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FLAME RETARDANT SURFACE MODIFICATION OF COTTON TEXTILES USING LAYER-BY-LAYER DEPOSITION

DOCTORAL DISSERTATION

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

Doktorski rad

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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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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].

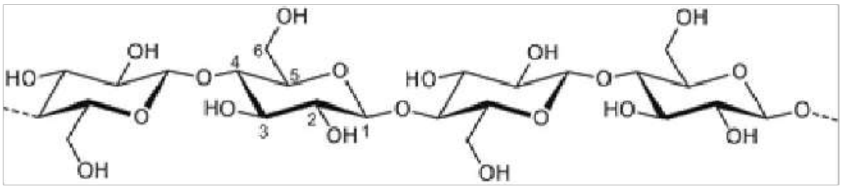

Figure 1: *Cellulose molecule [6]*

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].

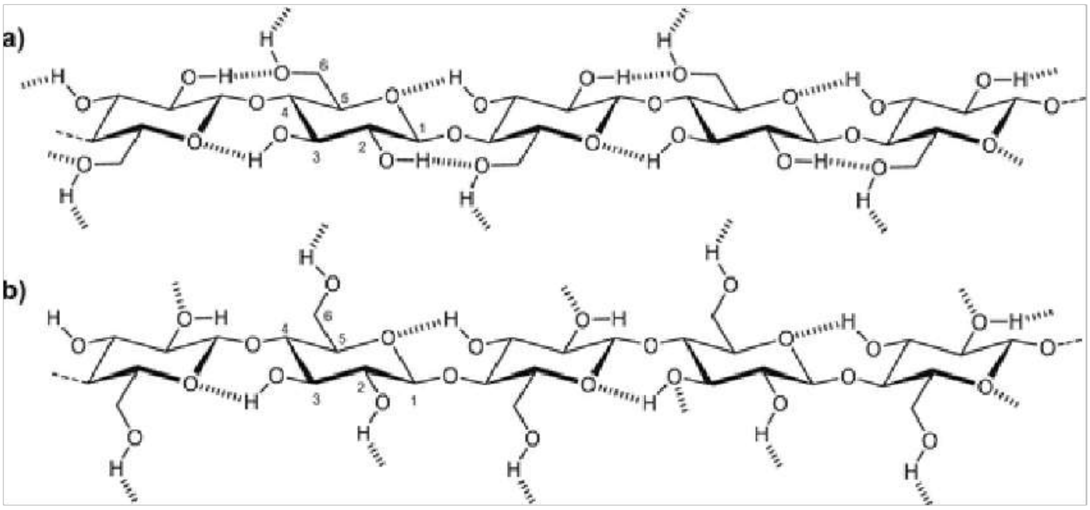

Figure 2: *A scheme of the H bonding in (a) cellulose I and (b) II [7]*

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.

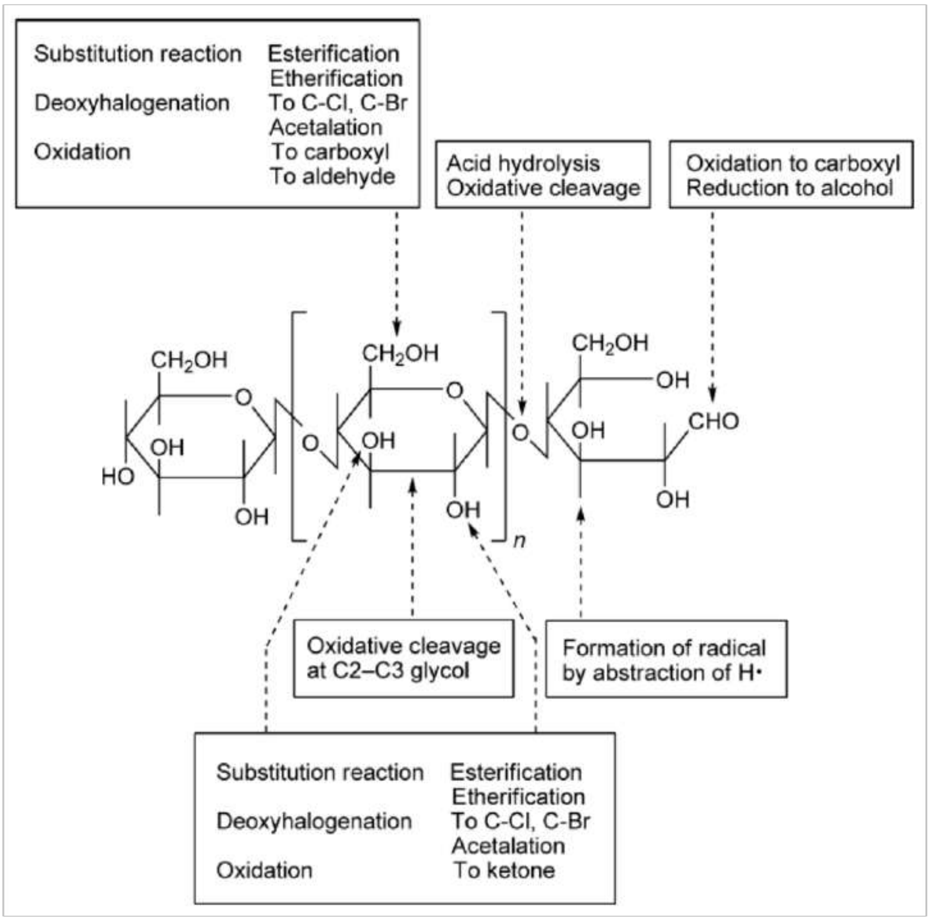

Figure 3: *Positions in cellulose structure for chemical reactions [8]*

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].

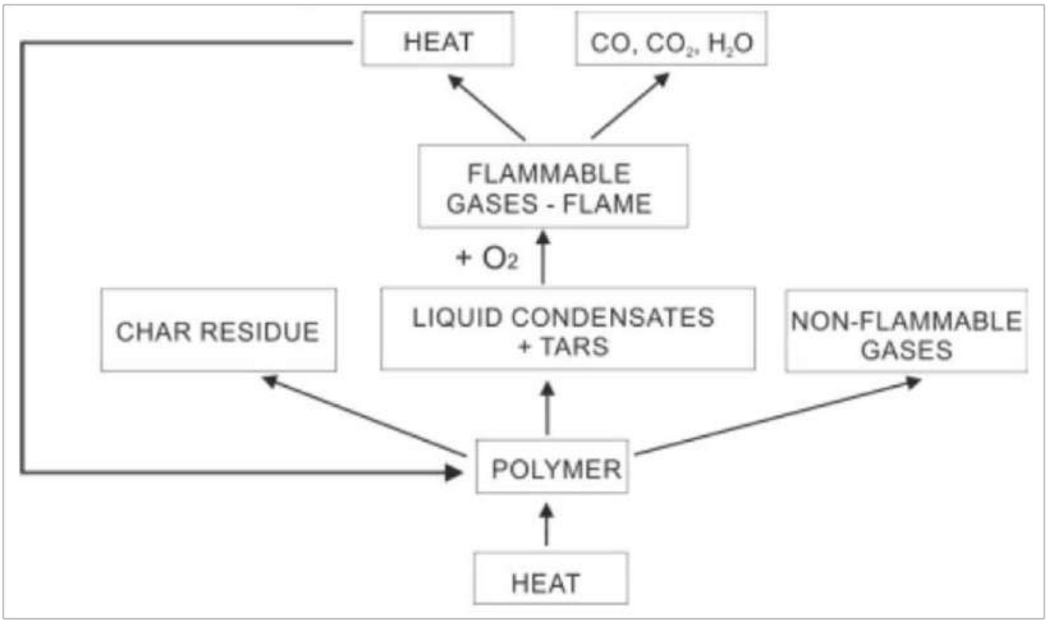

Figure 4: *Schematic of polymer burning [12]*

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]:

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

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]:

$H + MO + (X) = HMO + (X)$ (19)

$HMO + OH$ (or H) $= MO + H_2O$ (or H_2) (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].

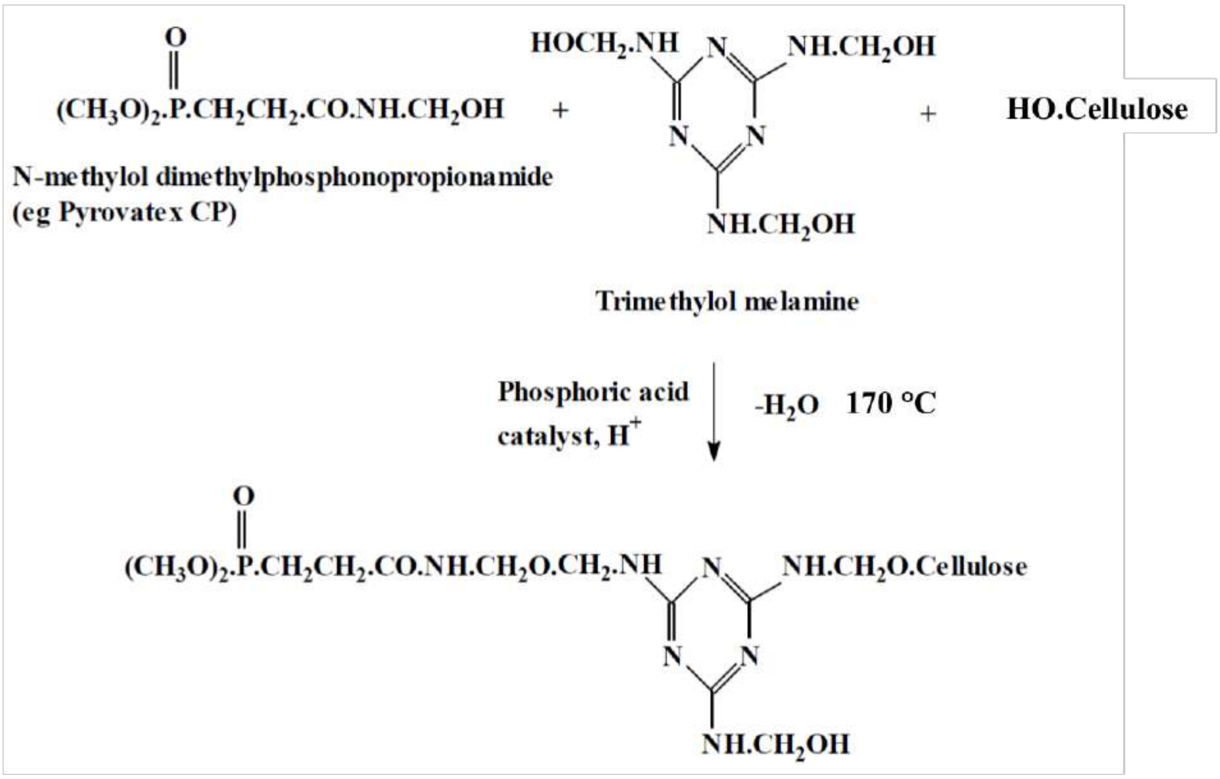

Figure 5: *Chemistry of Pyrovatex® [30]*

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].

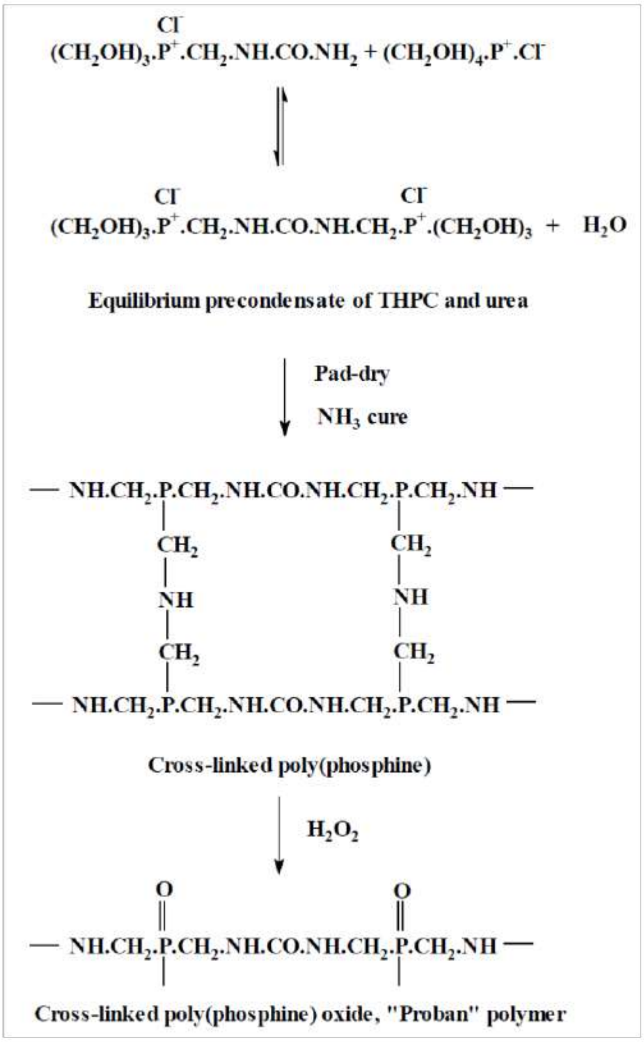

Figure 6: *Chemistry of the Proban® [30]*

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].

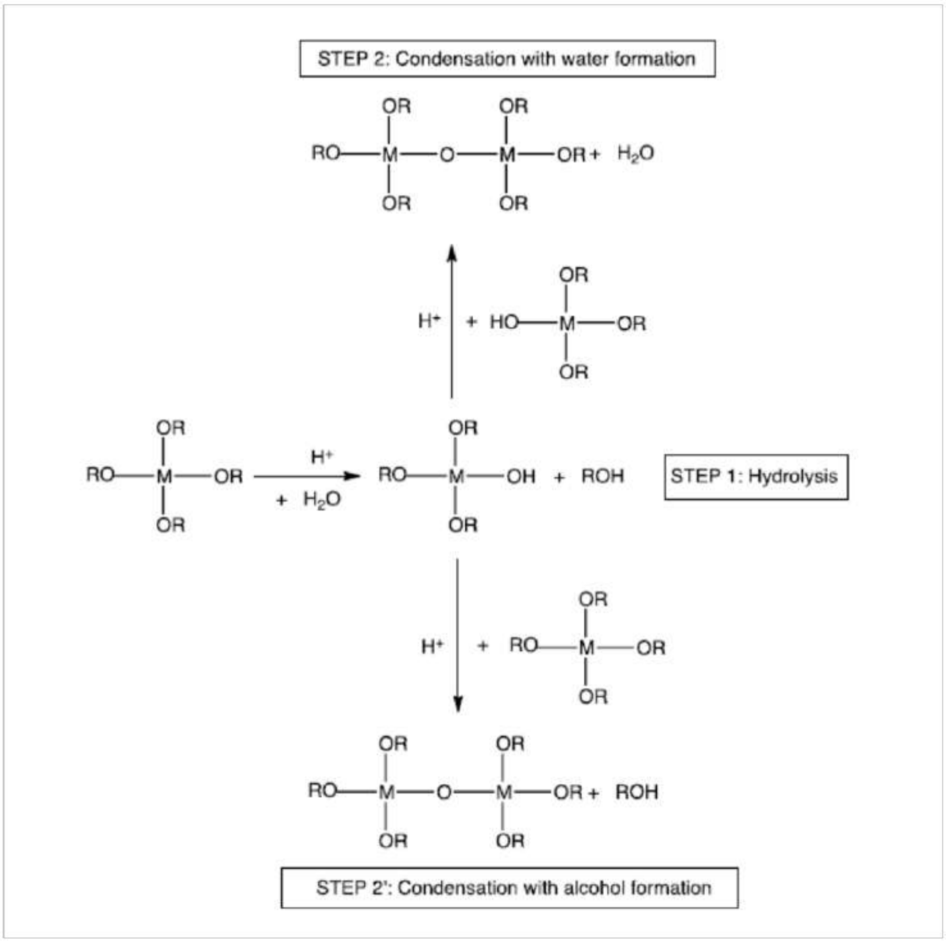

Figure 7: Chemistry of sol-gel [37]

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.

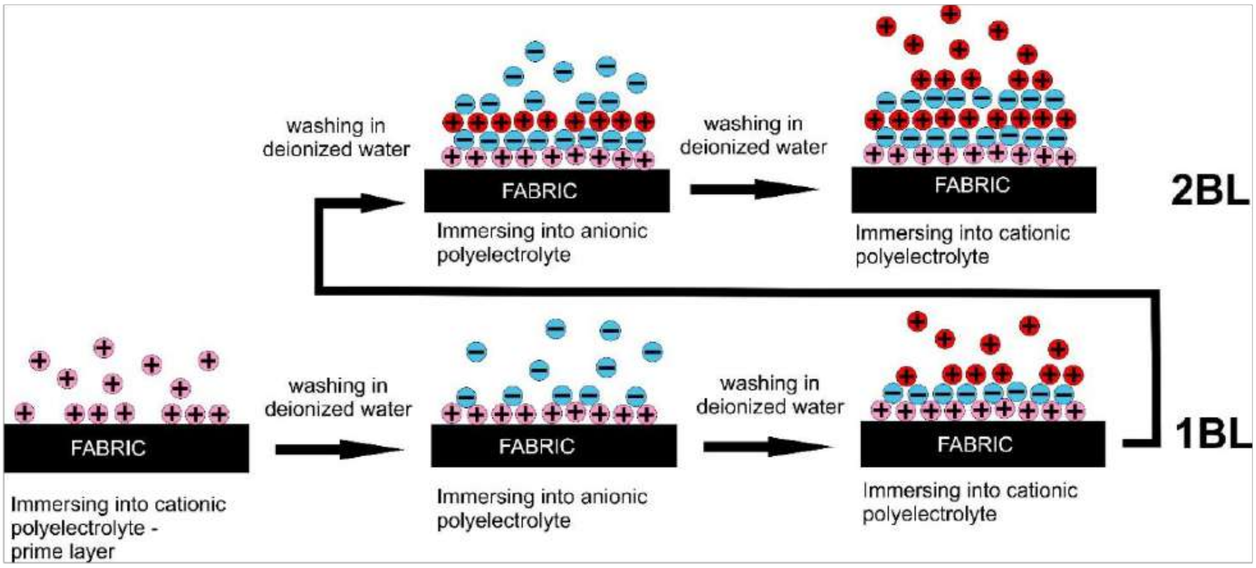

Figure 8: *Schematic of typical layer-by-layer deposition of fabrics*

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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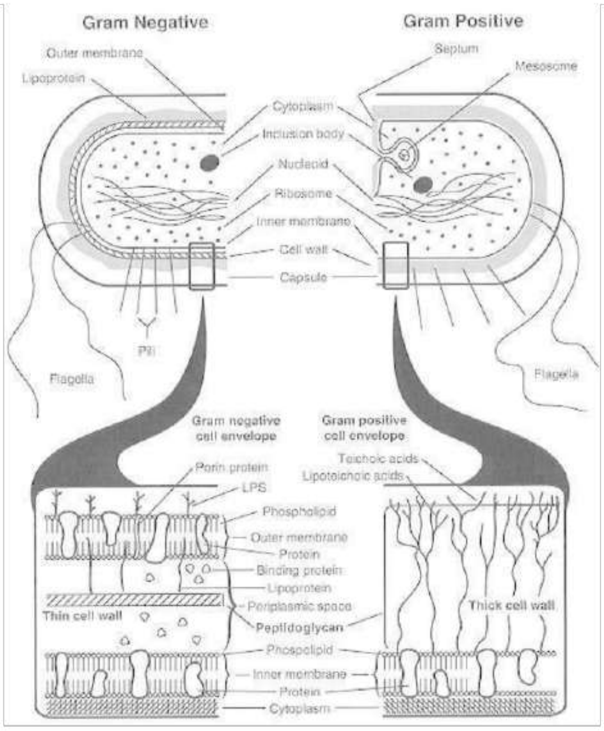


Figure 9: *Schematic of cell structures of Gram-negative and Gram-positive bacteria [49]*

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.

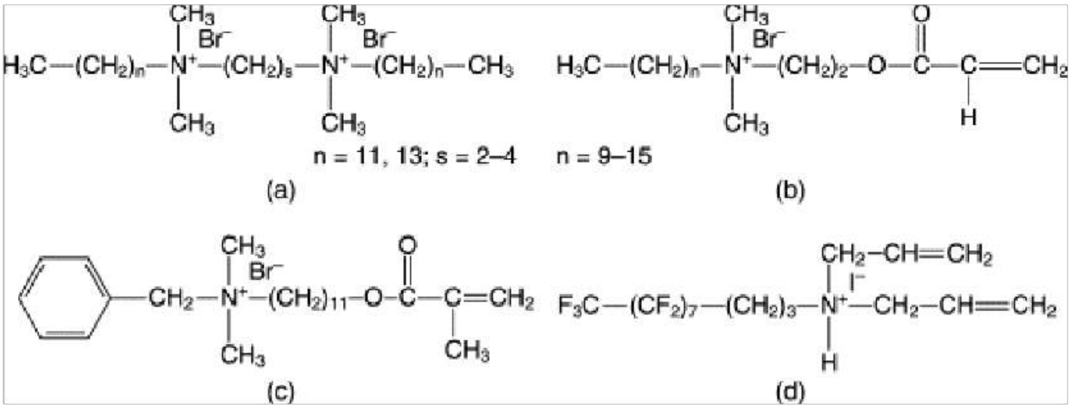


Figure 11: *Structural formula of different QACs: (a) diquaternary ammonium salt (alkanediyl- α, ω - bis(dimethylalkyl ammonium bromide)), (b) alkyl(2- (acryloyloxy)ethyl)dimethyl ammonium bromide, (c) benzyl(11-(acryloyloxy)undecyl) dimethyl ammonium bromide; (d) N -(4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11-heptadecafl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

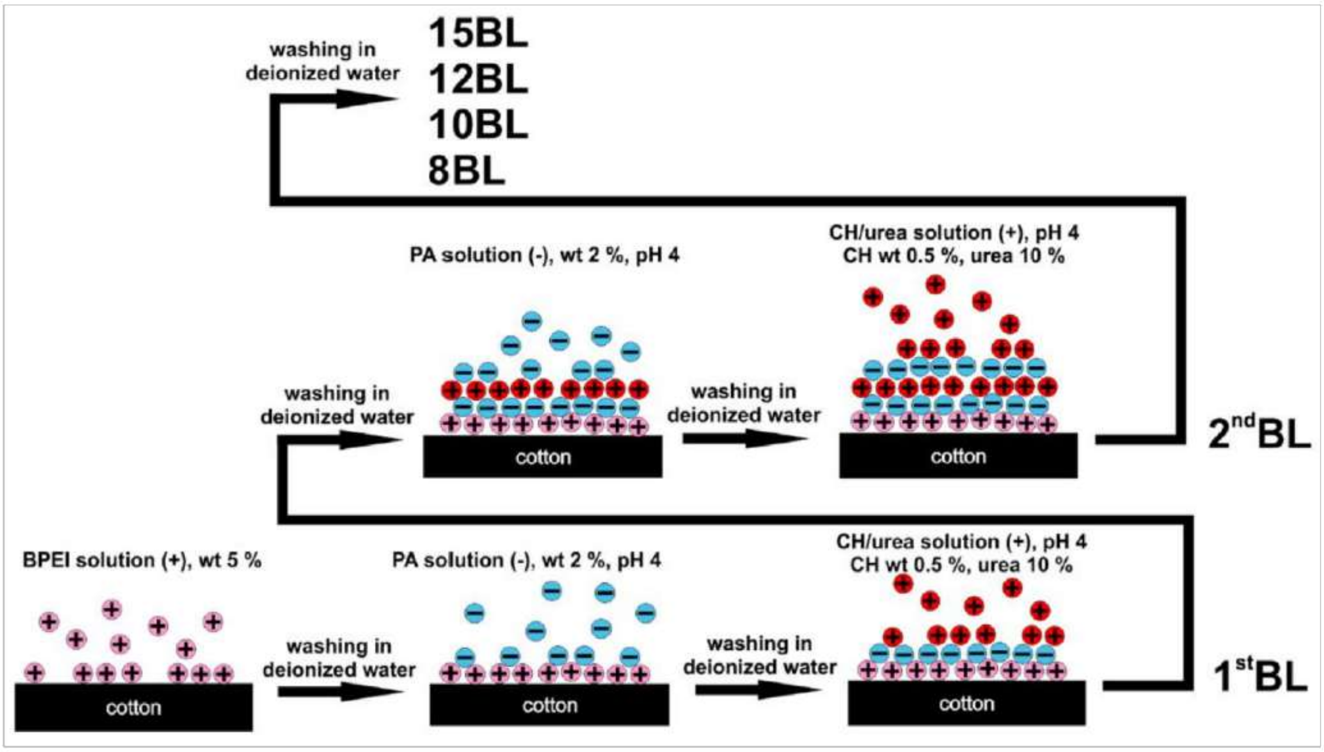


Figure 12: *LbL deposition of cotton with 8, 10, 12, and 15 BL of PA/CH-U* [76]

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

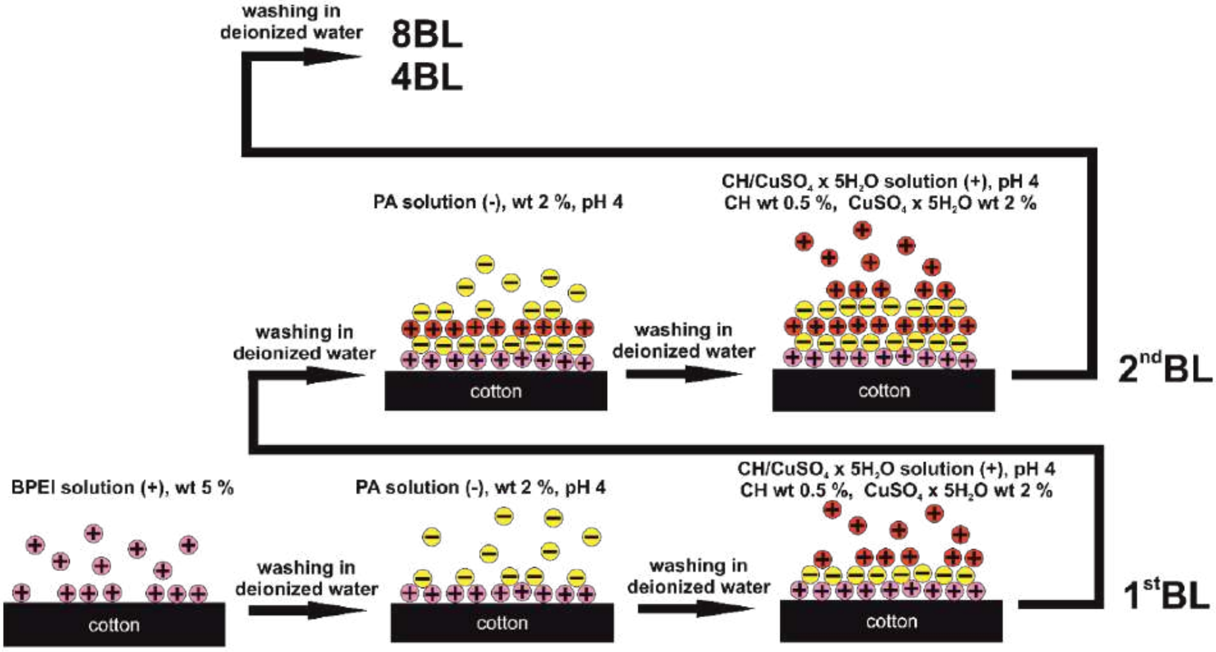


Figure 13: *LbL deposition of cotton with 4, 8 BL of PA^-/CH^+ and $PA^-/(CH\text{-}CuSO4\ x\ 5H_2O)^+$ [77]*

- 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].

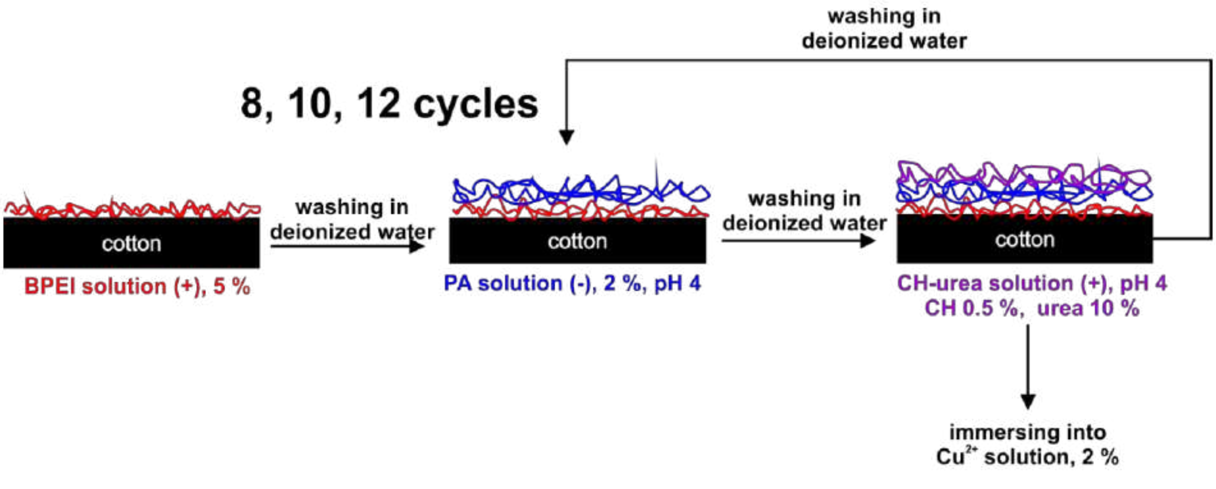


Figure 14: *LbL deposition of cotton with 8, 10, 12 BL of $PA^-/(CH\text{-}U)^+$ with immersion into $CuSO_4$ x $5H_2O$ solution [70]*

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:

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

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.

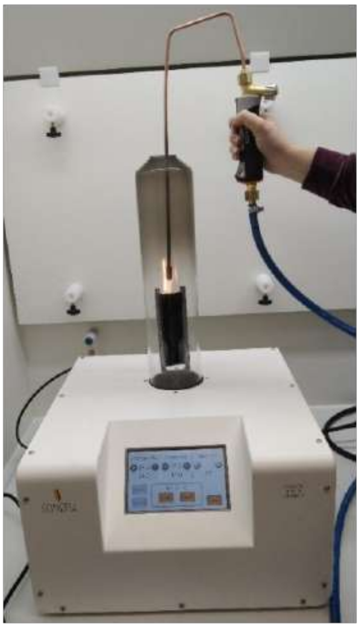


Figure 15: *LOI device, Concept Equipment*

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].

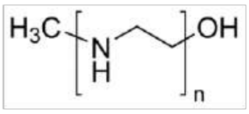


Figure 20: *Structural formula of linear PEI [104]*

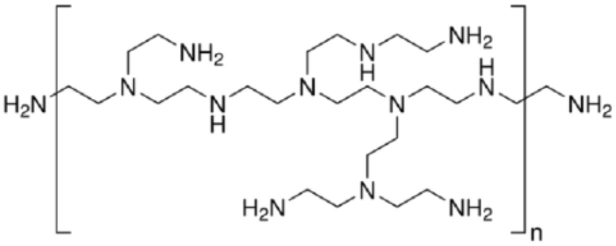


Figure 21: *Structural formula of branched PEI [103]*

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].

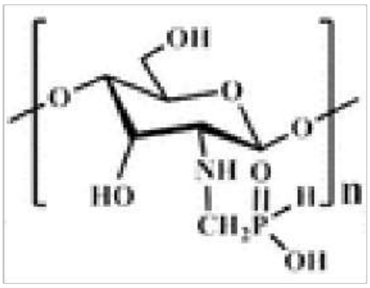


Figure 22: *Structural formula of HACH [108]*

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].

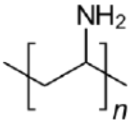


Figure 23: *Structural formula of PVAm [110]*

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].

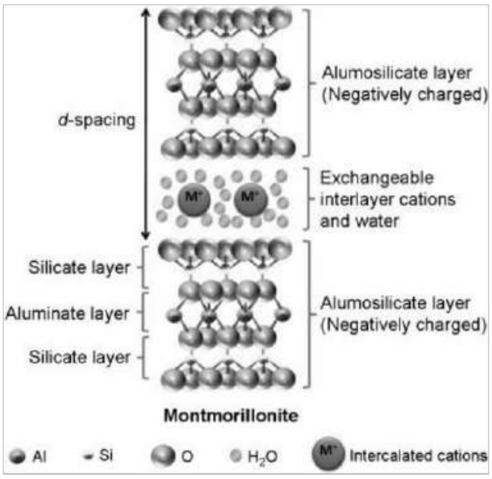


Figure 24: *Layered structure of MMT [112]*

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].

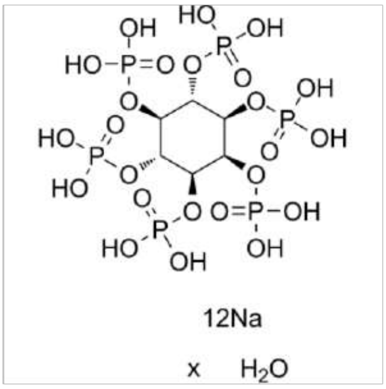


Figure 25: *Structural formula of PA [120]*

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].

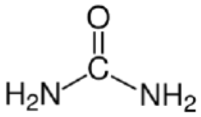


Figure 26: *Structural formula of U [125]*

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).

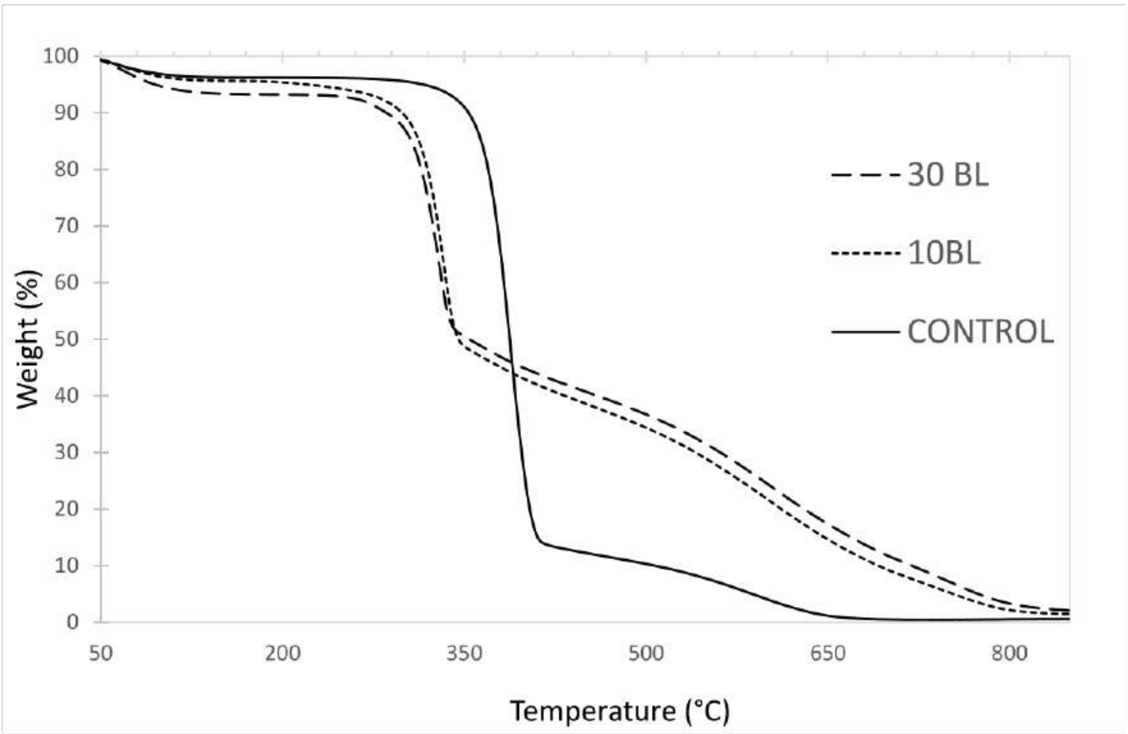


Figure 27: *TG curves of untreated cotton and cotton samples treated with 10 BL of PA/CH-U and 30 BL of PA/CH*

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].

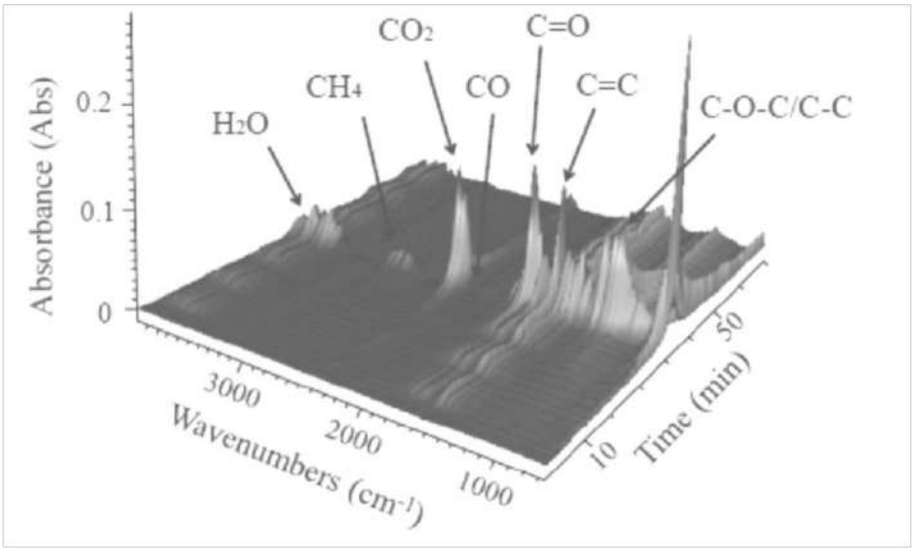


Figure 28: *TG-IR evolved gas analysis of cellulose in* N_2 *[131]*

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].

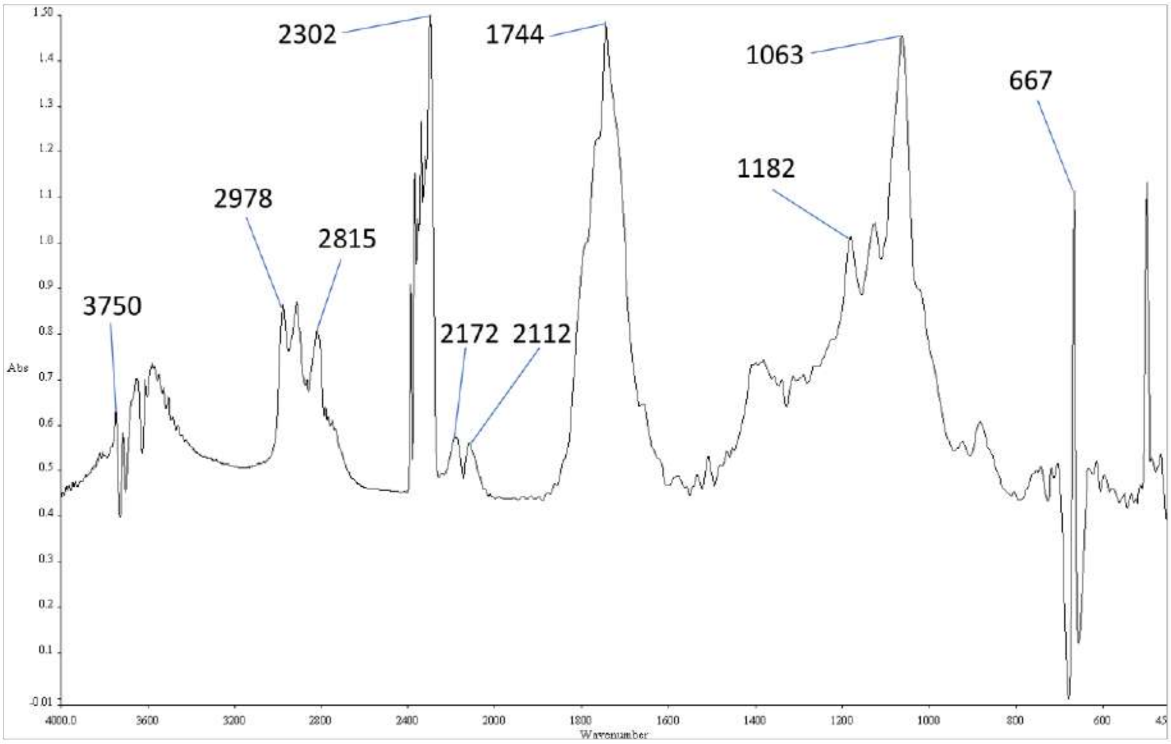


Figure 29: *TG-IR spectra of evolved gases of cellulose at the first decomposition stage ~ 396 °C [70]*

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.

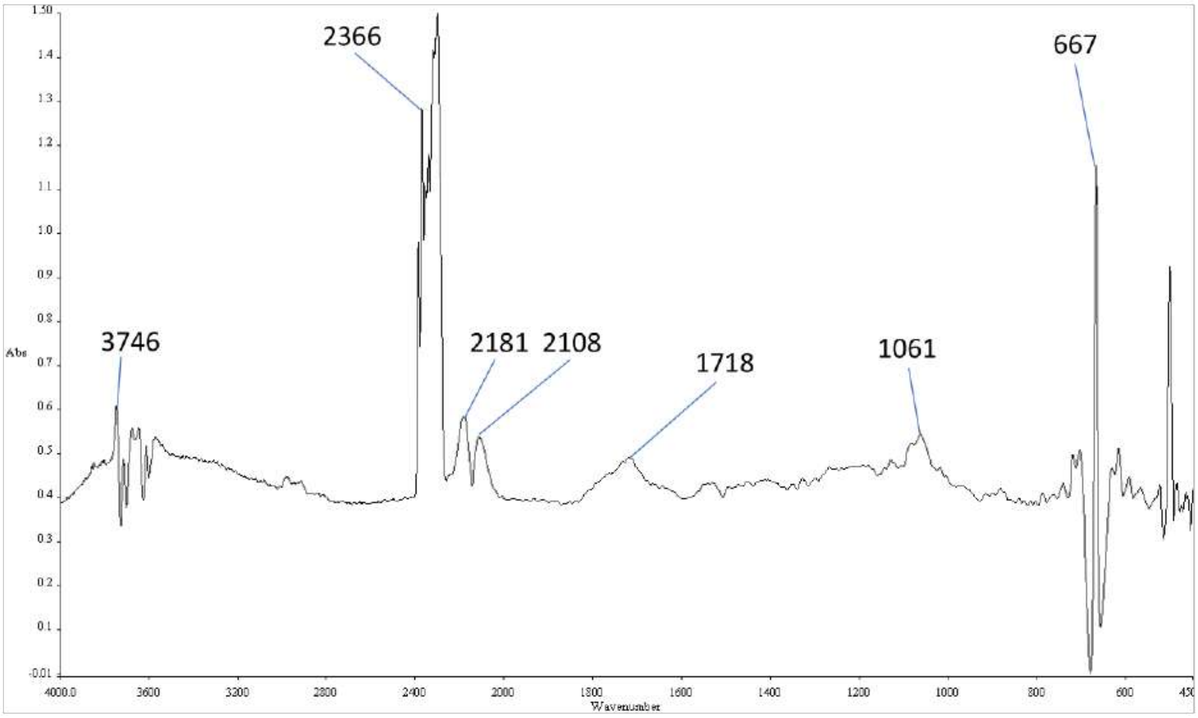


Figure 30: *TG-IR spectra of evolved gases of cellulose at the second decomposition stage ~ 578 °C [70]*

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_2O 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].

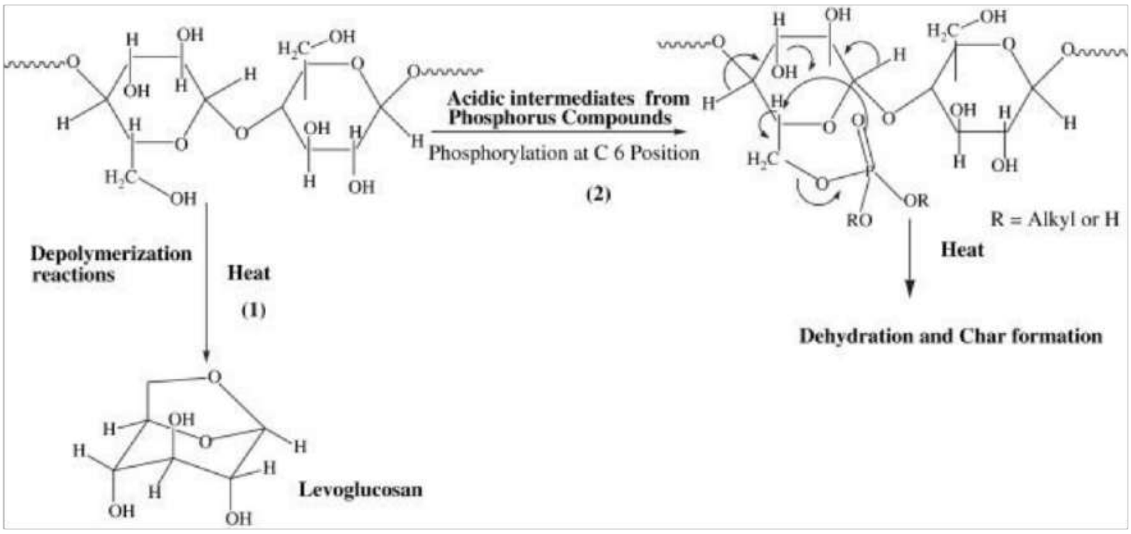


Figure 31: *Mode of action of phosphorus flame retardants [136]*

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].

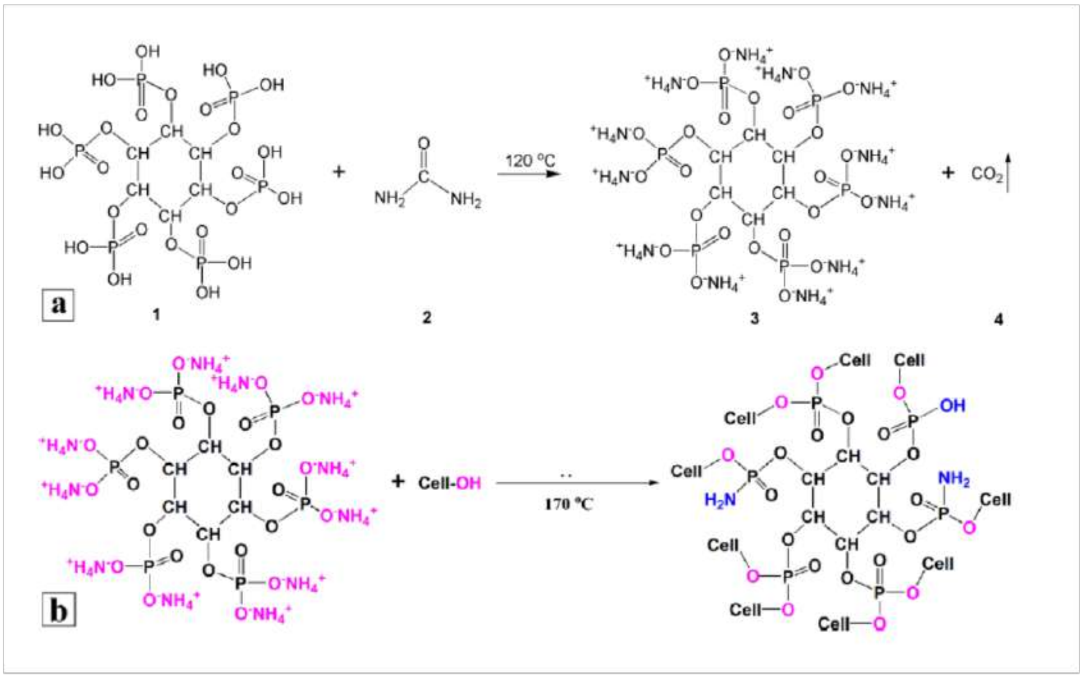


Figure 32: A possible reaction between a) PA and U b) PA-U intermediate and cellulose [139]

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].

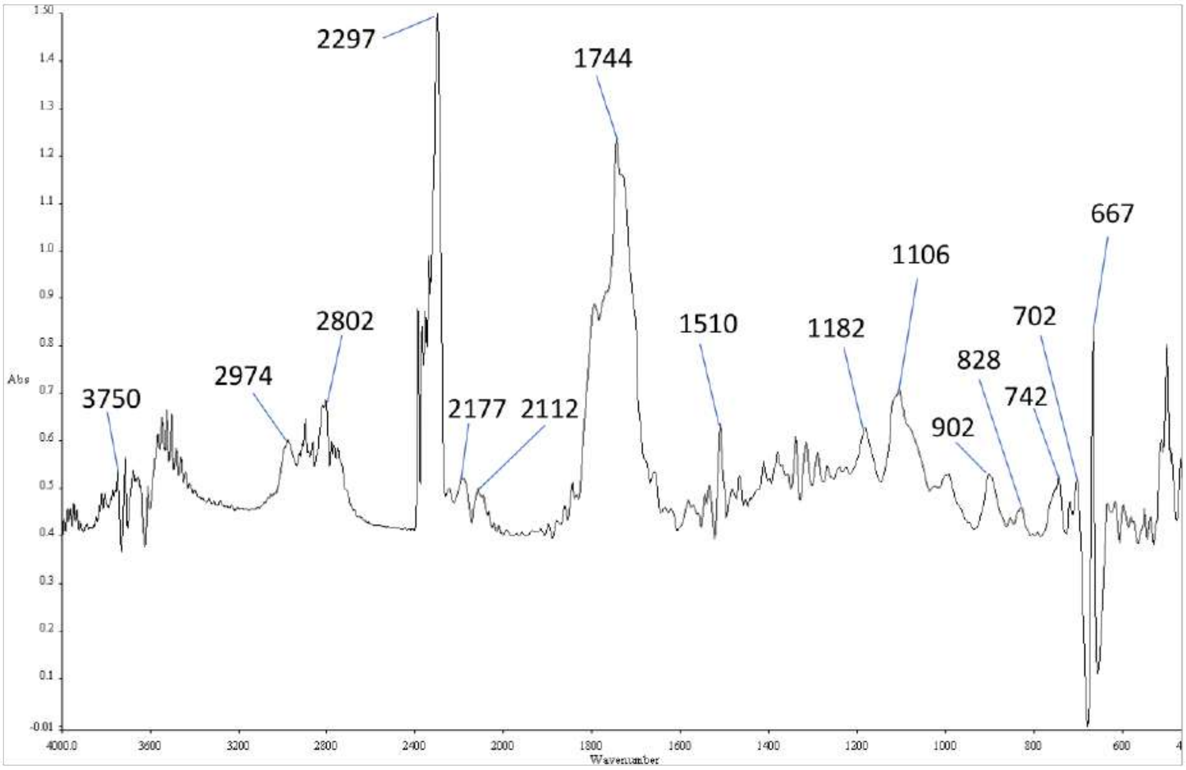


Figure 33: TG-IR spectra of evolved gases of 12 BL PA/CH-U treated cotton at ~ 339 °C

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].

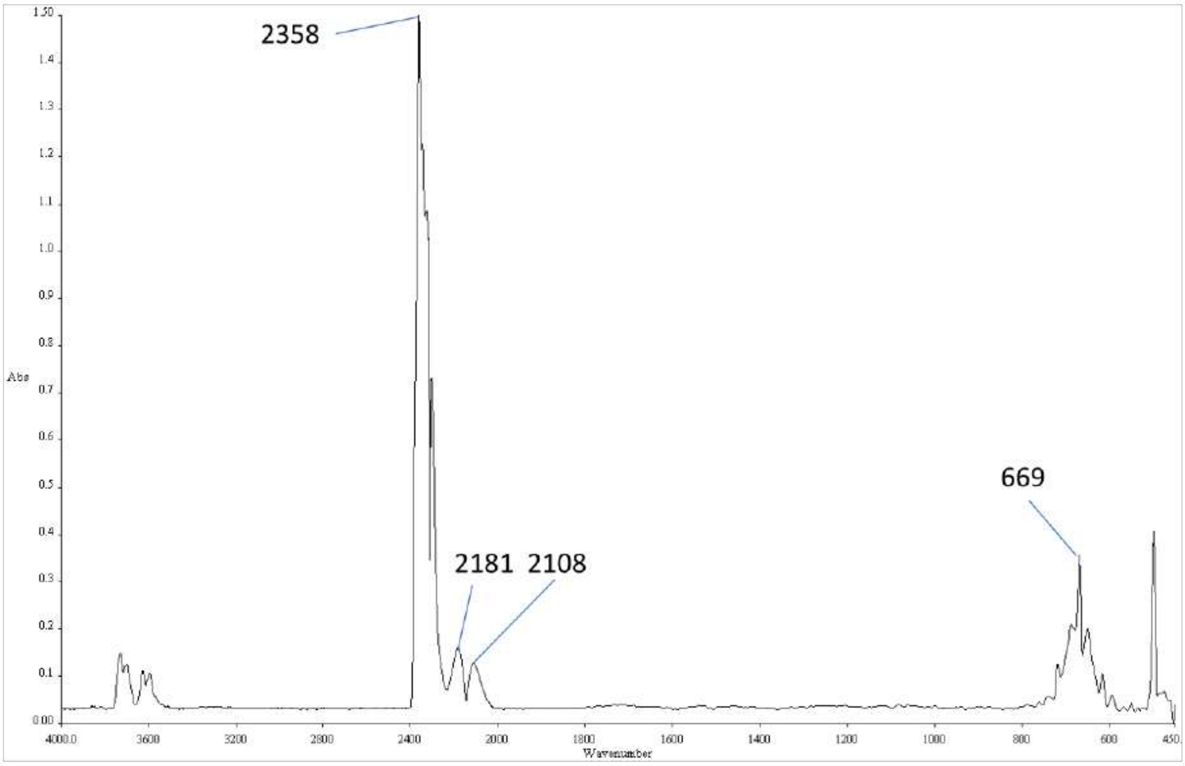


Figure 34: *TG-IR spectra of evolved gases of PA/CH-U treated cotton at ~ 636 °C*

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).

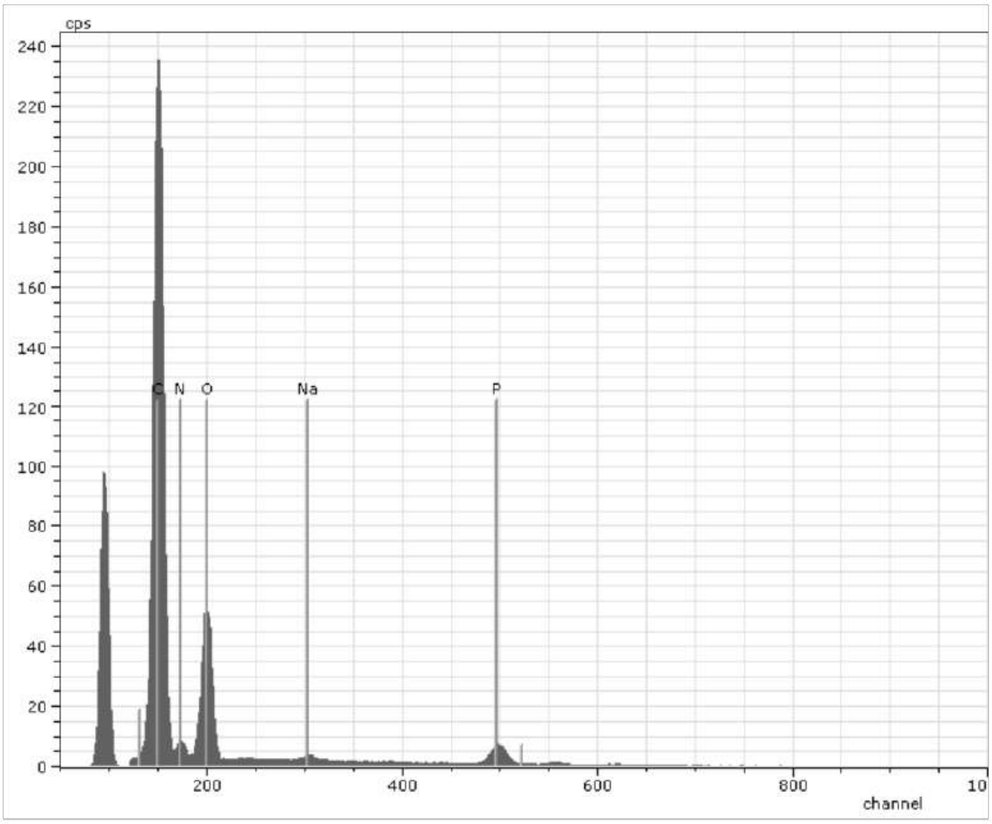
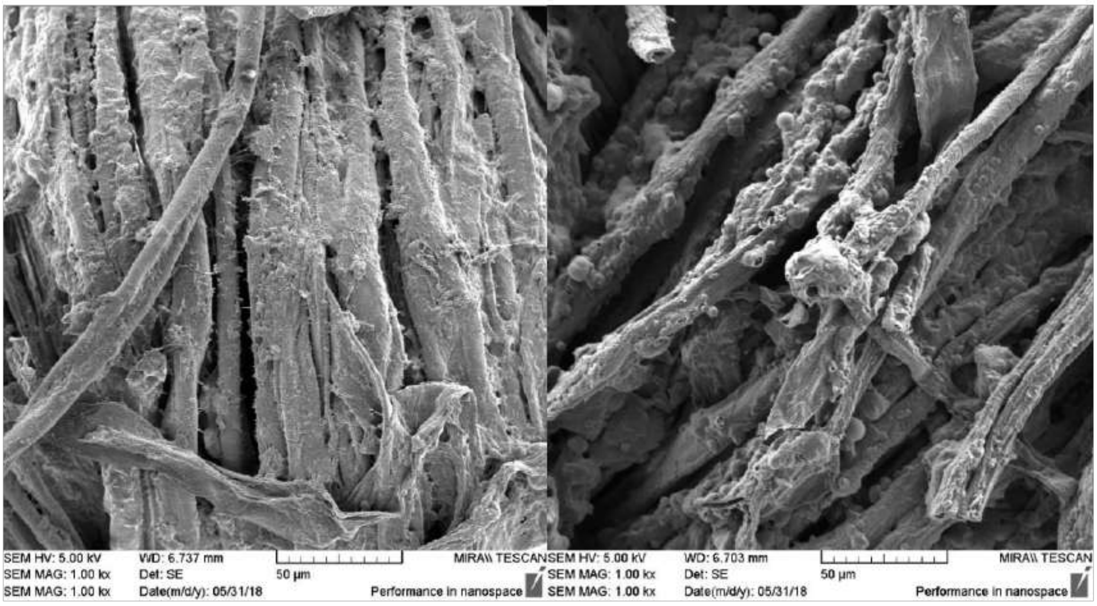


Figure 35: *EDS analysis of post-burn char of 12 BL PA/CH-U treated cotton*



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].

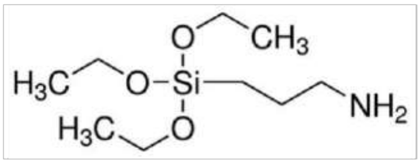


Figure 37: *Structural formula of APTES [160]*

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].

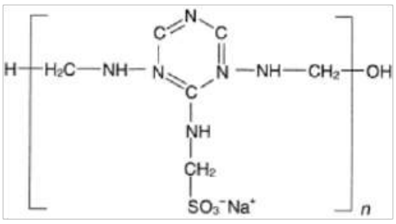


Figure 38: *Structural formula of SMF [161]*

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].

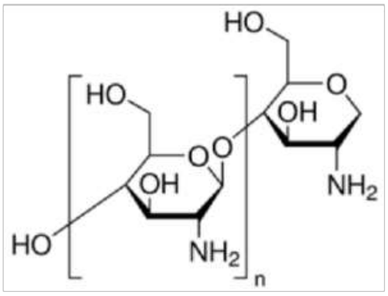


Figure 39: *Structural formula of CH [166]*

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].

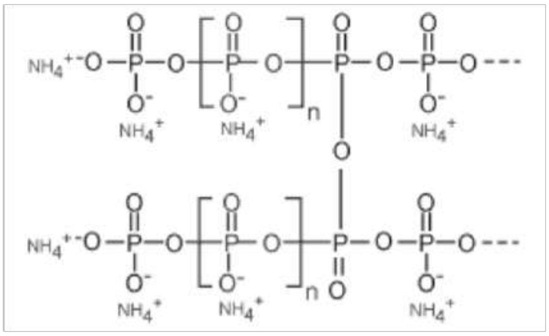


Figure 40: *Structural formula of APP (Form II)* [170]

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].

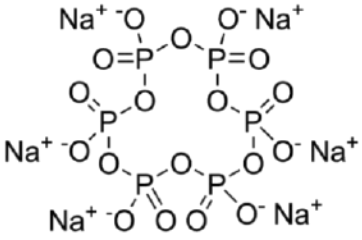


Figure 41: *Structural formula of PSP [174]*

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].

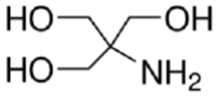


Figure 42: *Structural formula of THAM [176]*

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: $BaCl_2$ $C_4H_6O_4Ni$ x $4H_2O$ $C_4H_6O_4Co$ x $4H_2O$)			
	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$_2$O, 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$_2$O, 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$_3$OH	[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].

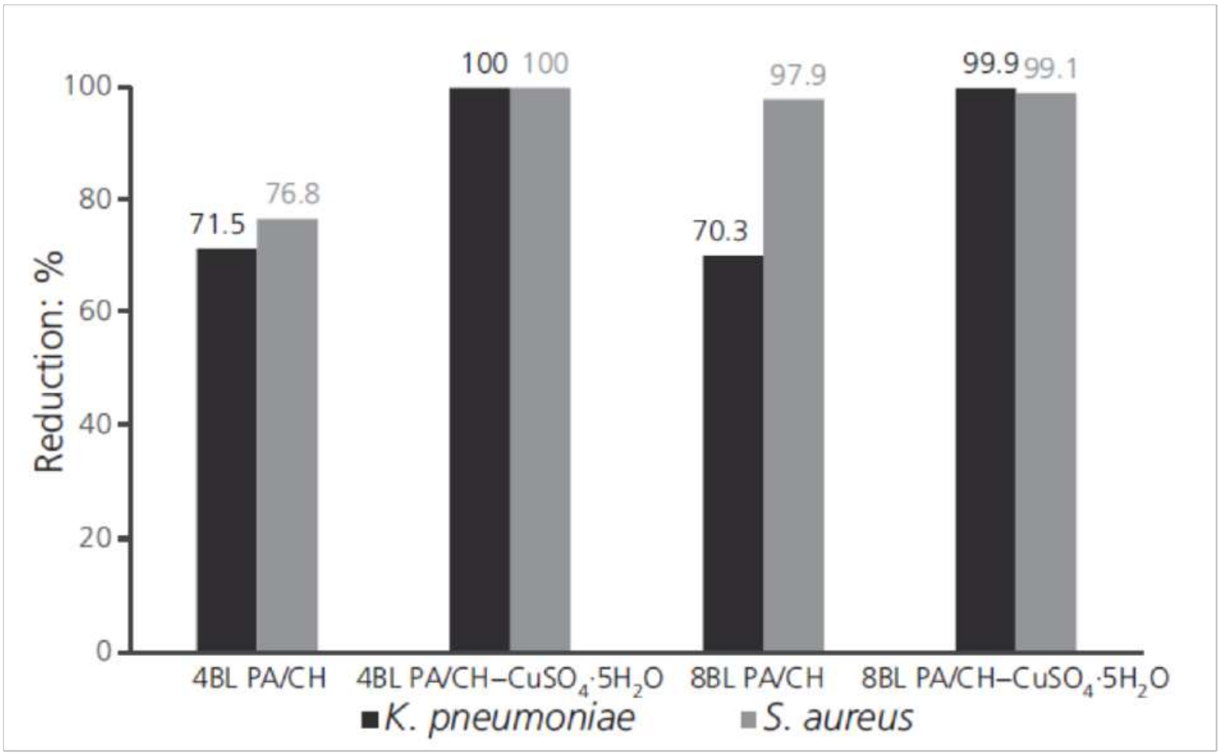


Figure 43: *Influence of treatment on reduction of K. Pneumoniae and S. aureus after 24 h of incubation (%) [77]*

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].

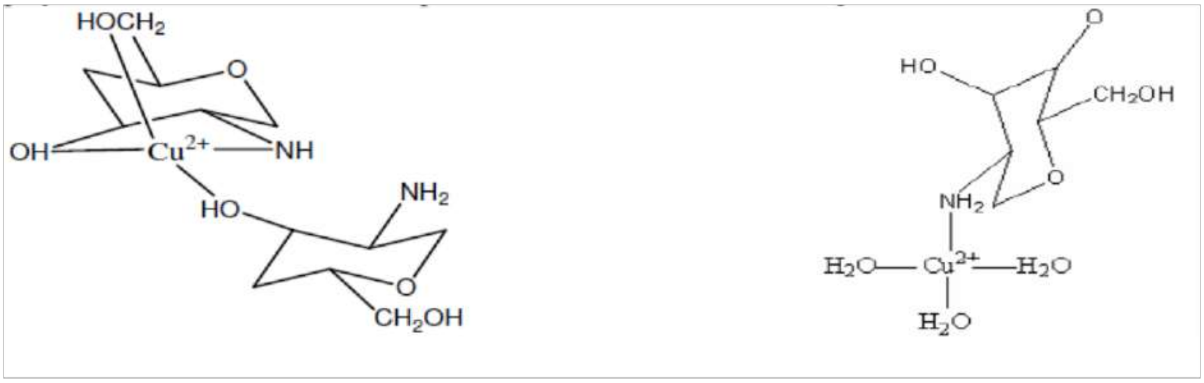


Figure 44: *Possible Cu^{2+}-CH complex structures [191]*

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]:

$$Cu^{2+} + O_2^{\bullet -} = Cu^{+} + O_2 \quad (23)$$

$$Cu^{+} + H_2O_2 = O_2 + OH^{\bullet} + OH^{-} \quad (24)$$

$OH^{\bullet}$ 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].

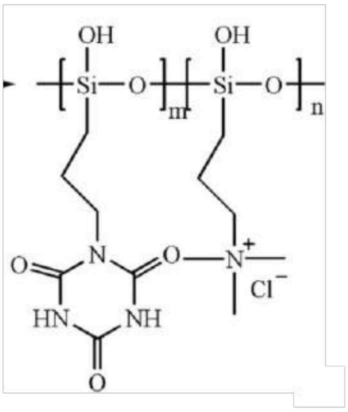


Figure 45: *Structural formula of PCQS [203]*

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.

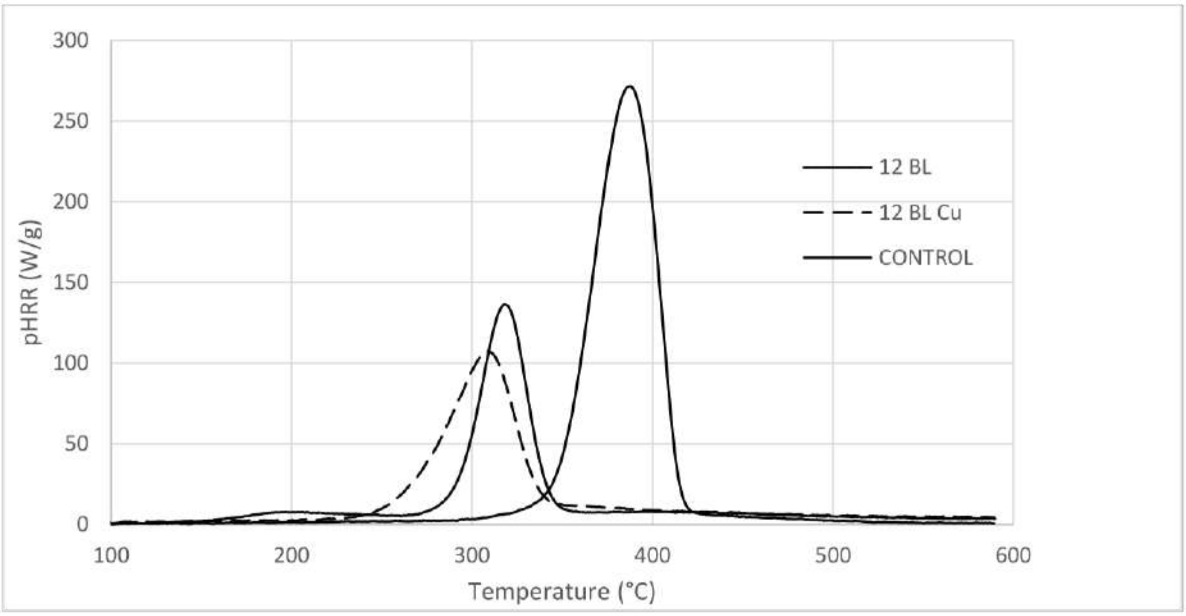


Figure 47: *MCC curves of untreated and 12 BL PA/CH-U and 12 BL PA/CH-U+$CuSO_4$ x $5H_2O$ treated cotton*

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

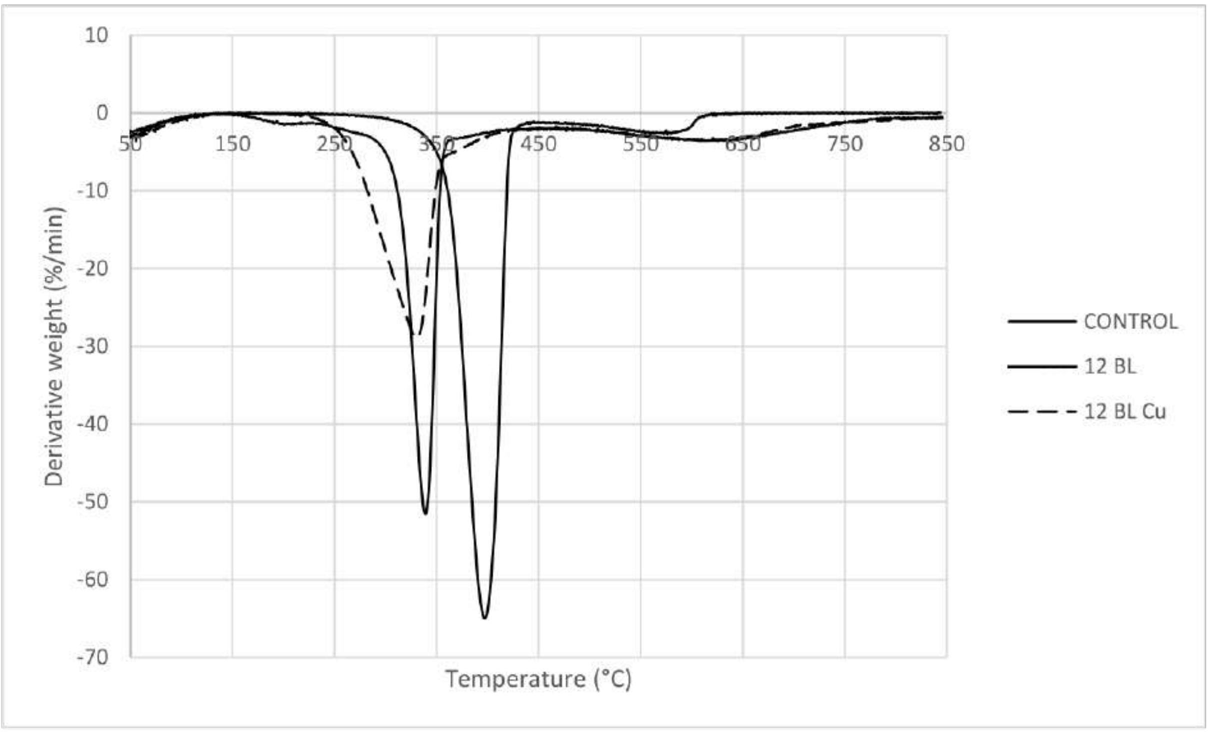


***Figure 48:** DTG curves of untreated and 12 BL PA/CH-U and 12 BL PA/CH-U+$CuSO_4$ x $5H_2O$ treated cotton*

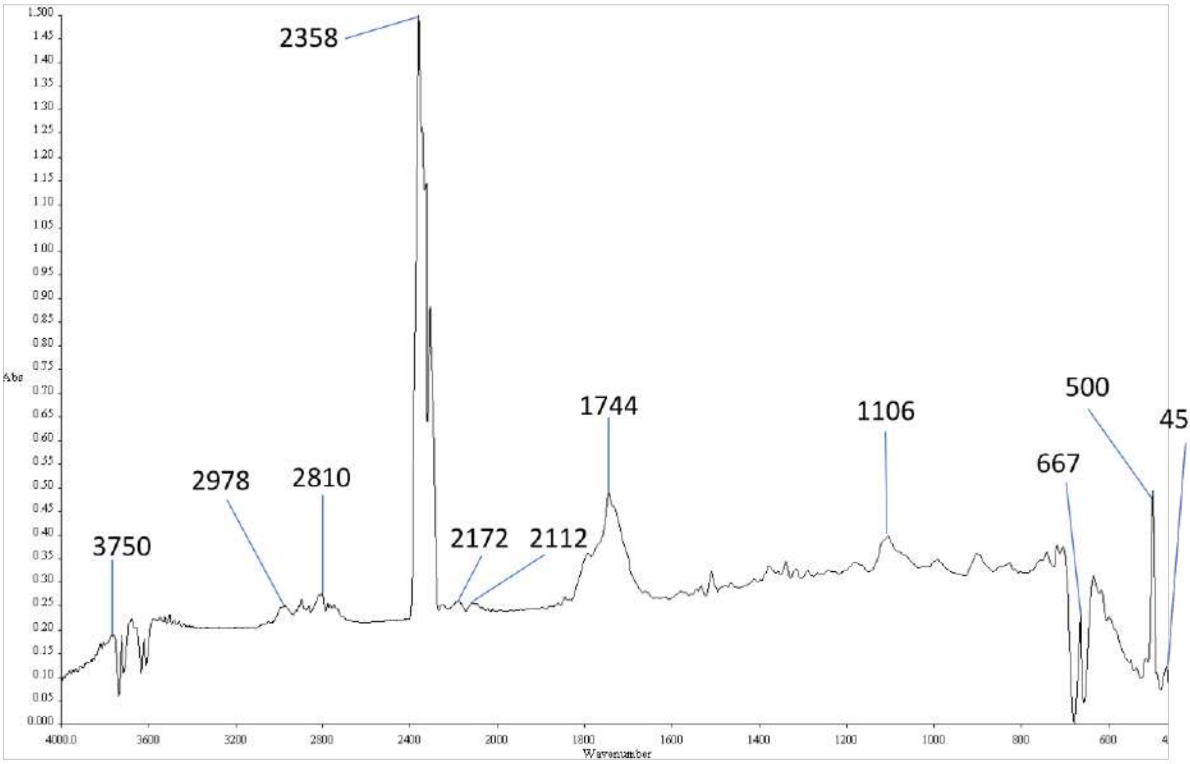


***Figure 49:** TG-IR spectra of evolved gases of 12 BL PA/CH-U+$CuSO_4$ x $5H_2O$ treated cotton at ~ 330 °C*

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).

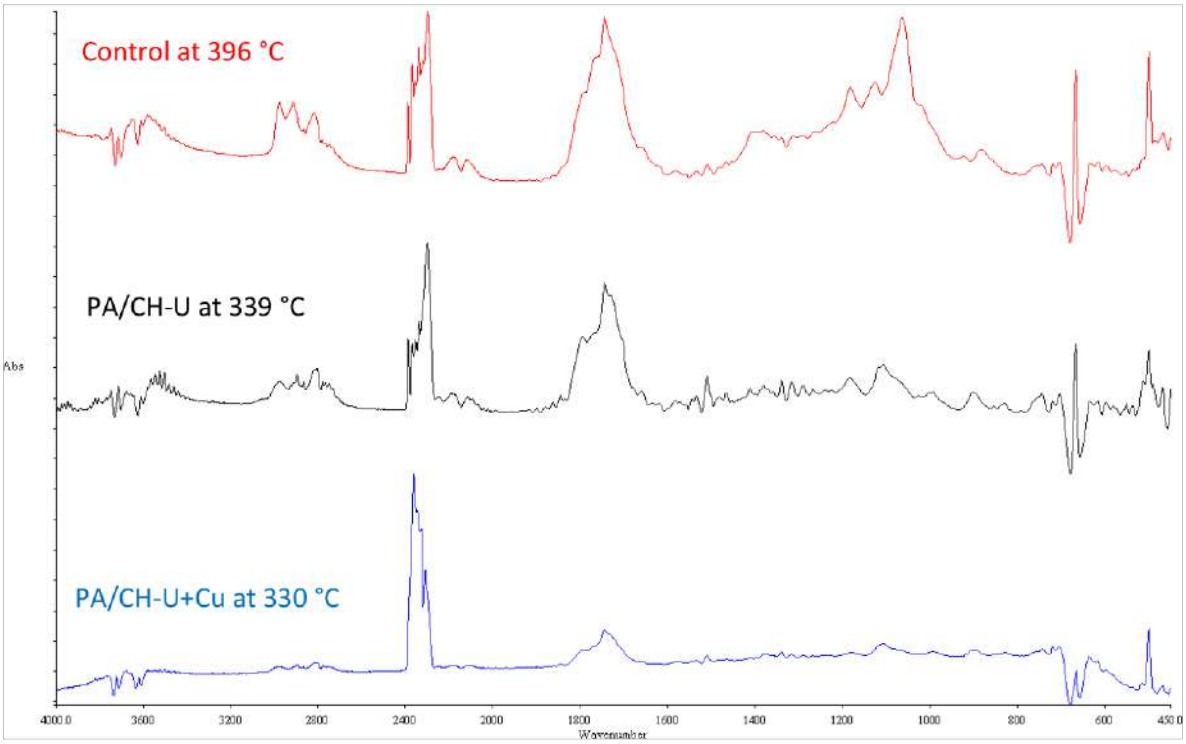


Figure 50: *TG-IR spectra of untreated (control), 12 BL PA/CH-U, and 12 BL PA/CH-U+CuSO*$_4$ *x 5H*$_2$*O treated cotton at the first decomposition stage (T*$_1$*) [70]*

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*$_2$*O 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

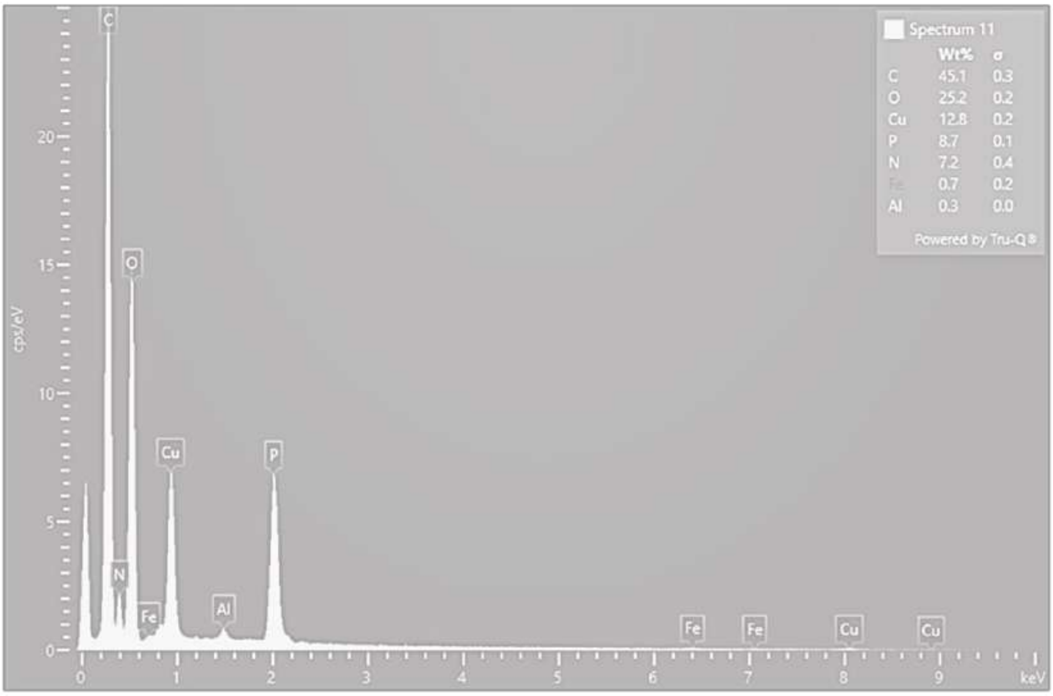
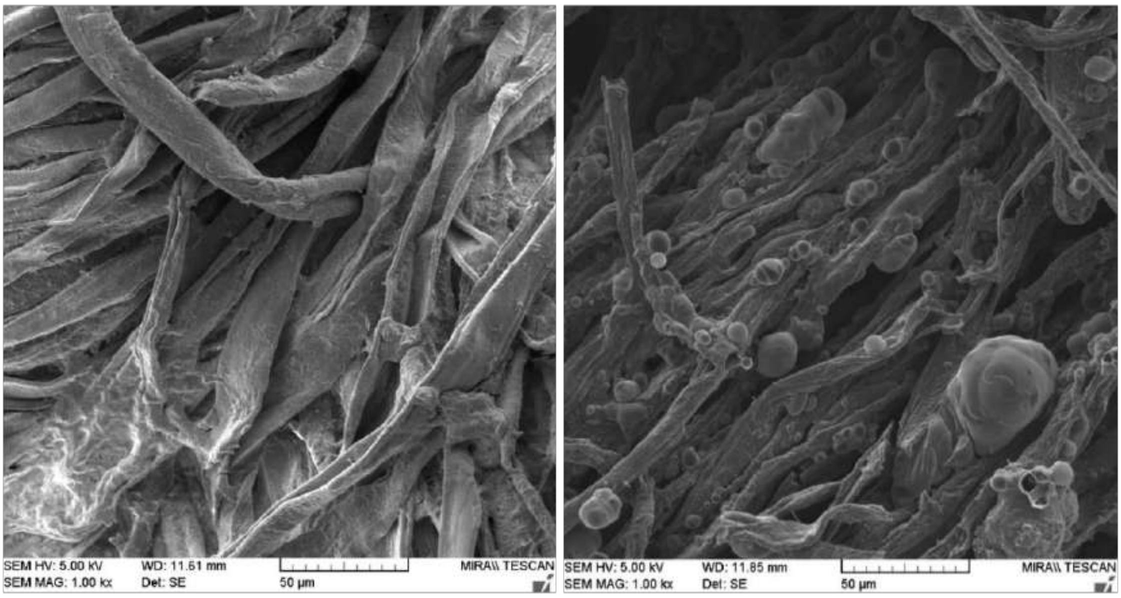


Figure 51: *EDS analysis of post-burn char of 12 BL PA/CH-U+Cu treated cotton*

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.

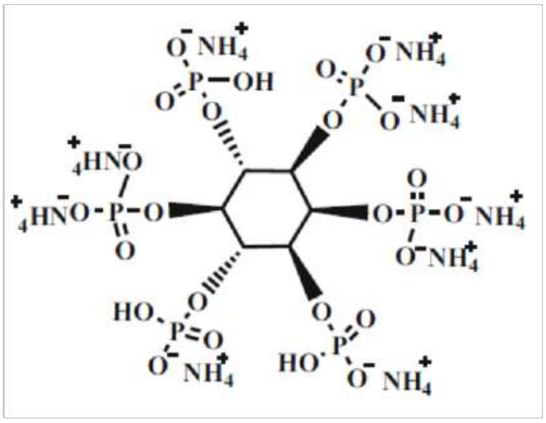


Figure 53: *Structural formula of AP [213]*

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].

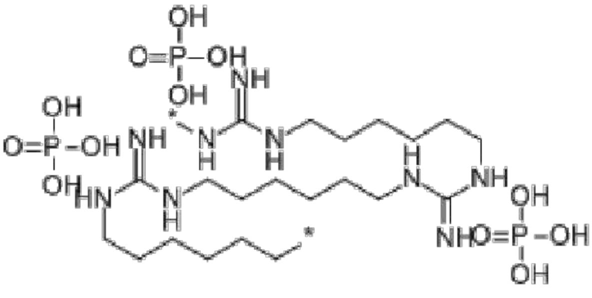


Figure 54: *Structural formula of PHMGP* [216]

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$_2$O	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$_2$O, almost no CH$_4$/CH$_3$OH, 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$_2$O, 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.

6. REFERENCES

1. Global Industry Analysts, I. *Textile Global Market Report 2021: COVID-19 Impact and Recovery to 2030*; London, UK, 2021;
2. Textile Exchange Organization *Preferred Fiber & Materials Market Report 2021*; Lamesa, TX, USA, 2021;
3. Lee, K.E. Environmental Sustainability in the Textile Industry. In *Sustainability in the Textile Industry*; Muthu, S.S., Ed.; Springer Nature Singapore Pte Ltd.: Singapore, 2017; pp. 17–55 ISBN 10.1007/9789811.
4. European Comission, D.-G. for E. A New Circular Economy Action Plan For a Cleaner and More Competitive Europe. *Doc. 52020DC0098* 2020, 1–20.
5. Segal, L.; Wakelyn, P.J. Cotton fibres. In *Handbook of natural fibres*; Kozłowski, R.M., Ed.; Woodhead Publishing Limited: Cambridge, UK, 2012; Vol. 1, pp. 11–23 ISBN 0824773357.
6. Heinze, T.; Heinze, T. Cellulose: Structure and Properties. In *Cellulose Chemistry and Properties: Fibers, Nanocelluloses and Advanced Materials. Advances in Polymer Science*; Rojas, O., Ed.; Springer, Cham, 2015; Vol. 271, pp. 1–52 ISBN 978-3-319-26015-0.
7. Tashiro, K.; Kobayashi, M. Theoretical Evaluation of Three-Dimensional Elastic Constants of Native and Regenerated Celluloses: Role of Hydrogen Bonds. *Polymer (Guildf).* **1991**, *32*, 1516–1526, doi:10.1016/0032-3861(91)90435-L.
8. Atalla, R.H.; Isogai, A. Celluloses. In *Comprehensive Natural Products II Chemistry and Biology*; Liu, H.-W., Mander, L., Eds.; Elsevier B.V: Amsterdam, Netherlands, 2010; Vol. 6, pp. 493–539 ISBN 978-0-08-045382-8.
9. Brushlinsky, N.; Ahrens, M.; Sokolov, S.; Wagner, P. World Fire Statistics Available online: https://www.ctif.org/sites/default/files/2020-06/CTIF_Report25.pdf (accessed on 28 November 2021).
10. Freedonia Group Global Flame Retardants Market by Country, Product and Market Available online: https://www.freedoniagroup.com/industry-study/global-flame-retardants-market-by-country-product-and-market-6th-edition-3499.htm (accessed on 28 November 2021).
11. Moldoveanu, S.C. General Information About Pyrolysis. In *Pyrolysis of Organic Molecules*; Moldoveanu, S.C., Ed.; Elsevier, 2019; pp. 1–33 ISBN 978-0-444-64000-0.
12. Magovac, E.; Bischof, S. Non-Halogen FR Treatment of Cellulosic Textiles. **2015**, *64*,

298–309.

13. Lewin, M.; Weil, E.D. Mechanisms and modes of action in flame retardancy of polymers. In *Fire Retardant Materials*; Horrocks, A.R., Price, D., Eds.; Woodhead Publishing Ltd.: Boca Raton, FL, USA, 2001; pp. 31–68 ISBN 1 85573 419 2.
14. Green, J. Mechanisms for Flame Retardancy and Smoke Suppression -A Review. *J. Fire Sci.* **1996**, *14*, 426–442, doi:10.1177/073490419601400602.
15. Scharte, B. Phosphorus-Based Flame Retardancy Mechanisms—Old Hat or a Starting Point for Future Development? *Materials (Basel).* **2010**, *3*, 4710–4745, doi:10.3390/MA3104710.
16. Zachariah, M.R.; Smith, O.I. Experimental and Numerical Studies of Sulfur Chemistry in H2/O2/SO2 Flames. *Combust. Flame* **1987**, *69*, 125–139, doi:10.1016/0010-2180(87)90026-5.
17. Rasmussen, C.L.; Glarborg, P.; Marshall, P. Mechanisms of Radical Removal by SO2. *Proc. Combust. Inst.* **2007**, *31 I*, 339–347, doi:10.1016/j.proci.2006.07.249.
18. Howell, B.A.; Daniel, Y.G. The Impact of Sulfur Oxidation Level on Flame Retardancy. *J. Fire Sci.* **2018**, *36*, 518–534, doi:10.1177/0734904118806155.
19. Feng, D.; Zhou, Z.; Bo, M. An Investigation of the Thermal Degradation of Melamine Phosphonite by XPS and Thermal Analysis Techniques. *Polym. Degrad. Stab.* **1995**, *50*, 65–70, doi:10.1016/0141-3910(95)00123-4.
20. Chen, J.P.; Isa, K. Thermal Decomposition of Urea and Urea Derivatives by Simultaneous TG/(DTA)/MS. *J. Mass Spectrom. Soc. Jpn.* **1998**, *46*, 299–303, doi:10.5702/MASSSPEC.46.299.
21. Grant, G.; Brenton, J.; Drysdale, D. Fire Suppression by Water Sprays. *Prog. Energy Combust. Sci.* **2000**, *26*, 79–130, doi:10.1016/S0360-1285(99)00012-X.
22. Nuessle, A.C.; Ford, F.M.; Hall, W.P.; Lippert, A.L. Some Aspects of the Cellulose-Phosphate-Urea Reaction. *Text. Res. J.* **1956**, *26*, 32–39, doi:10.1177/004051755602600105/ASSET/004051755602600105.FP.PNG_V03.
23. Hendrix, J.E.; Bostic, J.E.; Olson, E.S.; Barker, R.H. Pyrolysis and Combustion of Cellulose. I. Effects of Triphenyl Phosphate in the Presence of Nitrogenous Bases. *J. Appl. Polym. Sci.* **1970**, *14*, 1701–1723, doi:10.1002/APP.1970.070140705.
24. Langley, J.T.; Drews, M.J.; Barker, R.H. Pyrolysis and Combustion of Cellulose. VII. Thermal Analysis of the Phosphorylation of Cellulose and Model Carbohydrates during Pyrolsis in the Presence of Aromatic Phosphates and Phosphoramides. *J. Appl. Polym. Sci.* **1980**, *25*, 243–262, doi:10.1002/APP.1980.070250210.

25. Morgan, A.B. A Review of Transition Metal-Based Flame Retardants: Transition Metal Oxide/Salts, and Complexes. *ACS Symp. Ser.* **2009**, *1013*, 312–328, doi:10.1021/BK-2009-1013.CH019.
26. Ewing, C.T.; Faith, F.R.; Hughes, J.T.; Carhart, H.W. Evidence for Flame Extinguishment by Thermal Mechanisms. *Fire Technol.* **1989**, *25*, 195–212, doi:10.1007/BF01039778/METRICS.
27. Linteris, G.T.; Rumminger, M.D.; Babushok, V.I. Catalytic Inhibition of Laminar Flames by Transition Metal Compounds. *Prog. Energy Combust. Sci.* **2008**, *34*, 288–329, doi:10.1016/J.PECS.2007.08.002.
28. Mitani, T. A Flame Inhibition Theory by Inert Dust and Spray. *Combust. Flame* **1981**, *43*, 243–253, doi:10.1016/0010-2180(81)90024-9.
29. Wu, Y.; Zhou, X.; Xing, Z.; Ma, J. Metal Compounds as Catalysts in the Intumescent Flame Retardant System for Polyethylene Terephthalate Fabrics. **2018**, *89*, 2983–2997, doi:10.1177/0040517518805373.
30. Horrocks, A.R. Overview of Traditional Flame-retardant Solutions (including Coating and Backcoating Technologies). In *Update on Flame Retardant Textiles: State of the Art, Environmental Issues and Innovative Solutions*; Alongi, J., Horrocks, A.R., Carosio, F., Malucelli, G., Eds.; Smithers Rapra Technology Ltd.: Shawburry, UK, 2013; pp. 123–175 ISBN 9781909030176.
31. Tesfaye, S.; Hamba, N.; Gerbi, A.; Negeri, Z. Occupational Formaldehyde Exposure Linked to Increased Systemic Health Impairments and Counteracting Beneficial Effects of Selected Antioxidants. *Alexandria J. Med.* **2021**, *57*, 157–167, doi:10.1080/20905068.2021.1926172.
32. Dasarathy, S.; Mookerjee, R.P.; Rackayova, V.; Rangroo Thrane, V.; Vairappan, B.; Ott, P.; Rose, C.F. Ammonia Toxicity: From Head to Toe? *Metab. Brain Dis. 2016 322* **2016**, *32*, 529–538, doi:10.1007/S11011-016-9938-3.
33. Horrocks, A.R. Flame Retardant Challenges for Textiles and Fibres: New Chemistry versus Innovatory Solutions. *Polym. Degrad. Stab.* **2011**, *96*, 377–392, doi:10.1016/j.polymdegradstab.2010.03.036.
34. Schindler, W.D.; Hauser, P.J. Flame-retardant finishes. In *Chemical finishing of textiles*; Schindler, W.D., Hauser, P.J., Eds.; Woodhead Publishing: Cambridge, UK, 2004; pp. 98–116 ISBN 978-1-85573-905-5.
35. Commission Regulation (EU) 2017/227. *Off. J. Eur. Union* **2017**, *L 35/7*, 6–9.
36. Horrocks, A.R. Smart flame retardant textile coatings and laminates. In *Smart Textile*

Coatings and Laminates; Smith, W.C., Ed.; Woodhead Publishing Ltd.: Cambridge, UK, 2019; pp. 205–236 ISBN 9780081024287.

37. Malucelli, G. Sol-Gel and Layer-by-Layer Coatings for Flame-Retardant Cotton Fabrics: Recent Advances. **2020**, *10*, 333, doi:10.3390/coatings10040333.
38. Haji, A.; Kan, C.-W. Plasma treatment for sustainable functionalization of textiles. In *Green Chemistry for Sustainable Textiles*; Ibrahim, N., Hussain, C.M., Eds.; Woodhead Publishing, 2021; pp. 265–277 ISBN 978-0-323-85204-3.
39. Horrocks, A.R.; Eivazi, S.; Ayesh, M.; Kandola, B. Environmentally Sustainable Flame Retardant Surface Treatments for Textiles: The Potential of a Novel Atmospheric Plasma/UV Laser Technology. *Fibers 2018, Vol. 6, Page 31* **2018**, *6*, 31, doi:10.3390/FIB6020031.
40. Iler, R.K. Multilayers of Colloidal Particles. *J. Colloid Interface Sci.* **1966**, *21*, 569–594, doi:10.1016/0095-8522(66)90018-3.
41. Kirkland, J.J. Porous Thin-Layer Modified Glass Bead Supports for Gas Liquid Chromatography. *Anal. Chem.* **1965**, *37*, 1458–1461, doi:10.1021/ac60231a004.
42. Decher, G.; Hong, J.D.; Schmitt, J. Buildup of Ultrathin Multilayer Films by a Self-Assembly Process: III. Consecutively Alternating Adsorption of Anionic and Cationic Polyelectrolytes on Charged Surfaces. *Thin Solid Films* **1992**, *210–211*, 831–835, doi:10.1016/0040-6090(92)90417-A.
43. Ariga, K.; Yamauchi, Y.; Rydzek, G.; Ji, Q.; Yonamine, Y.; Wu, K.C.-W.; Hill, J.P. Layer-by-Layer Nanoarchitectonics: Invention, Innovation, and Evolution. *Chem. Lett.* **2014**, *43*, 36–68, doi:10.1246/cl.130987.
44. Alongi, J.; Carosio, F.; Frache, A.; Malucelli, G. Layer-by-Layer Coatings Assembled through Dipping, Vertical or Horizontal Spray for Cotton Flame Retardancy. *Carbohydr. Polym.* **2013**, *92*, 114–119, doi:10.1016/J.CARBPOL.2012.08.086.
45. Michel, M.; Toniazzo, V.; Ruch, D.; Ball, V. Deposition Mechanisms in Layer-by-Layer or Step-by-Step Deposition Methods: From Elastic and Impermeable Films to Soft Membranes with Ion Exchange Properties. *ISRN Mater. Sci.* **2012**, *2012*, 1–13, doi:10.5402/2012/701695.
46. Wu, G.; Zhang, X. Layer-by-Layer Assembly: From Conventional to Unconventional Methods. In *Multilayer Thin Films: Sequential Assembly of Nanocomposite Materials: Second Edition*; Decher, G., Schlenoff, J.B., Eds.; Wiley-VCH Verlag GmbH & Co. KGaA., 2012; Vol. 1, pp. 43–67 ISBN 9783527316489.
47. *World Health Statistics 2021: Monitoring Health for the SDGs, Sustainable*

Development Goals; World Health Organization: Geneva, Switzerland, 2021;

48. Gulati, R.; Sharma, S.; Sharma, R.K. Antimicrobial Textile: Recent Developments and Functional Perspective. *Polym. Bull.* **2021**, 1–25, doi:10.1007/S00289-021-03826-3/TABLES/2.
49. Salton, M.R.J.; Kim, K.-S. Structure. In *Medical Microbiology*; Baron, S., Ed.; University of Texas Medical Branch: Galveston, TX, USA, 1996; pp. 257–322 ISBN 0-9631172-1-1.
50. Reygaert, W.C. An Overview of the Antimicrobial Resistance Mechanisms of Bacteria. *AIMS Microbiol.* **2018**, *4*, 482, doi:10.3934/MICROBIOL.2018.3.482.
51. Schweizer, H.P. Triclosan: A Widely Used Biocide and Its Link to Antibiotics. *FEMS Microbiol. Lett.* **2001**, *202*, 1–7, doi:10.1111/J.1574-6968.2001.TB10772.X.
52. Halden, R.U.; Lindeman, A.E.; Aiello, A.E.; Andrews, D.; Arnold, W.A.; Fair, P.; Fuoco, R.E.; Geer, L.A.; Johnson, P.I.; Lohmann, R.; et al. The Florence Statement on Triclosan and Triclocarban. *Environ. Health Perspect.* **2017**, *125*, doi:10.1289/EHP1788.
53. Choudhury, R.; Kumar, A. Finishes for protection against microbial, insect and UV radiation. In *Principles of Textile Finishing*; Choudhury, R., Kumar, A., Eds.; Elsevier: Cambridge, UK, 2017; pp. 319–382 ISBN 978-0-08-100646-7.
54. Bischof-Vukušić, S.; Grgac, S.F.; Budimir, A.; Kalenić, S. Cotton Textiles Modified with Citric Acid as Efficient Anti-Bacterial Agent for Prevention of Nosocomial Infections. *Croat. Med. J.* **2011**, *52*, 68–75, doi:10.3325/cmj.2011.52.68.
55. Zhang, Y.Y.; Xu, Q.B.; Fu, F.Y.; Liu, X.D. Durable Antimicrobial Cotton Textiles Modified with Inorganic Nanoparticles. *Cellulose* 2016, *23*, 2791–2808.
56. Zhang, B.; Jiao, Y.; Kang, Z.; Ma, K.; Ren, X.; Liang, J. Durable Antimicrobial Cotton Fabrics Containing Stable Quaternarized N-Halamine Groups. *Cellulose* **2013**, *20*, 3067–3077, doi:10.1007/s10570-013-0031-3.
57. Zhang, Z.; Chen, L.; Ji, J.; Huang, Y.; Chen, D. Antibacterial Properties of Cotton Fabrics Treated with Chitosan. *Text. Res. J.* **2003**, *73*, 1103–1106, doi:10.1177/004051750307301213.
58. Nayak, R.; Padhye, R. Antimicrobial finishes for textiles. In *Functional Finishes for Textiles: Improving Comfort, Performance and Protection*; Paul, R., Ed.; Woodhead Publishing: Oxford, UK, 2015; pp. 361–385 ISBN 9780857098450.
59. Gerba, C.P. Quaternary Ammonium Biocides: Efficacy in Application. *Appl. Environ. Microbiol.* **2015**, *81*, 464, doi:10.1128/AEM.02633-14.

60. Burel, C.; Kala, A.; Purevdorj-Gage, L. Impact of PH on Citric Acid Antimicrobial Activity against Gram-negative Bacteria. *Lett. Appl. Microbiol.* **2021**, *72*, 332, doi:10.1111/LAM.13420.

61. Raafat, D.; Von Bargen, K.; Haas, A.; Sahl, H.G. Insights into the Mode of Action of Chitosan as an Antibacterial Compound. *Appl. Environ. Microbiol.* **2008**, *74*, 3764, doi:10.1128/AEM.00453-08.

62. Morais, D.S.; Guedes, R.M.; Lopes, M.A. Antimicrobial Approaches for Textiles: From Research to Market. *Mater. 2016, Vol. 9, Page 498* **2016**, *9*, 498, doi:10.3390/MA9060498.

63. Granados, A.; Pleixats, R.; Vallribera, A. Recent Advances on Antimicrobial and Anti-Inflammatory Cotton Fabrics Containing Nanostructures. *Mol. 2021, Vol. 26, Page 3008* **2021**, *26*, 3008, doi:10.3390/MOLECULES26103008.

64. Gomes, A.P.; Mano, J.F.; Queiroz, J.A.; Gouveia, I.C. Layer-by-Layer Deposition of Antimicrobial Polymers on Cellulosic Fibers: A New Strategy to Develop Bioactive Textiles. *Polym. Adv. Technol.* **2013**, *24*, 1005–1010, doi:10.1002/PAT.3176.

65. Zhang, J.; Chen, B.; Liu, J.; Zhu, P.; Liu, Y.; Jiang, Z.; Dong, C.; Lu, Z. Multifunctional Antimicrobial and Flame Retardant Cotton Fabrics Modified with a Novel N,N-Di(Ethyl Phosphate) Biguanide. *Cellulose* **2020**, *27*, 7255–7269, doi:10.1007/S10570-020-03256-W/TABLES/5.

66. El-Shafei, A.; Elshemy, M.; Abou-Okeil, A. Eco-Friendly Finishing Agent for Cotton Fabrics to Improve Flame Retardant and Antibacterial Properties. *Carbohydr. Polym.* **2015**, *118*, 83–90, doi:10.1016/J.CARBPOL.2014.11.007.

67. Podgornik, B.B.; Šandrič, S.; Kert, M. Microencapsulation for Functional Textile Coatings with Emphasis on Biodegradability—A Systematic Review. **2021**, *11*, 1371, doi:10.3390/COATINGS11111371.

68. Palaskar, S.S.; Desai, A.N.; Shukla, S.R. Development of Multifunctional Cotton Fabric Using Atmospheric Pressure Plasma and Nano-Finishing. *J. Text. Inst.* **2016**, *107*, 405–412, doi:10.1080/00405000.2015.1034932.

69. Oliver, S.; Lei, L.; Fan, K.W.; Wang, C.; Baena, J.C.; Pham, P.; Lin, Q.; Kabir, I.I.; Wong, E.H.H.; Yuen, A.C.Y.; et al. Wet or Dry Multifunctional Coating Prepared by Visible Light Polymerisation with Fire Retardant, Thermal Protective, and Antimicrobial Properties. *Cellulose* **2021**, *28*, 8821–8840, doi:10.1007/S10570-021-04095-Z.

70. 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. **2021**, *9*, 69, doi:10.3390/FIB9110069.

71. Li, Y.-C.; Schulz, J.; Mannen, S.; Delhom, C.; Condon, B.; Chang, S.; Zammarano, M.; Grunlan, J.C. Flame Retardant Behavior of Polyelectrolyte-Clay Thin Film Assemblies on Cotton Fabric. *ACS Nano* **2010**, *4*, 3325–37, doi:10.1021/nn100467e.
72. Choi, K.; Seo, S.; Kwon, H.; Kim, D.; Park, Y.T. Fire Protection Behavior of Layer-by-Layer Assembled Starch–Clay Multilayers on Cotton Fabric. *J. Mater. Sci.* **2018**, *53*, 11433–11443, doi:10.1007/s10853-018-2434-x.
73. Eremenko, A.M.; Petrik, I.S.; Smirnova, N.P.; Rudenko, A. V.; Marikvas, Y.S. Antibacterial and Antimycotic Activity of Cotton Fabrics, Impregnated with Silver and Binary Silver/Copper Nanoparticles. *Nanoscale Res. Lett.* **2016**, *11*, 28, doi:10.1186/S11671-016-1240-0.
74. Borkow, G.; Gabbay, J. Putting Copper into Action: Copper-impregnated Products with Potent Biocidal Activities. *FASEB J.* **2004**, *18*, 1728–1730, doi:10.1096/FJ.04-2029FJE.
75. Llorens, A.; Lloret, E.; Picouet, P.; Fernandez, A. Study of the Antifungal Potential of Novel Cellulose/Copper Composites as Absorbent Materials for Fruit Juices. *Int. J. Food Microbiol.* **2012**, *158*, 113–119, doi:10.1016/J.IJFOODMICRO.2012.07.004.
76. 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.
77. Magovac, E.; Budimir, A.; Jordanov, I.; Bischof, S.; Grunlan, J.C. Antibacterial Cotton from Novel Phytic Acid-Based Multilayer Nanocoating. *Green Mater.* **2021**, *0*, 1–6, doi:10.1680/JGRMA.20.00050.
78. ISO 4589-2:2017(En), Plastics — Determination of Burning Behaviour by Oxygen Index — Part 2: Ambient-Temperature Test Available online: https://www.iso.org/obp/ui/#iso:std:iso:4589:-2:ed-2:v1:en (accessed on 25 October 2021).
79. ASTM D6413 / D6413M - 15 Standard Test Method for Flame Resistance of Textiles (Vertical Test) Available online: https://www.astm.org/Standards/D6413.htm (accessed on 25 October 2021).
80. ASTM D7309 - 21a, Standard Test Method for Determining Flammability Characteristics of Plastics and Other Solid Materials Using Microscale Combustion Calorimetry Available online: https://www.astm.org/Standards/D7309.htm (accessed

on 25 October 2021).

81. Ebeid, E.-Z.M.; Zakaria, M.B. State of the art and definitions of various thermal analysis techniques. In *Thermal Analysis*; Ebeid, E.-Z.M., Zakaria, M.B., Eds.; Elsevier: Amsterdam, Netherlands, 2021; pp. 1–39 ISBN 978-0-323-90191-8.
82. AATCC Committee RA31 TM100-TM 100 Test Method for Antibacterial Finishes on Textile Materials: Assess Available online: https://members.aatcc.org/store/tm100/513/ (accessed on 2 March 2020).
83. Hyde, K.; Rusa, M.; Hinestroza, J. Layer-by-Layer Deposition of Polyelectrolyte Nanolayers on Natural Fibres: Cotton. *Nanotechnology* **2005**, *16*, S422, doi:10.1088/0957-4484/16/7/017.
84. Fang, F.; Xiao, D.; Zhang, X.; Meng, Y.; Cheng, C.; Bao, C.; Ding, X.; Cao, H.; Tian, X. Construction of Intumescent Flame Retardant and Antimicrobial Coating on Cotton Fabric via Layer-by-Layer Assembly Technology. *Surf. Coatings Technol.* **2015**, *276*, 726–734, doi:10.1016/j.surfcoat.2015.05.023.
85. Lacasse, K.; Baumann, W. Finishing. In *Textile Chemicals*; Lacasse, K., Baumann, W., Eds.; Springer: Berlin, Heidelberg, 2004; pp. 373–483 ISBN 978-3-642-62346-2.
86. Khandual, A. Green Flame Retardants for Textiles. *Environ. Footprints Eco-Design Prod. Process.* **2016**, 171–227, doi:10.1007/978-981-10-0245-8_6/COVER.
87. Li, P.; Wang, B.; Liu, Y.Y.; Xu, Y.J.; Jiang, Z.M.; Dong, C.H.; Zhang, L.; Liu, Y.; Zhu, P. Fully Bio-Based Coating from Chitosan and Phytate for Fire-Safety and Antibacterial Cotton Fabrics. *Carbohydr. Polym.* **2020**, *237*, 116173, doi:10.1016/j.carbpol.2020.116173.
88. Zhang, Y.; Tian, W.; Liu, L.; Cheng, W.; Wang, W.; Liew, K.M.; Wang, B.; Hu, Y. Eco-Friendly Flame Retardant and Electromagnetic Interference Shielding Cotton Fabrics with Multi-Layered Coatings. *Chem. Eng. J.* **2019**, *372*, 1077–1090, doi:10.1016/j.cej.2019.05.012.
89. Li, S.; Lin, X.; Li, Z.; Ren, X. Hybrid Organic-Inorganic Hydrophobic and Intumescent Flame-Retardant Coating for Cotton Fabrics. *Compos. Commun.* **2019**, *14*, 15–20, doi:10.1016/j.coco.2019.05.005.
90. Li, S.; Lin, X.; Liu, Y.; Li, R.; Ren, X.; Huang, T.-S.T.S. Phosphorus-Nitrogen-Silicon-Based Assembly Multilayer Coating for the Preparation of Flame Retardant and Antimicrobial Cotton Fabric. *Cellulose* **2019**, *26*, 4213–4223, doi:10.1007/s10570-019-02373-5.
91. Zilke, O.; Plohl, D.; Opwis, K.; Mayer-Gall, T.; Gutmann, J.S. A Flame-Retardant

Phytic-Acid-Based LbL-Coating for Cotton Using Polyvinylamine. *Polymers (Basel).* **2020**, *12*, 1202, doi:10.3390/POLYM12051202.

92. Huntsman Pte Ltd Pyrovatex CP New Pyrovatex CP-LF Available online: https://docplayer.net/32223760-Pyrovatex-cp-new-pyrovatex-cp-lf.html (accessed on 31 March 2023).
93. Pan, Y.; Liu, L.; Zhang, Y.; Song, L.; Hu, Y.; Jiang, S.; Zhao, H. Effect of Genipin Crosslinked Layer-by-Layer Self-Assembled Coating on the Thermal Stability, Flammability and Wash Durability of Cotton Fabric. *Carbohydr. Polym.* **2019**, *206*, 396–402, doi:10.1016/j.carbpol.2018.11.037.
94. Lin, D.; Zeng, X.; Li, H.; Lai, X. Facile Fabrication of Superhydrophobic and Flame-Retardant Coatings on Cotton Fabrics via Layer-by-Layer Assembly. *Cellulose* **2018**, *25*, 3135–3149, doi:10.1007/s10570-018-1748-9.
95. Xue, C.H.; Wu, Y.; Guo, X.J.; Liu, B.Y.; Wang, H. Di; Jia, S.T. Superhydrophobic, Flame-Retardant and Conductive Cotton Fabrics via Layer-by-Layer Assembly of Carbon Nanotubes for Flexible Sensing Electronics. *Cellulose* **2020**, *27*, 3455–3468, doi:10.1007/s10570-020-03013-z.
96. Haile, M.; Leistner, M.; Sarwar, O.; Toler, C.M.; Henderson, R.; Grunlan, J.C. A Wash-Durable Polyelectrolyte Complex That Extinguishes Flames on Polyester-Cotton Fabric. *RSC Adv.* **2016**, *6*, 33998–34004, doi:10.1039/c6ra03637f.
97. Laufer, G.; Kirkland, C.; Morgan, A.B.; Grunlan, J.C. Intumescent Multilayer Nanocoating, Made with Renewable Polyelectrolytes, for Flame-Retardant Cotton. *Biomacromolecules* **2012**, *13*, 2843–8, doi:10.1021/bm300873b.
98. Lazar, S.; Eberle, B.; Bellevergue, E.; Grunlan, J. Amine Salt Thickening of Intumescent Multilayer Flame Retardant Treatment. *Ind. Eng. Chem. Res.* **2020**, *59*, 2689–2695, doi:10.1021/acs.iecr.9b06359.
99. Li, Y.; Ju, D. The Application, Neurotoxicity, and Related Mechanism of Cationic Polymers. In *Neurotoxicity of Nanomaterials and Nanomedicine*; Jiang, X., Gao, H., Eds.; Academic Press, 2017; pp. 285–329 ISBN 978-0-12-804598-5.
100. Yuan, W.; Li, C.M. Exponentially Growing Layer-by-Layer Assembly to Fabricate PH-Responsive Hierarchical Nanoporous Polymeric Film and Its Superior Controlled Release Performance. *Chem. Commun.* **2010**, *46*, 9161–9163, doi:10.1039/C0CC03267K.
101. Curtis, K.A.; Miller, D.; Millard, P.; Basu, S.; Horkay, F.; Chandran, P.L. Unusual Salt and PH Induced Changes in Polyethylenimine Solutions. *PLoS One* **2016**, *11*,

e0158147, doi:10.1371/journal.pone.0158147.

102. Gibney, K.A.; Sovadinova, I.; Lopez, A.I.; Urban, M.; Ridgway, Z.; Caputo, G.A.; Kuroda, K. Poly(Ethylene Imine)s as Antimicrobial Agents with Selective Activity. *Macromol. Biosci.* **2012**, *12*, 1279, doi:10.1002/MABI.201200052.
103. Polyethylenimine, Branched Available online: https://www.sigmaaldrich.com/HR/en/product/aldrich/408727 (accessed on 1 March 2022).
104. Polyethylenimine Available online: https://www.sigmaaldrich.com/HR/en/product/aldrich/764582 (accessed on 1 March 2022).
105. Zong, E.; Guo, B.; Yang, J.; Shi, C.; Jiang, S.; Ma, Z.; Liu, X. Reusable Hyperbranched Polyethylenimine-Functionalized Ethyl Cellulose Film for the Removal of Phosphate with Easy Separation. *ACS Omega* **2021**, *6*, 505–515, doi:10.1021/ACSOMEGA.0C04955/SUPPL_FILE/AO0C04955_SI_001.PDF.
106. Li, S.; Ding, F.; Lin, X.; Li, Z.; Ren, X. Layer-by-Layer Self-Assembly of Organic-Inorganic Hybrid Intumescent Flame Retardant on Cotton Fabrics. *Fibers Polym.* **2019**, *20*, 538–544, doi:10.1007/s12221-019-8914-z.
107. Liu, L.; Huang, Z.; Pan, Y.; Wang, X.; Song, L.; Hu, Y. Finishing of Cotton Fabrics by Multi-Layered Coatings to Improve Their Flame Retardancy and Water Repellency. *Cellulose* **2018**, *25*, 4791–4803, doi:10.1007/s10570-018-1866-4.
108. Liu, L.; Pan, Y.; Wang, Z.; Hou, Y.; Gui, Z.; Hu, Y. Layer-by-Layer Assembly of Hypophosphorous Acid-Modified Chitosan Based Coating for Flame-Retardant Polyester-Cotton Blends. *Ind. Eng. Chem. Res.* **2017**, *56*, 9429–9436, doi:10.1021/ACS.IECR.7B02303/SUPPL_FILE/IE7B02303_SI_001.PDF.
109. Pan, Y.; Wang, W.; Liu, L.; Ge, H.; Song, L.; Hu, Y. Influences of Metal Ions Crosslinked Alginate Based Coatings on Thermal Stability and Fire Resistance of Cotton Fabrics. *Carbohydr. Polym.* **2017**, *170*, 133–139, doi:10.1016/j.carbpol.2017.04.065.
110. Poly(Vinylamine) Available online: https://www.polymersource.ca/index.php?route=product/category&path=2_2183_15_166_1098&subtract=1&categorystart=A-1.1.5.4&serachproduct= (accessed on 1 March 2022).
111. Pelton, R. Polyvinylamine: A Tool for Engineering Interfaces. **2014**, *30*, 15373–15382, doi:10.1021/LA5017214.

112. Ng, S.; Plank, J. Interaction Mechanisms between Na Montmorillonite Clay and MPEG-Based Polycarboxylate Superplasticizers. *Cem. Concr. Res.* **2012**, *42*, 847–854, doi:10.1016/J.CEMCONRES.2012.03.005.
113. Zhou, C.; Tong, D.; Yu, W. Smectite Nanomaterials: Preparation, Properties, and Functional Applications. In *Nanomaterials from Clay Minerals: A New Approach to Green Functional Materials*; Elsevier, 2019; pp. 335–364 ISBN 9780128145333.
114. Król-Morkisz, K.; Pielichowska, K. Thermal Decomposition of Polymer Nanocomposites With Functionalized Nanoparticles. In *Polymer Composites with Functionalized Nanoparticles: Synthesis, Properties, and Applications*; Elsevier, 2019; pp. 405–435 ISBN 9780128140659.
115. Kavaliauskaite, R.; Klimaviciute, R.; Zemaitaitis, A. Factors Influencing Production of Cationic Starches. *Carbohydr. Polym.* **2008**, *73*, 665–675, doi:10.1016/J.CARBPOL.2008.01.019.
116. Zhang, D.; Williams, B.L.; Liu, J.; Hou, Z.; Smith, A.T.; Nam, S.; Nasir, Z.; Patel, H.; Partyka, A.; Becher, E.M.; et al. An Environmentally-Friendly Sandwich-like Structured Nanocoating System for Wash Durable, Flame Retardant, and Hydrophobic Cotton Fabrics. *Cellulose* **2021**, *28*, 10277–10289, doi:10.1007/S10570-021-04177-Y/TABLES/2.
117. Graf, E. Applications of Phytic Acid. *J. Am. Oil Chem. Soc. 1983 6011* **1983**, *60*, 1861–1867, doi:10.1007/BF02901539.
118. Nauta, T. Chelating agents. In *Food Additive User's Handbook*; Springer, Boston, MA: Boston, MA, 1991; pp. 273–279.
119. Schlemmer, U.; Frølich, W.; Prieto, R.M.; Grases, F. Phytate in Foods and Significance for Humans: Food Sources, Intake, Processing, Bioavailability, Protective Role and Analysis. *Mol. Nutr. Food Res.* **2009**, *53 Suppl 2*, S330–S375, doi:10.1002/MNFR.200900099.
120. Phytic Acid Dodecasodium Salt Hydrate Available online: https://www.chemsrc.com/en/cas/123408-98-0_122854.html (accessed on 1 March 2022).
121. Sykam, K.; Försth, M.; Sas, G.; Restás, Á.; Das, O. Phytic Acid: A Bio-Based Flame Retardant for Cotton and Wool Fabrics. *Ind. Crops Prod.* **2021**, *164*, 113349, doi:10.1016/J.INDCROP.2021.113349.
122. Laufer, G.; Kirkland, C.; Morgan, A.B.A.B.A.B.; Grunlan, J.C.J.C.J.C. Intumescent Multilayer Nanocoating, Made with Renewable Polyelectrolytes, for Flame-Retardant

Cotton. *Biomacromolecules* **2012**, *13*, 2843–2848, doi:10.1021/bm300873b.

123. Petrila, L.M.; Bucatariu, F.; Mihai, M.; Teodosiu, C. Polyelectrolyte Multilayers: An Overview on Fabrication, Properties, and Biomedical and Environmental Applications. *Materials (Basel).* **2021**, *14*, 1–29, doi:10.3390/ma14154152.
124. Krase, N.W.; Gaddy, V.L. Synthesis of Urea from Ammonia and Carbon Dioxide. *Ind. Eng. Chem.* **2002**, *14*, 611–615, doi:10.1021/IE50151A009.
125. Urea - Carbonyldiamide, Carbamide Available online: https://www.sigmaaldrich.com/HR/en/substance/urea600657136 (accessed on 1 March 2022).
126. Shafizadeh, F.; Bradbury, A.G.W. Thermal Degradation of Cellulose in Air and Nitrogen at Low Temperatures. *J. Appl. Polym. Sci.* **1979**, *23*, 1431–1442, doi:10.1002/APP.1979.070230513.
127. Shafizadeh, F.; Furneaux, R.H.; Cochran, T.G.; Scholl, J.P.; Sakai, Y. Production of Levoglucosan and Glucose from Pyrolysis of Cellulosic Materials. *J. Appl. Polym. Sci.* **1979**, *23*, 3525–3539, doi:10.1002/APP.1979.070231209.
128. Shafizadeh, F.; Fu, Y. Pyrolysis of Cellulose. *Carbohydr. Res.* **1973**, *29*, 113–122, doi:10.1016/S0008-6215(00)82074-1.
129. Benítez-Guerrero, M.; López-Beceiro, J.; Sánchez-Jiménez, P.E.; Pascual-Cosp, J. Comparison of Thermal Behavior of Natural and Hot-Washed Sisal Fibers Based on Their Main Components: Cellulose, Xylan and Lignin. TG-FTIR Analysis of Volatile Products. *Thermochim. Acta* **2014**, *581*, 70–86, doi:10.1016/J.TCA.2014.02.013.
130. Horrocks, A.R.; Price, D.; Akalin, M. FTIR Analysis of Gases Evolved from Cotton and Flame Retarded Cotton Fabrics Pyrolysed in Air. *Polym. Degrad. Stab.* **1996**, *52*, 205–213, doi:10.1016/0141-3910(96)00017-1.
131. Xu, F. xiang; Zhang, X.; Zhang, F.; Jiang, L. qun; Zhao, Z. li; Li, H. bin TG-FTIR for Kinetic Evaluation and Evolved Gas Analysis of Cellulose with Different Structures. **2020**, *268*, 117365, doi:10.1016/j.fuel.2020.117365.
132. Jozef Lengyel; Milan Ončák; Andreas Herburger; Linde, C. van der; K. Beyer, M. Infrared Spectroscopy of O˙ − and OH − in Water Clusters: Evidence for Fast Interconversion between O˙ − and OH˙OH −. *Phys. Chem. Chem. Phys.* **2017**, *19*, 25346–25351, doi:10.1039/C7CP04577H.
133. Scarano, D.; Bertarione, S.; Spoto, G.; Zecchina, A.; Otero Areán, C. FTIR Spectroscopy of Hydrogen, Carbon Monoxide, and Methane Adsorbed and Co-Adsorbed on Zinc Oxide. *Thin Solid Films* **2001**, *400*, 50–55, doi:10.1016/S0040-

6090(01)01472-9.

134. Falk, M.; Miller, A.G. Infrared Spectrum of Carbon Dioxide in Aqueous Solution. *Vib. Spectrosc.* **1992**, *4*, 105–108, doi:10.1016/0924-2031(92)87018-B.

135. Stevulova, N.; Estokova, A.; Cigasova, J.; Schwarzova, I.; Kacik, F.; Geffert, A. Thermal Degradation of Natural and Treated Hemp Hurds under Air and Nitrogen Atmosphere. *J. Therm. Anal. Calorim.* **2017**, *128*, 1649–1660, doi:10.1007/S10973-016-6044-Z/FIGURES/8.

136. Gaan, S.; Rupper, P.; Salimova, V.; Heuberger, M.; Rabe, S.; Vogel, F. Thermal Decomposition and Burning Behavior of Cellulose Treated with Ethyl Ester Phosphoramidates: Effect of Alkyl Substituent on Nitrogen Atom. *Polym. Degrad. Stab.* **2009**, *94*, 1125–1134, doi:10.1016/j.polymdegradstab.2009.03.017.

137. Weil, E.D.; Levchik, S. V.; Ravey, M.; Zhu, W. A Survey of Recent Progress in Phosphorus-Based Flame Retardants and Some Mode of Action Studies. *Phosphorus. Sulfur. Silicon Relat. Elem.* **2008**, *144–146*, 17–20, doi:10.1080/10426509908546171.

138. Nuessle, A.C.; Ford, F.M.; Hall, W.P.; Lippert, A.L. Some Aspects of the Cellulose-Phosphate-Urea Reaction. *Text. Res. J.* **2016**, *26*, 32–39, doi:10.1177/004051755602600105.

139. Feng, Y.; Zhou, Y.; Li, D.; He, S.; Zhang, F.; Zhang, G. A Plant-Based Reactive Ammonium Phytate for Use as a Flame-Retardant for Cotton Fabric. *Carbohydr. Polym.* **2017**, *175*, 636–644, doi:10.1016/j.carbpol.2017.06.129.

140. Nyquist, R.A.; Fiedler, S.L. Infrared Study of Five- and Six-Membered Type Cyclic Imides. *Vib. Spectrosc.* **1995**, *8*, 365–386, doi:10.1016/0924-2031(94)00051-H.

141. Flakus, H.T.; Hachuła, B. Effect of the Resonance of the C-H and O-H Bond Stretching Vibrations on the IR Spectra of the Hydrogen Bond in Formic and Acetic Acid. *Spectrochim. Acta. A. Mol. Biomol. Spectrosc.* **2011**, *79*, 1276–1284, doi:10.1016/J.SAA.2011.04.054.

142. Sibert, E.L.; Tabor, D.P.; Lisy, J.M. Modeling the CH Stretch Vibrational Spectroscopy of M+[Cyclohexane] (M = Li, Na, and K) Ions. *J. Phys. Chem. A* **2015**, *119*, 10293–10299, doi:10.1021/ACS.JPCA.5B07461/ASSET/IMAGES/LARGE/JP-2015-07461E_0010.JPEG.

143. Lannon, J.A.; Nixon, E.R. Vibrational Spectra and Force Constants of Methylphosphine. *Spectrochim. Acta Part A Mol. Spectrosc.* **1967**, *23*, 2713–2732, doi:10.1016/0584-8539(67)80165-X.

144. Lin-Vien, D.; Colthup, N.B.; Fateley, W.G.; Grasselli, J.G. Compounds Containing –

NH2, –NHR, and –NR2 Groups. In *The Handbook of Infrared and Raman Characteristic Frequencies of Organic Molecules*; Lin-Vien, D., Colthup, N.B., Fateley, W.G., Grasselli, J.G., Eds.; Academic Press: Amsterdam, 1991; pp. 155–178 ISBN 978-0-12-451160-6.

145. Gilbert, A.S. IR Spectral Group Frequencies of Organic Compounds. In *Encyclopedia of Spectroscopy and Spectrometry*; Academic Press: Kent, 2017; pp. 408–418.

146. Kallonen, R. Smoke Gas Analysis by FTIR Method. Preliminary Investigation. *J. Fire Sci.* **1990**, *8*, 343–360, doi:10.1177/073490419000800503.

147. Wesolek, D.; Kozlowski, R. Toxic Gaseous Products of Thermal Decomposition and Combustion of Natural and Synthetic Fabrics with and without Flame Retardant. *Fire Mater.* **2002**, *26*, 215–224, doi:10.1002/fam.800.

148. Wodley, F.A. Pyrolysis Products of Untreated and Flame Retardant-Treated α-Cellulose and Levoglucosan. *J. Appl. Polym. Sci.* **1971**, *15*, 835–851, doi:10.1002/APP.1971.070150406.

149. Li, Z.F.; Zhang, C.J.; Cui, L.; Zhu, P.; Yan, C.; Liu, Y. Fire Retardant and Thermal Degradation Properties of Cotton Fabrics Based on APTES and Sodium Phytate through Layer-by-Layer Assembly. *J. Anal. Appl. Pyrolysis* **2017**, *123*, 216–223, doi:10.1016/j.jaap.2016.11.026.

150. Liu, Y.; Wang, Q.Q.; Jiang, Z.M.; Zhang, C.J.; Li, Z.F.; Chen, H.Q.; Zhu, P. Effect of Chitosan on the Fire Retardancy and Thermal Degradation Properties of Coated Cotton Fabrics with Sodium Phytate and APTES by LBL Assembly. *J. Anal. Appl. Pyrolysis* **2018**, *135*, 289–298, doi:10.1016/j.jaap.2018.08.024.

151. Pan, Y.; Zhao, H. A Novel Blowing Agent Polyelectrolyte for Fabricating Intumescent Multilayer Coating That Retards Fire on Cotton Fabric. *J. Appl. Polym. Sci.* **2018**, *135*, 46583, doi:10.1002/app.46583.

152. Chen, H.Q.; Xu, Y.J.; Jiang, Z.M.; Jin, X.; Liu, Y.; Zhang, L.; Zhang, C.J.; Yan, C. The Thermal Degradation Property and Flame-Retardant Mechanism of Coated Knitted Cotton Fabric with Chitosan and APP by LBL Assembly. *J. Therm. Anal. Calorim.* **2020**, *140*, 591–602, doi:10.1007/s10973-019-08834-0.

153. Salmeia, K.; Fage, J.; Liang, S.; Gaan, S. An Overview of Mode of Action and Analytical Methods for Evaluation of Gas Phase Activities of Flame Retardants. *Polymers (Basel).* **2015**, *7*, 504–526, doi:10.3390/polym7030504.

154. Massold, E.; Bähr, C.; Salthammer, T.; Brown, S.K. Determination of VOC and TVOC in Air Using Thermal Desorption GC-MS – Practical Implications for Test Chamber

Experiments. *Chromatogr. 2005 621* **2005**, *62*, 75–85, doi:10.1365/S10337-005-0582-Z.

155. Zhu, P.; Sui, S.; Wang, B.; Sun, K.; Sun, G. A Study of Pyrolysis and Pyrolysis Products of Flame-Retardant Cotton Fabrics by DSC, TGA, and PY–GC–MS. *J. Anal. Appl. Pyrolysis* **2004**, *71*, 645–655, doi:10.1016/J.JAAP.2003.09.005.
156. Talasek, R.T.; Daugherty, K.E. The Analysis of Nitrogen and Sulfur Oxides by Gas Chromatography—Mass Spectroscopy. *J. Chromatogr. Sci.* **1992**, *30*, 131–135, doi:10.1093/CHROMSCI/30.4.131.
157. Liu, X.; Zhang, Q.; Peng, B.; Ren, Y.; Cheng, B.; Ding, C.; Su, X.; He, J.; Lin, S. Flame Retardant Cellulosic Fabrics via Layer-by-Layer Self-Assembly Double Coating with Egg White Protein and Phytic Acid. *J. Clean. Prod.* **2020**, *243*, 118641, doi:10.1016/j.jclepro.2019.118641.
158. Zhu, D.; Hu, N.; Schaefer, D.W. Water-based sol–gel coatings for military coating applications. In *Handbook of Waterborne Coatings*; Zarras, P., Soucek, M.D., Tiwari, A., Eds.; Elsevier, 2020; pp. 1–27 ISBN 978-0-12-814201-1.
159. (3-Aminopropyl)Triethoxysilane Available online: https://www.sigmaaldrich.com/HR/en/product/aldrich/440140 (accessed on 3 March 2022).
160. (3-Aminopropyl)Triethoxysilane Available online: https://www.sigmaaldrich.com/HR/en/product/aldrich/440140 (accessed on 1 March 2022).
161. Edmeades, R.M.; Hewlett, P.C. Cement Admixtures. *Lea's Chem. Cem. Concr.* **1998**, 841–905, doi:10.1016/B978-075066256-7/50027-8.
162. Sulphonated Melamine Formaldehyde Available online: https://alphachem.com.au/wp-content/uploads/2021/07/SDS-Sulphonated-Melamine-Formaldehyde.pdf (accessed on 20 October 2021).
163. Sudhakar, Y.N.; Selvakumar, M.; Bhat, D.K. Methods of Preparation of Biopolymer Electrolytes. In *Biopolymer Electrolytes*; Sudhakar, Y.N., Selvakumar, M., Bhat, D.K., Eds.; Elsevier, 2018; pp. 35–52 ISBN 978-0-12-813447-4.
164. Mutreja, R.; Thakur, A.; Goyal, A. Chitin and chitosan: current status and future opportunities. In *Handbook of Chitin and Chitosan: Volume 1: Preparation and Properties*; Elsevier, 2020; pp. 401–417 ISBN 9780128179703.
165. Yilmaz Atay, H. Antibacterial Activity of Chitosan-Based Systems. *Funct. Chitosan* **2020**, 457, doi:10.1007/978-981-15-0263-7_15.

166. Chitosan Available online: https://www.sigmaaldrich.com/HR/en/substance/chitosan123459012764 (accessed on 1 March 2022).
167. Wang, W.; Guo, J.; Liu, X.; Li, H.; Sun, J.; Gu, X.; Wang, J.; Zhang, S.; Li, W. Constructing Eco-Friendly Flame Retardant Coating on Cotton Fabrics by Layer-by-Layer Self-Assembly. *Cellulose* **2020**, *27*, 5377–5389, doi:10.1007/s10570-020-03140-7.
168. Kulakovskaya, T. V.; Vagabov, V.M.; Kulaev, I.S. Inorganic Polyphosphate in Industry, Agriculture and Medicine: Modern State and Outlook. *Process Biochem.* **2012**, *47*, 1–10, doi:10.1016/J.PROCBIO.2011.10.028.
169. Ammonium Polyphosphate Available online: https://www.sigmaaldrich.com/HR/en/product/sigald/a1645 (accessed on 3 March 2022).
170. Ammonium Polyphosphate Available online: http://www.sinoharvest.com/products/Ammonium-polyphosphate.shtml (accessed on 1 March 2022).
171. P-Phenylazoaniline | Sigma-Aldrich Available online: https://www.sigmaaldrich.com/HR/en/product/sigma/p7144?region= (accessed on 2 March 2022).
172. Andersen, F.A. Final Report on the Safety Assessment of Sodium Metaphosphate, Sodium Trimetaphosphate, and Sodium Hexametaphosphate: **2016**, *20*, 75–89, doi:10.1080/10915810152630756.
173. Sodium Hexametaphosphate Available online: https://www.sigmaaldrich.com/HR/en/search/68915-31-1?focus=products&page=1&perpage=30&sort=relevance&term=68915-31-1&type=cas_number (accessed on 3 March 2022).
174. Sodium Hexametaphosphate Available online: https://www.sigmaaldrich.com/HR/en/product/vetec/v800380 (accessed on 1 March 2022).
175. Lu, C.; Leibner, E.; Wright, B. The Use of Tris-Hydroxymethyl Aminomethane in the Emergency Department. *Clin. Exp. Emerg. Med.* **2016**, *3*, 264, doi:10.15441/CEEM.16.165.
176. Tris(Hydroxymethyl)Aminomethane Available online: https://www.sigmaaldrich.com/HR/en/product/sial/252859 (accessed on 1 March

2022).

177. Carosio, F.; Alongi, J.; Malucelli, G. Flammability and Combustion Properties of Ammonium Polyphosphate-/ Poly(Acrylic Acid)-Based Layer by Layer Architectures Deposited on Cotton, Polyester and Their Blends. *Polym. Degrad. Stab.* **2013**, *98*, 1626–1637, doi:10.1016/j.polymdegradstab.2013.06.019.

178. Carosio, F.; Alongi, J.; Paravidino, C.; Frache, A. Improving the Flame Retardant Efficiency of Layer by Layer Coatings Containing Deoxyribonucleic Acid by Post-Diffusion of Hydrotalcite Nanoparticles. *Materials (Basel).* **2017**, *10*, 709, doi:10.3390/ma10070709.

179. Jang, W.; Chung, I.J.; Kim, J.; Seo, S.; Park, Y.T.; Choi, K. Improving Fire Resistance of Cotton Fabric through Layer-by-Layer Assembled Graphene Multilayer Nanocoating. *J. Korean Phys. Soc.* **2018**, *72*, 1052–1057, doi:10.3938/jkps.72.1052.

180. Poly(Diallyldimethylammonium Chloride) Available online: https://www.sigmaaldrich.com/HR/en/product/aldrich/409014 (accessed on 3 March 2022).

181. Singh, R.; Gautam, S.; Sharma, B.; Jain, P.; Chauhan, K.D. Biopolymers and their classifications. In *Biopolymers and their Industrial Applications*; Thomas, S., Gopi, S., Amalraj, A., Eds.; Elsevier: Amsterdam, Netherlands, 2021; pp. 21–44 ISBN 978-0-12-819240-5.

182. Poly(4-Styrenesulfonic Acid) Available online: https://www.sigmaaldrich.com/HR/en/product/aldrich/561223 (accessed on 1 March 2022).

183. Poly(Acrylic Acid) Available online: https://www.sigmaaldrich.com/HR/en/product/aldrich/323667 (accessed on 4 March 2022).

184. Graphene Nanoplatelets Available online: https://www.sigmaaldrich.com/HR/en/product/aldrich/900407 (accessed on 3 March 2022).

185. No, H.K.; Young Park, N.; Ho Lee, S.; Meyers, S.P. Antibacterial Activity of Chitosans and Chitosan Oligomers with Different Molecular Weights. *Int. J. Food Microbiol.* **2002**, *74*, 65–72, doi:10.1016/S0168-1605(01)00717-6.

186. Liu, N.; Chen, X.G.; Park, H.J.; Liu, C.G.; Liu, C.S.; Meng, X.H.; Yu, L.J. Effect of MW and Concentration of Chitosan on Antibacterial Activity of Escherichia Coli. *Carbohydr. Polym.* **2006**, *64*, 60–65, doi:10.1016/J.CARBPOL.2005.10.028.

187. Younes, I.; Sellimi, S.; Rinaudo, M.; Jellouli, K.; Nasri, M. Influence of Acetylation Degree and Molecular Weight of Homogeneous Chitosans on Antibacterial and Antifungal Activities. *Int. J. Food Microbiol.* **2014**, *185*, 57–63, doi:10.1016/J.IJFOODMICRO.2014.04.029.

188. Qin, C.; Li, H.; Xiao, Q.; Liu, Y.; Zhu, J.; Du, Y. Water-Solubility of Chitosan and Its Antimicrobial Activity. *Carbohydr. Polym.* **2006**, *63*, 367–374, doi:10.1016/J.CARBPOL.2005.09.023.

189. Nie, J.; Wang, Z.; Hu, Q. Chitosan Hydrogel Structure Modulated by Metal Ions. *Sci. Reports 2016 61* **2016**, *6*, 1–8, doi:10.1038/srep36005.

190. Guibal, E. Interactions of Metal Ions with Chitosan-Based Sorbents: A Review. *Sep. Purif. Technol.* **2004**, *38*, 43–74, doi:10.1016/J.SEPPUR.2003.10.004.

191. Mekahlia, S.; Bouzid, B. Chitosan-Copper (II) Complex as Antibacterial Agent: Synthesis, Characterization and Coordinating Bond- Activity Correlation Study. *Phys. Procedia* **2009**, *2*, 1045–1053, doi:10.1016/J.PHPRO.2009.11.061.

192. Li, J.; Zhuang, S. Antibacterial Activity of Chitosan and Its Derivatives and Their Interaction Mechanism with Bacteria: Current State and Perspectives. *Eur. Polym. J.* **2020**, *138*, 109984, doi:10.1016/J.EURPOLYMJ.2020.109984.

193. Claudel, M.; Schwarte, J. V.; Fromm, K.M. New Antimicrobial Strategies Based on Metal Complexes. *Chem. 2020, Vol. 2, Pages 849-899* **2020**, *2*, 849–899, doi:10.3390/CHEMISTRY2040056.

194. Moustakas, M. The Role of Metal Ions in Biology, Biochemistry and Medicine. *Materials (Basel).* **2021**, *14*, 1–4, doi:10.3390/MA14030549.

195. Dalecki, A.G.; Crawford, C.L.; Wolschendorf, F. Copper and Antibiotics: Discovery, Modes of Action, and Opportunities for Medicinal Applications. *Adv. Microb. Physiol.* **2017**, *70*, 193–260, doi:10.1016/BS.AMPBS.2017.01.007.

196. Glasauer, A.; Chandel, N.S. Targeting Antioxidants for Cancer Therapy. *Biochem. Pharmacol.* **2014**, *92*, 90–101, doi:10.1016/J.BCP.2014.07.017.

197. Bhamidimarri, S.P.; Young, T.R.; Shanmugam, M.; Soderholm, S.; Basle, A.; Bumann, D.; Van Den Berg, B. Acquisition of Ionic Copper by the Bacterial Outer Membrane Protein OprC through a Novel Binding Site. *PLoS Biol.* **2021**, *19*, doi:10.1371/JOURNAL.PBIO.3001446.

198. Pham, A.N.; Xing, G.; Miller, C.J.; Waite, T.D. Fenton-like Copper Redox Chemistry Revisited: Hydrogen Peroxide and Superoxide Mediation of Copper-Catalyzed Oxidant Production. *J. Catal.* **2013**, *301*, 54–64, doi:10.1016/J.JCAT.2013.01.025.

199. ASTM E2149-20 Standard Test Method for Determining the Antimicrobial Activity of Antimicrobial Agents Under Dynamic Contact Conditions Available online: https://www.astm.org/e2149-20.html (accessed on 26 December 2022).
200. GB/T 20944.3-2008 Standard English Version, China National Standards, GB/T 20944.3-2008 Textiles - Evaluation for Antibacterial Activity - Part 3: Shake Flask Method Available online: http://www.gbstandards.org/GB_standard_english.asp?code=GB/T 20944.3-2008 (accessed on 26 December 2022).
201. Kirby-Bauer Disk Diffusion Susceptibility Test Protocol | ASM.Org Available online: https://asm.org/Protocols/Kirby-Bauer-Disk-Diffusion-Susceptibility-Test-Pro (accessed on 26 December 2022).
202. Seffernick, J.L.; Wackett, L.P. Ancient Evolution and Recent Evolution Converge for the Biodegradation of Cyanuric Acid and Related Triazines. *Appl. Environ. Microbiol.* **2016**, *82*, 1638, doi:10.1128/AEM.03594-15.
203. Rózga-Wijas, K.; Mizerska, U.; Fortuniak, W.; Chojnowski, J.; Hałasa, R.; Werel, W. Quaternary Ammonium Salts (QAS) Modified Polysiloxane Biocide Supported on Silica Materials. *J. Inorg. Organomet. Polym. Mater.* **2007**, *17*, 605–613, doi:10.1007/S10904-007-9153-0/TABLES/4.
204. Grunlan, J.C.; Choi, J.K.; Lin, A. Antimicrobial Behavior of Polyelectrolyte Multilayer Films Containing Cetrimide and Silver. *Biomacromolecules* **2005**, *6*, 1149–1153, doi:10.1021/bm049528c.
205. Dvoracek, C.M.; Sukhonosova, G.; Benedikt, M.J.; Grunlan, J.C. Antimicrobial Behavior of Polyelectrolyte-Surfactant Thin Film Assemblies. **2009**, *25*, 10322–10328, doi:10.1021/LA901161Z/SUPPL_FILE/LA901161Z_SI_001.PDF.
206. Wu, Y.; Zhou, X.; Xing, Z.; Ma, J. Metal Compounds as Catalysts in the Intumescent Flame Retardant System for Polyethylene Terephthalate Fabrics. *Text. Res. J.* **2018**, *89*, 2983–2997, doi:10.1177/0040517518805373.
207. Zhang, J.; Ji, Q.; Wang, F.; Tan, L.; Xia, Y. Effects of Divalent Metal Ions on the Flame Retardancy and Pyrolysis Products of Alginate Fibres. *Polym. Degrad. Stab.* **2012**, *97*, 1034–1040, doi:10.1016/j.polymdegradstab.2012.03.004.
208. Weil, E.D.; Levchik, S. V. Flame Retardants in Commercial Use or Development for Textiles. *J. Fire Sci.* **2008**, *26*, 243–281, doi:10.1177/0734904108089485.
209. Dogan, M.; Dogan, S.D.; Savas, L.A.; Ozcelik, G.; Tayfun, U. Flame Retardant Effect of Boron Compounds in Polymeric Materials. *Compos. Part B Eng.* **2021**, *222*, 109088,

doi:10.1016/J.COMPOSITESB.2021.109088.

210. Riyaz, S.; Parveen, A.; Azam, A. Microstructural and Optical Properties of CuS Nanoparticles Prepared by Sol–Gel Route. *Perspect. Sci.* **2016**, *8*, 632–635, doi:10.1016/J.PISC.2016.06.041.

211. Peng, F.; Sun, Y.; Yu, W.; Lu, Y.; Hao, J.; Cong, R.; Ge, M.; Shi, J.; Dai, N. Studies on Sensing Properties and Mechanism of CuO Nanoparticles to H2S Gas. **2020**, *10*, doi:10.3390/NANO10040774.

212. Mostashari, S.M.; Nia, Y.K. Detection of Copper(II) Sulfate's Uniformity and Its Thermal Behavior in Flammability of Cotton Fabric: Spectrophotometric and TG Analysis. *J. Therm. Anal. Calorim.* **2008**, *92*, 489–493, doi:10.1007/S10973-007-7907-0/METRICS.

213. Liu, X. hui; Zhang, Q. yan; Cheng, B. wen; Ren, Y. lin; Zhang, Y. guang; Ding, C. Durable Flame Retardant Cellulosic Fibers Modified with Novel, Facile and Efficient Phytic Acid-Based Finishing Agent. *Cellulose* **2018**, *25*, 799–811, doi:10.1007/S10570-017-1550-0/SCHEMES/3.

214. Annalisa, C.; Francesca, B.; Giulio, M.; Chiara, M.; Monica, P. DNA-Chitosan Cross-Linking and Photografting to Cotton Fabrics to Improve Washing Fastness of the Fire-Resistant Finishing. *Cellulose* **2016**, *23*, 3963–3984, doi:10.1007/S10570-016-1067-Y/TABLES/6.

215. Fang, F.; Chen, X.; Zhang, X.; Cheng, C.; Xiao, D.; Meng, Y.; Ding, X.; Zhang, H.; Tian, X. Environmentally Friendly Assembly Multilayer Coating for Flame Retardant and Antimicrobial Cotton Fabric. *Prog. Org. Coatings* **2016**, *90*, 258–266, doi:10.1016/J.PORGCOAT.2015.09.025.

216. Polyhexamethyleneguanidine Phosphate Available online: https://m.chemicalbook.com/ProductChemicalPropertiesCB81014693_EN.htm (accessed on 4 March 2022).

217. Ginter, A.E.; Detring, K.; Henley, Shirley Titus Livingston, E. The Effects of a Borax-Boric Acid Solution on Cotton and Rayon Fabrics. *Res. Bull.* **1954**, 1–23.

218. Veerappagounder, S.; Nalankilli, G.; Shanmugasundaram, O.L. Study on Properties of Cotton Fabric Incorporated with Diammonium Phosphate Flame Retardant through Cyclodextrin and 1,2,3,4-Butane Tetracarboxylic Acid Binding System. *J. Ind. Text.* **2016**, *45*, 1204–1220, doi:10.1177/1528083714555780/ASSET/IMAGES/LARGE/10.1177_1528083714555780-FIG13.JPEG.

219. Pal, A.; Kumar Samanta, A.; Ranjan Kar, T. Eco-Friendly Fire-Retardant Finishing of Cotton Fabric with Mixture of Ammonium Sulfamate and Sodium Stannate. *Res. Sq.* **2022**, 1–15, doi:10.21203/RS.3.RS-2081673/V1.

220. Camino, G. Flame retardants: intumescent systems. In *Plastics Additives*; Pritchard, G., Ed.; Springer: Dordrecht, 1998; pp. 297–306 ISBN 978-94-010-6477-4.

221. Yang, J.; Zhao, Y.; Li, M.; Du, M.; Li, X.; Li, Y. A Review of a Class of Emerging Contaminants: The Classification, Distribution, Intensity of Consumption, Synthesis Routes, Environmental Effects and Expectation of Pollution Abatement to Organophosphate Flame Retardants (Opfrs). *Int. J. Mol. Sci.* 2019, *20*, 2874.

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.

7.2. 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.

7.3. 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.

7.4. 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.

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

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Bibliography (322272):

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Work Experience:

1. November 2014 – present: Associate, University of Zagreb Faculty of Textile Technology, Zagreb
2. June 2011 – November 2014: Associate, Croatian Chamber of Economy, Karlovac County Chamber, Karlovac
3. September 2009 – June 2011: Associate – Assistant on EU project FP7-REGPOT-2008-1: Unlocking the Croatian Textile Research Potentials T-Pot, University of Zagreb Faculty of Textile Technology, Zagreb
4. May 2008 – November 2008: Graphic Designer, Magma d.d., Jastrebarsko
5. October 2006 – January 2008: Development Manager, Lola Ribar d.d., Karlovac
6. March 2005 – September 2006: Development Technologist, Pazin Textiles d.o.o., Pazin
7. October 2003 – September 2004: Technologist - Trainee, Mr. Joseph d.o.o., Duga Resa
8. February 2003 – September 2003: Technologist - Trainee, MKZ d.o.o., Zagreb

Qualifications:

1. September 2011 – December 2011: EU Funding Project Manager, Algebra College, Zagreb
2. November 2008 – July 2009: Web Designer, Ivora – IT and Management, Karlovac
3. October 2005 – February 2008: Specialized Sales Clerk-Manager/Commerce Manager-Travel Agency Expert, Start – Business School
4. July 1996 – April 2002: BSc of Textile Technology, University of Zagreb Faculty of Textile Technology, Zagreb

Training:

1. 04/03/2018–28/04/2018: 2 -month research training on the development of eco-friendly flame retardants for cellulose by LbL deposition under the supervision of Dr. Jaime

Grunlan at Texas A & M University, Department of Mechanical Engineering, College Station, TX, USA

2. 08/03/2011–10/03/2011: a 3-day course in fundamentals, applications, and instrumentation of DSC and TG/FTIR under the supervision of Stefano Pera, PerkinElmer, Monza, Italy
3. 19/11/2010 – 19/12/2010: 1-month research training within a bilateral project BI-HR/11011-028 “Interactions of Surfactants in Detergent Solutions” under the supervision of Dr. Petra Forte – Tavčer, Department of Textiles, Faculty of Natural Sciences and Engineering University of Ljubljana, Slovenia
4. 06/09/2005 – 15/09/2005: 2-week temporary labor induction training on yarn preparation, weaving, and dyeing of fabrics under the supervision of Hiroshi Tsuchikura, Toray Textiles Europe Ltd., Mansfield, UK

Languages:

1. English, B2, First Certificate in English, University of Cambridge, 2005
2. German, B1.2, Teilnahmebestätigung, Goethe Institut, 2017

Award:

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Projects collaboration:

1. KK.01.1.1.04.0091: BIOCOMPOSITES Design of Advanced Biocomposites from Energy Sustainable Sources
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

INDEX:

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5. Science Citation Index Expanded (SCI-EXP) (7)
6. Emerging Sources Citation Index (ESCI) (2)

List of papers:

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.
2. Magovac, E. Eco-friendly multifunctional treatment of cotton - layer-by-layer deposition. In Book of Abstracts *PhD Day 2022*; Firšt Rogale, S., Ed.; Zagreb: University of Zagreb Faculty of Textile Technology, Zagreb, Croatia, 2022; pp. 248–249.
3. 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.
4. 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.
5. 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.
6. 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.
7. Tarbuk, A.; Đorđević, D.; Flinčec Grgac, S.; Kodrić, M.; Magovac, E.; Čorak, I. The influence of lipase surface modification to polyester crystallinity and absorbility. In Book of Proceedings *13th International Scientific Professional Symposium Textile*

Science & Economy; Petrak, S.; Zdraveva, E.; Mijović, B., Eds.; Zagreb: University of Zagreb Faculty of Textile Technology, Zagreb, Croatia, 2020; pp. 33–38.

8. Jordanov, I.; Kolibaba, T. J.; Lazar, S.; Magovac, E.; Bischof, S.; Grunlan, J. C.: Flame suppression of polyamide through combined enzymatic modification and addition of urea to multilayer nanocoating. *J. Mater. Sci.* **2020**, *30*, 15056–15067 doi:10.1007/s10853-020-05074-8.
9. Jordanov, I.; Magovac, E.; Fahami, A.; Lazar, S.; Kolibaba, T.; Smith, R. J.; Bischof, S.; Grunlan, J. C. Flame retardant polyester fabric from nitrogen-rich low molecular weight additives within intumescent nanocoating. *Polym. Degrad. Stab.* **2019**, *170*, 1–7, doi:10.1016/j.polymdegradstab.2019.108998.
10. Jordanov, I.; Stevens, D. L.; Tarbuk, A.; Magovac, E.; Bischof, S.; Grunlan, J. C. Enzymatic Modification of Polyamide for Improving the Conductivity of Water-Based Multilayer Nanocoatings. *ACS Omega*. **2019**, *7*, 12028–12035, doi:10.1021/acsomega.9b01052.
11. Magovac, E. Flame retardant surface modification of cotton textiles by means of Layer-by-Layer deposition. In Book of Abstracts *PhD Day 2018* Flinčec Grgac, S., Ed.; Zagreb: University of Zagreb Faculty of Textile Technology, Zagreb, Croatia, 2018; pp. 66–67
12. Magovac, E.; Bischof, S.; Grunlan, J. C.; Jordanov, I. LBL Deposition – An Innovative Method of Surface Modification of Cotton with Enhanced FR Properties. In Book of Proceedings *9th International Textile, Clothing & Design Conference - Magic World of Textiles*; Dragčević, Z.; Hursa Šajatović, A.; Vujasinović, E., Eds.; Dubrovnik: University of Zagreb Faculty of Textile Technology, Zagreb, Croatia, 2018; pp. 132–136
13. Zdraveva, E.; Magovac, E.; Mijović, B. Elektroispredanje – značajna tehnika 21. Stoljeća. *Tekstil.* **2016**, *65*, 397–409.
14. Bischof, S.; Magovac, E. LbL deposition of halogen free flame retardants based on phytic acid. In Book of Abstracts *Final Conference on "Innovations in Flame Retardancy of Textiles and Related Materials" (COST MP1105)*; Van Der Burght, Ed.; COST, Poznan, Poland, 2016; p. 19.
15. Magovac, E.; Bischof, S. Nanocoating of Cotton by a Halogen-Free Flame Retardant BPEI/PA via LbL Deposition. *International Conference on Nanomaterials and Nanotechnology*, Canberra, Australia, 2016.

16. Magovac, E.; Bischof, S. Non-halogen FR treatment of cellulosic textiles. *Tekstil.* **2015**, *64*, 298-309.
17. Furdek, D.; Kordiš, T.; Kosler, H.; Hudoklin, M., Žagar, T.; Magovac, E. In Book of Abstracts *Memorandum on creating a cross-border region of excellence Bela Krajina, Dolenjska, Kočevsko - Ribniško and Posavje*; Bukovec, B., Ed.; Novo mesto: Dolenjska akademska pobuda, Novo mesto, Slovenia, 2012; pp. 13–14.
18. Pfueller, T.; Illing-Guenther, H.; Naumann, R.; Franitza, P.; Kovačević, Z.; Magovac, E.; Flinčec Grgac, S.; Bischof, S. Investigation of thermal behaviour and ageing of thermoplastic polymers used for protective textiles. In Book of Proceedings *6th International Textile, Clothing & Design Conference - Magic World of Textiles*; Dragčević, Z.; Hursa Šajatović, A.; Vujasinović, E., Eds.; Dubrovnik: University of Zagreb Facuty of Textile Technology, Zagreb, Croatia, 2012; pp. 561–566.
19. Bischof-Vukušić, S.; Pušić, T.; Magovac, E.; Petrinić, I.; Luxbacher, T.; Aračić, J. Funkcionalnost dimenzijski stabiliziranog vunenog pletiva. U Zborniku radova *5. međunarodnog znanstveno-stručnog savjetovanja Tekstilna znanost i gospodarstvo*; Ujević, D.; Penava, Ž., ur.; Zagreb: Sveučilište u Zagrebu Tekstilno-tehnološki fakultet, Zagreb, 2012.; str. 119–122.
20. Forte-Tavčer, P.; Magovac, E.; Šumiga, B.; Boh, B.; Bischof Vukušić, S. Obdelava bombažne tkanine z mikrokapsuliranim zavarivalcem gorenja trifenilfosfatom. U Zborniku radova *42. Simpozija o novostih v tekstilstvu*; Forte Tavčer, P.; Simončić, B., ur.; Ljubljana: Univerza v Ljubljani Naravnotehniška fakulteta, Ljubljana, 2011; str. 197–203 ISBN 978-961-6045-93-3.
21. Magovac, E.; Šumiga, B.; Forte Tavčer, P.; Bischof Vukušić, S. Microcapsulation for protective purposes. In *Young scientists in the protective textiles research*; Bischof Vukušić, S.; Katović, D., Eds.; University of Zagreb Faculty of Textile Technology & FP7-REGPOT-2008-1229801: T-Pot, Zagreb, Croatia, 2011; pp. 215–237 ISBN 978-953-7105-41-9.
22. Magovac, E.; Katović, D.; Bischof Vukušić, S. Primjena materijala s promjenom faza (PCM) u tekstilstvu. *Tekstil.* **2011**, *60*, 102–108.