^+$/ZrP^- $POSS^{®+}$/ZrP^-	5, 10 BLs	[123]
	Ludox CL^+/Ludox $SM30^-$	5 BLs	[124]
	PAH^+/PSP^-/PAH^+/$TiO_2{}^-$	5, 10, 15 QLs	[125]
	CH^+/APP^- $(CH+GSM)^+$/APP^- $(CH+U)^+$/APP^- $(CH+THU)^+$/APP^-	10, 25, 30 BLs	[126]
	$BPEI^+$/APP^-	3, 5, 7 BLs	[127,128]
Primer layer $BPEI^+$	MMT^-/$OAPOSS^+$	5 BLs	[129]
1. Alkali hydrolysis 2. UV-grafting with AM and benzophenone	PEI^+/OSA^-	5, 10, 15 BLs	[130]
	SSP^+/PA^-/SSP^+	1 TL	[131]

Studies dedicated to polyester flame retardancy by means of LbL deposition show that compounds consisting of nitrogen, phosphorus, sulfur, or inorganic particles reduced the pHRR values by 65% and the THR values by 29%, relative to untreated polyester. By combining different compounds, varying their concentration and applying varying number of bilayers, polyester fabric exhibited no melt dripping and a self-extinguishing behavior. The same effect could be achieved by increasing the immersion time of the fabric in a polyelectrolyte solution [131]. Generally, LbL deposition did not degrade the strength of the polyester fabric [128]. Studies showed that the wash durability of FR treatment depended almost exclusively on the creation of covalent bonds between layers, which could be improved by post-curing with adequate crosslinking agent [131].

4.4. Layer-by-Layer Deposition to Reduce Flammability of Polyamide Textiles

The compounds used for FR LbL deposition of polyamide are similar to those applied to cotton and polyester. According to the literature, polyamide is mainly treated with cationic polymers, such as PAH, CH and PEI, as a primer layer or one of the polyelectrolyte pairs [125,133–136]. As a pre-treatment, chemical grafting with PAA as well as enzymatic modification have been reported [137,138]. Apaydin et al. experimented with a 1 mg/mL cationic PAH solution and a 1 wt% anionic MMT suspension to deposit 5, 10 and 20 BLs on PA6. Cone calorimetry revealed that 20 BLs reduced the pHRR values by more than 60% [133]. These same researchers deposited cationic PAH with anionic PSP to build 5, 10, 15 and 40 BLs on PA6.6. TGA showed that the amount of residue increased for 20 and 40 BLs, while the cone calorimeter data showed a significant decrease in pHRR (up to 36%) for all coated fabrics [134]. The same group of authors combined cationic PAH, anionic PSP and an anionic suspension of titanium dioxide (TiO_2) to deposit 5, 10 and 15 QLs of PAH/PSP/PAH/TiO_2 (Section 4.3). Cone calorimetry showed that the coating reduced pHRR by 26% for PA6.6 fabric treated with 15 QLs, but the presence of TiO_2 did not significantly improve the FR performance relative to the formulation without TiO_2 [125]. Kumar Kundu et al. deposited 5, 10 and 15 QLs of cationic CH, anionic PA and anionic oxide sodium alginate (OSA) on PA6.6. The aldehyde groups in OSA formed strong covalent bonds with CH and it could be used in LbL deposition as a cross linker. In the VFT, 10 and 15 QL coatings stopped the melt-dripping of PA6.6, with LOI values of ~22%. Cone calorimetry showed that a maximum reduction (24%) in the pHRR was achieved with five QL deposition [135]. In 2018, the same group of authors treated PA6.6 with 5 and 10 BLs of a 1 wt% cationic CH solution and a 2 wt% anionic PA solution to build 5 and 10 BLs. The fabrics were further impregnated in 1 and 5 wt% Na-tetraborate decahydrate solutions and cured at 90 °C. All the treated fabric samples could stop melt dripping in VFTs and pHRR values were lowered compared with the control. In terms of FR performance, the best results were with fabrics treated with 10 BLs (a 31% reduction in pHRR relative to untreated fabric). This coating remained durable up to five washing cycles for PA6.6 impregnated with borate [136]. In 2020, they deposited a 1 wt% cationic CH solution and an anionic solution of 1 wt% phosphorylated chitosan (PCH) and 0.25 wt% poly-acrylate sodium (PAS) onto PA6.6 via "one pot" and LbL deposition to compare the efficiency of these two methods in the reduction in the flammability of PA6.6. Fabric treated via "one pot" for 5 and 10 min was then UV-grafted. Layered fabric was immersed first into cationic CH, washed with DI and then immersed into anionic (PCH-PAS), forming 5 and 10 BLs, then either UV-cured (5 and 10 BLs) or thermally crosslinked (10 BLs). The results indicated that the UV-grafted fabric treated with 10 BLs, with a higher weight gain%, exhibited the highest LOI value of 23% and a 25% reduction in pHRR relative to untreated fabric. However, only the thermally cross-linked PA6.6 treated with 10 BLs retained the FR performance after 5 washing cycles [139]. One-pot synthesis is an expression denoting that all the reactants are subjected to successive chemical reactions in just one reactor, thus saving time and resources and improving the efficiency of a chemical reaction [140].

Ziaur Rahman et al. investigated the influence of pre-treatment and post-treatment on the thermal properties of PA6.6 deposited with two and five BLs of a cationic CH solution with added ME and U and an anionic PA solution. The fabrics were first chemically grafted with PAA in a solution of benzene and dibenzoyl peroxide (BPO). The fabrics were then dipped into cationic PEI, dried at 70 °C and then dipped into a polyacrylic acid–co-maleic acid solution (PAACM) and dried. After LbL treatment, the fabrics were impregnated in a cationic CH and graphene oxide (GO) solution through a pad–dry–cure process. Despite excellent hydrophilic properties achieved by adding GO, none of the treated fabrics passed VFTs either before or after washing [137]. In 2020, Jordanov et al. successfully deposited 15–25 BLs of a 1 wt% anionic APP suspension and a 1 wt% cationic CH solution, with added low-molecular-weight compounds 20 wt% THU or U, onto the enzymatically modified surface of PA6.6 fabrics. The process is schematically shown in Figure 7. By adding low-molecular-weight FR compounds into the CH network, the number of BLs passing the HFT was reduced from 25 BLs of APP/CH-U to 15 BLs, while the pHRR was reduced by 35% relative to untreated fabric [138]. A summation of polyelectrolytes used to achieve FR of polyamide fabrics is provided in Table 4.

There are relatively few studies about LbL deposition of FR compounds on polyamide fabrics, showing reductions in pHRR from 24 to 60% relative to untreated fabric. The results of VFTs and HFTs showed decreased melt dripping. By varying different coating parameters (FR compounds, concentration and number of bilayers), polyamide fabrics could be self-extinguishing. Wash durability (up to five washing cycles) of FR LbL treatment could be achieved by low-temperature thermal curing [139].

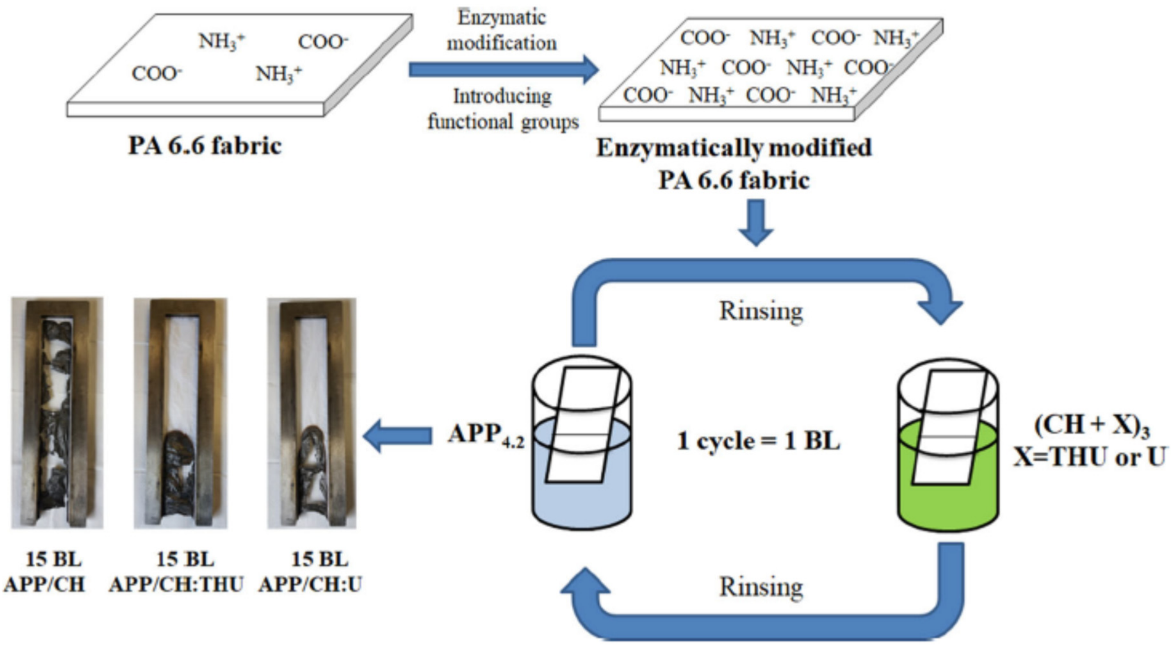


Figure 7. LbL deposition scheme of APP/CH+X on enzymatically modified PA6.6 fabric [138] Reproduced with permission from Jordanov, I.; Kolibaba, T.J.; Lazar, S.; Magovac, E.; Bischof, S.; Grunlan, J.C., J. Mater. Sci.; published by Springer Nature Switzerland AG., 2020.

Table 4. Polyelectrolytes used to achieve FR of polyamide fabric.

Pre-Treatment	Recipe	Number of Layers	Literature
	$PAH^+/PSP^-/PAH^+/TiO_2{}^-$	5, 10, 15 QLs	[125]
	PAH^+/MMT^-	5, 10, 20 BLs	[133]
	PAH^+/PSP^-	5, 10, 15, 40 BLs	[134]
	$CH^+/PA^-/CH^+/OSA^-$	5, 10, 15 QLs	[135]
	CH^+/PA^-	5, 10 BLs	[136]
	$CH^+/(PCH+PAS)^-$	1BL	[139]
1. Chemical grafting with PAA in solution of benzene and BPO 2. $PEI^+/PAACM^-$, dipping, drying	$(CH+ME+U)^+/PA^-$	2, 5 BLs	[137]
Enzymatic modification with protease from *Bacillus licheniformis*	APP^-/CH^+ $APP^-/(CH+THU)^+$ $APP^-/(CH+U)^+$	15, 30 BLs 10, 15 BLs 10, 15 BLs	[138]

4.5. Layer-by-Layer Deposition to Reduce Flammability of Cotton/Polyester and Cotton/Polyamide Blends

There are very few studies dealing with LbL deposition of cotton/polyester blends to obtain FR properties. Carosio et al. treated cotton/polyester fabrics with a quadlayer (QL) combination of PDAC/PAA/PDAC/APP. The resulting coating limited the flammability of the fabric by suppressing the afterglow and melt dripping, as well as lowering heat release during combustion (Section 4.1) [107]. Wattanatanom et al. studied the influence of polyelectrolyte concentration, as well as the number of layers, on the flammability of cotton/polyester blends. By using a cationic BPEI solution and a 5, 7 and 10 wt% anionic APP suspension, the flammability and anti-dripping properties of the fabric were reduced with three, five and seven BLs (Section 4.3). The study showed that the increase in the number of bilayers or the concentration of the solution improved the flame retardancy and anti-dripping of blends by decreasing the after-flame time of coated fabrics and self-extinguishing the flame [127]. Alongi et al. investigated whether different orders of layers with the same compounds and same concentration had any influence on the reduction in flammability and anti-dripping behavior of cotton/polyester blends. They used a 0.2 wt% cationic suspension of alumina-coated silica nanoparticles, 0.2 wt% cationic CH solution, 0.2 wt% anionic suspension of silica nanoparticles and 0.2 wt% anionic APP suspension to deposit 5 and 10 silica+/silica-/CH/APP QLs and 5 + 5 and 10 + 10 (CH/APP + silica$^+$/silica$^-$) BLs on fabric blends. The coated fabric did not pass VFTs, proving that only the thickness of the coating and weight gain had an influence on FR properties [141]. In 2012, Carosio et al. coated two blend fabrics, one with a 0.2 wt% cationic CH solution and a 0.2 wt% anionic APP suspension, depositing 5, 10 and 20 BLs, and a second fabric with a 0.2 wt% cationic suspension of alumina-coated silica nanoparticles with 0.2 wt% APP. Despite the fact that both FR coatings suppressed the afterglow phenomenon, leaving a remarkable residue after combustion, none of the fabrics passed VFTs [142]. In a previous study by Carosio et al. already mentioned in Section 4.1, the burning rate of cotton/polyester blends was successfully reduced in HFTs relative to untreated fabric by combining PDAC/PAA/PDAC/APP in 1, 5 and 10 QLs [107].

In 2016, Haile et al. compared the efficiency of two types of coating, LbL and "one pot" deposition, in extinguishing flames during VFTs, as well as the wash durability to home laundering of FR finishes. Blend fabrics were coated by means of LbL deposition with a 1 wt% cationic PAH solution and a 2 wt% anionic PSP suspension (20, 25 and 30 BLs) and by a "one pot" deposition of a water-soluble polyelectrolyte complex suspension (PEC) consisting of three different wt% concentrations (low, medium and high) of PAH and PSP. The LbL-coated fabric was dried at 70 °C, while "one pot" fabrics were dried and then immersed into a buffer solution consisting of citric acid and sodium citrate at pH 4 for 5 min, as shown in Figure 8. In the acidic environment, PAH and PSP formed an insoluble complex, durable up to five laundry cycles. VFTs showed that the highly concentrated "one pot"-coated cotton/polyester fabric with 17.9% weight gain was able self-extinguish, while the MCC data showed a reduction in pHRR of 78% and 31% for cotton and polyester, respectively. The coating process was reduced from more than 100 processing steps to only 5 [143].

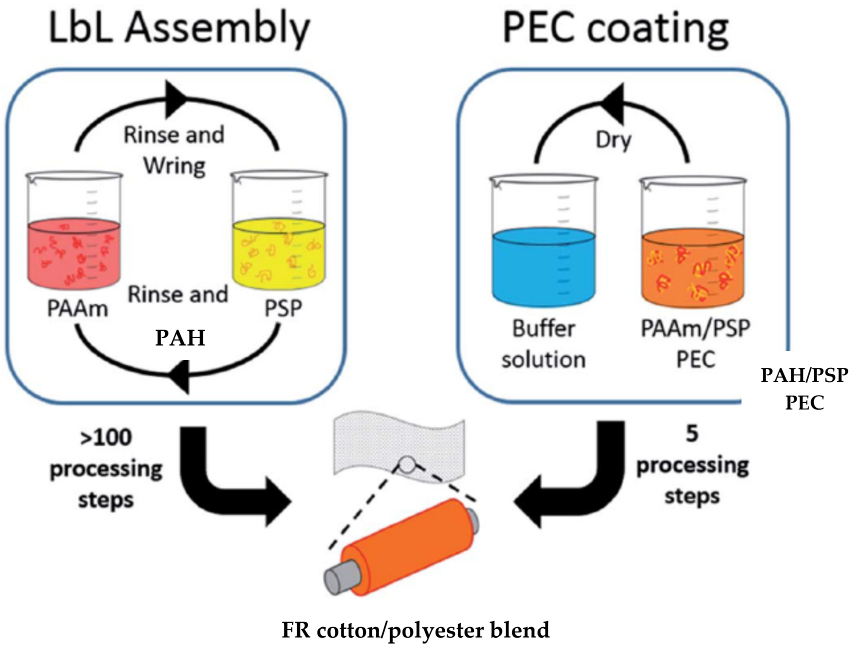


Figure 8. LbL and "one pot" deposition scheme of cotton/polyester fabric with PAH and PSP [143] Reproduced with permission from Haile, M.; Leistner, M.; Sarwar, O.; Toler, C.M.; Henderson, R.; Grunlan, J.C., RSC Adv.; published by Royal Society of Chemistry, 2016.

Leistner et al. investigated the influence of low-molecular-weight additives (e.g., melamine) into the cationic CH network for effective FR properties of cotton/polyester blends coated with a 1.4 w% cationic CH solution and a 2 wt% anionic PSP solution. In this study, the concentration of the cationic solution was held constant at 1.4 wt%, but the concentrations of single components in the cation solution (CH and ME) were different, as shown in Figure 9. The number of bilayers required for a 12.5 wt% coating was 8 BLs for 1.4 wt% CH and 15 BLs for 0.5 wt% and 0.9 wt% melamine, where the latter showed the best result in VFTs, with a char length of 4.5 in and char residue of 93% after performing a combustion calorimeter test [144].

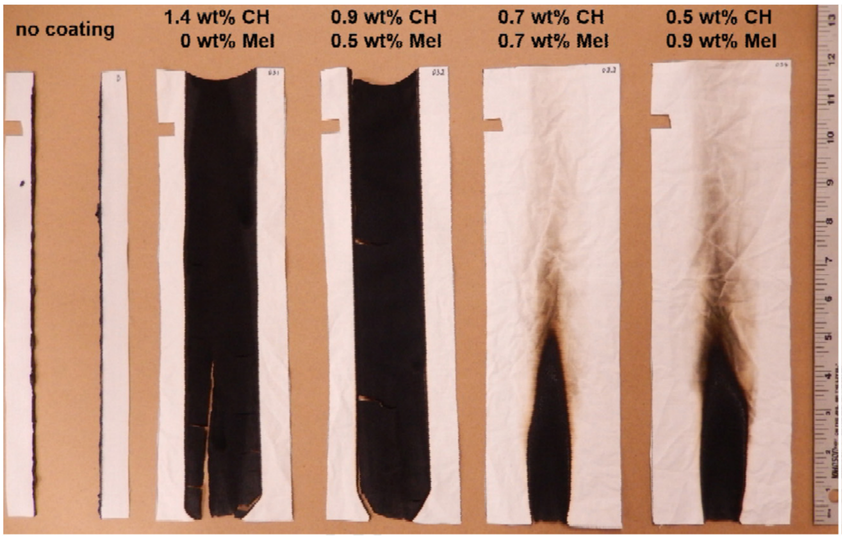


Figure 9. Results of VFT of CH/PSP coating on fabric with melamine addition [144] Reproduced with permission from Leistner, M.; Abu-Odeh, A.A.; Rohmer, S.C.; Grunlan, J.C., Carbohydr. Polym.; published by Elsevier Ltd., 2015.

Liu et al. also used ME as a low-molecular-weight additive in a cationic PAH solution. Cotton/polyester fabric was first pretreated with a 1 wt% anionic PAA solution for a better adhesion of LbL layers. The fabric was then immersed into a 1 wt% cationic PAH or PAH–ME solution and a 1 wt% anionic APP suspension, forming 10 BLs. Fabric treated with PAH–ME/APP self-extinguished, with a char length of 11.3 cm in VFTs and with an LOI value of 28.4%. The pHRR was reduced by 34.4%, with a 9 wt% coating [145]. The same group of authors pre-treated cotton/polyester fabric with 0.1 wt% anionic PAA and then immersed it into a 0.5 wt% cationic BPEI solution and a 1 wt% or 2 wt% anionic hypophosphorous acid-modified chitosan (PCH) solution, depositing 10 and 20 BLs. During HFTs, the flame was completely extinguished for the sample coated with 20 BLs of 2 wt% PCH [146]. By depositing alkali-hydrolyzed cotton/polyester blends with a 0.5 wt% cationic PEI solution and a 0.3 wt% anionic OSA solution, thus forming 5 and 10 BLs, and then soaking coated fabrics into a 10 wt% HA solution for cross-linking, it was possible to achieve self-extinguishing in HFTs with FR coating durable through 12 home laundry cycles [147]. Wang et al. combined a 1 wt% cationic γ-paperazinylproplymethyldimethoxy silane (GP-108) solution with a 1 wt% anionic APP solution to build up 5, 10 and 15 BLs. Fabric coated with 15 BLs achieved self-extinguishing in VFTs and showed a strong decrease in heat release during cone calorimetry tests [148].

The number of studies on LbL deposition to reduce the flammability of cotton/polyamide blends is very limited. Narkhede at al. first pre-treated these blends by immersing them into a pH 2 solution for cationization. The cationized fabric was then deposited with 5, 10, 15 and 20 BLs by dipping. For the anionic polyelectrolyte, a 2 wt% PSP solution was used and, for the polycationic, three different cationic polysiloxane compounds were used, namely, 6.8 wt% (trimethylammonium methyl phenythyl)-methyl siloxane and dimethyl siloxane copolymer chloride salt (QMS-435) solution, 4 wt% aminoethylaminopropyl silsesquioxane–methylsilsesquioxane copolymer oligomer (WSA-7021) solution and 4 wt% aminopropyl silesquioxane oligomers (WSA-9911) solution. Only fabrics coated with 20 BLs of WSA-7021 and WSA-9911 passed VFTs [149]. A summation of polyelectrolytes used to achieve FR of blend fabrics is provided in Table 5.

Table 5. Polyelectrolytes used to achieve FR of cotton/polyester and cotton/polyamide blends.

Pre-Treatments	Recipes	Number of Layers	Literature
Cotton/polyester			
	PDAC^{+}/PAA^{-}/PDAC^{+}/APP^{-}	1, 5, 10 QLs	[107]
	BPEI^{+}/APP^{-}	3, 5, 7 BLs	[127]
	alumina-coated silica nanoparticles^{+}/silica nanoparticles^{-}/CH^{+}/APP^{-} CH^{+}/APP^{-} +alumina-coated silica nanoparticles^{+}/silica nanoparticles^{-}	5, 10 QLs 5 + 5 BLs 10 + 10 BLs	[141]
	CH^{+}/APP^{-} alumina-coated silica nanoparticles^{+}/APP^{-}	5, 10, 20 BLs	[142]
	PAH^{+}/PSP^{-}	20, 25, 30 BLs	[143]
	CH^{+}/PSP^{-} (CH+ME)$^{+}$/PSP^{-}	8 BLs 10, 15 BLs	[144]
Primer layer PAA^{-}	PAH^{+}/APP^{-} (PAH+ME)$^{+}$/APP^{-}	10 BLs 10 BLs	[145]
Primer layer PAA^{-}	BPEI^{+}/PCH^{-}	10, 20 BLs	[146]
Alkali hydrolysis	OSA^{-}/PEI^{+}	5, 10 BLs	[147]
	GP-108^{+}/APP^{-}	5, 10, 15 BLs	[148]
Cotton/polyamide			
	PSP^{-}/QMS-435^{+} PSP^{-}/WSA-7021^{+} PSP^{-}/WSA-9911^{+}	5, 10, 15, 20 BLs	[149]

The reduced flammability of cotton blends can be easily achieved with a wide range of chemical compounds containing nitrogen, phosphorus, sulfur and inorganic compounds, as summarized in Table 5. As a pre-treatment, various primer layer chemicals have been used, such as BPEI or PAA, or the cotton blends have been treated with acid/alkali hydrolysis to achieve more functional groups on the fiber surface. By means of FR LbL deposition, the pHRR values were reduced by 78% and 31% for the cotton and polyester. Wash durability of FR LbL treated blends could be achieved by low-temperature thermal curing (up to 12 washing cycles) [147]. However, the role of each FR chemical compounds in LbL recipes and their mode of action on suppression of flames on cotton blends require further analyses, but the generally accepted opinion is that these compounds act as passive barriers and/or intumescent of known modes of actions.

5. Conclusions

LbL deposition has long been considered one of the green alternatives for current commercially available finishing technologies to impart flame retardancy to the most widely used fibers globally—cotton, polyester, polyamide and their blends. It is possible to use almost any compound consisting of nitrogen, phosphorus, sulfur, or metal in the form of small organic molecules (U, THU and MEL), synthetic long-chain macromolecules (APTES, PDAC, PAA, APP, BPEI, PAH, PSP and SSP), biomacromolecules (DNA, egg white protein, PA, CS, SA, CH and its derivates), or inorganic colloids, such as metal, metal oxides and clays. By means of FR LbL deposition, the pHRR values of cotton can be reduced up to 97%

and the THR values by 93% relative to untreated fabric, with minimal influence on break strength. With the same technique, the pHRR values of treated polyester can be reduced up to 65% and the THR values by 29% relative to untreated fabric. Additional benefits are the suppression of melt dripping and self-extinguishing behavior. Generally, LbL deposition does not degrade the strength of the polyester. Limited studies regarding LbL deposition of FR compounds on polyamide fabric showed the reduction in pHRR within the range 24–60%. The results of VFT and HFT showed improvements and a decrease in melt dripping. The pHRR values of cotton and polyester in blends were reduced by 78% and 31%, respectively. Comparable to commercially available and industrially feasible technologies of FR finishing, one of the advantages of the LbL technique is the use of deionized water as a solvent for a very low concentration of polyelectrolytes (up to 10 wt%).

Since the layers are bound by weak electrostatic and hydrogen bonds, sensitive to environmental conditions (pH, dipping time, electrolyte concentration and purity), flame-retardant (and multifunctional) LbL finishing is not durable to conventional laundering. This drawback can be partially eliminated by low-temperature thermal curing to form covalent bonds between layers. Technological drawbacks of LbL deposition are the use of high amounts of water as well as time to achieve the desired number of layers sufficient for effective reduction in flammability. In the case of using eco-friendly chemical compounds, such as DNA, PA, CH, or egg proteins, one should be aware of their high costs. LbL deposition of FR compounds onto the textile materials is a promising alternative to overcome the negative drawbacks of current commercially available technologies, via the elimination of free formaldehyde during the product life cycle or the use of eco-friendly chemicals from renewable sources.

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Abbreviations

AgNW	silver nanowires
AM	acrylamide
AMM	p—aminobenzene sulfonic acid modified melamine
AP	ammonium phytate
APP	ammonium polyphosphate
APTES	3-aminopropyl triethoxysilane
BA	boric acid
$BaCl_2$	barium chloride
BL	bilayer
BNNS	boron nitride nanosheets
BOD	biochemical oxygen demand
BPEI	branched polyethyleneimine
BPO	dibenzoyl peroxide
BTCA	butyl tetracarboxylic acid
$C_4H_6O_4Co{\cdot}4H_2O$	cobalt acetate tetrahydrate
$C_4H_6O_4Ni{\cdot}4H_2O$	nickel acetate tetrahydrate

CA	anionic caprolactam modified casein composite emulsion
CH	chitosan
CNT	carbon nanotubes
CO	carbon monoxide
CO_2	carbon dioxide
COD	chemical oxygen demand
CS	cationic starch
DI	deionized water
DMT	dimethyl terephthalate
DNA	deoxyribonucleic acid
FR	flame retardant
F-SiO_2	fluorinated silica
GNP	graphene nanoplatelets
GO	graphene oxide
GP-108	γ-paperazinylproplymethyldimethoxy silane
GSM	guanidine sulfamate
HA	hypophosphorus acid
HACH	hypophosphorous acid-modified chitosan
HBr	hydrogen bromide
HCl	hydrogen chloride
HCN	hydrogen cyanide
HF	hydrogen fluoride
HFT	horizontal flammability test
HT	hydrotalcite
IPA	isopropanol
LbL	layer-by-layer
LOI	limiting oxygen index
Ludox CL	alumina coated silica
Ludox SM30	silica
MCC	microscale combustion calorimeter
ME	melamine
MMT	sodium montmorillonite
MTES	methyltriethoxysilane
$NaBH_4$	sodium borohydride
NaCl	sodium chloride
NaClO	sodium hypochlorite
NH_3	ammonia
N-MDMPA	N-methylol dimethylphosphonopropionamide
NO_x	nitrogen oxide
OAPOSS	octapropylammonium polyhedral oligomeric silsesquioxane
OSA	oxide sodium alginate
PA	phytic acid
PAA	poly (acrylic acid)
PAACM	polyacrylic acid-co-maleic acid solution
PAH	poly (allylamine hydrochloride)
PAS	polyacrylate sodium
PCH	phosphorylated chitosan
PCQS	poly[3-(5,5-cyanuricacidpropyl)- siloxane-co-trimethylammoniumpropylsiloxane chloride]
PDAC	poly (diallyl dimethylammonium chloride)
PDDA	poly dimethyl diallyl ammonium chloride
PDMS	polydimethylsiloxane
PDMSOH	hydroxy-terminated polydimethylsilo
PEC	stable soluble polyelectrolyte complex (PSP and PAH)
PEI	polyethyleneimine

pHRR	peak heat release rate
POSS$^{\circledR}$	polyhedral oligomeric silsesquioxane cage molecule carrying eight n-propylammonium chloride groups
PPA	polyphosphoric acid
PSP	sodium polyphosphate
PSS	poly (4-styrenesulfonic acid);
PVA	polyvinyl alcohol
PVAm	polyvinyl amine
QL	quadlayer
QMS-435	(trimethylammonium methyl phenylethyl)-methyl siloxane and dimethyl siloxane copolymer chloride salt
SA	sodium alginate
SHP	Sodium Hypophosphite
SiO_2	alumina-coated silica nanoparticles
SLS	sodium lignin sulphonate
SMF	sulfonated melamine-formaldehyde
SSP	flexible polysiloxane prepared by sol-gel from methyltriethoxysilane (MTES), isopropanol (IPA) and hydroxy-terminated polydimethylsiloxane (PDMSOH)
TA	therephthalic acid
T_g	glass transition temperature
THAM	tris(hydroxymethyl)aminomethane
THPX	tetrakis(hydroxymethyl) phosphonium salt
THR	total heat release rate
THU	thiourea
TiO_2	titanium dioxide
TL	trilayer
T_p	melting point
T_p	thermal decomposition
U	urea
VFT	vertical flammability test
WSA-7021	aminoethylaminopropyl silsesquioxane–methylsilsesquioxane copolymer oligomer
WSA-9911	aminopropyl silesquioxane oligomers
ZrP	α-zirconium phosphate

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Article

Environmentally Benign Phytic Acid-Based Nanocoating for Multifunctional Flame-Retardant/Antibacterial Cotton

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Abstract: Environmentally benign layer-by-layer (LbL) deposition was used to obtain flame-retardant and antimicrobial cotton. Cotton was coated with 8, 10, and 12 phytic acid (PA) and chitosan (CH)-urea bilayers (BL) and then immersed into copper (II) sulfate ($CuSO_4$) solution. Our findings were that 12 BL of PA/CH-urea + Cu^{2+} were able to stop flame on cotton during vertical flammability testing (VFT) with a limiting oxygen index (LOI) value of 26%. Microscale combustion calorimeter (MCC) data showed a reduction of peak heat release rates (pHRR) of more than 61%, while the reduction of total heat release (THR) was more than 54%, relative to untreated cotton. TG-IR analysis of 12 BL-treated cotton showed the release of water, methane, carbon dioxide, carbon monoxide, and aldehydes, while by adding Cu^{2+} ions, the treated cotton produces a lower amount of methane. Treated cotton also showed no levoglucosan. The intumescent behavior of the treatment was indicated by the bubbled structure of the post-burn char. Antibacterial testing showed a 100% reduction of *Klebsiella pneumoniae* and *Staphylococcus aureus*. In this study, cotton was successfully functionalized with a multifunctional ecologically benign flame-retardant and antibacterial nanocoating, by means of LbL deposition.

Keywords: cotton; antimicrobial; flame-retardancy; chitosan; phytic acid; copper (II) sulfate

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1. Introduction

Cotton is one of the most frequently used textile materials for a variety of products, such as medical textiles, underwear, sportswear, fashion garments, footwear, safety clothes, etc. [1]. The reason why cotton is such a favorite material is its softness and water uptake, enabled by highly hydrophilic and reactive hydroxyl groups in the molecule of cellulose. The reactivity of these groups, however, makes cotton fabric very flammable and prone to microbial growth [2]. These properties are undesirable, especially for textiles used for protective clothing. Commercially available compounds to reduce the flammability of cotton and cotton-based materials are halogen, organo-halogen, antimony organo-halogen, and organophosphorus [3]. Halogens, as well as antimony compounds, are known to be toxic to the environment as well as humans, and the inhalation of the volatile gases generated in a fire can be fatal. Organophosphorus flame retardants (FRs) have been considered safe for many years [4]. To stop or at least reduce bacterial growth, cotton is treated with different antibacterial compounds, such as chitosan, citric acid, metal particles and metal salts, phenyl derivates, quaternary ammonium compounds, triclocarban and triclosan. However, phenyl derivates, triclocarban and triclosan are toxic [5]. Durable FR, as well as antibacterial finishes for cotton, are commercially applied by a pad-dry-cure process. The process is not ecological due to the release of toxic formaldehyde derivatives during production and usage [6,7]. The greener, formaldehyde-free alternatives for curing FRs and antibacterial finishes on cellulosic fabrics are polycarboxylic acid-based curing agents [8,9]. Another environmentally friendly approach could be layer-by-layer (LbL) deposition, which uses deionized water as a solvent for various active compounds (polymers, nanoparticles, small molecules, etc.) and is applicable to nearly any charged surface, such as textiles [10,11]. In LbL deposition, the charged fabric is immersed into oppositely charged polyelectrolyte solutions to deposit a layered nanocoating in the form of layers [12]. The process can be repeated as many times as necessary to obtain textiles with desirable properties such as flame retardancy [13] and antimicrobial action [14], or even multifunctional properties such as flame retardancy and antimicrobial action [15], hydrophobicity–flame retardancy–conductivity [16], and hydrophobicity–flame retardancy, etc. [17]. In a previous study, cotton was successfully deposited with anionic PA solution and cationic CH-urea solution by means of the LbL technique, forming 8, 10, 12, and 15 BL with effective FR properties that are comparable to commercial FR finishes of cotton [18]. In the second study, cotton was successfully LbL-deposited with anionic PA and cationic CH (with the addition of $CuSO_4$) to build an effective antibacterial 2- and 4-BL assembly that was able to eliminate 100% of Gram-negative *Klebsiella pneumoniae* and Gram-positive *Staphylococcus aureus* [19].

In the present study, 8, 10, and 12 BL of PA and CH-urea were deposited on cotton and the LbL-treated samples were then immersed in a 2% Cu^{2+} solution. The resulting cotton fabric was successfully functionalized with multifunctional ecologically benign flame-retardant and antibacterial nanocoating by means of LbL deposition. In the tests, 12 BL were sufficient for the self-extinguishing of cotton and to kill almost 100% of the bacteria.

2. Materials and Methods

USDA Southern Regional Research Center (New Orleans, LA, USA) supplied the chemically bleached cotton fabric (119 g/m^2). Sigma Aldrich (Milwaukee, WI, USA) supplied the branched polyethyleneimine (BPEI, M = 25,000 g/mol, ≤ 1% water), urea, chitosan (CH) powder (M ~ 190,000–310,000 g/mol, 75–85% deacetylated), copper (II) sulfate pentahydrate ($CuSO_4 \times 5H_2O$), hydrochloric acid (HCl) and sodium hydroxide (NaOH). Biosynth Carbosynth Ltd. (Compton, UK) supplied the phytic acid dodecasodium salt hydrate (PA, M ~ 923.82 g/mol, purity ≥ 75%). For the preparation of all polyelectrolyte solutions, as well as for the rinsing of fabrics, deionized (DI) water (18.2 mW) was used. A cationic BPEI solution (5 wt %) was prepared for prime layering of the cotton. An anionic PA solution (2 wt %) and a cationic CH solution (0.5 wt %) were magnetically stirred for 24 h. Urea (10 wt %) was added to the CH solution after 24 h. Cu^{2+} solution (2 wt %) was prepared by adding $CuSO_4 \times 5H_2O$ into DI. Prior to the LbL deposition, the pH of all solutions (except BPEI) was adjusted to 4, with 1 M NaOH or 1 M HCl. Six cotton samples were first immersed into the BPEI solution and then alternately immersed into the PA/CH-urea solutions, depositing 8, 10, and 12 BL. At the end of the process, the samples were immersed in 2% Cu^{2+} solution to achieve antibacterial properties. The whole process is shown in Figure 1.

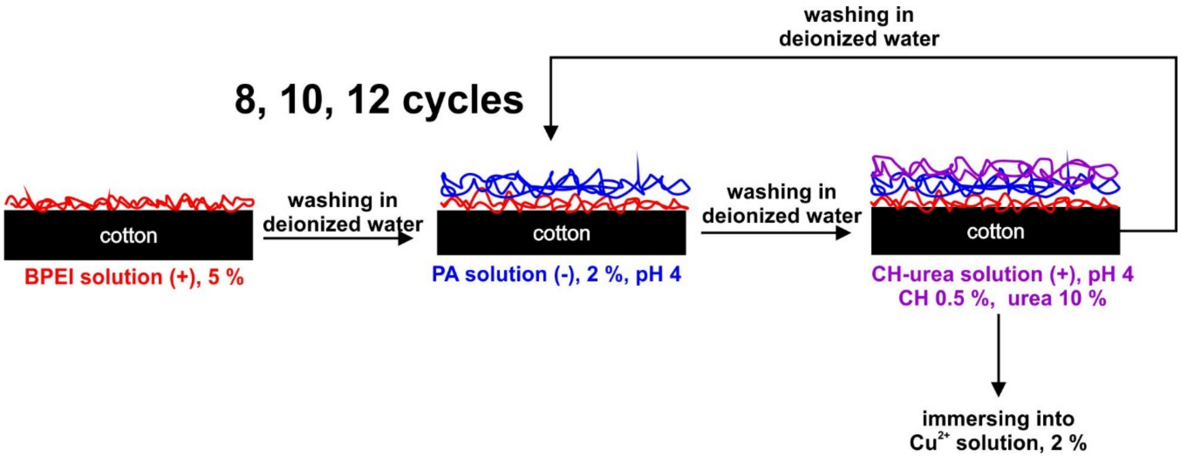


Figure 1. The LbL deposition process of FR/antimicrobial nanocoating on cotton.

The immersion time was 5 min for the first layer (BPEI/PA/CH) and 1 min for each additional layer (PA/CH). Between each immersion step into the polyelectrolyte solution, the fabric was rinsed in DI water. The samples were dried at 80 °C for 24 h at the end of the LbL deposition.

The weight gains (%) of samples were calculated according to the following equation:

$$\text{weight gain (\%)} = [\text{m (treated)} - \text{m (untreated)}]/\text{m (untreated)} \times 100 \quad (1)$$

Limiting oxygen index (LOI) measurements were performed according to ISO 4589-2:2017 with a Concept Equipment Oxygen Index Module (Poling, UK) [20]. Vertical flame testing (VFT) was carried out according to ASTM D6413/D6413M-15 [21].

Measurements of heat release were performed by means of a Govmark MCC-2 (Heilbronn, Germany) according to ASTM D7309–21a, Method A [22]. The samples were heated from 75 °C to 650 °C with a heating rate of 1 C°/min (flow rate: 100 mL/min). Three replicate samples were measured for the calculation of standard deviations.

Thermogravimetric analysis (TGA) was carried out with a PerkinElmer Pyris 1 (Shelton, CT, USA). All samples were heated from 50 to 850 °C, with a heating rate of 30 C°/min in air (flow rate: 30 mL/min). The TG data were analyzed via Pyris 1 software.

Evolved gas analysis was performed via a PerkinElmer Spectrum 100 FT-IR spectrometer with TL 8000 TG-IR interface (Shelton, CT, USA) in absorbance, wavelength range 4000–450 cm^{-1}, resolution 4.0 cm^{-1}, and with a 27-minute heating interval. The spectra were normalized and analyzed via the KnowItAll Informatics System 2020, IR spectroscopy edition (John Wiley & Sons, Ltd., Hoboken, NJ, USA) and available literature.

The morphology of the samples, before and after performing VFT, was analyzed with a Tescan MIRA LMU FE-SEM (SE detector, 5 kV, Brno, Czech Republic). All samples were coated with 5 nm of chromium (Q150T ES Sputter Coater, Quorum Technologies, Laughton, UK), with the exception of the char.

The chemical analysis of post-burn char was studied using a Tescan Mira LMU FE-SEM (backscattered electron BSE detector, 10 and 20 kV) equipped with an energy-dispersive X-ray spectroscopy (EDS) detector (Oxford Instruments, Oxford, UK).

Antimicrobial testing was performed according to AATCC Test Method 100-2019 against Gram-negative *Klebsiella pneumoniae* and Gram-positive *Staphylococcus aureus* [23]. The percentage of reduction of the bacteria was calculated according to the following equation:

$$\text{R (\%)} = (\text{C} - \text{A})/\text{C} \times 100 \quad (2)$$

where R (%) is reduction, C is the number of bacteria recovered from the inoculated untreated control specimen swatches in the jar at “zero” contact time, and A is the number of bacteria recovered from the inoculated treated test specimen swatches in the jar, incubated over the contact period of 24 h.

3. Results and Discussion

As presented in Table 1, cotton samples were coated with 8, 10, and 12 BL of PA/CH-urea. The weight gain increases linearly with the number of bilayers. Limiting oxygen index (LOI) values also follow linear growth. The resulting weight gains are consistent with the weight gains obtained in a previous study following linear growth from 12% (8 BL) to 18% (12 BL) [18]. The LOI value of untreated cotton is 18, whereas the values of treated cotton increase from 21.5% (8 BL) to 24.5% (12 BL). Compared with the findings of the previous study, the results of the LOI values are lower by approx. 4.3% [18]. The samples that were immersed in Cu^{2+} solution at the end of LbL deposition show a slight increase of LOI values (from 23.5% for 8 BL to 26.0% for 12 BL). The commercial requirements of LOI for durable FR cotton are 28% or above [24].

Table 1. Weight gain and LOI values of cotton coated with CH-urea/PA, with and without $CuSO_4$.

Batch	Number of BLs	Weight Gain (%)	LOI (%)
Control	n/a	n/a	18.0
PA/CH-urea	8	12.34	21.5
	10	17.58	24.0
	12	18.54	24.5
PA/CH-urea + Cu^{2+}	8	12.96	23.5
	10	18.05	25.5
	12	18.97	26.0

The results of the vertical flame test (VFT) show that only cotton treated with 12 BL passed the test, with a char length of 6.7 cm for cotton treated with PA/CH-urea and 6.5 cm for 12 BL cotton immersed in Cu^{2+} solution, as shown in Table 2. The results of VFT correlate with measured LOI values.

Table 2. The results of the VFT of cotton coated with different recipes.

	Control	PA/CH-Urea			PA/CH-Urea + Cu^{2+}		
Number of BL	n/a	8	10	12	8	10	12
Image							
Char length (cm)	n/a	n/a	n/a	6.7	n/a	n/a	6.5
After flame time (s)	n/a	n/a	n/a	0	n/a	n/a	0
After glow time (s)	n/a	n/a	n/a	0	n/a	n/a	0

Figures 2 and S1 show microscale combustion calorimeter (MCC) values, such as heat release rates (pHRR), as a function of temperature (T_{pHRR}) for untreated and differently treated cotton. The results of MCC measurements are summarized in Table 3. Parameters responsible for the MCC data are heating rate, chamber atmosphere, inhomogeneity of the sample as well as sample preparation [25]. There are three major groups of curves for: untreated (control) cotton, cotton treated with 8 BL (PA/CH-urea, PA/CH-urea + Cu^{2+}), and cotton treated with 10 and 12 BL (PA/CH-urea, PA/CH-urea + Cu^{2+}). According to Figure 2 and Table 3, the pHRR of untreated cotton is 269.4 W/g, while the total heat release rate (THR) is 11.6 kJ/g at 395 °C. In the present study, 8 BL cotton shows a reduction of peak release rate (ΔHRR) of more than 49%, while a reduction of total heat release rates (ΔTHR) is more than 30%. In the previous study, the ΔHRR values for 8, 10 and 12 BL were reduced by more than 57%, whereas the ΔTHR values were reduced by more than 67% [18]. By immersing 8 BL samples into Cu^{2+} solution, the ΔHRR is reduced by more than 59% (Figure S1 and Table 3). By adding more bilayers of the PA/CH-urea + Cu^{2+} system, from 10 to 12, the pHRR slightly decreases from 110.1 to 103.0 W/g, but there is no actual difference in the pHRR and THR values between 10 and 12 BL, with and without added Cu^{2+} ions. By adding Cu^{2+} ions, the pHRR values, as well as $T_{pHRR,}$ decrease for all treated samples, as shown in Table 3. The resulting MCC values correspond to LOI values in Table 1 and the VFT results in Table 2.

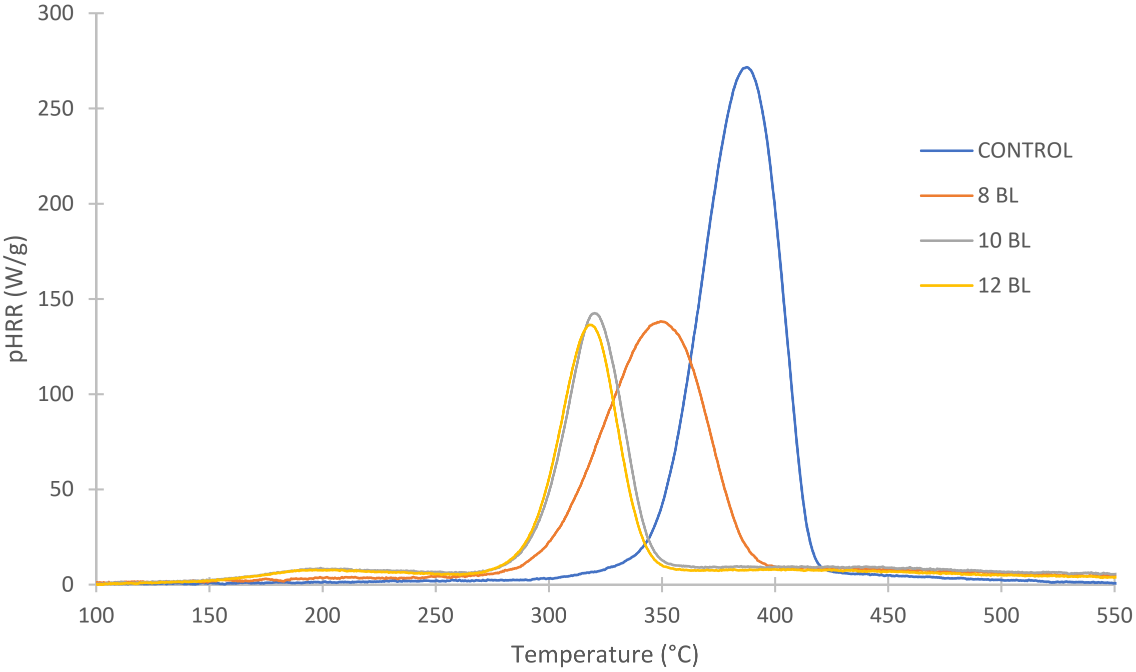


Figure 2. MCC curves for untreated cotton (control) and cotton coated with 8, 10 and 12 BL of PA/CH-urea.

Table 3. MCC data of cotton coated with different recipes (with standard deviations).

Sample	pHRR (W/g)	ΔHRR (%)	THR (kJ/g)	ΔTHR (%)	T_{pHRR} (°C)
control	269.4 ± 4.8	0.0	11.6 ± 0.9	0.0	395 ± 1.4
8 BL	133.2 ± 5.7	50.6	7.7 ± 0.8	33.6	360 ± 2.4
10 BL	136.7 ± 5.5	49.3	5.0 ± 0.6	56.9	322 ± 2.7
12 BL	132.2 ± 6.4	50.9	5.0 ± 1.1	56.9	318 ± 3.0
8 BL Cu	110.1 ± 6.1	59.1	7.9 ± 1.0	31.9	320 ± 2.9
10 BL Cu	108.8 ± 4.2	59.6	5.1 ± 0.7	56.0	310 ± 1.8
12 BL Cu	103.0 ± 4.1	61.8	5.3 ± 0.6	54.3	311 ± 1.7

Figure 3 represents the weight loss of untreated and PA/CH-urea-treated cotton samples as a function of temperature, while Table 4 summarizes the weight (%) of samples at the first decomposition (T_1) and the second decomposition temperature peak (T_2). As seen in Figure 3, between 50 °C and 100 °C, the evaporation of moisture of all samples occurs. The dehydration and depolymerization of cellulose molecules occur between 250 °C and 400 °C. At the end of this stage (at 420 °C), cotton loses almost 95% of its weight by generating non-flammable gases, such as CO_2 and CO, primary char residue, and the highly flammable levoglucosan [26]. The maximum peak temperature of the first stage of untreated cotton occurs at 396 °C, as shown in Table 4.

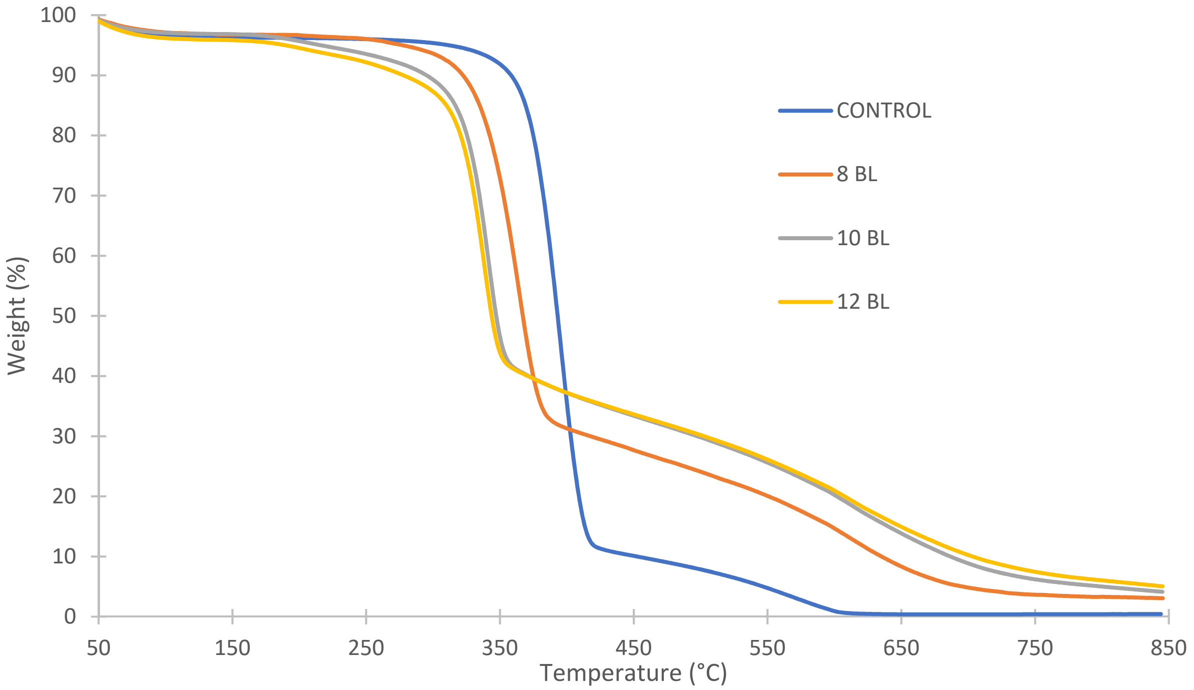


Figure 3. TGA curves for untreated (control) and 8, 10, 12 BL PA/CH-urea-treated samples.

Table 4. Summary of thermogravimetric analysis of untreated and LbL-treated cotton.

Sample	Onset 1 (°C)	T_1 (°C)	Time (s)	Weight at T_1 (%)	End 1 (°C)	Onset 2 (°C)	T_2 (°C)	Time (s)	End 2 (°C)	Weight at 650 °C (%)
control	360	396	727	43.6	420	496	578	1027	607	0.4
8 BL	324	364	646	54.4	388	604	623	1158	813	8.3
10 BL	316	342	602	58.7	357	527	640	1142	745	13.8
12 BL	312	339	609	57.8	354	512	636	1161	711	14.9
8 BL + Cu	258	334	588	54.9	376	488	578	1066	648	3.3
10 BL + Cu	267	328	576	58.5	350	502	634	1182	705	14.8
12 BL + Cu	261	330	597	56.2	354	464	636	1130	700	13.3

All treated cotton samples show a shift to lower T_1 by more than 32 °C due to the addition of the FR agent. At the second decomposition stage (between 500 °C and 650 °C and with its maximum at T_2), levoglucosan decomposes, generating highly flammable gases and secondary char [26]. As shown in Table 4, the highest rate of weight loss of untreated cotton (56%) appears at 396 °C, while at 650 °C it loses over 99% of its mass. The TG curves of 10 BL and 12 BL are almost identical, showing the first decomposition temperature peak (T_1) at around 340 °C and weight loss of around 42%. At 650 °C, both samples lost around 86% of their mass. According to Figure 3, the 8 BL sample lost 46%

of its weight at 364 °C, and around 92% at 650 °C. Compared with the previous study, the T_1 and T_2 values of 8, 10 and 12 BL samples are higher, and the char yield at T_1 is lower, while the values of char yield at 650 °C differ slightly [18]. The TG curves of 10 and 12 BL samples correspond to the LOI values of 24.0% and 24.5%, whereas only the 12 BL samples passed VFT (Figure 3, Tables 1 and 2). The differences in flammability (VFT, LOI) and thermal stability (MCC, TG) between the 8, 10 and 12 BL samples of PA/CH-urea in this study and the previous study [18] come from the slightly different chemicals used in the experiment, basically the MW of CH and the purity of PA.

Figure 4 shows the weight loss of untreated and PA/CH-urea + Cu^{2+}-treated cotton samples as a function of temperature, while Table 4 summarizes the weight (%) of samples at the characteristic first decomposition (T_1), as well as at the second decomposition temperature peak (T_2). Cotton samples treated with 8, 10, 12 BL of PA/CH-urea + Cu^{2+} exhibit a shift to lower first-stage decomposition temperatures by more than 62 °C, in comparison to untreated samples. The TG curves of 10 BL and 12 BL are almost identical, showing the first decomposition temperature peak (T_1) at around 329 °C and a weight loss of around 43%. At 650 °C, both samples lost around 86% of their mass, as shown in Table 4. The TG curves of 10 and 12 BL correspond to the LOI values of 25.5% and 26.0%, where only 12 BL passed the VFT (Figure 5, Tables 1 and 2). According to Table 4, the 8 BL samples lost 45% of weight at 334 °C and around 96.7% at 650 °C.

As shown in Table 4, by immersing treated cotton samples into 2% Cu^{2+} solution at the end of LbL deposition, the first decomposition stage exhibits a shift to lower temperatures for 30 °C for 8 BL, 14 °C for 10 BL, and 9 °C for 12 BL. The TG curves of 10 BL and 12 BL show almost identical behavior at the second decomposition stage, as shown in Figure 4. These curves correspond to the pHRR and T_{pHRR} values obtained by MCC, which show a strong reduction of MCC values by adding Cu^{2+} ions into the LbL system of PA/CH-urea, as seen in Table 3.

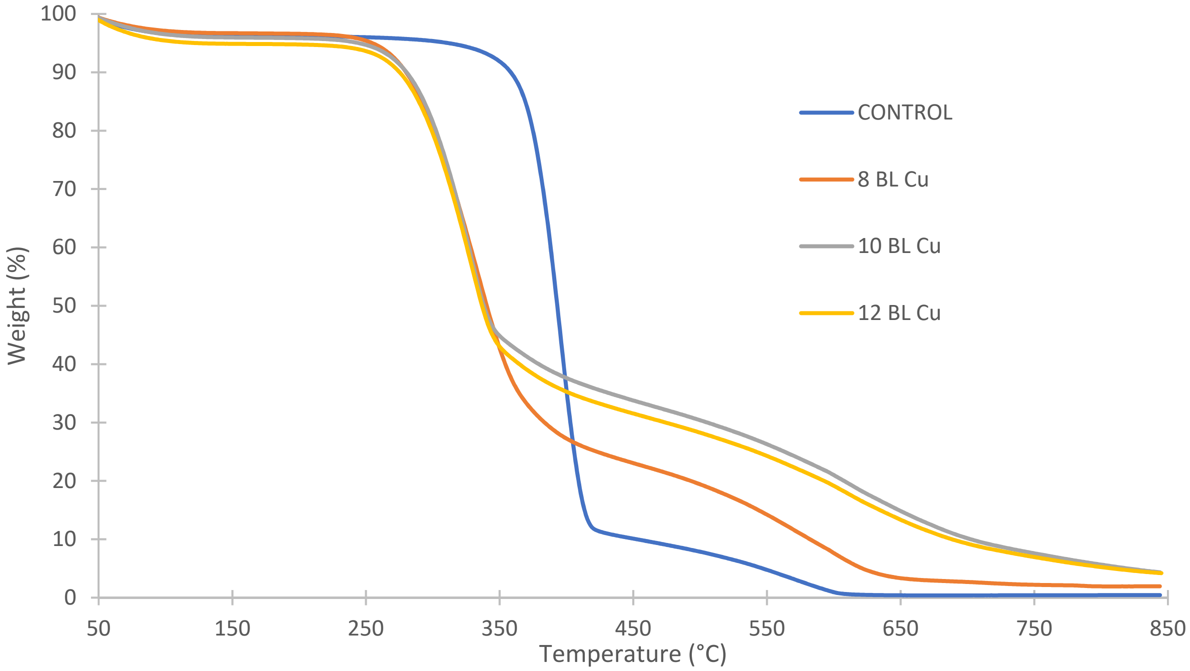


Figure 4. TGA curves for untreated (control) and 8, 10, 12 PA/CH-urea + Cu^{2+}-treated samples.

Only gas IR spectra of untreated and treated cotton samples (12 BL with and without added Cu^{2+}) were analyzed due to the strongest intensity profile of gaseous products generated during heating from 50 °C to 850 °C. The profile was taken at two measuring temperature/time points, where the derivative weight curves show the maximum temperature peaks at the first and second decomposition stages (T_1 and T_2), as presented in Table 4.

As seen from Figure 5, the first group of characteristic peaks of IR spectra of all untreated samples lies between 3800 cm^{-1} and 3500 cm^{-1}, which matches the medium stretching vibrations of O-H bonds in a molecule of water [27]. The second group of characteristic peaks lies between 3000 cm^{-1} and 2750 cm^{-1}, which is the C-H stretching of methane [28]. Untreated cotton produces more methane while heating relative to treated cotton. The third group of characteristic peaks lies between 2450 cm^{-1} and 2300 cm^{-1}, which belongs to the strong antisymmetric stretching and rotational bands from the R branch of the C=O bonds in carbon dioxide [29]. Double peaks at 2172 cm^{-1} and 2112 cm^{-1} represent the stretching vibrations of C=O molecules of carbon monoxide [28]. A peak at 1744 cm^{-1} matches the C=O stretching vibration of aldehyde (formaldehyde, acetaldehyde, acrolein). Treated cotton immersed in Cu^{2+} solution produces less aldehyde during heating, relative to untreated cotton and cotton treated only with PA/CH-urea. Cotton treated only with PA/CH-urea also shows a peak at 1410 cm^{-1} that matches that of propylene. At 1062 cm^{-1}, there is a very sharp peak of untreated cotton that can be assigned to levoglucosan, which is the compound responsible for the high flammability of cellulose. Cotton treated only with PA/CH-urea shows two peaks at 742 cm^{-1} and 702 cm^{-1}, probably belonging to the wagging of NH bonds [30]. Untreated and treated cotton show a very sharp peak (668 cm^{-1}) of weak bending vibrations from the Q branch of the C=O bonds from carbon dioxide [29]. Other phosphorus or nitrogen compounds may exist, but their spectra are overlapped by water and carbon dioxide [31].

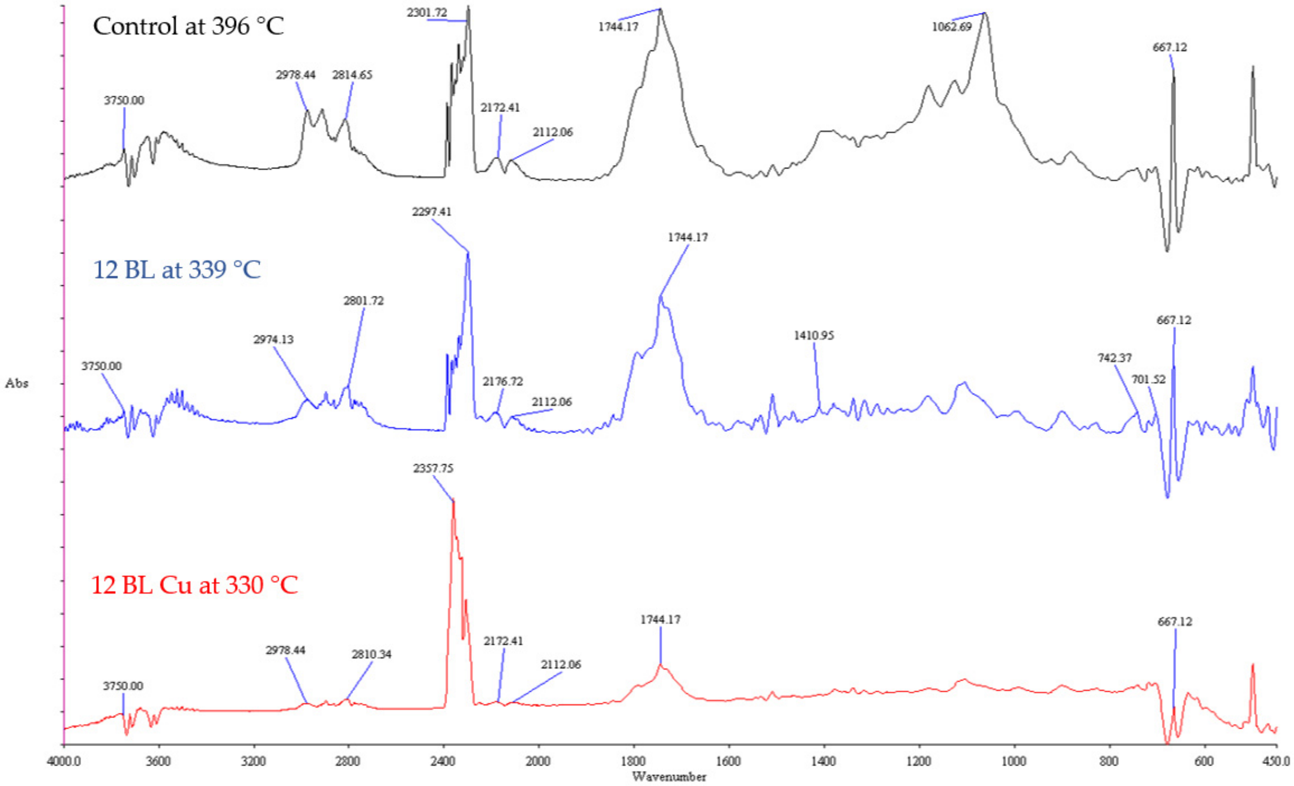


Figure 5. IR spectra of untreated and 12 BL-treated cotton at the first decomposition stage (T_1).

Figure 6 shows the IR spectra of gas products of untreated and treated at the second decomposition stage consisting of water (wavelength range from 3800 cm^{-1} to 3500 cm^{-1}), carbon dioxide (wavelength range from 2450 cm^{-1} to 2300 cm^{-1}, and a sharp peak at around 668 cm^{-1}), carbon monoxide (peaks at 2181 cm^{-1} and 2107 cm^{-1}), and levoglucosan for untreated cotton (1062 cm^{-1}) [27–29]. At the second decomposition stage, treated cotton shows no levoglucosan, which means that even a small fraction of FR compounds decreases the amount of levoglucosan responsible for the high flammability of cellulose, thus producing more post-burn char. Although the T$_2$ of the second decomposition stage of untreated cotton is lower by more than 58 °C than the treated ones, due to the small amount of levoglucosan more flammable gases are generated during its thermal decomposition, making the untreated cotton more flammable than the treated cotton. The FR compounds have little effect on the amount of water, carbon dioxide and carbon monoxide [32].

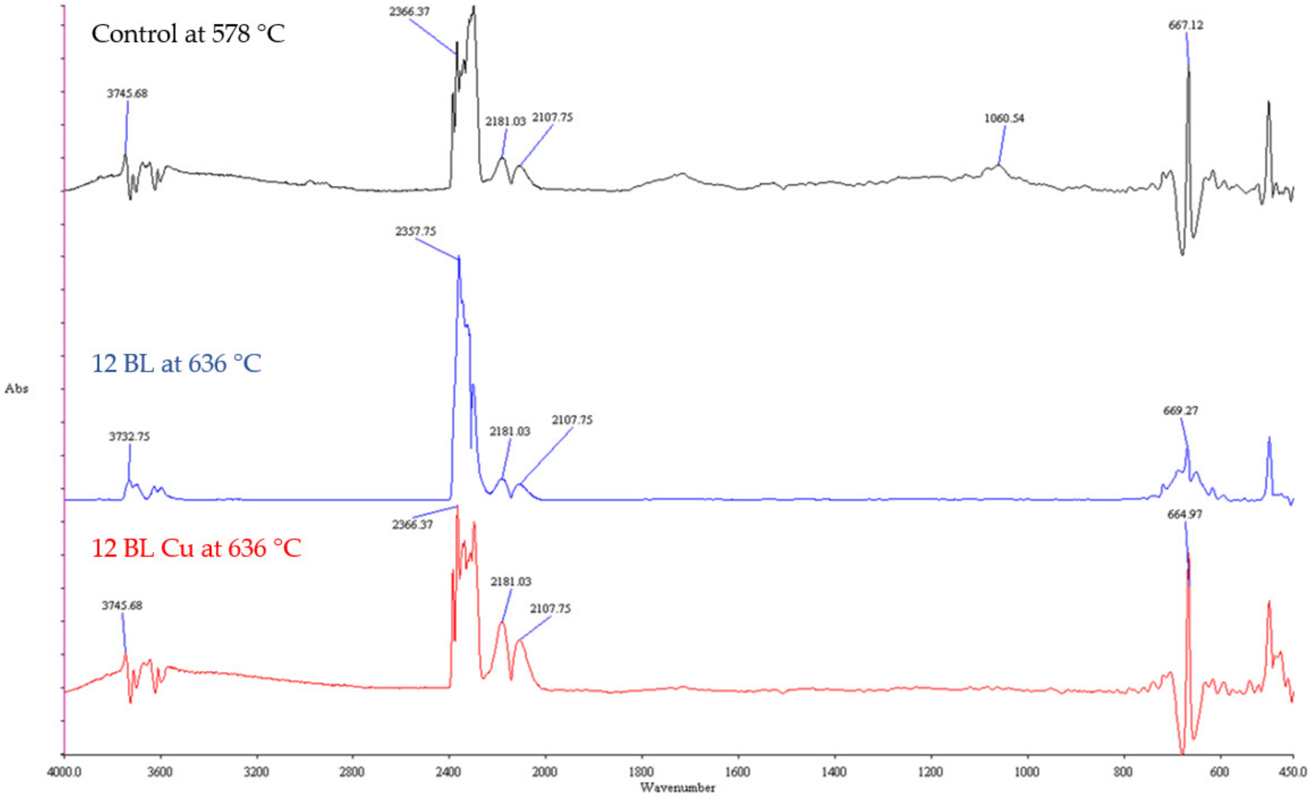
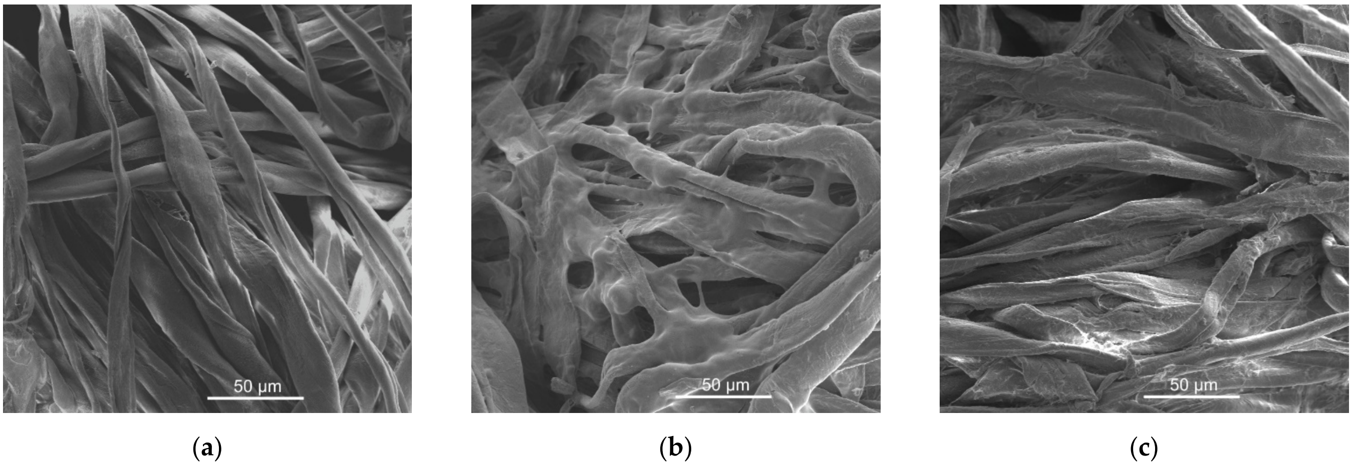


Figure 6. IR spectra of untreated and 12 BL-treated cotton at the second decomposition stage (T$_2$).

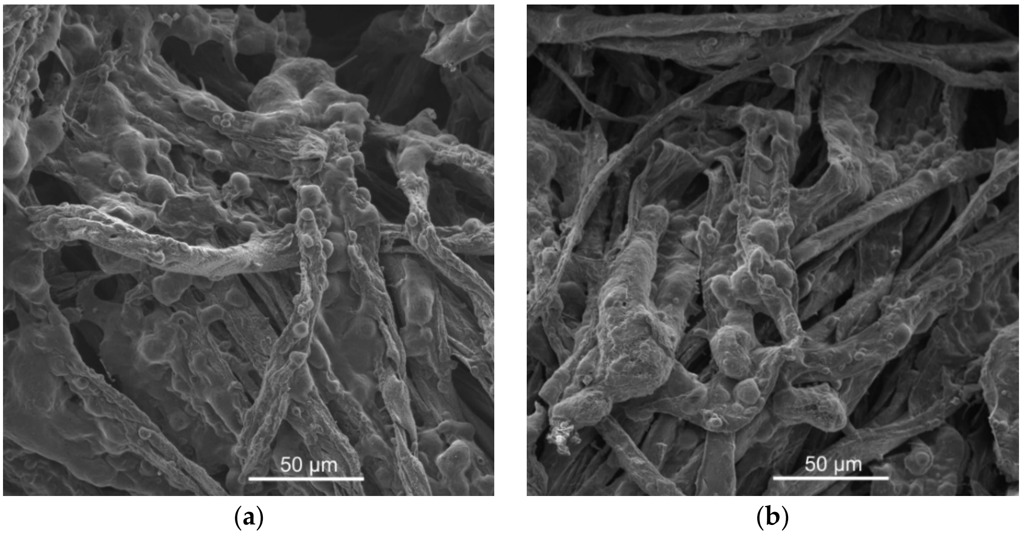
Figure 7 shows the SEM images of treated and untreated cotton. The surface of untreated cotton is smooth (Figure 7a), while treated samples have a rough, uneven, and paste-like structure (Figure 7b–c). There is also a very slight difference between PA/CH-urea- (Figure 7b) and PA/CH-urea + Cu^{2+} (Figure 7c)-treated samples. It seems that adding Cu^{2+} salts as a very top layer will peel off the upper PA/CH-urea layer, thus making the surface of the fibers more fibril-like. This structure corresponds to the thermal degradation of the FR properties of PA/CH-urea + Cu^{2+}-treated cotton by decreasing the char length after VFT, as well as by increasing the LOI values accordingly (Tables 1 and 2). This difference is more obvious when comparing the pHRR and T$_{pHRR}$ values obtained by MCC (Table 3) and the TG values of PA/CH-urea and PA/CH-urea + Cu^{2+} (Table 4).



(**a**) (**b**) (**c**)

Figure 7. SEM images of cotton: (**a**) untreated; (**b**) 8 BL; (**c**) 8 BL + Cu.

All the post-burn charred LbL samples shown in Figure 8 demonstrate a bubbled structure, one that is typical for intumescent flame-retardant systems with phytic acid acting as an acid donor, chitosan as a carbon donor, and urea as a blowing agent generating non-flammable gases. Cu^{2+} metal ions act as a shield that is capable of preventing heat from going into the fiber [33,34]. There is no difference between the post-burnt char of a sample treated with PA/CH-urea and PA/CH-urea + Cu^{2+} ions.



(**a**) (**b**)

Figure 8. SEM images of post-burn char: (**a**) 8 BL; (**b**) 8 BL + Cu.

To semi-quantify the amounts of phosphorus, nitrogen and copper, EDS measurements at 4 different points for each post-burn char of the treated cotton samples were performed and the average values of wt % for phosphorus, nitrogen and copper for each sample were calculated; the results are summarized in Table 5. The post-burn char mainly contains carbon, oxygen, phosphorus, and copper (for PA/CH-urea + Cu^{2+}-treated samples), along with impurities such as aluminum, iron, magnesium, calcium, sulfur, and potassium (derived from the technical-grade sodium phytate). These results suggest that the deposition of PA/CH-urea and PA/CH-urea + Cu^{2+} was successful.

Table 5. Quantity of phosphorus, nitrogen, and copper in post-burn for PA/CH-urea and PA/CH-urea + Cu^{2+} coated cotton.

Element	**Phosphorus**	**Nitrogen**	**Copper**
Atomic number	15	7	29
Series	K-series	K-series	L-series
Sample		Average wt %	
8 BL	12.1	5.2	n/a
10 BL	1.7	3.3	n/a
12 BL	11.7	6.8	n/a
8 BL Cu	5.8	2.6	17.0
10 BL Cu	8.3	2.3	6.6
12 BL Cu	14.0	4.6	8.2

The results of the antibacterial activity of Gram-negative *Klebsiella pneumoniae* and Gram-positive *Staphylococcus aureus* after immersing LbL-treated fabric into Cu^{2+} solution are summarized in Table 6. Metal ions such as Cu^{2+} and Zn^{2+} damage the cell membrane acting as a biosynthesis inhibitor, thus killing the bacteria [35]. As expected, all PA/CH-urea + Cu^{2+} treated samples killed almost 100% of the bacteria. These results are consistent with the results obtained in a previous study, where only 2.3 wt % of copper is sufficient to kill almost 100% of the bacteria [19].

Table 6. Influence of treatments on the reduction of *Klebsiella pneumoniae* and *Staphylococcus aureus* bacteria after 24 h of incubation (%).

	Bacterium Reduction (%)	
Sample	***Klebsiella pneumoniae***	***Staphylococcus aureus***
8 BL Cu	99.9	100
10 BL Cu	99.7	99.9
12 BL Cu	100.0	100.0

4. Conclusions

Cotton fabric was successfully treated with an environmentally benign flame-retardant coating consisting of PA/CH-urea, deposited via LbL deposition. The LOI value of cotton coated with 12 BL was 24.5% and the sample passed the VFT, with a char length of 6.7 cm. By immersing such treated cotton into Cu^{2+} solution, it is possible to achieve a higher FR effect, as well as to obtain antimicrobial properties. The result is in accordance with MCC values, where the pHRR for cotton, when treated with 12 BL of PA/CH-urea, is 132.2 W/g. The reduction of HRR is more than 50% and the reduction of T_{pHRR} is more than 23 °C, relative to untreated cotton. At the same time, the TG analysis showed that the 12 BL treatment moved the T_1 at the first decomposition stage to a lower temperature by 57 °C. By adding Cu^{2+} ions into the LbL system, the difference is even more visible. Antibacterial testing showed the reduction of Gram-negative *Klebsiella pneumoniae* and Gram-positive *Staphylococcus aureus* by almost 100%. By means of LbL treatment, it is possible to achieve an effective, environmentally friendly, multifunctional FR-antimicrobial nanocoating consisting of PA/CH-urea + Cu^{2+} on cotton as an alternative to commercial treatments.

Supplementary Materials: The following are available online at www.mdpi.com/article/10.3390/fib9110069/s1, Figure S1: Heat release rates as a function of temperature for untreated (control) and cotton treated with 8, 10 and 12 BL of PA/CH-urea + Cu^{2+}.

Author Contributions: Conceptualization, E.M.; methodology, I.J. and A.B.; validation, I.J. and A.B.; formal analysis, E.M.; investigation, E.M.; resources, I.J.; data curation, E.M.; writing—original draft preparation, E.M.; writing—review and editing, I.J., B.V., A.B., J.C.G. and S.B.; visualization, E.M.; supervision, S.B. All authors have read and agreed to the published version of the manuscript.

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Conflicts of Interest: The authors declare no conflict of interest.

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Antibacterial cotton from novel phytic acid-based multilayer nanocoating

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In an effort to impart antimicrobial behavior to cotton using renewable and environmentally benign components, fabric was treated using layer-by-layer (LbL) assembly. Alternating layers of phytic acid (PA) and chitosan (CH) were deposited from water. Cotton coated with four and eight bilayers (BLs) of anionic PA and cationic CH, with and without adding copper (II) sulfate ($CuSO_4$) into the CH solution, was evaluated in accordance with the American Association of Textile Chemists and Colorists (AATCC) TM 100-2019 test method. Gram-positive *Staphylococcus aureus* and gram-negative *Klebsiella pneumoniae* were used to determine whether the addition of copper salt into a CH network improves antibacterial efficacy. The copper ions were successfully incorporated into the CH network formed using LbL assembly onto cotton fibers. The location of deposited copper ions was determined with electron microscopy. Just four BLs of PA/CH–copper (II) sulfate kill 100% of gram-positive and gram-negative bacteria and add only 5.2 wt% to the fabric. This nanocoating provides a unique opportunity to impart antibacterial behavior to textiles without harming the environment.

Notation

A	number of bacteria recovered after 24 h
C	number of bacteria recovered at 'zero' contact time
R	reduction in bacteria

1. Introduction

Antimicrobial finishing of textiles is an important market segment worldwide, impacting a wide range of products such as medical textiles for use in hospitals, underwear, sportswear and footwear.[1] Among all of these products, cotton plays a vital role as a textile used for hundreds of years due to its softness and absorbency, which is enabled by hydroxyl groups in the cellulose molecule. These groups are highly reactive, generating derivates with useful properties.[2,3] Despite its many beneficial properties, the porosity and hydrophilicity of cotton make it prone to bacterial growth. As a result, many cotton textiles are treated with different types of antibacterial finishing (e.g. triclosan, triclocarban, phenyl derivates, quaternary ammonium compounds, citric acid, metal particles (and salts) and chitosan (CH)), which should not be toxic to humans at low concentrations.[4–8]

The commercial antimicrobial treatment of cotton fabric involves a pad–dry–cure process involving toxic formaldehyde derivatives that are released over time.[9] Layer-by-layer (LbL) deposition from water, using relatively benign polyelectrolytes, is a healthier alternative for antimicrobial fixation.[10] LbL deposition involves the surface adsorption of polyelectrolyte molecules of one charge onto the substrate of the opposite charge, followed by washing with deionized (DI) water. The second step is adsorption of an oppositely charged polyelectrolyte onto the first layer and so on. Compared with other methods of textile finishing, LbL processing is simple and uses low concentrations of polyelectrolytes in water.[11] As already mentioned, the ideal antimicrobial agent should be effective at low concentrations, non-toxic to humans, environmentally benign and low-cost. CH and copper (Cu) salts meet these criteria.[12,13]

CH is a linear polysaccharide composed of randomly distributed β-(1→4)-linked d-glucosamine and *N*-acetyl-d-glucosamine and produced commercially by deacetylation of chitin.[14] CH is soluble in aqueous acidic solutions, where it acts as a cationic polyelectrolyte with a high charge density, forming hydrogen bonds intermolecularly and chelating small molecules into its network.[15] Due to its unique behavior, CH has been widely used for LbL deposition.[16–18] Copper salts (i.e. blue vitriol or copper (II) sulfate pentahydrate ($CuSO_4 \cdot 5H_2O$)) are among the oldest antibacterial agents used, but due to their characteristic blue coloring of textile materials, they have not been widely used.[19,20] Additionally, high levels of copper (II) sulfate ($CuSO_4$) are toxic to humans, damaging the kidneys and liver.[21] On the other hand, copper has been used for decades in intrauterine devices due to the low sensitivity of tissues to copper and in dermatology as an anti-irritation skincare agent due to the high sensitivity of microorganisms to copper.[22,23]

In the present study, CH and phytic acid (PA) were deposited LbL onto cotton fabric, with and without copper (II) sulfate included in the CH solution. Weight gain and antimicrobial efficacy were

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evaluated with four and eight bilayers (BLs) of each recipe. Four BLs of PA/CH–copper (II) sulfate add 5.2 wt% to the cotton and are able to eliminate 100% of *Klebsiella pneumoniae* (gram negative) and *Staphylococcus aureus* (gram positive), while eight BLs of PA/CH could eliminate only 70% of the gram-negative bacteria, despite adding more than 14 wt% to the fabric. The conformal nature of the LbL-deposited nanocoating ensures that the bacteria are exposed to a very large surface area even though the concentration of the bactericidal agent is quite low. This unique nanocoating provides a more environment-friendly approach to imparting antibacterial behavior to high-surface-area substrates, such as textiles, by relying on renewable polyelectrolytes.

2. Materials and methods

2.1 Materials

Chemically bleached 100% cotton fabric, with a weight of 119 g/m^2, was supplied by the US Department of Agriculture Southern Regional Research Center (New Orleans, LA). Branched polyethylenimine (BPEI; molecular weight (MW) 25 000, ≤1% water), PA sodium salt hydrate (MW 660.04), copper (II) sulfate pentahydrate, hydrochloric acid (HCl) and sodium hydroxide (NaOH) pellets were all purchased from Sigma-Aldrich (Milwaukee, WI). CH powder (MW ~60 000) was purchased from G.T.C. Bio Corporation (Qingdao, China). For the preparation of all polyelectrolyte solutions, 18.2 mΩ DI water was used.

Table 1. Antimicrobial coatings evaluated in this study

Coating recipe	Number of BLs	Weight gain: %
PA/CH	4	8.3
PA/CH–copper (II) sulfate pentahydrate	4	5.2
PA/CH	8	14.5
PA/CH–copper (II) sulfate pentahydrate	8	5.6

A 5 wt% aqueous solution of positively charged BPEI was prepared with DI water and used as a primer layer for better adhesion to cotton. A 2 wt% aqueous solution of negatively charged PA and 0.5 wt% aqueous solution of positively charged CH water were both prepared with DI water that was magnetically stirred for 24 h. The 0.5 wt% CH solution was divided into two solutions (with and without adding copper (II) sulfate pentahydrate). Copper (II) sulfate pentahydrate (2 wt%) was added to the second 0.5 wt% aqueous solution of CH and magnetically stirred for 1 h. The pH of all of these solutions was adjusted to 4, with 1 M sodium hydroxide or 1 M hydrochloric acid, prior to LbL deposition.

2.2 LbL deposition

Five dry cotton samples were prepared. Two samples were immersed into aqueous solutions of negatively charged PA and positively charged CH, forming four and eight BLs. Two other cotton samples were immersed into aqueous solutions of negatively charged PA and positively charged CH–copper (II) sulfate pentahydrate, forming four and eight BLs, as shown in Table 1. One cotton sample was used as a control sample. The process of LbL deposition is shown schematically in Figure 1. The immersing time was 5 min for the first

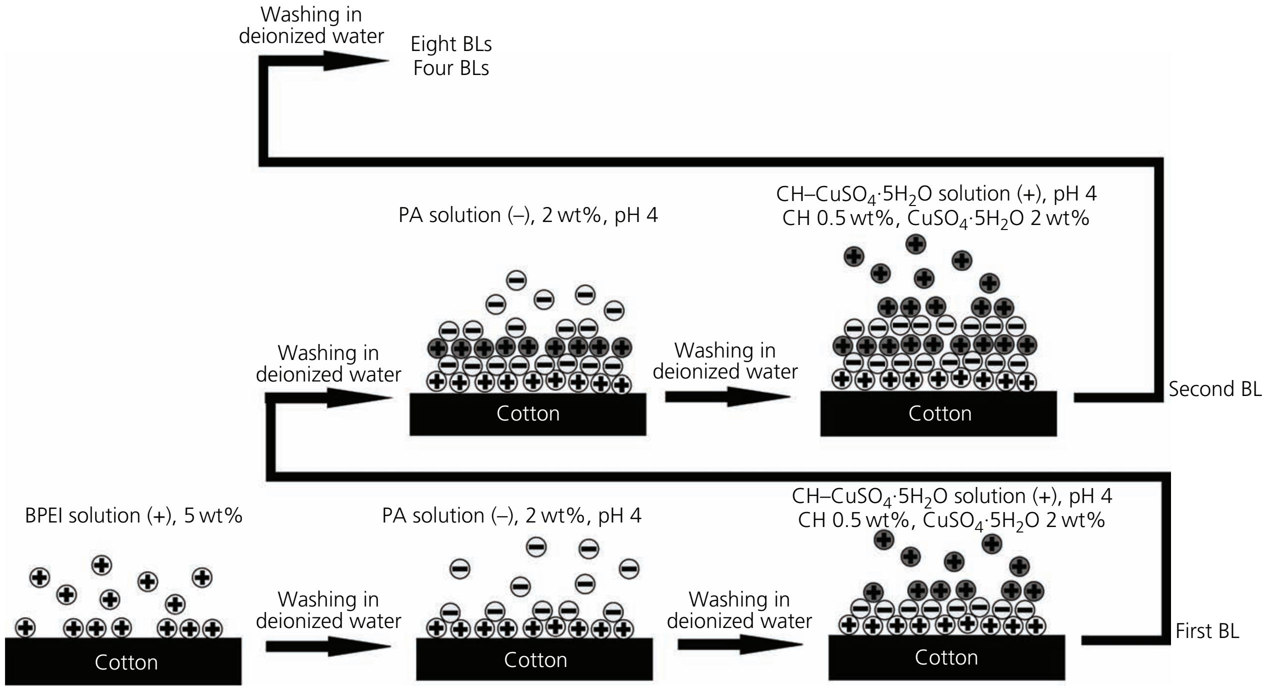

Figure 1. Schematic procedure of LbL deposition of antimicrobial nanocoatings on cotton fabric

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layer and 1 min for each additional layer. Each immersion step was followed by rinsing in DI water. All samples were dried in an oven at 70°C for 2 h before and after the LbL treatment.

2.3 Characterization

The weights of all samples were measured after drying. The morphology of all samples was imaged using a Tescan Mira LMU field emission scanning electron microscopy (FE-SEM) scanning electron microscope (secondary electron detector, 5 kV, Brno, Czech Republic) and an SC7620 sputter coater equipped with chrome target (Quorum Technologies, Laughton, UK). The chemical analysis of samples treated with copper (II) sulfate pentahydrate was studied using a Tescan Mira LMU FE-SEM scanning electron microscope (backscattered electron (BSE) detector, 10 kV) equipped with an energy-dispersive X-ray spectroscopy (EDS) detector (Bruker Nano, Berlin, Germany) for elemental analysis. No sputter-coating was performed prior to EDS analysis. Antimicrobial testing was performed according to AATCC TM 100-2019, which determines the bacteriostatic as well as bactericidal activity of the coated samples. Four circular specimens from each of five samples were cut (diameter 4.8 ± 0.1 cm) and stacked in a 250 ml wide-mouth glass jar (with a screw cap) so that the amount of cotton fabric used absorbs 1.0 ± 0.1 ml of inoculum, leaving no free liquid in the jar. The test bacteria applied were gram-positive *S. aureus* and gram-negative *K. pneumoniae*.[24] The percentage of the reduction in bacteria by the specimen treatment was calculated using the following formula:

$$R\ (\%) = \frac{C - A}{C} \times 100 \qquad (1)$$

where R (%) is reduction; C is the number of bacteria recovered from the inoculated untreated control specimen swatches in the jar immediately after inoculation (at ‘zero’ contact time); and A is the number of bacteria recovered from the inoculated treated test specimen swatches in the jar incubated over the desired contact period (24 h).

3. Results and discussion

Table 1 shows that eight BLs of PA/CH add 14.5 wt% to the cotton fabric, while inclusion of the copper salt dramatically reduces this weight gain. Comparing samples with the same antibacterial formulation but with a different number of BLs, it is evident that the weight gain increases with the number of BLs. The nearly doubled weight gain between four BLs (8.3 wt%) and eight BLs (14.5 wt%) treated only with PA/CH agrees with the literature, where the weight gain linearly increases up to 10 BLs.[25] Adding copper (II) (Cu^{2+}) salt into cationic CH only marginally increases weight (5.2 wt% for four BLs and 5.6 wt% for eight BLs of PA/CH–copper (II) sulfate), which seems contrary to previous research, where adding salt increases LbL growth.[26] One of the factors influencing the thickness of the layers is the ionic strength of the electrolytes. At low ionic strength, the polymer coil expands to form thin layers with a low adsorbed amount of mass. The increase in ionic strength causes repulsion between the charged polymer units, creating a more coiled chain and thicker layers with a higher adsorbed mass.[27]

The explanation for such a low increase in the weight gain of cotton samples treated with four and eight BLs of PA/CH–copper (II) sulfate (only 0.4 wt% between them) could be that the concentration of salt was too high, enabling copper (II) ions to bind PA anions that generate complex compounds deposited on the surface of cotton in the shape of fibrils, shown in Figures 2(c) and 2(d). An additional explanation could be that sulfate (SO_4^{2-}) groups neutralize positively charged CH amino groups, making them unavailable for electrostatic bonding with phytic anions. SEM images of the samples coated with four and eight BLs of PA/CH, shown in Figures 2(a) and 2(b), reveal non-uniform porous films around the fibers. The surface with the eight-BL treatment is clearly rougher than the four-BL sample. This stronger complexation is known to occur between polyanions and polycations of non-matching molar masses (e.g. PA is 660 g/mol and CH is ~60 000 g/mol).

SEM images of the samples coated with four and eight BLs of PA/CH–copper (II) sulfate also reveal a non-uniform porous film around the fibers (partially peeled off from the fiber surface), as shown in Figures 2(c) and 2(d). There is no real difference in layer structure and thickness between four and eight BLs when copper (II) sulfate is present, which agrees with the negligible difference in weight gain shown in Table 1. Regarding samples treated with PA/CH, treatment with the salt generates visibly thinner deposits in the shape of fibrils, which are likely copper–PA or CH–sulfate complexes. This is in accord with the results of EDS elemental analysis that revealed an average 0.31 wt% sulfur for four BLs and 1.24 wt% for eight BLs. The results in Table 2 represent the average weight percentage taken from 20 different points on these samples. Copper was also detected by the EDS detector. The average atomic weights of sulfur and copper correlate with the number of BLs deposited. Copper increases from 2.32% (four BLs) to 2.44% (eight BLs). EDS analysis of copper content agrees with the results of BSE imaging, which shows areas with light and heavy elements as darker and lighter areas, respectively.[28] The BSE image of the sample treated with four BLs PA/CH–copper (II) sulfate is almost black, suggesting significantly less copper than the sample treated with eight BLs, as shown in Figure 3.

Figure 4 shows the effectiveness of different antibacterial treatments. The number of gram-positive *S. aureus* decreased after 24 h of incubation to 76.8% for four BLs and 97.9% for eight BLs of PA/CH. More BLs increase the amount of CH that catches more bacteria in the porous network. According to some literature, the introduction of transition metal ions such as copper (II) ions into a CH network leads to a decrease in antibacterial activity due to complex formation.[29] This finding contradicts the results obtained in this work. The introduction of copper (II) ions into PA/CH results in a dramatic reduction in *S. aureus* (up to almost 100% for

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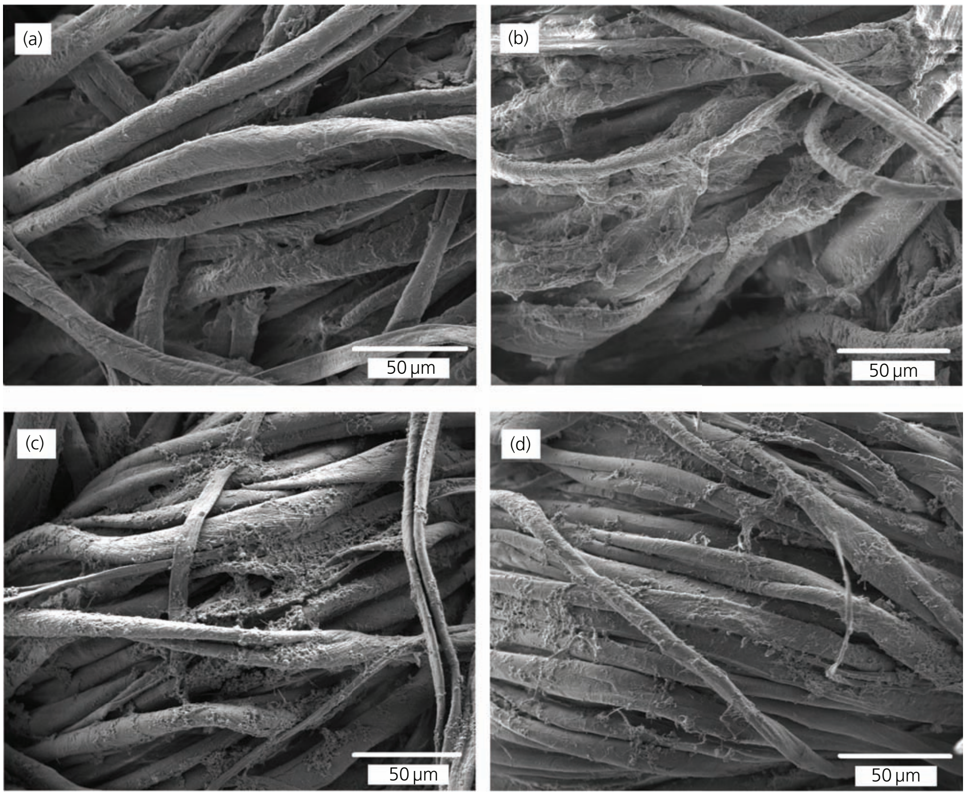

Figure 2. SEM images of cotton samples treated with (a) four and (b) eight BLs of PA/CH and (c) four and (d) eight BLs of PA/CH–copper (II) sulfate

Table 2. EDS analysis of samples treated with PA/CH–copper (II) sulfate

Element	Atomic number	Series	Average wt%	
			Four BLs	Eight BLs
Copper	29	L series	2.32	2.44
Sulfur	16	K series	0.31	1.24

both four and eight BLs). This could be explained by the fact that the top layer of positively charged copper (II) ions is the most important factor responsible for contact killing of bacteria.[30] In contrast, the number of PA/CH BLs, as well as the amount of available CH, has little influence on *K. pneumoniae* reduction. For four BLs, the reduction is 71.5% after 24 h and 70.3% for eight BLs. This is due to differences in the structure of the *S. aureus* and *K. pneumoniae* outer membranes.[31] The generally accepted difference between these two types is their cell membrane structure, which in both cases consists of peptidoglycan (macromolecules composed of *N*-acetylglucosamine and *N*-acetylmuramic acid cross-linked by short peptides of teichoic acid that provide strength and shape). Gram-positive bacteria consist of several layers of peptidoglycan, whereas gram-negative bacteria form a single thin layer internal to the outer membrane layer, a capsule, consisting of murein lipoproteins, lipopolysaccharides and phospholipids, which provide environmental protection.[32]

Outer bacterial cell membranes are generally negatively charged and for that reason highly attracted by the positively charged amino groups of CH, as well as metal ions such as copper. The higher the opposite charge between the outer membrane and the antibacterial agent, the more effective the antibacterial activity in general.[33] CH is effective against both gram-positive and gram-negative bacteria due to protonation of amino groups at pH 4–6, which become positively charged and interact electrostatically with the negatively charged bacterial cell membrane. It disrupts the permeability barrier, causing metabolic imbalance and leakage of small cellular nutrients such as potassium (K^+) and calcium (Ca^{2+}) ions that result in cell death.[34,35] In contrast, metal ions such as copper (II) ions damage the cell membrane by entering the cytoplasm and inhibiting biosynthesis, which kills the bacteria.[36] The evidence for the major importance of the top layer for bacterial killing is the reduction of ~100% of *S. aureus* and *K. pneumoniae* for samples treated with four and eight BLs of PA/CH–copper (II) sulfate, independent of the amount of copper salt present.

4. Conclusion

Cotton fabric was treated with an innovative and eco-friendly multilayer nanocoating, composed of renewable polyelectrolytes that rendered it antibacterial. Concentrated electrolytes, such as copper (II) sulfate, were also incorporated, but only in a very small quantity. CH is an effective antibacterial agent against *S. aureus* and

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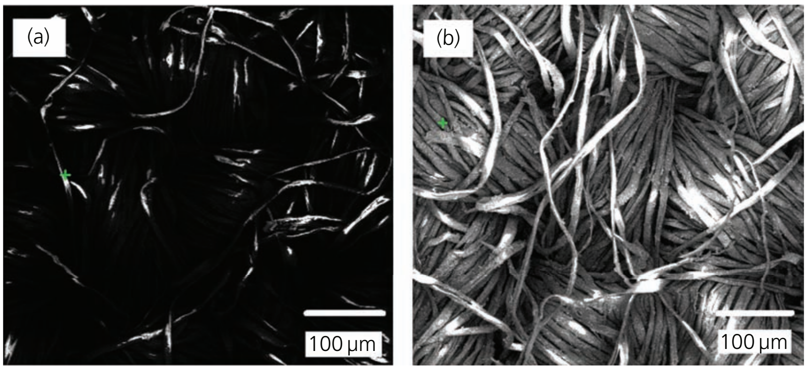

Figure 3. BSE images of samples treated with (a) four and (b) eight BLs of PA/CH–copper (II) sulfate

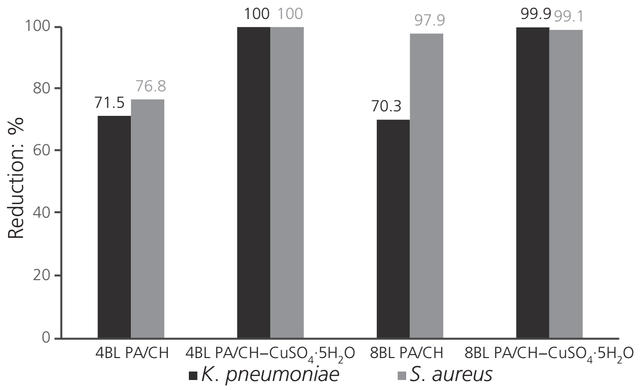

Figure 4. Influence of treatment on reduction of *K. pneumoniae* and *S. aureus* after 24 h of incubation (%)

K. pneumoniae. The number of CH/PA BLs, as well as the amount of available CH, increases the antibacterial activity, but efficacy depends on the structure of the outer bacterial cell membrane. Salt ions such as copper (II) ions are very effective against *S. aureus* and *K. pneumoniae* if they are located on a top layer of a multilayer thin film. The presence of the copper salt in a four-BL CH/PA nanocoating resulted in 100% reduction of both types of bacteria while adding only 5.2 wt% to cotton fabric. Future research will be focused on obtaining improved bactericidal cotton and combining this with additional functionality such as flame-retardant properties.

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Article

Environmentally-Benign Phytic Acid-Based Multilayer Coating for Flame Retardant Cotton

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Abstract: Chemically bleached cotton fabric was treated with phytic acid (PA), chitosan (CH) and urea by means of layer-by-layer (LbL) deposition to impart flame retardant (FR) behavior using only benign and renewable molecules. Samples were treated with 8, 10, 12 and 15 bilayers (BL) of anionic PA and cationic CH, with urea mixed into the aqueous CH solution. Flammability was evaluated by measuring limiting oxygen index (LOI) and through vertical flame testing. LOI values are comparable to those obtained with commercial flame-retardant finishes, and applying 10 or more bilayers renders cotton self-extinguishing and able to pass the vertical flame test. Microscale combustion calorimeter (MCC) measurements show the average reduction of peak heat release rate (pHRR) of all treated fabrics of ~61% and the reduction of total heat release (THR) of ~74%, in comparison to untreated cotton. Decomposition temperatures peaks (T_{1max}) measured by thermogravimetric analyzer (TG) decreased by approximately 62 °C, while an average residue at 650 °C is ~21% for 10 and more bilayers. Images of post-burn char indicate that PA/CH-urea treatment is intumescent. The ability to deposit such a safe and effective FR treatment, with relatively few layers, makes LbL an alternative to current commercial treatments.

Keywords: layer-by-layer assembly; flame retardant; cotton; phytic acid; chitosan; urea

1. Introduction

Cotton is one of the best-selling textiles in the world, used for a wide range of products such as sportswear, fashion garments as well as protective clothing due to its softness and moisture absorption, which makes it comfortable to wear. This absorption is enabled by hydroxyl groups in the cellulose molecule that attract water and make it hydrophilic. However, high flammability is the primary undesirable property of cotton, making it inappropriate for protective clothing and safety workwear requiring fire safety. To reduce flammability, cotton has been treated with commercially available flame-retardant finishes based on halogen, organo-halogen, antimony organo-halogen or organophosphorus chemistries [1]. Many of these flame retardants are toxic to humans, as well as to the environment, causing endocrine disruption, infertility, cancer, neurobehavioral problems, as well as embryotoxic and teratogenic effects [2]. Inhalation of toxic volatile products generated in a fire (e.g., carbon monoxide, hydrogen cyanide, hydrocarbons, dioxin, acrolein, formaldehyde, etc.) can lead to death. Until recently, flame retardants based on organophosphorus compounds have been considered safe, but in recent studies they have been found to be persistent in the atmosphere, soil, water and in biological samples [3].

The most durable flame retardant (FR) finishes for cotton fabric are typically organophosphorus compounds based on tetrakis (hydroxymethyl) phosphonium derivatives and N-methyloldimethyl phosphonopropioamide applied by a pad-dry-cure process, which produces toxic smoke during curing [4]. Formaldehyde is one of the toxic compounds released in these finishing processes. Formaldehyde-free alternatives for cotton finishing are polycarboxylic acid-based flame retardants, such as 1,2,3,4-butanetetracarboxylic acid (BTCA), succinic acid (SA), citric acid and malic acid (MA) [5,6]. Layer-by-layer (LbL) deposition of more environmentally-benign compounds based on phosphorus-nitrogen synergy has emerged as another promising approach for cotton flame retardancy [7,8]. This aqueous treatment consists of polyanion and polycation solution exposure, resulting in a multilayer nanocoating [9,10]. This versatile technique is applicable to nearly any surface and can make use of polymers, nanoparticles and various small molecules.

Chemically bleached cotton fibers are generally negatively-charged due to the presence of carboxyl and hydroxyl-groups [11]. However, cotton cellulose modified by quaternary ammonium compounds that block anionic groups results in a positive charge [12]. Charged surface of cotton fibers make them an ideal substrate for the LbL deposition [13]. LbL treatment of cotton involves dipping/immersing of fabric into the oppositely-charged polyelectrolyte solutions or simply spraying with polyelectrolyte solutions [14]. Repeated exposure to oppositely-charged polyelectrolytes can be used to deposit bilayers (BL), trilayers (TL) or quadlayers (QL) with a desired functionality, such as combination of hydrophobicity-flame retardancy-conductivity [15], hydrophobicity-flame retardancy [16,17], or antimicrobial-flame retardancy [18,19].

In the present study, three environmentally-benign compounds have been used: phytic acid (PA), chitosan (CH) and urea, where negatively-charged PA and positively-charged CH are known to form an FR nanocoating on cotton [20]. Phytic acid stores phosphorus in plants [21], while chitosan is a linear polysaccharide produced commercially by deacetylation of the chitin shells in the crustaceans [22]. For FR purposes, chitosan acts as a source of nitrogen as well as blowing agent [23]. Urea is the principal end product of metabolism in mammals and provides an additional source of nitrogen [24]. Thirty bilayers of CH/PA has been shown to impart self-extinguishing behavior to cotton [20]. Thirty bilayers can be reduced to 4 BL by adding divalent metal ions such as barium into CH [25]. Here it is shown that the addition of nitrogen-rich urea reduces the number of bilayers from 30 to 10 for the same level of flame retardancy saving the energy by skipping drying at 80 °C after each immersing/padding step. Additionally, this 10 BL nanocoating increases the LOI of cotton from 18 to 28%. Accomplishing such effective fire protection using only environmentally-benign chemistries and relatively few processing steps makes this a very scalable treatment.

2. Materials and Methods

Chemically bleached, desized cotton fabric, with a weight of 119 g/m^2, was supplied by the USDA Southern Regional Research Center (New Orleans, LA, USA). Branched polyethyleneimine (BPEI, M = 25,000 g/mol, ≤1% water), phytic acid sodium salt hydrate (PA), urea, hydrochloric acid (HCl) and sodium hydroxide-pellets (NaOH), were all purchased from Sigma Aldrich (Milwaukee, WI, USA). Chitosan (CH) powder (M ~ 60,000 g/mol 75–85% deacetylated) was purchased from G.T.C. Bio Corporation (Qingdao, China). For the preparation of all polyelectrolyte solutions, 18.2 mΩ deionized (DI) water was used.

In an effort to improve coating adhesion to cotton, an aqueous cationic solution of BPEI (5 wt%) was prepared and the textile was immersed to deposit a primer layer. An aqueous anionic solution of PA (2 wt%) and cationic CH (0.5 wt%), both prepared with DI, were magnetically stirred for 24 h. Urea (10 wt%) was added to the CH solution and magnetically stirred until completely dissolved. The pH of all of these solutions was adjusted to 4, with 1 M NaOH or 1 M HCl, just before LbL deposition. Cotton was washed in a standard detergent solution, dried in an oven for 24 h at 80 °C and cut into five 3 inch × 12 inch samples. Four cotton samples were alternately immersed in the PA and CH-urea solutions, depositing 8, 10, 12 and 15 BL, as shown in Table 1. The remaining cotton sample was left untreated as a control. The process of LbL deposition is shown in Figure 1.

Table 1. Weight gain and limiting oxygen index data.

Number of BL	Weight Gain (%)	LOI (%)	Time (s)
Control	-	18	25
8	12.36	26	26
10	17.29	28	40
12	18.19	29	34
15	20.12	31	30

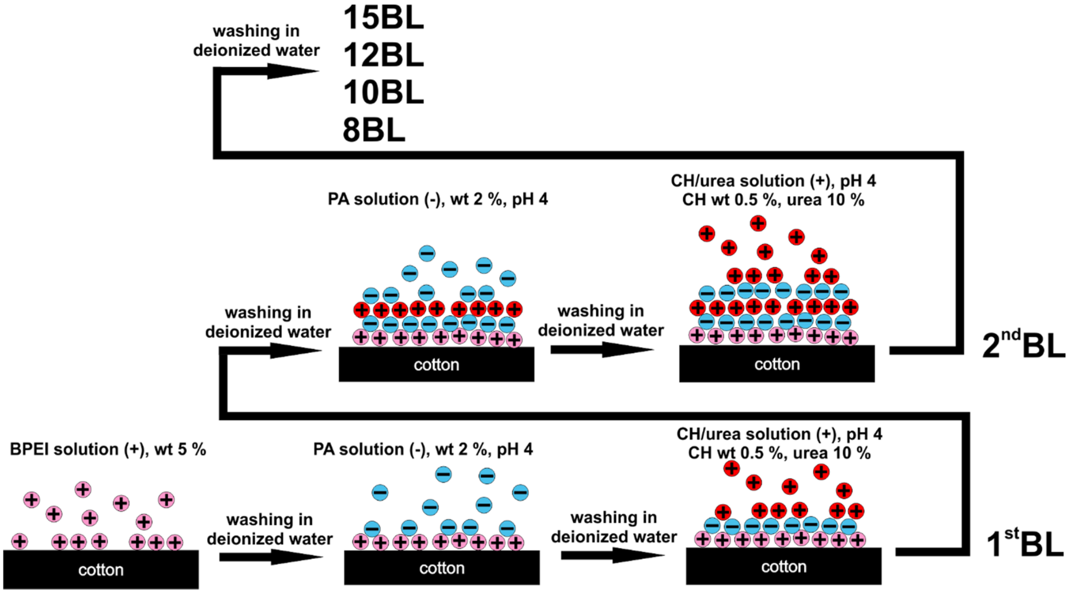


Figure 1. Schematic of layer-by-layer deposition of flame retardant nanocoatings on cotton fabric.

The immersion time is 5 min for the first layer and 1 min for each additional layer. Each immersion step is followed by rinsing in DI water. All samples are dried in the oven at 80 °C for 24 h after the LbL treatment.

The weights of all samples were measured after drying in the oven at 80 °C for 24 h, before and after LbL treatment, to calculate weight gain (%) using the following equation:

$$\text{weight gain } (\%) = \frac{\text{m (treated)} - \text{m(untreated)}}{\text{m (untreated)}} \times 100 \tag{1}$$

Limiting oxygen index (Dynisco, Heilbronn, Germany) was measured according to ISO 4589-2:2017 [26].

Vertical flame testing was carried out in a standard chamber (Govmark, Farmingdale, NY, USA) according to ASTM D6413/D6413M-15 [27].

A Govmark MCC-2 (Heilbronn, Germany) microscale combustion calorimeter (MCC) was used to measure heat release of cotton samples according to ASTM D7309-19a [28]. A temperature range of 75–650 °C was used with the mixture of gases consisting of 20% N_2 and 80% O_2, 100 mL/min gas flow rate) and heating rate of 1 °C/min. The repeatability of the MCC measurement was determined on three replicated samples for each treatment with standard deviations.

Thermogravimetric analysis (TGA) was performed with a PerkinElmer Pyris 1 (Shelton, CT, USA). All samples were heated from 50 to 850 °C with a heating rate of 30 °C/min in air (flow rate: 30 mL/min). The morphology of all samples, as well as post-burn char, was imaged using a Tescan MIRA\\LMU FE-SEM (Scanning Electron Microscope, SE detector, 5 kV, Brno, Czech Republic). All samples were coated with 5 nm of chromium for better conductivity (Q150T ES Sputter Coater, Quorum Technologies, Laughton, UK), with the exception of the char samples.

3. Results and Discussion

Cotton samples were treated with a varying number of chitosan-urea/phytic acid bilayers. The tendency toward linear weight gain can be seen in Table 1.

The minimum oxygen fraction in an O_2/N_2 mixture that supports combustion, as well as the time required to complete combustion, was measured for these treated samples. LOI for untreated cotton is between 18% and 19%, depending on the type of fabrics, construction, weight, moisture, ambient temperature, etc. For cotton treated with commercial durable flame retardants, the LOI is usually within the range of 28–29% [29]. Here, LOI increases with the number of CH-urea/PA bilayers deposited. Cotton treated with 8 BL has an LOI of 26%, which increases to 31% with 15 BL. Cotton treated with 10, 12 and 15 BL satisfy commercial requirements, with the values of 28% or above. Burning time of samples treated with 10, 12, 15 BL is ~35 s, which means that samples burn more slowly than untreated cotton.

The results of vertical flame testing correlate with the LOI results. Samples treated with 10, 12 and 15 BL pass the vertical flame test (VFT) with char lengths between 12.0 and 13.0 cm, with no afterflame and afterglow time, as summarized in Table 2.

Table 2. Vertical flame test results for cotton samples treated with varying number of bilayers.

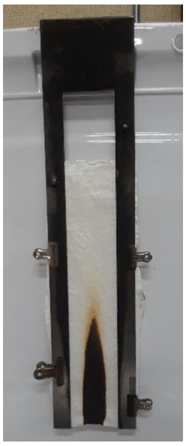
Number of BL	8	10	12	15
				
Char length (cm)	n/a	13.0	12.0	12.5
After flame time (s)	n/a	0	0	0
After glow time (s)	n/a	0	0	0

Figure 2 shows microscale combustion calorimetry (MCC) heat release rates (pHRR) as a function of temperature for cotton LbL-treated with varying bilayers of PA/CH-urea.

Factors influencing pHRR curves are homogeneity, sample weight, flow rate perturbation, oxygen level and loading/types of additives [30,31]. Three different groups of curves are observed: untreated cotton (control), cotton treated with 8 BL and cotton treated with 10, 12 or 15 BL. These results correlate well with VFT results. Table 3 summarizes the MCC results.

Table 3. Heat release values of layer-by-layer (LbL) treated cotton fabric (with standard deviations).

Number of BL	pHRR (W/g)	ΔHRR (%)	THR (kJ/g)	ΔTHR (%)	T_{pHRR} (°C)
Control	234.8 (5.7)	-	11.1 (0.9)	-	380 (1.7)
8 BL	101.0 (4.8)	57.0	3.6 (0.8)	67.6	302 (2.3)
10 BL	95.1 (6.3)	59.5	3.3 (0.7)	70.3	303 (3.0)
12 BL	88.6 (4.5)	62.3	3.0 (0.5)	73.0	299 (1.8)
15 BL	86.2 (6.1)	63.3	2.2 (0.8)	80.2	303 (2.1)

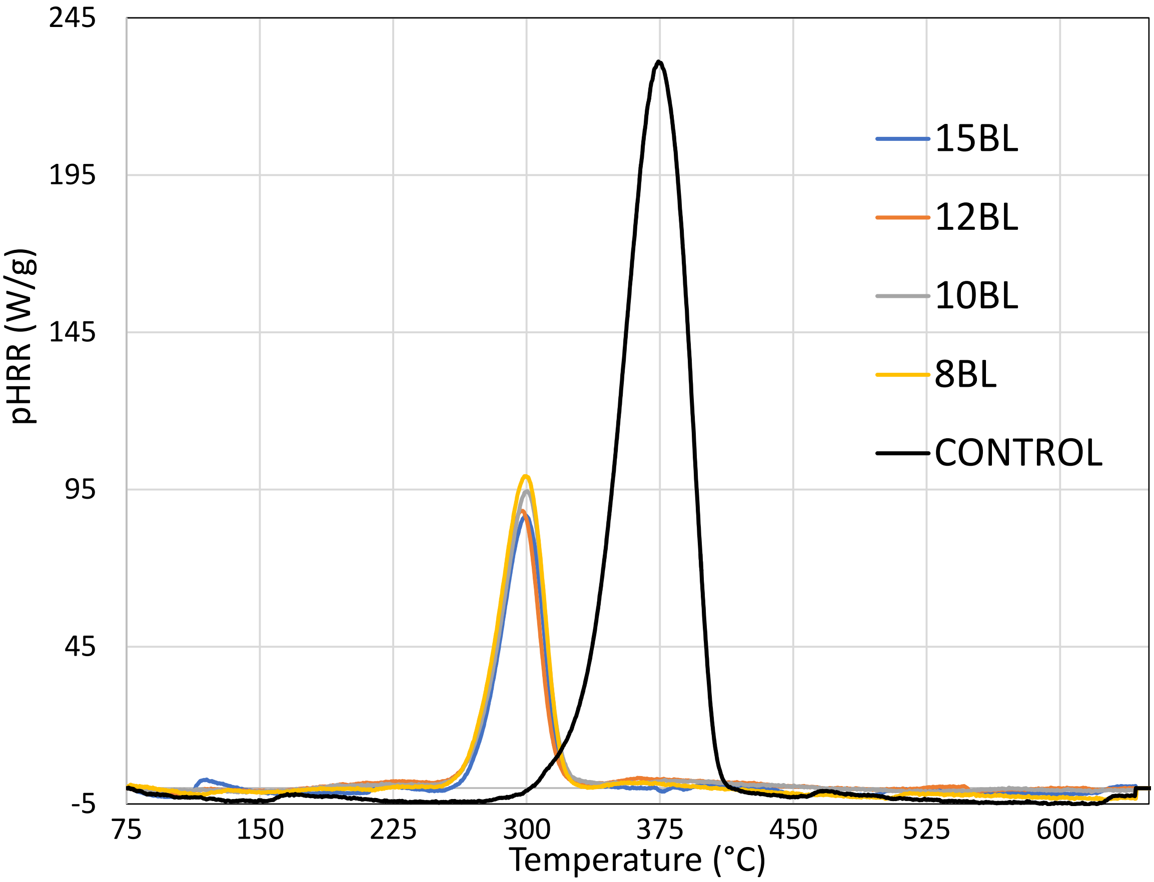


Figure 2. Heat release rates as a function of temperature for cotton treated with varying bilayers (8 BL-15 BL) of PA/CH-urea.

Peak release rates (pHRR) of untreated cotton is 234.8 W/g, while total heat release (THR) is 11.1 kJ/g at ~380 °C. pHRR values for cellulose materials vary depending on their chemical composition (content of lignin, hemocellulose, impurities, etc.). Peak heat release rate of FR treated cotton is decreased by 50%, compared to untreated cotton. Among all treated samples, 8 BL exhibits the lowest reduction of pHRR (57.0%) and THR (67.6%), which correlates with the results of vertical flame testing (where the 8 BL sample burns completely). Cotton treated with 10, 12 or 15 BL reduces pHRR by ~61% and THR ~74%. In all cases, pHRR, THR and T_{pHRR} values decrease steadily with increasing bilayers deposited.

Figure 3 shows TGA curves of untreated and LbL-treated cotton samples with three stages of weight loss, while Figure 4 shows derivative weight as a function of temperature for all samples.

The first weight loss starts between 50 and 100 °C, due to evaporation of moisture, and is identical for untreated and treated samples. The first decomposition stage begins between 250 and 400 °C, with dehydration and depolymerization. At this stage, T_{1max} cellulose loses 95% of its weight, generating non-flammable gases, primary char residue and levoglucosane. All LbL-treated cotton samples exhibit a shift to lower temperatures, by ~60 °C. The curves differ more dramatically at the second decomoposition stage, which starts between 500 and 650 °C. Its maximum is T_{2max}, where levoglucosane produces flammable gases and secondary char [32]. As shown in Table 4, the highest mass loss of untreated cotton (59%) appears at ~389 °C, while at ~585 °C it loses 95% of its mass.

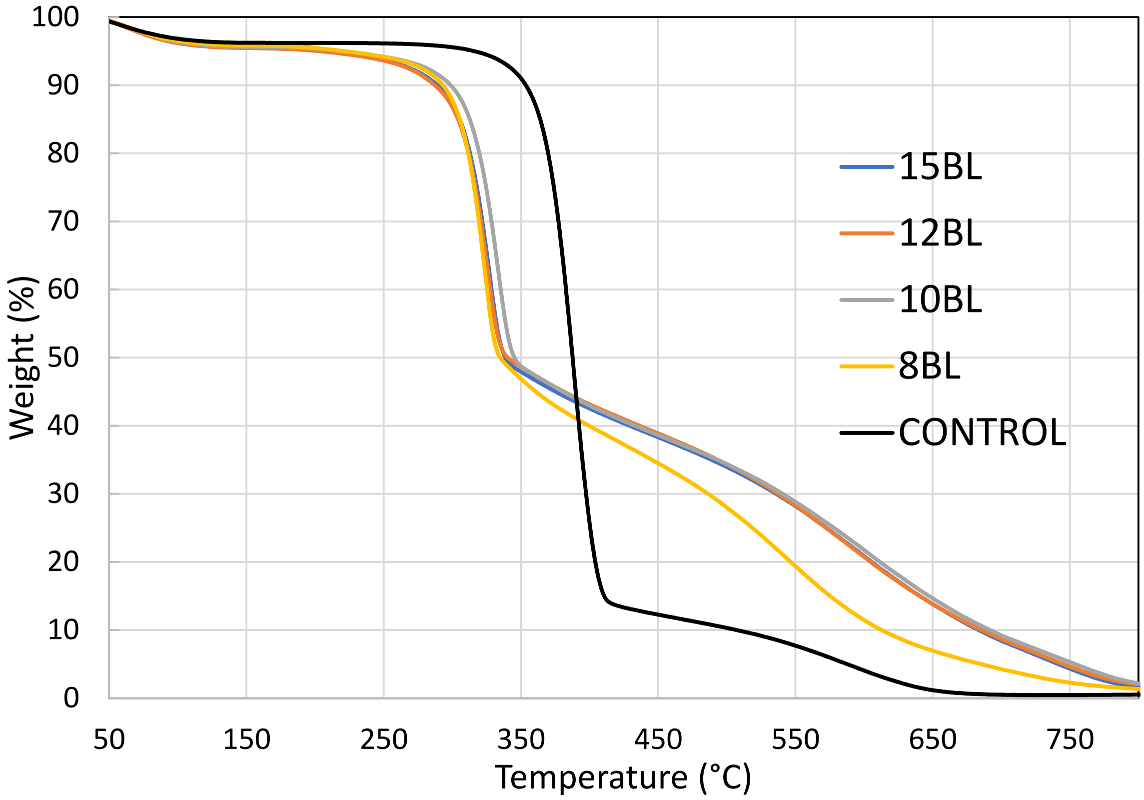


Figure 3. Cotton weight as a function of temperature for untreated and LbL-treated samples.

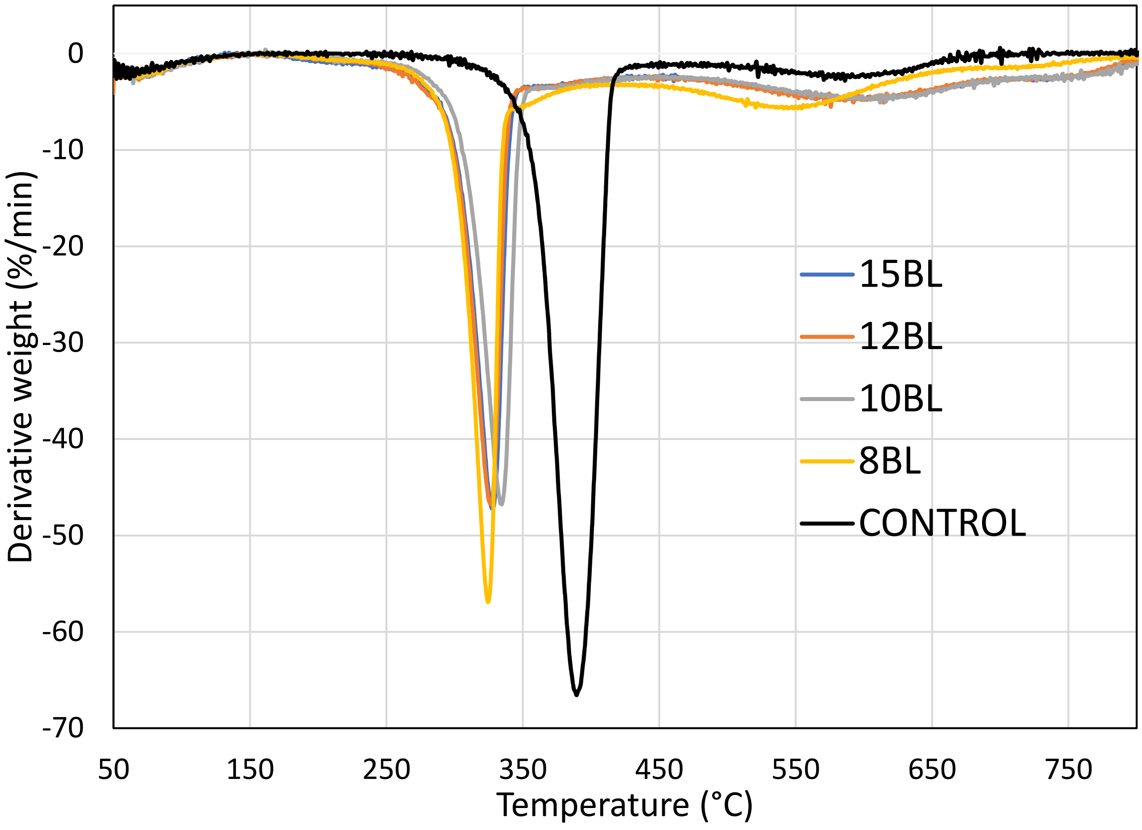


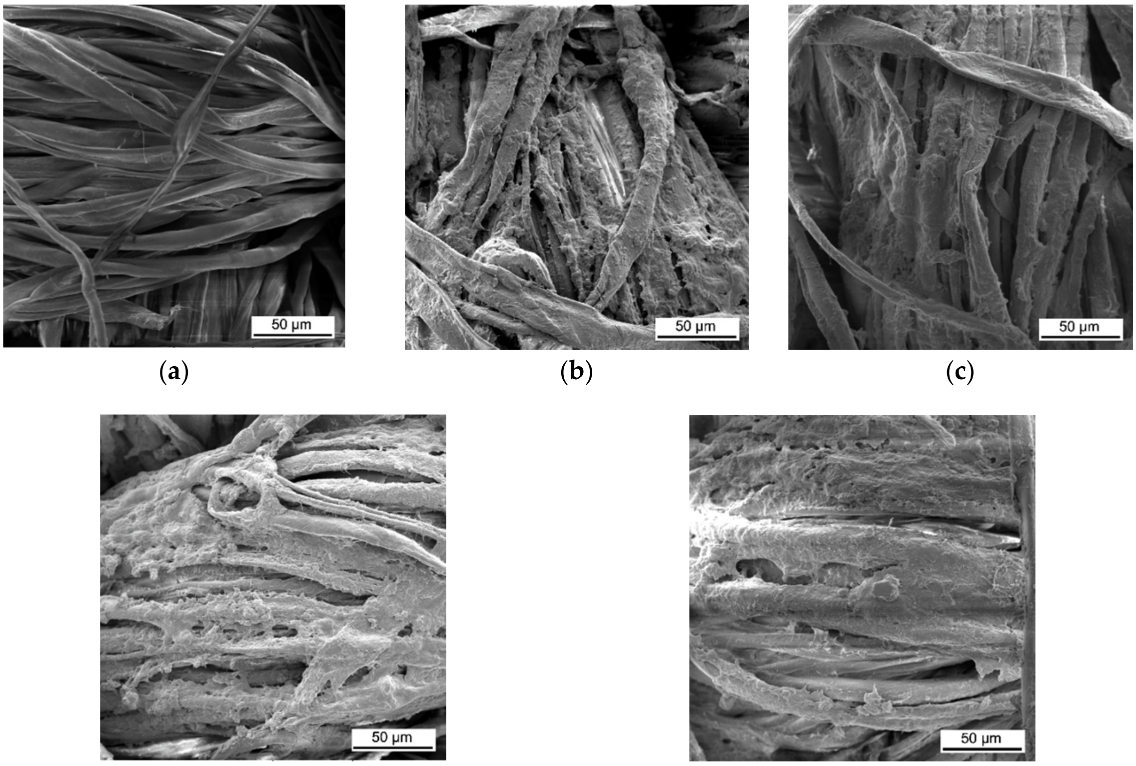
Figure 4. Derivative weight as a function of temperature for untreated and LbL-treated samples.

Table 4. Summary of thermogravimetric analysis of treated and untreated cotton.

Number of BL	T_{1max} (°C)	Char Yield at T_{1max} (%)	T_{2max} (°C)	Char Yield at T_{2max} (%)	Char Yield at 650 °C (%)
Control	389	46.28	585	5.20	1.17
8	323	63.53	552	19.10	6.96
10	334	62.50	604	21.13	14.63
12	326	62.63	592	21.93	13.82
15	327	63.00	607	19.76	13.80

The char consists of impurities or inorganic compounds, making up 1–5% of untreated cotton. On the other hand, T_{1max} of LbL-treated cotton appears at ~327 °C, with an average mass loss of 37%. This means that the CH-urea/PA coating decreases the decomposition temperature of cotton. At this stage non-flammable gases generate that dilute the concentration of the combustible gases and absorb heat causing bubbling [33]. At the same time, urea catalyzes the reaction of PA as well as the decomposition of cellulose at low temperature, thus forming intumescent char, which acts as physical barrier that blocks heat and oxygen [34]. At T_{2max} the average mass loss for all treated samples is around 80 %. At 800 °C the oxidation of all organic compounds occurs. At 650 °C, the 8 BL coated cotton has a char of ~7%, while the char yield of 10, 12 and 15 BL is ~14%.

Figure 5 shows SEM micrographs of untreated and LbL-treated cotton fabric. Untreated cotton fabric's smooth surface (Figure 5a) contrasts with the rough, uneven and paste-like surface of the treated samples (Figure 5b–e).

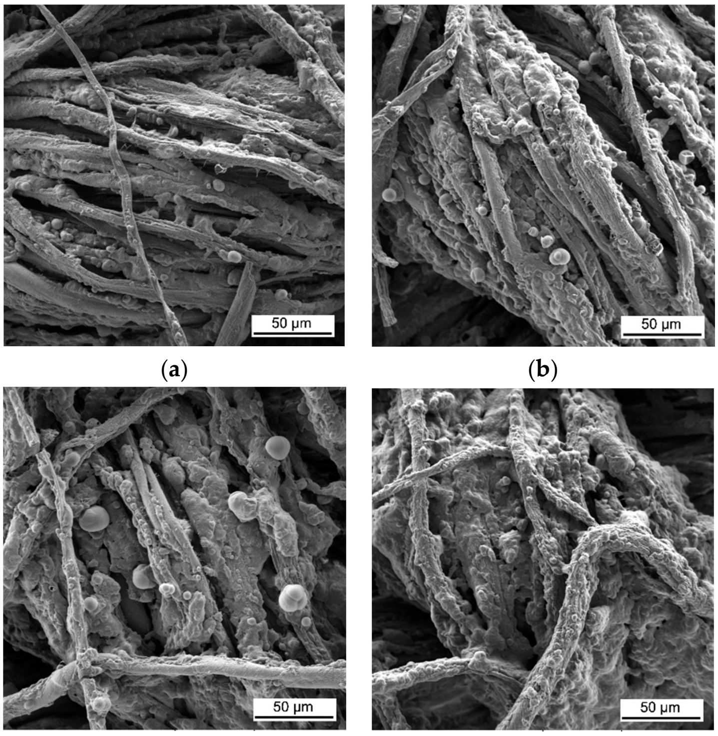


(**a**) (**b**) (**c**)

(**d**) (**e**)

Figure 5. SEM images of (**a**) untreated cotton and (**b**) cotton treated with 8, (**c**) 10, (**d**) 12, and (**e**) 15 bilayers (BL) chitosan (CH)-urea/phytic acid (PA).

These images confirm that CH-urea/PA was successfully deposited onto the fabric and visually the thickness increases with the number of bilayers deposited. SEM images of char after performing vertical flame testing are shown in Figure 6.



(**a**) (**b**)

(**c**) (**d**)

Figure 6. SEM images of the char residue of treated cotton after performing vertical flame testing: (**a**) 8, (**b**) 10, (**c**) 12, and (**d**) 15 BL.

Untreated cotton completely combusts, so no char residue was obtained. All of the charred fabric samples reveal a bubbling effect, which is characteristic of intumescent flame-retardant systems. Chitosan acts as a carbon donor, phytic acid as an acid donor and low-molecular weight urea as a blowing agent that generates gas. The foamed char acts as a physical barrier to slow heat and mass transfer between the gas and condensed phases [35].

4. Conclusions

Cotton fabric was successfully treated with an environmentally-benign multilayer nanocoating to reduce flammability. Layer-by-layer deposition of chitosan-urea and phytic acid solutions produced this effective intumescent treatment. LOI of cotton coated with 10, 12 and 15 BL is in the range 28–31%, confirming that LbL-treated fabric is comparable to commercially available cotton flame retardant finishes. 10 BL of CH-urea/PA applied to cotton passes the standard vertical flame test. The average reduction of pHRR of all treated fabrics is 61% and the reduction of THR, in comparison to untreated cotton, is 74%. TGA reveals an average residue at 650 °C of ~14% for 10, 12 and 15 BL, confirming the intumescent effectiveness of the treated cotton. SEM images of post-burn char show characteristic intumescent bubbles. This work demonstrates that the number of CH/PA bilayers can be dramatically reduced to 10 BL, by adding urea to the CH solution, which makes this treatment much easier to process. The ability to deposit such a safe and effective FR treatment, makes LbL an ecologically-friendly alternative to current commercial treatments.

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Nehalogene obrade protiv gorenja celuloznih tekstilnih materijala

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Pregled

U radu je dan pregled najčešće korištenih sredstava za obrade protiv gorenja celuloznih tekstilnih materijala, s naglaskom na nehalogena sredstva. Prikazan je i mehanizam njihovog djelovanja na usporavanje gorenja. Budući da je velik broj halogenih sredstava toksičan ili potencijalno toksičan za organizme i okoliš, potrebna je njihova zamjena ekološki povoljnim sredstvima. Predstavljena su alternativna sredstva koja se nastoji uvesti u praksu, a također su prikazane i uspoređene različite metode nanašanja sredstva za obradu protiv gorenja. Jedan od mogućih pravaca razvoja zamjenskih sredstava protiv gorenja, mogla bi biti primjena biomakromolekula kao što su hitosan, fitinska kiselina, kazein, sirutka, hidrofobini ili DNK.

Ključne riječi: *obrada protiv gorenja, nehalogena sredstva, usporivači gorenja, tekstil*

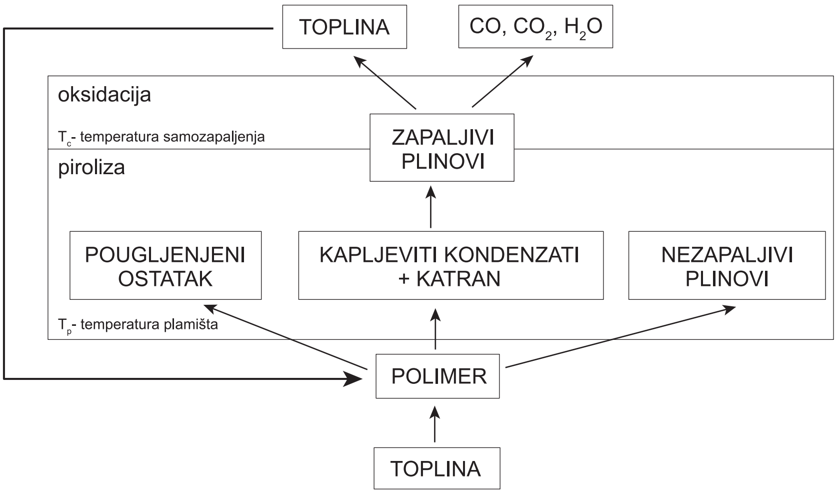
1. Uvod

Laka zapaljivost celuloznih tekstilnih materijala bio je problem kroz čitavu povijest, što je rezultiralo i prvim detaljnim istraživanjima početkom 19. i tijekom 20. stoljeća o tvarima kojima bi se oblagale pamučne, lanene i jutene tkanine, a koje bi spriječile ili barem usporile gorenje. Premda su sredstva bila vrlo učinkovita, glavni im je nedostatak bio nepostojanost na pranje [1, 2]. Tzv. zlatno razdoblje razvoja sredstava za obrade protiv gorenja započinje nakon II. svjetskog rata, kada su razvijena dva najznačajnija sredstva za obradu protiv gorenja, odnosno usporivača gorenja celuloznih materijala postojana na pranje koja su još i danas u upotrebi bez značajnije alternative [3]. Zbog niza ekoloških dvojbi u pogledu proizvodnje, uporabe i zbrinjavanja tekstilnih materijala obrađenih komercijalnim usporivačima gorenja (*engl. flame retardant – FR*) javlja se potreba za njihovom djelomičnom ili potpunom zamjenom novim ekološki povoljnijim sredstvima i/ili tehnološkim rješenjima. Naime, 2013. svjetska potrošnja usporivača gorenja bila je veća od 2 mil. t, a komercijalno najvažniji sektor primjene bio je građevinarstvo, u prvom redu u Aziji, SAD-u i EU [4].

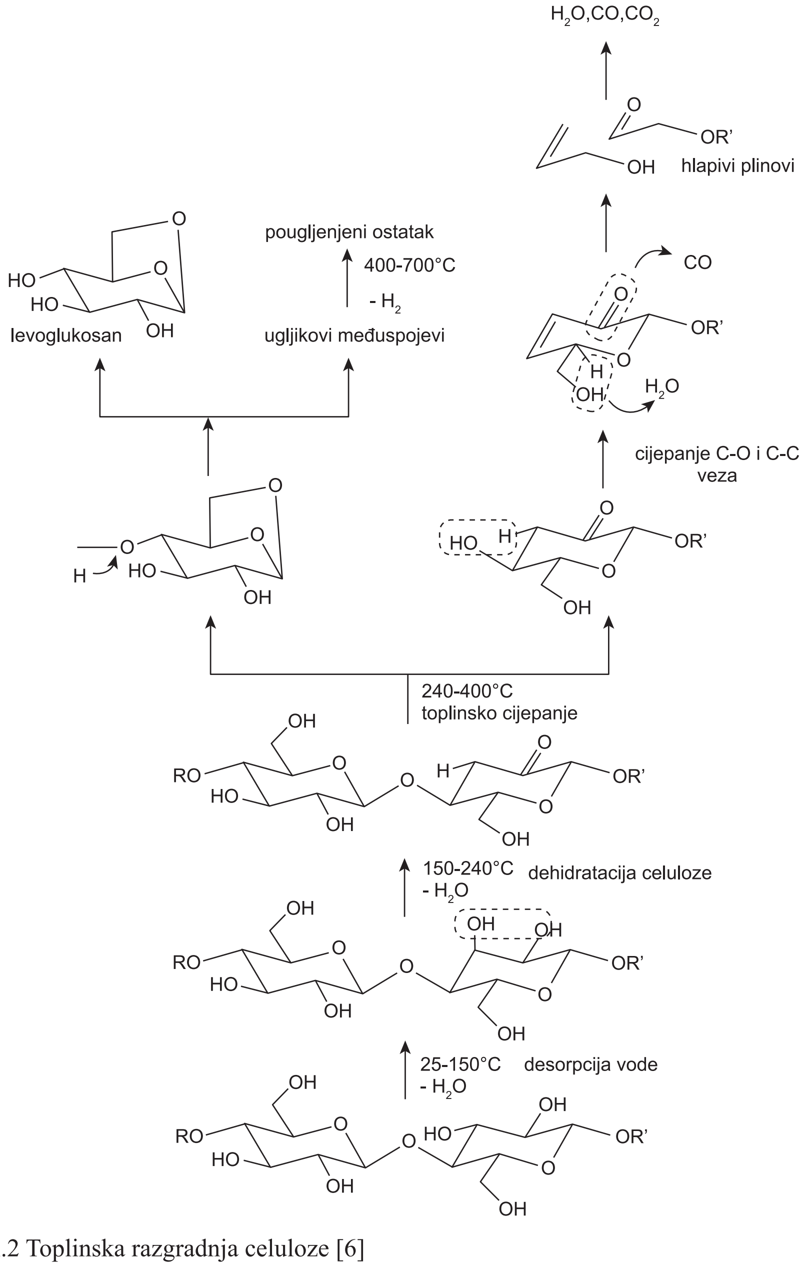
2. Zapaljivost tekstilnih celuloznih materijala i mehanizam djelovanja usporivača gorenja

Na gorenje tekstilnih materijala utječu fizikalni i kemijski čimbenici, sastav i struktura tekstilnog materijala, kao i okoliš, a ponašanje vlakana pri gorenju ovisi o temperaturama toplinskih prijelaza i termodinamičkim parametrima: temperatura staklastog prijelaza (T_g), temperatura mekšanja (T_m), temperatura plamišta (T_p), temperatura samozapaljenja (T_c), granični indeks kisika (LOI) i toplina izgaranja (ΔH_c). Mehanizam gorenja kao mehanizam povratne sprege (*engl. Feedback mechanism*) prikazan je na sl.1 [5].

Toplina koja se prenosi od izvora gorenja prema polimeru, odnosno vlaknu uzrokuje pirolizu (na T_p karakterističnoj za svako vlakno) u kojem se dugolančane polimerne molekule razgrađuju u niskomolekularne kapljevite kondenzate i katran, uz stvaranje pougljenjenog ostatka i nezapaljivih plinova. Kapljeviti kondenzati i katran (kondenzirana faza) se dalje



Sl.1 Mehanizam gorenja tekstilnih vlakana

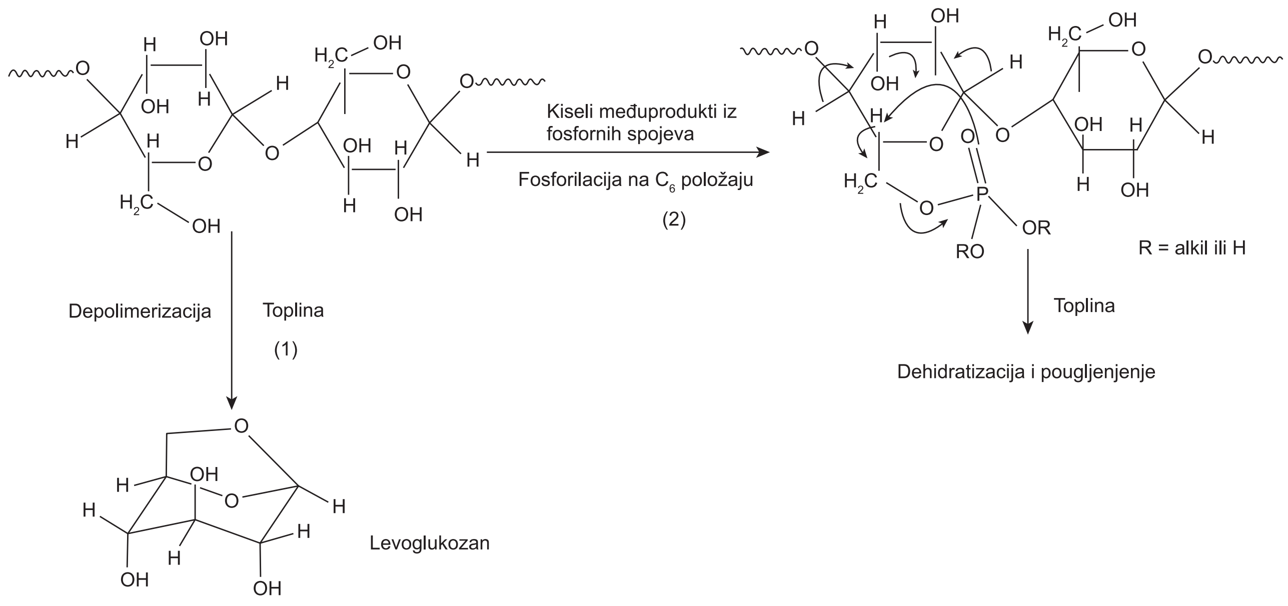


Sl.2 Toplinska razgradnja celuloze [6]

razgrađuju u male molekule zapaljivih plinova. Plinovi (plinovita faza) sa zrakom tvore zapaljivu smjesu u kojoj zapaljivi plinovi oksidiraju uz prisutnost kisika iz zraka (na temperaturi samozapaljenja T_c karakterističnoj za svako vlakno). Dio topline koji se oslobađa oksidacijom vraća se na polimer i izaziva nastavak pirolize. Oksidacija se pritom odvija na višim temperaturama od pirolize. Materijal, dakle, gori jedino ako tijekom pirolize nastaju zapaljivi plinovi. Oksidacijom nastaju slobodni radikali visoke energije ($R^{\cdot}$, $O^{\cdot}$, $H^{\cdot}$, $OH^{\cdot}$), koji potiču daljnju reakciju gorenja plinova. Produkti idealnog gorenja celuloze bi teoretski trebali biti voda i ugljični dioksid, no u stvarnosti nastaju i ugljični monoksid, policiklički aromatski ugljikovodici, cijanovodik itd. [5].

Na sličan način odvija se i toplinska razgradnja celuloze. Zagrijavanjem celuloze u zraku na temperaturama između 25 i 150 °C dolazi do desorpcije vode. Na temperaturama od 150 do 240 °C započinju dvije paralelne kemijske reakcije. Jedna je dehidratacija celuloze, koja dovodi do stvaranja primarnog pougljenjenog ostatka stabilnog na temperaturama od 400 °C do 600 °C uz stvaranje nezapaljivih plinova (voda, ugljični monoksid, ugljični dioksid), a druga je depolimerizacija na temperaturama između 240 i 400 °C kojom se cijepaju acetilne veze glukozidnih jedinica primarnog pougljenjenog ostatka uz stvaranje levoglukozana koji na temperaturama između 400 i 700 °C daje zapaljive plinove i potiče stvaranje sekundarnog pougljenjenog ostatka stabilnog na temperaturama od najmanje 800 °C [6].

Usporivači gorenja, odnosno sredstva za obrade protiv gorenja kemijskim i/ili fizikalnim djelovanjem usporavaju ili blokiraju proces gorenja za vrijeme pojedinih faza gorenja na način da uklanjaju dovod topline na polimer, blokiraju pristup kisiku, povećavaju stvaranje nezapaljivih plinova ili smanjuju stvaranje zapaljivih plinova i povećavaju stvaranje pougljenjenog



Sl.3 Toplinska razgradnja celuloze bez usporivača gorenja (1) i s usporivačem gorenja (2) na bazi fosfora [11]

ostatka djelujući u plinovitoj i kondenziranoj fazi. Često se ti mehanizmi djelovanja međusobno isprepliću [7, 8]. Usporivači gorenja, koji djeluju u plinovitoj fazi tijekom gorenja zapaljivih plinova, vežu se za slobodne radikale visoke energije ($R^{\cdot}$, $O^{\cdot}$, $H^{\cdot}$, $OH^{\cdot}$) nastale oksidacijom, stvarajući pritom stabilne nezapaljive plinove koji „guše“ plamen. Tako djeluju halogeni usporivači gorenja, metalni hidroksidi, usporivači gorenja na bazi fosfora i dušika [9].

Mehanizam usporavanja gorenja u kondenziranoj fazi očituje se međudjelovanjem polimera i usporivača gorenja na temperaturama nižim od temperature pirolize, te se odvija kroz dvije faze: dehidratacije i umrežavanja, odnosno stvaranja pougljenjenog ostatka, čime se smanjuje nastanak zapaljivih plinova te se ograničava pristup kisiku [10]. Na ovaj način djeluju usporivači gorenja na bazi fosfora te silikatni i silikonski usporivači gorenja.

Ako se celuloza obradi usporivačima gorenja na bazi fosfora (reakcija 2, sl.3), tijekom razgradnje na temperaturi nižoj od T_c dolazi do fosforilacije hidroksilne skupine na C_6 atomu koja uzrokuje dehidrataciju i pojačava pougljenjenje, čime se smanjuje ukupna količina zapaljivih plinova. Bez usporivača gorenja nastaje levoglukozan koji potiče stvaranje zapaljivih plinova na temperaturama višim od 400 °C [11].

Usporivači gorenja koji djeluju fizikalnim putem dijele se na:

1. anorganske soli koje se pod djelovanjem topline tale stvarajući sloj koji štiti površinu polimera od izvora topline,
2. toplinski nestabilne anorganske karbonate i hidrate koji pod djelovanjem topline otpuštaju ugljični dioksid i/ili vodu koja hladi polimer, te formiraju sloj koji štiti površinu polimera od izvora topline,
3. tvari dobre toplinske vodljivosti (metali) i materijali s promjenom faze (*eng. Phase-Change Materials - PCM*) koji apsobiraju velike količine topline tijekom razgradnje ili isparavanja, te otklanjaju toplinu s polimera prije nego što se postignu uvjeti za zapaljenje [12].

Anorganski usporivači gorenja uključuju metalne okside, zeolite, hidrokside, borate, stanate, anorganske fosforne spojeve (crveni fosfor i amonijev polifosfat) i grafit. Uglavnom se kombiniraju s halogenim usporivačima gorenja, te onima na bazi fosfora i/ili dušika [7, 8].

Usporivači gorenja na bazi fosfora (P) najučinkovitiji su ukoliko se kombiniraju sa dušikovim (N) spojevima, tzv. N-P sinergizam [13]. Postoji nekoliko teorija N-P sinergizma:

1. dušikovi spojevi (melamin, urea i njihovi derivati) otpuštaju dušik koji se veže za slobodne radikale visoke energije nastale oksidacijom, stvarajući pritom stabilne nezapaljive plinove koji „guše“ plamen (NO - dušikov monoksid, NO_2 - dušikov dioksid) [14, 15];
2. dušikovi spojevi olakšavaju reakciju fosforilacije fosfornih usporivača gorenja jer se vežu za fosforne usporivače gorenja tvoreći vezu između fosfora i dušika bolje toplinske stabilnosti nego veze između fosfora i kisika, te se time povećava zadržavanje fosfora i dušika u pougljenjenom ostatku [16].

U posljednjih deset godina pojavljuju se i bubreći usporivači gorenja, namijenjeni u prvom redu za zaštitu drva, plastike i metala, koji se nanose na površinu materijala, te pod utjecajem visoke temperature ekspandiraju formirajući pritom izolacijski vatrootporni sloj na površini materijala koji ga štiti od daljnje pirolize i gorenja. Ostatak nakon gorenja ima karakterističan pjenušavi izgled. Ovi sustavi djeluju u kondenziranoj fazi i uključuju vrlo složene međuovisne komponente. U bubrećem sustavu fosforni spoj (fosforna kiselina i njeni derivati, amonijev polifosfat) uzrokuje fosforilaciju polimera (sa C-O vezom) potičući njegovu dehidrataciju i pougljenjenje. Kapljeviti polimer se tijekom pougljenjenja pjeni zbog otpuštanja negorivih plinova (NO, NO_2) nastalih dekompozicijom dušikovih spojeva (melamina, uree, dicijandiamina itd.) [17].

3. Komercijalna sredstva za obradu protiv gorenja

Godina 1783. službeno se smatra godinom početka primjene prvog usporivača gorenja na pamuku. Te godine su, naime, braća Montgolfier svoje zračne balone naslojili aluminijem kako bi spriječili gorenje [18]. Početkom 20. st. Perkin je izradio i prvu sustavnu studiju usporivača gorenja celuloznih materijala, koja je bila u primjeni do 1950-ih godina, a uključivala je: amonijev klorid, amonijev fosfat, amonijev sulfat, zinkov klorid, kalcijev klorid, magnezijev klorid, aluminijev hidroksid, cinkov sulfat, natrijev borat, bornu kiselinu, magnezijev sulfat, natrijev klorid, natrijev silikat, silikatna kiselina, kalijev klorid, natrijev fosfat, aluminijev borat, aluminijev fosfat, kalcijev fosfat, magnezijev fosfat, cinkov borat, volframsku kiselinu, natrijev volframat, amonijev volframat i glinu. Glavni nedostatak ovih sredstava je nepostojanost na pranje [2].

1950-ih godina započinje tzv. zlatni period koji će potrajati sve do kasnih 1980-ih. U tom periodu komercijalizirani su postojani usporivači gorenja celuloznih materijala na bazi:

1. organofosfornih spojeva temeljenih na umrežavanju kondenzata tetrakis(hidroksimetil)fosfonijevih soli (THPX) i uree, trgovačkog naziva Proban®,
2. derivata N-alkil supstituiranih fosfonopropionamida (npr. MDPA - N-metiloldimetilfosfonopropionamid), odnosno reaktivni spojevi trgovačkog naziva Pyrovatex CP®,
3. antimon-organohalogenih spojevima: heksabromociklododekan (HBCD) + antimonov(III)-oksid i dekabromodifeniloksid (DECA) + antimonov(III)-oksid,
4. kloriranih parafinskih voskova [3, 8, 18].

Usporivači gorenja na bazi THPX i MDPA su i danas u upotrebi bez značajnije alternative, te se na tekstilni materijal nanose impregnacijom. Glavni im je nedostatak otpuštanje slobodnog formaldehida tijekom procesa kondenzacije, odnosno impregnacije tekstilnog materijala, kao i tijekom njegove uporabe. Kao zamjena za spojeve koji otpuštaju slobodni formaldehid, od 1980-ih do 2010-ih godina komercijalizirani su umreživači na bazi polikarboksilnih kiselina. Njihov glavni nedostatak je smanjenje čvrstoće obrađene tkanine, te utjecaj na ton obojena i na pH vrijednost obrađene tkanine u odnosu na neobrađenu [12]. Mehanizam djelovanja polikarboksilnih kiselina u obradama protiv gorenja pamučnih materijala detaljno je opisano u literaturi [19-25]. U tab.1 su navedena neka od sredstava bez sadržaja slobodnog formaldehida razvijenih u periodu od 1980-ih do danas [18, 26-29].

Usporivači gorenja celuloznih materijala budućnosti moraju zadovoljiti sljedeće uvjete:

1. moraju biti netoksični,
2. moraju biti ekonomski isplativi,
3. ne smiju mijenjati izgled, boju ili ton boje tkanine,
4. moraju jamčiti ugodan opip (hrapavost), zadovoljavajuću čvrstoću (prekidnu silu, prekidno istezanje), otpornost na habanje,
5. moraju biti postojani na 50 ciklusa pranja u alkalnom na visokim temperaturama, neovisno o tvrdoći vode,
6. ne smiju otpuštati formaldehid tijekom i nakon obrade tkanine,
7. obrađena tkanina ne smije izgubiti svojstvo propusnosti zraka zbog nanosa usporivača gorenja [30-33].

4. Alternativna sredstva

4.1. Biomakromolekule

Biomakromolekule ili biopolimeri su dugolančane molekule bitne za funkcioniranje svakoga živog bića. Obuhvaćaju nukleinske kiseline - polimere nukleotida (deoksiribonukleinska kiselina – DNK i ribonukleinska kiselina - RNK), a služe kao geni i posrednici u prijenosu genetičke infor-

Tab.1 Sredstva za obrade protiv gorenja razvijene u periodu od 1980.-tih do danas

- MDPA i limunska kiselina;
- N-hidroksimetil-3-dimetilfosfonpropionamid i butantetrakarboksilna kiselina (BTCA)/ limunska kiselina (CA);
- aminometilfosfonski diamid;
- trietilaminofosfonski oksidi;
- fosfat-fosfonat oligomer;
- hidroksifunkionaliziran organofosforni oligomer i multifunkcionalna karboksilna kiselina;
- hidroksialkilorganofosforni oligomer (Fyroltex®)/ trimetilamin/ dimetiloldihidroksietilen urea (DMDHEU);
- BTCA fosforilirana hidroksialkil organofosfornim oligomerom (Fyroltex®);
- BTCA fosforilirana hidroksialkil organofosfornim oligomerom (Fyroltex®) - trietanolamin (TEA);
- maleinska kiselina - natrijev hipofosfit;
- jantarna, jabučna, vinska kiselina - natrijev hipofosfit;
- oligomeri maleinske kiseline koji sadržavaju fosfor - natrijev hipofosfit - TEA;
- alkilfosforamidat stabiliziran amonijevim kloridom;
- diamonijev fosfat (DAP), fosforna kiselina (PA), tributilfosfat (TBP), trialilfosfat (TAP) i trialilfosfornitriamid (TPT);
- TBT - spojevi na bazi dušika (urea, guanidinkarbonat, melaminformaldehid);
- trietilfosfat (TEP) -dietilfosforamidat, -fosforamidna kiselina, N(2-hidroksietil) dietilester, -dietiletilfosforamidat ili -dietil 2-metoksietilfosforamidat

macije (biosintezi bjelančevina), zatim bjelančevine - polimeri peptida, a obavljaju najrazličitije funkcije u svakoj živoj stanici (enzimi, prijenosnici kisika i elektrona itd.), te polisaharide - polimere šećera, a služe kao građa (npr. celuloza, hitin) ili energetska zaliha u organizmu (škrob, glikogen) [34]. Najčešće primjenjivane biomakromolekule u obradama protiv gorenja tekstilnih materijala u laboratorijskim uvjetima su derivati hitina, proteini kazeina, sirutke, hidrofobini i DNK [35].

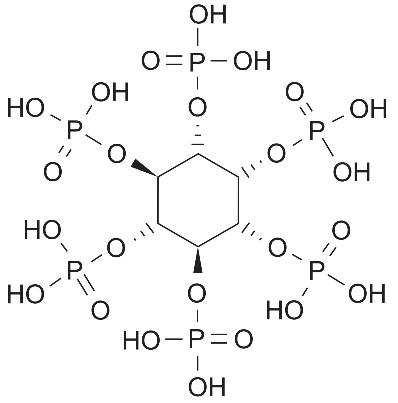
4.1.1. Hitosan

Hitosan je linearni polisaharid koji se sastoji od nasumično raspoređenih β(1→4)-D-glukozamina i N-acetil-D-glukozamina. Hitosan se komercijalno dobiva alkalnom deacetilacijom hitina, strukturalnog elementa oklopa ljuskara (rakova, škampa) i gljiva (šampinjona). Variranjem stupnja deacetilacije dobivaju se različita svojstva hitosana različitih primjena. Hitosan ima pKa vrijednost oko 6.5, zbog amino skupina u molekuli polimera, dok naboj ovisi o pH otopine i stupnju deacetilacije. Kao pozitivno nabijeni biopolimer u kiselom okruženju, hitosan je bioadhesivan i lako se veže na negativno nabijenu površinu [36, 37]. Biokompatibilan je i biorazgradljiv te dobrih antibakterijskih svojstava, što mu omogućuje široku primjenu u poljoprivredi za tretiranje sjemenja, kao biopesticid, u vinarstvu za finu filtraciju i bistrenje vina, u farmaciji za proizvodnju/prijenos inzulina, a isto tako i smanjuje apsorpciju masnoća (dijetalna prehrana). Hitosan je biopolimer sa tisuću lica zbog mogućnosti kemijskih modifikacija esterifikacijom, eterifikacijom, polimerizacijom cijepljenjem, fosforilacijom itd [38]. Hitosan je do sada pokazao dobra antibakterijska svojstva i svojstva usporavanja gorenja, te je u posljednih 10-ak godina zabilježen veliki broj znanstvenih radova o njegovoj primjeni na poliuretanskim (PU) pjenama i u tekstilu metodom impregnacije/iscrpljenja ili naslojavanja „sloj-po-sloj“ (*engl. Layer-by-layer LbL deposition*).

Teli i sur. su pokazali kako se dodatkom hitosana u klasičnim multifunkcionalnim obradama pamuka protiv gužvanja, gorenja i antibakterijskim obradama, smanjuje otpuštanje slobodnog formaldehida [39]. Postupkom fosforilacije u kupelji s diamonijevim hidrogenfosfatom (DAPH), natrijevim hipofosfitom (SHP) i 1,2,3,4-butantetrakarboksilnom kiselinom (BTCA) kao umreživačem dobiva se hitosanski fosfat koji zbog dušične komponente u sinergiji s fosforom daje dobra FR svojstva pamuka. Pritom se s povećanjem koncentracije DAPH-a povećava i postojanost FR obrada pamuka na pranje [40]. El-Tahlawy i sur. su kombinirali natrijev stanat i hitosan u obradama protiv gorenja pamuka. Pritom su upotrijebili hitosan (CH), limunsku kiselinu (CA), natrijev hipofosfit (SHP), diamonijev hidrogenfosfat (DAHP) i natrijev stanat ($NaSnO_3$). U prisustvu DAHP-a dolazi do reakcije fosforilacije s hidroksilnim skupinama celuloze i aminoskupinama hitosana, te se stvara fosforilirana celuloza i hitosanski fosfat. Limunska kiselina umrežuje hitosanski fosfat i celulozu, a istovremeno djeluje i protiv gužvanja pamuka. Ona također otapa hitosan stvarajući topljive hitosanlimunske soli. Natrijev stanat daje odlična FR svojstva, no krut je na dodir, zahtijeva veliku koncentraciju DAHP-a i uree, te nekoliko stupnjeva umrežavanja [41]. El-Shafei i sur. su eksperimentirali multifunkcionalnim FR i antibakterijskim obradama pamuka protiv gužvanja upotrebom titanovog dioksida (TiO_2) nanočestica, hitosanovog fosfata, BTCA, natrijevog hipofosfita (SHP) kao katalizatora. Hitosan kao derivat hitina pokazao je dobra svojstva otpornosti na gorenje u kombinaciji s fosfornim spojevima zbog N-P sinergije uz istovremeno antibakterijsko djelovanje. On može smanjiti količinu komercijalnih organofosfornih spojeva, a također se pokazalo da smanjuje otpuštanje slobodnog formaldehida u klasičnim formulacijama sredstava za obrade protiv gorenja [42].

4.1.2. Fitinska kiselina

Fitinska kiselina se u prirodi nalazi u mekinjama žitarica, sjemenki i grahorica, kao i u orašastim plodovima u obliku fitina, sl.4. Nije probaljiva za ljudski organizam, a na OH skupine vrlo lako veže po život važne minerale kao što su kalcij, magnezij, željezo i cink. Njeno djelovanje može biti štetno jer inhibira enzime potrebne za probavu bjelančevina i škroba, čime minerale i fosfor čini nedostupnima za ljudski organizam, no svejedno je na neki način sveprisutna u organizmima sisavaca i smatra se da ima veliku ulogu u „popravku“ mutirane DNK. Pa ipak, o ulozi fitinske kiseline u organizmima zna se vrlo malo. Fitinska kiselina i njene soli dobivaju se ekstrakcijom mekinja bogatih fitinom vodenim otopinama sulfatne ili kloridne kiseline, precipitiranima natrijevim hidrogenkarbonatom i pročišćenima ekstrahiranjem u eteru iz otopine kloridne kiseline. U prehrambenoj industiji se upotrebljava kao konzervans E391 [43]. Budući da u svojoj strukturi sadrži fosfor i OH skupine koje na sebe vrlo lako vežu metale i druge organske spojeve, idealna je za obrade protiv gorenja koja bi u teoriji mogla zamijeniti amonijeve polifosfate. Do sada je objavljen mali broj znanstvenih radova u kojima je upotrijebljena fitinska kiselina u obradama protiv gorenja. Laufer i sur. su primijenili polielektrolitne otopine fitinske kiseline i hitosana LbL metodom na pamuku [44]. Wang i sur. su pamučnu tkaninu



Sl.4 Fitinska kiselina

obradili fitinskom kiselinom i hibridom silana [45].

4.1.3. Proteini - kazein, hidrofobini i sirutka

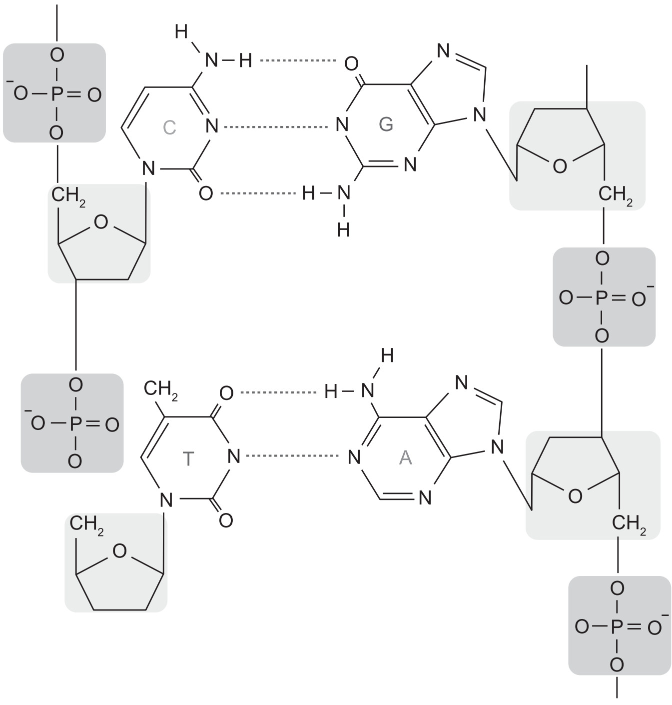
Kazein je fosforom bogat protein koji nastaje kao nusprodukt u proizvodnji potpuno obranog mlijeka, te čini 80 % mliječnih proteina. Sastoji se od αs1-kazeina, αs2-kazeina, β-kazeina i Ƙ-kazeina [46]. Osim u proizvodnji sira, kazein se tradicionalno upotrebljava za proizvodnju emulgatora, vezivnih sredstava, u proizvodnji papira, doradi kože, u proizvodnji vlakana itd [47]. Hidrofobini su prirodni površinski aktivni proteini male molarne mase bogati sumporom (cisteini) koji se nalaze u površinskim izlučevinama stijenki gljiva oblikujući monoslojeve. Pokazuju amfifilna svojstva, što znači da ovisno o okolini u kojoj se nalaze od hidrofobnih dobivaju hidrofilna svojstva. Pojavljuju se u dvije različite kristalne strukture klasa I i klasa II. Klasu I čine stabilni teško topljivi polimerni monoslojevi sastavljeni od fibrilarnih štapićastih struktura koje se otapaju jedino u jakim kiselinama. Proces je reverzibilan, što znači da se štapići pod određenim uvjetima vrlo brzo ponovno polimeriziraju. Klasu II hidrofobina čine polimerni monoslojevi bez fibrilarne štapićaste strukture dobro topljivi u organskim otapalima i deterdžentima. Hidrofobini smanjuju površinsku napetost supstrata na kojem gljiva raste omogućavajući joj interakciju sa zrakom i vodom. Drugim riječima, sporama gljiva omogućavaju raspršivanje u zraku i otpornost na vlagu, te vezivanje za pogodno tlo, a jednom kada se spora veže, omogućavaju joj dovod vlage/vode, rast i daljnje razmnožavanje. Smatra se također da hidrofobini imaju veliku ulogu u deaktivaciji imunološkog sustava domaćina na kojem gljiva raste. Hidrofobine je vrlo teško proizvesti u obliku primjerenom za laboratorijsku ili industrijsku primjenu [48]. U posljednje vrijeme pronalaze primjenu u sredstvima za pjenjenje i nanokapsuliranje aktivnih tvari u farmaceutskoj i prehrambenoj industriji [49]. Alongi i sur. su impregnirali pamučne tkanine vodenom suspenzijom kazeina i otopinom hidrofobina, te su usporedili njihove termogravimetrijske (TG) krivulje s krivuljama neobrađenog pamuka, kao i pamuka obrađenog amonijevim polifosfatom (APP). Pamučni uzorci obrađeni kazeinom/hidrofobinom pokazali su dobra i gotovo identična FR svojstva, no znatno lošija u odnosu na uzorke obrađene APP-om [50]. Carosio i sur. su dokazali da kazein ima utjecaj na FR svojstva čistog pamuka i čistog poliestera (PES), no da istovremeno nema nikakvog utjecaja na mješavine pamuka/PES-a [51].

Proteini sirutke čine 20 % mliječnih proteina, slični su građi α-heliksa u kojem se izmjenjuju kiselo/bazne i hidrofobno/hidrofilne aminokiseline sa sadržajem sumpora unutar polipeptidnog lanca (metionin, cistein). Glavni sastojci sirutke su β-laktoglobulin, α-laktalbumin, serum albumin i imunoglobulin. Zbog amfifilnih svojstava upotrebljavaju se u proizvodnji emulgatora. Bosco i sur. su proučavali utjecaj denaturiranja proteina sirutke na FR svojstva pamuka. Denaturacija je narušavanje prirodne strukture proteina (i nukleinskih kiselina) izazvana povišenom temperaturom, zračenjem, mehaničkim faktorima, solima teških metala ili djelovanjem jakih kiselina i lužina. Dokazali su da denaturacija proteina sirutke nema nikakvog utjecaja na FR svojstva obrađenog pamuka [52].

4.1.4. Deoksiribonukleinska kiselina (DNK)

Deoksiribonukleinska kiselina je polimer nukleotida koji su građeni od pentoze deoksiriboze, fosfatne skupine i dušične baze koja kod DNK može biti adenin (A), gvanin (G), timin (T) i citozin (C).

„Kralježnica“ je izgrađena od polisaharidnih i fosfatnih skupina povezanih esterskim vezama. DNK sadrži, dakle, sve tri komponente bubrećeg FR sustava u samo jednoj molekuli - fosfatne skupine koje mogu razviti fosfornu kiselinu, deoksiribozu sa C-O vezama koje mogu dehidratirati i razviti pougljenjeni ostatak, te spojeve dušika (adenina, gvanina, citozina i timina), sl.5. Tijekom zagrijavanja fosfatne skupine unutar DNK stvaraju fosfornu kiselinu koja oslo-



Sl.5 Struktura deoksiribonukleinske kiseline DNK [53]

bađa vodu uz dehidrataciju i pougljenjenje. Istovremeno dušikove baze stvaraju amonijak koji zaustavlja gorenje i reagira s kapljevitim polimerom pritom stvarajući zaštitni sloj na materijalu [54]. Izvori dobivanja pročišćene DNK su sperma i ikra bakalara i haringe. Alongi i sur. su prvi put impregnirali DNK na pamučni materijal kao sredstvo za obradu protiv gorenja [55]. Carosio i sur. su upotrijebili hitosan/DNK u LbL naslojavanju na pamuku [56]. Alongi i sur. su uspoređivali FR svojstva DNK, kazeina i amonijevog polifosfata (APP), a dobiveni rezultati pokazali su da APP postiže neusporedivo najbolje rezultate, nakon čega slijedi DNK [54]. Međutim, veliki nedostatak svih ovih ekološki prihvatljivih obrada je nepostojanost na pranje, čak i na 30 °C bez upotrebe deterdženta [57].

Tab.2 Primjena prekursora u sol-gel postupcima obrade protiv gorenja

Tip sustava	Prekursor
anorganski metalni alkoksidi	– tetraetilortosilikat (TEOS) – tetrametilortosilikat (TMOS) – tetrabutilortosilikat (TBOS) – alkoksilan s različitim brojem hidroliziranih skupina, – tetraetilortotitanat, – tetraetilortocirkonat, – aluminijev isopropilat, – TMOS + mikro i nanočestice aluminija
anorgansko-organski hibridi na bazi N-P sustava	– TMOS + aluminijev fosfinat, – TMOS + aluminijev fosfinat/melamin(poli)fosfat/cinkov oksid/boronov oksid, – TMOS + α-cirkonijev fosfat, – TEOS + H_3PO_4 ili etildiklorofosfat, – dietilfosfatoetiltrietoksisilan (DPTES) – DPTES + 3-aminopropiltrietoksisilan (APTES) ili APTES i smola na osnovi melamina, – DPTES + 1-hidroksietan 1,1-difosfonska kiselina, – DPTES + N,N,N´,N´,N″,N″-heksakismetoksimetil-[1,3,5]triazin-2,4,6-triamin, – DPTES + urea, – natrijev metasilikat + urea/amonijev dihidrogenfosfat – DPTES/APTES (3-aminopropiltrietoksisilan)+ melamin/urea

5. Postupci nanošenja usporivača gorenja na celulozne tekstilne materijale

Usporivači gorenja se na celulozne tekstilne materijale nanose postupkom impregnacije i sušenja (*engl. Pad – Dry*) ili naslojavanjem na naličju (*engl. Back – Coating*). Impregnacijom se materijal potpuno uroni u kupelj sa usporivačima gorenja, ocijedi i osuši, no nakon takvih obrada materijal može postati krut, neugodnog opipa, a često gubi čvrstoću i elastični oporavak. Naslojavanje označava postupak u kojem se usporivač gorenja nanosi na površinu materijala, ne prodire u njegovu strukturu i zadržava njegova osnovna i poželjna svojstva (u slučaju pamuka udobnost, dobru apsorpciju vlage itd.). U posljednjih nekoliko godina impregnacija se svrstava u kategoriju 1-slojnog naslojavanja. Od površinskih funkcionalizacija celuloznih tekstilnih materijala u industrijskoj su primjeni jedino impregnacija i naslojavanje na naličju, i to isključivo nebubrećim sredstvima za obrade protiv gorenja. U posljednjih se nekoliko godina eksperimentira i sljedećim nanotehnologijama:

1. adsorpcija nanočestica,
2. sol-gel postupak naslojavanja,
3. obrade plazmom,
4. naslojavanje sloj-po-sloj (*engl. Layer-by-Layer deposition*) [18, 58].

5.1. Adsorpcija nanočestica

Adsorpcija nanočestica je jednostavan, brz i jeftin, no ne i trajan postupak u kojem se tkanina impregnira u stabilnoj vodenoj suspenziji nanočestica, a vezivanje se temelji na ionskoj interakciji negativno nabijenog tekstilnog supstrata i pozitivno nabijene nanočestice. Adsorpcija nanočestica se danas svrstava u kategoriju 1-slojnog naslojavanja. U literaturi se spominju:

- prirodni i sintetski zeoliti (montmorilonit, klinoptilolit),
- nanoglina (karbonatni hidrotalcit, sulfonatni bohemit),
- nanočestice (cinkov oksid, titanijev dioksid, silicijev dioksid, oktapropilamonijev polihedralni oligomerni silseskvioksan (POSS®) [18, 59-64].

5.2. Sol-gel postupak

Sol-gel postupak je jednostavan, jeftin i ekološki prihvatljiv postupak sinteze homogenih anorganskih metalnih oksida, kao i organsko-anorganskih hibrida (*engl. dual-cure sol-gel*) dobrih mehaničkih, optičkih, električnih i toplinskih svojstava na temperaturama nižim od 100 °C. Postupak obuhvaća reakcije hidrolize i kondenzacije metalnih alkoksida (prekursora) pri čemu iz koloidne otopine (sol) nastaje kruti gel s neprekinutom trodimenzijskom metaloksidnom mrežom uz kiselinu ili bazu kao katalizator [65]. Postupak nanošenja sredstava sol-gel postupkom na tekstilnom materijalu započinje hidrolizom prekursora. Hidrolizirani prekursor se zatim dodaje u kupelj s organskim usporivačima gorenja kojom se zatim impregnira tekstilni materijal. Nakon impregnacije slijedi sušenje i kondenzacija, prilikom čega nastaje kruti gel na materijalu [66]. U tab.2 su navedeni neki od prekursora koji se koriste u ovim postupcima [18, 66-69].

5.3. Obrade plazmom

Obrada hladnom plazmom je postupak kojim se funkcionalne skupine i makromolekule cijepe (*engl. grafting*) na polimer vlakna, i to na površini tekstilnog materijala bez modifikacije u unutrašnjosti:

1. jetkanjem (*eng. etching*) površine materijala i/ili funkcionalizacijom pomoću nepolimerizirajućih plinova (N_2, H_2, O_2, Ar, NH_3, CO_2 itd.)
2. sintezom kopolimera cijepljenjem nehlapljivih vrsta fosfora u hladnoj plazmi,
3. polimerizacijom (taloženjem) organosilikonskih spojeva pomoću plazme,
4. upotrebom hladne N_2 plazma tehnike,
5. upotrebom akrilnih monomera za sintezu kopolimera cijepljenjem [58].

Primjenom hladne plazme u obradama protiv gorenja celuloznih tekstilnih materijala postižu se zadovoljavajuće vrijednosti granične vrijednosti kisika (engl. Limiting Oxygen Index) čak i nakon 50 ciklusa pranja (27 %), no ovaj postupak još uvijek ne nalazi široku industrijsku primjenu zbog visokih troškova investicija u odnosu na postojeće komercijalne postupke obrada protiv gorenja, kao i na visoku cijenu gotovog proizvoda [70, 71].

5.4. Naslojavanje sloj-po-sloj

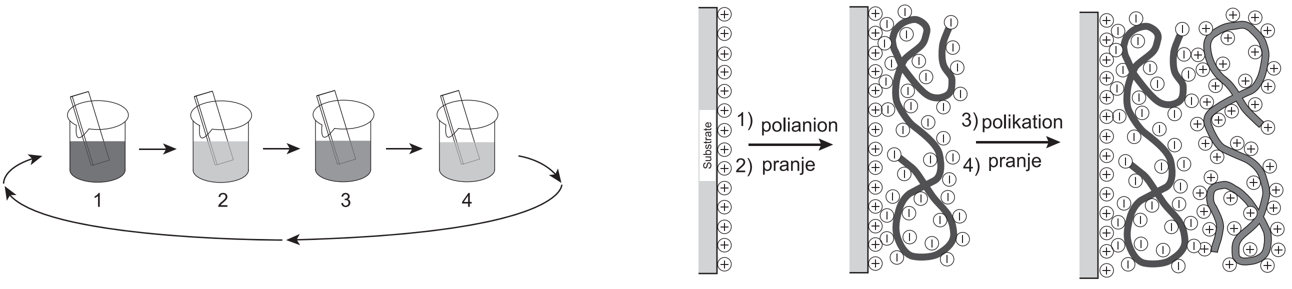
Naslojavanje sloj-po-sloj (*engl. Layer-by-Layer deposition – LbL*) predstavlja površinsku adsorpciju dugolančanih molekula polielektrolita jednog naboja (+) na kruti supstrat suprotnog naboja (-). Zatim slijedi faza ispiranja deioniziranom vodom. U drugoj fazi se pozitivno nabijeni polielektrolit veže na negativno nabijeni polielektrolit, sl.6. I tako naizmjence [72].

Na taj način moguće je slagati nekoliko slojeva jednakih ili potpuno različitih elektrolita jedan na drugi kao dvostruki (*eng. Bilayer - BL*), trostruki (*eng. Trilayer - TL*) i četverostruki slojevi (*eng. Quadlayer - QL*).

Tab.3 LbL sustavi u obradama protiv gorenja

Pamuk	
BPEI/CH/PSP	BPEI – razgranati polietilenimin; CH – hitosan; PSP – natrijev polifosfat
BPEI+urea+ DAP/kaolin	BPEI – razgranati polietilenimin; DAP – diamonijev fosfat
BPEI/kaolin	BPEI – razgranati polietilenimin
BPEI/PAA-P/AA	BPEI – razgranati polietilenimin; PAA-P – fosfonatni poli(alilamin); AA – oligoalilamin
CH/PA	CH – hitosan; PA – fitinska kiselina
CH/APP	CH – hitosan; APP – amonijev polifosfat
CH/PSP	CH – hitosan; PSP – natrijev polifosfat
FR-PAA/MMT	FR-PAA – aminoderivirana poli(akrilna kiselina); MMT – montmorilonit
FR-PAM/GO	FR-PAM – FR derivat poliakrilamida; GO – grafenov oksid
BPEI/PSP/PAA	BPEI – razgranati polietilenimin; PSP – natrijev polifosfat; PAA – poli(alilamin);
SiN/PA	SiN – hibrid silana modificiran dušikom i dobiven prekursor – kondenzacija postupkom; PA – fitinska kiselina
CH/PT	CH – hitosan; PT – fosforilirani hitin
CH/PCL	CH – hitosan; PCL – fosforilirana celuloza
CH/DNK	CH – hitosan; DNK – deoksiribonukleinska kiselina
AP/-POSS	AP – aminopropilsilseskvioksan; -POSS – oktakis(tetrametilamonij) pentaciklo$[9.5.1.1.^{3,9}.1^{5,15}.1^{7,13}]$oktasiloksan1,3,5,7,9,11,13, 15-oktakis(siloksid)hidrat
+POSS/-POSS	+POSS – okta(3-amonijpropil)oktasilseskvioksanoktaklorid -POSS -oktakis(tetrametilamonij)pentaciklo$[9.5.1.1.^{3,9}.1^{5,15}.1^{7,13}]$ oktasiloksan1,3,5,7,9,11,13,15-oktakis(siloksid)hidrat
BPEI/MMT	BPEI – razgranati polietilenimin; MMT – montmorilonit
BPEI/-SiO_2	BPEI – razgranati polietilenimin -SiO_2 – negativno nabijeni silicijev dioksid
-Al_2O_3/+Al_2O_3, uz kationizaciju pamuka	-Al_2O_3 – anionska koloidna otopina aluminijevog oksida +Al_2O_3 – kationska koloidna otopina aluminijevog oksida
-Ag/PDDA	-Ag – anionska koloidna otopina srebrnih nanočestica PDDA – poli(dialildimetilamonijev klorid
CH/TNT	CH – hitosan; TNT – titanske nanocjevčice
Ramija	
DMF + MWNT-NH_2/APP	DMF – N,N- dimetilformamid; MWNT-NH_2 – aminofunkcionalizirane višeslojne ugljikove nanocjevčice; APP – amonijev polifosfat
BPEI-$CuSO_4$ /PVPA	BPEI – razgranati polietilenimin; $CuSO_4$ – bakarni sulfat; PVPA – poli(vinilfosfonska) kiselina
BPEI-$ZnCl_2$ /PVPA	BPEI – razgranati polietilenimin; $ZnCl_2$ – cinkov klorid; PVPA – poli(vinilfosfonska) kiselina

LbL naslojavanje se u eksperimentalnoj fazi ispituje na obradama protiv gorenja tekstilnih materijala upotrebom različitih sredstava protiv gorenja. Glavni nedostatak ove metode je nepostojanost obrade protiv gorenja



Sl.6 Shematski prikaz metode taloženja sloj-po-sloj (LbL) [72]

na pranje, budući da se vezanje polielektrolita temelji na elektrostatskim vezama ili H-vezama. Nešto bolji rezultati postignuti su naknadnim obradama UV umrežavanjem. Prednost u odnosu na ostale metode je jednostavnost postupka, mogućnost kontrole broja, debljine i homogenosti slojeva (što ovisi o odabiru i koncentraciji polielektrolita, pH otopine, dodatnoj ultrazvučnoj obradi itd.), kao i upotreba ekoloških otapala - vode [58]. LbL naslojavanje se u laboratorijskim uvjetima provodi sljedećim tehnikama:

1. uranjanjem (*engl. dipping*),
2. horizontalnim ili vertikalnim prskanjem (*engl. spraying*) [73].

U literaturi je nađen mali broj radova u kojima se ispituju mogući komercijalni pristupi kontinuiranog industrijskog postupka LbL naslojavanja na tekstilnom materijalu metodom uranjanja [74, 75]. LbL naslojavanje se do sada primijenilo na sljedećim celuloznim vlaknima: pamuk, ramija, sisal, a upotrijebljeni kationsko-anionski ili anionsko-kationski BL, TL i/ili QL sustavi prikazani su u tab.3 [44, 45, 56, 74-91].

6. Toksikologija

Američka nacionalna akademija znanosti je 2000. objavila opsežnu studiju o toksikološkim rizicima upotrebe komercijalnih sredstava za obrade protiv gorenja. Studijom su obuhvaćena sva do tada poznata sredstva, pa tako i ona koja se upotrebljavaju u tekstilnoj industriji. Studija je pokazala da sredstva za obrade protiv gorenja u većoj ili manjoj mjeri ometaju rad imunološkog sustava i endokrilnog sustava, izazivaju neurološke promjene na mozgu, te fizičke malformacije ploda, zaostajanje u rastu i razvoju, depigmentaciju kože, inhibiraju rad enzima, izazivaju spontane pobačaje, gastroenterološke probleme, potencijalno su kancerogena, pa čak i oštećuju DNK strukturu. Toksikološka studija iz 2000. pokazala je da su najštetnija sredstva za obrade protiv gorenja tekstilnih materijala ona na bazi halogenih, organo halogenih i antimonovih organohalogenih spojeva. Komercijalna sredstva na bazi organofosfornih spojeva smatrana su do 2000. sigurnima za upotrebu [92]. Van der Veen i de Boer su 2012. objavili pregledni rad o toksičnosti samo nekih organofosfornih sredstava za obrade protiv gorenja, u kojem se navodi sljedeće:

1. Bisfenol-A difenilfosfat se zbog nedostatka podataka o njegovim razinama u okolišu, a na osnovi ispitivanja *in vivo*, za sada ne smatra toksičnim, no može izazvati iritaciju kože i očiju,
2. Trifenilfosfat je manje ili više neurotoksičan, može izazvati alergije, ometa rad imunološkog i endokrinog sustava, toksičan je za vodene organizme, zaustavlja rast algi,
3. Difenilcresilfosfat može izazvati iritaciju kože i očiju, toksičan je za vodene organizme, izaziva reproduktivne i razvojne probleme, no zbog nedostatka podataka za sada se smatra sigurnim,
4. Melamin-polifosfat može izazvati iritaciju očiju, toksičan je na alge, no zbog nedostatka podataka, za sada se smatra sigurnim za upotrebu,
5. Dietilfosfinska kiselina može izazvati iritaciju očiju, toksična je na alge, no zbog nedostatka podataka se za sada smatra sigurnom za upotrebu,
6. Tricresilfosfat je neurotoksin, reproduktivni toksin, toksičan za vodene organizme [93].

Europsko udruženje za fosforna, anorganska i dušična sredstva za obrade protiv gorenja, a koje čine Chemische Fabrik Budenheim, Ciba Inc. (koja je sada dio BASF-a), Clariant Produkte (D) GmbH, Italmatch Chemicals S.p.A., Lanxess Deutschland GmbH i Nabaltec AG., je 2009. izdalo kratki pregled o nehalogenim sredstvima za obrade protiv gorenja, u kojem se navodi da su nehalogeni organofosforni spojevi sasvim sigurni za upotrebu, odnosno da nisu bioakumulativni, toksični, kancerogeni ili mutageni, budući da je fosfor neophodan kemijski element kod ljudi, životinja i biljaka, te je glavna komponenta kostiju i DNA. U izvješću se čak navodi i primjer jedne studije slučaja u Japanu, u kojoj se fosfor u obliku fosforne kiseline u pepelu reciklira za mineralno gnojivo. Europska komisija, dakle, nema službenih procjena rizika nehalogenih sredstava za obrade protiv gorenja jer ona nisu stavljena na tzv. listu prioriteta kemikalija koje su bile temelj za obavljanje procjene rizika u Europi [94].

Sljedeći problem obrada protiv gorenja, prije svega celuloznih materijala, je otpuštanje slobodnog formaldehida tijekom proizvodnje i upotrebe. Da bi se, naime, sredstvo za obradu protiv gorenja na bazi organofosfornih spojeva trajnije vezalo za celulozno vlakno, potreban je umreživač na bazi formaldehida (fenolformaldehid, ureaformaldehid, melaminformaldehid) koji se tijekom proizvodnje i upotrebe postupno otpušta. Međunarodna agencija za istraživanje raka Svjetske zdravstvene organizacije označava formaldehid kao kancerogen (izaziva rak nazofarinksa i leukemiju) [95]. Zbog potencijalne ili dokazane toksičnosti intenzivno se eksperimentira novim alternativnim sredstvima i/ili tehnološkim rješenjima koja bi djelomično ili u potpunosti zamijenila sva do sada postojeća komercijalna sredstva za obrade protiv gorenja.

7. Zaključak

Da je laka zapaljivost i gorivost tekstilnih materijala bio problem s kojim su se susretali ljudi od davnina, govori podatak da je već krajem 18. stoljeća izrađena detaljna studija o tvarima kojima bi se mogle oblagati pamučne, lanene i općenito celulozne tkanine koje se koriste za izradu balona, kazališnih zastora itd., a koje bi spriječile ili barem usporile gorenje. Radilo se o sredstvima koja su se mogla pronaći u prirodi na bazi metalnih soli i gline, vrlo učinkovitih, no i potpuno nepostojanih na pranje. Nakon II. svjetskog rata i procvatom kemijske industrije, pojavila su se i vrlo obećavajuća sredstva na bazi halogenih i halogenfosfornih spojeva odličnih FR svojstava, te postojanih na pranje. Nakon desetljeća komercijalne upotrebe počele su se javljati osnovane sumnje da se radi o potencijalno štetnim kemikalijama za okoliš. Prije 15 godina dokazana je njihova iznimna toksičnost (ometanje rada endokrinog i imunološkog sustava, neurotoksičnost, kancerogenost, inhibicija rada enzima, spontani pobačaji, malformacije ploda, fizička i mentalna zaostalost itd.). Sredstva su u nekim zemljama zabranjena, a u nekima je ograničena njihova upotreba. Organofosforni spojevi se za sada smatraju sigurnima za upotrebu. U posljednjih desetak godina intenzivno se eksperimentira novim alternativnim ekološki povoljnim sredstvima i/ili tehnološkim rješenjima koja bi djelomično ili u potpunosti zamijenila sva do sada postojeća komercijalna sredstva za obrade protiv gorenja. Jedan od pravaca bi mogao biti i primjena biomakromolekula kao što su hitosan, fitinska kiselina, kazein, sirutka, hidrofobini i DNK.

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SUMMARY

Non-halogen FR treatments of textiles

E. Magovac, S. Bischof

The paper gives a historical overview of the most commonly used textile flame retardants, with emphasis on halogen-free FRs with the mechanism of their action to slow down or prevent burning. Since a large number of halogen FRs are toxic or potentially toxic to organisms and environment, there is a need for their replacement by eco-friendly agents. The paper presents new alternative FRs that should be put into practice, as well as different methods of their application onto the textile in comparison to one another. One of the possible ways of development of alternative FRs could be the application of bio-macromolecules such as chitosan, phytic acid, casein, whey, hydrophobins or DNA.

Key words: FR treatment, non-halogen agents, fire retardants, textile

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Halogenfreie flammhemmende Behandlungen von Textilien

Der Artikel gibt einen historischen Überblick über die am meisten verwendete Flammschutzmittel zur Behandlung von Textilien aus Zellulose. Es wird dargestellt, wie man die Verbrennung verlangsamen kann. Da zahlreiche Halogen enthaltende Mittel für Organismen und Umwelt toxisch oder potentiell toxisch sind, ist es erforderlich, sie durch umweltfreundliche Mittel zu ersetzen. Alternative Mittel, die in die Praxis eingeführt werden sollen, werden auch vorgestellt. Darüber hinaus werden unterschiedliche Auftragsmethoden von Flammschutzmitteln dargestellt und gegenübergestellt. Eine der möglichen Richtungen der Entwicklung von alternativen Flammschutzmitteln könnte die Verwendung von Biomakromolekülen wie Chitosan, Phytinsäure, Kasein, Molke, Hydrophobine oder DNS sein.

Non-halogen FR treatment of cellulosic textiles

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Review

A historical overview of the most commonly used textile flame retardants (FR) is given, with an emphasis on halogen-free FRs acting through their mechanism to slow down or prevent burning. Since a large number of halogen FRs are toxic, or potentially toxic, to the organisms and the environment, there is a need for them to be replaced by eco-friendly agents. The paper presents new alternative FRs that are trying to be put into practice, as well as different methods of their application onto textiles in comparison to one another. One of the possible ways of developing alternative FRs could be the application of bio-macromolecules such as chitosan, phytic acid, casein, whey, hydrophobins or DNA.

***Key words**: FR treatment, non-halogen agents, textile*

1. Introduction

Cellulosic textile materials have always been prone to easy burning, and it has been a problem throughout the history of humankind. This was why the first systematic studies were started in the 19th and 20th centuries concerning the substances which could coat cotton, linen and jute fabrics, so as to prevent, or at least retard, burning. The substances tested were quite effective; however, their main disadvantage was they were not resistant to washing [1, 2]. So called golden period in the development of flame retardants and procedures started after the World War II, when two most important flame retardants for cellulosic fabrics were developed, both of them resistant to washing, and both of them used even today, with no important alternative [3]. Due to a number of environment-protection issues regarding the manufacture, use and disposal of textile materials treated with commercial flame retardants, a need arose to substitute them partially or completely with new alternative and more environment-friendly agents and/or technological solutions. As statistics show, the consumption of FRs globally was more than 2 million tons in 2013, with commercially outstanding sectors of building and construction, primarily in Asia, the USA and the European Union [4].

2. Flammability of cellulosic textiles and mechanisms of FRs functioning

Textile material flammability is affected by numerous physical and chemical factors, by the content and structure of the material, as well as by the environment, while fibre behaviour in burning depends upon the temperatures of thermal transitions and thermodynamic parameters: glass transition temperature (T_g), melting temperature (T_m), pyrolysis temperature (T_p), combustion (oxidation) temperature (T_c), limiting oxygen index (LOI) and heat of combustion (ΔH_c). The mechanism of burning as a feedback mechanism can be seen in Fig. 1 [5].

The heat that is transferred from the source of flame towards the polymer results in pyrolysis (at T_p specific for a particular fibre), where long-chain polymer molecules are split into low-molecular liquid condensates and tar, with char residue and non-flammable gases. Liquid condensates and tar (condensed phase) are further split into small molecules of flammable gases. The gases (gaseous phase) form, together with the air, a flammable mixture, where flammable gases are oxidised with the oxygen from the air (at T_c characteristic for a particular fibre). A part of the heat released by oxidation returns to the polymer and causes pyrolysis to continue. In this case, oxidation temperature is higher than pyrolysis temperature. The material burns, as can be seen, only if flammable gases are generated in the course of pyrolysis. Oxidation generates free radicals of high energy ($R^{\cdot}$, $O^{\cdot}$, $H^{\cdot}$, $OH^{\cdot}$), which stimulate further burning reaction of the gases. The product of ideal burning of cellulose should theoretically be water and carbon dioxide. However, in reality, carbon monoxide, polycyclic aromatic hydrocarbons, hydrogen cyanide, etc. [5] are created as well.

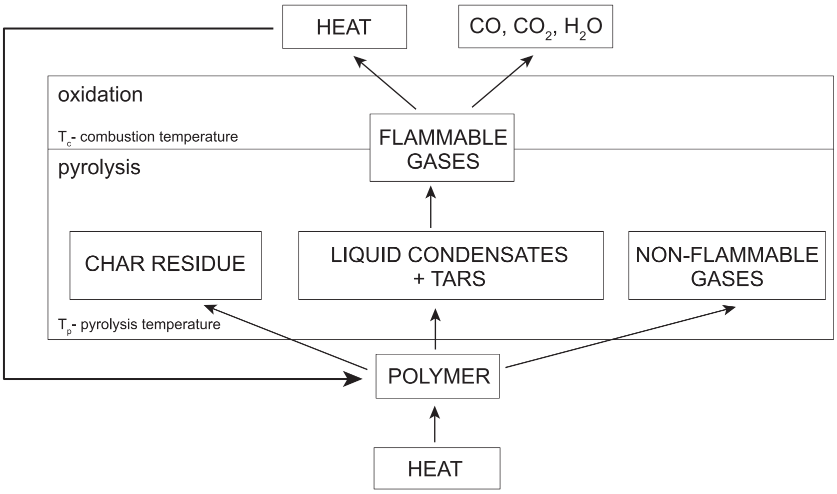

Fig.1 Mechanism of polymer burning

Thermal decomposition of cellulose occurs in a similar manner. When cellulose is heated in the air at the temperatures between 25 °C and 150 °C, water desorption occurs. At the temperatures between 150 °C and 240 °C two parallel chemical reactions are started. One is cellulose dehydration, which results in the generation of primary char residue, stable at the temperatures from 400 °C to 600 °C, with non-flammable gases (water, carbon monoxide, carbon dioxide), while the other is depolymerisation at the temperatures between 240 °C and 400 °C, due to which acetyl bonds are broken in glucoside units of the primary char residue, and levoglucosane is generated, which, at the temperatures between 400 °C and 700 °C yields flammable gases and initiates the generation of secondary char residue, stable at the temperatures below 800 °C [6].

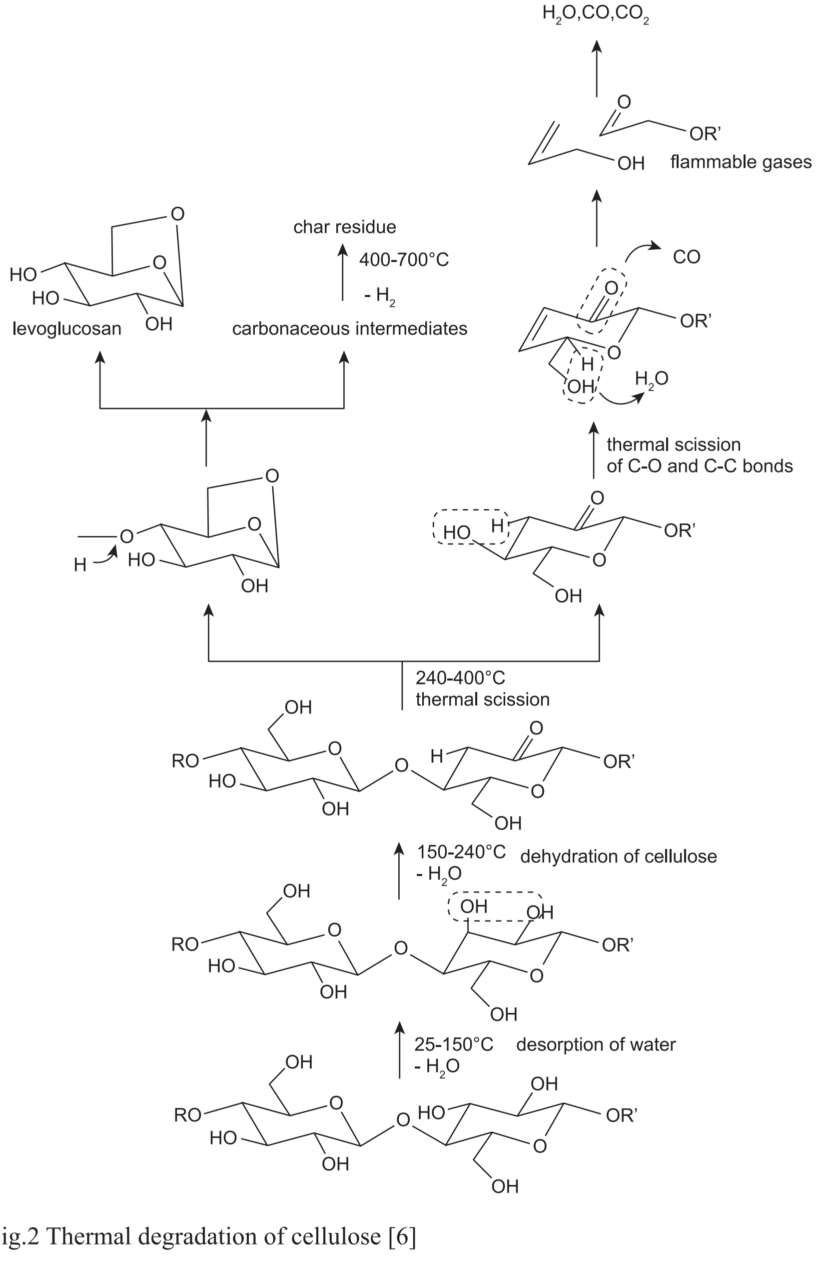

Fig.2 Thermal degradation of cellulose [6]

Flame retardants with chemical and/or physical action retard or block the process of burning in particular phases of burning so that they stop the inflow of heat to the polymer, block the access of oxygen, increase the generation of non-flammable gases or reduce the generation of flammable

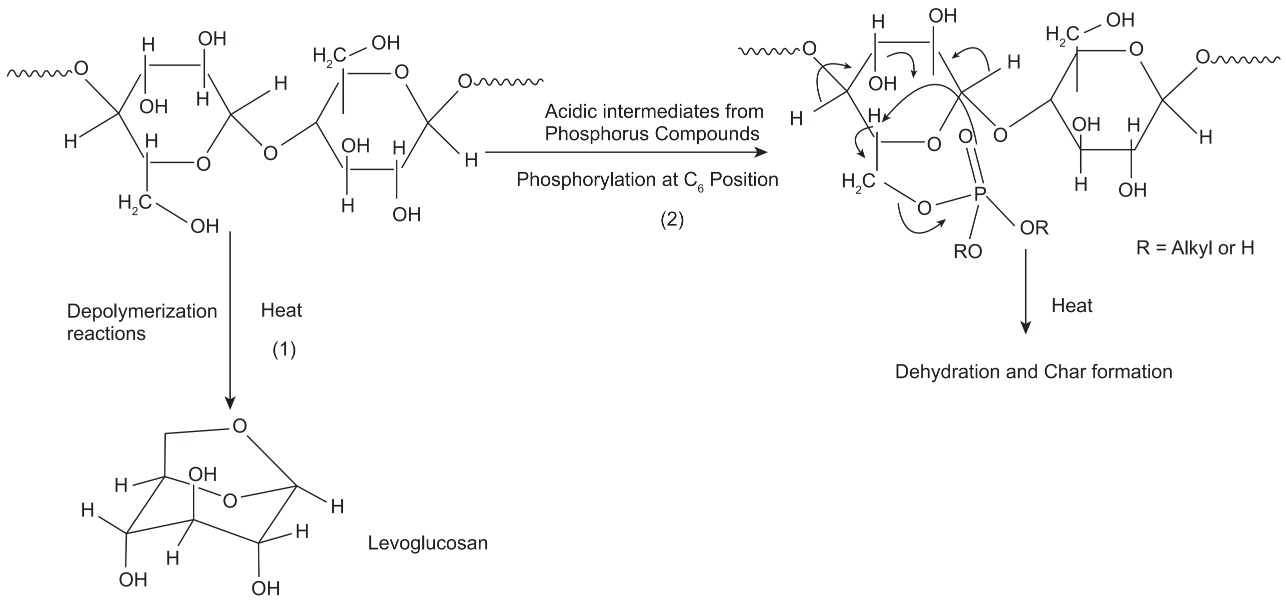

Fig.3 Thermal decomposition of cellulose without a phosphorus-based FR (1) and with it (2) [11]

ones and increase the content of char residue, acting in the gaseous and condensed phases. These mechanisms often cannot be clearly separated [7, 8]. Flame retardants that act in the gas phase, during the burning of flammable gases, are bonded to high-energy free radicals ($R^{\cdot}$, $O^{\cdot}$, $H^{\cdot}$, $OH^{\cdot}$), generated by oxidation, which results in non-flammable gases that extinguish the flame. Halogen FRs act in this manner, as well as metal hydroxides, phosphorus- or nitrogen-based FRs [9].

FR mechanism in the condensed phase can be seen in reaction of the polymer and flame retardant at the temperatures below the temperature of pyrolysis and is realised in two stages: dehydration and cross-linking, or the generation of char residue, which reduces the generation of flammable gases and limit the access of oxygen [10]. Phosphorus-based FRs, as well as silicone and silicon FRs act in this manner.

If cellulose is treated with phosphorus-based FRs (reaction 2, Fig.3), during decomposition at the temperature below T_c, phosphorilation of hydroxyl group occurs at the C_6 atom, caused by dehydration, which increases carbonisation and reduces the total amount of flammable gases. If no FR is used, levoglucosan is generated, which stimulates the generation of flammable gases at the temperatures above 400 °C [11].

Flame retardants with physical action are divided into:

1. inorganic salts which melt under the impact of high temperature and create a layer that protects the polymer surface from the heat source,
2. thermally unstable inorganic carbonates and hydrates which yield carbon dioxide when heated and/or water to cool down the polymer, forming a layer to protect the polymer surface from the heat source,
3. heat conductors (metals) and phase-change materials (PCM), which absorb huge amounts of heat when decomposing or evaporating, thus removing the heat from the polymer before the conditions for ignition are reached [12].

Inorganic FRs include metal oxides, zeolites, hydroxides, borates, stannates, inorganic phosphorus compounds (red phosphorus and ammonium polyphosphate) and graphite. They are usually combined with halogen FRs, as well as with phosphorus- and/or nitrogen-based ones [7, 8].

Phosphorus-based (P) FRs reach their maximum efficiency if they are combined with nitrogen (N) compounds, in so called N-P synergism [13]. There are more theories on N-P synergism:

1. nitrogen compounds (melamines, urea and their derivatives) release nitrogen which is bonded to high-energy free radicals, generated by oxidation, creating in the process stable non-flammable gases which quench the flame (NO – nitrous monoxide, NO_2 – nitrous dioxide) [14, 15]
2. nitrogen compounds make the reaction of phosphorilation of phosphorus-based FRs easier as they are bonded to phosphorus-based FRs, creating a link between phosphorus and nitrogen, of much better thermal stability than is the case with the link of phosphorus and oxygen, which increases the phosphorus and nitrogen content remaining in the carbonised residue [16].

Past decade has witnessed the development of so called intumescent FRs, intended primarily for the protection of wood, plastics and metals. They are applied to the material surface and expand under the influence of high temperature, forming an insulatory fire-resistant layer at the surface of the material, protecting it from further pyrolysis and burning. The char residue has a characteristic foamy appearance. These systems act in the condensed phase and involve some highly complex mutually dependent components. A phosphorous compound (phosphoric acid and their derivatives, polyphosphate) in the intumescent system cause the polymer to phosphorilate (with a C-O bond), stimulating its dehydration and carbonisation. Liquid polymer foams during carbonisation as it releases non-flammable gases (NO, NO_2) generated by the decomposition of nitrous compounds (melamine, urea, dicyandiamine etc.) [17].

3. Commercial flame retardants

The year 1783 is officially considered to be the year when the first FR was used on cotton. Brothers Montgolfier coated their air balloons with aluminium to prevent burning [18]. In early 20th century Perkin released the first systematic study of fire retardants for cellulosic materials, which was used until the fifties and included: ammonium chloride, ammonium phosphate, ammonium sulphate, zinc chloride, calcium chloride, magnesium chloride, aluminium hydroxide, zinc sulphate, sodium borate, boracic acid, magnesium sulphate, sodium chloride, sodium silicate, silicic acid, potassium chloride, sodium phosphate, aluminium borate, aluminium phosphate, calcium phosphate, magnesium phosphate, zinc borate, tungstic acid, sodium tungstate, ammonium tungstate and clay. A chief disadvantage of these agents is their poor resistance to washing [2].

The 1950s are noted as a start of so called golden period, which will last until the end of the 1980s. This was the period when resistant FRs for cellulosic materials were marketed, based on:

1. organophosphorous compounds created by cross-linking of tetraoxi(hydroxymethil)phosphonium salts (THPX) condensates and urea, under the trade name of Proban®,
2. derivatives of N-alkyl substituted phosphonopropionamides (e.g. MDPA - N-methyldimethylphosphonopropionamide), which were reactive compounds under the trade name of Pyrovatex CP®,
3. antimony-organo-halogen compounds: hexabromocyclododecan (HBCD) + antimony III oxide and decabromodipheniloxide (DECA) + antimony III oxide,
4. chlorinated paraffin waxes [3, 8, 18].

THPX- and MDPA-based FRs have been used until present days with no substantial alternative and are applied to textile materials by pad-dry method. Their chief disadvantage is that they release free formaldehyde during condensation, or impregnation of textile material, as well in use. As an alternative to formaldehyde-free flame retardants cross-linking agents based on polycarboxile acids were developed and launched in the market in the period from 1980 to 2010. However, their chief disadvantages were that treated fabrics treated experienced considerable strength reduction, they had a detrimental impact on the colouring shade, as well as on the pH value of the fabric treated [12]. The mechanism of polycarboxylic acid action in fire-resistant treatments for cotton fabrics has been described in literature in detail [19-25]. Table 1 shows some of the formaldehyde-free agents developed or experimented with in the period from 1980s until today [18, 26-29].

Future FRs for cellulosic material should:

1. be non-toxic,
2. be economically feasible,
3. not change the appearance, colour or shade of the fabric treated,
4. ensure pleasant feel (roughness), adequate strength (breaking strength, elongation at break) and be wear resistant,
5. be water-proof for at least 50 washing cycles in alkaline medium, at high temperatures, independent of water hardness,
6. not release free formaldehyde during processing or after it,
7. have high air-permeability after the treatment, regardless of the

Tab.1 FR agents developed in the period from 1980s until today

- N-methylol dimethylphosphonpropionamide (MDPA) and citric acid (CA);
- N-hydroxymethil-3-dimethylphosphonpropionamide and butanetetracarboxylic acid (BTCA)/ citric acid (CA);
- aminomethilphosphonic diamide;
- triethylamoinophosohonic oxides;
- phosphate-phosphonate oligomer;
- hydroxy-functionalise organophosphorous oligomer and multifunctional carboxylic acid;
- hydroxyalkilorganophosphorous oligomer (Fyroltex®)/ trimethylamine/ dimethiloldihydroxyethilene urea (DMDHEU);
- BTCA phosphated by hydroxyalkyl organophosphorous oligomer (Fyroltex®);
- BTCA phosphated hydroxyalkyl organophosphorous oligomer (Fyroltex®) – triethanolamin (TEA);
- maleic acid – sodium hypophosphite;
- succinic, mallic, racemic acid - sodium hypophosphite;
- oligomers of maleic acid which contain phosphorus.sodium hypophosphite – TEA;
- alkylphosphorusamidate stabilised as a salt product with ammonium chloride;
- diammmonium phosphape (DAP), phosphoric acid (PA), tributylphosphate (TBP), triallylphosphate (TAP) and triallylphosphoroustriamide (TPT);
- TBT – nitrogen-based compounds (urea, guanidinecarbonate, melaminformaldehyde);
- triethylphosphate (TEP) -diethylphosphorusamidate, -phosphorousamide acid, N(2-hydroxyethyl)diethylester -diethylethylphosphorusamidate or –diethyl 2-metoxiethylphosphorusamidate

high amount of the FR coating [30-33].

4. Alternative flame retardants

4.1. Biomacromolecules

Biomacromolecules or biopolymers are long-chain molecules essential for the functioning of every living being. They include nucleic acids – polymers of nucleotides (deoxyribonucleic acid – DNA and ribonucleic acid – RNA), and are used as genes and intermediates in transferring genetic information (biosynthesis of proteins), then proteins – polymers of peptides, which perform various functions in every living cell (enzymes, transferring oxygen and electrons, etc.), and finally polysaccharides – polymers of sugar, which serve as building blocks (e.g. cellulose, chitin) or to store energy in the organism (starch, glycogen) [34]. The biomacromolecules most frequently used in fire-resistant and fire-retardant treatments for textile materials in laboratory conditions are chitin derivatives, casein proteins, wheys, hydrophobins and DNA [35].

4.1.1. Chitosan

Chitosan is a linear polysaccharide consisting of randomly distributed β-(1→4)-linked D-glucosamine and N-acetyl-D-glucosamine. Chitosan is commercially obtained by alkali deacetylation of chitine, which is a building element of crustacean (crabs, lobsters) shells and of some mushrooms (button mushrooms). Varying the deacetylation degree various properties are obtained in chitosan, adequate for various applications. The amino group in chitosan has the pKa value of about 6.5, while the charge depends upon the solution pH and degree of deacetylation. Being a positively charged biopolymer in an acidic environment, chitosan is bioadhesive and is easily bonded to negatively charged surfaces [36, 37]. It is biocompatible and biodegradable, possesses good antibacterial properties, which makes it adequate for wide application in agriculture, for treatment of seeds, as a biopesticide, in wine production for fine filtration and wine clearing, in pharmacy for the production and transfer of insulin, as well as for reduced absorption of fats (dietary food). Chitosan is a polymer with thousand faces, as it can be chemically modified through estherification, etherification, graft polymerisation, phosphorylation, etc. [38]. Chitosan has proved to have good antibacterial and flame retardant properties and a number of research papers have been published in the last decade dealing with its application on polyurethane (PU) foams and in textiles, both by impregnation/exhaustion and by layer-by-layer (LbL) deposition.

Teli et al. have shown that adding chitosan to conventional multifunctional crease-proof, flame retardant and antibacterial treatments of cotton, results in lower free-formaldehyde release [39]. The treatment of phosphorilation in a bath of diammonium hydrogenphosphate (DAPH), sodium hypophosphite (SHP) and 1,2,3,4-butanetetracarboxylic acid (BTCA) as a cross-linking agent, yields chitosan phosphate, which, due to its nitrogen component, in synergy with phosphorus, offers good FR properties to cotton. Raising the DAPH concentration also raises resistance of cotton to washing [40]. El-Tahlawy et al. combined sodium stannate and chitosan in treating cotton against burning. They used chitosan (CH), citric acid (CA), sodium hipophosphite (SHP), diammonium hydrogenphosphate (DAHP) and sodium stannate ($NaSnO_3$). A reaction of phosphorilation occurs in the presence of DAHP with hydroxylic groups in cellulose and amino groups in chitosan, yielding phoshphorilised cellulose and chitosan phosphorus. Citric acid cross-links the chitosan phosphorus and cellulose, acting simultaneously as a crease-resistant agent. It also solutes chitosan into chitocan citric salts. Sodium stannate offers excellent FR properties. However it feels hard to touch, requires a high concentration of DAHP and ureas, as well a few phases of cross-linking [41]. El-Shafei et al. experimented with multifunctional FRs, antibacterial treatments and crease-resistant treatments of cotton using titanium dioxide (TiO_2) nanoparticles, chitosan phosphate, BTCA, and sodium hipophosphite (SHP) as a catalyst. Chitosan, as a derivative of chitin, exhibited good FR properties in combination with phosphorous compounds, due to the N-P synergy, with a simultaneous antibacterial activity. It can reduce the amount of commercial organophosphorous compounds, and experiments have shown it reduces the release of free formaldehyde in conventional recopies for flame retardant treatments [42].

4.1.2. Phytic acid

Phytic acid can be found in cereal bran, various seeds and vetch, as well as in various nuts in the form of phytin (Fig. 4). Human organism cannot digest it, while it can readily take various minerals important for life and link them to its OH groups, such as calcium, magnesium, iron and zinc. It can have a detrimental impact to health, as it inhibits enzymes necessary for digesting proteins and starch, which makes minerals and phosphorus inaccessible to human organism. However, it is still widely present in a manner in the organisms of mammals and is attributed with the

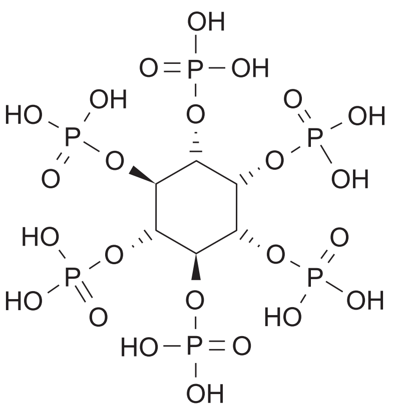

Fig.4 Phytic acid

ability to „repair“ mutated DNA. Still, not much is known of the role of phytic acid in human organism. Phytic acid and its salts are obtained by extraction from the bran rich in phytin, using aqueous solutions of sulphonic or hydrochloric acids, precipitated by sodium hydrogen carbonate and purified by extracting in ether from the solution of hydrochloric acid. It is used as a preservative E391 in food industry [43]. As it contains phosphorus in its structure, together with OH groups which readily bond to metals and other organic compounds, it is an ideal FR agent, which could, in theory replace ammonium polyphosphates. Only a few papers have been published on the use of phytic acid in flame-retardant treatments. Laufer at al. used polyelectrolytic solutions of phytic acid and chitosan applied by LbL method on cotton [44]. Wang et al. treated cotton fabric with phytic acid and a silane hybrid [45].

4.1.3. Proteins – casein, hydrophobines and whey

Casein is a phosphorus-rich protein, a by-product in the manufacture of completely skimmed milk, containing about 80% of milk proteins. It consists of αs1-casein, αs2-casein, β-casein and Ꝁ-casein [46]. Besides cheese manufacture, casein is traditionally used in the production of emulsifiers, binders, in paper manufacture, leather tanning, manufacture of fibres etc. [47]. Hydrophobines are natural surface active proteins of low molecular mass, rich in sulphur (cisteins) occurring as surface spew on some mushrooms and fungi, where they form monolayers. They exhibit amphiphilic properties, meaning that, depending upon the environment, they can have either hydrophobic or hydrophilic properties. It occurs in two different crystalline structures – class I and class II. Class I includes stable and hard to dissolve polymer monolayers, consisting of fibrillated rod-like structures which can only be dissolved in strong acids. The process is reversible, meaning that the rods, under favourable conditions, can be readily polymerised again. Class II hyrophobines includes polymer monolayers with no fibrillated rod-like structure, readily soluble in organic solvents and detergents. Hydrophobins reduce surface tension of the substrate where the mushroom grows, making its interaction with air and water easier. In other words, mushroom spores can be dissipated in the air and protected from moisture, embedded into favourable ground, while once they are stable in the ground the spore can take moisture/water, grow and further propagate. Hydrophobins are also considered to play a major role in deactivating the immune system of the host on which the mushrooms (or fungi) grow. Hydrophobic is very hard to make in the form adequate for laboratory or industrial use [48]. Hydrophobian have recently been applied in foaming agents and nanoencapsulating active substances in pharmaceutical and food industries [49]. Alongi et al. impregnated cotton fabrics with aqueous suspensions of casein and solution of hydrophobin, and compared thermogravimetric curves (TG) obtained with TG curves of untreated cotton and of cotton treated with ammonium polyphosphate (APP). Cotton samples treated with casein/hydrophobin exhibited good and almost identical FR properties, but considerably lower than the samples treated with APP [50]. Carosio et al. proved that casein has an impact on FR properties of pure cotton and pure polyester (PES); having at the same time no influence on cotton/PES blends [51].

Whey proteins make 20% of milk proteins, with the structure similar to α-helixes, with alternating acidic/basic and hydrophobic/hydrophilic aminoacids, with sulphur contained within the peptide chain (methionine, cysteine). Chief components of whey are β-lactoglobulin, α-lactalbumin, serum albumin and immunoglobulin. Due to their amphiphilic properties, these proteins are used in the manufacture of emulsifiers. Bosco et al. studied the impact of whey protein denaturation on cotton FR properties. Denaturation means disturbing secondary (tertiary) structure in proteins (and nucleic acids) by high temperature, irradiation, mechanical factors, heavy metal salts, or actions of strong acids and alkalis. They proved that denaturation of whey protein has no effect on FR properties of cotton treated with them [52].

4.1.4. Deoxyribonucleic acid (DNA)

DNA molecule consists of long chain nitrogen-based polymers – adenine, guanin, cytosine and thymine, with the backbone made of polysaccharide and phosphate groups linked with ester linkages. It could be said that DNA contains all three components of a swelling FR system in a single molecule – phosphate groups that can yield phosphoric acid, deoxyribose with C-O linkages which can be dehydrated and yield carbonised residue, and nitrogen compounds (adenine, guanin, cytosine and thymine) (Fig.5). When heated, phosphate groups in DNA yield phosphoric acid, which releases water, accompanied by dehydration and carbonisation. At the same time, nitrogen-rich bases yield ammonium, which retards burning and reacts with the liquid polymer to create a protecting layer on the material [54]. The sources for purified DNA are codfish and herring sperm and spawn. Alongi et al. were the first to impregnate cotton fabric with DNA, with the idea of using DNA as a FR [55]. Carosio et al. used chitosan/DNA in LbL layering on cotton [56]. Alongi et al. compared DNA flame retardant properties with casein and ammonium polyphosphate (APP), and the results obtained showed that APP offers much better results than the other agents, DNA being the second [54]. Chief disadvantage of all of these environment-friendly treatments is their poor fastness to washing, even at 30 °C with no detergent used [57].

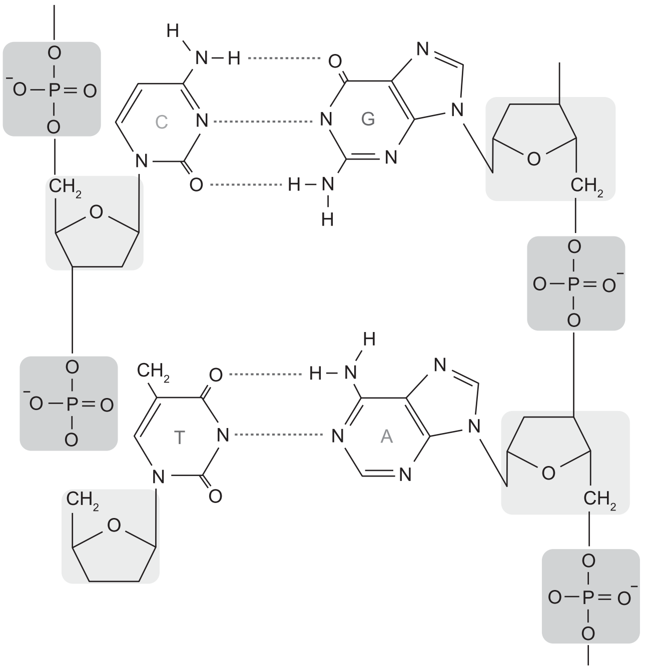

Fig.5 DNA structure [53]

5. Processes of applying FRs to cellulose textile fabrics

Flame retardants can be applied to textile fabrics using either the process of pad-drying or back-coating. Pad-drying consists in immersing the material in the bath containing a flame retardant, wringing it and drying. However, after such a treatment the fabric is often stiff, of unpleasant feel, and sometimes of reduced strength and no elastic recovery. Back-coating is the process in which FR is applied to the fabric surface, does not penetrate its structure, so that the material can retain its basic and favourable properties (in the case of cotton it means comfort, good absorption of moisture etc.). Back-coating has recently been classified as a single-layer coating. Pad-dry process and back coating are the only surface functionalisation techniques used for cellulose textile fabrics in industry, using non-intumescent FRs exclusively. Some other nanotechnologies have also been experimented with in the course of past few years:

1. nanoparticle adsorption,
2. sol-gel process,
3. plasma treatment and
4. layer-by-layer deposition [18, 58].

5.1. Nanoparticle adsorption

Nanoparticle adsorption is a simple, fast and cheap, but not permanent process, in which the fabric is impregnated in an aqueous suspension of nanoparticles, while bonding is based on ionic interaction of negatively charged textile substrate and positively charged nanoparticle. Nanoparticle adsorprion is classified as a single-layer coating. Literature references mention:

- natural and synthetic zeolites (montmorillonite, klinoptilolit),
- nanoclays (carbonate hydrotalcite, sulphonate bohemite),
- nanoparticles (zinc oxide, titanium dioxide, silicon dioxide, octapropylammonium polyhedral oligomeni silsesquioxane (POSS®) [18, 59-64].

5.2. Sol-gel process

Sol-gel process is a simple, inexpensive and environmentally friendly procedure of synthesizing homogenous metal oxides, or organic-inorganic hybrids (dual-cure sol-gel) of good mechanical, optical, electric and thermal properties, at the temperatures below 100 °C. The procedure includes hydrolisis and condensation reactions of metal alkoxides (precursors), which changes the colloidal solution (sol) into s solid gel with uninterrupted three-dimensional metaloxide network, with an acid or alkali as a catalyst [65]. The process of applying FR by sol-gel technique onto a textile material starts with precursor hydrolysis. Hydrolysed pre-

Tab.2 Precursor in different systems type in Sol-Gel process in flame retardant treatments

System type	Precursor
Inorganic meal alkoxides	– tetraethyl orthosilicate (TEOS), – tetramethyl orthosilicate (TMOS), – tetrabutyl orthosilicate (TBOS), – alkoxysilane with various numbers of hydrolysed groups, – tetraethyl ortho-titanate, – tetraethyl ortho-zirkonate – aluminium isopropylate, – TMOS + aluminium micro and nanoparticles
Inorganic--organic hybrids based on N-P systems	– TMOS + aluminium phosphinate – TMOS + aluminium phosphinate/melamine(poly)phosphate/zinc oxide/boron oxide, – TMOS + α-zirconium phosphate, – TEOS + H_3PO_4 or ethyl dichlorophosphate – diethylphosphatoethyltrioxysilan (DPTES), – DPTES + 3-aminopropyltriethoxylane (APTES) or APTES melamine-based resin, – DPTES + 1-hydroxyethanal 1,1-diphosphonic acid, – DPTES + N,N,N′,N′,N″,N″-hexametoxymethyl-[1,3,5]triazine-2,4,6-triamine, – DPTES + urea, – sodium metasilicate + urea/ammonium dihydrogen phosphate – DPTES/APTES (3-aminopropyiltrietoxysilane)+ melamine/urea

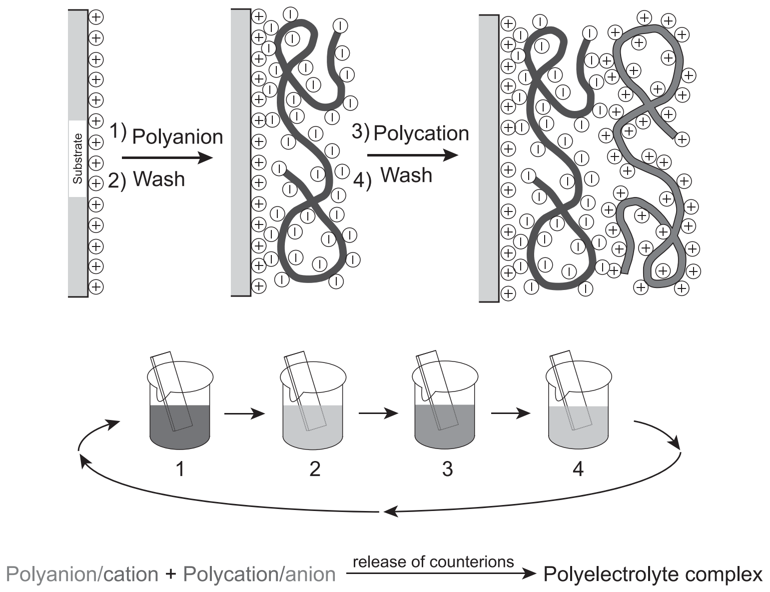

Fig.6 Schemes of the layer-by-layer deposition method (LbL) [72]

cursor is then added into the bath with organic FRs, which is then used to impregnate the textile fabric to be treated. Drying follows after impregnation, together with condensation, creating a solid gel on the fabric [66]. Tab. 2 lists some of the precursors used in these processes [18, 66-69].

5.3. Plasma treatment

Plasma treatment is a process in which functional groups and macromolecules are synthesised by grafting onto the surface of textile fabric, with no internal modification of the textile, through:

1. etching fabric surface and/or functionalisation with the help of non-polymerising gases (N_2, H_2, O_2, Ar, NH_3, CO_2 etc.)
2. polymer synthesis with the help of shoots from non-volatile kinds of phosphorus in cold plasma,
3. deposition of organosilicone compounds with the help of plasma polymerisation,
4. using cold N_2 plasma technique,
5. using acrylic monomers for graft polymerisation [58].

Cold plasma in flame retardant treatments of cellulosic fabrics offer satisfactory values of limiting oxygen index, even after 50 washing cycles (27%). However, the process has not been widely accepted by the industry, primarily due to high necessary investments, as compared to the conventional commercial FR processes, which results in too high a price for the final product [70, 71].

5.4. Layer-by-layer deposition

Layer-by-layer deposition (LbL) is a surface adsorption of long-chain polyelectrolyte molecules of one charge (+) on a solid substrate of the opposite charge (-), followed by rinsing with deionised water. The second phase consists in linking positively charged polyelectrolyte to negatively charged polyelectrolyte (Fig.6). The process is alternately repeated [72].

It is thus possible to arrange a few layers of the same or completely different electrolytes one on the other as a bilayer (BL), trilayer (TL) or quadlayer (QL).

LbL coating has been experimentally tested for FR treatments of textile fabrics, using various FR agents. Chief disadvantage of this method is again poor wash-fastness, as polyelectrolyte links are based on electrostatic bonds or H-bonds. Somewhat better results have been achieved by post-treatments of UV cross-linking. The advantage of this process is its simplicity, possibility to control the number, thickness and homogeneity of individual layers (which depends upon the choice and concentration of polyelectrolytes, solution pH, additional ultrasonicating etc.), as well as the usage of green solvent - water [58]. LbL coating is implemented in laboratories using the following techniques:

1. dipping and
2. horizontal or vertical spraying [73].

Only a few papers could be found dealing with possible commercial approaches to a continuous industrial LbL process of coating textile materials by dipping technique [74, 75]. LbL coating has until now been applied to the following cellulosic fibres: cotton, ramie and sisal. Cationic/anionic or anionic/cationic BL, TL, and/or QL systems used can be seen in Tab.3 [44, 45, 56, 74-91].

6. Toxicology

American National Academy of Science published a comprehensive study in 2000 on the toxicological risks in using commercial flame retardants. The study encompassed all the FRs known at the time, together with those used in textile industry. It proved that FRs to certain extent disturb the functioning of human immune system and endocrine system, cause neurological changes in the brain and physical malformation of foetus, disorders in child growth and development, skin depigmentation, they inhibit the workings of certain enzymes, can cause spontaneous miscarriage, gastroenterological problems, potentially are carcinogenic and can even damage the DNA structure. The toxicological study from 2000 also showed that most damaging agents used as FR on textiles were those halogen-based, organohalogen and anitimony organohalogen compounds. Commercial agents based on organophosphorus compounds were considered safe until 2000 [92]. Van der Veen and de Boer published a review in 2012 on toxicity of some organophosphorous FRs, where they stated the following:

1. bisphenol-A diphenilphosphate is not, for the time being, considered

toxic, due to insufficient data on its level of presence in the environment, based on in-vivo experiments. However, it can cause eye and skin irritation,

2. triphenilphosphate is more or less neurotoxic for aquatic organisms, can cause allergies, disturbs the workings of immune and endocrine systems, blocks the growth of algae,
3. diphenil cresyl phosphate can cause skin and eye irritation, is toxic for aquatic organisms, causes reproductive and development problems, but is considered safe for the time being due to insufficient data available,
4. melaminpolyphosphate can cause eye irritation, is toxic for algae, but is considered safe for the time being due to insufficient data available,
5. diethylphosphinic acid can cause eye irritation, it is toxic to algae, but is considered safe for the time being due to insufficient data available,
6. tricresyl phosphate is a neurotoxin, reproductive toxin and toxic for aquatic organisms [93].

Phosphorus, Inorganic and Nitrogen Flame Retardants Association, the member of which are Chemische Fabrik Budenheim, Ciba Inc. (a part of BASF now), Clariant Produkte (D) GmbH, Italmatch Chemicals S.p.A., Lanxess Deutschland GmbH and Nabaltec AG., published in 2009 a short report of non-halogen FRs, where they stated that non-halogen organophosporous compounds were completely safe to use, meaning they were not bioaccumulative, toxic, carcinogenic or mutagenic as phosphorus was a necessary chemical element for humans, animals and plants, being a major component of bones and DNA. The report even stated an example of a case-study in Japan where phosphorus was, in the form of phosphoric acid, recycled for mineral fertilisers. European Commission, as it is, has no official assessments of the risk of non-halogen FRs, as they have not been included into the so called list of priority chemicals to be a basis for risk assessment in Europe. [94].

Tab.3 LbL systems in flame retardant treatments

Cotton	
BPEI/CH/PSP	BPEI – branched polyethyleneimine; CH – chitosan; PSP – sodium polyphosphate
BPEI+urea+ DAP/kaolin	BPEI – branched polyethyleneimine; DAP – diammonium phosphate
BPEI/kaolin	BPEI – branched polyethyleneimine
BPEI/PAA-P/AA	BPEI – branched polyethyleneimine; PAA-P – phosphonate poly(allylamine); AA – oligoallylamine
CH/PA	CH – chitosan; PA – phytic acid
CH/APP	CH – chitosan; APP – ammonium polyphosphate
CH/PSP	CH – chitosan; PSP – sodium polyphosphate
FR-PAA/MMT	FR-PAA – aminoderived poly(acrylic acid); MMT – montmorillonite
FR-PAM/GO	FR-PAM – FR polyacrylamide derivative; GO – graphene oxide
BPEI/PSP/PAA	BPEI – branched polyethyleneimine; PSP – sodium polyphosphate; PAA – poly(allylamine);
SiN/PA	SiN – silane hybrid modified by nitrogen and obtained by sol-gel process; PA – phytic acid
CH/PT	CH – chitosan; PT – phosphorilated chitine
CH/PCL	CH – chitosan; PCL – phosphorilated cellulose
CH/DNA	CH – chitosan; DNA – deoxyribonucleic acid
AP/-POSS	AP – aminopropyil silsesquioxane -POSS – octakis(tetramethylammonium)pentacyclo[9.5.1.1.^{3,9}.1^{5,15}.1^{7,13}] octasiloxane1,3,5,7,9,11,13,15-octakis(cyloxide)hydrate
+POSS/-POSS	+POSS – octa(3-ammoniumpropyl)octasilsesquioxane octachloride -POSS – octakis(tetramethylammonium)pentacyclo[9.5.1.1.^{3,9}.1^{5,15}.1^{7,13}] octasiloxane1,3,5,7,9,11,13,15-octakis(cyloxide)hydrate
BPEI/MMT	BPEI – branched polyethyleneimine; MMT – montmorillonite
BPEI/-SiO_2	BPEI – branched polyethyleneimine -SiO_2 – negatively charged silicon dioxide nanoparticles
-Al_2O_3/+Al_2O_3, with cotton cationisation	-Al_2O_3 – anionic aluminium oxide colloidal solution +Al_2O_3 – cationic aluminium oxide colloidal solution
-Ag/PDDA	-Ag – anionic colloidal solution of silver nanoparticles PDDA – poly(diallyldimethylammonium chloride)
CH/TNT	CH – chitosan; TNT – titanium nanotubes
Ramie	
DMF + MWNT-NH_2/APP	DMF – N,N-dimethylformamide; MWNT-NH_2 – aminofunctionalised multilayered carbon nanotubes; APP – ammonium polyphosphate
BPEI-$CuSO_4$ /PVPA	BPEI – branched polyethyleneimine; CuSO4 – cupric sulfate; PVPA – poly(vinylphosphonic) acid
BPEI-$ZnCl_2$ /PVPA	BPEI – branched polyethyleneimine; ZnCl2 – zinc chloride; PVPA – poly(vinylphosphonic) acid

Another problem of FR treatments for primarily cellulosic fabrics is the release of free formaldehyde in processing and use. As the technology goes, in order to bond an organophosphorous compound-based FRs more permanently to a cellulosic fibre, a formaldehyde-based cross-linking agent is necessary (phenolformaldehyde, ureaformaldehyde, melaminformaldehyde), which is gradually released in the course of processing and use. International Agency for Research on Cancer, of the World Health Organisation, classified formaldehyde as a carcinogenic chemical (causes nasopharynx cancer and leukaemia) [95]. Because of its potential or proved toxicity, intensive research has been done with new alternative agents and/or technological solutions, which could partially or completely replace all the existing commercial FRs.

7. Conclusion

The ease with which textile fabrics caught flame and burned was a problem which faced people from prehistoric time. As early as the end of 18th century a detailed study was made on the substances to coat cotton, linen and generally cellulose fabrics used in the manufacture of balloons, stage curtains in theatres etc., which would prevent, or at least retard, burning. These were natural substances, mostly based on mineral salts and clay, highly efficient, but completely nonfast to washing. After the World War II chemical industry developed at a fast pace and some promising substances were created, based on halogen and halogenphosphorus compounds of excellent FR properties, resistant to washing. After a few decades of commercial use doubts appeared of their potential detrimental impact on the environment. Some 15 years ago, their extreme toxicity was proved (disturbing the workings of immune and endocrine systems, neurotoxicity, carcinogenicity, inhibiting the function of enzymes, spontaneous miscarriages, foetus malformations, physical and mental retardation etc.). Some countries banned these substances while some limited their use. Organophosporous compounds are for the time being considered safe. Past decade or so has witnessed intensive experimenting with new alternative and environment-friendly agents and/or technological solutions, which could partially or completely replace all the existing commercial FRs. One of the solutions could be the implementation of biomacromolecules, such as chitosan, phytic acid, casein whey, hydrophobins and DNA.

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2. KK.01.1.1.02.0024: MI-TSRC Modernization of Infrastructure of the Textile Science Research Center
3. Croatian Science Foundation 2013-11 9967 ADVANCETEX Advanced textile materials by targeted surface modifications
4. IPA4.1.1.1.05.01.c34: Labour Market Council of Karlovac County – Work in Progress!
5. FP7-REGPOT-2008-1-229801: T-Pot Unlocking the Croatian Textile Research Potentials, EU, 2009–2011
6. E! 5785 FLAMEBLEND, Improvement in the flame retardant properties of cotton and wool blends, 2010–2013

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1. Zain, G.; Jordanov, I.; Bischof, S.; Magovac, E.; Šišková, A. O.; Vykydalová, A.; Kleinová, A.; Mičušík, M.; Mosnáčková, K.; Nováčiková, J.; Mosnáček, J. Flame-retardant finishing of cotton fabric by surface-initiated photochemically induced atom transfer radical polymerization. *Cellulose*. **2022**, *44*, 1–22, doi:10.1007/s10570-022-04982-z.
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