FACULTY OF TEXTILE ENGINEERING TUL

Dissertation Thesis

Biopolymer for Reduction of Cotton Flammability

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DEDICATION

Dedicated to my great and beloved late parents

whose countless efforts and prayers are the basis of my success

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“Seek knowledge from the cradle to the grave”

- Prophet Muhammad (P.B.U.H)

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ABSTRACT

Cotton is an extensively utilized natural textile fiber but its applicability is negatively influenced by high flammability due to its cellulosic nature. Cotton ignites very easily with a rapid flame spread and quickly consumes as fuel ensuing perilous fires that can cause huge materials loss and fatal accidents. The desire to improve flame retardant properties of cellulosic textile materials for the reduction of fire hazards has been a major preoccupation over the years for the safety of ultimate consumers under many circumstances.

However, most of the high-performing flame retardants for cellulosic textile products have been banned or limited from industrial/commercial use facing several changes and challenges of health issues and environmental concerns. Due to these considerations, researchers and manufacturers have been deploying their endeavors to find, design, and develop some efficient but more environmentally benign specialty flame retardant finishing materials/products for cellulosic textile substrates to reduce their flame vulnerabilities. Contextually, in recent years, bio-based natural and renewable materials/products, i.e., biopolymers have become of growing interest and gained significant importance because of their environmental friendliness.

The focal intent of the present work was to scrutinize the applications of a biopolymer, i.e., bovine milk casein (bovine milk protein; a phosphoprotein) on cotton fabrics as green and environment-friendly flame retardant finishing material to provide an attractive solution for the valorization of the dairy industry by utilization of its by-product or waste in the improvement of flame retardant performance, char formation, and intumescence effect of cotton fabrics. Casein was applied on cotton fabrics just as it alone and in combination with other environment-friendly materials (such as ammonium polyphosphate and polyvinyl alcohol) for synergistic/hybrid effects in different concentrations through non-hazardous aqueous solvents/solutions and simple industrial applicable textile finishing techniques/methods (such as roller padding, roller coating, and electrospray coating). Physiological comfort, mechanical properties, and washing durability accompanying flame retardancy and thermal properties of cotton fabrics finished with casein and casein-based synergistic/hybrid systems were also perused.

Different kinds of measurements, characterization, and testing techniques were employed on control and finished cotton fabrics to determine, investigate and evaluate the different parameters, features, and properties such as surface properties (surface morphology, surface chemical structure, elemental contents analysis), thermal properties (thermo-oxidative stability, flame retardancy, limiting oxygen index, radiant heat resistance, intumescent system performance), comfort properties (air permeability, water vapor permeability, thermal conductivity, bending rigidity) mechanical properties (tensile performance, tear performance), and durability properties (durability to washing) according to feasible standard test methods. Results were analyzed, interpreted, discussed, and concluded to study and investigate causes with logical reasons for observance of different functional properties. Casein finished cotton fabrics demonstrated, slow flame propagation as also revealed from the image analysis data of burn length and burn area, and enhancement in limiting oxygen index, producing a higher amount of thermally stable char residues. Casein was ascertained to develop flame retardant intumescent systems in combined applications with other synergistic chemicals/compounds. Cotton fabrics indicated stronger sensitization of cellulose decomposition and exhibited higher thermo-oxidative stability properties after treatments with casein macromolecules alone and in combination with other thermally stable and phosphorous-rich flame retardant compounds. As in the case of other flame retardant chemicals finishing, likewise, physiological comfort and mechanical properties of casein finished cotton fabrics were affected depending on the deposited amount of chemicals/finishes as well as governing by application methods. In addition, after-treatments of casein finished cotton fabrics, with certain suitable less toxic and/or environmentally friendly chemical agents pertaining to different crosslinking/binding systems (such as phenols, aldehydes, carboxylic acids, resins, silanes), facilitated the improvement of their durability against washing.

Keywords: Cotton fabric; Flammability; Casein; Flame retardant; Flame retardancy; Char residue; Intumescent

ABSTRAKT

Bavlna je hojně využívané přírodní textilní vlákno, ale její použitelnost je negativně ovlivněna vysokou hořlavostí díky obsahu celulózy. Bavlna se velmi snadno vzněcuje, plamen se rychle šíří a rychle se mění v popel. Je příčinou nebezpečných požárů, které mohou způsobit obrovské materiální škody a smrtelné nehody. Snaha zlepšit vlastnosti celulózových textilních materiálů zpomalující hoření za účelem snížení nebezpečí požáru byla v průběhu let hlavním zájmem řešení nehořlavých úprav zajištujících bezpečnost spotřebitelů.

Nicméně, většina vysoce účinných zpomalovačů hoření pro celulózové textilní výrobky byla zakázána nebo omezena pro průmyslové/komerční použití, pro svoji zdravotní závadnost a negativní vliv na životní prostředí. Výzkumní pracovníci a výrobci se tedy snaží najít, navrhnout a vyvinout některé účinné, ale k životnímu prostředí šetrnější speciální materiály/produkty zpomalující hoření celulózových textilních substrátů. V souvislosti s tím se v posledních letech zkoumají přírodní materiály/produkty na biologické bázi, tj. biopolymery.

Hlavním záměrem této práce bylo prozkoumat aplikace speciálního biopolymeru, tj. kaseinu z hovězího mléka (bílkovina z hovězího mléka; fosfoprotein) na bavlněné tkaniny. Kasein je ekologický přijatelný materiál zpomalující hoření. Umožňuje atraktivní zhodnocení vedlejšího produktu/odpadu mlékárenského průmyslu ke zpomalování hoření, tvorby zuhelnatělého zbytku a intumescenčního efektu na bavlněných tkaninách. Bylo zkoumáno ovlivnění fyziologického komfortu, mechanických vlastností, trvanlivosti při praní a tepelných vlastnosti kaseinem upravených bavlněných tkanin. Kasein byl aplikován na bavlněné tkaniny samostatně a v kombinaci s dalšími materiály šetrnými k životnímu prostředí (jako je polyfosfát amonný a polyvinylalkohol). Byla použita bezpečná vodná rozpouštědla/roztoky a jednoduché, průmyslové textilní zušlechťovací techniky/metody (jako je válečkové nanášení, zátěry a elektrosprejová úprava). Fyziologický komfort, mechanické vlastnosti a trvanlivost při praní doprovázející zpomalování hoření a tepelné vlastnosti bavlněných tkanin s kaseinovou a synergické/hybridní systémy na bázi kaseinu úpravou byli také stíháni.

U kontrolních a upravených bavlněných tkanin byly použity různé druhy měření, charakterizace a testovacích technik pro stanovení, zkoumání a hodnocení různých parametrů a vlastností, jako jsou povrchová struktura (morfologie povrchu, chemická struktura povrchu, analýza obsahu prvků), tepelné vlastnosti (termooxidační stabilita, zpomalení hoření, limitní kyslíkové číslo, odolnost proti sálavému teplu, intenzita bobtnání), vlastnosti související s komfortem (propustnost vzduchu, propustnost vodní páry, tepelná vodivost, tuhost v ohybu) mechanické vlastnosti (tažnost, odolnost proti protržení) a trvanlivosti úprav (odolnost v opakovaném praní) podle standardních zkušebních metod. Výstupní data byla analyzována, interpretována, diskutována a komplexně zhodnocena. Byly zkoumány příčiny a logické důvody pro docílení různých funkčních vlastností. Bavlněné tkaniny upravené kaseinem prokázaly pomalé šíření plamene (jak bylo určeno z dat analýzy obrazu délky hoření a oblasti hoření), zlepšení limitního kyslíkového čísla a produkci vyššího množství tepelně stabilních zuhelnatělých zbytků. Bylo zjištěno, že kasein vyvíjí intumescentní systémy zpomalující hoření v kombinovaných aplikacích s jinými synergickými chemikáliemi/sloučeninami. Bavlněné tkaniny vykazovaly vyšší odolnost proti tepelnému rozkladu a vyšší termooxidační stabilitu po ošetření samotnými kaseinovými makromolekulami a v kombinaci s jinými tepelně stabilními a na fosfor bohatými samozhášecími sloučeninami. Stejně jako v případě jiných chemických úprav zpomalujících hoření byl ovlivněn fyziologický komfort a mechanické vlastnosti bavlněných tkanin s úpravou kaseinem. Míra ovlivnění závisela na naneseném množství chemikálií/apretur a také na aplikačních metodách. Kromě toho následná úprava kasein obsahujících bavlněných tkanin s vhodnými méně toxickými a/nebo ekologicky šetrnými síťovacími/vazebnými systémy (jako jsou aldehydy, karboxylové kyseliny, pryskyřice, silany), vedla ke zlepšení odolnost v praní.

Klíčová slova: Bavlněné textilie; Hořlavost; Kasein; Zpomalovače hoření; Zpomalení hoření; Zuhelnatělé zbytky; Intumescentní vrstvy

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LIST OF ABBREVIATIONS

AATCC	American Association of Textile Chemists and Colorists
AP	Air Permeability
APP	Ammonium Polyphosphate
ASTM	American Society for Testing and Materials
ATR	Attenuated Total Reflectance/Reflection
CAS	Casein
CF	Cotton Fabric
COI	Critical Oxygen Index
ČSN	Czech Technical Standard / České Technické Normy
DTG	Derivative thermogravimetric
ECE	European Colorfastness Establishment
FRs	Flame Retardants
FTIR	Fourier Transform Infrared Spectroscopy
ICP-AES	Inductively Coupled Plasma Atomic Emission Spectrometer
ICP-OES	Inductively Coupled Plasma Optical Emission Spectrometry
IFRs	Intumescent Flame Retardants
IR	Infrared Radiation
ISO	International Organization for Standardization
KES-F	Kawabata Evaluation System of Fabric
LOI	Limiting Oxygen Index
MTPS	Modified Transient Plane Source
PVA	Polyvinyl Alcohol
RH	Relative Humidity
RWVP	Relative Water Vapor Permeability
SEM	Scanning Electron Microscope/Microscopy
TCi	Thermal conductivity instrument
TG	Thermogravimetric
TGA	Thermogravimetric Analysis

Chapter 1

INTRODUCTION

Textiles play an important role in everyday life. Like most polymeric materials such as foams and plastics [1], textiles are extremely vulnerable to flame and fire exposures. The flammability of textile materials/products (i.e., fibers, yarns, and fabrics) signifies an area of the safety issue, which evinces that textiles are the first thing to be ignited even by small flames (such as matchsticks, cigarettes, candles, etc.) thus resulting in the most common fire [2]. As far as the burning of textiles is concerned, one main drawback refers to their primitive matter. Such as they are mostly based on organic polymers, which are usually flammable contrarily if not inherently flame retarded [3].

Flame and/or fire retardants (i.e., additives/chemicals/finishes) are commonly applied to different kinds of materials to make them non-flammable or self-extinguishing, as the principle of flame/fire retardants (FRs) is to reduce their propensity to flame spread and further to ignite/burn when subjected to a heating source or open flame [4, 5]. Therefore a flame retardant fabric does not stimulate to propagate the flame, although it may burn and/or char when it is exposed to any form of heat source. Char formation confines the amount of flammable volatiles and gases acting as a diffusion barrier and reduces heat transmission into textile material providing a thermally insulating layer at the surface [6].

Among all textiles, cellulosic fibers are most susceptible to flame and/or fire. When ignited they undergo rapid thermal degradation, forming combustible volatile gaseous compounds that further get involved to propagate fire, and leaving no char residues (almost negligible amount) behind except traces of ash [7, 8]. Production of flame-retardant cellulose-based textiles has always been the most challenging task. Providentially cellulose has a chemical composition that makes it easily susceptible to conjoint flame retardant treatments. Flame retardant treatments are generally applied to textile materials through chemical finishing [9] and it is also the most commonly used method to produce flame-retardant cotton fabrics as well.

Cotton is a natural cellulosic fiber and one of the most important natural biopolymers in the world. It is commonly used in wide application areas indeed due to its availability in large quantities and plentiful diverse advantages such as good mechanical properties, hydrophilicity, physiological comfort, biodegradability, absence of static charge problems, etc. [10, 11]. However thermal properties such as high flammability, ease of ignition, low thermal stability, and quick burning/combustion of cotton textiles [12–14] restricted many of their specific applications in transportation, automotive, protective garments, military, home/furniture upholstery, apparel, bed/nightwear, etc.

When cotton fabrics are exposed to any kind of heating source, it starts to degrade and undergoes thermal decomposition. More precisely, degradation phenomena usually involve the dehydration of glycosyl units to produce a thermally stable carbonaceous structure (usually called char) and/or depolymerization of such units to release volatile species/gases able to further fuel the process [15]. Hence, one possible strategy to hinder the degradation process is to assist dehydration rather than depolymerization. This could be attained by using species/compounds efficient enough to interfere with the degradation process. However, it is generally expected that an effective flame retardant controls pyrolysis by instigating cellulose, to carbonize through dehydration, at temperatures below 300°C. Preferably an ideal flame retardant system, for cellulose chars generation, prevents afterglow and minimizes the release of toxic gases and smoke. Alternatively, intumescent flame retardant systems also provide some potential promises for flame and heat protection [16].

Most of the existing successful commercial flame retardant treatments, formulations/finishes, and chemicals/additives for textiles are primeval and old over fifty years and derived from chemistry developed in the golden period of 1950-1980 [17–19]. Currently, the most common flame retardants that are being used for cotton and other cellulosic textile materials/products are mainly halogens, phosphorous, and nitrogen elements based compounds [20, 21]. As a research and development results in the last fifty years, most of the high performing halogen-based (release toxic fumes and harmful/corrosive gases on thermal degradation) and phosphorous-based (release formaldehyde during manufacturing and also on heating at application and end-use stages) flame retardants for cellulosic fabrics have been banned or limited from industrial and commercial use. They have also been facing several changes and challenges and suspecting to evoke some specific health and environmental concerns as they have already proven to be bioaccumulative, persistent, toxic and/or carcinogenic for animals and humans [22–27]. According to these perspectives, the use of bio-based natural and renewable materials (i.e., biopolymers) including biowastes has been the focus of the scientific research community towards all environmental preservation and sustainability of resources. In very recent times, biopolymer-based materials have attracted considerable attention and exploded interest in the field of flame retardancy because of their low environmental impact and toxicity [28–32].

Biopolymers such as protein fractions derived from animals have shown unexpected flame retardant/suppressant potentials when deposited on selected cellulosic and synthetic textile substrates like cotton, polyester, or cotton-polyester blends [33, 34]. The use of bovine milk-derived casein protein as a flame retardant is a significant advantage since it can be considered as a waste or co-product obtained from the milk industry during the production of skim milk and cheese [35, 36]. Casein is a major fraction (80%) of bovine milk proteins. It is actually a family of proteins synthesized in the mammary glands [37, 38]. Perhaps the most widely studied and investigated protein due to its latent bio- and techno-functional properties. Casein is a phosphoprotein (i.e., polyamino acids bearing several phosphate groups in its micellar structure) and exists in milk in form of large self-assembled colloidal particles, known as "micelles". It is a globular protein with an amphiphilic structure and usually composed of α_{S1}-, α_{S2}-, β-, κ- casein, according to the nomenclature developed for bovine milk caseins [39, 40].

Flame retardant effectiveness or conformance of casein (a natural green, eco-friendly, and renewable biomacromolecule) can be attributable to its chemical composition. As, cellulosic fibers such as cotton can suitably be flame retarded with phosphorus-based flame retardants, owing to the presence of the hydroxyl groups [41, 42]. Furthermore, the phosphorus and phosphorous-nitrogen based compounds are regarded as effective flame retardants for cotton fabrics [43, 44]. They can dehydrate cellulose during the thermal decomposition process rather than its depolymerization and enhance the formation of a thermally stable carbonaceous structure (char) instead of the production of combustible volatile products. Additionally, the flame retardant efficiency of phosphorous-based compounds also improves due to the synergistic effect of nitrogen elements [45, 46].

Chapter 2

SIGNIFICANCE, SCOPE, AND OBJECTIVES

The urge to improve flame retardant properties of cellulosic textile materials for the reduction of fire hazards has been a major concern over the years and most of the efforts have been purported primarily to develop efficient and environmentally benign flame retardant finishing for cotton fabrics to reduce their flame vulnerabilities. In this regard, the research and development emphasizing bio-based materials/polymers, to study and investigate their flame retardant properties for textiles, is relatively a novel thought and also an emerging potential field of the recent decade.

In this context, the current research work idea/plan was postulated and presented, overall aiming to assess different hidden and inherent key techno-functional features of bovine milk casein protein (owing to its chemical composition/structure) for flame retardancy, char formation, and intumescence effect for cotton fabrics, furthermore, its impact on basic essential and desired properties of cotton fabrics.

This was expected to be done by exploiting casein application on cotton fabrics just as it alone and in combination with other environmentally friendly materials for synergistic/hybrid effects. In particular, the exploration of its application on cotton fabrics through non-hazardous solvents/solutions, i.e., aqueous solutions by using simple, time-saving, and industrially applicable techniques/methods. As traditional potential flame retardant treatments may cause deleterious effects on the physiological comfort as well as on the mechanical properties of textile fabrics. Therefore simultaneously the determination of physiological comfort, mechanical performance, and washing durability accompanying flame retardancy and thermal properties of casein finished cotton fabrics was also intended to contemplate in this research work.

Comprehending the canvass as discussed in the previous section, the overall originated major aims and objectives of this research work study are as follows:

- **Flame retardant performance and char formation properties of casein for cotton fabrics**
    - Preparation of casein aqueous solutions of different possible concentrations revealing its swelling and solubility limits as well as consistent and stable solution-forming properties as a prerequisite, and their application on cotton fabrics.
    - Proving commonly used parameters/conditions of the textile fabric finishing process, to observe ease and compliance of casein solutions' application through roller padding method, as well as, to attain an adequate amount of casein add-on/uptake on treated cotton fabrics.

  - Conforming to its effectiveness, for flame retardant and char formation properties of casein treated cotton fabrics.
  - Examination of physiological comfort and mechanical properties accompanying flame retardancy and thermal properties of casein treated cotton fabrics.
- **Comparative evaluation of flame retardant behavior and inherent intumescent phenomenon of alkaline and acidic casein solution coatings for cotton fabrics**
  - Attempting the dissolution of casein in water at alkaline and acidic pH conditions to prepare solutions of different possible concentrations revealing its swelling and solubility limits as well as consistent and stable solution-forming properties.
  - Application of alkaline and acidic casein solutions on cotton fabrics through roller/bar coating method, as well as, essaying to deposit higher amounts of casein (add-on/weight gain) on coated cotton fabrics.
  - Evaluation of the comparative performance of flame retardant and char formation properties in conjunction with an inherent intumescent phenomenon of alkaline and acidic casein solutions coated cotton fabrics.
- **Intumescent flame retardant system based on casein in combination with ammonium polyphosphate for cotton fabrics**
  - Developing an efficient and effective flame retardant intumescent system for cotton fabrics using halogen-free and environment-friendly resources; casein as a biopolymer-based carbonization agent and ammonium polyphosphate as an acid-releasing agent.
  - Building up the polyelectrolyte bilayer assemblies/coatings of casein and ammonium polyphosphate on cotton fabrics from aqueous solutions by depositing and coupling positively charged casein (as polycations) with negatively charged ammonium polyphosphate (as polyanions) by using roller/bar coating method.
  - Examination of the effect of different concentrations of casein and ammonium polyphosphate in bilayer assemblies/coatings for the changes in thermal properties and flame retardant behavior of cotton fabrics.
  - Exploration of intumescent char layers formation phenomenon controlling the thermal transmission and release of cellulose's gaseous products and conforming to the effectiveness of the developed intumescent flame retardant system.
- **Flame retardant and intumescent char formation potentials of casein and polyvinyl alcohol based bicomponent composite nanoparticles for cotton fabrics**
  - Endeavoring the processability of casein to fabricate submicron size droplets/particles by utilization of the electrospraying technique starting with aqueous solutions.

  - Deposition of electrosprayed casein/polyvinyl-alcohol bicomponent composite nanoparticles on the surface of cotton fabrics as very fine and uniform layers/coatings, in order to develop an ecologically acceptable flame retardant and intumescent char forming system.
  - Approximation of the effect of different composition casein/polyvinyl-alcohol nanoparticles' coatings for the changes in thermal properties and flame retardant behavior of cotton fabrics.
  - Examination of physiological comfort and mechanical properties accompanying flame retardancy and thermal properties of cotton fabrics electrospray coated with casein/polyvinyl-alcohol nanoparticles.

- **Washing durability of casein treated cotton fabrics**
  - Evaluation of durability against washing/laundering of a proffered biopolymer-based flame retardant material, i.e., casein protein.
  - Improving the washing durability of casein treated cotton fabrics by suitable chemical crosslinking/binding systems.
  - Comparing the chemical crosslinking systems based on glutaraldehyde (a dialdehyde), citric acid (a polycarboxylic acid), tannic acid (a polyphenol), Texapret LF (a resin), and tetraethoxysilane (a silane) for washing durability of casein treated cotton fabrics.

Chapter 3

LITERATURE REVIEW

According to ISO 13943 and ASTM E176-18a standards, a material is said to be flammable if it is susceptible to easy ignition and rapid flaming combustion [47, 48].

Textile is a material, available in the form of fibers, yarns, and fabrics. Fiber is the basic building block of any textile product and that may be a natural, regenerated, and synthetic polymer [49, 50]. Most of the textile fibers are flammable under normal ambient conditions and cause serious fire hazards in case of fire accidents. The main reason is that a major part of these fibers is organic polymers, representing a bountiful source of hydrocarbons, that act as an excellent source of fuel for burning processes.

The flammability of textiles is a critical aspect with respect to their end uses and application areas. The term "flame retardant textiles" usually alludes to textiles or textile-based materials that resist flame and/or inhibit the spread of fire. Flame-resistant/flame-retardant textiles can be manufactured by using; any one or combination of the following different techniques, methods, and/or routes [51].

- ***Using inherent flame-resistant fibers:***

Fibers that contain inherently flame-resistant polymers; such as wool, polyaromatic amides/aramids, polyimide, polybenzimidazole, melamine, glass, basalt, halogen-containing olefins, polyvinyl chlorides, polyphenylene benzobisoxazole, oxidized polyacrylonitrile, and polyphenylene sulfide-based fibers are some examples of inherently flame-resistant polymers.

Fibers from polymers that contain special flame-resistant co-monomers; such as Trevira CS (modified polyester) and modacrylics are common examples of fibers that contain special monomers with flame-resistant characteristics.

- ***Using manufactured flame-resistant fibers:***

Fibers that contain special non-reactive flame-resistant additives; such as Viscose FR® and Visil® are flame-retardant cellulosic fibers (melt/wet spun viscose fibers) that contain a high concentration of flame-resistant additives, which are usually incorporated in polymer bulk before the spinning process.

- ***Using surface treatments with flame-resistant compounds:***

Chemicals/finishes with various chemistries can be applied and/or deposited on the surface of textiles (also known as chemical finishing) by using different finishing/coating and subsequent fixation processes/routes.

Flame retardant textiles aid to save lives, obviate injuries and property losses, and protect the environment by facilitating to prevent of fires from starting and limiting fire damages. Flame retardant textiles are requisite and have been used in several application areas (consumer and industrial) such as; apparel, uniforms for firefighters, military/police personnel, and industrial workers, high-performance sports applications, upholstery for home furnishing, office/commercial infrastructure, and transportation systems, sleepwear for children and elderly people, architectural fabrics, etc. [21].

3.1 Flammability and thermal stability of cotton

Cellulose $(C_6H_{10}O_5)_n$; a biopolymer, is a long-chain carbohydrate polymer of repeating β-D-glucopyranose units. It is the most abundant natural polymer that exists on earth as a major structural component of various plants' cell walls and an important constituent of many living species (marine animals and microorganisms) [52]. Cotton, a natural cellulosic fiber (creamy white or yellowish); seed hair of the plants of order "Malvales", family "Malvaceae", tribe "Gossypieae" and genus "Gossypium", is the purest form of cellulose. The cellulose present in cotton fibers has the highest content and molecular weight, and the highest structural order (i.e., highly crystalline 70-80%, oriented and fibrillar) among all kinds of plant fibers [53–55]. Each cotton fiber is a single, elongated, and complete cell, which develops in the surface layer of cells of cottonseed as shown in Figure 3.1.

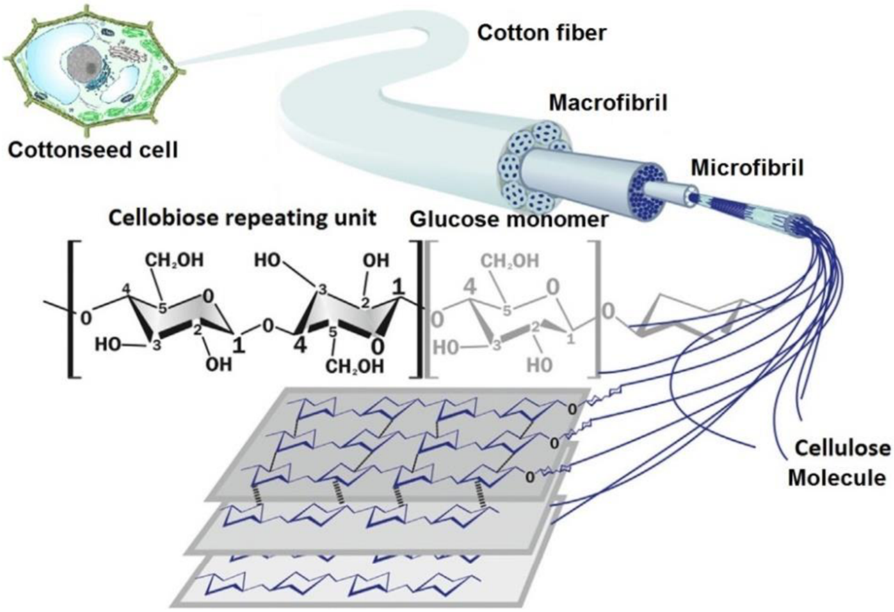


Figure 3.1. Representation of a cotton fiber organization, adapted and modified [56]

Cotton cellulose exists in linear chain condensation homo-polymer form consisting of several D-anhydroglucopyranose monomer units (also known as anhydroglucose). These units are linked together covalently by β-1,4-glycosidic bonds/linkages between the equatorial hydroxyl (–OH) group of C1 and the C4 carbon atoms through the polymerization process that make a long, strong, and rigid chain molecular structure, in which each monomer unit is corkscrewed at 180° with respect to its neighbors as shown in Figure 3.2. The steric effects restrain the free rotation of anhydroglucopyranose C–O–C link [57–59]. The repeating unit of this natural polymer is a dimer of glucose, known as the anhydrobeta-cellobiose or simply cellobiose. The number of repeating units linked together gives the degree of polymerization (DP), which is usually between 9000 and 15000 in native cotton [52].

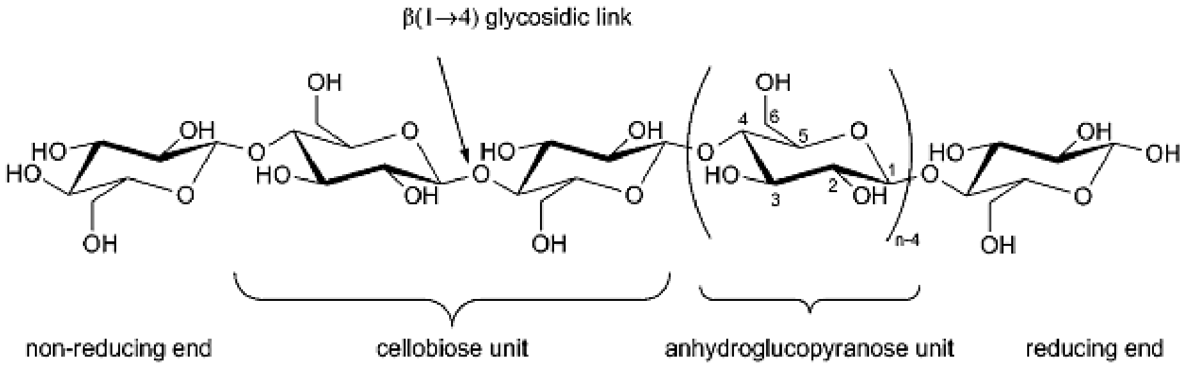


Figure 3.2. Chemical structure of cotton fiber cellulose chains [58, 59]

When any solid polymer material including textile fibers is heated, several physical and chemical changes take place at different specific thermal transition temperatures and thermodynamic parameters depending on the chemical nature and structure of the solid, thus ultimately affecting its flammability [60]. The four thermal transition temperatures such as; softening/glass transition temperature (T_g), melting temperature (T_m), pyrolysis temperature (T_p), and combustion (T_c), are very important (see Table 3.1) while considering the flame retardancy of fibers. When natural cellulosic fibers (i.e., non-thermoplastic fibers) are exposed to a heat/ignition source, pyrolysis and combustion temperatures are encountered before softening and melting temperatures and eventually they ignite. Usually, the lower the value of T_c, the more flammable is the fiber [60, 61]. Another related factor that is considered important in burning is the limiting oxygen index (LOI) value; the minimum volumetric amount of oxygen, required by any material to support combustion and usually expressed in percentage [62, 63]. It has been used to specify the relative flammability or flame retardancy of different polymeric materials [64] and has also broadly been applied to textile materials [65, 66]. The thermal transition temperatures and LOI values of cotton and some other commonly available fibers are enlisted in Table 3.1.

Overall at the macro-scale, the burning/combustive process is an exothermic process (oxidation) that involves three essential components (i.e., fire triangle components) [67, 68], such as:

- a fuel; a combustible substance
- an oxidant; an oxidizing gas, i.e., primarily oxygen
- an ignition/heating source; an external or from a combustion process itself

Table 3.1. Thermal transitions of cotton and some other commonly used fibers [65]

Fiber	**T_g (softens)**	**T_m (melts)**	**T_p (pyrolysis)**	**T_c (combustion)**	**LOI (limiting oxygen index)**
	(°C)	**(°C)**	**(°C)**	**(°C)**	**(%)**
Wool	-	-	245	600	25
Cotton	-	-	350	350	18.4
Viscose rayon	-	-	350	420	18.9
Triacetate	172	290	305	540	18.4
Nylon 6	50	215	431	450	20-21.5
Nylon 6.6	50	265	403	530	20-21.5
Polyester	80-90	255	420-447	480	20-21
Acrylic	100	>220	290	>250	18.2
Polypropylene	-20	165	469	550	18.6
Modacrylic	< 80	>240	273	690	29-30
Polyvinyl chloride	< 80	>180	>180	450	37-39
Polyvinylidene chloride	-17	180-210	>220	523	60
Polytetrafluoroethylene	126	≥327	400	560	95
Oxidized acrylic	-	-	≥640	-	55
Nomex	275	375	410	>500	28.5-30
Kevlar	340	560	>590	>550	29
Polybenzimidazol	>400	-	≥500	>500	40-42

The burning of materials, including cotton cellulose, generally involves two thermal degradation/decomposition processes [69], such as:

- Pyrolysis, and
- Combustion

As cotton is basically cellulose and so its pyrolysis behavior has a significant influence on cotton flammability. Cotton textiles (i.e., fiber, yarn, or fabric) have low flame resistance, and burn easily and vigorously with a prolonged afterglow, leaving no char residues (almost negligible amount) behind except usually the traces of ash. A number of researchers have proposed, reported, and published as scientific literature the numerous possible theories and mechanisms of cotton/cellulose pyrolysis and thermal degradation/decomposition on ignition [70–76]. The cellulosic materials are combustible but actually not volatile since they are not directly involved in the instigation of fire. However, at the initial stage for burning, through the availability and support of an ignition source, these materials encounter endothermic degradation reactions in which larger polymeric molecules are broken into smaller, volatile species and combustible compounds as fuel. Then, these pyrolysis products diffuse to the fiber/yarn/fabric surface and mix with the oxygen from the air so that flame can propagate and combustion can take place. This combustion then becomes exothermic, and the heat and fumes so generated partially transfer back to fiber/yarn/fabric surfaces, so maintaining voluntarily a continuous quick supply/feedback of volatile gaseous fuel to sustain polymer pyrolysis and/or combustion [17, 65]. It can be concluded that the overall cellulose burning may be modeled and exhibited as a cyclic process as shown in Figure 3.3, maintaining a continuous supply of gaseous fuel for further flame propagation.

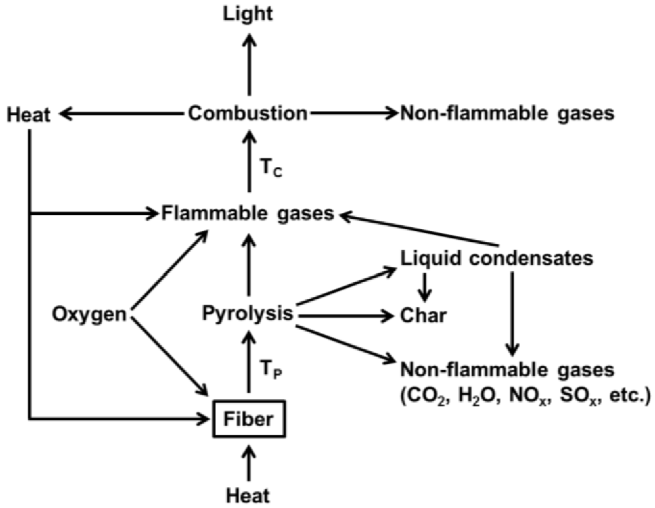


Figure 3.3. Schematic description of combustion cycle for textiles, adapted and reproduced [65]

Combustion typically refers to the act of burning and in literature both burning and combustion are often considered the same and these terms are used interchangeably. The combustion of cotton cellulose can be explained as the following two discrete fire phenomena [77]:

- Glowing, and
- Flaming

That takes place at different temperatures and usually presents individual different possible potential hazards and should be approached accordingly in different ways [69, 78]. Furthermore, the combustion (glowing and flaming) can be explained as the following two distinct phases/states, based on the nature of fire [69, 78]:

- Solid/condensed (oxidation of solid cellulose or its degradation products/residues), and
- Gas/vapor (combustion process of flammable gases and volatile species)

Glowing combustion is generally slow combustion (afterglow or smoldering/smolder combustion) that involves only a solid phase. While flaming combustion is a complex process, which involves both solid and gas phases, and may be modeled as a cyclic process [78].

The pyrolysis of cotton cellulose is a very complex chemical process and is generally believed that it involves and/or takes place as two different phase change mechanisms [79–82], such as:

- Dehydration
- Depolymerization

These two mechanisms are dramatically influenced by the existence of impurities as well as by temperature and heating rate. The dehydration reactions are favored in presence of acid catalysts, whereas, the depolymerization reactions (more specifically decomposition reactions) are privileged in presence of alkaline media. The dehydration usually occurs at low heating rates and increases the subsequent char (carbonaceous structure) formation [79–82]. Whereas, depolymerization usually occurs at high heating rates and increases the consequent rapid volatilization via the formation of levoglucosan and more gaseous combustible products. Greater dehydration also decreases the levoglucosan formation and successively lessens the volatile species [79–82]. The competition between these two reactions subsists throughout the thermal decomposition process of cellulose. It has been suggested and experimentally confirmed, in particular, that pyrolytic decomposition usually occurs as two reactions at controlled temperatures as shown in Figure 3.4. In the first reaction, at about 200-280°C (low temperature), cellulose decomposes to produce 1,2-anhydrocellulose / 1,2-anhydro-β-D-glucopyranose (active cellulose; cellulose*) [72, 73] and water is released and then vanished. In the second reaction, at an elevated temperature, i.e., at about 300-340°C (high temperature), 1,2-anhydrocellulose further decomposes to produce various volatile species/products (alkanes, alcohols, aldehydes, ketones, organic acids, etc.), flammable gases (methane, ethane, ethylene, carbon monoxide, hydrogen, many oxidizable organic molecules, etc.), non-flammable gases (carbon dioxide, water vapor, higher oxides of nitrogen and sulfur, etc.), water and carbonaceous char residues. The second reaction usually involves levoglucosan formation and predominates at a temperature above 280°C. The levoglucosan(1,6-anhydrocellulose / 1,6-anhydro-β-D-glucopyranose) is the main product that produces by the pyrolysis of cellulose. It is a cyclic monomer of cellulose generated due to the thermal scission of β-1,4-glucosidic linkages and loss of water molecules between C1 and C6 hydroxyl groups of anyhydroglucose [69, 83].

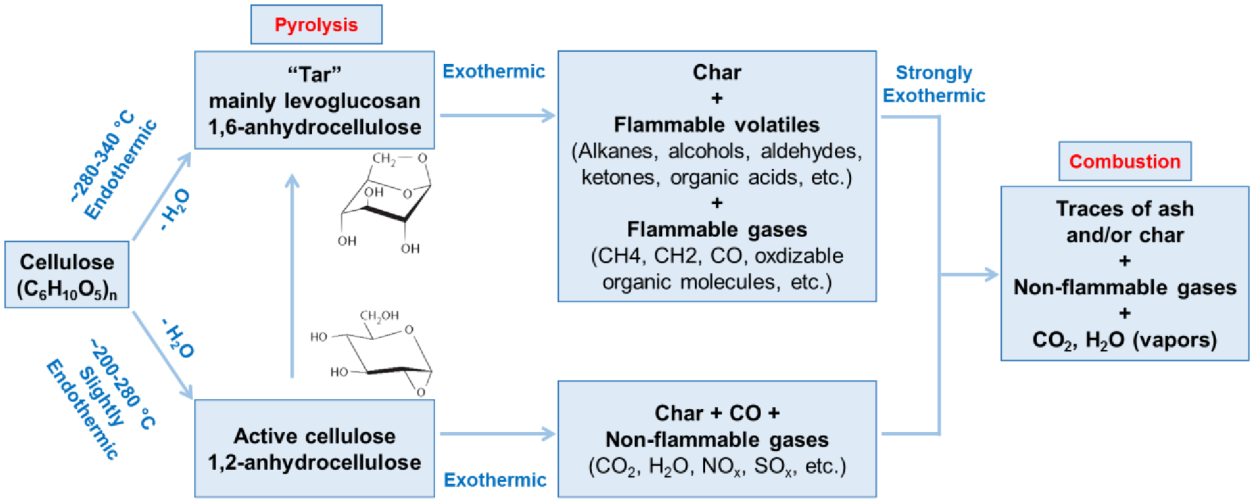


Figure 3.4. General scheme for phase change mechanisms/reactions involved in cotton cellulose thermal degradation, adapted and modified [78, 79]

However, in general, it can be concluded that cotton cellulose thermal degradation is three stages volatile species and char formation/decomposition competitive process as shown in Figure 3.5, and that depends on both the temperature and the exact nature/composition of a material/substrate [69, 84].

Stage I (temperature range 300 – 400 °C)**:** shows a well-established balance between two competitive processes (dehydration and depolymerization) of volatilization and char formation and decides ease of ignition. These competing reactions lead to the formation of thermally stable aliphatic structures/forms (char I) and volatile fuel-forming levoglucosan.

Stage II (temperature range 400 – 800 °C)**:** shows the competitive processes of char I oxidation and conversion of aliphatic char to aromatic structures/forms (char II) with the release of water, methane, carbon monoxide, and carbon dioxide. The volatile species produced in stage I are also oxidized at this stage to produce similar products as from char I oxidation and aromatization. The char II is usually stable at least up to 800 °C.

Stage III (temperature range 800 – 900 °C)**:** during this higher temperature range, the decomposition of some char II to acetylene occurs. While above 800°C, complete combustion of all types of remaining carbonaceous products to carbon- monoxide and dioxide takes place.

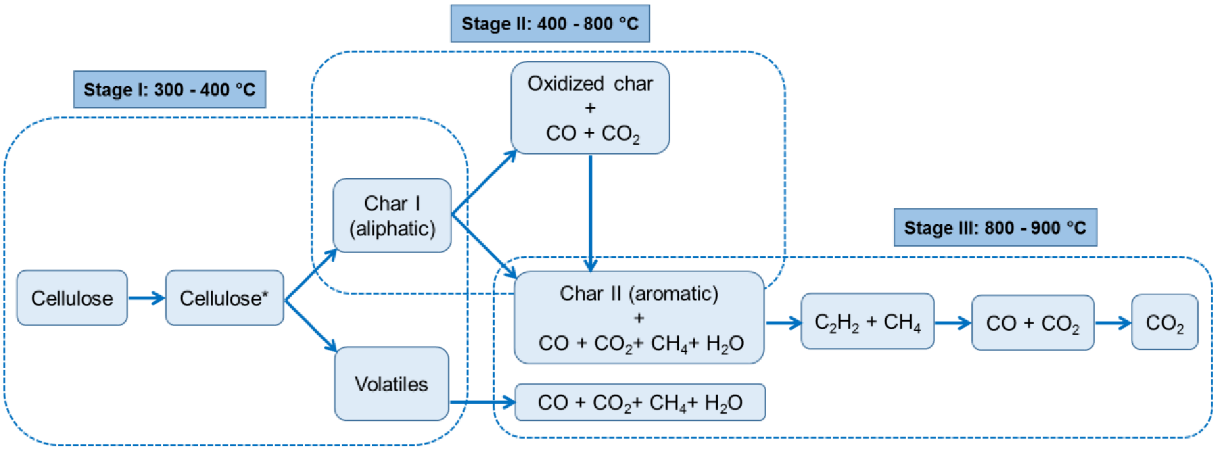


Figure 3.5. Basic scheme depiction for stages involved in cotton cellulose thermal degradation, adapted and modified [69, 78]

3.2 Flame retardants and flame retardancy general aspects

“Flame retardants are chemicals that are added or applied to materials in order to prevent or slow the start or growth of fire” [4, 85], and usually composed of organic and inorganic compounds of phosphorous (P), nitrogen (N), sulfur (S), halogens (X; Br, Cl, F), silicon (Si), aluminium (Al), magnesium (Mg), antimony (Sb), tin (Sn), boron (B), zinc (Zn), carbon (C; graphite), zirconium (Zr), titanium (Ti) and calcium (Ca). The flame retardants could comprise one or more of these elements and their effectiveness is usually a direct function of the fraction of an active element present in the flame retardants [21, 86]. For ease of understanding, flame retardants have been classified into different groups/classes under different situations/conditions, according to several different ways [78, 87, 88], such as based on origin/source, nature of textile material, way/means of incorporation to textile materials, end-uses/application areas of textile materials, chemical-composition/elemental-constituents, general chemical nature, chemical type, or mode of action. Figure 3.6 illustrates how the major flame retardants could be subdivided based on their working mechanisms.

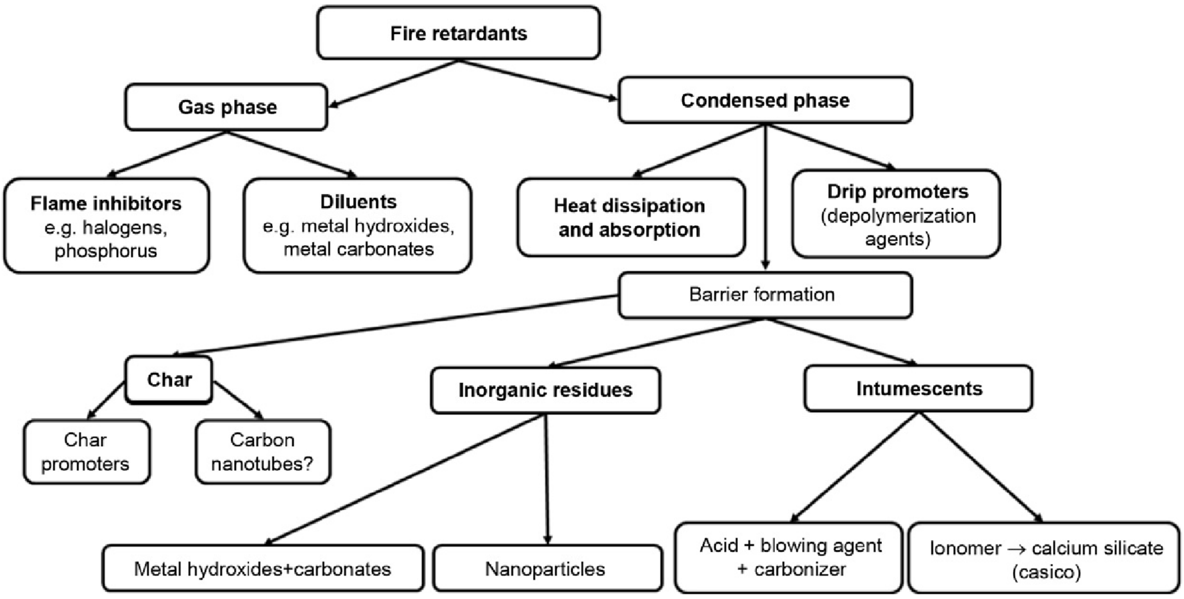


Figure 3.6. Classification of flame retardants based on working mechanisms [87]

As the particular hazards associated with quick burning/combustibility of textiles, especially cellulosic materials (such as cotton and flax) were recognized during ancient civilizations [89]. Salts such as alums have been used since those times to suppress/reduce their combustibility and so confer flame retardancy. In 1735, borax, vitriol (a metal sulfate; ferrous sulfate), and some other mineral substances (alum) were then patented by Obadiah Wyld [90] for flame retarding canvas and linen. The state of the art for different commercially available flame retardants for textile materials has been reviewed, summarized, and classified into different periods (from almost 1735 to onward) according to their key research and development findings [17–19].

Most of the potential and successful additives, formulations, and treatments are derived from chemistry developed in the 1950-1980 period, which is usually considered the “Golden Period” for flame retardant research and developments [19]. That period was particularly remarkable and interesting for the development of two important flame retardants, which are still currently being used. These represent two major and commercially dominant main generic types of durable flame retardants for cotton and cotton-rich blends, specifically those based on tetrakis(hydroxymethyl) phosphonium-urea (THPX) condensates, epitomized by Proban® (Rhodia now Solvay), and those based on N-methylol dimethylphosphonopropionamide (N-MDMPE) derivatives, epitomized by Pyrovatex® (Ciba now Huntsman).

Flame retardant chemicals and finishes for cotton fabrics have been reviewed in a large number of research publications, encyclopedia articles, and books [91–103]. Flame retardant chemical and/or finishing treatments for cotton cellulose and cellulose-based textiles, i.e., flame retardancy can be generally achieved through and/or categorized as non-durable flame retardants, semi-durable flame retardants, and durable flame retardants. Definitely, a large number of different compounds and formulations, from simple processes including deposition of inorganic salts to sophisticated processes involving modifications of cellulose molecules and/or in situ polymerization of suitable monomers, have been proposed [51, 104]. Although many of these compounds, formulations, and processes are documented in scientific and/or patent literature to improve flame retardancy of cotton cellulose and cellulose-based materials and products, their utilization has been limited due to undesirable side effects and high costs [17–20]. However, phosphorus-containing materials are so far the most significant class of compounds commonly used to impart flame resistance to cotton cellulose. Meanwhile, in parallel to the development of new flame retardants, processing technology for flame retardancy has evolved significantly and is still being developed as depicted in Figure 3.7. Flame retardants and processing methods have mutually adapted to each other from simple coating treatment in Ancient Egypt to new 3D and 4D printing technologies. The flame retardant treatment of textiles is one of the oldest forms of textile finishing. Traditionally flame retardants are normally applied to textile substrates through padding, coating, spraying, etc., techniques. A number of advanced techniques like plasma deposition, physical/chemical vapor deposition, layer by layer and sol-gel, etc., have also attracted increasing attention for coating applications in the flame retardant domain [105, 106].

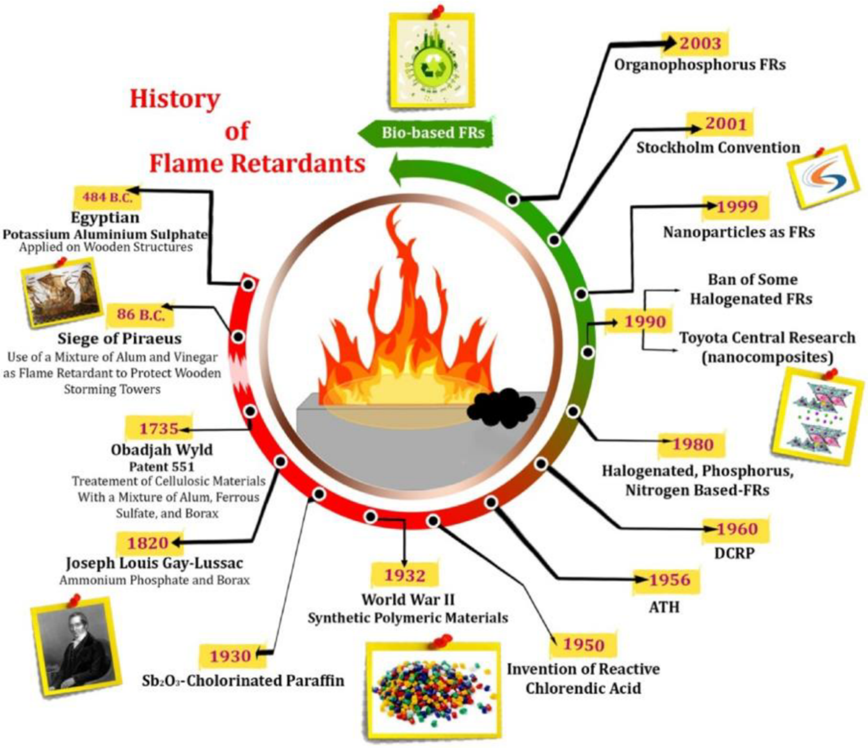


Figure 3.7. Evolution of flame retardants [107]

On exposure to flame, fire, or heating source, flame retardants become active depending on their nature as well as their chemical interaction with the polymers/fibers and can interfere with or disrupt the combustion process/cycle in the solid, liquid, or gas phase (see Figure 3.8 and Figure 3.9) during a particular stage of burning (i.e., heating, decomposition, ignition or flame propagation) through physical actions, and/or chemical actions [65, 108]. They do not happen individually but should be considered as composite/complex processes in which many single distinct stages occur simultaneously with one dominating.

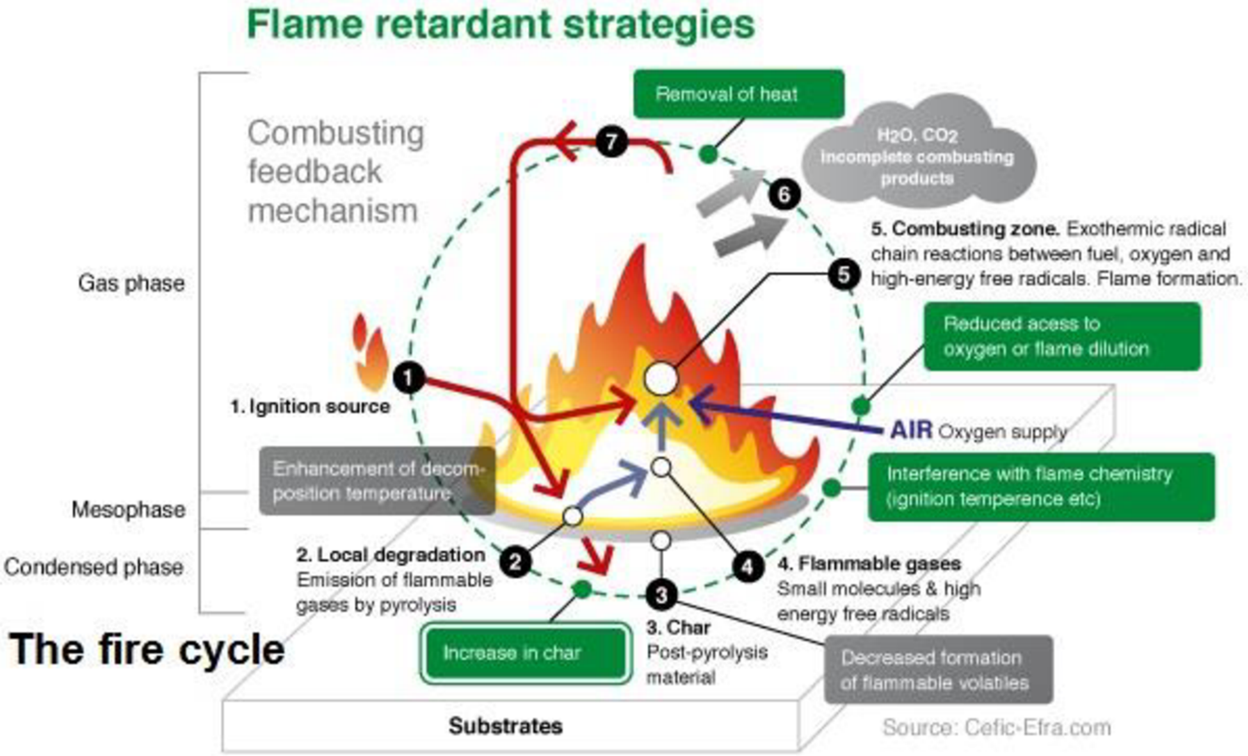


Figure 3.8. Flame retardant working mechanisms and strategies [109]

There are several physical phenomena that may interfere with the combustion process:

- ***By formation of protective layers:*** The combustible/flammable material (polymer/fiber) in the condensed phase can be protected with a protective solid layer that prevents heat transfer from the heat source as well as from the gas phase and inhibits oxygen flow. It then helps to reduce the degradation rate of polymer and also the supply of pyrolysis gases to materials' surfaces. It is also a basic principle of the intumescence phenomenon [110, 111]. This same mechanism can be experienced by using phosphorus- and silicon-containing compounds, boric acid based additives, inorganic borates, or low-melting glasses [112, 113].
- ***By cooling:*** The combustible/flammable substrate can be cooled down to a temperature below that required for ignition and sustaining the combustion process by triggering endothermic processes such as decomposition/degradation of additives, e.g., inorganic/ organic phosphorus-containing agents, aluminium hydroxide, or alumina trihydrate [114].

- ***By dilution:*** The concentration of flammable gases in the condensed and gas phase can be lowered by using inert substances/additives, e.g., fillers (such as talc, chalk) [115] as well as hydrates, char-promoting, and halogen-containing compounds. They release non-flammable gases on decomposition and dilute the fuel in both phases, ultimately the flammable gases concentration falls under the ignition limit.

There are some important chemical reactions that may interfere with the combustion process:

- ***Reactions in the gas/vapor phase:*** The free radical reactions that usually take place in the gas phase of the combustion process can be interrupted by flame retardants. The concentration of free radicals drops down to a critical value, thus flaming cannot occur. The exothermic processes and resulting thermal feedback to the condensed phase are then also declined due to less release of flammable volatiles that ultimately is completely suppressed. The halogenated and some phosphorous-based compounds can interfere with chain reactions by preventing the reaction of hydroxide and hydrogen free radicals with oxygen and carbon monoxide [116, 117].
- ***Reaction in the solid/condensed phase:*** The amount of volatile species produced in the condensed phase can be reduced by changing the pyrolytic path using flame retardants. Consequently, instead, carbonaceous char, carbon dioxide, and water are then often produced [116, 117]. Most of these phenomena occur in the case of nitrogen and phosphorous-based compounds as well as heavy metal complexes. These both are recognized to take place in cellulosic as well as synthetic fibers.

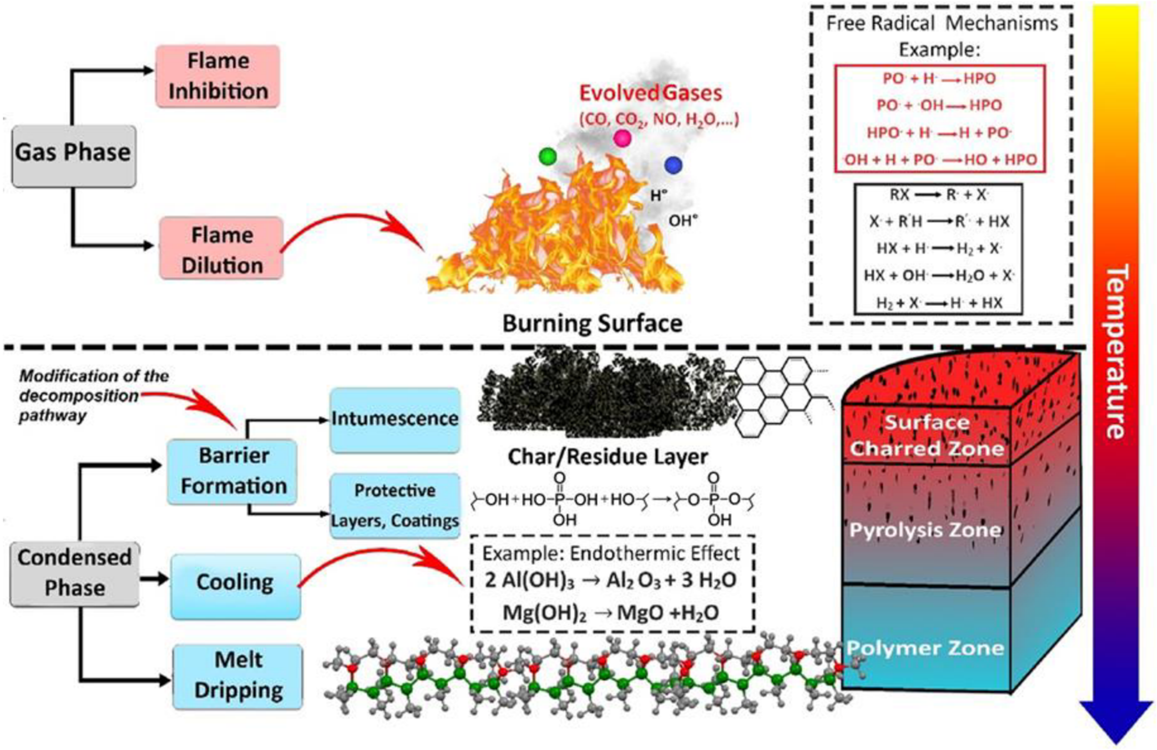


Figure 3.9. Possible action mechanisms of flame retardants in condensed and gas phases [107]

3.3 Char formation and intumescence phenomenon

Char formation during polymer decomposition/degradation, with heat and/or on flame/fire exposure, directly affects the degree of flame retardancy of the polymer. Van Krevelen [118] has shown that the inherent flammability tendency of any polymer decreases as its char-forming propensity increases as char formation always happens at expense of volatile fuel. During burning, char formation act as a thermal insulating layer at the surface to reduce heat transmission into the material and also provides a diffusion barrier to combustible volatiles and gases (fuel) emanating to extinguish the fire in most cases [6]. Additionally, char formation also accompanies the release of water condensates that can dilute combustible volatiles [119]. Char residues are mostly composed of noncombustible carbon derivatives that proffer protection from flaming [119]. In general, for flammable cotton cellulose, most of the effective and efficient flame retardants are ones that stimulate and promote the transformation of polymeric chains into carbonaceous char [16]. Such as, it is notable, that phosphorus-containing flame retardants may wield different modes of action for flame retardancy. They may ensue through the condensed phase or vapor phase, or as a combination of both. The condensed phase action generally results in an increased non-tumescent char formation, and in some cases, tumescent char formation through a mechanism known as intumescence [120].

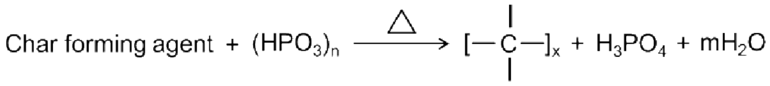
Intumescence or expanded carbonaceous char formation is one of the most efficient ways of imparting flame/fire retardancy to combustible materials [16]. Intumescent coatings (ICs) and intumescent flame retardants (IFRs) systems/technologies have emerged and attracted attention progressively and have been considered the most promising materials to displace halogen-containing flame retardants because they generate low smoke and no toxic and/or corrosive gases. The intumescence phenomenon was observed and reported by Gay Lussac in 1821, with reference to flame retardancy of textiles, but the word “intumescence” was not used at that time. The intumescent flame/fire retardant systems have been employed widely and successfully for almost sixty years for different combustible materials such as for coatings of building structures (mainly on wood boards and steel structures) to facilitate protection against flame/fire. Though, it was the first time reported in the literature, on a fire retardant intumescent coating material mainly applied to wood for fire protection in 1938; a patent by Tramm et al. [121], and first reviewed in the 1970s by Vandersall [110] and updated later by Kay et al. [122]. However, Olsen and Bechle [123] used the term "intumescent" for the first time in this field, in 1948. In the 1980s, it was the comprehensive pioneer work of Camino et al., who successfully applied and permitted this basic concept to bulk polymers (mainly thermoplastics) [124–128]. In more recent years this approach was experienced to apply for polymers and flexible structures such as textiles and is acquiring considerable attention [129].

On the basis of new chemical synthesis, several efforts at academic and industrial levels have been proposed and carried out in the last twenty years by reconsidering conventional perceptions of intumescent formulations and intumescence phenomenon [110, 130]. Available detailed review articles/papers [131–137], cover and present core concepts of intumescence (formulations and developments), highlighting innovations for intumescent flame retardants and their application methods, accompanying the most significant results achieved in flame retardancy of polymeric materials (such as wood, steel, metals, plastics as well as foams, films, and textiles), in last fifteen to twenty years. The intumescent flame retardant system most commonly comprises the integration of three components, although only one single material can have more than one role [108], [135]. Other components that may also be used include binders, resins, viscosity modifiers, fillers, pigments, and fibers as required [129, 138]. The three main components are:

- ***a catalyst; dehydrating agent*** – supply acid for dehydration, accelerate the process, substances that release acid during their thermal decomposition (usually at a temperature between 100 and 250°C), and then acid esterifies hydroxyl groups of carbonizing agents (at slightly above the temperature of acid release), often an inorganic acid and/or its thermal precursors such as phosphoric acid and/or its ammonium, aminic salt and esters (ammonium polyphosphate; APP), boric acid and its derivatives.

$$\text{Acid producing agent} \xrightarrow{\triangle} (HPO_3)_n + nNH_3$$

- ***a carbonific; carbonizing agent*** – supply raw material for char formation, substances with a large number of carbon atoms (as a source of carbon; either provides its own carbon or uses polymer substrate as a carbon source such as cellulose), thermal degradation of which results in the formation of carbonaceous material, and/or, having a huge number of hydroxyl groups, able to be esterified with acids such as polyols, polyphenols, saccharides, polysaccharides.



$$\text{Char forming agent} + (HPO_3)_n \xrightarrow{\triangle} [-\overset{|}{\underset{|}{C}}-]_x + H_3PO_4 + mH_2O$$

- ***a spumific; blowing agent*** – supply evolving gases for foam formation or char expansion, substances able to release a large amount of nonflammable gases during its thermal decomposition to form the foamed structure of carbonaceous char layers such as nitrogen- and halogen-containing compounds.

$$\text{Gas releasing agent} \xrightarrow{\triangle} NH_3 \xrightarrow{O_2} N_2 + H_2O$$

The most basic and earliest intumescent flame retardant system is; pentaerythritol (carbon source), ammonium polyphosphate (acid-releasing source), and melamine (gases forming source) which has been thoroughly and systematically studied by Camino et al. [139–144]. Flame retardancy exhibited by polymers and/or textiles through intumescence is principally a special case of condensed phase mechanism [111]. Intumescent flame retardants certain compounds (either initially incorporated into or merely coated onto polymeric material), on heating beyond a critical high temperature, either decompose or react with other materials in the condensed phase [145–147]. The intumescence phenomenon happens due to the combined effect of charring and foaming of the surface of the burning polymer. The intumescent coatings cover the polymer/textile surface and interfere with thermal degradation and self-sustained combustion at its very earlier stages with the formation and/or evolution of gaseous fuels aiding to insulating polymer/textile surface from heat and gaseous oxidant [16, 145], as shown in Figure 3.10.

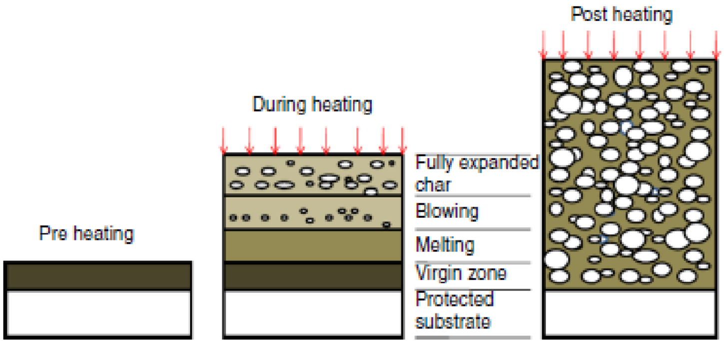


Figure 3.10. Schematic representation of intumescence process [136]

The formation of foamed char depends on a series of complex chemical reactions and physical processes in the condensed phase of polymer/textile burning that occur simultaneously but sequentially at an appropriate time via respective liquid stages in the development of the intumescence phenomenon can be described as follows [108, 127, 135]. Consequently, produced foamed cellular stable charred layer (protective barrier) on the polymer/textile surface protects the underlying substrate from the action of heat-flux/flame and further excessive rise of temperature and oxygen penetration, thus ultimately thermal degradation and combustion [110, 131]. Furthermore, intumescence also fills up interstices between fibers and yarns of textile fabrics as it chars. After that, it also interjects with adjacent charring fibers and yarns, if compatible liquefied phases are present in course of initial pyrolysis stages [148, 149]. As a part of the overall flame retardancy of polymeric materials, the formation of intumescent chars also stimulates to reduce the toxic fire gases and smoke emissions [132, 135].

3.4 Ecotoxicological issues related to flame retardant chemicals and finishes

Chemical finishing has always been an essential part of textile processing that requires complete knowledge and consideration of several important factors [150, 151]. During the last few decades, apart from the inevitable pressure of all these factors, knowledge about the toxicity and environmental impact of chemicals has been growing rapidly and people have become more conscious of potential hazards associated with them [152–154]. Nowadays, the major and most important highlighted issue and challenge throughout the textile and/or chemical finishing industry is the ever-increasing influence of environmental and ecological factors and in general associated present concerns leveled at the use of flame retardants [155–160]. Flame retardancy future is obstructed significantly by the eco-toxicological and environmental considerations, the flame retardants used, and the toxic nature of products released on combustion of textiles.

At present, a major part of commercially available potent flame retardants are petrochemical-based organic compounds (e.g., organo-halogenated, organo-phosphorous, organo-nitrogen compounds). Phosphorus-based flame retardant counterparts seem real as a suitable, potential, and efficient alternative to halogen-based compounds for different types of fibers/fabrics [161]. Though, it is not overall a general case that all phosphorus-based flame retardants are nontoxic, as the development of new flame retardants based on phosphorus compounds has revealed that they have lower toxicity profiles as compared to that halogen-based counterparts [162, 163]. However, considering the pros and cons, and according to very strict proclamations/directives concerning the chemistry of flame retardants used, a large number of flame retardant compounds including some of the currently used halogenated and phosphorous-based compounds received a bad press. They have been limited, are no longer produced, and have been removed from the market or even banned. They are on special lists of national and/or international environmental concerns committees, as they are suspected to stimulate specific health and environmental issues. Because they release toxic products (furans, dioxins, ammonia, formaldehyde, other volatile organic compounds, etc.) during; manufacturing, application to textiles, upon combustion of textiles, etc. [20]. They also have certainly divulged high toxicity for both animals and humans as they do not easily break down, can build up in animals and humans over time (bioaccumulation), and can remain persistent in the environment for years [158].

Environmental benefits require terms/labels such as; green, sustainable, environmentally responsible, environmentally friendly, eco-safe, and recyclable materials and have often been used to describe, advertise, and promote materials/products that are supposedly and/or evidently considered to have nominal negative environmental impacts [152]. However, there are many concerns about the use of flame retardants in all kinds of textiles. Exposures (namely pathways exposure and route exposure) may occur at numerous points in the whole life-cycle of a flame retardant typified by; occupational exposure (during manufacturing/industrial operations), consumer exposure (during end use), and public and environment exposure to releases (during product disposal or from manufacturing/industrial facilities). Any type of products that humans can be exposed to either by direct contact, dermal adsorption, inhalation, or oral ingestion and through a breakdown in the environment as well as ingestion by animals is of concern [164]. In general, ideal flame retardant chemicals and finishes should not be persistent, bioaccumulative, and/or toxic to humans, animals, and/or ecosystems. They should not cause adverse health effects to ultimate consumers and/or adversely affect the overall environment such as air, water, soil, etc. [156, 164]. Therefore, it stimulated both the academic and industrial scientific communities to endow continuous efforts towards research and development in order to find out worthy alternatives and counterparts to traditional flame retardants. In the last few years, extensive consideration and attention have been concentrated on biomass-based (bio-based, i.e., biopolymers; biomacromolecules) natural products due to their renewable resources and environmental friendliness [165–168].

3.5 Biopolymers as green environmentally sustainable initiatives toward flame retardancy

Biopolymers generally refer to bio-based compounds that can be obtained and/or derived from biomass. Biomass exists on earth in the form of biological matter including plants, animals, and microorganisms, which represents about 560 billion tons of carbon apart from bacteria. Vassilev et al. analyzed and presented an overview particularly related to the chemical composition of biomass relying on the general organization of biomass into groups, subgroups, varieties, and species [169]. Although depending on groups, this composition is quite different and very variable but they were able to identify the most abundant elements such as; C, H, N, Ca, K, Si, Mg, Al, S, Fe, P, Cl, Na, Mn, and Ti, in decreasing order. It is commendable to mention that some of these elements are commonly known to possess a flame-retardant effect.

In order to use biomass as a raw matter to produce useful forms such as fuels, heat, power, or chemicals, it has to be converted by passing through various value-added biorefinery processes to separate, extract, and modify different biochemical intermediates and/or compounds [170]. Hence, four main families/classes of biochemical compounds can be differentiated as carbohydrates, proteins, lipids, and phenolic compounds. These biomacromolecules can be used as such or further converted to derivatives employing chemical or biological treatments. Thus, a better approach, to understanding how biomass building blocks can be procured, and further, to develop flame retardant functionalities, comprises in considering its biochemical composition [30]. The bio-based polymers/biopolymers may be classified according to different ways such as based on; source/origin, method of production, chemical composition, applications, etc. But according to the source/origin and the method of production, biopolymers can usually be divided into three main classes/categories [171], as schematically summarized in Figure 3.11.

Up to almost ten years ago, utilization of these biopolymers/biomacromolecules was absolutely allocated for other application fields and have been used as edible films, food emulsifiers, adhesives, papermaking, printing, leather finishing systems, as well as, for the design of biosensors and environmental monitoring systems [172, 173].

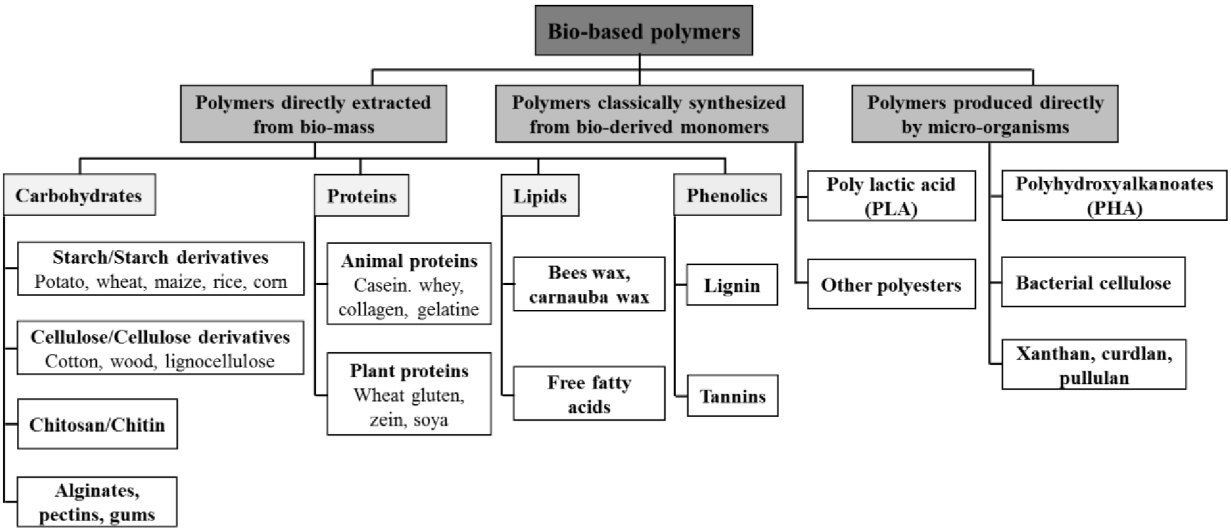


Figure 3.11. Schematic overview for classification of bio-based polymers based on their origin and method of production [174]

In very recent years, continuous efforts have been expended by researchers, pursuing and looking for novel cost-effective, and environmentally sustainable flame retardants for textiles based on the use of biomacromolecules due to enhanced awareness of environmental protection. In this connection, biopolymers, in particular, animal-derived natural products, i.e., proteins such as casein, whey, hydrophobins, deoxyribonucleic acid, etc., presented a potentially innovative strategy and worthy alternatives to traditional chemicals/finishes and approaches for improving the textile materials' thermal stability and flame retardancy. Despite this, some issues relating to the durability of these treatments are still unresolved [28–34]. Actually, the chemical structure of some of these natural products evinces the presence of nitrogen, phosphorus, sulfur, etc., which can impart flame-retardant features to different types of fibers and fabrics.

Alongi et al. [175] investigated the effect of casein protein coating on the thermal stability, flammability, and combustion behavior of cotton fabrics. The results revealed that protein coating was recognized to be responsible for a strong sensitization of cotton cellulose during its thermal degradation. Simultaneously, the flammability and heat flow features of cotton fabric were considerably changed favoring an enhanced flame retardance, heat flow resistance, and char residue formation of the treated fabric. It was indicated by an increase in total burning time (+40%), a decrease in burning rate (-35%) as well as an increase in char residue (+34%).

In another study, the effectiveness of casein protein coating treatment on polyester and polyester-cotton blend fabrics deposited through a simple impregnation method as well as its influence on thermal stability, flammability, and combustion behavior of treated fabrics was evaluated by Carosio et al. [176]. The thermal stability of the treated fabrics, as well as their resistance to a flame application and an irradiative heat flux of 35 kW/m^2, was substantiated to be stoutly affected by casein. Indeed, for polyester fabric, a remarkable reduction in the burning rate

(−67%) and a notable increase in char residue (+79%) after the flame test as well as in its limiting oxygen index from 21 to 26% were observed. While, for polyester-cotton blend fabric, casein coating was worked out to slow down the fabric burning rate (−36%) with an increase in char residue (+62%) after the flame test and a slight increase in its limiting oxygen index from 19 to 21% as well as its resistance to an irradiative flux.

Zhang et al. [177] conducted research work to prepare flame-retardant silk fabric through the application of casein phosphopeptide followed by mordanting with metal salts such as ferrous and titanium sulfates. The treated fabrics presented good flame retardant and smoke suppressant effects. The treated fabrics demonstrated an improvement in limiting oxygen index values from 23.4 to 28. 0% and reached a B1 rating on the vertical burning test even after twenty repeated washing cycles. The enhanced thermal stability at high temperatures and increased good charring ability of treated silk fabrics contributed to their flame retardant capability. Interestingly, casein phosphopeptide and ferrous sulfate treated cotton fabric exhibited a bright yellow color with good washing and rubbing fastness as well as a medium level of light fastness.

In one study by Chang et al. [178], flame retardant properties were imparted to cotton fabrics through coating layer-by-layer assemblies of casein protein with eco-friendly inorganic chemicals (such as polyethylenimine with urea and diammonium phosphate). The effect of layer-by-layer assemblies on the thermal stability, flammability, and combustion behavior of cotton fabrics was characterized and found to be significantly greater than the uncoated cotton fabric. The cotton fabrics coated with twenty bilayers of different compositions showed higher limiting oxygen index values of 29-34% and passed flame tests with char lengths less than 50% of the original length presenting after-flame and after-glow times between 0 and 2 seconds.

A research study was carried out by Uddin et al. [179] to synthesize a simple green fire retardant composite by using casein protein and magnesium hydroxide and examined its functional performance as a self-adhesive coating paste for wood. The casein-magnesium composites were able to produce thermally stable insulating magnesium oxide and char as a result of a synergistic combination of physical and chemical actions - the intumescent action of casein that facilitated suppressing fire spread and smoke. The most effective fruition was obtained with a sample of the highest coating weight for which time to ignition of wood substrate was increased by 147% while peak heat release rate and smoke production rate were decreased by 30% and 53% respectively.

3.6 Casein; bovine milk protein

Bovine milk (a complex biological fluid) is a mixture of water, fats (lipids), lactose (carbohydrate), proteins, vitamins, minerals (or ash), enzymes, and organic acids secreted by mammals that play an essential role to provide nutrition and immunity to offspring [180, 181].

The major general constituents of commercial raw/whole milk are illustrated in Figure 3.12. Bovine milk contains approximately 3.0-3.5% of proteins, which can vary in concentration and composition, according to breed and during different stages of lactation. Milk proteins are usually a heterogeneous mixture of different proteins and categorized into two types; caseins (~2.8%) and whey proteins (~0.6%), making up to 80% and 20% nitrogenous material of milk respectively [182–185]. Caseins and whey proteins have very different physiochemical properties, such as chemistry, structure, functionality, nutrition, etc., that have been extensively and comprehensively studied over the past few centuries.

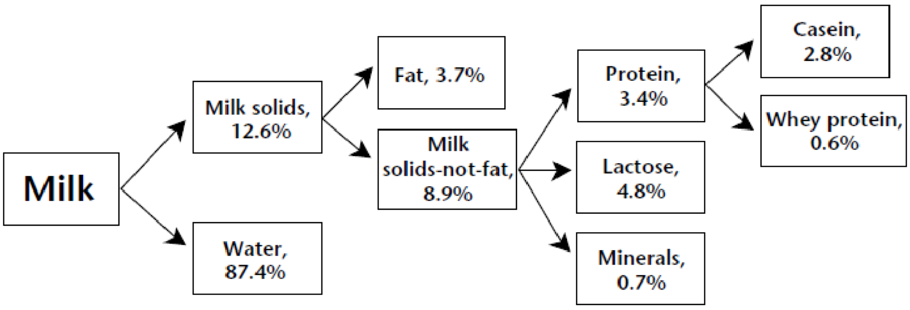


Figure 3.12. Gross composition of milk with major constituents [186]

Caseins are major proteins in milk that are extracted for various applications, as a co-product or by-product during the production of skim milk and cheese, and possibly, are the most broadly investigated food proteins. It is precipitated at its isoelectric pH (~4.6-4.8) and 20°C from skim milk. Pure casein is usually a white/slightly yellowish, tasteless/sweet, and odorless/milky odor powder. The casein chemical structure is that of a block bio-copolymer sparingly soluble in water at almost neutral pH and room temperature. Caseins are phosphoproteins (polyamino acids bearing several phosphate groups in their micelle structure) and characteristically contain phosphorus covalently attached to the protein by a serine ester linkage [182, 187] as depicted in Figure 3.13. Caseins are globular proteins, that build up by a single polypeptide chain of 209 amino acids residues, with molecular weight ranging from 19,007 to 25,230 daltons [39].

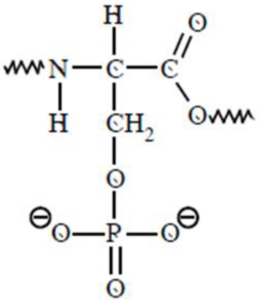


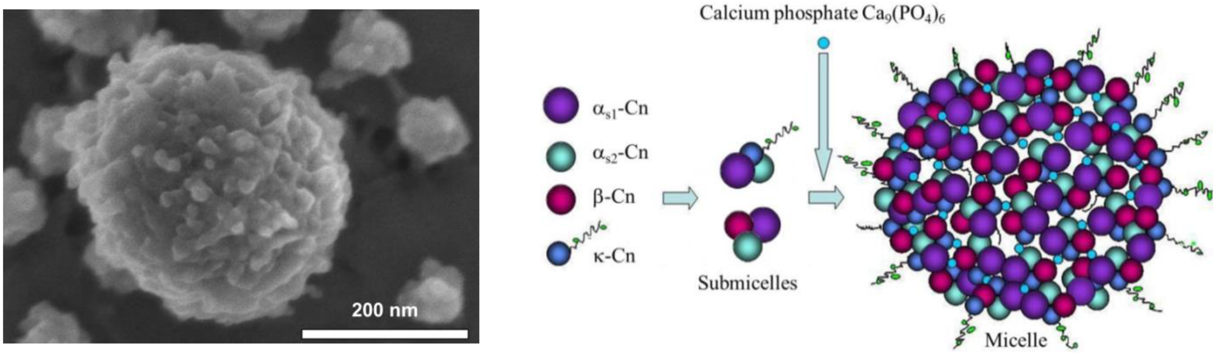
Figure 3.13. General chemical molecular structure representation of casein phosphoprotein [188]

Over 55% of the amino acids in casein proteins contain polar side groups [189], such as 26% carboxyl (–COOH), 15% amino (–NH_2), and 15% hydroxyl (–OH), which facilitate the formation of inter- and intra- molecular hydrogen bonding among macromolecules of casein protein. Casein protein is usually heterogeneous and it is composed of distinct fractions of four main types of proteins: α_{S1}-casein (~38%), α_{S2}-casein (~10%), β-casein (~36%), and κ-casein (~13%), ranging in mass ~19-25kDa, as described and validated by analysis of deoxyribonucleic acid sequences [40, 190]. There are sometimes trace amounts of γ-casein also present, occurring naturally due to limited proteolysis of β-casein by plasmin. Each major sub-constituent of casein has various genetic variants, may be distinguished by electrophoresis, and varies primarily in amino acid composition, proline residues, level of phosphorylation (phosphoseryl residues), molecular weight, isoelectric point, and hydrophobicity/hydrophilicity [39, 191], as specified in Table 3.2.

Table 3.2. various casein fractions in bovine milk and some of their properties [39, 191]

Protein subunit	**Content in skim milk (g/L)**	**Molecular weight (kDa)**	**Isoelectric point (pl)**	**Phosphate residues (per mole)**
α_{S1}-casein	12-15	22-23.7	4.2-4.7	8-10
α_{S2}-casein	3-4	25	-	10-13
β-casein	9-11	24	4.6-5.1	4-5
κ-casein	2-4	19	4.1-5.8	1

Caseins are amphiphilic and have poorly defined structures [192–194]. In milk, 80-95% of casein in its native state, form the larger size of macromolecules that exist in the water phase of milk as self-assembled micellar aggregates (known as “micelles”) of spherical shape [195, 196] with 50-600 nm in diameter size and stable as a colloidal dispersion [197, 198]. These highly hydrated micelles have high proline contents and are highly phosphorylated for the binding of calcium. Many attempts have been to propose diverse models that elucidate casein micelle structure. One most commonly and widely accepted model is that casein micelles consist of spherical subunits (submicelles). Casein micelle is actually a porous, randomly coiled, and spherical complex aggregate (subunits or submicelles) of proteins (α_{S1}-, α_{S2}-, β- and κ-casein) and colloidal calcium phosphate (CCP) held together by hydrophobic interactions as well as by bridging of calcium phosphate nano-clusters that are attached to phosphorylated serine residues of casein side chains, which helps to stabilize the micelle in solution [199–201]. CCP plays a fundamental role in stabilizing and maintaining micellar integrity. There are two main types of submicelles. One consists of α_{S1}-, α_{S2}-, β- casein (center of phosphorylation) that constitutes the hydrophobic center of the micelle. While, another type, consisting of α_{S1}-, α_{S2}-, κ- casein, is distributed and circulated outside of the micelle with a hydrophilic part (i.e., sugar residues of κ-caseins) creating an outer charged hairy surface/layer that aids to stabilize micelles through inter-micellar steric and electrostatic repulsion, as shown in Figure 3.14. These micelles have been extensively studied due to their importance for a number of physico-chemical properties (functional behavior) of milk and various milk products, their structure, composition, properties, and the effects of their composition and processing conditions [202, 203]. However, the exact nature and structure of these casein micelles are still under dispute.



(a) Electron micrograph [204]

(b) Schematic diagram [205]

Figure 3.14. Structure of casein submicelles and casein micelles composed of submicelles held together by calcium phosphate

There are two major types of casein are available, acid and rennet caseins, depending on separation processes [206]. For both types, production starts with skim milk which is produced after the removal of fat from whole milk through centrifugal separation. Then casein is separated from milk serum by; using a mineral acid (aping natural milk souring), using an enzyme (aping cheese making) [207], or using membrane filtration [208]. Acid casein is usually obtained through precipitation, by adjusting the pH of skim milk to its isoelectric point, i.e., ~4.6-4.8, with mineral acids such as hydrochloric or sulfuric acid or lactic acid (produced in situ by microbiological fermentation) [209]. While rennet casein is usually obtained through coagulation in skim milk by the action of chymosin/rennin (rennet) [210]; a key functional enzyme that cleaves/hydrolyzes the bond between methionine and phenylalanine in κ-casein resulting in casein micelle is destabilized and coagulated as a three-dimensional structure. After separation from milk serum, casein (precipitates/coagulates) is cut, stirred, drained, and washed before drying into a powder.

Protein solubility (at least partial) and swelling is a prerequisite for a consistent and stable dispersion to be applied as coating film/layer as well as for inducing viscosity and network formation. It conduces to loosening the molecular structure of a protein, thus countenancing interactions with both the solvent and further protein macromolecules, as functional groups of protein macromolecules require to be available to develop highly viscous solutions and to form networks. Most of the proteins are soluble in water or some other polar solvents, whereas, a few proteins are soluble in moderately polar solvents such as alcohols [211]. Despite this, proteins are the major class of natural polymers, but notoriously, it is still more difficult and challenging to be processed the proteins' solutions into fibrous and/or particle forms than that of other synthetic polymers [212–215]. It is due to their complex macromolecular and three-dimensional structures as well as with strong inter- and/or intra-molecular forces, spurring their structure stability that reduces their capability to unravel in an extensional flow field and obviates the viscoelastic response necessary for jet stabilization. Since, the fact, that casein solutions could not be electrospun, is believed to be due to the high elasticity of polymer, which is caused as a result of the globular structures and strong inter-molecular and intra-molecular forces of casein molecules. However, it was suggested that by reducing these inter-molecular and intra-molecular forces/bondings, the casein solutions could have become electrospinnable. One approach, to interrupt the three-dimensional structure and to dissociate the casein molecules, is by adding another polymer, which has a dissimilar structure and capacity to form secondary bonding with the casein proteins. The addition of another secondary polymer, such as either polyvinyl alcohol or polyethylene oxide (the most easily electrospinnable polymers), can dissociate the inter-connected poly-peptide chains of the protein and therefore reduce its elasticity [212–215].

Thermal behavior/properties, such as thermal stability and pyrolysis products of proteins, sturdily depend on their amino acid composition [216]. As an illustration, the thermal degradation of milk protein; casein in air and under a nitrogen atmosphere, was studied by Mocanu et al. [217]. From the results, they concluded that the thermal degradation of casein in air and under a nitrogen atmosphere is symptomatic of a specific and complex degradation mechanism. The characteristic temperatures signify that the thermal stability of casein does not depend on the degradation atmosphere nature. Casein remains thermally stable and undergoes a little weight loss below 170°C due to the release of physically retained water within casein. The main degradation occurs at 250-425°C, with a slight difference in air and under nitrogen, with the release of the same gaseous species such as carbon dioxide (CO_2), water (H_2O), ammonia (NH_3), isocyanic acid (HNCO), carbon monoxide (CO) in the endothermic domains and carbon dioxide (CO_2), methane (CH_4) and ammonia (NH_3) in the exothermic domain.

Chapter 4

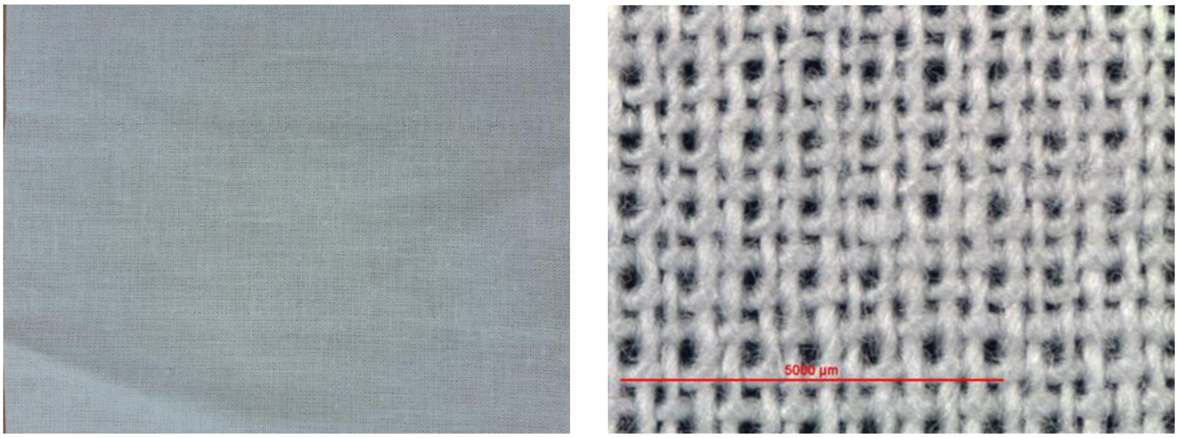
EXPERIMENTAL PART

4.1 Materials

The pretreated, standard bleached, 100% cotton woven fabric was used as a substrate. The fabric was purchased from Licolor, a.s., Czech Republic. The weave of the fabric was plain with a well-balanced construction. The photographs of cotton fabric are shown in Figure 4.1. The preliminary fabric characterization tests were performed according to the standard test methods. The investigated and evaluated different specifications of fabric are given in Table 4.1.

Table 4.1. Technical specifications of cotton fabric used for research work

Fabric specification	**Value**
Warp yarns composition	100 % cotton
Weft yarns composition	100 % cotton
Weave structure/pattern	Plain 1/1
Areal Density (g/m^2)	145
Warp yarns count (tex)	29.5
Weft yarns count (tex)	29.5
Ends (warp yarns) / cm	26
Picks (weft yarns) / cm	22
Fabric thickness (mm)	0.33
Fabric volume porosity (%)	72
Tegewa rating of fabric	9
Fabric absorbency (s)	3
pH of fabric	7.1



(a) Digital photograph (b) Digital Photomicrograph

Figure 4.1. Photographs of cotton fabric used for research work

The details of the chemicals' specifications and sources are given in Table 4.2. All these chemicals were used as received without any kind of further purification.

Table 4.2. List of chemicals used for research work

Chemical	**Specifications**	**Source**
Bovine milk casein	Purified powder, composition (g/l) of: α-s_1(~12-15), α-s_2(~3-4), β(~9-11) and κ(~2-4), technical grade	Sigma Aldrich Czech Republic
Ammonium polyphosphate	Fine granular powder, crystal phase II, n>1000, technical grade	Aako Chemicals Netherland
Polyvinyl alcohol	Crystalline solid, average M_w. 9000-1000, 80% hydrolyzed, technical grade	Sigma Aldrich Czech Republic
Glutaraldehyde	Aqueous solution, 50%, reagent grade	Sigma Aldrich Czech Republic
Citric acid	Anhydrous, granular powder, ≥99%, reagent grade	Sigma Aldrich Czech Republic
Tannic acid	Powder, specific form of tannin, ≥99%, reagent grade	Sigma Aldrich Czech Republic
Texapret LF	Liquid, nonionic, modified dimethylol-dihydroxy-ethylene-urea based resin, commercial grade	Inotex Czech Republic
Tetraethoxy silane	Liquid, 98%, reagent grade	Sigma Aldrich Czech Republic
Sodium hydroxide	Pearls, ≥99%, reagent grade	Lach-Ner Czech Republic
Hydrochloric acid	Aqueous solution, 35%, reagent grade	Lach-Ner Czech Republic
Acetic acid	Liquid, 98%, reagent grade	Lach-Ner Czech Republic
Ethyl alcohol	Liquid, 96%, reagent grade	Lach-Ner Czech Republic
Trisodium citrate	Anhydrous, granular powder, ≥98%, reagent grade	Lach-Ner Czech Republic
Magnesium chloride	Hexahydrate, granular powder, ≥99%, reagent grade	Lach-Ner Czech Republic

The laboratory-scale apparatuses and instruments were used for the preparation of solutions of different chemicals and auxiliaries. These are given in Table 4.3 with the details of their purpose of the use or performed function, model number, and manufacturer.

Table 4.3. List of apparatuses and instruments used for solutions preparation

Equipment	**Function**	**Model**	**Manufacturer**
Weighing balance	Weighing of materials (with accuracy up to 4 decimals)	Kern 770-14	Kern, Germany
pH meter	pH measurements	Eutech, pH 510	Thermo Fisher, USA
Thermometer	Temperature measurements	ČSN	Exatherm, Czech Republic
Glass rods, cylinders, beakers, flasks, etc.	Solutions/suspensions preparation	ČSN	Simax, Czech Republic
Hot plate magnetic stirrer	Controlled stirring and heating of solutions/suspensions	MR Hei-Standard	Heidolph, Germany
Thermostatic water bath	Controlled heating of solutions / suspensions	GFL 1041	GFL, Germany

The laboratory-scale devices and machines were used for the application of different chemical solutions on cotton fabric to develop the final samples. The details of these devices and machines including their purpose of the use or function performed, type/model number, and manufacturer are given in Table 4.4.

Table 4.4. List of devices and machines used for samples development

Machine	**Function**	**Model**	**Manufacturer**
Padding mangle (Roller padding unit)	Uniform chemicals impregnation of fabrics and squeezing with variable pneumatic load and speed adjustment	HVF	Werner Mathis, Switzerland
Coating device (Roller coating unit)	Uniform chemicals coating on fabrics with variable pneumatic load and speed adjustment	SV	Werner Mathis, Switzerland
Stenter dryer (Pin frame drying unit)	Drying and curing of chemical treated fabrics with controllable parameters, i.e., dwell time, temperature, fan speed, etc.	LTE	Werner Mathis, Switzerland
Elmarco’s nanospider (Electrospinning unit)	Needleless electrospinning system for nanofiber and nanoparticles generation	NS1W S500U	Elmarco Czech Republic

The different types of instruments, devices, and machines were used for the characterization and testing of control/pristine and developed/prepared fabric samples. The details of all these equipment including their purpose of use or function performed, model number, and manufacturer are given in Table 4.5.

Table 4.5. List of equipment used for characterization and testing of fabric samples

Equipment	**Function**	**Model**	**Manufacturer**
Weighing balance	Weighing of fabric samples (with accuracy up to 3 decimals)	L 420 P	Sartorius, Germany
Magnifying pick counter glass	Counting of number of ends/picks yarns of fabrics	M240F	Sdl Atlas, USA
GSM cutter	Cutting of standard-sized fabric samples for measuring of fabric areal density	240/100	James H.Heal, UK
Optical/light microscope	Creating a magnified image of fabric samples	Navitar	Nikon Inc., Japan
Digital fabric thickness tester	Determination of fabric thickness	D-2000-T	Hans Schmidt, Germany
Digital stop watch	Measuring of time amount/interval	Fisherbrand 24 Hours	Thermo Fisher, USA
Scanning electron microscope	Featuring of surface morphology of fabric samples	Vega 3 & TS 5130	Tescan, Czech Republic
Fourier transform infrared spectrometer	Identification of surface chemical structure of fabric samples	Nicolet iN10 MX	Thermo Fisher, USA
Inductively coupled plasma atomic emission spectrometer	Detection of elements contents present in fabric samples	Optima 2100 DV	Perkin Elmer, USA
Thermogravimetric analyser	Determination of materials' thermal stability and residues	TGA/SDTA 851	Mettler Toledo, USA
Horizontal flame chamber/tester	Evaluation of burn rate and burn resistance of fabric samples	HMV	Sdl Atlas, USA
High speed video camera	Video recording of burning of fabric samples	HDR-SR12E	Sony, Japan
Limiting oxygen index apparatus	Quantification of limiting oxygen index values of fabric samples	OI-1-X	Govmark, USA
Radiant heat transmission analyzer	Analyzing radiant heat flux density through fabric samples	X637 B	Wazau, Germany
Thermal conductivity instrument/analyzer	Thermal analysis of char residues of the burnt fabric samples	TCI-2-A	C-Therm, Canada
Air permeability tester	Air flow/permeability testing of fabric samples	FX 3300	Textest AG, Switzerland

Water vapor permeability tester	Water vapor flow/permeability testing of fabric samples	Permetest	Sensora, Czech Republic
Alambeta instrument	Thermal conductivity/resistivity analysis of fabric samples	Alambeta	Sensora, Czech Republic
Stiffness tester	Measuring of stiffness/bending rigidity of fabric samples	TH-7	Unireg, Czech Republic
Tensile testing machine	Measuring of tensile force/strength of fabric samples	TIRA test 2300	Tira, Germany
Tear testing machine	Measuring of tear force/strength properties of fabric samples	M006B Digital	UTS International, China
Electrolux-wascator washing machine	Washing performance/durability testing of fabric samples	FOM71CSL	James H. Heal, UK

4.2 Methodology

The solutions of different chemicals, used in this research work, were prepared in the distilled water complying with the different specified time, temperature, and pH conditions. These different conditions were finalized after reviewing the literature and conducting different trials to find out the best parameters that confirmed the solubility of these chemicals and materials in water to form homogeneous aqueous solutions/colloids/emulsions/suspensions. Although the materials used, such as casein and polyvinyl alcohol are also soluble in their other respective solvents. Nonetheless, all the solutions were prepared in water due to addressing ecologically-safe systems.

4.2.1 Preparation of casein solution

The aqueous solutions of casein (CAS) were prepared, under alkaline condition, at six different concentrations such as 5, 10, 15, 20, 25, 30% w/v (i.e., 50, 100, 150, 200, 250, 300 g/l). At first, the calculated quantity of casein powder was added to distilled water under continuous magnetic stirring/agitation (300 rpm) at room temperature for 10 min. It contributed to loosening the molecular structure of casein thus allowing interactions with both the water and further the casein molecules. Then, the temperature of the mixture was raised slowly and it was heated to 80°C in a thermostatic bath. Meanwhile, the pH was adjusted to 9 with a dropwise addition of 1M NaOH, under continuous magnetic stirring (600 rpm). The process was later stopped when the casein was completely dissolved in water. Finally, the solutions were cooled down to almost 30°C before applying to cotton fabrics. The whole process for casein solution preparation, under alkaline conditions, is explained in the process profile as shown in Figure 4.2.

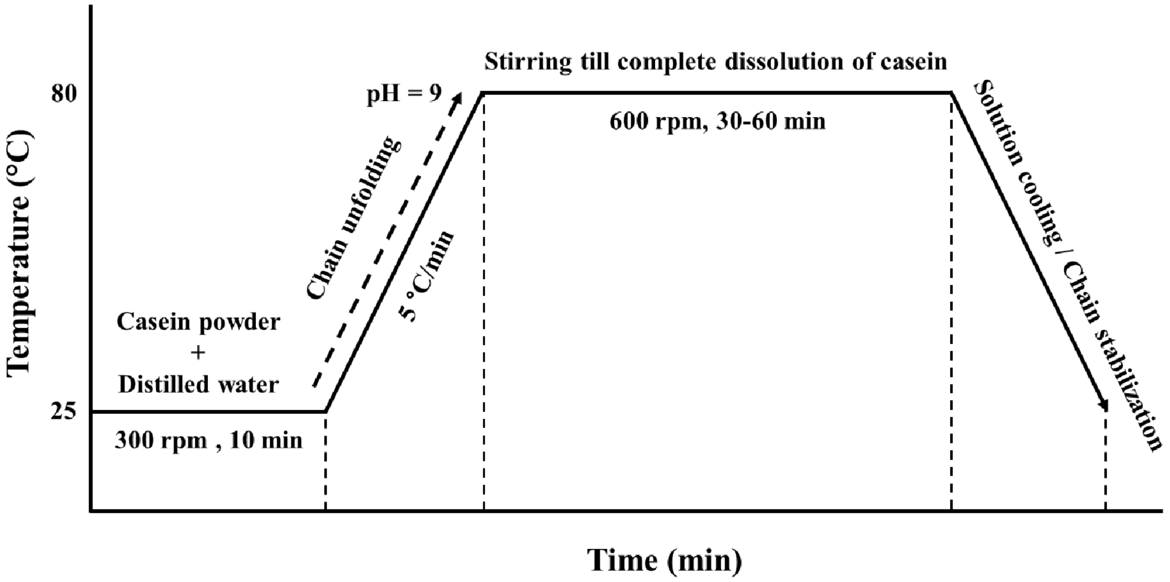


Figure 4.2. Process profile for casein solution preparation in alkaline condition

The aqueous solutions of casein (CAS) were also prepared, under acidic condition, at three different concentrations such as 5, 10, 15% w/v (i.e., 50, 100, 150 g/l). At first, the calculated quantity of casein powder was added to distilled water under continuous magnetic stirring/agitation (300 rpm) at room temperature for 10 min. It contributed to loosening the molecular structure of casein thus allowing interactions with both the water and further the casein molecules. Then, the temperature of the mixture was raised slowly and it was heated to 80°C in a thermostatic bath. Meanwhile, the pH was adjusted to 3 with a dropwise addition of 1M HCl, under continuous magnetic stirring (600 rpm). The process was later stopped when the casein was completely dissolved in water. Finally, the solutions were cooled down to almost 30°C before applying to cotton fabrics. The whole process for casein solution preparation, under acidic conditions, is explained in the process profile as shown in Figure 4.3.

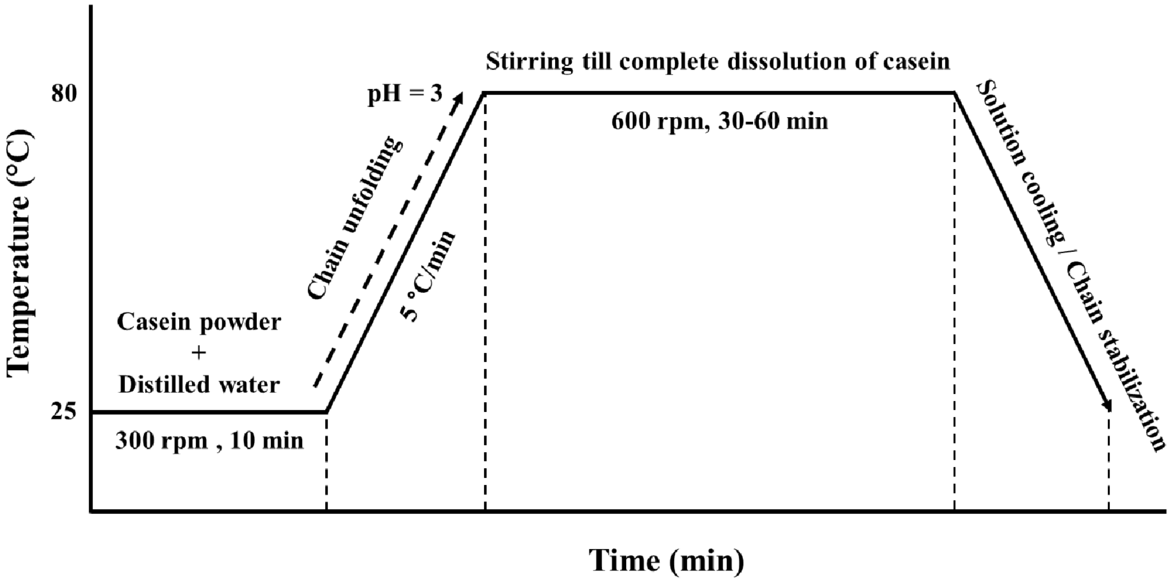


Figure 4.3. Process profile for casein solution preparation in acidic condition

4.2.2 Preparation of ammonium polyphosphate solution

The aqueous solutions of ammonium polyphosphate (APP) were prepared, under alkaline conditions, at three different concentrations such as 2.5, 5, 7.5% w/v (i.e., 25, 50, 75 g/l). At first, the calculated quantity of APP powder was added to distilled water under continuous magnetic stirring/agitation (300 rpm) at room temperature for 10 min. It contributed to loosening the molecular structure of the APP thus allowing interactions with both the water and further the APP molecules.

Then, the solution preparation process was continued at room temperature. Meanwhile, the pH of the mixture was adjusted to 11 with a dropwise addition of 1M NaOH, under continuous magnetic stirring (600 rpm). The process was later stopped when the APP was completely dissolved in water at room temperature. The whole process for APP solution preparation is explained in the process profile as shown in Figure 4.4.

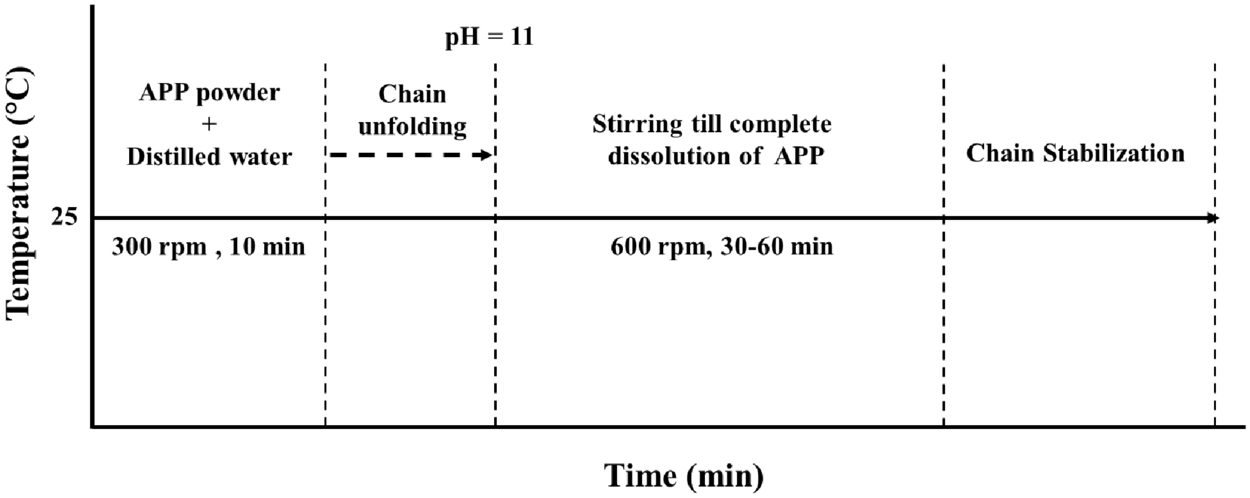


Figure 4.4. Process profile for ammonium polyphosphate solution preparation

4.2.3 Preparation of polyvinyl alcohol solution

The aqueous solution of polyvinyl alcohol (PVA) was prepared at 10% w/v (i.e., 100 g/l) concentration. At first, the calculated quantity of PVA granules was added to distilled water under continuous magnetic stirring/agitation (300 rpm) at room temperature for ~24 h. It contributed to loosening the molecular structure of PVA thus allowing interactions with both the water and further the PVA molecules.

Then, the temperature of the mixture was raised slowly and it was heated to 50°C under continuous magnetic stirring (600 rpm). The process was later stopped when the PVA was completely dissolved in water. Finally, the solutions were cooled down to room temperature. The whole process for PVA solution preparation is explained in the process profile as shown in Figure 4.5.

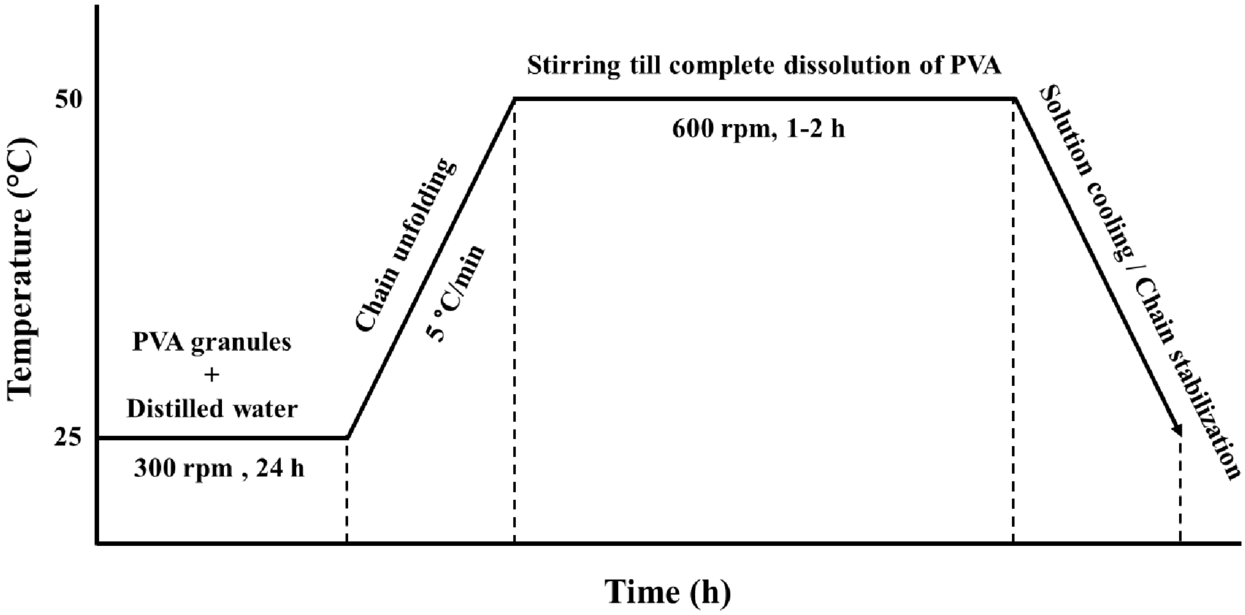


Figure 4.5. Process profile for polyvinyl alcohol solution preparation

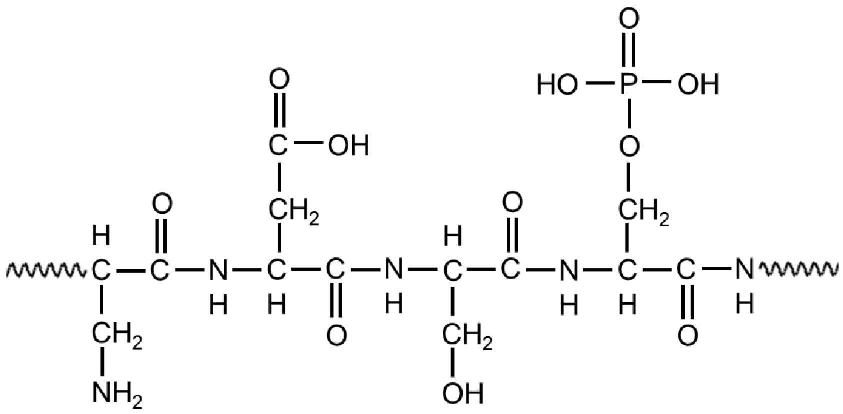
4.2.4 Preparation of crosslinking chemicals solution

The solutions of crosslinking/binding chemical agents (see Figure 4.6), belonging to different chemical classes such as; dialdehydes, polycarboxylic acids, polyphenols, resins, silanes, were prepared separately at the same defined concentration of 5% w/v (i.e., 50 g/l). All these solutions were prepared in distilled water at the suitable and applicable conditions of pH, catalyst, time, and temperature as follows.

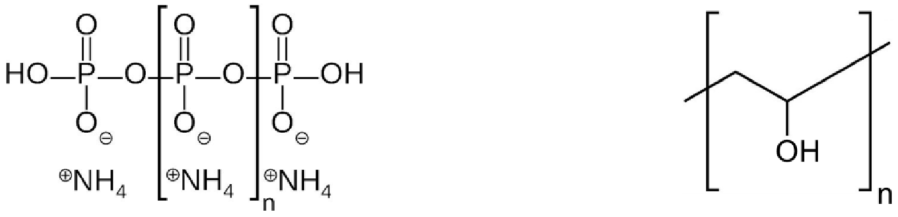
- **Glutaraldehyde solution preparation:** At first, the calculated quantity of glutaraldehyde solution was added to distilled water under continuous magnetic stirring/agitation (200 rpm) at room temperature. After that, the calculated quantity of magnesium chloride (10 g/l) was added as a catalyst. Then, the solution preparation process was continued at room temperature. Meanwhile, the pH of the mixture was adjusted to 5.0-5.5 with a dropwise addition of acetic acid solution. Thenceforth, the stirring (400 rpm) was continued for 5 min to mix all the ingredients appropriately. The process was later stopped when the homogeneous solution was achieved.

- **Citric acid solution preparation:** At first, the calculated quantity of citric acid powder was added to distilled water under continuous magnetic stirring/agitation (200 rpm) at room temperature. After that, the calculated quantity of trisodium citrate (15 g/l) was added as a catalyst. Then, the solution preparation process was continued at room temperature. Meanwhile, the pH of the mixture was adjusted to 3.5-4.0 with a dropwise addition of sodium hydroxide solution. Thenceforth, the stirring (400 rpm) was continued for 5 min to mix all the ingredients adequately. The process was later stopped when a homogeneous solution was obtained.

- **Tannic acid solution preparation:** At first, the calculated quantity of tannic acid powder was added to distilled water under continuous magnetic stirring/agitation (200 rpm) at room temperature. Then, the solution preparation process was continued at room temperature. Meanwhile, the pH of the mixture was adjusted to 5.0-5.5 with a dropwise addition of sodium hydroxide solution. Thenceforth, the stirring (400 rpm) was continued for 5 min to mix all the ingredients precisely. The process was later stopped when a homogeneous solution was attained.
- **Texapret LF resin solution preparation:** At first, the calculated quantity of Texapret LF resin (modified dimethylol-dihydroxy-ethylene-urea (DMDHEU) based resin) was added to distilled water, under continuous magnetic stirring/agitation (200 rpm) at room temperature. After that, the calculated quantity of magnesium chloride (10 g/l) was added as a catalyst. Then, the solution preparation process was continued at room temperature. Meanwhile, the pH of the mixture was adjusted to 4.5-5.0 with a dropwise addition of acetic acid solution. Thenceforth, the stirring (400 rpm) was continued for 5 min to mix all the ingredients properly. The process was later stopped when a homogeneous solution was gained.
- **Tetraethoxysilane solution preparation:** The silica phase (silica sol) was synthesized by a sol-gel technique using tetraethyl orthosilicate (tetraethoxysilane; TEOS) as a silicon alkoxide precursor. The pure silica sol was prepared via acidic hydrolysis of TEOS. At first, the calculated quantity of ethanol (25 g/l) was added to distilled water, under continuous magnetic stirring/agitation (200 rpm) at room temperature. After that, the calculated quantity of TEOS was added in parts. Then, the solution preparation process was continued at room temperature. Meanwhile, the pH of the mixture was adjusted to 4.5-5.0 with a dropwise addition of acetic acid solution. Thenceforth, the stirring (400 rpm) was continued for 60 min to mix all the ingredients perfectly and to hydrolyze the TEOS sufficiently. The process was later stopped when a homogeneous and clear solution was acquired.

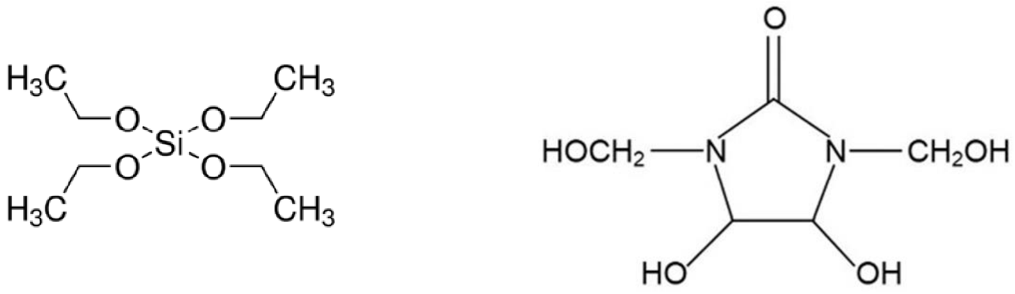


(a) Bovine milk casein

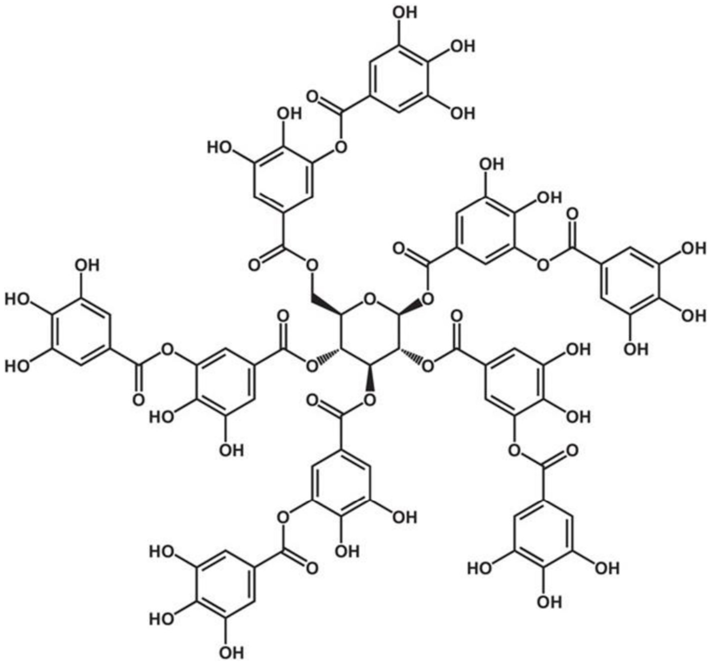


(b) Ammonium polyphosphate (c) Polyvinyl alcohol

(d) Glutaraldehyde (e) Citric acid



(f) Tetraethoxysilane (g) Texapret LF resin



(h) Tannic acid

Figure 4.6. General schematic molecular graphs of main chemicals used in research work

The prepared aqueous solutions of chemicals were applied on cotton fabric, to develop the final samples, by using different industrially applicable methods. These methods are depicted in the flow chart diagram as shown in Figure 4.7 and explained in the following sections. The rationale for using and switching the methods step by step was to attain the intended aims and objectives.

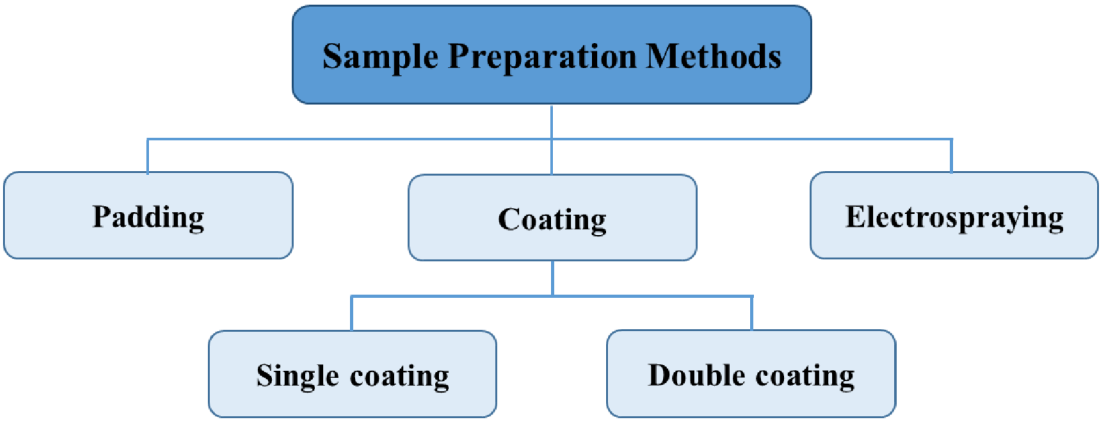


Figure 4.7. Sample preparation methods

4.2.5 Sample preparation of casein treated cotton fabrics

The different concentrations of casein solutions were applied on cotton fabric (CF) by a padding method as demonstrated in Figure 4.8 using the lab-scale padding mangle/machine (two bowl/roller vertical padding unit) in 30±2% relative humidity 30±2°C temperature atmosphere.

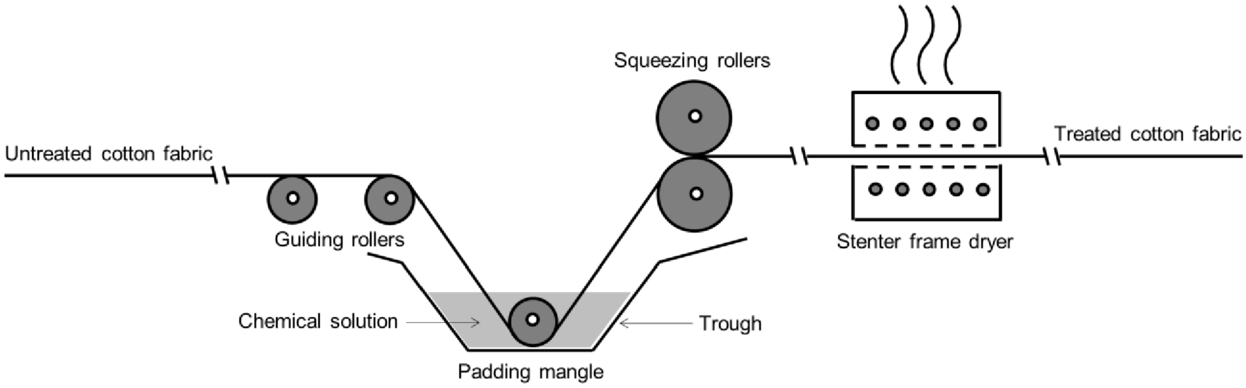


Figure 4.8. Schematic illustration of sample preparation process through padding method

First, the cotton fabric samples were cut up according to the dimensions of the padding/squeezing rollers. Then, the fabric sample was immersed in the padding mangle/trough containing a finishing solution, i.e., casein solution. Simultaneously, the solution-impregnated fabric sample was squeezed while passing through padding rollers, adjusting the pressure and speed to render 80% wet pick up of the solution on the weight of the fabric.

The casein solution padded fabric sample was then placed over a pin frame (stenter frame) in open-width stretched form to avoid any unevenness and dried at 100°C in the lab-scale hot air dryer (stenter frame dryer) for uniform drying. The process was repeated to produce the replicas of treated cotton fabrics for each casein solution respectively, according to the defined experimentation as stated in Table 4.6. Then, the total dry solid uptake (add-on/weight-gain) for casein treated fabric samples was calculated according to the gravimetric principle from the weight of fabric samples by using Equation 1:

$$\text{Add-on (wt.\%)} = \frac{w_f - w_i}{w_i} \times 100 \qquad (1)$$

where 'w_i' is the weight of the cotton fabric sample before impregnation/coating and 'w_f' is the weight of the cotton fabric sample after impregnation/coating and the subsequent drying.

Table 4.6. Details of casein treated cotton fabrics

Sample ID	CF_5% casein	CF_10% casein	CF_15% casein	CF_20% casein	CF_25% casein	CF_30% casein
Casein solution concentration	5%	10%	15%	20%	25%	30%

4.2.6 Sample preparation of alkaline and acidic casein solutions coated cotton fabrics

The single coatings (single-/mono- layer coatings) of different concentrations of casein solutions (prepared at alkaline and acidic pH conditions) were applied on cotton fabric (CF) by a coating method as demonstrated in Figure 4.9 using the lab-scale bar/roller coating unit in 30±2% relative humidity 30±2°C temperature atmosphere.

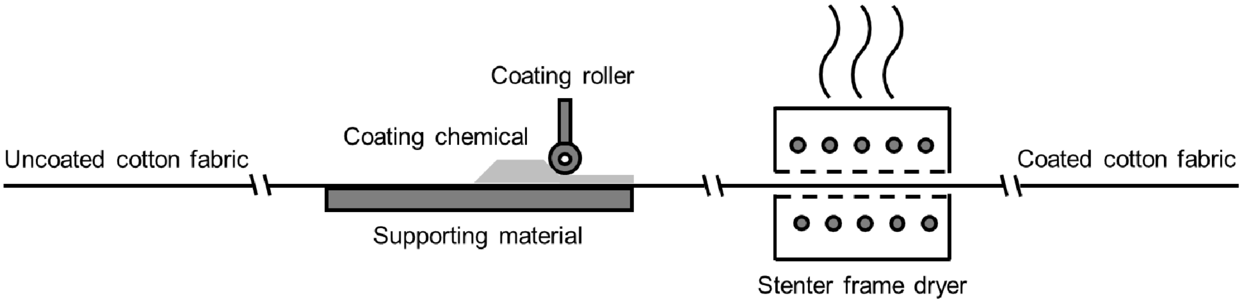


Figure 4.9. Schematic illustration of sample preparation through single-layer coating method

First, the cotton fabric samples were cut up according to the dimensions of the sample mounting head/frame. Then, the fabric sample was mounted over the frame. After mounting, the casein solution was spread over the fabric sample with a spatula so that the amount of solution applied was three times the weight of the uncoated cotton fabric sample. Simultaneously, the coating on the solution-steeped fabric sample was evened out by pressing very gently with a rotary bar while adjusting the pressure and speed. Casein solution coated fabric sample was then placed over a pin frame (stenter frame) in open-width stretched form to avoid any unevenness and dried at 100°C in the lab-scale hot air dryer (stenter frame dyer) for uniform drying.

The process was repeated to produce the replicas of coated cotton fabrics for each casein solution respectively, according to the defined experimentation as specified in Table 4.7. Then, the total dry solid uptake (add-on/weight-gain) for casein coated fabric samples was calculated according to the gravimetric principle from the weight of fabric samples by using Equation 1.

Table 4.7. Details of alkaline and acidic casein coated cotton fabrics

Sample ID	Casein solution concentration	Sample ID	Casein solution concentration
	alkaline pH conditions		acidic pH conditions
CF_50 g/l casein-alkaline	50 g/l	CF_50 g/l casein-acidic	50 g/l
CF_100 g/l casein-alkaline	100 g/l	CF_50 g/l casein-acidic	100 g/l
CF_150 g/l casein-alkaline	150 g/l	CF_50 g/l casein-acidic	150 g/l

4.2.7 Sample preparation of casein in combination with ammonium polyphosphate bilayer coated cotton fabrics

The double coatings (double-/bi- layer coatings/assemblies) of different concentrations of CAS and APP solutions were applied on cotton fabric (CF) by a coating method as demonstrated in Figure 4.10 using the lab-scale bar/roller coating unit in 30±2% relative humidity 30±2°C temperature atmosphere.

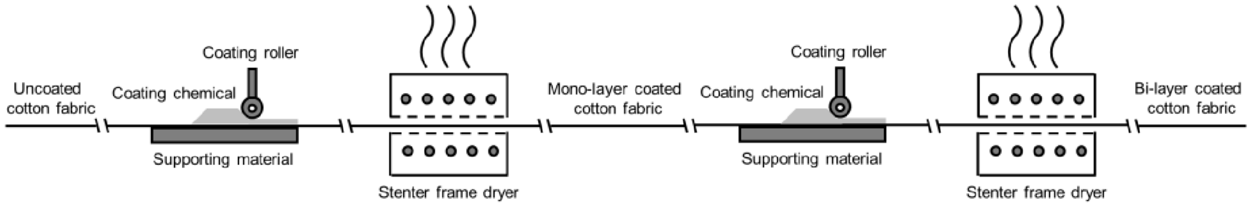


Figure 4.10. Schematic illustration of sample preparation through double-layer coating method

First, the cotton fabric samples were cut up according to the dimensions of the sample mounting head/frame. Then, the fabric sample was mounted over the frame. After mounting, the casein solution was spread over the fabric sample with a spatula so that the amount of solution applied was three times the weight of the uncoated cotton fabric sample. Simultaneously, the coating on the solution-imbued fabric sample was evened out by pressing very gently with a rotary bar while adjusting the pressure and speed. The casein coated fabric sample (monolayer coated) was then placed over a pin frame (stenter frame) in open-width stretched form to avoid any unevenness and dried at 100°C in the lab-scale hot air dryer (stenter frame dryer) for uniform drying. After drying, the casein monolayer coated fabric sample was again mounted over the frame. After mounting, the APP solution was spread over the fabric sample with a spatula so that the amount of solution applied was three times the weight of the uncoated cotton fabric sample. Concurrently, the coating on the solution-imbued fabric sample was evened out by pressing very gently with a rotary bar while adjusting the pressure and speed. The casein-ammonium polyphosphate (CAS-APP) coated fabric sample (bilayer coated) was then again placed over a pin frame (stenter frame) in open width stretched form to avoid any unevenness and dried at

100°C in the lab-scale hot air dryer (stenter frame dryer) for uniform drying. The process was repeated to produce the replicas of CAS-APP bilayer coated cotton fabrics for different bilayer assemblies of CAS and APP solutions respectively, according to the defined experimentation as presented in Table 4.8. Then, the total dry solid uptake (add-on/weight-gain) for CAS-APP bilayer coated fabric samples was calculated according to the gravimetric principle from the weight of fabric samples by using Equation 1.

Table 4.8. Details of CAS-APP bilayer coated cotton fabrics

Sample ID	**1st coating layer**	**2nd coating layer**
	CAS solution concentration	**APP solution concentration**
CF_CAS$_{5\%}$+APP$_{2.5\%}$	5%	2.5%
CF_CAS$_{5\%}$+APP$_{5\%}$	5%	5%
CF_CAS$_{5\%}$+APP$_{7.5\%}$	5%	7.5%
CF_CAS$_{10\%}$+APP$_{2.5\%}$	10%	2.5%
CF_CAS$_{10\%}$+APP$_{5\%}$	10%	5%
CF_CAS$_{10\%}$+APP$_{7.5\%}$	10%	7.5%
CF_CAS$_{15\%}$+APP$_{2.5\%}$	15%	2.5%
CF_CAS$_{15\%}$+APP$_{5\%}$	15%	5%
CF_CAS$_{15\%}$+APP$_{7.5\%}$	15%	7.5%

4.2.8 Sample preparation of casein and polyvinyl alcohol based bicomponent composite nanoparticles coated cotton fabrics

The casein/polyvinyl alcohol (CAS/PVA) nanoparticles (i.e., bicomponent composite nanoparticles) were deposited on cotton fabric (CF) by electrospraying method as demonstrated in Figure 4.11 using the lab-scale Elmarco's Nanospider. Electrospraying is a well-known robust and versatile technique of liquid atomization and is based on similar principles of the electrospinning method [218]. It principally involves electrohydrodynamic processes where a polymer solution can be sprayed in the form of fine mist and/or fine droplets employing a high-potential electric field. The polymer droplets are highly charged, which prevents coagulation and stimulates self-dispersion that results in producing particles of micro and/or nano size range as uniform coatings (i.e., layers or films) on the surface of different types of substrates [219, 220]. Electrospraying technology has also been potentially attempted and successfully employed, as a promising coating technique, to coat textile substrates [221–227]. Elmarco's Nanospider NS 1WS500U (needless setup), is a wire electrode-based nanofiber-producing needless electrospinning machine. It is based on “free surface technology” and generates nanofibers owing to the potential difference between two wire electrodes. In current research work, this needless system was used for electrospraying to produce and deposit nanodroplets/nanoparticles on the surface of cotton fabric.

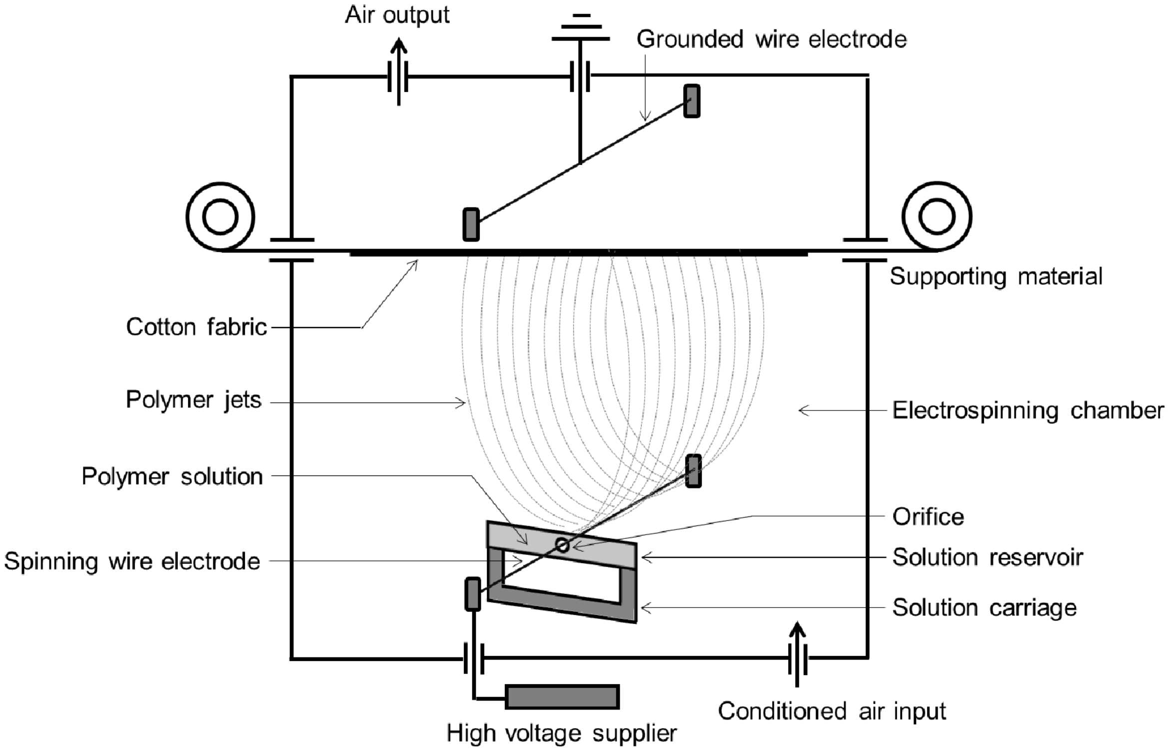


Figure 4.11. Schematic illustration of sample preparation through electrospraying method

The final blended solutions of polymers for electrospraying, i.e., CAS/PVA blended solutions were prepared by mixing the individually prepared aqueous solutions of CAS and PVA, in different specific proportions to achieve the desired compositions, according to the defined experimentation as described in Table 4.9. After mixing, the CAS/PVA solutions of different compositions were homogenized under continuous magnetic stirring/agitation (300 rpm) at room temperature for 5 min. Then, the blended solution of polymers was filled in the reservoir (equipped with a small orifice) of a solution-carriage. The lower wire electrode (stainless-steel wire of 0.2 mm diameter) was passed through an orifice (with a 0.7 mm inner diameter that allows the solution to come in contact with wire) of the reservoir in a concentric manner after mounting the solution-carriage on its support in the electrospinning/electrospraying chamber. The lower wire electrode was moved at a very slow speed of 0.5 mm/s in order to replenish the electrospinning/electrospraying surface, as a solid film was formed over it by polymers solution. The polymer solution was coated on this lower wire electrode (positively charged) through a solution-carriage. The carrier was moved on the wire at 200 mm/s speed, while, the airflow into the chamber was 80 m^3/h and out of it was 130 m^3/h. These ambient conditions inside the closed chamber were controlled through a built-in system included in the machine. The relative humidity and temperature were kept constant (30 ± 2% RH and 30 ± 2°C) and adjusted by controlling the conditions of the lab room using an electronic system. As the solution-carriage shuttled back and forth on the wire, an even layer of the polymer solution was coated on its surface. Under the action of electrostatic force, fine spray jets of polymers solution were emitted from the surface of the wire (positive electrode) and started to move toward the upper wire (negative electrode). These fine spray jets were prevented to reach the upper wire by a cotton fabric (i.e., collector substrate) and collected on its surface in the form of nanodroplets/nanoparticles. The process was repeated to produce the replicas of CAS/PVA electrospray coated cotton fabrics for all final CAS/PVA blended solutions so as to coat the surface of cotton fabrics with CAS/PVA nanoparticles of different compositions, according to the described procedure and the suitable defined parameters of experimentation, as summarized in Table 4.9. All these parameters were specifically selected on the basis of previous studies in the related research field and subsequently were finalized after conducting a number of experimental trials (pre-trials before final samples development). After sample preparation, the surface morphology and other results were evaluated from the scanning electron microscope (SEM) images at different magnifications. Moreover, the average size of CAS/PVA nanoparticles, deposited on the surface of cotton fabrics, was measured by observing the SEM images on the "Image J" software [228].

Table 4.9. Details of CAS/PVA electrospray coated cotton fabrics and input variables

Sample ID	**CAS solution concentration**	**PVA solution concentration**	**CAS/PVA blended solution composition**	**Applied voltage**	**Electrodes distance**
CF_CAS/PVA-75:25	10%	10%	75:25	65 kV	20.5 cm
CF_CAS/PVA-50:50			50:50		
CF_CAS/PVA-25:75			25:75		

4.2.9 Sample preparation for crosslinking of casein with cotton fabrics

The solutions of crosslinking/binding chemical agents of 5% concentration were applied on 30% casein concentration treated cotton fabric samples separately as an after-/post-treatment finishing process using the lab-scale padding mangle/machine (two bowl/roller vertical padding unit) and stenter dryer (pin frame drying unit). This finishing process was executed by applying the glutaraldehyde, citric acid, tannic acid, Texapret LF resin, and tetraethoxysilane chemicals solution according to the pad-dry-cure method at the suitable and applicable conditions of impregnation time, drying/curing time, and temperature. The casein treated cotton fabric sample was first immersed for 5 min in the pad/treatment bath containing a crosslinking chemical solution. Simultaneously, the solution-impregnated fabric sample was squeezed while passing through padding rollers to remove excess solution as well as to uniformly impart wet pick up of solution on the weight of the fabric. The solution padded fabric sample was then placed over a pin frame (stenter frame) in open-width stretched form to avoid any unevenness and dried at 85°C and cured at 150°C for 3 min in the lab-scale hot air dryer (stenter frame dryer) for uniform drying and curing. The after-/post-treatment finishing process was repeated for casein treated cotton fabrics applying each crosslinking chemical formulation respectively, according to the described procedure. Subsequently, all fabric samples after/post treated with glutaraldehyde, citric acid, and Texapret LF resin were thoroughly washed in warm water and dried, except only that, after/post treated with tetraethoxysilane were first rinsed with ethanol, then thoroughly washed with warm water and dried. The after/post treated fabric samples were washed to remove the unreacted deposits of crosslinking chemicals from their surface.

4.2.10 Characterization and testing

The different types of measurements, characterization, and testing techniques were employed in the research work. The intended significance of using these methods was to determine, investigate and evaluate the different parameters, features and properties of solutions, control/pristine and developed/prepared cotton fabrics. These methods are depicted in the flow chart diagram as shown in Figure 4.12 and explained in the following sections. All fabric samples were conditioned, in a standard atmosphere with 65±2% relative humidity and 20±2°C temperature for 24 h, according to the standard test method ISO 139 [229], before conducting any characterization and testing.

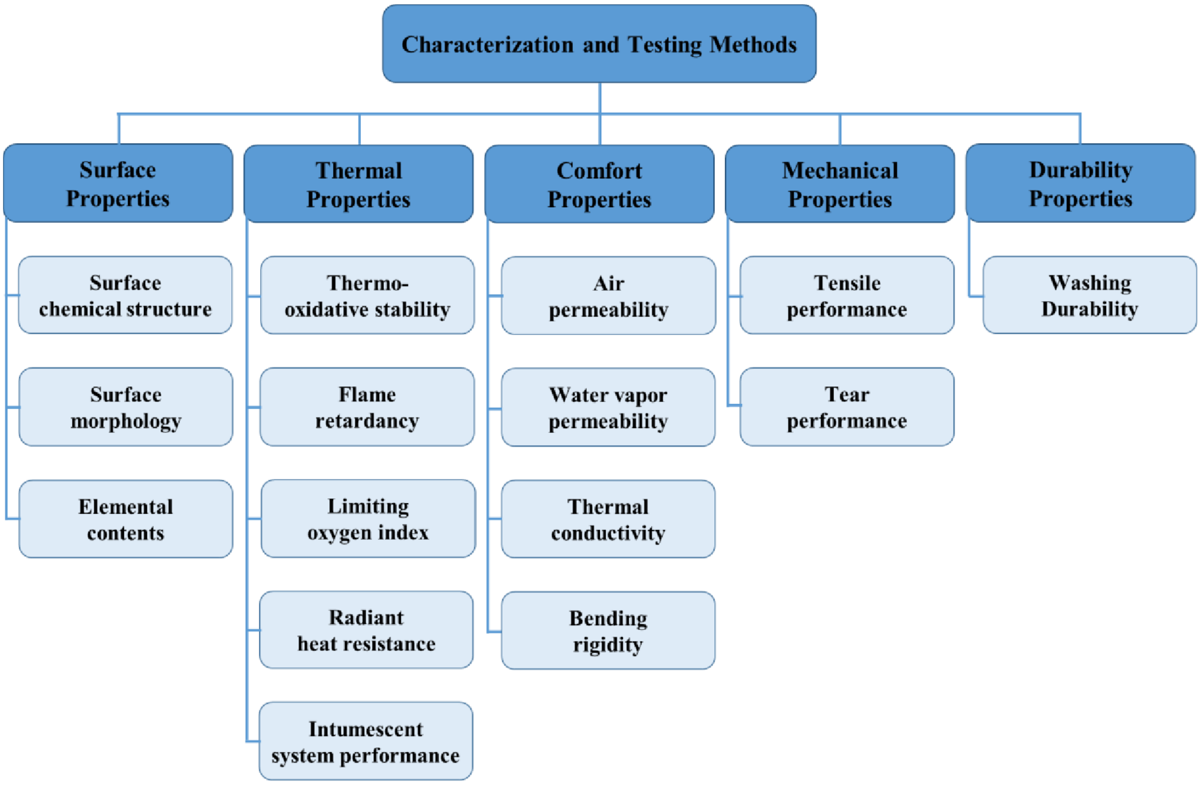


Figure 4.12. Characterization and testing techniques

The different specifications of bleached 100% cotton woven fabric are given in Table 4.1. These parameters of control cotton fabric were determined according to the standard test methods as mentioned in Table 4.10.

Table 4.10. Cotton fabric specifications analysis

Fabric specification	**Standard test method**	**Reference**
Fiber contents/composition	ISO 1833-11	[230]
Weave structure/pattern	ISO 7211-1	[231]
Number of ends and picks	ISO 7211-2	[232]
Warp and weft yarns count	ISO 7211-5	[233]
Areal density	ISO 3801	[234]
Fabric thickness	ISO 5084	[235]
Fabric absorbency	AATCC 79	[236]
pH of fabric	AATCC 81	[237]
Fabric porosity	Volume porosity	[238]
Tegewa rating of fabric	Tegewa solution test	[239]

Surface chemical structure

The surface chemical structure of cotton fabric samples was assessed by the fourier transform infrared (FTIR) spectra. The FTIR spectra of all fabric samples were recorded on an attenuated total reflectance-fourier transform infrared ATR-FTIR spectrometer, at room temperature in the spectra range between 4000-400 cm^{-1}, by using the ATR reflection technique on an adapter with a crystal of ZnSe. The spectra were collected as a result of 32 running scans at a resolution of 4 cm^{-1}. FTIR spectroscopy is a preferred method of infrared (IR) spectroscopy. In IR spectroscopy, infrared radiation is passed through a sample. Some of the infrared radiation is absorbed by the sample and some of it is passed (transmitted) through. The resulting IR spectrum, which represents the molecular absorption and/or transmission, identifies the chemical bonds, creating a distinctive molecular fingerprint of the sample. An IR spectrum of a sample, with absorbance and/or transmittance peaks, corresponds to the frequencies of vibrations between the bonds of atoms making up a material. In addition, the size of peaks in the spectrum is a direct indication of the amount of material present [240]. The attenuated total reflection (ATR) is a special accessory unit and a sampling technique used in conjunction with the fourier transform infrared (FTIR) spectroscopy, which enables samples to be examined directly in the solid or liquid state without any further preparation. The ATR uses a property of total internal reflection resulting in an evanescent wave. A beam of infrared light is passed through the ATR crystal in such a way that it reflects at least once off the internal surface in contact with the sample. This reflection forms an evanescent wave that extends into the sample. The beam is then collected by a detector as it exits the crystal [241].

Surface morphology

The surface morphology of cotton fabric samples, as well as, the charred samples of burnt cotton fabrics (char residues) obtained after the horizontal flame burning test was examined by using scanning electron microscopy (SEM). The SEM images of fabric samples and char residues were taken by using a scanning electron microscope. The samples were mounted rigidly on a specimen holder/stub using a conductive adhesive. Before SEM analysis, the surface of all samples was sputter-coated with gold (a conductive layer). Sputter coating was done to improve the electrical conductivity and stability of samples. So that, they can withstand the high vacuum conditions and the high energy (voltage) beam of electrons generated by a tungsten-heated filament electron gun/source (cathode). The images were taken at different suitable accelerating voltages and magnifications with a slow-scanning speed to obtain higher-quality images. The scanning electron microscope is a type of high-resolution electron microscope that produces the image of a sample by scanning its surface with a focused beam of high-energy electrons (typically ranging from 0.2 - 30 KeV). The high-energy primary electrons interact with atoms in the sample. The low-energy secondary electrons are emitted from each spot where the focused electrons beam impacts, producing various signals. The detectable intensity of secondary electron emission is a function that contains information about the surface morphology, topography, and composition of a sample. The electron beam is scanned in a raster scan pattern, and the position of the beam is combined with the intensity of the detected signal to produce an image. In the most common SEM mode, the secondary electrons emitted by atoms (i.e., excited by an electron beam) are detected using a secondary electron detector. The number of secondary electrons that can be detected and thus the signal intensity depends among other things on specimen topography [242].

Elemental contents

The phosphorus element content of cotton fabric samples was measured by using the inductively coupled plasma atomic emission spectrometer (ICP-AES). ICP-AES (also known as inductively coupled plasma optical emission spectrometry; ICP-OES) is an analytical technique used for the detection of chemical elements. It is a type of emission spectroscopy that uses inductively coupled plasma (often argon) to produce excited atoms and ions that emit electromagnetic radiations at wavelengths characteristic of a particular element. It works by determining the light intensity at elemental specific wavelengths that come from the emission of exited atoms and ions. The intensity of emission from various wavelengths of light is proportional to the concentration of an element within the sample [243]. Prior to analysis, the fabric samples are usually required to be prepared into a solution form by adapting one of the acid digestion methods. Therefore, at first, the treated fabric sample was cut into very small pieces. Then, approximately 0.1 g of treated fabric sample pieces was added to an Erlenmeyer flask with a reflux condenser containing 8 ml of concentrated HNO_3 (65%). The mixture was kept under reflux at 80°C for 2 h and digested until it was completely dissolved. After that, the digested fabric sample as a clear viscous solution was transferred to a 100 ml volumetric flask and diluted to be in the calibration range with deionized water. A phosphorus standard solution was used for calibration. At least, three replicas of each treated fabric sample were digested and analyzed respectively, and the average of measured values was considered as the final representative values. The analysis was performed by using the ICP-OES with argon plasma at a wavelength of 213.617 nm. The measured phosphorous (P) content was defined by Equation 2:

$$\text{P content (mg/g)} = \frac{C_s}{W \times V} \qquad (2)$$

where 'C_s' is the phosphorous concentration of the digestion solution analyzed by ICP-OES (mg/L), 'V' is the volume of the digestion solution (L), and 'W' is the weight of the treated fabric sample used for the digestion solution (g).

Thermo-oxidative stability

The thermogravimetric or thermal gravimetric analysis (TG analysis; TGA) is an analytical technique used to determine the thermal stability/degradation (under oxygen and inert atmosphere) of substances/materials by monitoring the weight change that occurs as a sample/specimen is subjugated to a controlled temperature program in a controlled atmosphere. The weight loss, due to the formation of volatile products, after degradation at high temperatures is monitored as a function of temperature or time [244]. The thermal stability in the air represents one of the most important issues in the design of a new flame retardant for fabrics. In particular, before ignition, any polymeric material undergoes thermo-oxidation and subsequently starts to burn [69, 245]. Therefore, the thermal behavior of cotton fabric samples was assessed by the TG analysis (TGA). It was conducted by using a thermogravimetric analyzer. All fabric samples were analyzed under oxidative (O_2) atmospheres, i.e., in air, to characterize thermo-oxidative processes. The fabric sample (~10 mg) was placed in an alumina crucible and distributed evenly across the pan bottom. The sample was heated in the air from 30 to 800°C at a controlled heating rate of 10°C/min. The experiment was repeated, at least, for three replicas of each fabric sample respectively, and the average of collected data values was considered as the final representative values. The data, obtained from testing results, were plotted as thermogravimetric (TGA/TG) and derivative thermogravimetric (DTG/dTG) curves for comparison. The data were also concluded and presented as $T_{onset10\%}$ (the temperature at 10% weight loss of sample), T_{max1} (the temperature at first maximum weight loss of sample), T_{max2} (the temperature at second maximum weight loss of sample), and char residue percentage at different degradation temperatures. The derivative thermogravimetric data was calculated to acquire T_{max1}, $T_{max2,}$ and char residues at these temperatures.

Flammability / flame retardancy

The flammability test methods generally measure how easily substrates/materials ignite, how quickly they burn, and how they react to burning. A flame retardant fabric does not propagate flame, although, it may burn or char when subjected to any form of heat source. In other words, the burning process must be interrupted by flame retardant compounds as a means to induce flame retardancy. Hence, in order to designate a realistic fire scenario and reaction to flame application, the cotton fabric samples were tested for ignitability (ease of ignition/burning) and flame propagation behavior (flame spread time/speed) in a horizontal configuration by employing a horizontal flame setup, according to the standard test method ASTM D4986 [246]. This setup is an essential flame chamber and is commonly used at a lab scale to determine the comparative burn rate (extent) and/or burn resistance (time of burning/total burning time) of textiles, plastics, and other automotive interior materials. The test determines if and when the flame extinguishes and/or the time in which the flame passes a measured distance. A fabric sample, having a length of 100 mm and a width of 50 mm, was clamped horizontally in a U-shaped sample holder. The small ignition source was provided by a gas burner, known as a Bunsen burner. The methane flame of 25±2 mm height was applied for 3 seconds (ignition time) to the shorter free-side end/edge of the fabric sample [247, 248]. Then, the different parameters such as total burning time (s), burning rate (mm/s), and final char residue (wt. %), for the fabric sample of specified dimensions, were recorded. The test was repeated and at least five replicas were tested for each fabric sample respectively, and the average of recorded values was considered as the final representative values.

Furthermore, the surface morphology of char residues obtained from burnt fabric samples was examined on a scanning electron microscope at different suitable accelerating voltages and magnifications with a slow-scanning speed to obtain higher-quality images. Irrespective of the measurement conditions of the above-described test (i.e., flame height, flame application time, fabric to flame position/angle, etc.), an additional method for flame retardancy evaluation using image analysis was also employed to detect small differences in flame propagation. The burning of fabric samples was recorded on videos using a high-speed video camera. The video file was composed of frames of size 1080x1920x3 pixels in RGB 8-bit depth at 25 frames per sec (fps) rate. The MATLAB video reader function/program was used to extract each frame as an image from a video file [249]. These images were further modified by using basic image processing tools/operations such as conversion to grey level image; subtraction of non-burned sample for suppression of sample texture. The global thresholding (at threshold 0.3) of grey-scale images was done for conversion to binary images; morphological opening for removing small connected objects and closing for filling holes in a burned area. Finally, the length and area of the burned region for burned fabric samples were estimated for every one second interval of burning time.

Limiting oxygen index

The limiting oxygen index values of cotton fabric samples were obtained by using the digital display oxygen index apparatus at ambient/room temperature, according to the standard test method ISO 4589-2 [250]. The limiting oxygen index (LOI), sometimes referred to as oxygen index (OI) or critical oxygen index (COI) is an important dynamic with respect to combustion. It is a fire reaction property that is very widely used as a research and quality control tool for quantifying the relative/comparative flammability and/or flame retardant properties of different materials including textiles. The LOI test is a quantitative, repeatable, and reproducible method for the evaluation of flammability, i.e., the ignition and ease of extinction of a material. It is a numerical index that is defined as the minimum volumetric amount/concentration/fraction of oxygen in a controlled atmosphere consisting of a gas stream/flowing mixture of oxygen and nitrogen, required by materials to support and sustain downward flame combustion under specified conditions in a candle-like fashion, and usually expressed in percentage [62, 63]. The higher the LOI value of a material (i.e., should also be greater than the natural atmospheric oxygen concentration), the lesser the propensity of that material to ignite and burn, representing its better flame retardancy. It is determined by propelling an upward-flowing mixture of oxygen and nitrogen gases over a vertically supported burning specimen in the downward position, then reducing the oxygen concentration until a critical level is reached. At least, five replicas of each fabric sample were tested respectively, and the average of calculated values was considered as the final representative values. The calculated LOI value can be represented by Equation 3:

$$\mathrm{LOI\ (vol.\%)} = \frac{[\mathrm{O_2}]}{[\mathrm{O_2}] + [\mathrm{N_2}]} \times 100 \qquad (3)$$

where '$[O_2]$' is the volume concentration of oxygen gas and '$[N_2]$' is the volume concentration of nitrogen gas in a gas mixture of oxygen and nitrogen.

Radiant heat resistance

The transmission of radiant heat (heat flux/heat flux density) through cotton fabric samples was evaluated by employing the radiant heat transmission analyzer (combustion behavior test equipment) [251], according to the standard test method ISO 6942-Method B [252]. The equipment consists of a heating arrangement, a curved copper plate calorimeter, and a moveable frame assembly. The heating arrangement comprises six carbide rods serving as a radiation heat source, which can generate heat flux density up to 80 kW/m^2. The calorimeter (with an area of 50 mm x 50.3 mm and a mass of 35.9-36.0 g) is mounted on a non-combustible block and determines the heat flux. Its face is coated with a thin film of an optically black paint having a coefficient of absorption greater than 0.9. The moveable frame assembly is constantly cooled with water flowing in cooling pipes. It contains a holder for the calorimeter and a moveable screen to expose the calorimeter (without and/or with a fabric sample, mounted over it) to radiant heat. At first, the calibration was performed by exposing the calorimeter to a radiation heat source without mounting the fabric sample on its face side. The moveable screen was withdrawn and reverted to the point when the rise of temperature reached 30°C and incident heat flux density Q_o was evaluated. Then, the fabric sample of the specified size, having a length of 230 mm and a width of 80 mm, was clamped in such a way that it was in contact with the face side of the calorimeter applying a mass of 200 g. The calorimeter, with a mounted fabric sample over it, was subjected to heat radiations (medium heat flux density of 40 kW/m^2) by lifting the moveable screen in its open position. It was reverted to its closed position as the temperature reached 30°C. Then, the time in seconds for temperature acceleration/rise of 12°C and 24°C in the calorimeter was recorded by a copper constantan thermocouple, mounted on its back. The experiment was repeated, at least, for five replicas of each fabric sample respectively, and the average of output data values was considered as the final representative values. The test was performed in a room that was free of any air currents and any system capable of producing stray heat radiations. The temperature of the test room was maintained between 15°C and 35°C. The output results of this test were concluded and expressed in the form of two threshold times i.e., the radiant heat transfer indexes; $RHTI_{12}$ (threshold time in seconds (t_{12}), when the temperature of the calorimeter increase in 12°C) and $RHTI_{24}$ (threshold time in seconds (t_{24}), when the temperature of calorimeter increase in 24°C) respectively, incident heat flux density; Q_o (kW/m^2), transmitted heat flux density; Q_c (kW/m^2) and the heat transmission factor TFQ_o(%) [251]. The heat transmission factor (TFQ_o) for incident heat flux density level can be elucidated by Equation 4:

$$TFQ_{\circ}\,(\%) = \frac{Q_c}{Q_{\circ}} \times 100 \qquad (4)$$

Thermal performance of intumescent char residues

The heat transmission characteristics of the stable structure of burnt cotton fabrics (i.e., intumescent char residues) after the flammability test were investigated by employing the thermal conductivity analyzer / thermal conductivity instrument (TCi). The test was conducted to evaluate and verify the working efficiency/potential of the CAS-APP intumescent system for the formation of porous foam/structure of char layer. The TCi conveniently measures the thermal conductivity of small samples/specimens using the modified transient plane source (MTPS) method that conforms to the standard test method ASTM D7984 [253]. It is versatile to test solids, liquids, powders, and pastes and has the flexibility to operate in various environmental enclosures. In addition, it can measure thermal conductivity using only one side of a sample/specimen [254]. The TCi consists of a sensor, a power control device, and a computer software. A spiral-type heating source is located at the center of the sensor, and heat is generated at the center. The heat that has been generated enters the material through a sensor during which a voltage decrease occurs rapidly at the heating source, and the thermal conductivity is calculated through voltage decrease data. On the basis of this similar principle, the burnt fabric sample was placed on a preheated sensor and the thermal conductivity measured by the program was noted. The test was repeated and at least five replicas were tested for each burnt fabric sample respectively, and the average of noted values was considered as the final representative values.

Air permeability

The air permeability of cotton fabric samples was measured by utilizing an air permeability tester, according to the standard test method ISO 9237 [255]. Any part of the textile fabric, to be tested, can be placed without its destruction between the sensing circular clamps/discs of this instrument. The air permeability instrument depends on the measurement of airflow passing through the fabric at a certain pressure gradient. For this purpose, pressurized air is passed perpendicularly through a specified area of the fabric sample subjected to testing. The airflow is automatically adjusted by the equipment to achieve a pre-set pressure differential across the two surfaces of the samples. The air permeability is obtained from the value of airflow. At least, ten measurements were performed at different places of the replicas for each fabric sample respectively, and the average of measured values was considered as the final representative values. The air permeability (AP) of the uniform textile fabric is usually defined by Equation 5.

$$\mathrm{AP}\ (\mathrm{l/m^2.s}) = \frac{\mathrm{q_v}}{\mathrm{A}} \tag{5}$$

where 'q_v' is the average rate of airflow passing through a fabric sample and 'A' is the fabric sample area.

Water vapor permeability

The relative water vapor permeability (RWVP) of cotton fabric samples was measured by utilizing a water vapor permeability instrument (Permetest device) [256]. The Permetest device provides all kinds of measurements very similar to the standard test method ISO 11092, and the results data are evaluated by an identical procedure as required in ISO 11092 [257]. This instrument is a so-called skin model that simulates dry and wet human skin surfaces in terms of its thermal feeling. The porous membrane (porous sweating surface) of the device simulates skin and records cooling heat flow caused by perspiration. The heat required for water to evaporate from the porous membrane, without and with covering it with a fabric sample, was recorded by the instrument to calculate RWVP. At least, five measurements were conducted at different places of the replicas for each fabric sample respectively, and the average of measured values was considered as the final representative values. The RWVP of the homogeneous textile fabric is usually defined by Equation 6.

$$\mathrm{RWVP}\ (\%) = \frac{\mathrm{q_s}}{\mathrm{q_o}} \times 100 \tag{6}$$

where ‘q_s’ is the heat flow (w/m^2) passing through the covered measuring head (i.e., covered by a fabric sample) and ‘q_o’ is the heat flow (w/m^2) passing through the uncovered measuring head.

Thermal conductivity

The thermal conductivity coefficient (λ) of cotton fabric samples was measured by utilizing an Alambeta instrument [258]. The Alameda instrument provides all kinds of measurements very similar to the standard test method ISO 8301, and the results are evaluated by an identical procedure as required in ISO 8301 [259]. The Alameda instrument enables fast measurements of both steady-state and transient-state thermal characteristics of textile fabrics. This instrument simulates, to some extent, the heat flow from human skin to the fabric during a short initial contact in the absence of body movement and external wind flow. It operates on the principle of heat emitted by a hot upper plate (around 32°C) in one direction through the fabric sample to a cold bottom plate (around 20°C) adjoined to the fabric sample. The flow of heat due to the temperature gradient between an upper heated plate and a fabric sample on a cold plate was recorded by the instrument to calculate (λ). At least, five measurements were executed at different places of the replicas for each fabric sample respectively, and the average of measured values was considered as the final representative values. The thermal conductivity coefficient of the uniform textile fabric is usually defined by Equation 7.

$$\lambda\ (\mathrm{W/m.K}) = \frac{\mathrm{qh}}{\mathrm{A\Delta T}} \tag{7}$$

where ‘q’ is the heat transferred/transmitted through a fabric sample (W), ‘h’ is the fabric sample thickness (m), ‘A’ is the fabric sample area (m^2), and ‘ΔT’ is the temperature gradient (K).

Stiffness / Bending rigidity

The stiffness/bending rigidity of cotton fabric samples was measured by utilizing a stiffness measuring device, a TH-7 bending rigidity tester [260], according to the standard test method

ČSN 80 0858 (800858) [261]. The TH-7 instrument has the same working principle as the Kawabata Evaluation System of fabric; the KES-F system (a device used for testing low-stress mechanical properties and surface characteristics of textile fabrics) [262, 263]. The bending rigidity results measured on the TH-7 instrument are similar and comparable to that measured on the standard Kawabata (KES-FB2) system [260]. The output of this instrument is bending force (F_m) in millinewtons that can be used to calculate bending rigidity. The range of this instrument, to measure bending force, is from 40 to 4000 mN. The greater the bending force that is required to bend a fabric sample at a particular angle, the greater will be the bending rigidity, which ultimately results in higher stiffness of the fabric. The test was repeated five times for one replica of each fabric sample and the average value of bending force was calculated. At least, five replicas were tested for each fabric sample respectively. The average values of resultant bending forces for five replicas of each fabric sample were then considered as the final representative values of bending force. The stiffness/bending rigidity (B) of the homogeneous textile fabric sample was determined from the measured bending force and it is usually defined by Equation 8.

$$\mathrm{B}\,(\mathrm{N.m^2/m}) = 0.7 \times 10^{-6} \times \mathrm{F_m} \qquad (8)$$

where 'F_m' is the force applied to bend a fabric sample and 0.7×10^{-6} is the multiplying factor (multiplication constant) [260].

Tensile properties

The tensile properties such as the tensile strength of cotton fabric samples were measured by utilizing the tensile testing machine, according to the standard test method ISO 1924-2 [264]. The tensile strength is also called breaking strength, which is usually referred to as the maximum tensile force when a substrate sample such as textile fabric is stretched to break. The tensile strength is generally used to evaluate the ability of a fabric to resist external forces/tensile damage. At least, five replicas of each fabric sample were tested respectively, and the average of obtained values was considered as the final representative values.

Tear properties

The tear properties such as tear strength of cotton fabric samples were measured by utilizing the tear testing machine, according to the standard test method ASTM D1424 [265]. The tear strength is also called tearing resistance, which is usually referred to as the average force applied during a tearing process of a substrate sample such as textile fabric. The tear strength is generally used to evaluate the ability of a fabric to resist external forces/tearing damage. At least, five replicas of each fabric sample were tested respectively, and the average of obtained values was considered as the final representative values.

Washing durability

The untreated and casein treated (without and with after-/post-treatment finishing) cotton fabric samples were laundered in the Electrolux-wascator (a front-loading, horizontal rotating drum type standard reference washing machine), according to the standard test method ISO 6330 [266]. The ECE non-phosphate reference detergent was used and the washing temperature was 40°C. The washing was conducted for 15 wash/laundry cycles, each of which comprised standard washing and rinsing steps. In order to inspect the durability of casein films/layers/coatings to washing, all the untreated, treated, unwashed, and washed cotton fabric samples were then evaluated for flame retardant performance through the horizontal flame test, at zero wash cycle (i.e., before washing) and after 1, 5, 10 & 15 wash cycles (i.e., after washing). The different variables such as total burning time (s), burning rate (mm/s), and final char residue (%), for all the fabric samples of specified dimensions, were noted and compared. The test was repeated and at least five replicas were tested for each fabric sample respectively, and the average of noted values was considered as the final representative values.

Chapter 5

RESULTS AND DISCUSSION

5.1 Flame retardant performance and char formation properties of casein treated cotton fabrics

The casein uptake (add-on/weight gain) by the cotton fabrics (CF) was assessed after treatment with the casein solutions of different concentrations. The effect of different concentrations of casein solutions on the casein add-on of cotton fabrics is shown in Figure 5.1. The add-on was found to increase remarkably with an increase in casein concentration. It was also observed that the higher casein add-on was obtained beyond the 20% casein concentration. It was due to the increased viscosity of casein solutions usually at the higher concentrations [267] beyond 20% that results in the maximum wetting and binding of individual fibers and yarns, and ultimately retaining in the fabric structure after squeezing and drying. Furthermore, to scrutinize the flame retardant performance, the phosphorous content (P content) of casein treated cotton fabrics was also determined. When it was plotted, the phosphorous content values were found to increase with an increase in casein concentration, as shown in Figure 5.1.

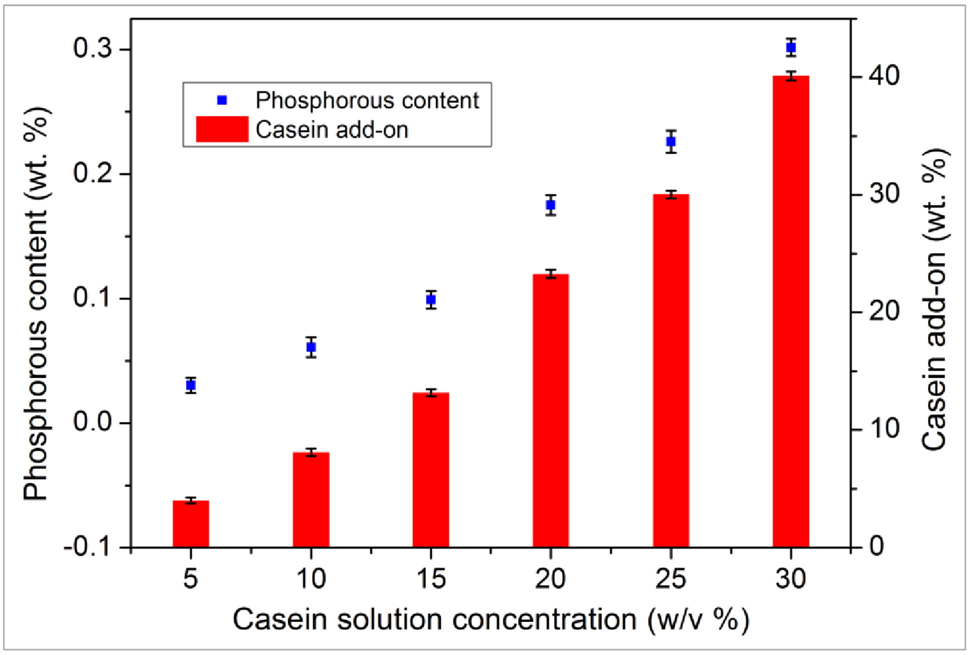


Figure 5.1. Add-on and phosphorous content of casein treated cotton fabrics

5.1.1 Surface chemical structure

The chemical/molecular structure, of cotton fabric samples, was assessed by the ATR-FTIR spectroscopy to conform to the effective presence of casein protein on the cotton fabrics. The ATR-FTIR spectra of untreated and casein treated cotton fabrics are given in Figure 5.2. In the case of untreated cotton fabric, the characteristic vibration modes of cellulose were detected, i.e., υ(OH) at ca. ~3300, υ(CH_2) at ~2900, δ(OH) at ~1640, δ(CH_2) at ~1425, δ(CH) at ~1370, δ(OH) at ~1310, υ(C–C) at ~1020, υ(OH) at ~894 cm^{-1}, etc. [268, 269]. On the other hand, the casein treated cotton fabrics showed the additional two peaks centered at 1647 and 1530 cm^{-1} for the respective vibrations of amide I and amide II groups [268, 270, 271]. As, the characteristic bands, in the infrared spectra for the polypeptides and proteins, include amide I (due to the stretching vibrations of C=O) and amide II (due to the bending vibrations of N–H) bands, resulting from the amide bonds that connect the amino acids. This confirmed the presence of protein coating on the surface of cotton fibers, due to the casein film/layer. The shifting of the aforementioned peaks/bands indicated the hydrogen bond interactions between the functional groups of cotton cellulose and casein protein. Moreover, an increase in the peak intensity/height depicted the deposition of a greater amount of casein on cotton fabrics treated with higher concentrations of casein, which was also evidenced by the spectra of these cotton fabrics showing the weak characteristic signals of cellulose.

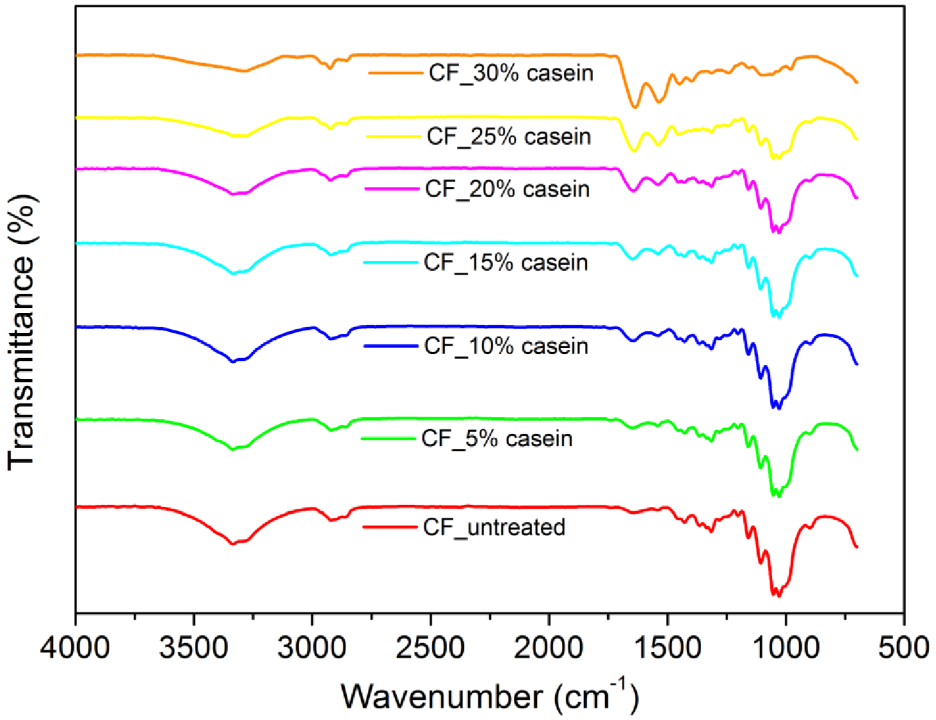
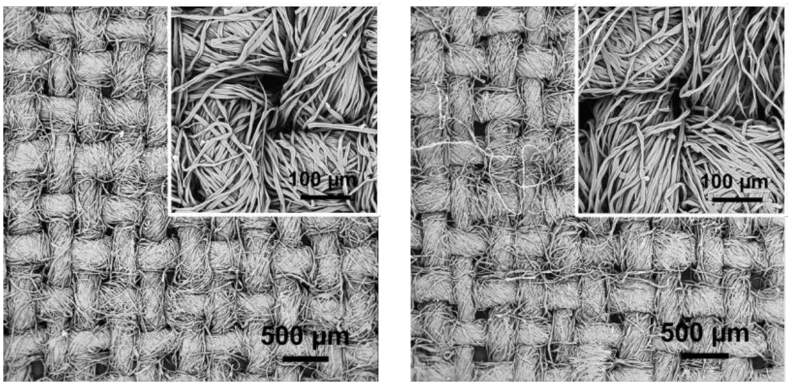


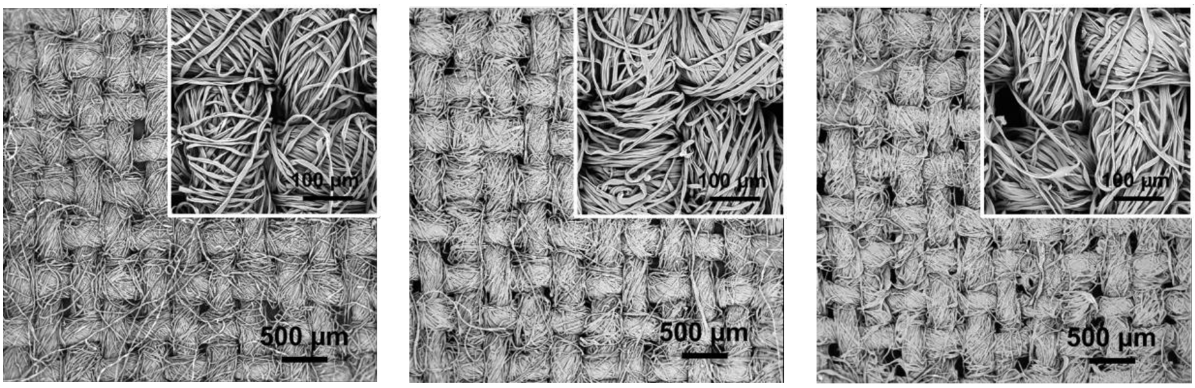
Figure 5.2. ATR-FTIR spectra of untreated and casein treated cotton fabrics

5.1.2 Surface morphology

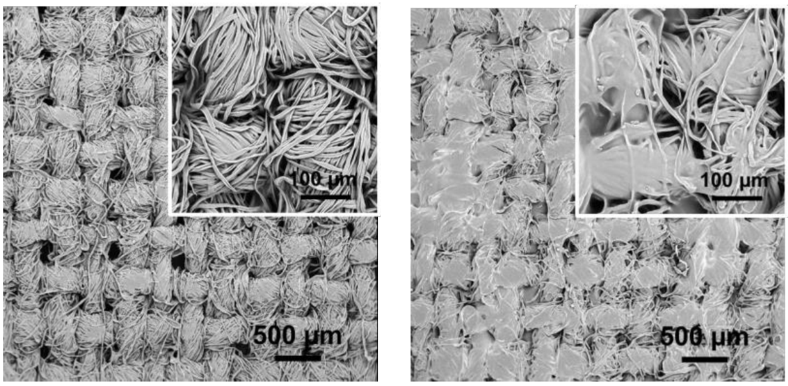
The scanning electron microscopy provided information concerning the morphology of casein treated cotton fabric samples. The typical SEM micrographs of untreated and casein treated cotton fabrics are shown in Figure 5.3. The treatment of cotton fabric samples; with the lower casein concentrations, exhibited distinct individual cotton fibers and yarns, whereas, with the higher casein concentrations, the individual cotton fibers and yarns were together grouped. A continuous, homogeneous, and coherent thin film/layer of casein can be observed on the cotton fibers below 20% casein concentrations. This uniform deposition of casein was found due to the maximum wetting and binding of individual cotton fibers.



(b) CF_5% casein (c) CF_10% casein



(a) CF_untreated (d) CF_15% casein (e) CF_20% casein



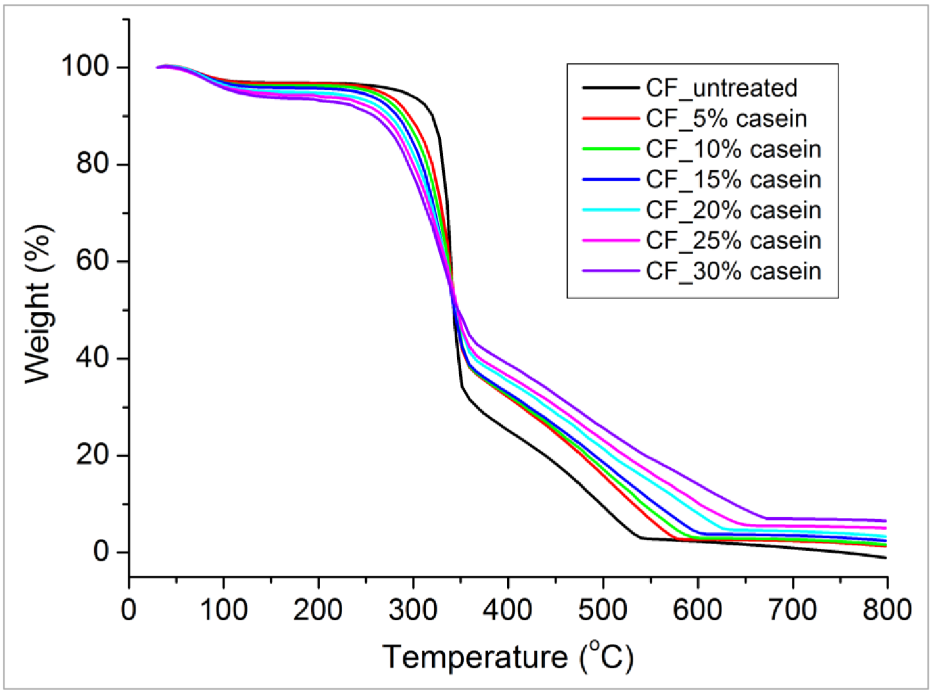
(f) CF_25% casein (g) CF_30% casein

Figure 5.3. SEM images of untreated and casein treated cotton fabrics

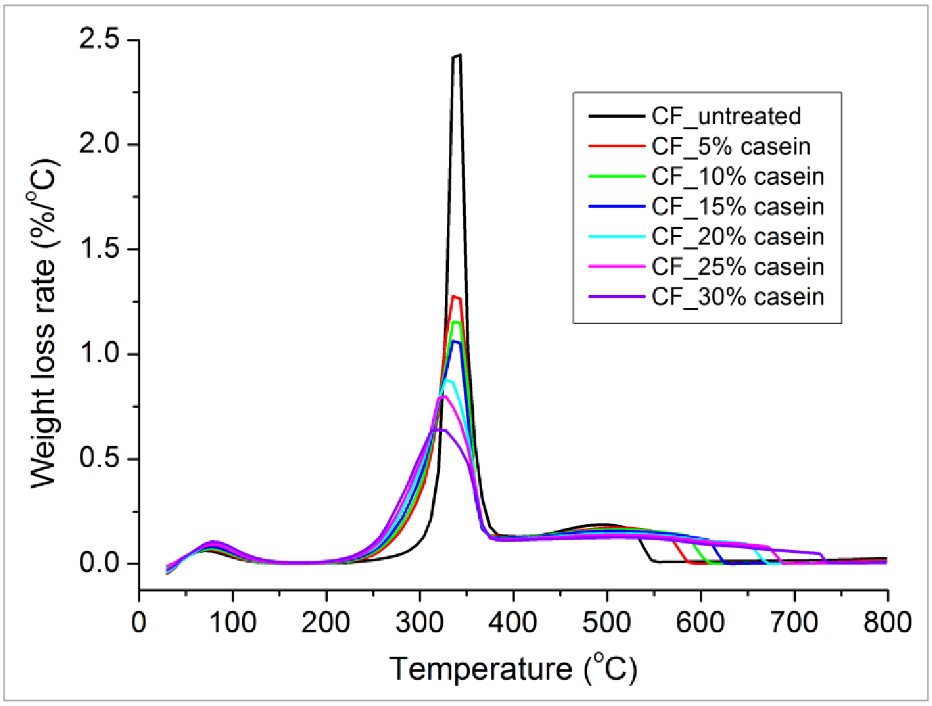
The absence of cracks indicated better compatibility between the casein and cotton fibers. In general, the proteins' hydrophilicity endorses their good compatibility with the polar surfaces [211], and hence, the formation of homogeneous films/layers can be attributed to the strong interactions via hydrogen bonds between the functional groups of cotton cellulose and casein protein. However, with a further increase in casein concentration beyond 20%, the film was also continuous, homogeneous, and coherent but it was thick, and therefore, the possible stiffening of fabric structure was observed due to the blocking of pores. This indicated a possible deterioration in the wearing comfort of cotton fabrics after the treatment of higher casein concentrations.

5.1.3 Thermo-oxidative stability

The thermo-oxidative stability, of untreated and casein treated cotton fabrics, was assessed by the thermogravimetric analysis. The TG and DTG curves of all fabric samples were plotted, as shown in Figure 5.4, which represents the weight loss and weight loss rate with an increase in the temperature. The detailed characteristics data obtained from the testing results were also summarized, as given in Table 5.1, which presents the values of different decomposition temperatures and residue percentages for untreated and casein treated cotton fabric samples.



(a) TG curves plot



(b) DTG curves plot

Figure 5.4. Thermo-oxidative stability of untreated and casein treated cotton fabrics

Insofar as the thermo-oxidative stability of cotton is cogitated, its degradation generally occurs in three main steps [69]. The first step, at 300-400°C, involves two competitive routes that produce aliphatic char and volatile products. During the second step, at 400-800°C, some aliphatic char transforms into an aromatic form generating carbon mono (CO) and carbon dioxide (CO_2), as a result of the simultaneous carbonization and char oxidation. In the last and final step, at 800°C, the char is further oxidized mainly to carbon mono- and di- oxide. In the present work, two decomposition peaks were observed between 300 and 500 °C, for the untreated cotton fabric, which was at 343°C (T_{max1}) and 492°C (T_{max2}). All fabric samples exhibited an initial mass loss in the ~50-150°C region that was attributable to the evaporation of free/residual water contained by the cotton and casein protein. Indeed, the pure proteins usually twitch to decompose at ~100°C to lose the water [217, 272], accompanying to generate the oligopeptides and amino acids that bear carboxylic groups and possess the ability to catalyze the decomposition of cellulose. The shift of $T_{onset10\%}$ values toward the lower temperatures indicated a stronger sensitization of the cotton cellulose decomposition after the treatment with casein macromolecules. Despite these findings, T_{max1} was also altered and observed to descent. But the residue percentage after the first degradation step at T_{max1} (at 300-400°C) was higher and attributed to the formation of a thermally stable product in the form of aliphatic char. With a further increase in the temperature at T_{max2} (at 400-800°C), aliphatic char was converted to a less volatile aromatic form, yielding carbon mono and dioxide. The percentage of residue at T_{max2} was found to increase with the increase in casein concentration. This behavior was ascribed to the dehydration of glycosyl units of the cotton cellulose due to the release of acidic species (like phosphoric acids) from the casein macromolecules [175, 217, 272].

Table 5.1. Thermo-oxidative stability data of untreated and casein treated cotton fabrics

				Residue at		
Sample	**$T_{onset10\%}$ (°C)**	**T_{max1} (°C)**	**T_{max2} (°C)**	**T_{max1} (wt. %)**	**T_{max2} (wt. %)**	**800°C (wt. %)**
CF_untreated	320.11±0.51	343.33±0.23	492.17±0.45	48.1±0.3	11.3±0.4	0.0±0.0
CF_5% casein	296.33±0.71	335.95±0.19	507.83±0.65	51.9±0.5	15.8±0.2	1.3±0.1
CF_10% casein	288.50±0.66	335.50±0.21	515.67±0.59	53.5±0.4	16.7±0.3	1.7±0.1
CF_15% casein	280.67±0.59	334.64±0.20	523.43±0.73	55.3±0.6	17.9±0.2	2.5±0.2
CF_20% casein	274.71±0.81	332.75±0.25	527.50±0.57	58.9±0.7	24.6±0.4	3.1±0.1
CF_25% casein	270.83±0.75	331.43±0.32	531.33±0.69	61.2±0.5	26.1±0.3	5.9±0.2
CF_30% casein	265.53±0.93	329.25±0.35	533.82±0.71	63.4±0.7	27.7±0.5	7.6±0.2

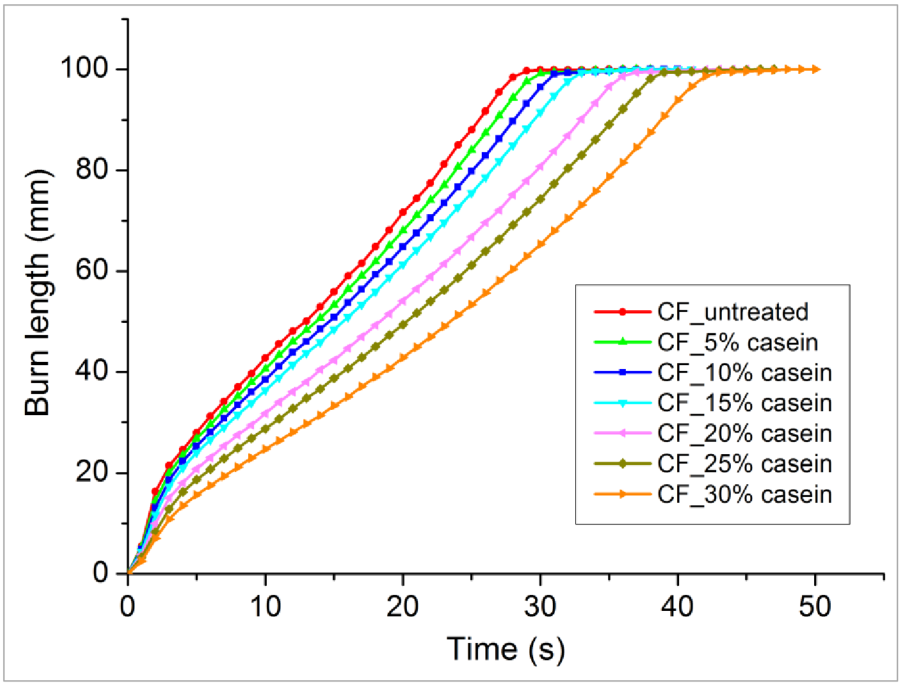
5.1.4 Flame retardancy

The flame retardant properties of untreated and casein treated cotton fabrics were measured through the flammability tests, in terms of the limiting oxygen index (LOI) and horizontal configuration flame spread/burning tests, relating an actual fire scenario to test the flammability of textile fabrics during the prevalence of flame spread. However, the LOI measurements have a good correlation to the char formation and the results of other practically applicable testing methods [273–275]. The LOI value of 18.3% was obtained for the untreated cotton fabric, as due to its cellulosic nature it catches the flame/fire very quickly and burns very easily in the open atmospheric air under normal ambient conditions. The LOI value of cotton fabric was far below the flame retardant standard LOI value of 26.0-28.0% [66]. Whereas, the LOI values of casein treated cotton fabrics were found to increase noticeably from 18.7% to 23.5%, with the increase in casein concentration, as given in Table 5.2. This was accredited to the enhanced char residue yields of treated fabric samples, as also revealed from the TGA results provided in Table 5.1, which acted as an effective thermal insulating barrier to hinder the transfer of heat and fuel and stop the combustion process. In general, an increased LOI value usually results in lower combustibility and better flame retardant properties of any polymeric materials including textile materials/substrates [66], [276], which was evinced from the horizontal flame test results such as; the total burning time, burn rate and char residue of untreated and casein treated cotton fabrics, as presented in Table 5.2. These observed different parameters were then used to estimate the resistance for flame propagation.

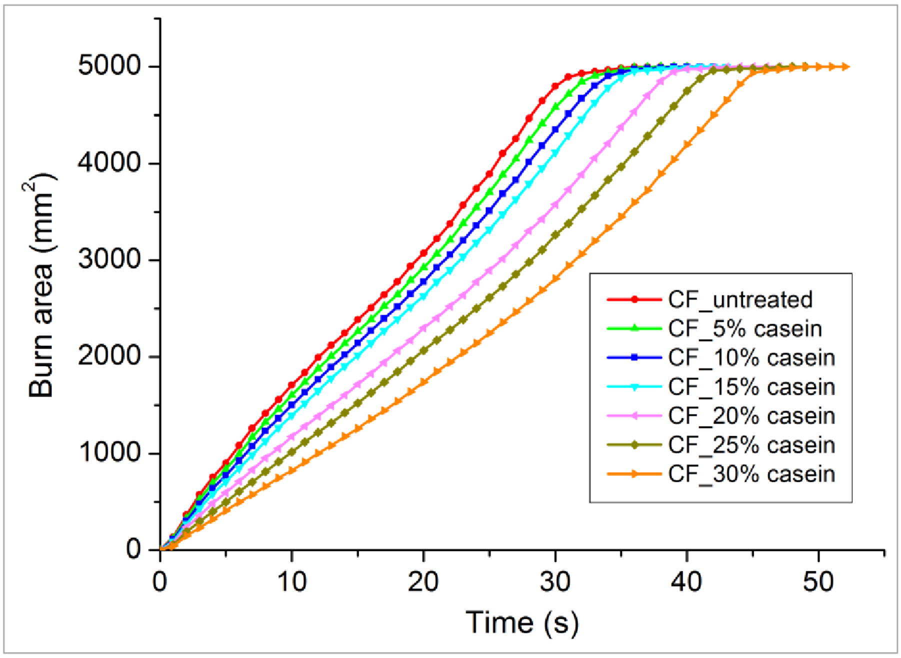
Table 5.2. Flammability characteristics of untreated and casein treated cotton fabrics

Sample	**LOI (vol. %)**	**Total burning time (s)**	**Burn rate (mm/s)**	**Char residue (wt. %)**
CF_untreated	18.28±0.22	36.21±0.25	3.63±0.04	3.1±1.1
CF_5% casein	18.86±0.25	37.95±0.36	3.39±0.03	12.4±1.5
CF_10% casein	19.52±0.31	39.43±0.41	3.21±0.05	23.2±1.8
CF_15% casein	20.18±0.29	40.81±0.33	3.05±0.06	31.5±2.1
CF_20% casein	21.48±0.27	44.53±0.39	2.78±0.04	37.4±1.7
CF_25% casein	22.20±0.30	45.97±0.45	2.57±0.06	43.9±2.2
CF_30% casein	23.52±0.28	48.42±0.51	2.34±0.07	53.1±1.9

The untreated cotton fabric was found to undergo vigorous and rapid combustion when a methane flame was applied for the specified time. It was completely burnt with an almost negligible amount of char residue left behind. Obviously, after ignition, the appeared vigorous flame on untreated cotton fabric was brighter all the time as compared to that on each casein treated cotton fabric sample, which conferred the fainter flames as well as the vanished afterglow phenomenon. On the contrary, the casein treatments promoted an increase in total burning time, thus exhibiting their ability for flame protection. The treated samples burnt at a slower rate and resulted in a stronger char residue while preserving the original texture of the fabrics. A substantial increase in total burning time (+34%) and a considerable reduction of burning rate (-36%), as well as a consistent final char residue (+53.1%), was found for the cotton fabric treated with 30% casein concentration. This flame retardant effectiveness of casein macromolecules was attributed to the phosphate groups located on the shell of casein micelles, which, upon heating, released phosphoric acid that favored the degradation of cellulose towards the formation of a stable char [175, 217, 272]. Furthermore, the produced char exerted a protective effect on the underlying cotton fabric, limiting the oxygen diffusion, avoiding the formation of combustible volatile products, and absorbing the heat evolved during the combustion.

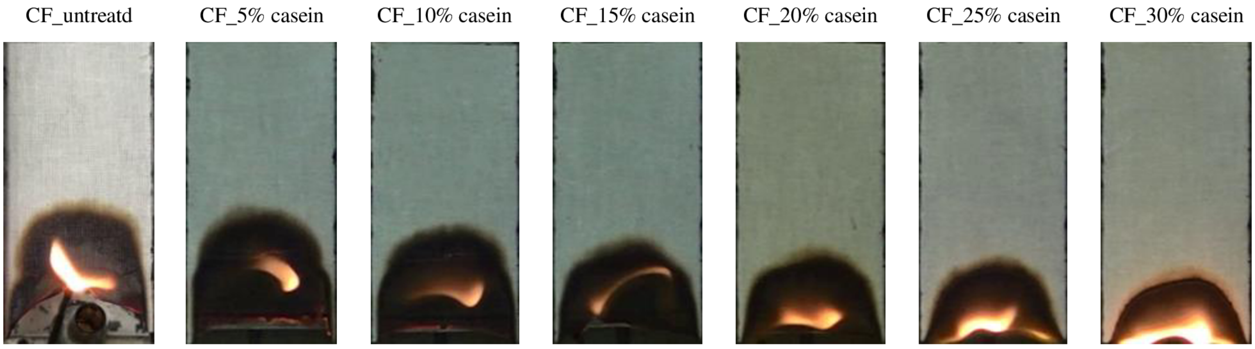


(a) Burn length

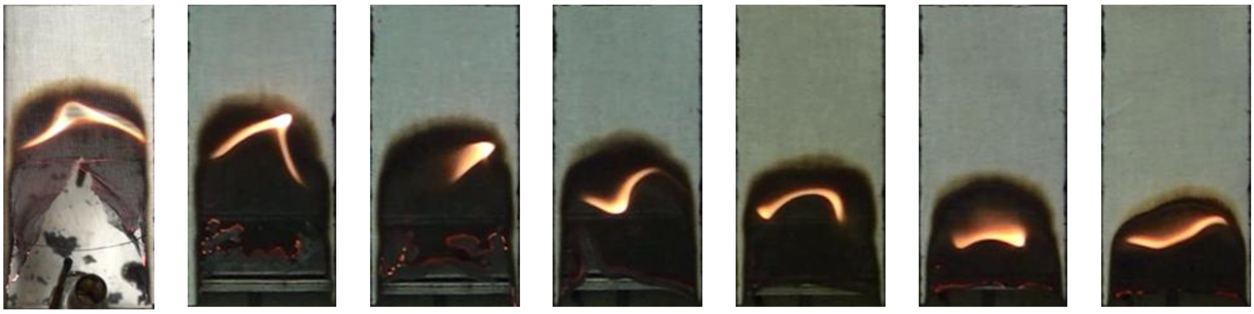


(b) Burn area

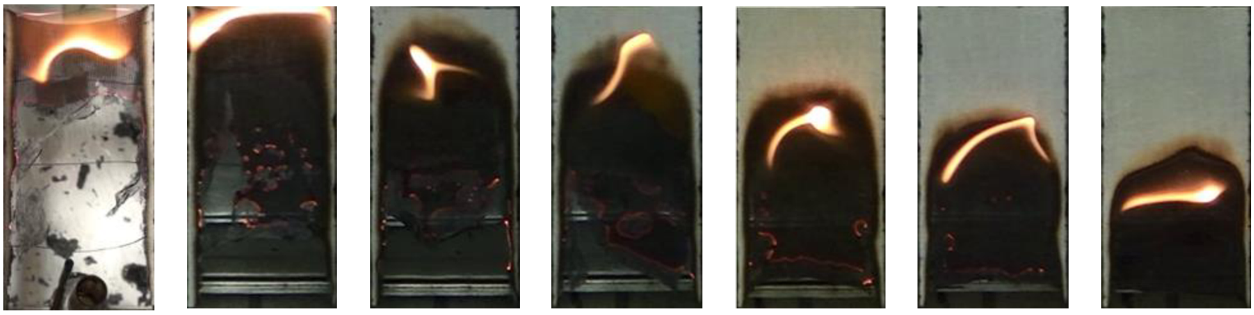
Figure 5.5. Plots for estimation of flame propagation with time from image analysis data



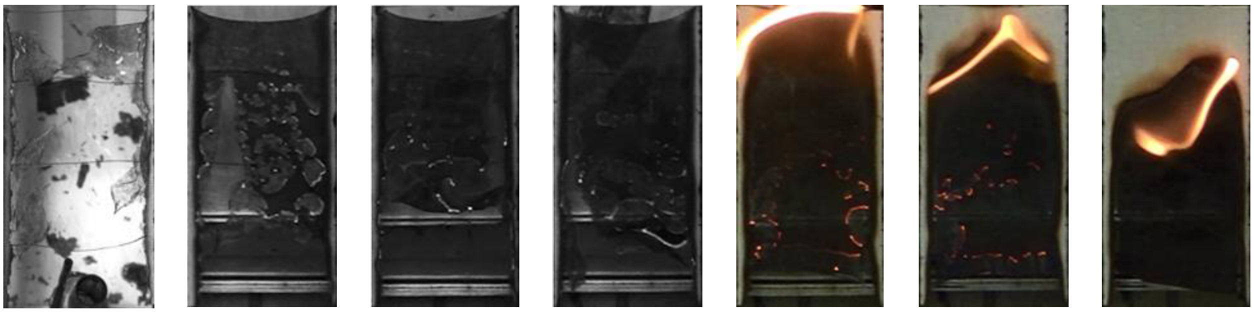
After 10 seconds time interval



After 20 seconds time interval



After 30 seconds time interval

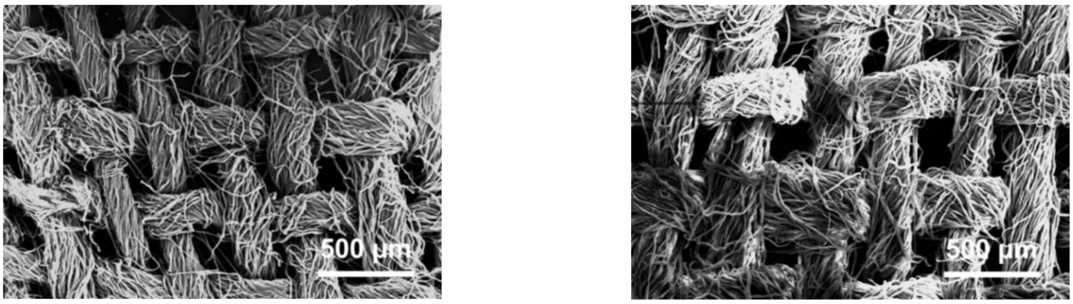


After 40 seconds time interval

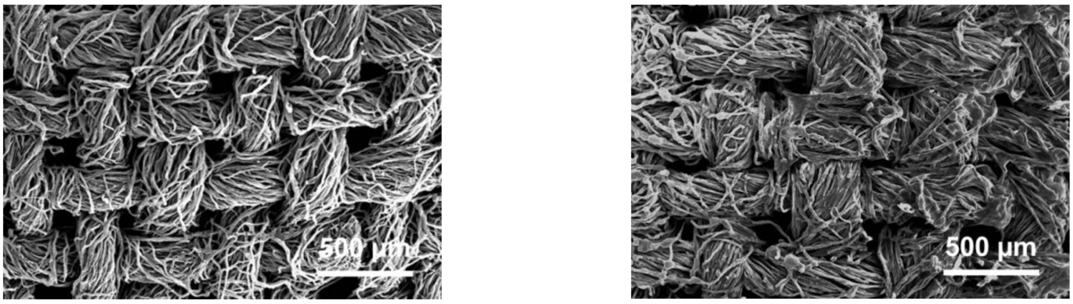
Figure 5.6. Photographs of burnt untreated and casein treated cotton fabrics at different time intervals during flame test

An additional method, for the flame resistance evaluation using image analysis, was employed to detect the small differences in flame propagation. Figure 5.5(a) and Figure 5.5(b) depict the burn length and burn area of untreated and casein treated cotton fabric samples with an increase of time interval in seconds. According to this analysis, the burn length and burn area plotted curves for the casein treated cotton fabric samples revealed a lesser steepness as compared to that for untreated cotton fabric. Furthermore, the steepness of curves was also observed to decrease with an increase in casein concentration. From these results, it was endorsed, a slow propagation/spread of the flame for the casein treated fabric samples and an improvement in self-extinguishing properties could be perceived for the cotton fabrics treated with higher casein concentrations. As the cotton fabrics treated with casein solutions of different concentrations exhibited lower burn length and lower burn area values as compared to that of untreated cotton fabric, this was further vindicated by the photographs of carbonized areas of all fabric samples as shown in Figure 5.6, which were taken after 10, 20, 30, and 40 seconds of the burning time. After the flammability test, scrutiny of the morphology of residues was also conducted through scanning electron microscopy. It revealed the preservation of the original texture of all the burnt casein treated cotton fabric samples in the form of stable and consistent char, which was verified from the SEM images, as shown in Figure 5.7. A very high amount of mechanically strong and extremely coherent char was observed for the burnt samples of cotton fabric treated with higher casein concentrations. The morphology of char residues of fabrics treated with higher casein concentrations indicated the formation of globular micrometric structures of phosphorus-rich bubbles that blow up during combustion [175]. The presence of bubbles in the residues was ascribed to the evolution of ammonia, released by the casein macromolecules upon heating [217, 272, 277].

(a) CF_5% casein (b) CF_10% casein



(c) CF_15% casein (d) CF_20% casein



(e) CF_25% casein (f) CF_30% casein

Figure 5.7. SEM magnifications of char residues of burnt casein treated cotton fabrics

5.1.5 Radiant heat resistance

The thermal resistance behavior, of untreated and casein treated cotton fabrics, as protection against radiant heat, was evaluated by exposing the cotton fabric samples to a radiant heat source at the specified incident heat flux density (Q_o). The rise of temperature was measured at the back of fabric samples by a calorimeter, which subsequently resulted in; two threshold times (namely radiant heat transfer indexes), i.e., time for the rise of 12°C ($RHTI_{12}$) and time for the rise of 24°C ($RHTI_{24}$), transmitted heat flux density (Q_c) and heat transmission factor (TFQ_o), as listed in Table 5.3. The lower values of Q_c were noticed for casein treated cotton fabric samples as compared to that of untreated cotton fabric. Consequently, an analogous pattern was observed in TFQ_o values, dropping from 57.8% to 42.3% for the treated cotton fabric samples with different casein concentrations. The reduction in Q_c and TFQ_o was due to an increase in the values of $RHTI_{12}$ and $RHTI_{24}$ indexes and their difference ($RHTI_{24}$ - $RHTI_{12}$).

Table 5.3. Radiant heat resistance parameters of untreated and casein treated cotton fabrics

Sample	Q_0 (kW/m^2)	$RHTI_{12}$ (s)	$RHTI_{24}$ (s)	$RHTI_{24}$-$RHTI_{12}$ (s)	Q_c (kW/m^2)	TFQ_0 (%)
CF_untreated	40	3.8±0.04	6.7±0.05	2.9±0.04	23.10±0.37	57.76±0.92
CF_5% casein	40	3.9±0.08	6.9±0.08	3.0±0.07	22.19±0.52	55.46±1.31
CF_10% casein	40	4.1±0.07	7.2±0.08	3.1±0.04	21.33±0.30	53.32±0.75
CF_15% casein	40	4.2±0.07	7.4±0.09	3.2±0.05	20.54±0.35	51.35±0.86
CF_20% casein	40	4.5±0.09	7.9±0.11	3.4±0.08	19.46±0.48	48.66±1.20
CF_25% casein	40	4.7±0.08	8.3±0.08	3.6±0.07	18.49±0.36	46.21±0.91
CF_30% casein	40	5.1±0.10	9.0±0.11	3.9±0.09	16.89±0.39	42.23±0.98

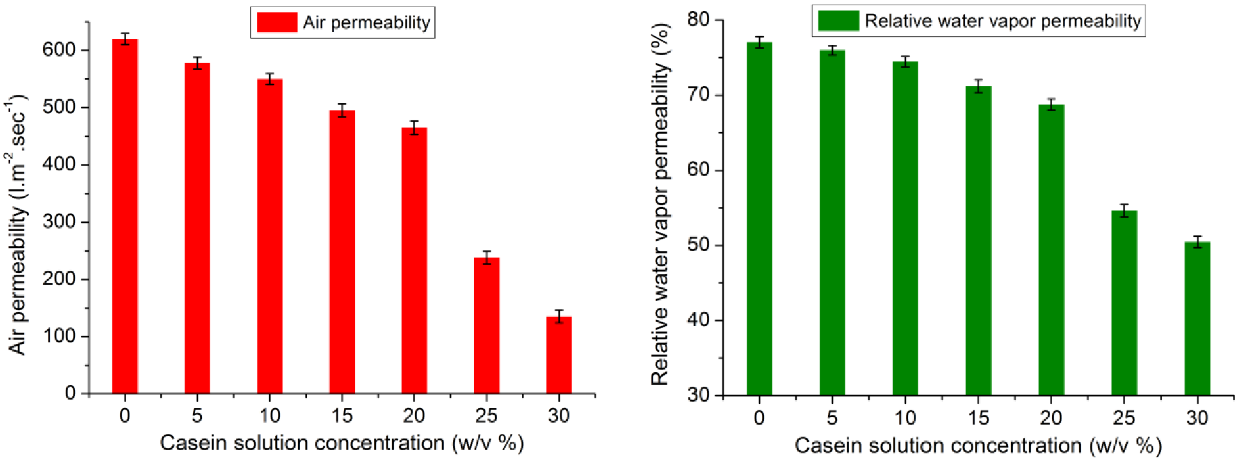
The higher values of radiant heat transmission indexes and their differences**,** for the casein treated cotton fabrics, as compared to the untreated cotton fabric, demonstrated that the temperature rise with respect to occurred at a lower rate, indicating the dilatory exchange of radiant heat towards calorimeter, i.e., the slower transmission of radiant heat. The increased values of $RHTI_{12}$, $RHTI_{24,}$ and ($RHTI_{24}$ - $RHTI_{12}$) indexes were owed to the thicker casein layer/films due to the higher casein add-on as an increase in casein concentration [278–280], blocking of the spaces/interstices between the cotton fibers and yarns as corroborated from the SEM micrographs (see Figure 5.3). The time differences ($RHTI_{24}$ - $RHTI_{12}$) provided a good indicator of the skin pain alarm time [281–283], as the investigation of thermal resistance performance of single-layer woven fabrics is highly relevant in order to procure and further develop the thermal protective multi-layer clothing and their overall thermal protective performance [284–289]. These larger values of ($RHTI_{24}$ - $RHTI_{12}$) for the casein treated fabric samples were endorsed for the reason that the infrared radiations which performed a pertinent part in the heat transference were also absorbed by the casein layers/films. Due to this casein layers/films provided improved thermal resistance and insulation. That might be helpful to prevent the wearer from acquiring burn injuries. Simultaneously, a reduction in the value of transmitted heat flux density, i.e., the lower quantity of transmitted radiant heat, is also considered beneficial for the textile substrate, resulting in its later on slower burning, as also validated from the flammability test results of casein treated cotton fabrics (see Table 5.2). More accurately, it was inferred that the resistance of casein layers/films to a radiant heat flux could also dramatically reduce the time to ignition of casein treated fabrics as compared to the untreated cotton fabric. This was accredited to the degradation/decomposition of casein to release phosphoric acid exerting a deleterious effect that sensitizes the early ignition of cotton fabric and favors the cellulose dehydration to produce more thermally stable char residues instead of volatile release [175].

5.1.6 Physiological comfort and mechanical properties

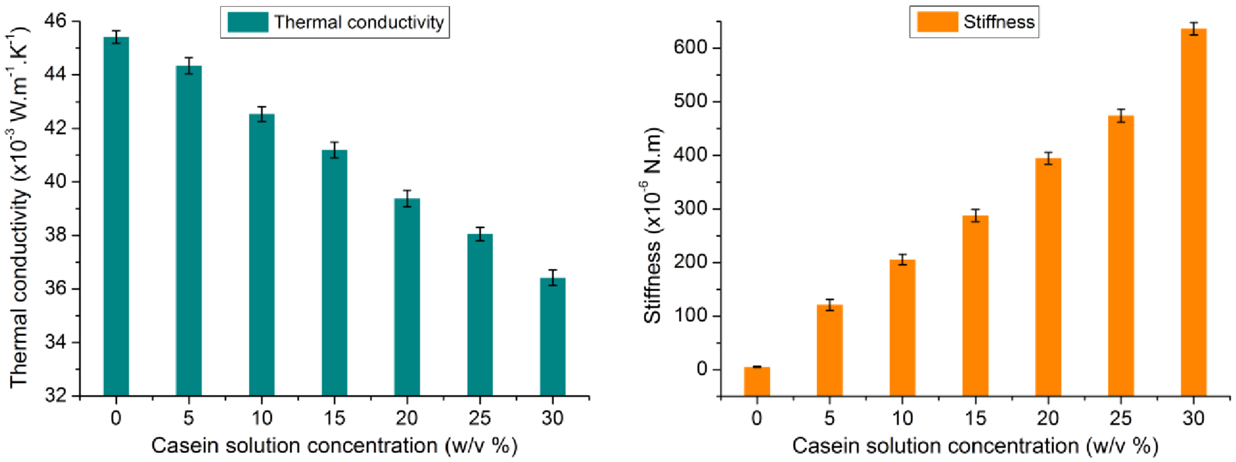
The air permeability, water vapor permeability, thermal conductivity, stiffness/bending rigidity, and tensile and tear testing, of untreated and casein treated cotton fabrics, were carried out to investigate properties connected with physiological comfort and mechanical performance, as discussed in the following sections.

Air Permeability

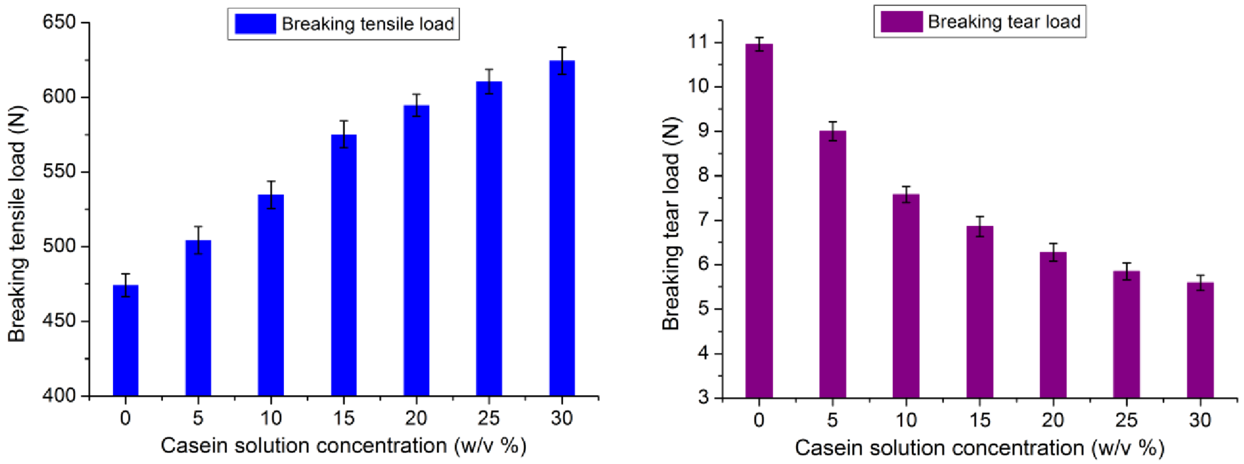
Despite their chemical compositions, all textile fibers are impermeable to air, and therefore, the air can only pass through a textile fabric via spaces/interstices between the fibers and yarns [290, 291]. Air permeability is interrelated to and/or affected by the characteristic structure and the ratio of empty spaces/voids (pores) in fabrics through which the air permeation eventuates. The fabrics with higher air permeability values mean that more amount of air can flow through them [292, 293]. Figure 5.8(a) shows the effect of casein treatments, from the solutions of different concentrations, on the air permeability of cotton fabrics. The air permeability of untreated cotton fabric was determined ~620.05 $l.m^{-2}.s^{-1}$. However, it can be seen that there is no considerable drop in the air permeability of casein treated cotton fabrics with an increase in casein concentration up to 20%. This behavior was explained by the formation of thin casein films on the surface of cotton fabric samples, which partially covered the interspaces between the fibers and yarns. Whereas, with a further increase in casein concentration beyond 20%, the air permeability of casein treated cotton fabrics was significantly dropped. The reduced airflow through these fabrics was attributed to, the closing and/or lessening of the size of inter-fiber and inter-yarn spaces/pores by the treatments of higher casein concentrations [174, 211].



(a) Air permeability (b) Water vapor permeability



(c) Thermal conductivity (d) Stiffness



(e) Tensile strength (f) Tear strength

Figure 5.8. Comfort and mechanical properties of untreated and casein treated fabrics

Water Vapor Permeability

Two processes are involved, when the water vapors pass through a layer of textile substrate, namely, diffusion and sorption-desorption. The diffusion rate through a textile material, at a specific concentration gradient, depends on the porosity of the textile material and also on the water vapor diffusivity of the textile fiber. It is not crucial how much water is absorbed by the fibers, but rather, how much water vapor the fibers can transport. In other words, it means, when the human body has stopped exuding sweat, the textile fabrics should release the detained water vapors to the external atmosphere, in order to lessen the humidity/moisture on the surface of the skin [290, 291]. Figure 5.8(b) shows the effect of casein treatments, from the solutions of different concentrations, on the relative water vapor permeability of cotton fabrics. The relative water vapor permeability of untreated cotton fabric was determined ~77.04 %. Likewise, the air permeability, a similar trend of casein treatments, was also observed for the water vapor permeability [174, 211]. The moisture vapor transport properties of treated cotton fabrics were less affected below 20% casein concentrations. The loss of moisture vapor transport, for the cotton fabrics treated with solutions of casein concentration beyond 20%, was recognized due to; the higher deposited amount of casein increasing the weight and thickness, and ultimately closing or decreasing the size of inter-fiber and intra-yarn spaces/pores [294–296].

Thermal Conductivity

Thermal conductivity is an intensive property, of any polymeric material including textile substrates, which represents the heat transfer process by a conduction mechanism. The thermal conductivity of untreated cotton fabric was determined ~$45.42\text{x}10^{-3}$ $\text{W.m}^{-1}.\text{K}^{-1}$. Figure 5.8(c) shows a reduction in the thermal conductivity of casein treated cotton fabrics with an increase in casein concentration. This behavior was explained by the deposition of the higher amount and/or the thick layers/films of casein on the surface of treated cotton fabric samples with an increase in the casein concentrations [297], eventually partially/fully covering the inter-spaces between the fibers and yarns. As the films produced from the casein protein usually have a rough structure and present several very small-sized pores inside their structure. The rough structure probably emanates from the substantial self-aggregation of the polar, nonpolar, and peptide chains during the drying process [298]. Perhaps, in addition to the effect of the amount/thickness of casein films, a reduction in the thermal conductivity, of casein treated cotton fabrics with higher casein concentration, might be due to the supplemental contribution and/or the effect of the entrapped air inside the inherent pores of the film structure of casein.

Stiffness

The deformation/bending properties describe the stiffness and/or flexibility of fabrics. It is a special property of fabrics, for the desirable handling, draping, and wrinkling behavior, which further can influence the physical comfort of clothing. The fabric stiffness may not be desired too high; for a considerate drape and handle in apparel, clothing, and garment fabrics, though, it may be a significant requirement, particularly for industrial fabrics. Figure 5.8(d) shows the effect of casein concentrations on the bending properties of cotton fabrics. The stiffness value of untreated cotton fabric was determined ~$5.17\text{x}10^{-6}$ N.m. It was observed that the stiffness of casein treated cotton fabric samples increased noticeably with an increase in the concentration of casein solutions. This could be associated with the deposition of casein over the cotton fabric structure that formed the bridges between the fibers and/or yarns due to its gluing and binding properties [299, 300], increasing the inter-fiber/yarn friction at the fibers/yarns cross-over points (i.e., inhibiting the free movement of fibers/yarns) and making the fabric difficult to bend [292, 301]. The lower stiffness values at the lower concentration of casein below 20% indicated the lesser detrimental effect on the draping behavior of treated cotton fabrics and a satisfactory physical comfort behavior.

Tensile Properties

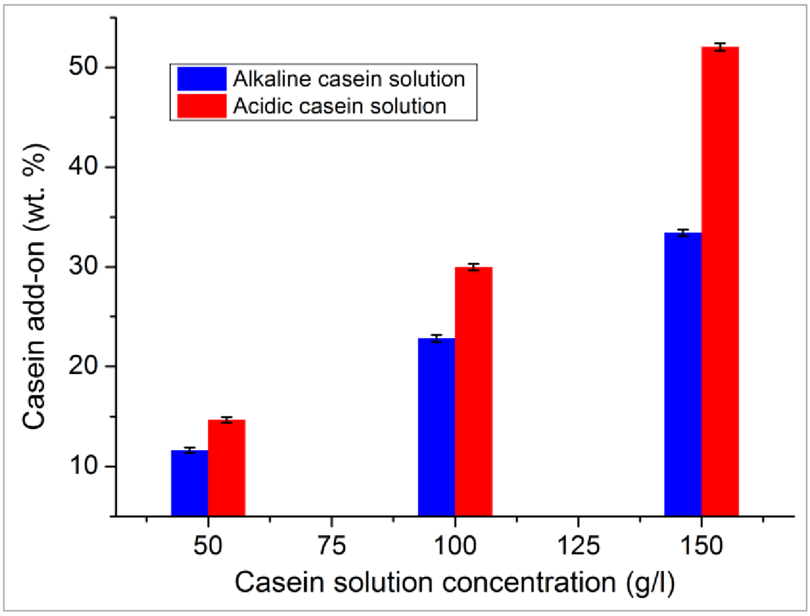
The tensile strength is a measure of the ability of a textile fabric, to resist breaking under tension (tensile stress), which is dependent on the length and the strength of fibers, their surface area, and also the bonding strength between them. Figure 5.8(e) shows the results of tensile testing and the effect of casein concentrations on the tensile breaking force (tensile breaking load/stress in newton) of cotton fabrics. The value of the breaking tensile load for the untreated cotton fabric was determined ~474.18 N. While, it was observed that the breaking tensile load for the treated cotton fabrics increased with an increase in the concentration of casein solutions [174, 211], [294–296]. The increased breaking force can be explained by a contribution of the load-bearing capacity of attached casein layers/films on the surfaces of fibers and yarns in the fabric structure. This can also be ascribed due to the reason that the casein solution pierces into the fabric structure during its application on the cotton fabrics through the padding method. Then it fills the spaces between the fibers and yarns and binds them together, which results in; an increase in the bending rigidity and ultimately the tensile breaking load of treated fabrics [302, 303].

Tear Properties

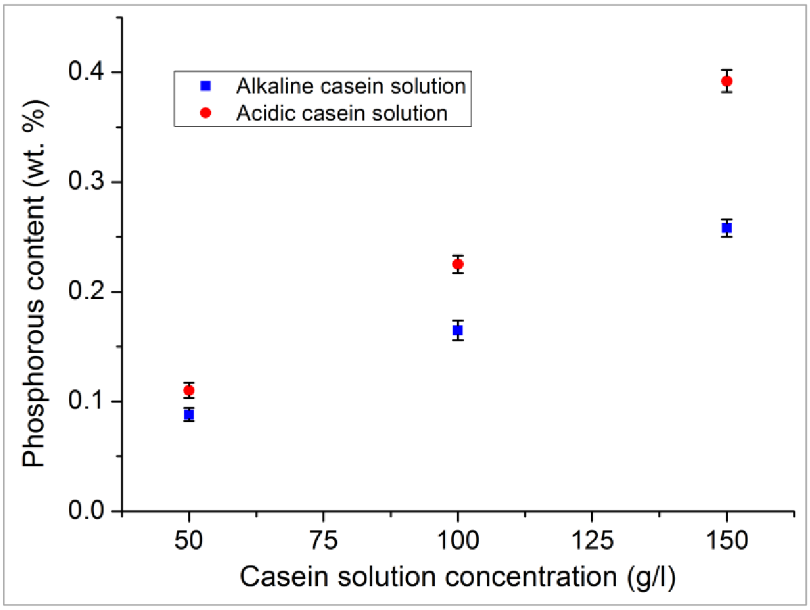
The tearing strength (tearing resistance) of a textile fabric corresponds to the average force applied during a tearing process, as a measure of the resistance offered by the fabric against tearing, which is likely that it relates to the fracture resistance and/or the fracture stress or the toughness of a material. Figure 5.8(f) shows the results of tear testing and the effect of casein concentrations on the tear breaking force/tearing force (tear breaking load/stress in newton) of cotton fabrics. The value of the breaking tear load for the untreated cotton fabric was determined ~10.96 N. Unlike the tensile testing results, it was observed that the tearing force for the treated cotton fabrics decreased with an increase in the concentration of casein solutions [174, 211], [294–296]. The reduced tearing force can be explained by an increase in cotton fabric rigidity after casein treatments, offering less resistance to an applied force for rupture/tearing. This can also be ascribed due to the reason that the casein solution penetrates the voids between the fibers and yarns, during its application on the cotton fabrics through the padding method. After drying the casein remains in the fabric structure and interferes with fiber-to-fiber and yarn-to-yarn interactions by binding them, which results in; a reduction of their free movement and sliding, as well as, the flexibility of fabric structure [303–306]. When the yarns are bonded together at a place in the fabric structure, the tearing force applied on individual yarns one at a time, results in a lower tearing force value.

5.2 Flame retardant behavior and inherent intumescent phenomenon of alkaline and acidic casein solutions coated cotton fabrics

The effect on the casein add-on (weight gain) of cotton fabric (CF) samples, coated with casein solutions of different concentrations (i.e., prepared under both alkaline and acidic pH conditions), is shown in Figure 5.9(a).



(a) Casein add-on



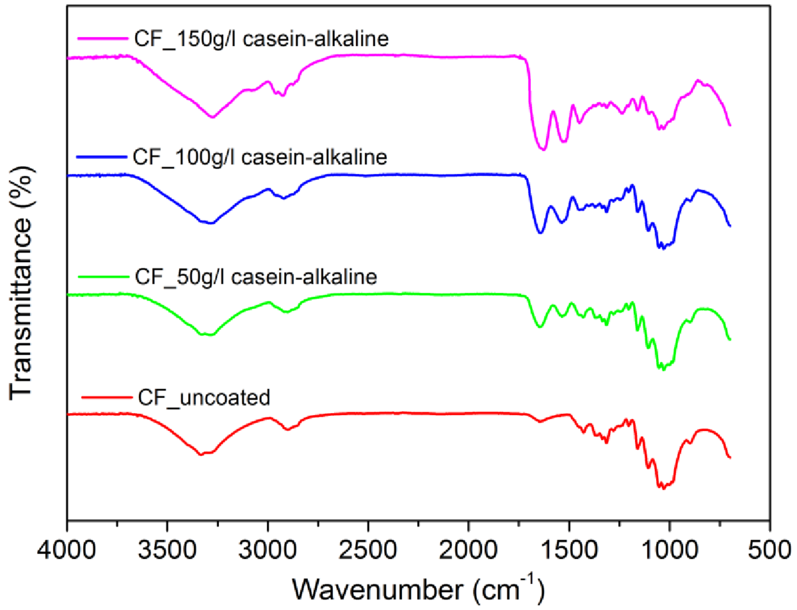
(b) Phosphorous content

Figure 5.9. Add-on and phosphorous content of casein coated cotton fabrics

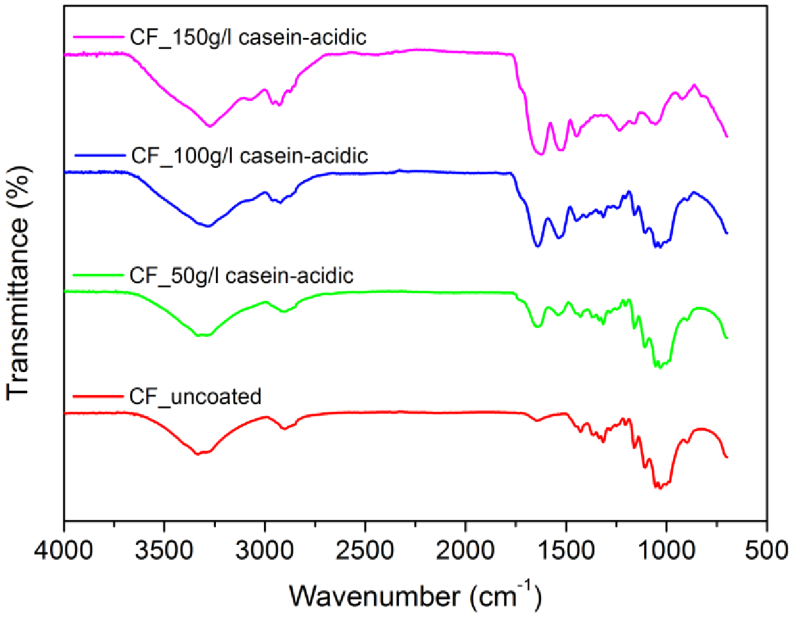
The add-on was found to increase with an increase in casein concentration due to the maximum wetting and binding of individual fibers and yarns, and eventually seizing inside as well as depositing on the fabric structure after coating and drying. Further, the solution of casein prepared under an acidic pH delivered a higher add-on of casein than that of the solution prepared under an alkaline pH [267], which was explained by the observed higher viscosity of casein solutions prepared under the acidic pH conditions. Additionally, to examine the flame retardant behavior, the phosphorous content (P content) of casein coated cotton fabrics was also evaluated. When plotted, the phosphorous content values were found to increase with an increase in casein concentration, as shown in Figure 5.9(b).

5.2.1 Surface chemical structure

The chemical/molecular structure, of cotton fabric samples, was appraised by ATR-FTIR spectroscopy to conform to the effectual existence of casein protein coatings on the cotton fabrics. Figure 5.10(a), (b) shows the ATR-FTIR spectra of uncoated cotton fabric and cotton fabric samples coated with both alkaline and acidic pH casein solutions respectively. For uncoated cotton fabric, typical vibration modes of cellulose were identified, such as; υ(OH) at ca. ~3300, υ(CH_2) at ~2900, δ(OH) at ~1640, δ(CH_2) at ~1425, δ(CH) at ~1370, δ(OH) at ~1310, υ(C–C) at ~1020, υ(OH) at ~894 cm^{-1}, etc. [268, 269]. As, the characteristic bands, in infrared spectra for proteins and polypeptides, include amide I (due to the stretching vibrations of C=O) and amide II (due to the bending vibrations of N–H) bands, resulting from the amide bonds that connect amino acids. Therefore, the two other peaks, located at 1624 and 1528 cm^{-1}, were substantially attributed to the respective vibrations of the amide I and amide II groups of casein. The same peaks were also credited to the presence of end amino acids; the respective asymmetric and symmetric vibrations of $-NH_3^+$ groups [268, 270, 271].



(a) ATR-FTIR spectra of alkaline casein coatings



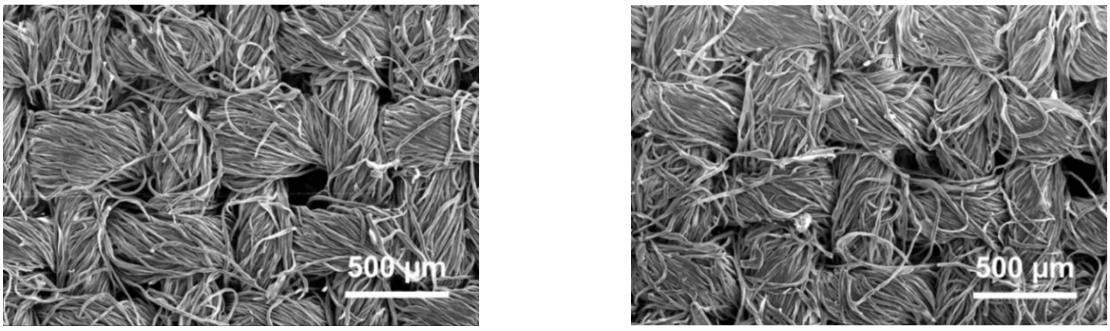
(b) ATR-FTIR spectra of acidic casein coatings

Figure 5.10. ATR-FTIR spectra of uncoated and casein coated cotton fabrics

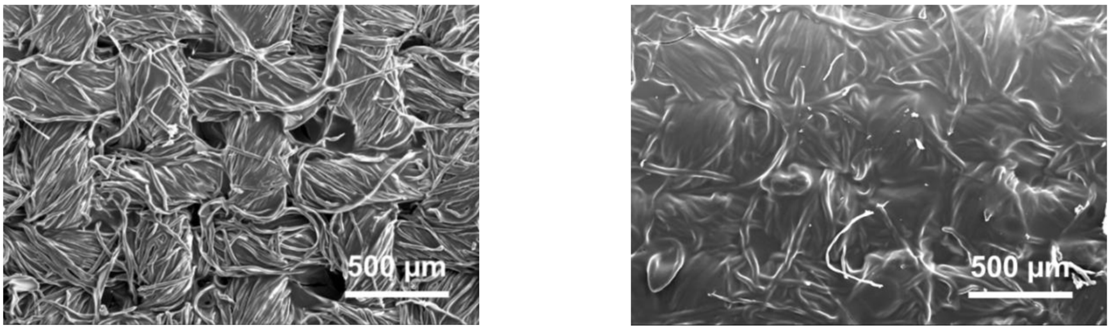
Furthermore, the cotton fabrics coated with the acidic casein solutions exhibited one another band at 1710 cm^{-1}, which was manifestly endorsed for the protonation of casein protein macromolecules that were dissolved in water under acidic pH conditions [307, 308]. Moreover, the deposition of a greater amount of casein on fabric samples for the acidic casein solutions was confirmed based on their higher peak intensities, and that was also supported by the spectra of these fabrics showing the weak characteristic signals of cellulose.

5.2.2 Surface morphology

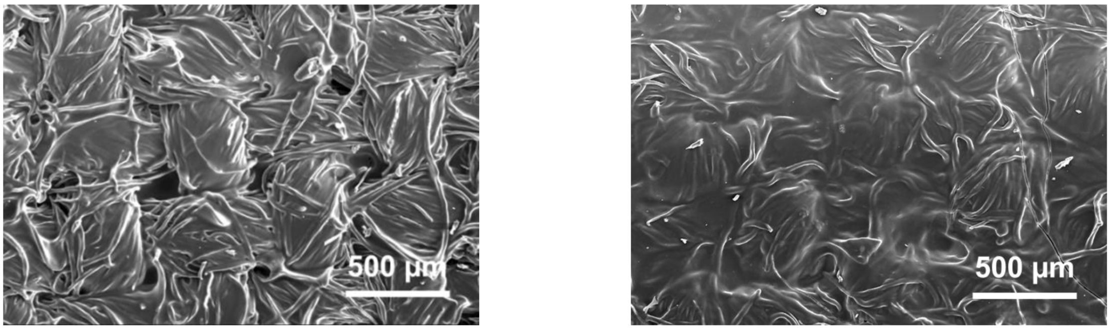
The scanning electron microscopy rendered information relating to the morphology of casein coated cotton fabric samples. Figure 5.11(a) to (f) shows the characteristic SEM micrographs of cotton fabrics coated with both alkaline and acidic casein solutions of different concentrations. The uniform deposition of casein was observed on the coated cotton fabrics and the absence of cracks indicated the better compatibility between the casein protein and cotton cellulose fibers for both solutions. The coating of a low concentration of alkaline casein solution exhibited distinct individual cotton fibers than the coating of acidic casein solution (see Figure 5.11(a), (b)). However, the grouping of individual cotton fibers increased with an increase in casein concentration (see Figure 5.11(c) to (f)). Moreover, both casein solutions were found to produce continuous, homogeneous, and coherent coatings. But, the greater deposited amounts and/or thickness of casein coatings were obtained in the case of acidic casein solutions, due to their higher viscosity than the alkaline casein solutions [309]. This indicated higher chances of possible deterioration in the wearing comfort of cotton fabrics after coating with an acidic casein solution than an alkaline casein solution.



(a) CF_50g/l casein-alkaline (b) CF_50g/l casein-acidic



(c) CF_100g/l casein-alkaline (d) CF_100g/l casein-acidic

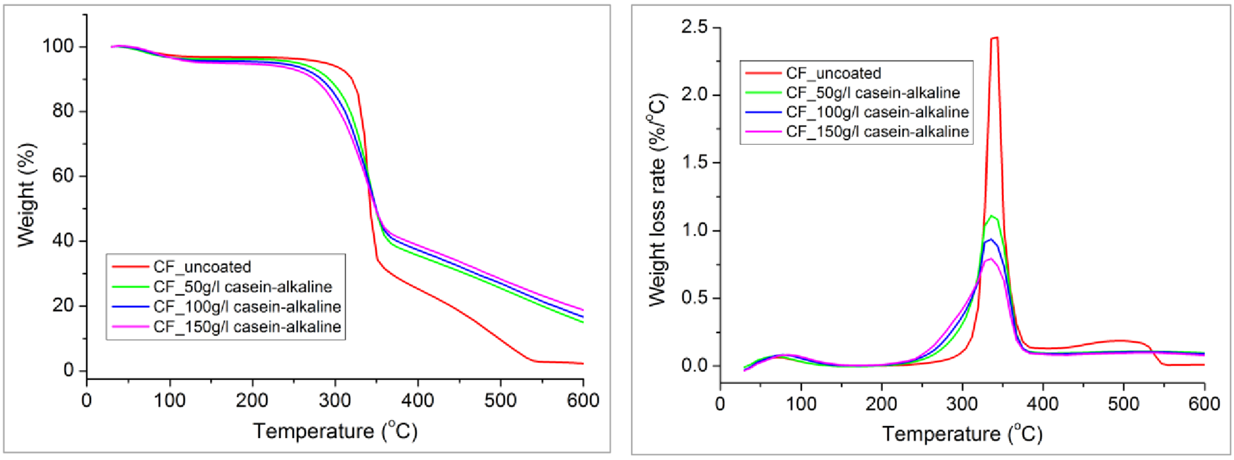


(e) CF_150g/l casein-alkaline (f) CF_150g/l casein-acidic

Figure 5.11. SEM images of casein coated cotton fabrics

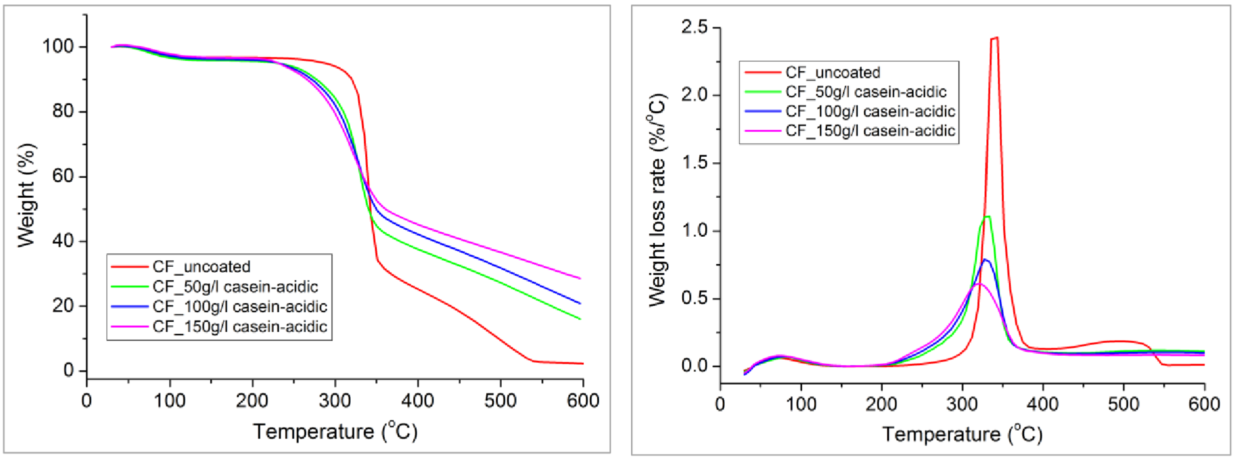
5.2.3 Thermo-oxidative stability

The effect of alkaline and acidic casein solutions' coatings on the thermo-oxidative stability of cotton fabrics was analyzed through thermogravimetric analysis. The plots of TG and DTG curves of all fabric samples were drawn, as shown in Figure 5.12, which represents the weight loss and weight loss rate with an increase in the temperature. The widespread characteristics data achieved from the testing results were also abridged, as given in Table 5.4, which presents the values of different decomposition temperatures and residue percentages of uncoated and casein coated cotton fabric samples. As far as, the thermo-oxidative stability of cotton is contemplated, its degradation generally occurs in three main steps [69]. The first step, at 300-400°C, involves two competitive routes that produce aliphatic char and volatile products. During the second step, at 400-800°C, some aliphatic char transforms into an aromatic form generating carbon mono (CO) and carbon dioxide (CO_2), as a result of the simultaneous carbonization and char oxidation. In the last and final step, at 800°C, the char is further oxidized mainly to carbon mono- and di-oxide. In the present work, two decomposition peaks were observed between 300 and 500 °C for the uncoated cotton fabric at 343°C (T_{max1}) and 492°C (T_{max2}). The reduced decomposition temperatures in the first step were confirmed from $T_{onset10\%}$ and T_{max1} values, which were discerned to shift to much lower temperature in the case of cotton fabric samples coated with acidic casein solutions than those with alkaline casein solutions. The shifting of $T_{onset10\%}$ to lower values indicated stronger sensitization of the cellulose decomposition after coating with casein macromolecule solutions prepared under different pH conditions.



(a) TG curves plot
(coatings of alkaline casein solutions)

(b) DTG curves plot
(coatings of alkaline casein solutions)



(c) TG curves plot
(coatings of acidic casein solutions)

(d) DTG curves plot
(coatings of acidic casein solutions)

Figure 5.12. Thermo-oxidative stability of uncoated and casein coated cotton fabrics

The residue percentage after the first degradation step at T_{max1} (at 300-400°C) was observed to increase. It was attributed to the formation of a thermally stable product in the form of aliphatic char that subsequently delayed the second degradation step of fabrics coated with the higher casein concentrations, as evidenced by an increase in T_{max2} values. With a further increase in temperature at T_{max2} (at 400-600°C), aliphatic char was converted to a less volatile aromatic form, yielding carbon mono and dioxide. The residue percentage at T_{max2} was also found to increase with an increase in the casein concentrations. Furthermore, the fabric samples coated with acidic casein solutions produced a higher amount of residues, at T_{max2} and 600°C, than those with alkaline casein solutions. This behavior was regarded to the higher casein add-on percentages obtained for the fabric samples coated with acidic casein solutions. However, the higher casein add-on percentage was ultimately the main cause of the growth of a higher phosphorous content (P content) on the fabric samples, as ascertained from Figure 5.9. Due to the higher deposited P content, a greater amount of acidic species such as phosphoric acid was released from casein macromolecules. That functioned the dehydration of more number of glycosyl units of cellulose, instead of depolymerization [175, 217, 272], leading to the formation of higher residues at higher temperatures. Therefore due to these reasons, it was differentiated manifestly that cotton fabrics coated with both alkaline and acidic 150 g/l casein solutions produced 19.2% and 27.6% residue respectively at 600°C as compared to 2.3% of uncoated cotton fabric.

Table 5.4. Thermo-oxidative stability data of uncoated and casein coated cotton fabrics

Sample	**$T_{onset10\%}$ (°C)**	**T_{max1} (°C)**	**T_{max2} (°C)**	**Residue at T_{max1} (wt. %)**	**Residue at T_{max2} (wt. %)**	**Residue at 600°C (wt. %)**
CF_uncoated	320.11±0.51	343.33±0.23	492.17±0.45	48.1±0.3	11.3±0.4	2.3±0.3
CF_50g/l casein-alkaline	289.15±0.58	334.43±0.21	523.50±0.51	54.3±0.5	22.9±0.3	14.5±0.2
CF_100g/l casein-alkaline	280.63±0.74	332.25±0.35	526.16±0.47	56.1±0.4	27.1±0.2	16.4±0.4
CF_150g/l casein-alkaline	272.83±0.69	330.31±0.29	530.43±0.63	59.9±0.6	31.4±0.4	19.2±0.3
CF_50g/l casein-acidic	275.51±0.61	328.15±0.26	538.10±0.49	62.8±0.3	24.5±0.2	15.9±0.3
CF_100g/l casein-acidic	270.16±0.71	325.83±0.37	541.33±0.54	64.6±0.5	28.8±0.3	20.5±0.5
CF_150g/l casein-acidic	263.33±0.83	322.33±0.41	543.67±0.65	67.2±0.7	33.4±0.5	27.6±0.4

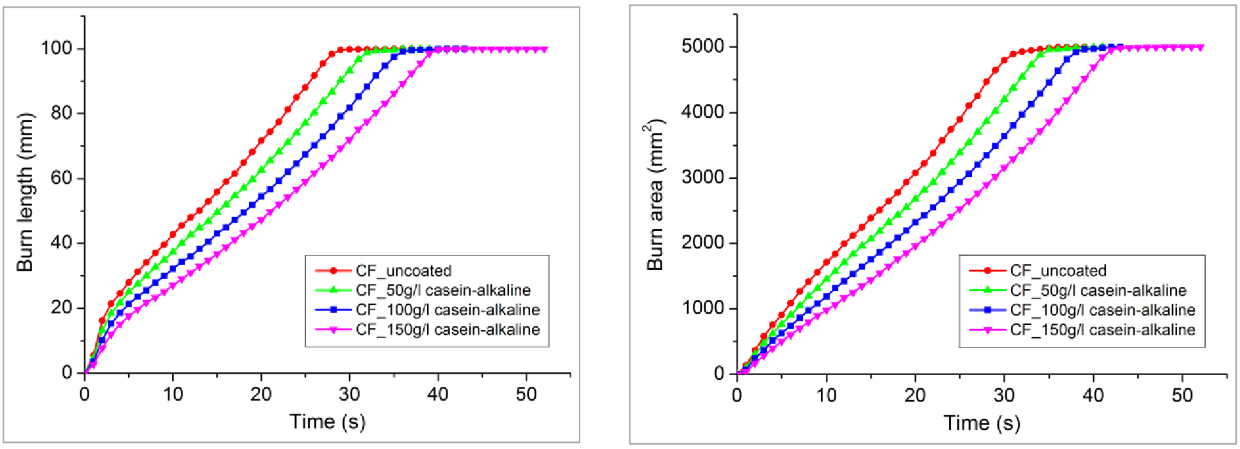
5.2.4 Flame retardancy

The effect of alkaline and acidic casein solutions' coatings on the flame retardancy of cotton fabrics was examined through flammability tests, i.e., limiting oxygen index (LOI) and horizontal configuration flame spread tests. The LOI value of 18.3% was obtained for the uncoated cotton fabric. Nevertheless, the LOI values of casein coated cotton fabrics were found to increase considerably with an increase in casein concentration, as given in Table 5.5. Besides, a greater improvement of LOI values was presented by the fabric samples coated with acidic casein solutions (from 21% to 25%) as compared to those with alkaline casein solutions (from 20% to 23%). This was accredited to the enhanced char residue yields of fabric samples coated with acidic casein solutions owing to the higher deposited casein add-on percentage and phosphorous content [276, 310, 311], as also revealed from the TGA results provided in Table 5.4, which acted as an effective thermal insulating barrier to hinder the transfer of heat and fuel and stop the combustion process. In general, an increased LOI value usually results in lower combustibility and better flame retardant properties of any polymeric materials including textile materials/substrates [66, 276], which was demonstrated from the horizontal flame test results such as; the total burning time, burn rate and char residue of uncoated and casein coated cotton fabrics, as presented in Table 5.5. These observed different parameters were then used to estimate the resistance for flame propagation.

Table 5.5. Flammability characteristics of uncoated and casein coated cotton fabrics

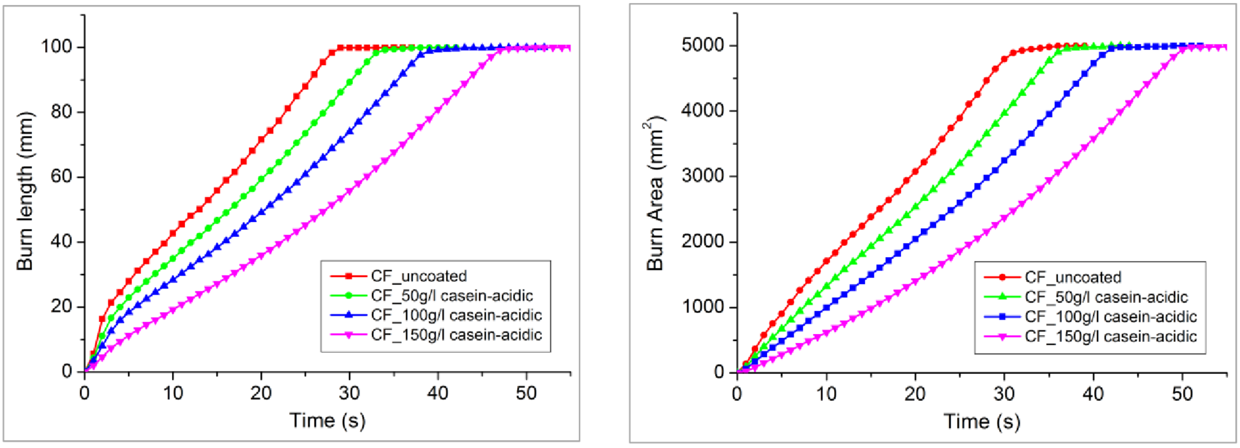
	Alkaline casein solution				**Acidic casein solution**			
Sample	**LOI (vol. %)**	**Total burning time (s)**	**Burn rate (mm/s)**	**Char residue (%)**	**LOI (vol. %)**	**Total burning time (s)**	**Burn rate (mm/s)**	**Char residue (%)**
CF_uncoated	18.28±0.22	36.21±0.25	3.63±0.04	3.1±1.1	18.28±0.22	36.21±0.25	3.63±0.04	3.1±1.1
CF_50 g/l casein	20.31±0.24	38.41±0.59	3.34±0.05	23.9±1.6	20.85±0.23	44.35±0.61	2.75±0.03	29.3±2.1
CF_100 g/l casein	21.63±0.25	43.97±0.73	2.83±0.04	36.5±1.8	22.48±0.24	52.41±0.78	2.31±0.05	45.1±1.4
CF_150 g/l casein	22.98±0.21	52.12±0.67	2.42±0.05	48.2±1.5	24.82±0.26	58.24±0.81	2.05±0.06	52.9±1.9

When a methane flame was applied for the specified time, the uncoated cotton fabric completely burnt vigorously without leaving any significant amount of char residue. Conversely, the casein coating treatments were found to assist an increase in the total burning time, and thus exhibited their ability for flame protection. The burning time was found to increase in a linear trend with an increase in casein concentration. Moreover, the cotton fabrics coated with both alkaline and acidic casein solutions preserved their original structure even after burning. Whereas, after burning the samples coated with acidic casein solutions preserved their original texture in the form of consistent and stable char residues even at low concentrations as compared to the less consistent and less stable, i.e., fractured structure of the char residues of samples coated with an alkaline casein solution (see Figure 5.14). Furthermore, the fabrics coated with acidic casein solutions burnt at a slower rate and resulted in stronger and higher char residues as compared to those treated with alkaline casein solutions. The 44% increase in total burning time, as well as 48.2% final residue, was found for the cotton fabric sample coated with 150 g/l alkaline casein solution; while, it was 61% and 52.9%, respectively for that one coated with 150 g/l acidic casein solution. This behavior was also supported by the results of TGA. Likewise, this was also construed to the obtained higher casein add-on percentage and eventually the higher phosphorous content for the fabrics coated with acidic casein solutions. Due to the deposited higher casein add-on and phosphorous content, a greater amount of acidic species like phosphoric acid was released from casein macromolecules on heating. That served the dehydration of more number of glycosyl units of cellulose, instead of depolymerization leading to a higher amount of char residues [175, 217, 272]. The produced char also exerted a protective effect on the underlying cotton fabric, limiting the oxygen diffusion, avoiding the formation of combustible volatile products, and absorbing the heat evolved during the combustion.



(a) Burn length
(coatings of alkaline casein solutions)

(b) Burn area
(coatings of alkaline casein solutions)

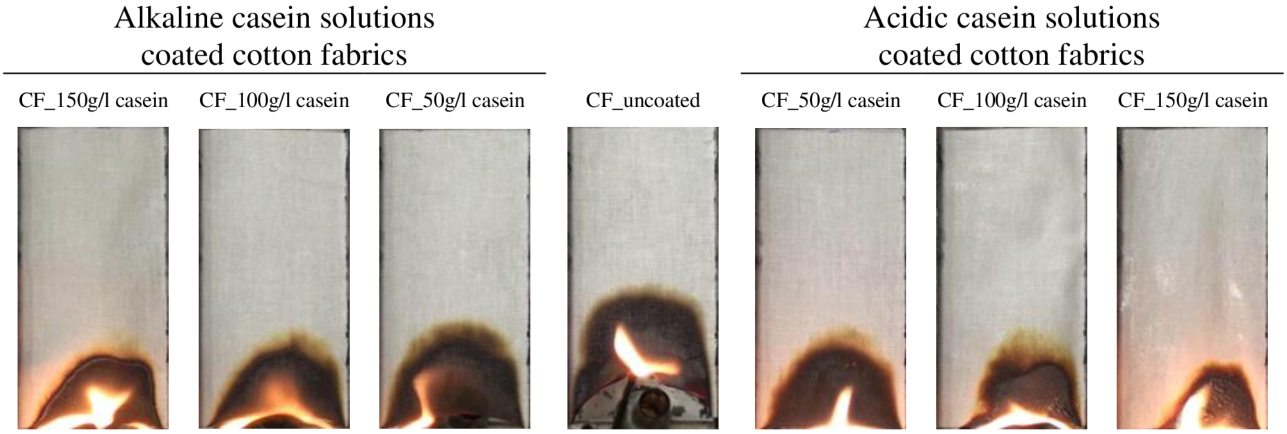


(c) Burn length
(coatings of acidic casein solutions)

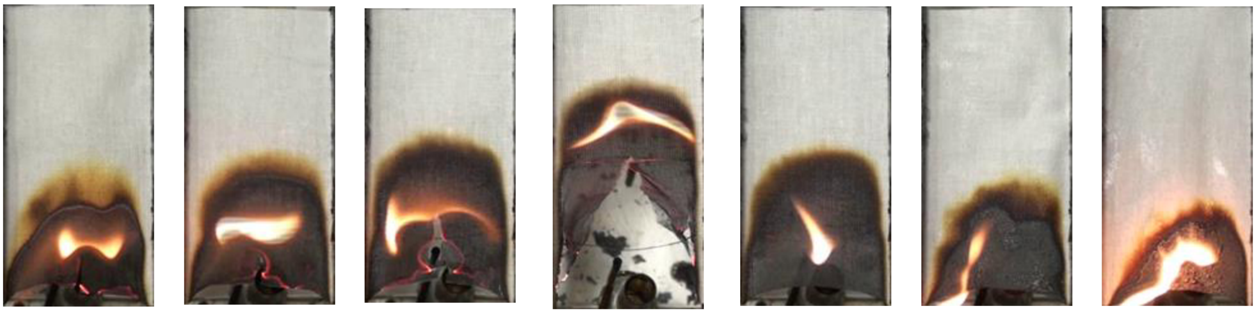
(d) Burn area
(coatings of acidic casein solutions)

Figure 5.13. Plots for estimation of flame propagation with time from image analysis data

The image analysis tools were employed, for the estimation of flame propagation over the small intervals of time, on uncoated and casein coated cotton fabric samples. The effect of coatings, of different concentration casein solutions prepared under both alkaline and acidic pH conditions, on the burn length and burn area can be seen in Figure 5.13. The cotton fabrics coated with different concentrations of acidic casein solutions presented less burning behavior and revealed a lesser burn length and lesser burn area as compared to those coated with the same concentrations of alkaline casein solutions. This was further justified by the photographs as given in Figure 5.14 that were taken after 10, 20, 30, and 40 s of the burning time. These photographs show the carbonized areas for all samples after the specified intervals of burning time. Surprisingly, more intumescence with the release of oily substances was observed while burning of the cotton fabrics treated with acidic casein solutions. The morphology of char residues, of burnt casein coated fabrics after the flammability test, was also examined through scanning electron microscopy, which can be observed from the SEM images as given in Figure 5.15. The char residues of fabrics coated with alkaline casein solutions showed the formation of globular micrometric structures (i.e. local intumescence) at localized spaces (see Figure 5.15(a), (c), (e)).

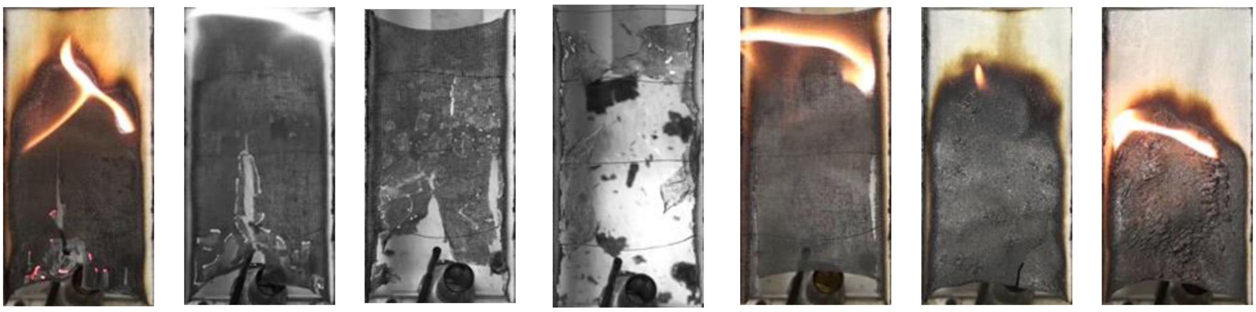


After 10 seconds time interval



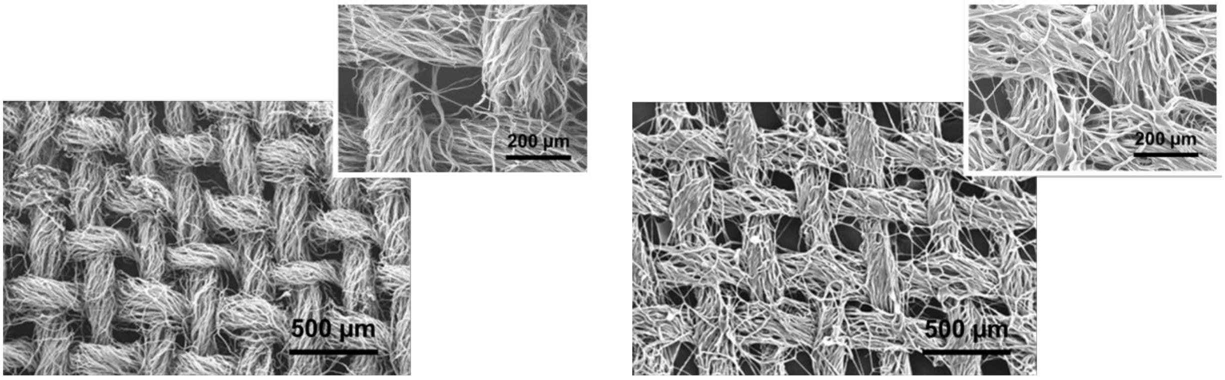
After 20 seconds time interval

After 30 seconds time interval

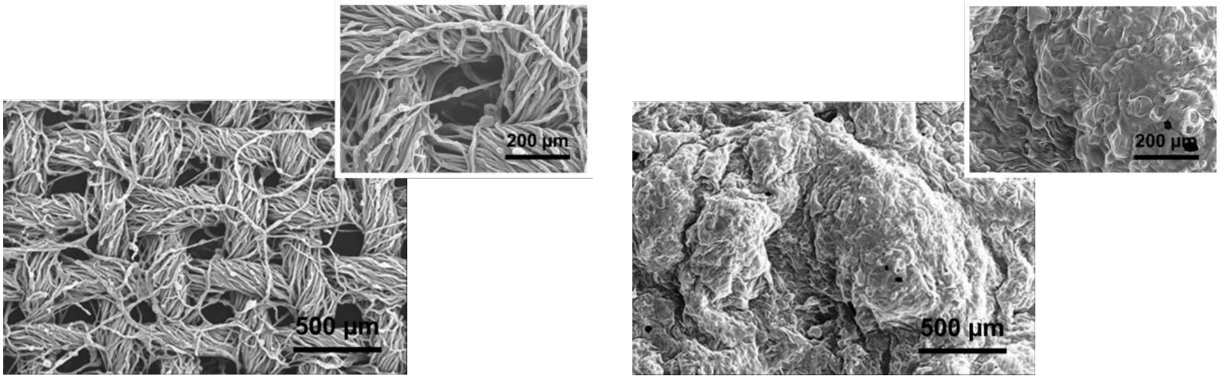


After 40 seconds time interval

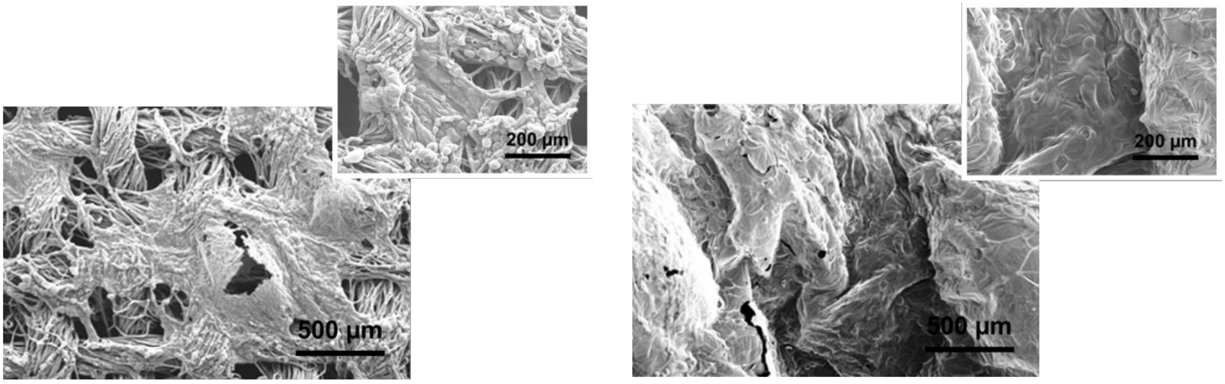
Figure 5.14. Photographs of burnt uncoated and casein coated cotton fabrics at different time intervals during flame test



(a) CF_50g/l casein-alkaline (b) CF_50g/l casein-acidic



(c) CF_100g/l casein-alkaline (d) CF_100g/l casein-acidic



(e) CF_150g/l casein-alkaline (f) CF_150g/l casein-acidic

Figure 5.15. SEM magnifications of char residues of burnt casein coated cotton fabrics

Contrarily, the char residues of fabrics coated with acidic casein solutions showed the formation of more expanded globular micrometric structures (i.e., global intumescence) at enlarged spaces (see Figure 5.15(b), (d), (f)). These micrometric structures were phosphorus-rich bubbles that blow up during the combustion, exhibiting an intumescence phenomenon [175]. The emergence of more bubbles, i.e., global intumescence, in the case of char residues of fabrics coated with acidic casein solutions, was ascribed to the release of ammonia [217, 272, 277], comparative in higher amounts, due to the protonation of casein protein macromolecules under acidic pH conditions (see section "Mechanism of proteins behavior under different pH conditions").

5.2.5 Radiant heat resistance

The effect of alkaline and acidic casein solutions' coatings on the thermal resistance characteristic of cotton fabrics, as protection against radiant heat, was assessed by exposing the cotton fabric samples to a radiant heat source at the specified incident heat flux density (Q_o). The rise of temperature was calculated at the back of fabric samples by a calorimeter, which eventually resulted in; two threshold times (namely radiant heat transfer indexes), i.e., time for the rise of 12°C ($RHTI_{12}$) and time for the rise of 24°C ($RHTI_{24}$), transmitted heat flux density (Q_c) and heat transmission factor (TFQ_o), as enumerated in Table 5.6. A drop in Q_c values was observed for casein coated cotton fabric samples as compared to that of uncoated cotton fabric. However, the reduction in Q_c values was comparatively more in the case of cotton fabrics coated with acidic casein solutions than those coated with alkaline casein solutions. Accordingly, an identical pattern was noticed in TFQ_o values, lowering from 57.8% to 43.3% and 57.8% to 41.0% for the cotton fabric samples coated with different concentrations of both alkaline and acidic casein solutions respectively. The reduction in Q_c and TFQ_o was due to an increase in the values of $RHTI_{12}$ and $RHTI_{24}$ indexes and their difference ($RHTI_{24}$ - $RHTI_{12}$). The higher values of radiant heat transmission indexes and their differences**,** for the casein coated cotton fabrics, as compared to the uncoated cotton fabric, highlighted that the temperature rise concerning time ensued at a lower rate, representing the tardy exchange of radiant heat towards the calorimeter, i.e., the slower transmission of radiant heat. The increased values of $RHTI_{12}$, $RHTI_{24,}$ and ($RHTI_{24}$ - $RHTI_{12}$) indexes, for the fabric samples coated with acidic casein solitons than those with alkaline casein solutions, were rendered to the comparative thicker casein coatings due to the higher casein add-on [278–280], blocking of the spaces/interstices between the cotton fibers and yarns as validated from the SEM micrographs (see Figure 5.11).

Table 5.6. Radiant heat resistance parameters of uncoated and casein coated cotton fabrics

Sample	**Q_0 (kW/m^2)**	**$RHTI_{12}$ (sec)**	**$RHTI_{24}$ (sec)**	**$RHTI_{24}$-$RHTI_{12}$ (sec)**	**Q_c (kW/m^2)**	**TFQ_0 (%)**
CF_uncoated	40	3.8±0.04	6.7±0.05	2.9±0.04	23.10±0.37	57.76±0.92
CF_50g/l casein-alkaline	40	4.3±0.05	7.5±0.08	3.2±0.04	20.66±0.28	51.66±0.70
CF_100g/l casein-alkaline	40	4.6±0.08	8.1±0.04	3.5±0.07	19.01±0.38	47.54±0.96
CF_150g/l casein-alkaline	40	4.9±0.07	8.7±0.09	3.8±0.05	17.33±0.25	43.32±0.61
CF_50g/l casein-acidic	40	4.4±0.05	7.7±0.08	3.3±0.04	20.04±0.26	50.10±0.66
CF_100g/l casein-acidic	40	4.8±0.04	8.4±0.05	3.6±0.05	18.18±0.27	45.45±0.68
CF_150g/ casein-acidic	40	5.4±0.08	9.5±0.04	4.1±0.09	16.39±0.36	40.98±0.89

These larger values of ($RHTI_{24}$ - $RHTI_{12}$) for the casein coated fabric samples were accredited to the reason that the infrared radiations which performed an apposite part in the heat transference were also absorbed by the casein coatings. Due to this casein coatings provided improved thermal resistance and insulation. That might be helpful to prevent the wearer from acquiring burn injuries. Concurrently, a reduction in the values of transmitted heat flux density, i.e., the lower quantity of transmitted radiant heat, is also regarded as favorable for the textile substrate, causing later on its slower burning, as also demonstrated by the flammability test results of casein coated cotton fabrics (see Table 5.5). More specifically, it was concluded that the resistance of casein coatings to a radiant heat flux could also vividly reduce the time to ignition of casein coated fabrics as compared to the uncoated cotton fabric. This was ascribed to the degradation/decomposition of casein to release phosphoric acid employing a detrimental effect that sensitizes the early ignition of cotton fabric and favors the cellulose dehydration to generate more thermally stable char residues instead of volatile release [175].

Mechanism of proteins behavior under different pH conditions**:** Such as, the casein protein macromolecules are poly amino acids bearing several phosphate groups in their micellae structure [223]. While, the amino acids are ampholytes; i.e., they contain both the acidic and basic groups and exhibit amphoterism, i.e., amphoteric ionic behavior [312]. Amphoterism is the reactivity of a substance, with both acids and bases, acting as a base in the presence of an acid and as an acid in the presence of a base. However, the amino acids are basic building blocks of proteins, hence, the amphoteric ionic behavior has also been considered as one of the characteristics of proteins and attributed to the presence of amino ($–NH_2$; a basic group) and carboxyl (–COOH; an acidic group) groups in the side chains of the poly-peptide chain [313]. Free amino acids and peptides do not exist as non-ionic molecules; instead, they occur as zwitterions (neutral molecules). A zwitterion is a molecule that contains both the positively and negatively charged functional groups but the net charge of the entire molecule is always zero. The net charge is influenced by the pH value. Each protein has a fixed value of the isoelectric point (pl). The isoelectric point (isoionic point) is the pH value at which the number of cations is equal to that of anions. Thus, at the isoelectric point, the net electric charge of a protein is always zero. But the total charge on the protein molecule (sum of positive and negative charges) at this point is always maximum. Therefore, the proteins are regarded as the dipolar ions or internal salts or zwitterions (German for ‘ion of both kinds’; amphoteric ions) at isoelectric point [314], [315], and exist in the solution as $(H_3N^+)_m$ — R— $(COO^-)_n$. This general structure of amino acids, represented as an inner salt, was originally proposed by Adam in 1916 [316] and Bjerrum in 1923 [317]. The formula depicts the carboxyl group as being dissociated while the amino group is protonated. It means that the protein macromolecules, at pH values lower than pl, will have a net positive charge as a cation. On contrary, at pH values higher than pl, the protein macromolecules will have a net negative charge as an anion, as shown in Figure 5.16. While at pl, the proteins are found to be least soluble and can be precipitated most easily. Hence, any protein’s solubility is highly dependent on the pH of the solution and ionic strength.

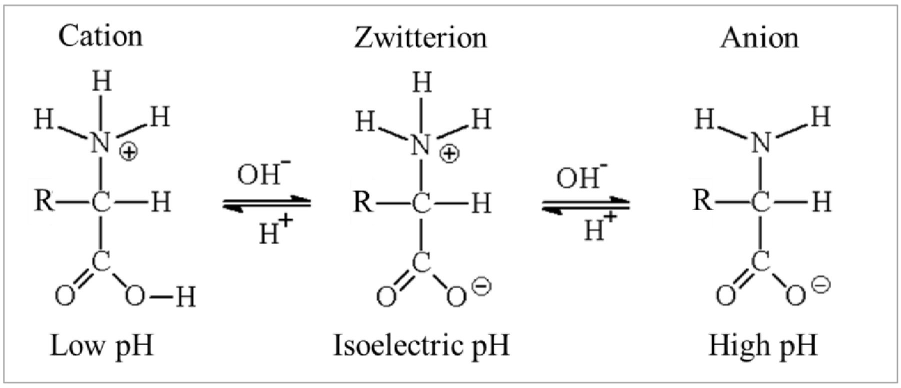
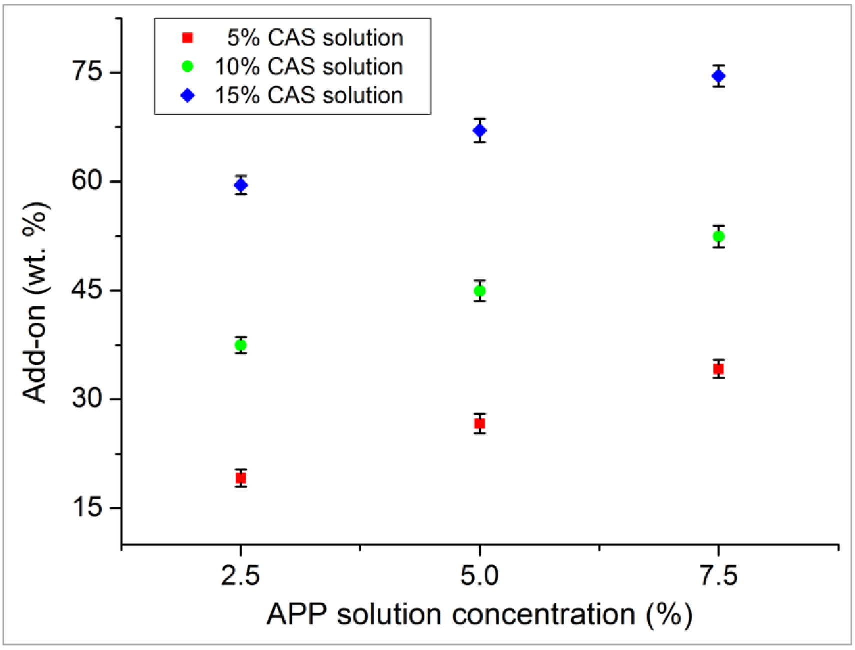


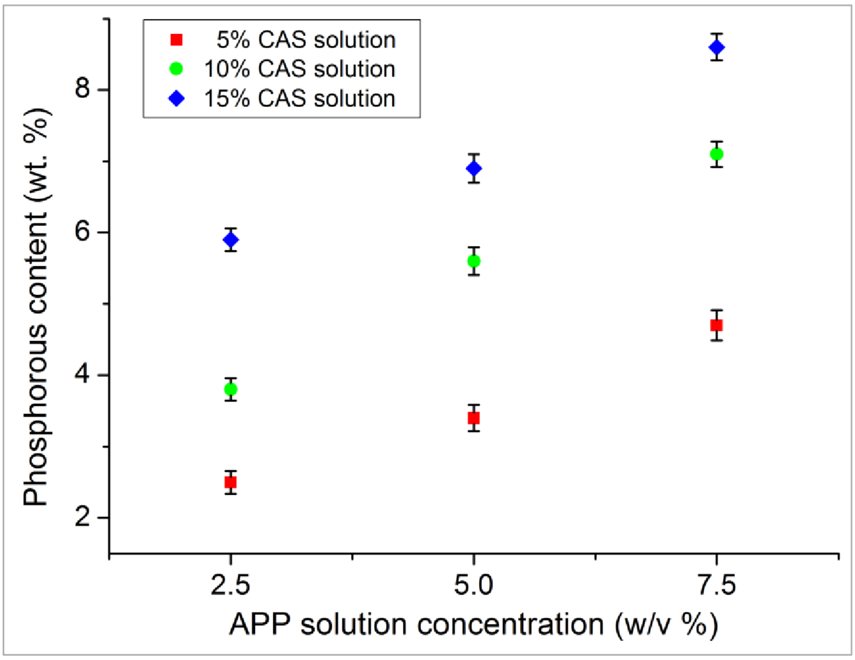
Figure 5.16. General mechanism for amphoteric nature of amino acids and proteins

5.3 Intumescent flame retardant system based on casein in combination with ammonium polyphosphate

The effect on the add-on (weight gain) of cotton fabric (CF) samples, coated with CAS-APP bilayer assemblies from the casein and ammonium polyphosphate solutions of different concentrations, is shown in Figure 5.17(a). It can be seen that the add-on of bilayer coated cotton fabric samples was increased with an increase in CAS concentration as well as APP concentration, due to the maximum wetting and binding of individual fibers and yarns, and ultimately confining inside as well as depositing on the fabric structure after bilayer coating and drying. Moreover, to predict the flame retardant function, the phosphorous content (P content) of cotton fabrics coated with the different compositions of CAS-APP bilayer assemblies were also analyzed. When plotted, the phosphorous content values of CAS-APP bilayer coatings were found to increase with an increase in CAS and APP concentrations, as shown in Figure 5.17(b). The maximum increase of ~9 wt. % was observed for a fabric sample coated with CAS-APP bilayer assembly of 15% CAS and 7.5% APP concentrations.



(a) Add-on



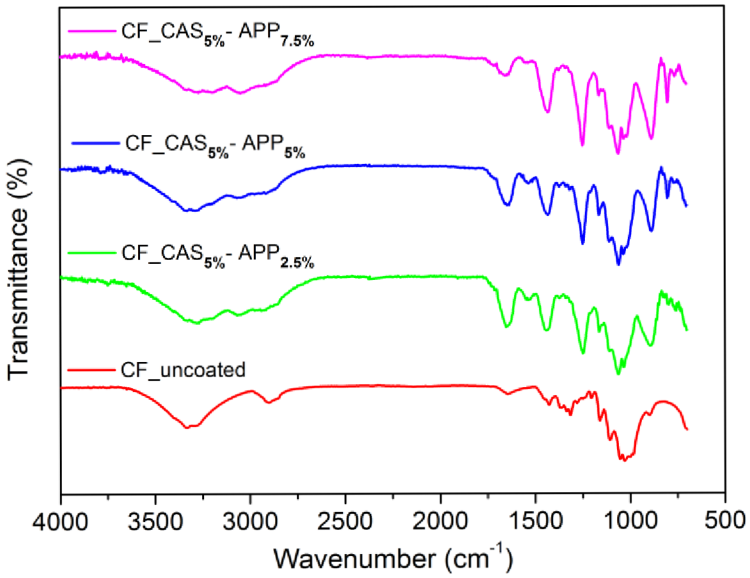
(b) Phosphorus content

Figure 5.17. Add-on and phosphorous content of CAS-APP bilayer coated cotton fabrics

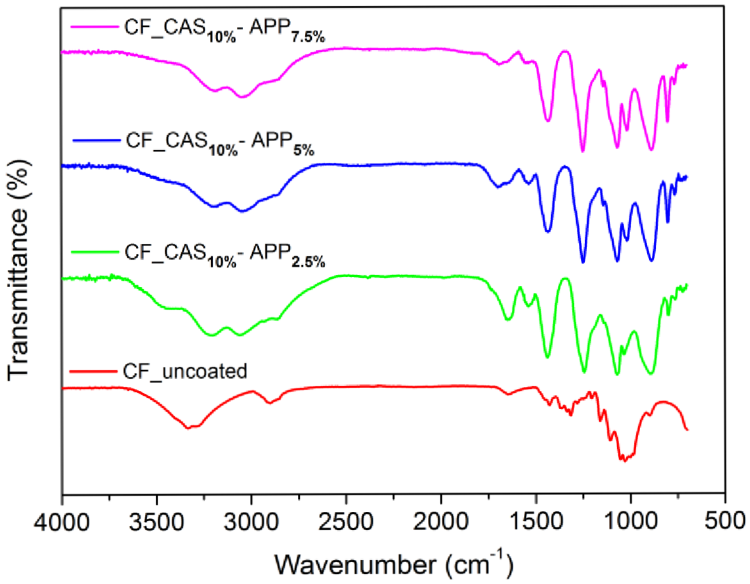
5.3.1 Surface chemical structure

The chemical/molecular structure, of cotton fabric samples, was scrutinized by ATR-FTIR spectroscopy to conform to the efficacy of different bilayer assemblies and the presence of CAS and APP on the cotton fabrics. The ATR-FTIR spectra, of uncoated cotton fabric and cotton fabric samples bilayer coated with different concentrations of CAS and APP, are given in Figure 5.18(a), (b), (c) respectively.

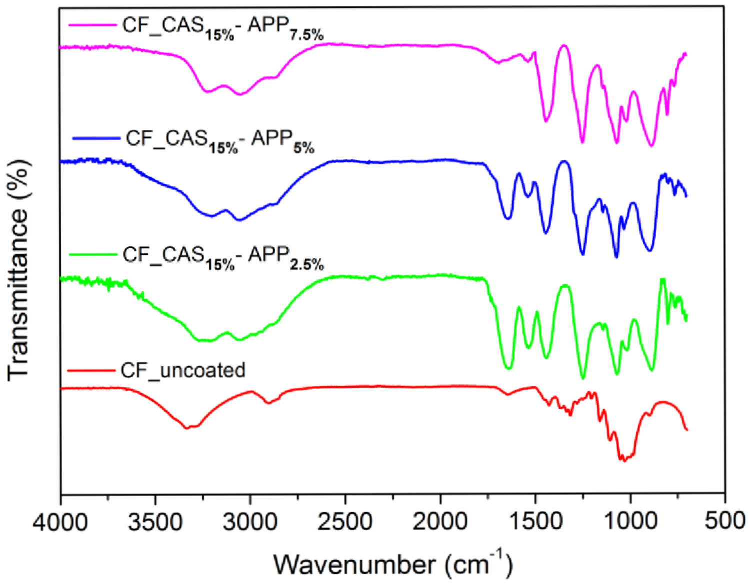
The spectra of CAS-APP bilayer coated cotton fabrics exhibited the weak characteristic signals of cellulose backbone indicating the presence of deposited CAS-APP bilayer coatings. Besides the weak distinctive vibration modes of cellulose, namely; υ(OH) at ca. ~3300, $\upsilon(CH_2)$ at ~2900, δ(OH) at ~1640, $\delta(CH_2)$ at ~1425, δ(CH) at ~1370, δ(OH) at ~1310, υ(C–C) at ~1020, υ(OH) at ~894 cm^{-1}, etc. [268, 269], the bilayer coated cotton fabrics showed some additional peaks for the presence of CAS and APP. The two peaks, positioned at 1624 and 1528 cm^{-1}, were significantly assigned for the respective vibrations of amide I and amide II groups of casein protein [268, 270, 271]. As, the characteristic bands, in infrared spectra for proteins and polypeptides, include amide I (due to the stretching vibrations of C=O) and amide II (due to the bending vibrations of N–H) bands, resulting from the amide bonds that connect the amino acids. In the region, at 1500-500 cm^{-1}, many overlapped signals/peaks were present. Whereas, the two peaks located at 1250 and 884 cm^{-1} were referred to as the vibrational modes of P=O and P–O–P of ammonium polyphosphate respectively, accompanying the typical signals of ammonium group stretching and bending [318, 319].



(a) ATR_FTIR spectra of 5%CAS-APP bilayer coatings



(b) ATR-FTIR spectra of 10%CAS-APP bilayer coatings



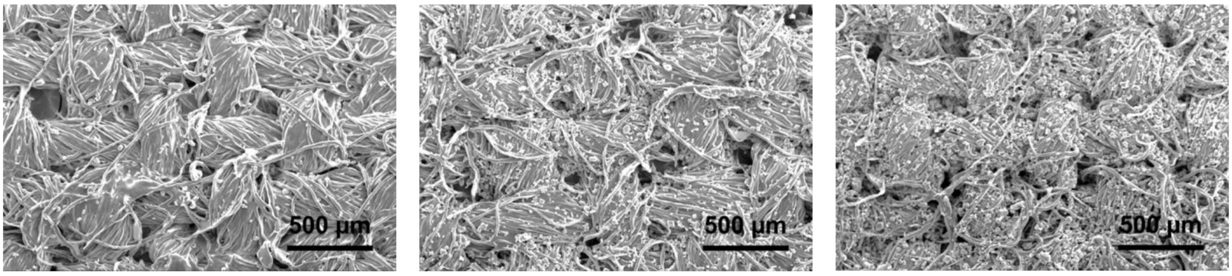
(c) ATR-FTIR spectra of 15%CAS-APP bilayer coatings

Figure 5.18. ATR-FTIR spectra of uncoated and CAS-APP bilayer coated cotton fabrics

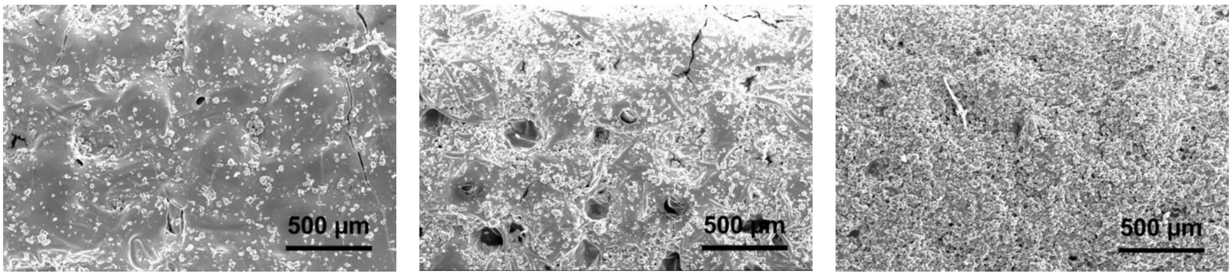
Moreover, an increase in the intensity/height of these peaks indicated the deposition of a greater amount of casein and ammonium polyphosphate on the cotton fabrics bilayer coated with the higher concentrations of CAS and APP, which was also verified by the spectra of these cotton fabrics showing the weak characteristic signals of cellulose.

5.3.2 Surface morphology

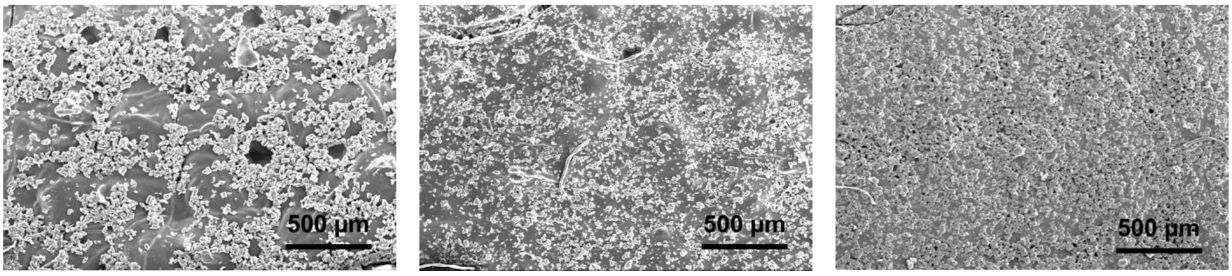
The scanning electron microscopy presented information regarding the morphology of CAS-APP bilayer coated cotton fabric samples. The representative SEM micrographs of cotton fabrics bilayer coated with different concentrations of CAS and APP are shown in Figure 5.19. A continuous, homogeneous, and coherent film was observed on the surface of bilayer coated fabric samples due to the maximum wetting and binding of cotton fibers and yarns with the casein and ammonium polyphosphate solutions of different concentrations. The cotton fibers exhibited better compatibility with bilayer coatings of CAS and APP, as was evidenced by the observations of no cracks on the surface coatings.



(a) CF_CAS$_{5\%}$-APP$_{2.5\%}$ (b) CF_CAS$_{5\%}$-APP$_{5\%}$ (c) CF_CAS$_{5\%}$-APP$_{7.5\%}$



(d) CF_CAS$_{10\%}$-APP$_{2.5\%}$ (e) CF_CAS$_{10\%}$-APP$_{5\%}$ (f) CF_CAS$_{10\%}$-APP$_{7.5\%}$



(g) CF_CAS$_{15\%}$-APP$_{2.5\%}$ (h) CF_CAS$_{15\%}$-APP$_{5\%}$ (i) CF_CAS$_{15\%}$-APP$_{7.5\%}$

Figure 5.19. SEM images of CAS-APP bilayer coated cotton fabrics

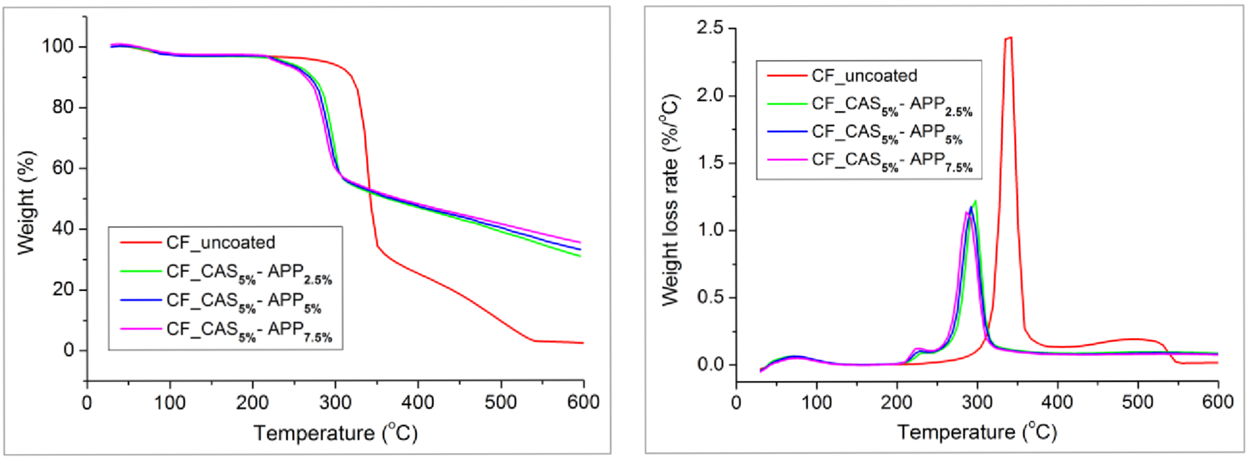
At a low concentration of CAS, the bilayer coated fabrics' surfaces showed distinct individual cotton fibers even with an increase in APP concentration (see Figure 5.19(a), (b), (c)). Whereas, at higher concentrations of CAS even with an increase in APP concentration, the bilayer coated fabrics' surfaces showed an increased grouping of individual fibers and yarns (see Figure 5.19(d), (e), (f) and also Figure 5.19(g), (h), (i)), which resulted in the reduction of inter-fiber and/or inter-yarn spaces/pores, due to the higher amount and thickness of deposited bilayer coatings.

5.3.3 Thermo-oxidative stability

The thermogravimetric analysis was employed to evaluate the effect of CAS-APP bilayer coatings on the thermo-oxidative stability of cotton fabrics. The TG and DTG curves of all fabric samples were plotted, as shown in Figure 5.20, which represents the weight loss and weight loss rate with an increase in the temperature. The broad characteristics data attained from the analysis results were also condensed, as given in Table 5.7, which presents the different decomposition temperatures and residue percentages of uncoated and CAS-APP bilayer coated cotton fabric samples.

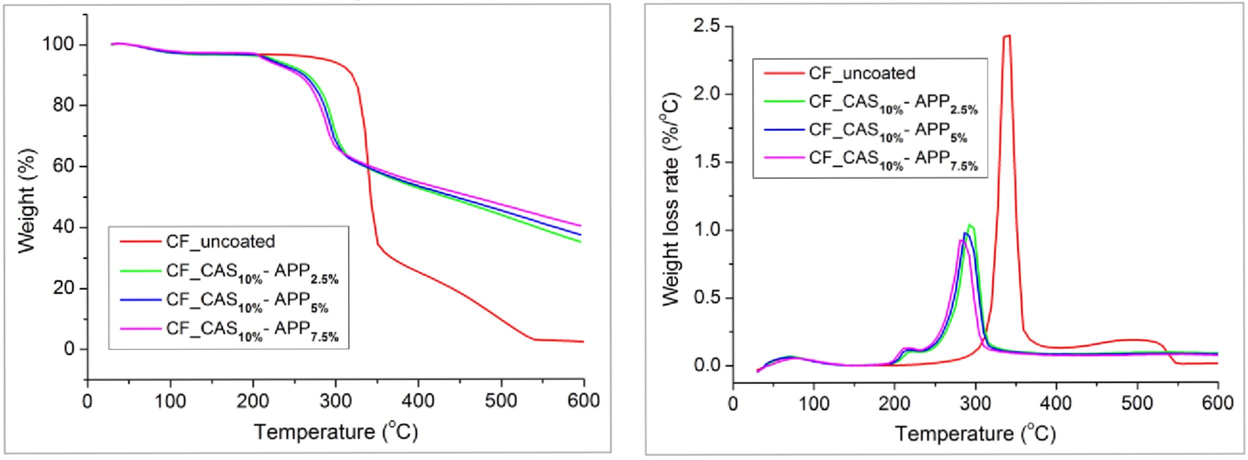
It can be viewed that the thermal degradation of all samples consists of two steps, i.e., 200-400°C and 400-600°C. The decomposition of uncoated cotton fabric was started at 298°C and then the maximum weight loss rate was observed at 343°C (T_{max1}) in the first degradation step. The residue percentage after the first degradation step at T_{max1} was attributed to the formation of a thermally stable form of aliphatic char due to the depolymerization and dehydration of cellulose. Nevertheless, on a further increase of temperature, the second maximum weight loss rate appeared at 492°C (T_{max2}) during the second degradation step, which corresponded to the carbonization of aliphatic char into aromatic char and then further oxidation into carbon mono (CO) and dioxide (CO_2) [69]. The $T_{onset10\%}$ values of cotton fabric samples were noticed to shift towards the lower temperatures when coated with CAS-APP bilayer assemblies of different concentrations of CAS and APP. The effect of increasing APP concentration was found more prominent in shifting the $T_{onset10\%}$ values as compared to increasing CAS concentration. This indicated a stronger performance of ammonium polyphosphate for sensitization of the cellulose decomposition as compared to casein.

Furthermore, the initial decomposition temperature (T_{max1}), of cotton fabric samples coated with different compositions of CAS-APP bilayer assemblies, was also reduced withal to a greater extent with increased concentration of APP than that of CAS due to the catalyzed thermal degradation of cotton in the presence of APP [320–322]. The anticipated first degradation step was regarded to be advantageous for the thermal stability of cotton in the whole degradation process, because the thermo-stable carbonaceous structure, formed at lower temperatures, is obviously considered favorable to suppress the further degradation of cotton at higher temperatures [320].



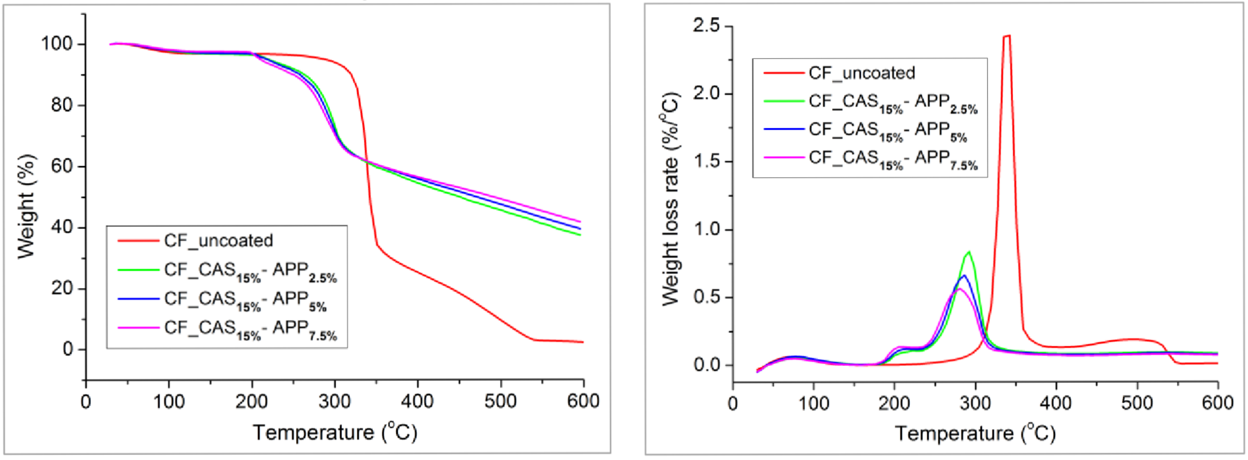
(a) TG curves plot (5%CAS-APP bilayer coatings)

(b) DTG curves plot (5%CAS-APP bilayer coatings)



(c) TG curves plot (10%CAS-APP bilayer coatings)

(d) DTG curves plot (10%CAS-APP bilayer coatings)



(e) TG curves plot (15%CAS-APP bilayer coatings)

(f) DTG curves plot (15%CAS-APP bilayer coatings)

Figure 5.20. Thermo-oxidative stability of uncoated and CAS-APP bilayer coated cotton fabrics

Irrespective of APP concentration, the higher concentration of CAS was found to produce a higher residue percentage at T$_{max1}$ as evidence of the catalyzed charring of casein by ammonium polyphosphate. This subsequently resulted in, the delayed occurrence of the second degradation step as confirmed by T$_{max2}$ values, and thus the formation of more stable char at higher temperatures compared to that of uncoated cotton fabric. However, the final char residues of

CAS-APP bilayer coated cotton fabrics with CAS and APP solutions of higher concentrations evinced a large-scale growth at 600°C. This increase in catalyzed charring was ascribed to the growth of higher phosphorous content (P content) on CAS-APP bilayer coated cotton fabric samples, as shown in Figure 5.17(b). The fabric sample coated with CAS-APP bilayer assembly of 15% CAS and 7.5% APP concentrations produced a maximum of 42.3% residue at 600°C as compared to that of 2.3% of uncoated cotton fabric.

Table 5.7. Thermo-oxidative stability data of uncoated and CAS-APP bilayer coated fabrics

				Residue at		
Sample	**$T_{onset10\%}$ (°C)**	**T_{max1} (°C)**	**T_{max2} (°C)**	**T_{max1} (wt. %)**	**T_{max2} (wt. %)**	**600°C (wt. %)**
CF_uncoated	320.11±0.51	343.33±0.23	492.17±0.45	48.1±0.3	11.3±0.4	2.3±0.3
CF_CAS$_{5\%}$-APP$_{2.5\%}$	269.50±0.42	298.13±0.29	520.11±0.49	74.2±0.3	40.7±0.2	30.9±0.3
CF_CAS$_{5\%}$-APP$_{5\%}$	265.87±0.51	293.56±0.35	525.83±0.61	75.5±0.4	42.4±0.4	33.1±0.4
CF_CAS$_{5\%}$-APP$_{7.5\%}$	262.45±0.44	290.17±0.42	531.67±0.55	77.2±0.2	44.4±0.3	35.2±0.5
CF_CAS$_{10\%}$-APP$_{2.5\%}$	264.55±0.39	292.50±0.31	528.85±0.47	76.5±0.3	43.5±0.4	34.3±0.2
CF_CAS$_{10\%}$-APP$_{5\%}$	261.43±0.41	288.15±0.45	534.48±0.58	77.9±0.4	45.1±0.3	36.8±0.5
CF_CAS$_{10\%}$-APP$_{7.5\%}$	258.12±0.51	284.67±0.51	540.21±0.66	79.6±0.3	47.4±0.5	38.9±0.4
CF_CAS$_{15\%}$-APP$_{2.5\%}$	260.33±0.43	287.10±0.33	536.43±0.54	78.8±0.3	46.3±0.3	37.9±0.4
CF_CAS$_{15\%}$-APP$_{5\%}$	256.45±0.53	283.33±0.48	541.95±0.64	80.4±0.2	48.6±0.5	40.1±0.3
CF_CAS$_{15\%}$-APP$_{7.5\%}$	253.51±0.57	280.25±0.53	547.65±0.62	82.1±0.4	49.9±0.4	42.3±0.5

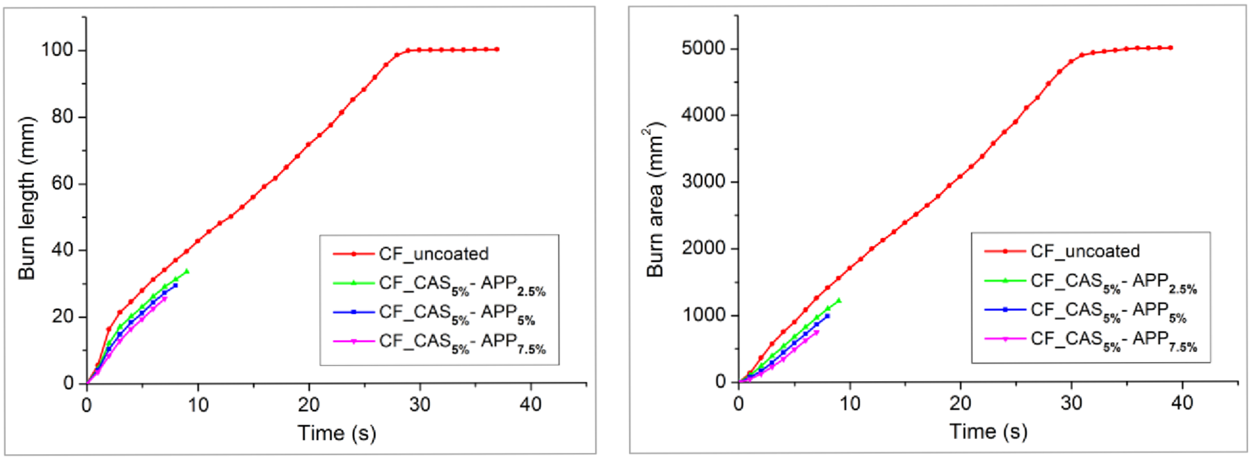
5.3.4 Flame retardancy

The flammability tests such as limiting oxygen index (LOI) and horizontal configuration flame spread tests were employed to assess the combustion behavior and flame retardant performance of CAS-APP bilayer coated cotton fabric samples. The LOI value of 18.3% was obtained for the uncoated cotton fabric. While, the LOI values were discerned to enhance significantly with the increased concentrations of CAS and APP, for the cotton fabric samples coated with different compositions of CAS-APP bilayer assemblies, as given in Table 5.8. This was accredited to the enhanced char residue yields of bilayer coated cotton fabrics owing to the higher deposited add-on percentage and phosphorous content [276, 310, 311], as also revealed from the TGA results provided in Table 5.7, which acted as an effective thermal insulating barrier to hinder the transfer of heat and fuel and stop the combustion process. In general, an increased LOI value usually results in lower combustibility and better flame retardant properties of any polymeric materials including the textile materials/substrates [66, 276], which was corroborated by the horizontal flame test results such as; the total burning time, burn rate and char residue of uncoated and CAS-APP bilayer coated cotton fabrics, as presented in Table 5.8. These observed different parameters were then used to evaluate the resistance for flame propagation.

Table 5.8. Flammability characteristics of uncoated and CAS-APP bilayer coated cotton fabrics

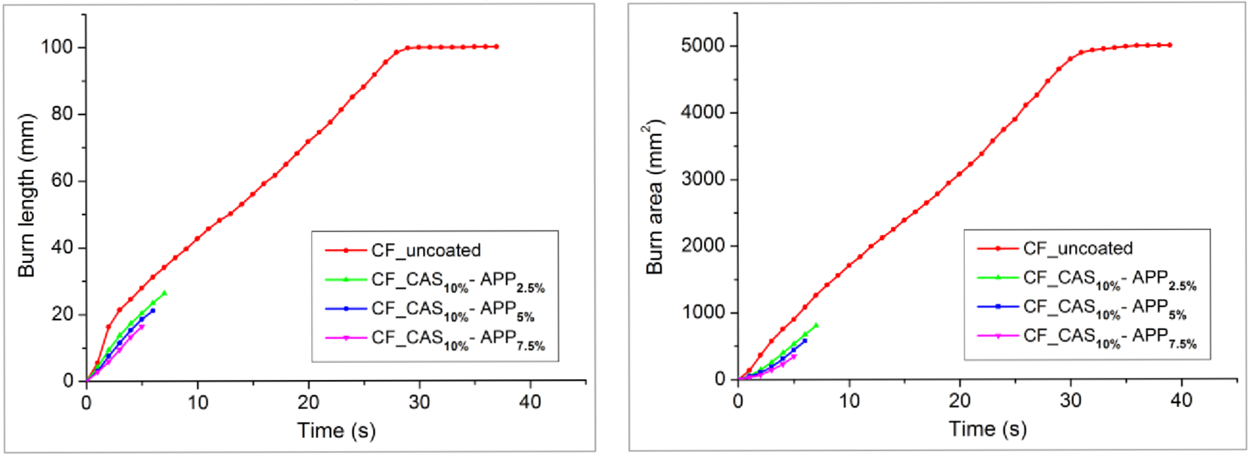
Sample	**LOI**	**Total burning time**	**Flame stoppage time**	**Char residue**
	(vol. %)	**(s)**	**(mm/s)**	**(wt. %)**
CF_uncoated	18.28±0.22	36.21±0.25	-	3.1±1.1
CF_CAS$_{5\%}$-APP$_{2.5\%}$	27.31±0.23	-	8.43±0.17	26.8±0.8
CF_CAS$_{5\%}$-APP$_{5\%}$	29.98±0.28	-	7.15±0.23	31.2±0.6
CF_CAS$_{5\%}$-APP$_{7.5\%}$	32.79±0.25	-	5.67±0.19	34.3±0.7
CF_CAS$_{10\%}$-APP$_{2.5\%}$	31.27±0.30	-	6.46±0.21	32.6±0.6
CF_CAS$_{10\%}$-APP$_{5\%}$	34.11±0.27	-	5.15±0.17	35.7±0.5
CF_CAS$_{10\%}$-APP$_{7.5\%}$	37.45±0.24	-	3.91±0.25	39.3±0.8
CF_CAS$_{15\%}$-APP$_{2.5\%}$	35.52±0.31	-	4.75±0.19	36.9±0.6
CF_CAS$_{15\%}$-APP$_{5\%}$	38.31±0.25	-	3.41±0.21	40.8±0.5
CF_CAS$_{15\%}$-APP$_{7.5\%}$	41.27±0.29	-	2.34±0.23	43.9±0.7

Besides burning vigorously, the uncoated cotton fabric was found to leave insignificant char residue, when a methane flame was applied for a specified time. The flame lasted for approximately 36 s followed by a prolonged afterglow. On the other hand, the flame stopped after some seconds, for the cotton fabrics coated with different compositions of CAS-APP bilayer assemblies, extinguishing the flame propagation, yielding enough char residues, and showing intumescence phenomena, depending on the CAS and APP solutions of different concentrations. However, the flame stoppage time was reduced more by the coated fabrics with higher APP contents/concentrations for either any constant casein concentration in the coatings of bilayer assemblies. Furthermore, the char residues were increased more by the coated fabrics with higher casein contents/concentrations for either any fixed APP concentration in the coatings of bilayer assemblies, which was analogous to the results of TGA. The maximum char of 43.9% was produced by a cotton fabric sample coated with CAS-APP bilayer assembly of 15% CAS and 7.5% APP concentrations as compared to that of 3.1% of uncoated cotton fabric. The burnt residues of bilayer coated cotton fabrics also perfectly maintained the weave/structure. Interestingly, for the burnt char residues of fabric samples coated with bilayer assemblies of higher casein contents for either any constant APP contents, the distinct appearance of higher intumescence phenomena was observed, in comparison with the fabrics that coated with bilayer assemblies of lower casein contents/concentrations. Therefore, an increase in casein concentration is more advantageous for the production of more intumescent char residues. These combustion behavior results proposed that the CAS-APP bilayer coatings could efficiently control the fire and ultimately lead to self-extinguishing on the cotton fabrics, acting as an intumescent flame retardant system.



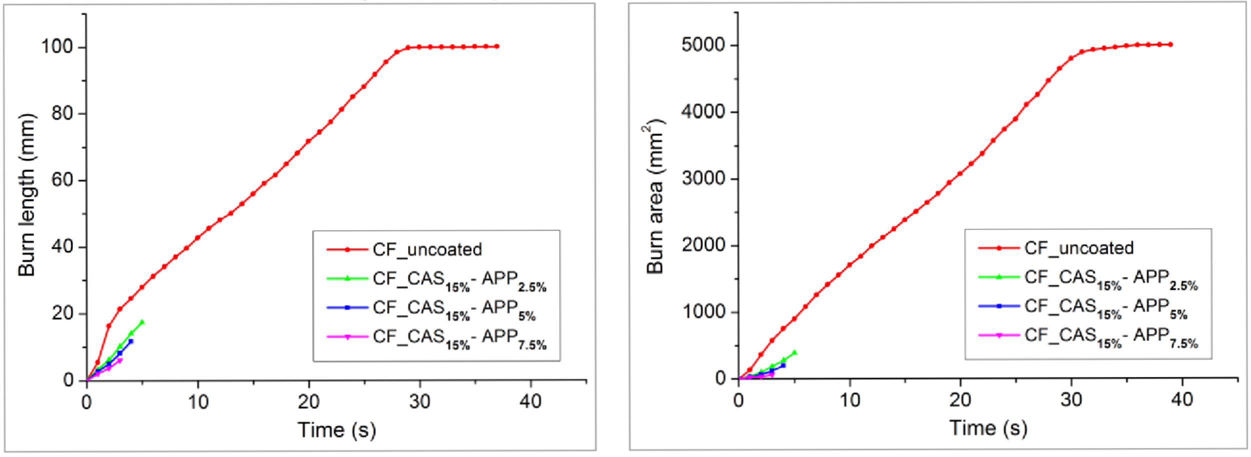
(a) Burn length (5%CAS-APP bilayer coatings)

(b) Burn area (5%CAS-APP bilayer coatings)



(c) Burn length (10%CAS-APP bilayer coatings)

(d) Burn area (10%CAS-APP bilayer coatings)



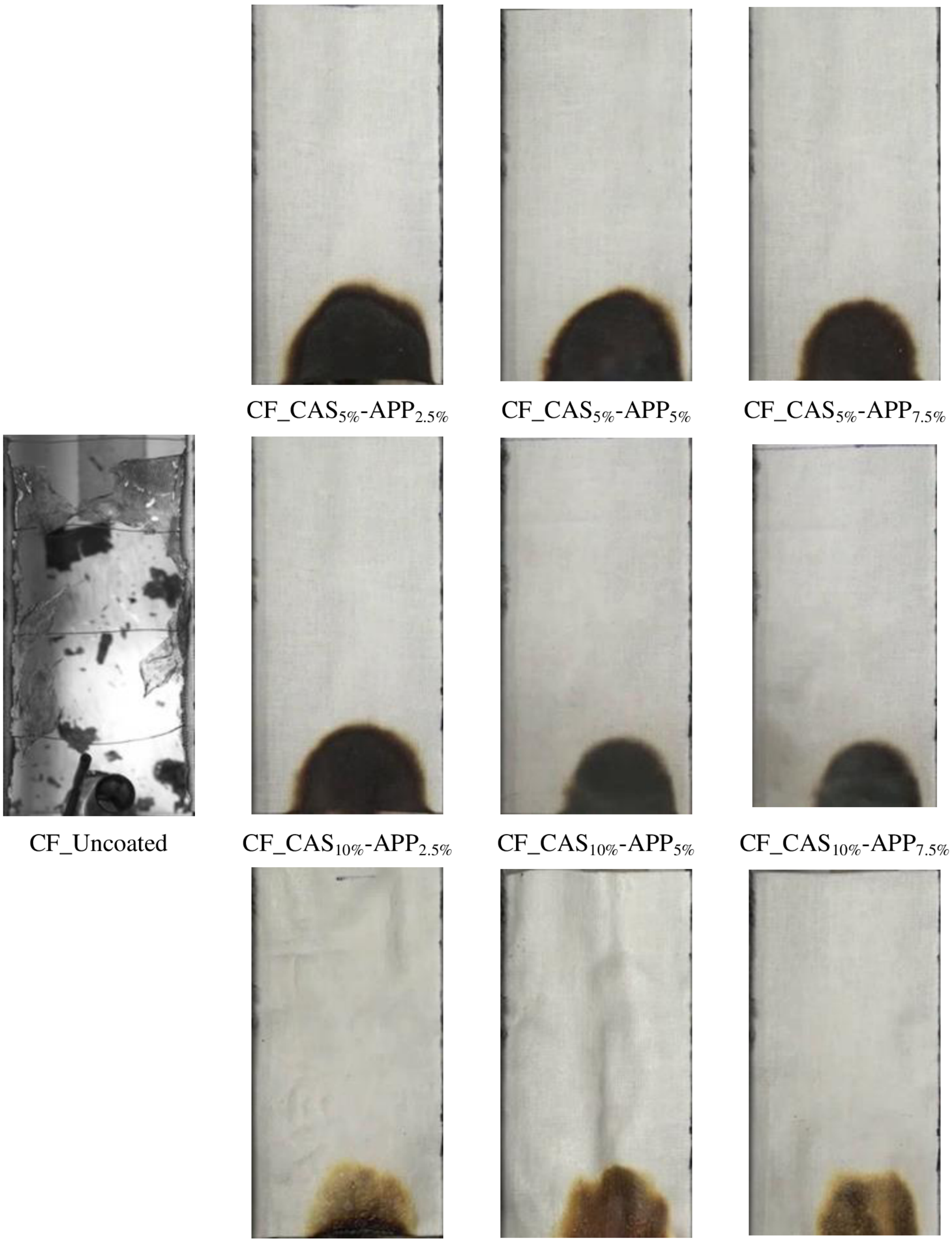
(e) Burn length (15%CAS-APP bilayer coatings)

(f) Burn area (15%CAS-APP bilayer coatings)

Figure 5.21. Plots for estimation of flame propagation with time from image analysis data

The dynamics of flame propagation were also studied using the image analysis method. It was performed to measure the changes in burn length and burn area over small intervals of time. Figure 5.21 shows the effect of CAS-APP bilayer assemblies of different compositions on the flame propagation dynamics of cotton fabrics. The CAS-APP bilayer coated fabric samples with higher APP contents/concentrations, for either any constant casein concentration in the coatings of bilayer assemblies, exhibited a lesser burn length and burn area. The least burning behavior among all fabric samples was observed for that one coated with a CAS-APP bilayer assembly of 15% CAS and 7.5% APP concentrations, as also affirmed in Figure 5.22. This behavior was credited to the greater release of phosphoric acid and ammonia, which completely extinguished the flame propagation and produced the multicellular swollen (intumescence) char residues through the catalyzed degradation of cotton cellulose and casein. Furthermore, the protective effect on the underlying cotton fabrics can be observed from the photographs of burnt fabric samples after the flame test, as given in Figure 5.22, which reveals the formation and presence of intumescence char layers. The produced foam of char limited the oxygen diffusion, avoided the formation of combustible volatile products, and absorbed the heat evolved during the combustion. This confirmed the promising applications of the bilayer assemblies of casein and ammonium polyphosphate for the formation of a body-fitted intumescent char layer, especially at higher casein contents.

Afterward, the intumescent flame retardant mechanism of CAS-APP bilayer assemblies was investigated by observing the surface morphology of burnt fabric samples through scanning electron microscopy. The SEM images of all burnt samples' residues after the flame test are given in Figure 5.23. It can be observed manifestly that in the case of burnt residues of the fabric samples that were bilayer coated with lower CAS and lower APP concentration, a thin protective char layer formed on the surface of fibers, containing less expanded globular micrometer structure at localized spaces (i.e., local intumescence) and few fibers fractured during the burning (see Figure 5.23(a)). Instead, as the APP concentration was increased in the bilayer coatings for the lower CAS concentration, the burnt residues also produced in the form of a thin protective char layer but containing a larger size and less expanded globular micrometer and bubbled structure with some cavities (see Figure 5.23(b), (c)). The globular micrometer structures are phosphorus-rich bubbles that blow up during combustion [175]. Contrarily, with an increase in CAS contents either for any of fixed APP contents in the bilayer assemblies coated on cotton fabrics, the char layer became denser containing more expanded globular micrometric and porous structures at enlarged spaces (i.e., global intumescence), and the underlying weaves structures of bilayer coated fabrics greatly retained (see Figure 5.23(d), (e), (f) & Figure 5.23(g), (h), (i)).



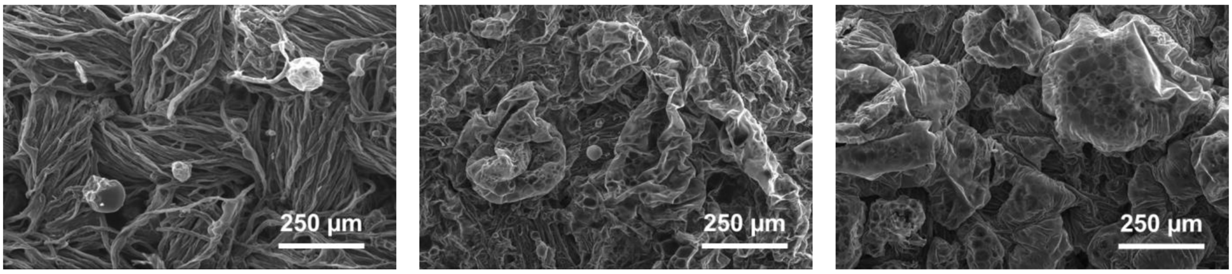
CF_CAS$_{5\%}$-APP$_{2.5\%}$ CF_CAS$_{5\%}$-APP$_{5\%}$ CF_CAS$_{5\%}$-APP$_{7.5\%}$

CF_Uncoated CF_CAS$_{10\%}$-APP$_{2.5\%}$ CF_CAS$_{10\%}$-APP$_{5\%}$ CF_CAS$_{10\%}$-APP$_{7.5\%}$

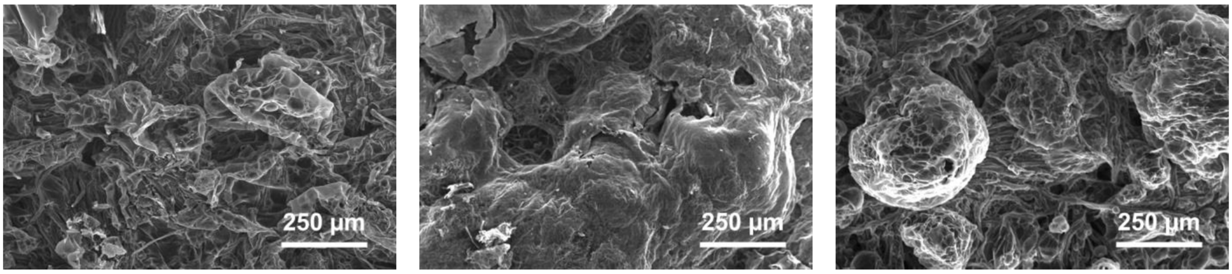
CF_CAS$_{15\%}$-APP$_{2.5\%}$ CF_CAS$_{15\%}$-APP$_{5\%}$ CF_CAS$_{15\%}$-APP$_{7.5\%}$

Figure 5.22. Photographs of burnt uncoated and CAS-APP bilayer coated cotton fabrics after flame test

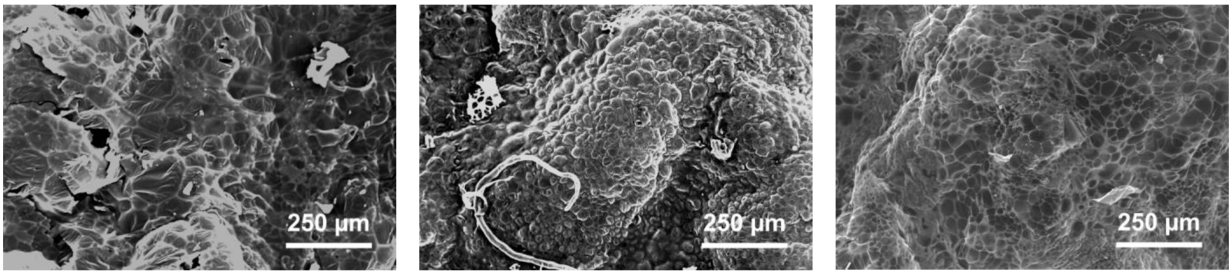
These results indicated the formation of additional char residues by the catalytic dehydration of CAS in the presence of APP, and thus the potential use of casein protein as a carbonization agent (carbon source) in intumescent systems. The greater char expansion by the release of more volatile gases (such as ammonia gas) can be validated from the observation of more bubbles in the case of higher APP contents [140, 143, 323]. Furthermore, the greater expansion of char during burning could also be attributed to the contribution of casein protein behavior as a blowing agent [217, 272]. Therefore, the CAS-APP based intumescent systems can be considered effective and efficient as the casein protein could perform a number of functions such as catalyzed dehydration, accelerated charring, and intumescent char formation.



(a) CF_CAS$_{5\%}$-APP$_{2.5\%}$ (b) CF_CAS$_{5\%}$-APP$_{5\%}$ (c) CF_CAS$_{5\%}$-APP$_{7.5\%}$



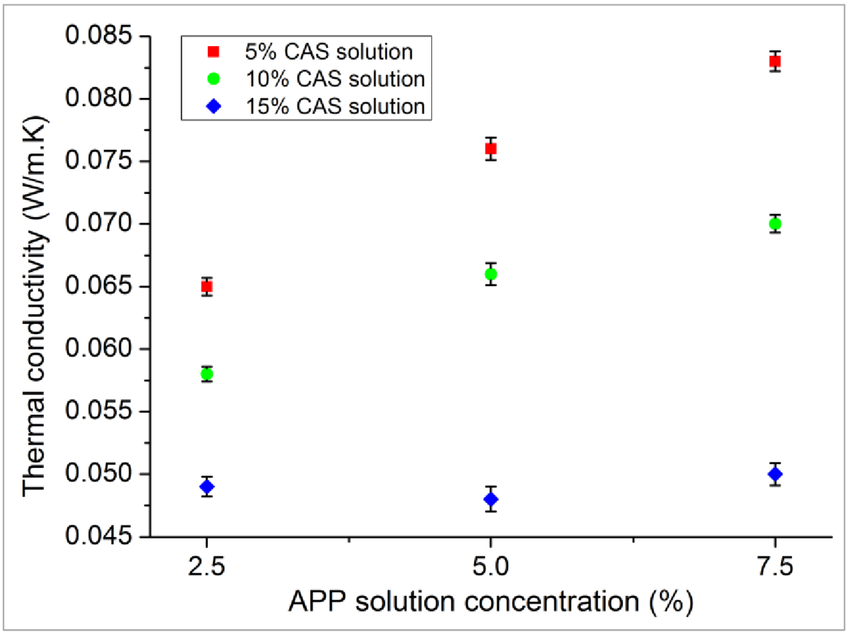
(d) CF_CAS$_{10\%}$-APP$_{2.5\%}$ (e) CF_CAS$_{10\%}$-APP$_{5\%}$ (f) CF_CAS$_{10\%}$-APP$_{7.5\%}$



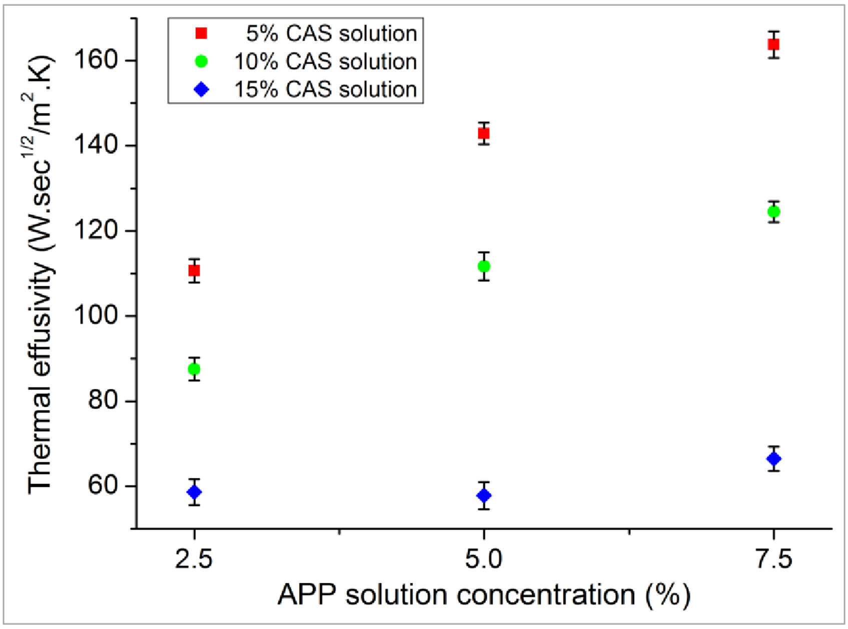
(g) CF_CAS$_{15\%}$-APP$_{2.5\%}$ (h) CF_CAS$_{15\%}$-APP$_{5\%}$ (i) CF_CAS$_{15\%}$-APP$_{7.5\%}$

Figure 5.23. SEM magnifications of char residues of burnt CAS-APP bilayer coated cotton fabrics

As the ultimate objective of an intumescence coating is the creation of a structurally stable and highly porous insulative material (tumescent/cellular/expanded/layered char) on the substrate's surface that limits heat transfer and/or heat diffusion to slow down the substrate's degradation. The thermal performance of an intumescence char is determined by its insulation characteristics, which basically depend on its structure. If the structure of char (i.e., the morphology and distribution of pores/voids inside the char) is appropriate, the thermal conductivity of intumescent chars is very low [135], [324–327]. On these bases, furthermore, to validate the formation of voluminous char after the flame test due to the burning of CAS-APP bilayer coated cotton fabrics, the heat transmission characteristics of the residual chars were measured by using the thermal conductivity instrument (TCi). The results obtained from the analysis were the values of thermal effusivity (heat penetration coefficient) and thermal conductivity of residual chars. It can be seen from Figure 5.24(a), (b) that the thermal conductivity and thermal effusivity values of residual chars of burnt bilayer coated fabric samples reduced with an increase in CAS concentration for either any constant APP concentration in the bilayer assemblies. The lower values of thermal conductivities and thermal effusivities were attributed to the formation of a greater amount of thicker, more porous, and more coherent intumescent chars. On the contrary, the residual chars of burnt fabric samples coated with low CAS concentration for either any fixed APP concentrations in bilayer assemblies depicted higher values of thermal conductivity and thermal effusivity. The relatively higher values of thermal conductivities and thermal effusivities were ascribed to the formation of a comparatively lesser amount of thinner, less porous, and less coherent intumescent chars.



(a) Thermal conductivity



(b) Thermal effusivity

Figure 5.24. Heat transmission characteristics of char residues of burnt CAS-APP bilayer coated cotton fabrics

5.3.5 Radiant heat resistance

The thermal performance of uncoated and CAS-APP bilayer coated cotton fabrics, as thermal resistance and/or protection against radiant heat, was estimated by exposing the cotton fabric samples to a radiant heat source at the specified incident heat flux density (Q_o). The rise of temperature was computed at the back of fabric samples by a calorimeter, which resulted in; two threshold times (namely radiant heat transfer indexes), i.e., time for the rise of 12°C ($RHTI_{12}$) and time for the rise of 24°C ($RHTI_{24}$), transmitted heat flux density (Q_c) and heat transmission factor (TFQ_o), as listed in Table 5.9.

Table 5.9. Radiant heat resistance parameters of uncoated and CAS-APP bilayer coated fabrics

Sample	**Q_0 (kW/m^2)**	**$RHTI_{12}$ (sec)**	**$RHTI_{24}$ (sec)**	**$RHTI_{24}$-$RHTI_{12}$ (sec)**	**Q_c (kW/m^2)**	**TFQ_0 (%)**
CF_uncoated	40	3.8±0.04	6.7±0.05	2.9±0.04	23.10±0.37	57.76±0.92
CF_$CAS_{5\%}$-$APP_{2.5\%}$	40	6.1±0.05	9.6±0.04	3.5±0.04	19.12±0.25	47.80±0.63
CF_$CAS_{5\%}$-$APP_{5\%}$	40	6.4±0.07	10.1±0.09	3.7±0.05	18.18±0.27	45.45±0.68
CF_$CAS_{5\%}$-$APP_{7.5\%}$	40	6.6±0.04	10.5±0.04	3.9±0.07	17.06±0.31	42.66±0.77
CF_$CAS_{10\%}$-$APP_{2.5\%}$	40	6.5±0.08	10.3±0.05	3.8±0.04	17.60±0.21	44.01±0.53
CF_$CAS_{10\%}$-$APP_{5\%}$	40	6.7±0.07	10.7±0.05	4.0±0.05	16.47±0.22	41.17±0.56
CF_$CAS_{10\%}$-$APP_{7.5\%}$	40	7.0±0.05	11.2±0.09	4.2±0.04	15.55±0.16	38.86±0.41
CF_$CAS_{15\%}$-$APP_{2.5\%}$	40	6.9±0.08	11.0±0.05	4.1±0.05	15.99±0.21	39.99±0.53
CF_$CAS_{15\%}$-$APP_{5\%}$	40	7.3±0.07	11.7±0.08	4.4±0.08	15.06±0.29	37.64±0.72
CF_$CAS_{15\%}$-$APP_{7.5\%}$	40	7.7±0.04	12.4±0.04	4.7±0.09	14.04±0.26	35.10±0.65

The lower values of Q_c were noted for cotton fabric samples coated with CAS-APP bilayer assemblies as compared to that uncoated cotton fabric. Correspondingly, an equivalent pattern was perceived in TFQ_o values, dropping from 57.8% to 35.1% for the cotton fabric samples bilayer coated with different concentrations of CAS and APP. The reduction in Q_c and TFQ_o was due to an increase in the values of $RHTI_{12}$ and $RHTI_{24}$ indexes and their difference ($RHTI_{24}$ - $RHTI_{12}$). The higher values of radiant heat transmission indexes and their difference, for the cotton fabrics coated with the different compositions of CAS-APP bilayer assemblies, as compared to the uncoated cotton fabric, emphasized that the temperature rise over time happened at a lower rate, signifying the delayed exchange of radiant heat towards calorimeter, i.e., the slower transmission of radiant heat. The increased values of $RHTI_{12}$, $RHTI_{24,}$ and ($RHTI_{24}$ - $RHTI_{12}$) indexes were assigned to the thicker bilayer coatings due to the higher add-on of the different compositions of CAS-APP assemblies [278–280], blocking of the spaces/interstices between the cotton fibers and yarns as verified from the SEM micrographs (see Figure 5.19). These larger values of ($RHTI_{24}$ - $RHTI_{12}$) for CAS-APP bilayer coated fabric samples were recognized for the reason that the infrared radiations which performed a germane part in the heat transference were also absorbed by CAS-APP bilayer coatings of different compositions. Due to this, these CAS-APP bilayer coatings provided improved thermal resistance and insulation. That might be helpful to prevent the wearer from acquiring burn injuries. Synchronously, a reduction in the value of transmitted heat flux density, i.e., the lower quantity of transmitted radiant heat, is also deemed advantageous for the textile substrate, resulting in its later on slower burning, as also revealed from the flammability test results of CAS-APP bilayer coated cotton fabrics (see Table 5.8). More precisely, it was deduced that the resistance of CAS-APP bilayer coatings to a radiant heat flux could also intensely reduce the time to ignition of bilayer coated fabrics as compared to the uncoated cotton fabric. This was attributed to the degradation/decomposition of casein and ammonium polyphosphate to release phosphoric acid exerting a deleterious effect that sensitizes the early ignition of cotton fabric and favors the cellulose dehydration to yield more thermally stable char residues instead of volatile release [175, 320]. This detrimental effect by intuition, and additionally, the catalyzed charring of casein and cotton cellulose in the presence of ammonium polyphosphate, could be extremely favorable to produce more char residues with an intumescence phenomenon, as a protective layer in advance at early thermal degradation stages, resulting in ineffective combustion of cotton due to the constricted diffusion of oxygen into the pyrolysis zone and also inhibiting the further release of volatile species at higher temperatures [110, 111].

5.4 Flame retardant and intumescent char formation potentials of casein and polyvinyl alcohol based bicomponent composite nanoparticles coated cotton fabrics

5.4.1 Surface chemical structure

The chemical/molecular structure, of cotton fabric (CF) samples, was inspected by the ATR-FTIR spectroscopy to confirm the competence of different composition electrospray coatings and the existence of CAS and PVA on the cotton fabrics. The ATR-FTIR spectra, of uncoated cotton fabric and cotton fabric samples electrospray coated with CAS/PVA blended solutions of different compositions, are given in Figure 5.25. Apart from the typical vibration modes of cellulose viz. υ(OH) at ca. ~3300, υ(CH_2) at ~2900, δ(OH) at ~1640, δ(CH_2) at ~1425, δ(CH) at ~1370, δ(OH) at ~1310, υ(C–C) at ~1020, υ(OH) at ~894 cm^{-1}, etc. [268, 269], the electrospray coated cotton fabrics showed the additional peaks for the presence of CAS and PVA. As, the characteristics bands, in infrared spectra for proteins and polypeptides, include amide I (due to the stretching vibrations of C=O) and amide II (due to the bending vibrations of N–H) bands, resulting from the amide bonds that connect the amino acids. Therefore, the two other peaks, situated at 1624 and 1528 cm^{-1}, were substantially attributed to the respective vibrations of amide I and amide II groups of casein [268, 270, 271]. Whereas, a broader band observed around 3340 cm^{-1} and a peak at 1096 cm^{-1} were credited to the stretching vibration of (–OH) (due to the inter- and intra- hydrogen bonding) and (C–O) of PVA respectively. The vibration band observed at 2942 and 2910 cm^{-1} were linked to the stretching (C–H) from alkyl groups and the peaks at 1735 and 1245 cm^{-1} due to the stretching (C=O) and (C–O–C) from the remaining acetate groups [328, 329]. The shifting of the abovementioned peaks/bands depicted the hydrogen bond interactions between the functional groups of cotton cellulose, casein protein, and polyvinyl alcohol polymers. Furthermore, an increase and/or a decrease in the intensity/height of the peaks indicated the deposition of higher and/or lower amounts of CAS and PVA in the form of CAS/PVA nanoparticles on cotton fabrics electrospray coated with CAS/PVA blended solutions of different compositions, which was also demonstrated by the spectra of these cotton fabrics showing the weak characteristic signals of cellulose.

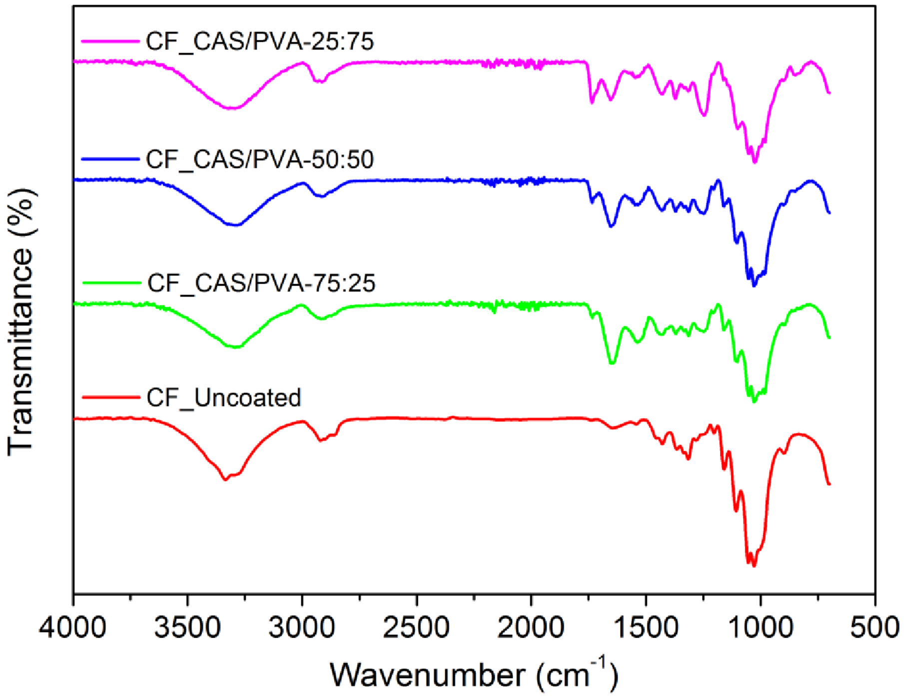
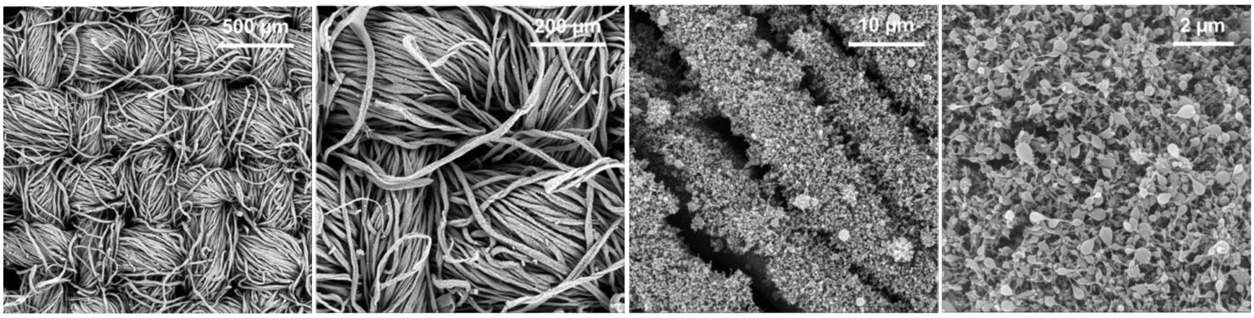


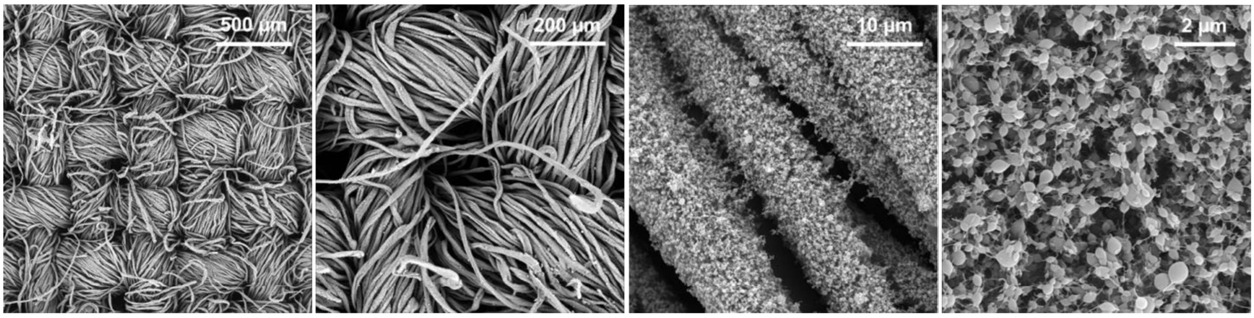
Figure 5.25. ATR-FTIR spectra of uncoated and CAS/PVA electrospray coated cotton fabrics

5.4.2 Surface morphology

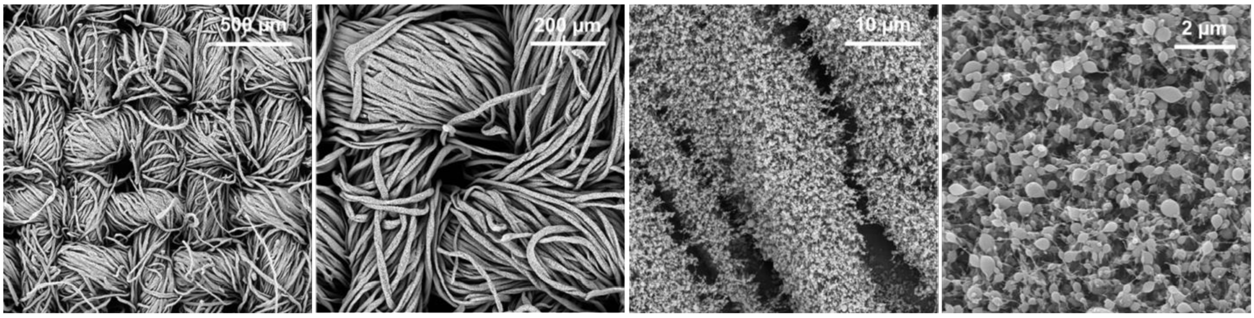
The scanning electron microscopy generated information referring to the morphology of CAS/PVA electrospray coated cotton fabric samples. The distinctive SEM images of cotton fabrics electrospray coated with CAS/PVA blended solutions of different compositions are shown in Figure 5.26. It was revealed from the SEM images that the uniform distribution of CAS/PVA nanoparticles as very fine layers/coatings, on the surface of cotton fabrics, was achieved through the electrospraying coating technique. A continuous, homogeneous, and coherent coating of CAS/PVA nanoparticles was clearly observed on the fibers/yarns of electrospray coated cotton fabric samples with CAS/PVA blended solutions of different compositions. The CAS/PVA nanoparticles presented better compatibility with cotton fibers as was verified by the absence of voids/cracks on surface coatings. Moreover, the CAS/PVA nanoparticles coated cotton fabric samples exhibited distinct individual cotton fibers, without blocking inter- and/or intra- fiber and/or yarn spaces/pores. This was an indication of probable, a less stiffening of fabrics' structure, and thus, a lower deterioration in the wearing comfort and mechanical properties of cotton fabrics after electrospray coatings. Additionally, the SEM images were also precisely observed and analyzed on "Image J" software, to measure the average particle size [228]. The homogeneity (regularity in shape) and the average size of CAS/PVA nanoparticles was found to increase with an increase in the ratio/amount of PVA [330].



(a) CAS/PVA-75:25 nanoparticles coated cotton fabric (average particle size = 314.6±73.5 nm)



(b) CAS/PVA-50:50 nanoparticles coated cotton fabric (average particle size = 346.4±71.2 nm)

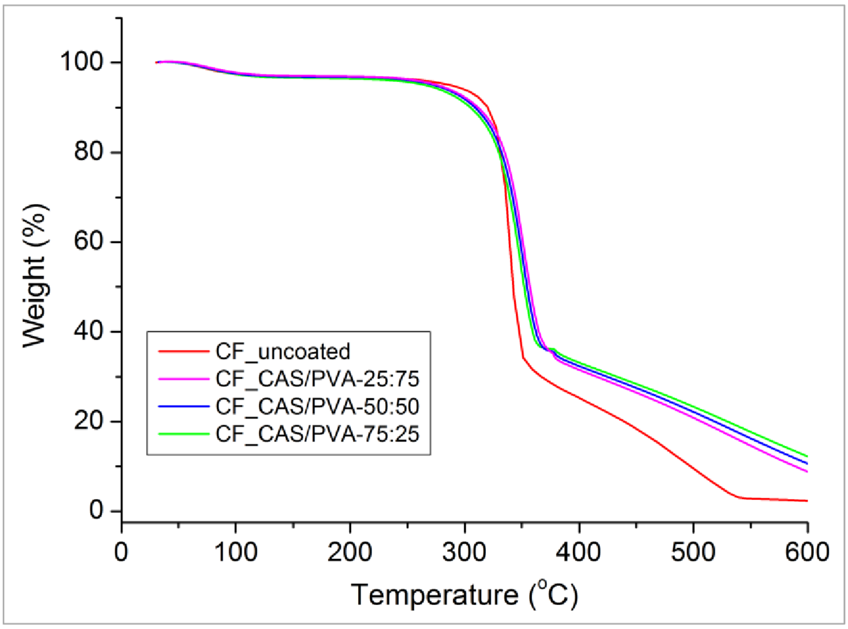


(c) CAS/PVA-25:75 nanoparticles coated cotton fabric (average particle size = 373.5±77.6 nm)

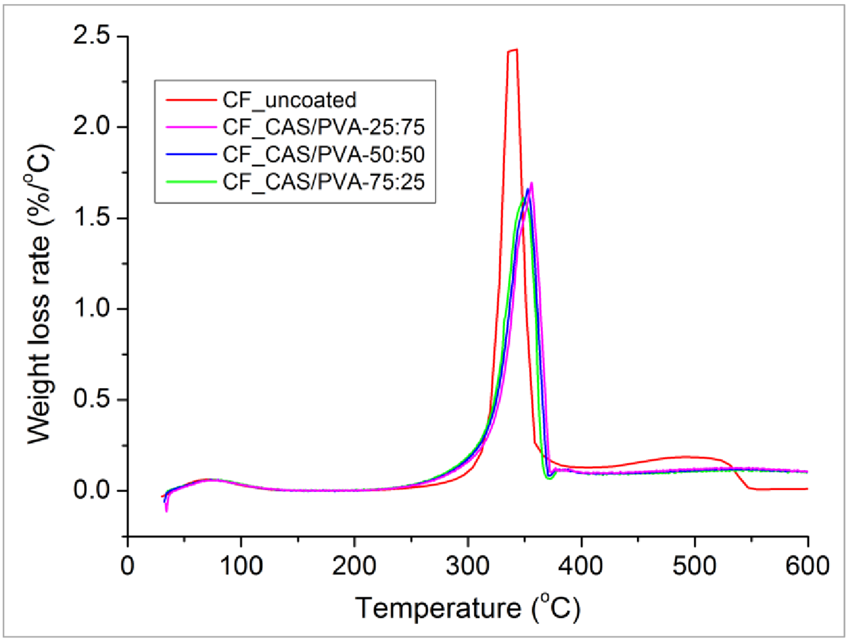
Figure 5.26. SEM images of CAS/PVA electrospray coated cotton fabrics

5.4.3 Thermo-oxidative stability

The thermogravimetric analysis was conducted to determine the effect of CAS/PVA nanoparticles' coatings on the thermo-oxidative stability of cotton fabrics. The plots of TG and DTG curves of all fabric samples were charted, as shown in Figure 5.27, which represents the weight loss and weight loss rate with an increase in the temperature. The wide range of characteristics data acquired from the testing results were also wrapped up, as given in Table 5.10, which presents the different decomposition temperatures and residue percentages of uncoated and CAS/PVA nanoparticles coated cotton fabric samples.



(a) TGA curves plot



(b) DTG curves plot

Figure 5.27. Thermo-oxidative stability of uncoated and CAS/PVA electrospray coated cotton fabrics

All fabric samples indicated an initial mass loss in the ~50-150°C region that was imputable to the evaporation of free/residual water contained by the cotton and casein protein and polyvinyl alcohol polymers. In fact, the pure proteins generally flinch to decompose at low temperatures ~100°C to lose the water [217, 272], accompanying to produce oligopeptides and amino acids that bear carboxylic groups and possess the ability to catalyze the decomposition of cellulose. It can be noticed that the thermal degradation of all samples consists of two steps, i.e., 200-400°C and 400-600°C. The decomposition of uncoated cotton fabric was started at 298°C and then the maximum weight loss rate (T_{max1}) was observed at 343°C in the first degradation step. The residue percentage after the first degradation step at T_{max1} was attributed to the formation of a thermally stable form of aliphatic char due to the depolymerization and dehydration of cellulose. Nevertheless, on a further increase of temperature, the second maximum weight loss rate appeared at 492°C (T_{max2}) during the second degradation step, which corresponded to the carbonization of aliphatic char into aromatic char and then further oxidation into carbon mono (CO) and dioxide (CO_2) [69].

Table 5.10. Thermo-oxidative stability data of uncoated and CAS/PVA electrospray coated cotton fabrics

Sample	$T_{onset10\%}$ (°C)	T_{max1} (°C)	T_{max2} (°C)	Residue at T_{max1} (wt. %)	Residue at T_{max2} (wt. %)	Residue at 600°C (wt. %)
CF_uncoated	320.11±0.51	343.33±0.23	492.17±0.45	48.1±0.3	11.3±0.4	2.3±0.3
CF_CAS/PVA-25:75	311.67±0.64	355.65±0.31	523.25±0.57	50.3±0.5	16.2±0.3	8.9±0.4
CF_CAS/PVA-50:50	308.18±0.73	352.40±0.27	530.13±0.65	52.8±0.4	18.5±0.4	11.1±0.3
CF_CAS/PVA-75:25	304.61±0.59	348.49±0.34	537.83±0.71	55.5±0.5	21.1±0.4	13.4±0.5

The $T_{onset10\%}$ values of cotton fabric samples were noted to shift towards the lower temperatures when coated with CAS/PVA nanoparticles of different compositions. The effect was observed more prominent in shifting the $T_{onset10\%}$ value for the CAS/PVA electrospray coated fabric sample containing CAS/PVA nanoparticles with a higher amount of CAS with respect to PVA. This indicated a stronger performance of casein for sensitization of the cellulose decomposition as compared to polyvinyl alcohol. In spite of these findings, the initial decomposition temperature (T_{max1}), of cotton fabric samples coated with CAS/PVA nanoparticles of different compositions, was also changed and descried to shift toward the higher temperatures as compared to that of uncoated cotton fabric. This phenomenon was related to the reason that when PVA is heated, above decomposition temperature, it commences a quick chain stripping and elimination of water. This process, couples with melting, causes the material, to foam or intumesce as it decomposes, to yield insoluble rigid foam-like residues [331]. Therefore, in the first stage, the thermal degradation of cellulose and polyvinyl alcohol also resulted in; producing the polyene structures through dehydration, as well as, forming the three-dimensional crosslinked structures by degradation products of cellulose and polyvinyl alcohol via conjugated bond formation [332, 333]. Such crosslinked structures (in the form of foam or intumesce) enveloped the cotton fibers/yarns and showed enhanced thermal stability by preventing the degradation/decomposition of cotton fabrics, causing the shift of degradation temperatures to higher ones [333]. Most of these polyene structures also served as intermediate species and were further reacted/degraded into other lower molecular weight products in the next degradation step T_{max2} to form residues as char [331, 334, 335]. In the thermal degradation process, these crosslinked structures are usually formed and destroyed simultaneously. The percentage of residue at T_{max2} and 600°C was found to increase for the CAS/PVA electrospray coated cotton fabrics, but higher for the CAS/PVA electrospray coated fabric sample containing CAS/PVA nanoparticles with a greater amount of CAS with respect to PVA. This comportment was imputed to the dehydration of glycosyl units of the cotton cellulose due to the release of acidic species such as phosphoric acids from the casein macromolecules [175, 217, 272]. The fabric sample electrospray coated with nanoparticles from CAS/PVA-75:25 blended solution compositions produced a maximum of 13.4% residue at 600°C as compared to that of 2.3% of uncoated cotton fabric.

5.4.4 Flame retardancy

The effect of different composition CAS/PVA nanoparticles' coatings on the flame retardancy of cotton fabrics was evaluated through flammability tests, i.e., limiting oxygen index (LOI) and horizontal configuration flame spread tests. The LOI value of 18.3% was obtained for the uncoated cotton fabric. Nonetheless, the LOI values were recognized to improve notably with the increased amount of CAS with respect to PVA, for the cotton fabric samples electrospray coated with the different compositions of CAS/PVA blended solutions, as given in Table 5.11. This was accredited to the enhanced char residue yields of electrospray coated cotton fabrics owing to the higher deposited phosphorous content (see Figure 5.28) [276, 310, 311], as also revealed from the TGA results provided in Table 5.10, which acted as an effective thermal insulating barrier to hinder the transfer of heat and fuel and stop the combustion process.

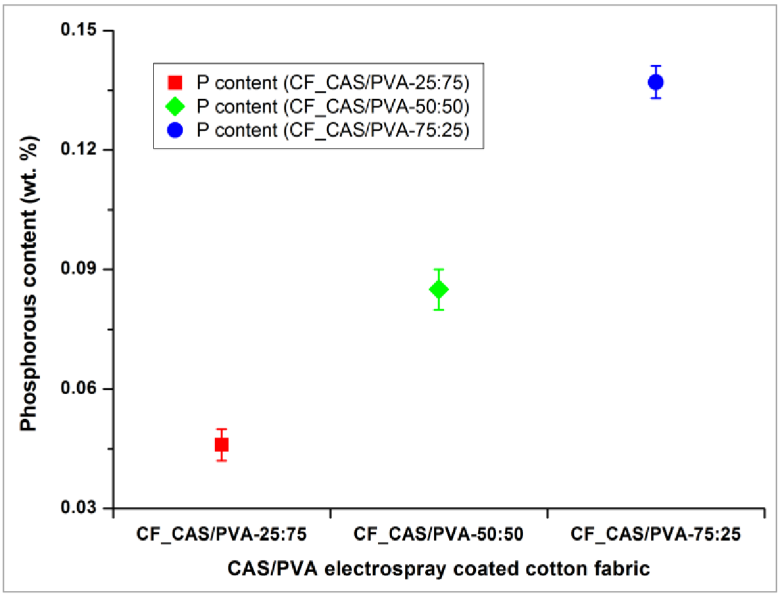


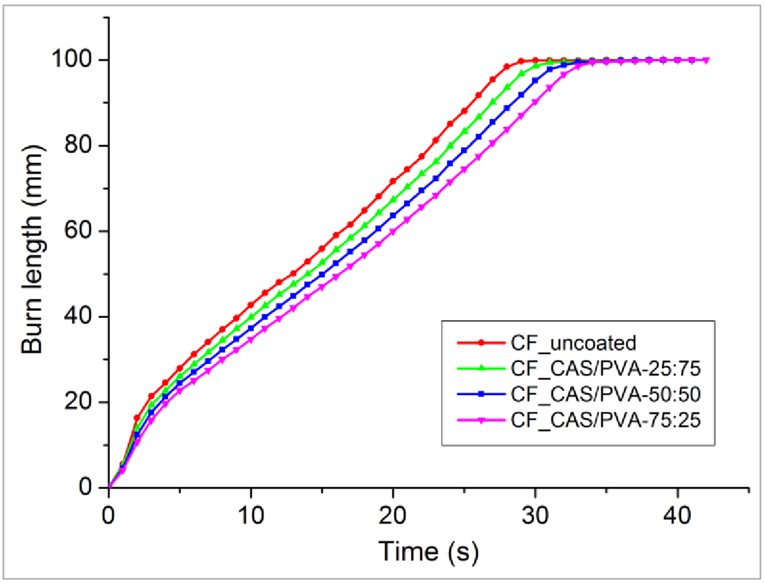
Figure 5.28. Phosphorous content of CAS/PVA electrospray coated cotton fabrics

In general, an increased LOI value usually results in lower combustibility and better flame-retardant properties of any polymeric materials including textile materials/substrates [66, 276], which was evidenced from the horizontal flame test results such as; the total burning time, burn rate and char residues of uncoated and CAS/PVA nanoparticles coated cotton fabrics, as presented in Table 5.11. These observed different parameters were then used to appraise the resistance for flame propagation. When a methane flame was applied for the specified time, it was noted that the uncoated cotton fabric expressed fast combustion and burnt vigorously. It was completely burnt, leaving behind a negligible amount of char residue. Contrarily, the coatings of CAS/PVA nanoparticles on cotton fabrics were observed to facilitate an increase in total burning time, thus exhibiting their ability for flame protection. The electrospray coated samples burnt at a slower rate and resulted in stronger char residues while preserving the original structure of the fabrics. Furthermore, the produced char exerted a protective effect on the underlying cotton fabric, limiting the oxygen diffusion, avoiding the formation of combustible volatile products, and absorbing the heat evolved during the combustion. The increase of total burning time and decrease in burn rate, as well as, consistent final char residues was noticed for the CAS/PVA nanoparticles coated cotton fabric samples as compared to that of uncoated cotton fabric, as validated from the flame retardant characteristics results given in Table 5.11. The 14% increase in total burning time, as well as, 33.7% final residue was found for the fabric sample electrospray coated with nanoparticles from CAS/PVA-75:25 blended solution compositions.

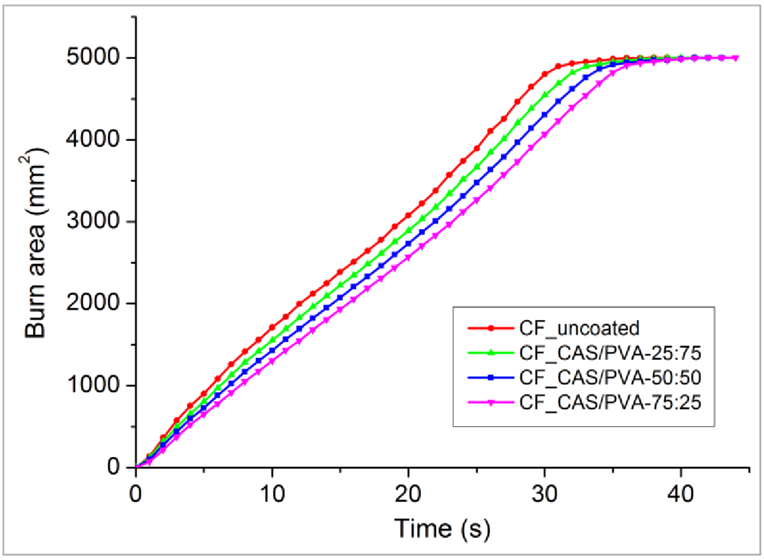
Table 5.11. Flammability characteristics of uncoated and CAS/PVA electrospray coated cotton fabrics

Sample	**LOI**	**Total burning time**	**Burn rate**	**Char residue**
	(vol. %)	**(s)**	**(mm/s)**	**(%)**
CF_uncoated	18.28±0.22	36.21±0.25	3.63±0.04	3.1±1.1
CF_CAS/PVA-25:75	19.11±0.27	38.13±0.31	3.37±0.03	14.8±1.7
CF_CAS/PVA-50:50	20.05±0.30	39.54±0.27	3.17±0.04	24.1±2.1
CF_CAS/PVA-75:25	21.13±0.25	41.25±0.33	2.95±0.05	33.7±1.8

On the whole, it is can be deduced that the casein contributed to improving both the flame suppression and char formation, while, the polyvinyl alcohol assisted more in thermal stability at early stages of fire pyrolysis by diluting the flame and improving the char formation at high temperature (as also evident from the TGA results) of CAS/PVA nanoparticles coated cotton fabrics. However, the flame retardant effectiveness of casein macromolecules was accredited to the phosphate groups located on the shell of casein micelles. These phosphate groups, upon heating, release phosphoric acids that favor the degradation of cellulose towards the formation of a stable char, through dehydration instead of depolymerization [175, 217, 272]. Whereas, the char formation effectiveness of polyvinyl alcohol was attributed to some fundamental condensed phase processes during its fire like pyrolysis. These processes involve the chain-stripping elimination of water and chain-scission reactions, which take place during its pyrolysis and lead to char formation [331], [334–337]. The dynamics of flame propagation were also calculated using the image analysis technique. It was conducted to identify the changes in burn length and burn area over small intervals of time. The effect of different composition CAS/PVA nanoparticles' coatings on the flame propagation dynamics (i.e., burn length and burn area) of cotton fabrics can be perceived from Figure 5.29(a), (b). Rendering to this assay, the burn length and burn area plotted curves for the CAS/PVA electrospray coated cotton fabric samples demonstrated a lesser steepness as compared to that for uncoated cotton fabric. Furthermore, the steepness of curves was also observed to decrease with an increase in CAS contents with respect to PVA contents. From these results, it was endorsed, a slow propagation/spread of the flame for the CAS/PVA nanoparticles coated fabrics and an improvement in self-extinguishing properties could be perceived for the cotton fabrics electrospray coated with higher CAS contents.



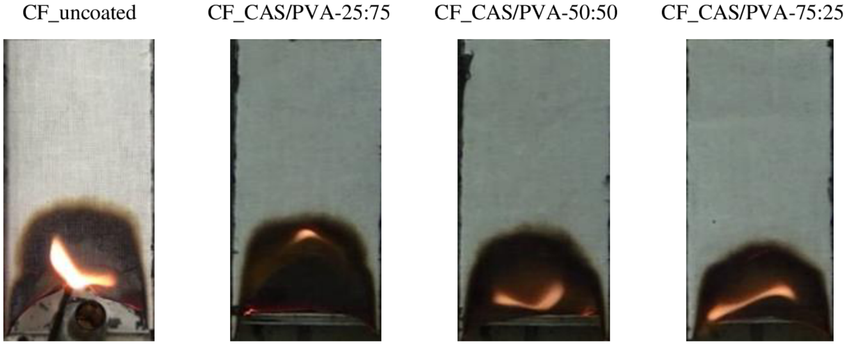
(a) Burn length



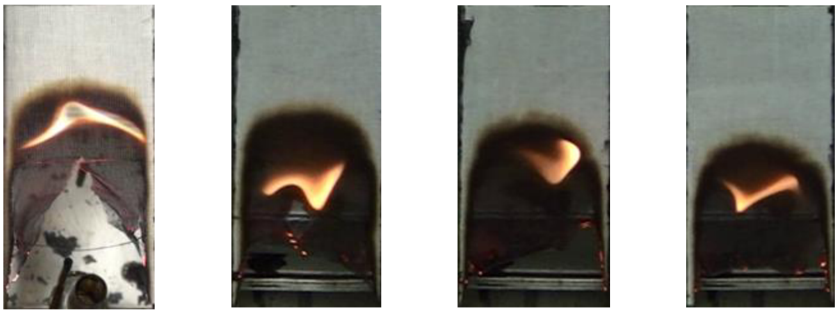
(b) Burn area

Figure 5.29. Plots for estimation of flame propagation with time from image analysis data

The fabric sample electrospray coated with nanoparticles from CAS/PVA blended solution compositions containing a greater amount of CAS with respect to PVA exhibited about lower burn length and lower burn area value as compared to the uncoated cotton fabric as well as to those electrospray coated with nanoparticles from CAS/PVA blended solution compositions containing a lower amount of CAS with respect to PVA. This was further verified from the photographs of carbonized areas of all fabric samples as shown in Figure 5.30, which were taken after 10, 20, 30, and 40 seconds of the burning time.

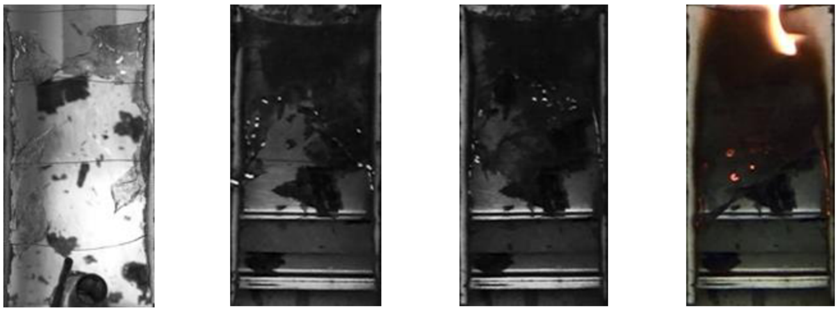


After 10 seconds time interval



After 20 seconds time interval

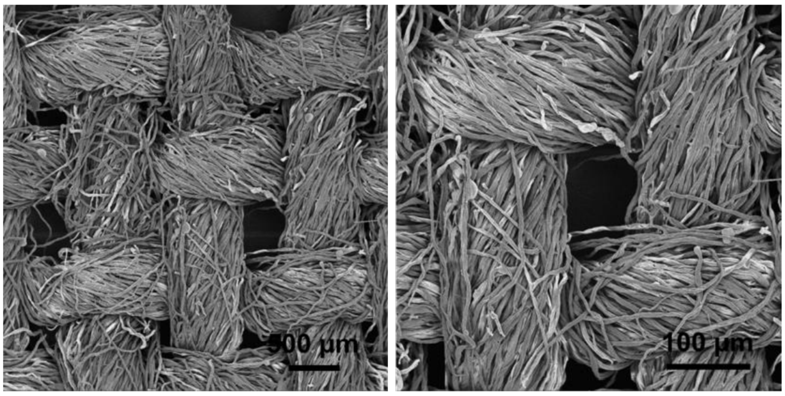
After 30 seconds time interval



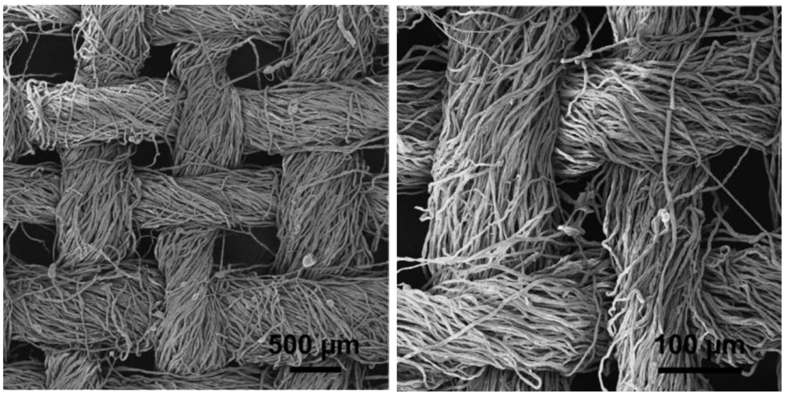
After 40 seconds time interval

Figure 5.30. Photographs of burnt uncoated and CAS/PVA electrospray coated cotton fabrics at different time intervals during flame test

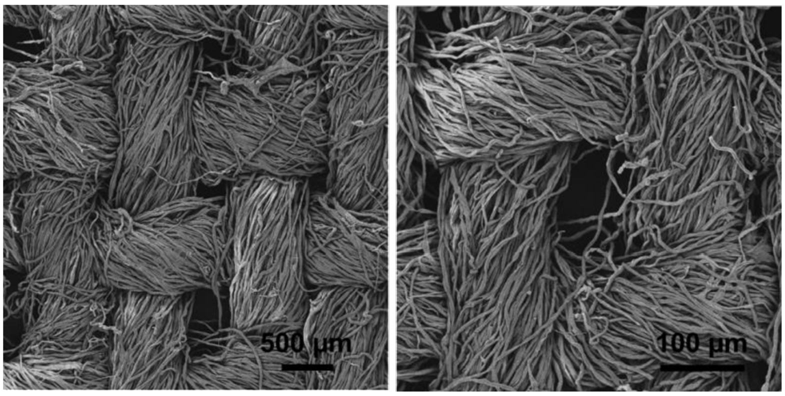
Thenceforth, the morphology of char residues, of burnt CAS/PVA electrospray coated cotton fabrics after the flammability test, was also reconnoitered through scanning electron microscopy, which can be observed from the SEM images as given in Figure 5.31. It revealed the preservation of the original structure of all the burnt CAS/PVA electrospray coated cotton fabric samples in the form of stable and consistent char, which was corroborated by the SEM images.



(a) CAS/PVA-75:25



(b) CAS/PVA-50:50



(c) CAS/PVA-25:75

Figure 5.31. SEM magnifications of char residues from burnt CAS/PVA electrospray coated cotton fabrics

A higher amount of mechanically strong and coherent char was observed for the burnt samples of cotton fabrics electrospray coated with CAS/PVA nanoparticles of different compositions. The morphology of char residues showed the formation of globular micrometric structures at localized spaces. Therewithal, the char residues of cotton fabric electrospray coated with CAS/PVA blended solution containing higher casein contents indicated the formation of more globular micrometric structures (i.e., local intumescence). The globular micrometric structures are phosphorus-rich bubbles that blow up during combustion [175]. The occurrence of bubbles in the residues was attributed to the evolution of ammonia, released by the casein macromolecules upon heating [217, 272, 277].

5.4.5 Radiant heat resistance

The thermal protection demeanor of uncoated and CAS/PVA electrospray coated cotton fabrics, as thermal resistance and/or protection against radiant heat, was estimated by exposing the cotton fabric samples to a radiant heat source at the specified incident heat flux density (Q_o). The rise of temperature was computed at the back of fabric samples by a calorimeter, which resulted in; two threshold times (namely radiant heat transfer indexes), i.e., time for the rise of 12°C ($RHTI_{12}$) and time for the rise of 24°C ($RHTI_{24}$), transmitted heat flux density (Q_c) and heat transmission factor (TFQ_o), as listed in Table 5.12. A drop in Q_c values was discerned for cotton fabric samples coated with CAS/PVA nanoparticles of different compositions as compared to that of uncoated cotton fabric. Subsequently, a similar pattern was perceived in TFQ_o values, dropping from 57.8% to 49.2% for the cotton fabric samples electrospray coated with the different compositions of CAS/PVA blended solutions.

Table 5.12. Radiant heat resistance parameters of uncoated and CAS/PVA electrospray coated cotton fabrics

Sample	**Q_0 (kW/m^2)**	**$RHTI_{12}$ (sec)**	**$RHTI_{24}$ (sec)**	**$RHTI_{24}$-$RHTI_{12}$ (sec)**	**Q_c (kW/m^2)**	**TFQ_0 (%)**
Uncoated	40	3.8±0.04	6.7±0.05	2.9±0.04	23.10±0.37	57.76±0.92
CAS/PVA-25:75	40	4.3±0.05	7.7±0.04	3.3±0.05	19.92±0.32	49.81±0.81
CAS/PVA-50:50	40	4.4±0.07	7.8±0.05	3.4±0.05	19.80±0.31	49.53±0.80
CAS/PVA-75:25	40	4.5±0.07	7.9±0.04	3.5±0.04	19.69±0.27	49.21±0.66

The reduction in Q_c and TFQ_o was due to an increase in the values of $RHTI_{12}$ and $RHTI_{24}$ indexes and their difference ($RHTI_{24}$ - $RHTI_{12}$). The higher values of radiant heat transmission indexes and their difference, for the cotton fabrics coated with CAS/PVA nanoparticles of different compositions, as compared to the uncoated cotton fabric, accentuated that the temperature rise with reference time resulted in a lower rate, specifying the deferred exchange of radiant heat towards calorimeter, i.e., the slower transmission of radiant heat. The increased values of $RHTI_{12}$, $RHTI_{24,}$ and ($RHTI_{24}$ - $RHTI_{12}$) indexes were apportioned to the CAS/PVA nanoparticles' coatings//layers of different compositions [338, 339], causing to covering partially and/or reducing, as well as, homogenizing the sizes of larger interstices (i.e., spaces and/or voids) between the cotton fibers and yarns as confirmed from the SEM micrographs (see Figure 5.26).

These larger values of ($RHTI_{24}$ - $RHTI_{12}$) for the CAS/PVA electrospray coated fabric samples were indorsed for the reason that the infrared radiations which performed an apropos part in the heat transference were also absorbed by the CAS/PVA nanoparticles' coatings/layers. Due to this the CAS/PVA nanoparticles' coatings/layers provided improved thermal resistance and insulation. That might be helpful to prevent the wearer from acquiring burn injuries. Concomitantly, a reduction in the value of transmitted heat flux density, i.e., the lower quantity of transmitted radiant heat, is also reckoned valuable for the textile substrate, resulting in its later on slower burning, as also revealed from the flammability test results of CAS/PVA electrospray coated cotton fabrics (see Table 5.11). More correctly, it was reasoned that the resistance of CAS/PVA nanoparticles' coatings/layers to a radiant heat flux could also radically reduce the time to ignition of electrospray coated fabrics as compared to the uncoated cotton fabric. This can be credited to the degradation/decomposition of casein to release phosphoric acid exerting a deleterious effect that sensitizes the early ignition of cotton fabric, and favors the cellulose dehydration to yield more char residues instead of volatile release [175]. This detrimental effect by perception, as well as, the three-dimensional crosslinked structures (in the form of foam or intumesce) formed by thermal degradation products of cellulose and polyvinyl alcohol, could be enormously beneficial to produce more char residues [332, 333], as a protective layer in advance at early thermal degradation stages, resulting in ineffective combustion due to the restricted diffusion of oxygen into the pyrolysis zone and also inhibiting the further release of volatile species at higher temperatures.

5.4.6 Physiological comfort and mechanical properties

The air permeability, water vapor permeability, thermal conductivity, stiffness/bending rigidity, tensile and tear testing, of uncoated and CAS/PVA electrospray coated cotton fabrics, was executed to determine properties connected with physiological comfort and mechanical performance, as discussed in the following sections.

Air permeability

Figure 5.32(a) shows the effect of CAS/PVA nanoparticles' coatings, electrosprayed from blended solutions of different compositions, on the air permeability of cotton fabrics. The air permeability of uncoated cotton fabric was quantified ~620.05 $l.m^{-2}.s^{-1}$. However, it can be seen that there is no substantial drop in the air permeability of CAS/PVA electrospray coated cotton fabrics. This behavior was explicated by the formation of CAS/PVA nanoparticles' coatings/layers on the surface of cotton fabric samples, which partially covered the interspaces between the fibers and yarns, unlike the other traditional coating methods [340, 341]. A little obstruction in airflow through these fabrics was accredited to, the reduced size of inter-fiber and inter-yarn spaces/pores by the coatings of CAS/PVA nanoparticles [342, 343].

Water vapor permeability

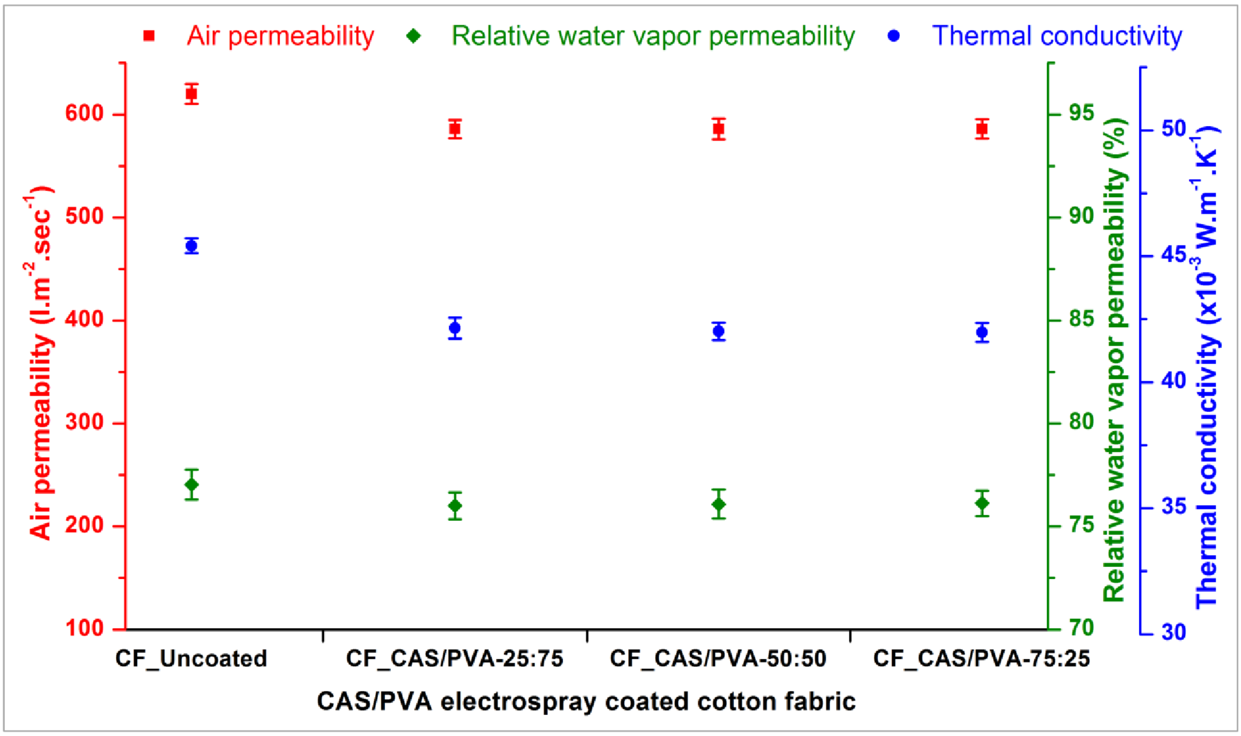
Figure 5.32(a) shows the effect of CAS/PVA nanoparticles’ coatings, electrosprayed from blended solutions of different compositions, on the relative water vapor permeability of cotton fabrics. The relative water vapor permeability of uncoated cotton fabric was quantified ~77.04 %. As well, the air permeability, an analogous trend of CAS/PVA nanoparticles’ coatings, was also noticed for the water vapor permeability. The moisture vapor transport properties of cotton fabrics were less affected after that of the CAS/PVA electrospray coatings [224, 341]. A slight loss of moisture vapor transport, for the cotton fabrics electrospray coated with CAS/PVA nanoparticles from the blended solutions of different compositions, was conceded due to; the deposited CAS/PVA nanoparticles’ coatings/layers on the surface of cotton fabric samples, and eventually partial closing or minimizing the size of inter-fiber and intra-yarn spaces [342, 344].

Thermal conductivity

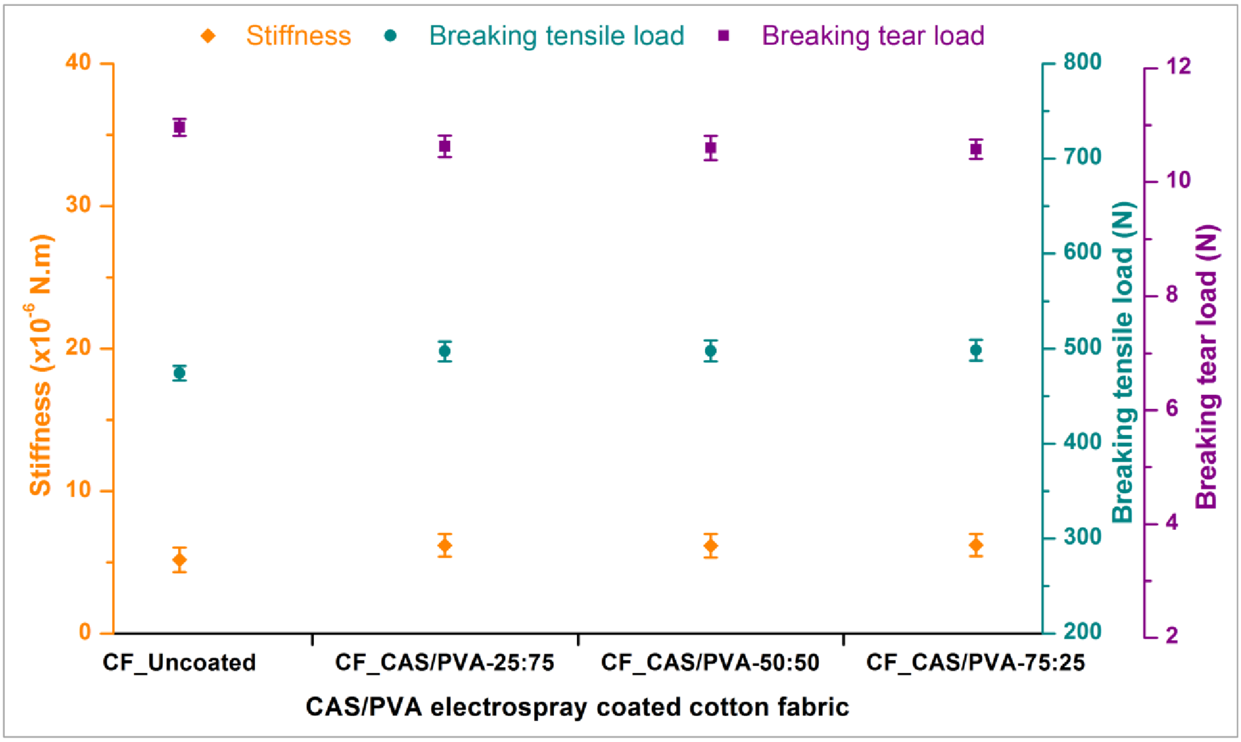
Figure 5.32(a) shows the effect of CAS/PVA nanoparticles’ coatings, electrosprayed from blended solutions of different compositions, on the thermal conductivity of cotton fabrics. The thermal conductivity of uncoated cotton fabric was quantified ~45.42x10^{-3} W.m^{-1}.K^{-1}. It was analyzed a reduction in the thermal conductivity of CAS/PVA electrospray coated cotton fabrics. This comportment was elucidated by the deposition of CAS/PVA nanoparticles’ coatings/layers on the surface of cotton fabric samples [339], ultimately partially blocking the interspaces between the fibers and yarns. As, the nanoparticles' coatings/layers typically possess a higher surface area to volume ratio, ensuing a highly porous structure [345]. Perhaps, in addition to the effect of partial covering the interspaces between the fibers and yarns by CAS/PVA nanoparticles’ coatings/layers, a reduction in the thermal conductivity, of CAS/PVA electrospray coated cotton fabrics, might be due to the supplemental contribution and/or the effect of the entrapped air inside the characteristic pores of the coating/layer structure of CAS/PVA nanoparticle [341, 344].

Stiffness

Figure 5.32(b) shows the effect of CAS/PVA nanoparticles’ coatings, electrosprayed from blended solutions of different compositions, on the bending properties of cotton fabrics. The stiffness value of uncoated cotton fabric was quantified ~5.17x10^{-6} N.m. It was examined that the stiffness of CAS/PVA electrospray coated cotton fabric samples increased a trivial. This could be correlated with the deposition of CAS/PVA nanoparticles over the cotton fabric structure that built the links/bonds between the fibers and/or yarns due to the gluing and binding properties of casein and polyvinyl alcohol [300, 346], heightening the inter-fiber/yarn friction at the fibers/yarns cross-over points (i.e., restraining the free movement of fibers/yarns) and letting the fabric difficult to bend [342, 343, 347].



(a) Air permeability, water vapor permeability, thermal conductivity



(c) Stiffness, tensile strength, tear strength

Figure 5.32. Comfort and mechanical properties of uncoated and CAS/PVA electrospray coated cotton fabrics

Tensile properties

Figure 5.32(b) shows the tensile testing results and the effect of CAS/PVA nanoparticles' coatings, electrosprayed from blended solutions of different compositions, on the tensile breaking force (tensile breaking load/stress in newton) of cotton fabrics. The value of the breaking tensile load for the uncoated cotton fabric was quantified ~474.18 N. Whereas, it was ascertained that the breaking tensile load for CAS/PVA electrospray coated cotton fabrics increased marginally. The increased breaking force can be explicated by a contribution of the load-bearing capacity [348], of attached CAS/PVA nanoparticles' coatings/layers on the surfaces of fibers and yarns in the fabric structure. This can also be recognized due to the reason that the CAS/PVA nanoparticles pierce into the fabric structure during their application on the cotton fabrics through the electrospraying method. Then the CAS/PVA nanoparticles partially cover the spaces between the fibers and yarns and bind them together, causing an increase in the bending rigidity and eventually the tensile breaking load of electrospray coated fabrics [348].

Tear Properties

Figure 5.32(b) shows the tear testing results and the effect of CAS/PVA nanoparticles' coatings, electrosprayed from blended solutions of different compositions, on the tear breaking force/tearing force (tear breaking load/stress in newton) of cotton fabrics. The value of breaking tear load for the uncoated cotton fabric was quantified ~10.96 N. Unalike the tensile testing results, it was ascertained that the tearing force for CAS/PVA electrospray coated cotton fabrics decreased slightly. The reduced tearing force can be explicated by an increase in cotton fabric rigidity after electrospray coatings of CAS/PVA nanoparticles, offering less resistance to an applied force for rupture/tearing. This can also be recognized due to the reason that the CAS/PVA nanoparticles impale the voids between the fibers and yarns during their application on the cotton fabrics through the electrospraying method. Subsequently, the CAS/PVA nanoparticles situate in the fabric structure and intervene with fiber-to-fiber and yarn-to-yarn interactions by binding them, causing a reduction of their free movement and sliding, as well as, the flexibility of fabric structure [348]. When the yarns are bonded together at a place in the fabric structure, the tearing force applied on individual yarns one at a time, results in a lower tearing force value.

5.5 Washing durability and crosslinking of casein with cotton fabrics

The casein treatments to cotton fabrics were determined to impart flame retardancy by suppressing flame propagation. As, the cotton fabric treated with 30% casein concentration, exhibited improved flame retardant characteristics in terms of the total burning time (~48.4 s), burning rate (~2.34 mm/s), and char residue (~53.1 %) as compared to that of untreated cotton fabric. But, the casein films/layers/coatings on casein treated cotton fabrics were found not to be resistant and/or less durable to washing treatments. It was observed that these casein coatings went off in water from cotton fabrics when subjected to washing according to some specific standard test methods, instead, even in mild conditions washings; i.e., at a low temperature (30°C) for short cycles and with and/or without using any detergent. This could be due to the reason that the proteins usually bind to cotton fibers' surface through the van der waals forces and hydrogen bonding [349–353]. The chemical affinity of casein protein to cotton cellulose has been considered and adduced to be associated with the interactions between the hydrogen of hydroxyl groups of cellulose and the carboxylate groups as well as the peptide bonds of amino acids of casein [354, 355], as shown in Figure 5.33. In addition, the possible and propounded binding mechanism may also involve the carbohydrate-π interactions [356–358].

At present, various chemical substances belonging to different classes have been studied and used, for the self-crosslinking of molecular/polymeric chains of proteins [359–371], and also for the self-crosslinking of molecular/polymeric chains of cotton cellulose fibers [372–384], ultimately improving their different special kind of properties regarding the end-use applications. But in the literature, the present research studies and works on crosslinking/binding of proteins with textile substrates are very limited, especially that of casein protein with cellulosic-based cotton fabric (to make it durable to washing) has not been well attempted and explored yet. Correspondingly, the different chemical crosslinking/binding systems were conjectured as probable for crosslinking of casein (i.e., protein) to cotton (i.e., cellulose) as an after-/post-treatment finishing process for the casein treated cotton fabrics, simultaneously emphasizing an adequate balance of green features.

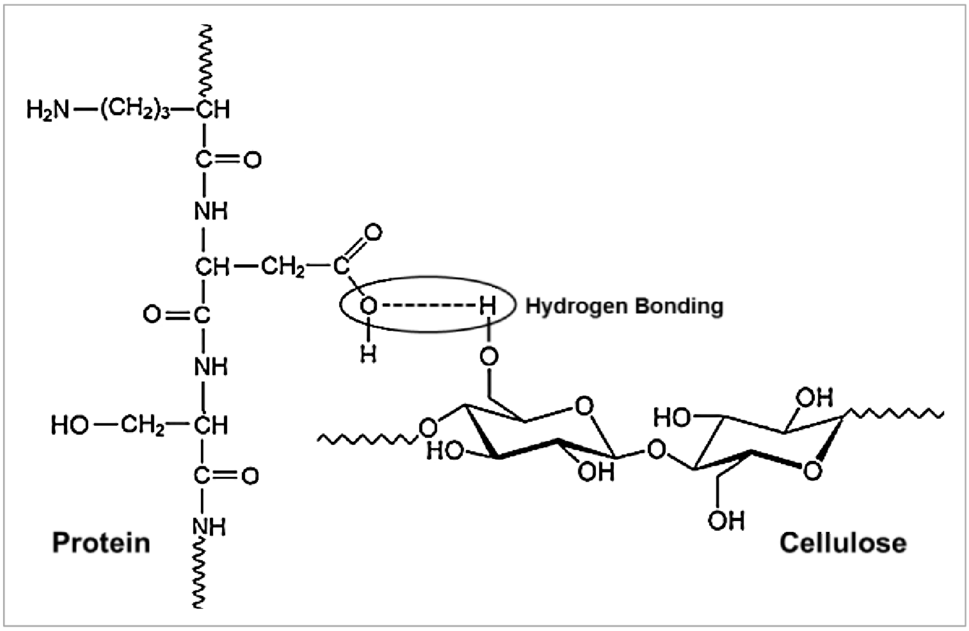
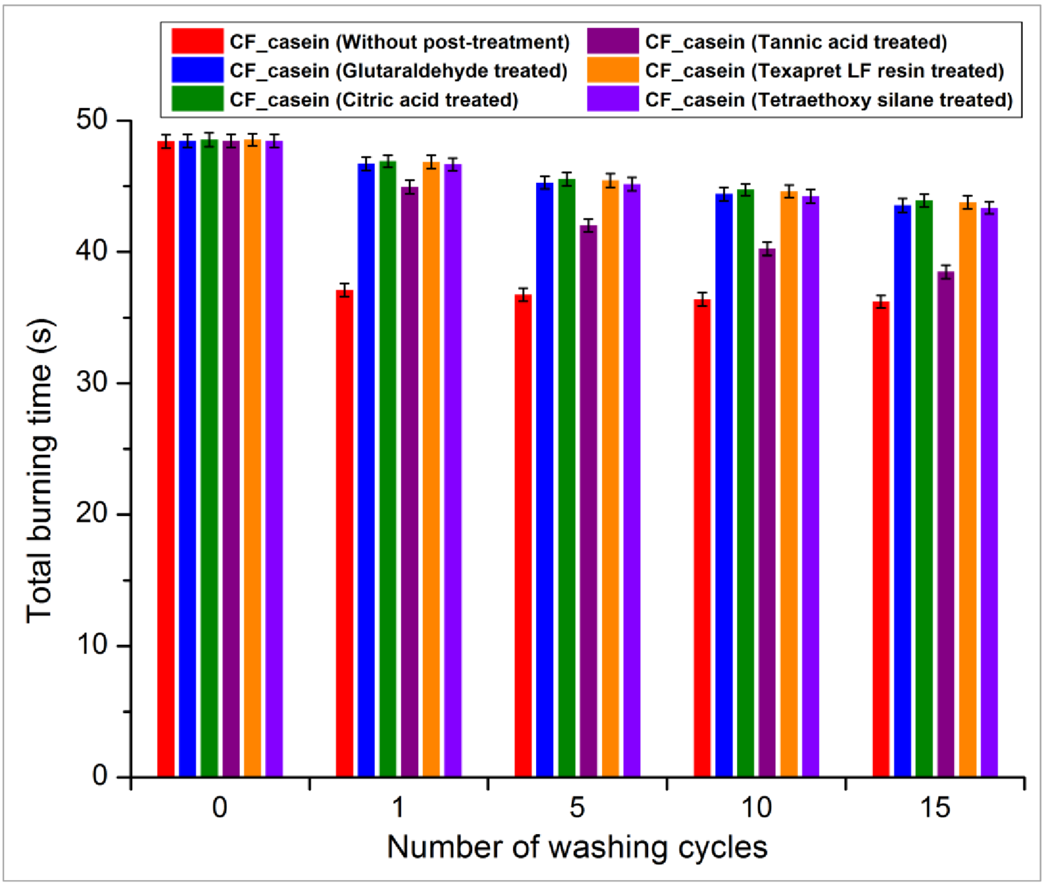


Figure 5.33. General mechanism of interaction between casein protein and cotton cellulose

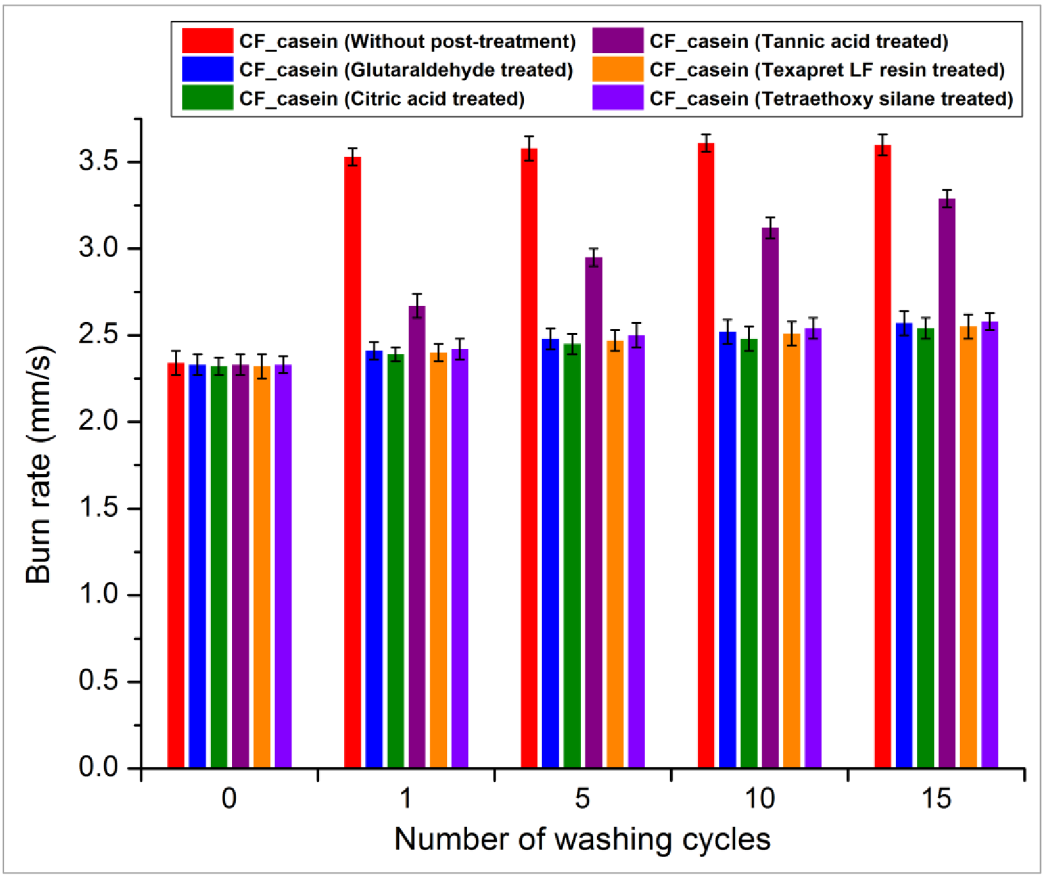
These different chemical crosslinking systems such as; glutaraldehyde (a dialdehyde), citric acid (a polycarboxylic acid), tannic acid (a polyphenol), Texapret LF (a resin), tetraethoxysilane (a silane), also their certain suitable and applicable application conditions were anticipated, due to their ability to react with the common functional groups present in the molecular/polymeric structure of casein and cotton.

Consequently, after post-treatment finishing of 30% casein concentration treated cotton fabric samples with 5% concentration of different types of crosslinking chemical agents, all fabric samples were washed/laundered according to the standard test method in order to examine the durability of casein coatings on cotton fabrics to multiple washing/laundering cycles. For this purpose the horizontal flame test was performed, for all untreated, treated, unwashed, and washed fabric samples, at zero wash cycle (i.e., before washing) and after 1, 5, 10 & 15 wash cycles (i.e., after washing), to assess the flame retardant performance. The different variables such as the total burning time, burn rate, and final char residues, for all fabric samples, were then noted and compared, as shown in Figure 5.34(a), (b), (c) respectively.

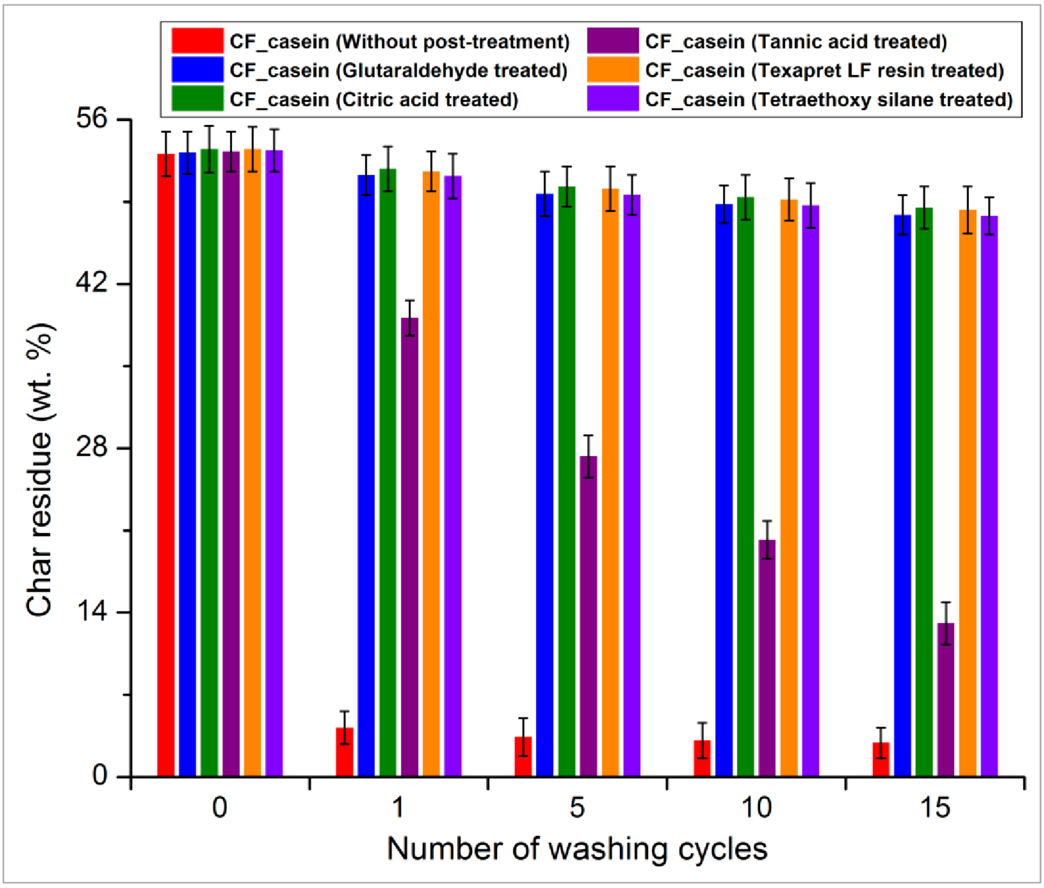
Though, the casein treated cotton fabric sample (i.e., without any post-treatment) was found to burn just like the untreated cotton fabric with very little char residues, even after one washing cycle. Nevertheless, it was distinctly evidenced from the obtained results that the different types of defined crosslinking systems were potentially substantiated to improve the washing durability of casein coatings on cotton fabrics. This improved phenomenon was varied comparatively up to certain washing/laundering cycles (see Figure 5.34(a), (b), (c)), relating to the chemical nature of crosslinking systems, and hence their crosslinking capability, at the specified and applied fixed concentration and application conditions.



(a) Total burning time



(b) Burn rate



(c) Char residue

Figure 5.34. Flammability characteristics of casein treated cotton fabrics after post-treatment finishing and washing

The possible crosslinking mechanisms and reactions of used chemicals, for enhancing the washing durability of casein coatings on cotton fabrics, are explained following.

The dialdehydes react with the hydroxyl (–OH) groups of cotton cellulose leading to the formation of hemiacetals/acetals through an acetylation reaction [377, 378]. Whereas, the dialdehydes react with the amino (–NH_2) and hydroxyl (–OH) groups of casein protein leading to the formation of; imine (Schiff base) through Schiff base reaction, and hemiacetal through acetylation reaction respectively, depending on the pH conditions of reaction [367, 385]. Therefore, the probable crosslinking interactions between cotton cellulose and casein protein in presence of glutaraldehyde can be considered, as illustrated in Figure 5.35.

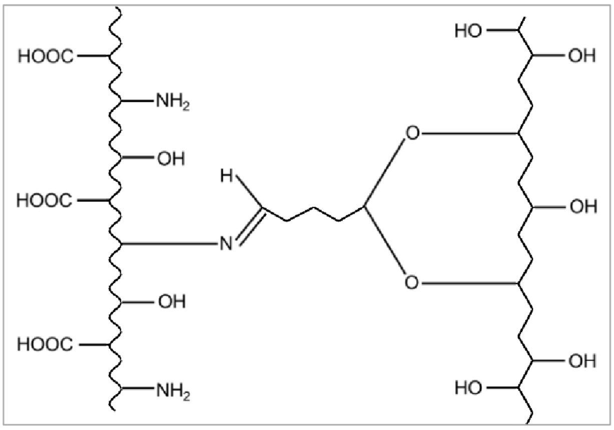


Figure 5.35. Schematic representation of crosslinking mechanism of casein protein with cotton cellulose using glutaraldehyde

The polycarboxylic acids form ester crosslinks with the hydroxyl (–OH) groups of cotton cellulose through an esterification reaction [386–389]. Whilst, the free amino (–NH_2) groups present in proteins undergo a nucleophilic substitution reaction with the carboxyl (–COOH) groups present in polycarboxylic acids to form a new amide linkage/bond through acylation reaction during this process [390, 391]. Therefore, the probable crosslinking interactions between cotton cellulose and casein protein in presence of citric acid can be regarded, as depicted in Figure 5.36.

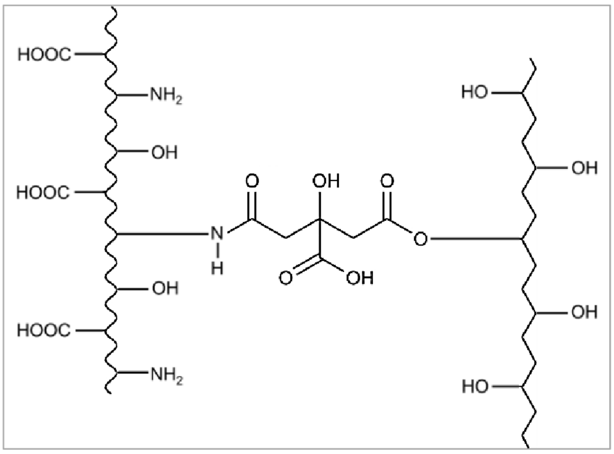


Figure 5.36. Schematic representation of crosslinking mechanism of casein protein with cotton cellulose using citric acid

The mechanisms of interaction between polyphenols (e.g., tannins) and macromolecules such as polysaccharides (e.g., cellulose) and/or proteins are primarily regulated by the noncovalent forces, involving the hydrogen bonding and hydrophobic interactions as well as the ionic interactions, van der Waals forces, and π-π stacking [392–399]. Withal, hydrogen bonding usually involves the polar groups of cellulose and proteins (i.e., amino, carboxyl, and hydroxyl groups) and the hydroxyl and carbonyl groups of polyphenols. While hydrophobic interactions typically comprise the nonpolar domains/regions of macromolecules and polyphenols molecules. Therefore, the probable crosslinking interactions between cotton cellulose and casein protein in presence of tannic acid can be speculated, as demonstrated in Figure 5.37.

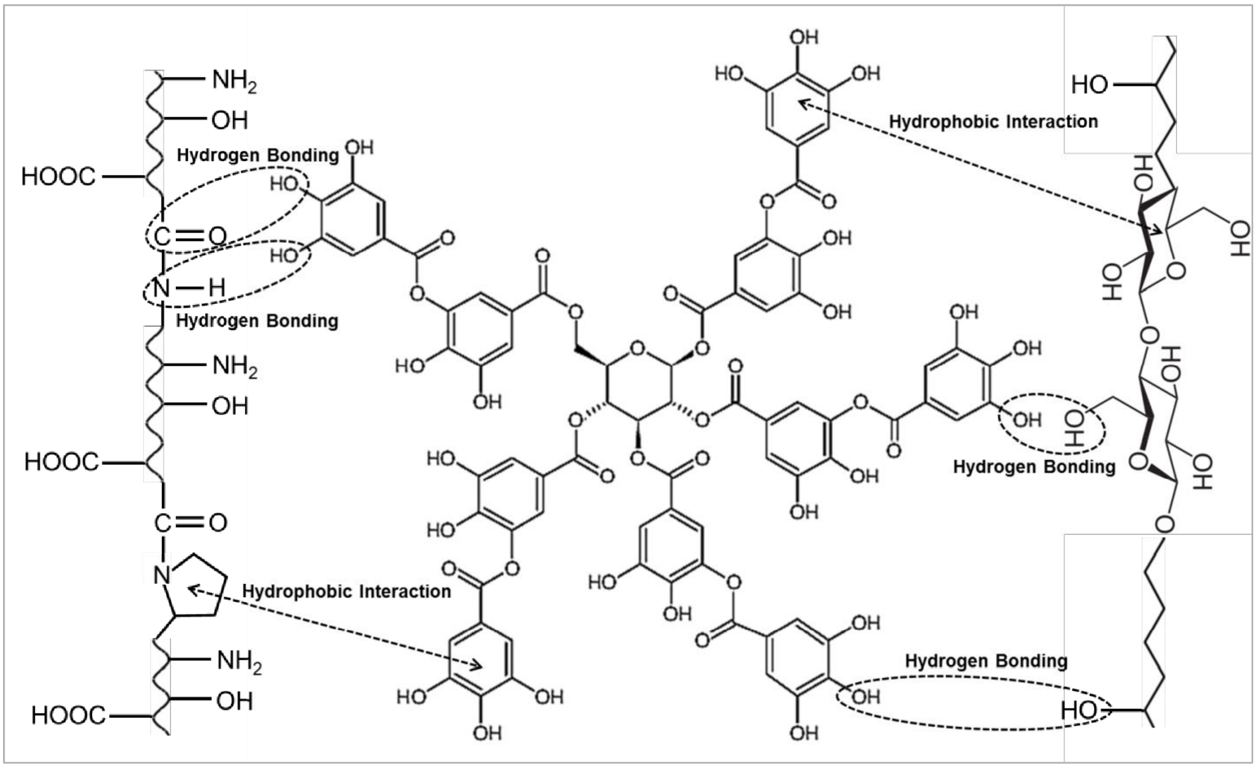


Figure 5.37. Schematic representation of crosslinking mechanism of casein protein with cotton cellulose using tannic acid

The principle crosslinking reaction of the N-methylol groups in DMDHEU (N,N’-dimethylol-4,5-dihydroxyethylene urea / 1,3-dimethylol-4,5-dihydroxyethylene urea) with cotton cellulose is an etherification of the hydroxyl (–OH) groups [153], [400–403]. Despite this, the DMDHEU can react and crosslink with the casein protein through an esterification reaction between the N-methylol groups of DMDHEU and the carboxyl (–COOH) groups of casein. In addition, the chemical reaction between the N-methylol groups of DMDHEU and the amino (–NH_2) groups of casein protein is also possible [353, 404, 405]. Therefore, the probable crosslinking interactions between cotton cellulose and casein protein in presence of DMDHEU-based resin (TEXAPRET LF resin) can be figured, as exhibited in Figure 5.38.

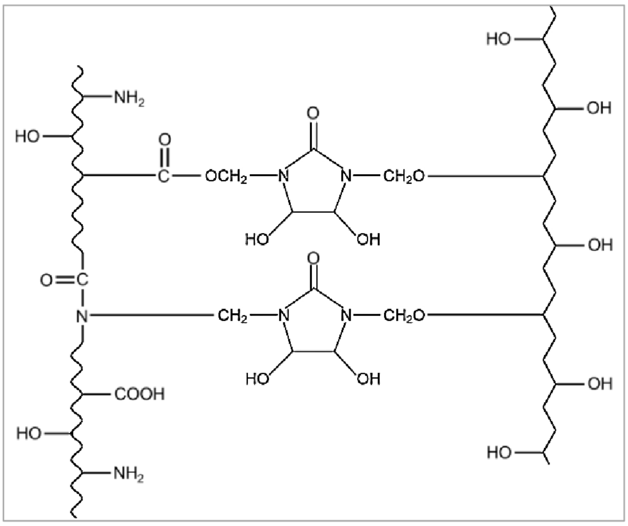


Figure 5.38. Schematic representation of crosslinking mechanism of casein protein with cotton cellulose using DMDHEU-based resin

The adsorption phenomenon of organosilanes/silanes (i.e., organoalkoxysilanes/alkoxysilanes) with cotton fibers ensues through the hydrogen bonding between the hydroxyl (–OH) groups of cellulose and the silanol (≡Si–OH) groups of prehydrolyzed alkoxysilanes first [406]. Finally, the heat treatment allows the water evaporation via a condensation reaction, which results in the formation of siloxane (≡Si–O–Si≡) bridges and the chemical grafting with cotton cellulose through (≡Si–O–C≡) covalent bonding [407–410]. Whilst, the adsorption behavior and reactivity mechanism of prehydrolyzed alkoxysilanes with proteins involve electrostatic attractions, hydrogen bonding, and hydrophobic interactions [411–413]. Then condensation reaction takes place upon heat treatment and releases water molecules in vapor form. The condensation reaction favors the generation of chemical grafting/covalent bonding (≡Si–O–Si≡ & ≡Si–O–C≡) between the silanol (≡Si–OH) groups of prehydrolyzed alkoxysilanes and the hydroxyl groups (–OH) and carboxyl (–COOH) groups of casein protein [414–417]. Therefore, the probable crosslinking interactions between cotton cellulose and casein protein can be deemed in presence of tetraethoxysilane (TEOS), as exemplified in Figure 5.39.

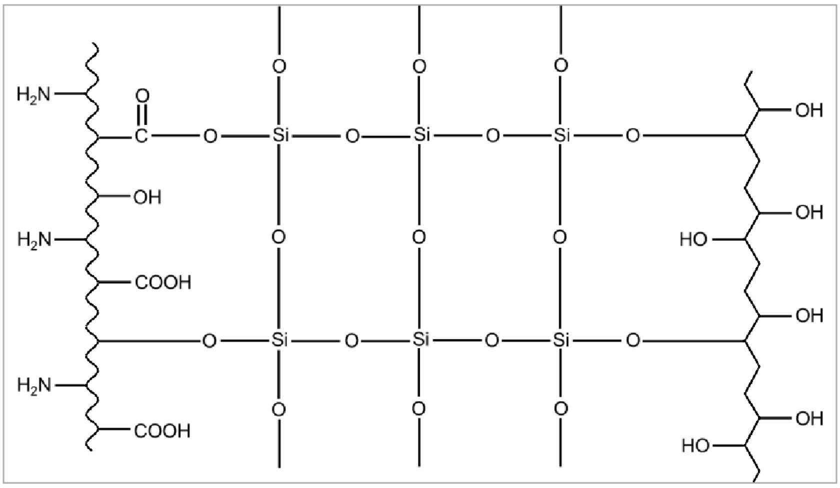


Figure 5.39. Schematic representation of crosslinking mechanism of casein protein with cotton cellulose using tetraethoxysilane

Chapter 6

CONCLUSIONS AND FUTURE PERSPECTIVES

This research work study was an endeavor to present an attractive solution for the valorization of the dairy industry by exploitation of its by-product or waste as green and environment-friendly flame retardant finishing material, i.e., a biopolymer; bovine milk casein (bovine milk protein; phosphoprotein) to impart flame retardancy to cotton fabrics. A detailed literature review was conducted on available literature about the subject matter. The literature review provided the necessary theoretical background, baseline data, and insights into related research work conducted in past as well as identified certain gaps and limitations. The objectives were crystallized to add to this knowledge base and also address the current state of the research problem. The broad objectives of this research work were; to contemplate flame retardant performance, char formation, and intumescence effect of casein for cotton fabrics, as well as, to explore the simultaneous conduct of their physiological comfort, mechanical performance, and washing durability accompanying flame retardancy and thermal properties. The certain different chemical crosslinking/binding systems were pursued to probe as an after-/post-treatment finishing process for the casein treated cotton fabrics for possible crosslinking of casein protein to cotton cellulose. Based on specific aims and objectives envisioned for this research work, casein was applied on cotton fabrics just as it alone and in combination with other environment-friendly materials for synergistic/hybrid effects through non-hazardous aqueous solvents/solutions and simple industrial applicable textile finishing techniques/methods. The output results data attained from characterization and testing were analyzed, interpreted, and discussed. On these bases, various significant information, interpretations, and inferences as well as considerable future viewpoints were deduced from this research work, which express its significant impacts.

The overall derived findings from this research work study are as follows:

Surface structure features

- The SEM images and ATR-FTIR spectra confirmed effective application and deposition as well as the presence of films/layers/coatings of casein-alkaline/acidic, casein-ammonium polyphosphate intumescent system, and casein/polyvinyl bicomponent composite nanoparticles on cotton fabrics.
- The films/layers/coatings were continuous, homogeneous, and coherent without the existence of any voids and/or cracks indicating better compatibility of casein protein and its synergistic/hybrid systems with cotton cellulose.

- The treatments of cotton fabrics with casein coatings through traditional padding and coating methods appeared to cover more interstices and/or pores between individual fibers and/or yarns within fabric structure eventually increasing fabric stiffness as compared to that with casein-based nanoparticles coatings through modernized electrospraying technique.

Thermal characteristics and flame retardant behavior

- The thermos-oxidative stability of casein-alkaline/acidic, casein-ammonium polyphosphate, and casein/polyvinyl alcohol finished cotton fabrics were ascertained to enhance, anticipating stronger sensitization of cellulose degradation/decomposition as well as favoring the formation of higher amounts of thermally stable residues (i.e., char) depending on treatments of cotton fabrics with casein alone or casein-based synergistic/hybrid systems, as revealed by higher residue percentages at the end of thermogravimetric analyses.
- The decrease in burn rates and flame stoppage time, as well as the increase in total burning times during flame tests, vindicated delayed flame propagation/spread for cotton fabrics finished with casein-alkaline/acidic, casein-ammonium polyphosphate intumescent system, and casein/polyvinyl bicomponent composite nanoparticles, producing larger amounts of char residues as well as exhibiting intumescence effects corresponding to treatments of cotton fabrics with casein alone or casein-based synergistic/hybrid systems, as also validated by image analysis data and justified by an increase in limiting oxygen index values.
- The flame retardant performance, limiting oxygen index, char formation, and intumescence effect were obtained higher for cotton fabrics finished with acidic casein solutions as compared to that finished with alkaline casein solutions.
- An intumescent flame retardant system based on casein in combination with ammonium polyphosphate as bilayer coatings was efficaciously constituted for cotton fabrics. Casein was determined as char forming and blowing agent when applied as bilayer coatings in combination with ammonium polyphosphate on cotton fabrics that were able to generate a voluminous char functioning as a thermal shield/barrier and self-extinguish the flame.
- An intumescent char-forming system based on casein in combination with polyvinyl alcohol as bicomponent composite nanoparticles coatings was adequately contrived for cotton fabrics. Polyvinyl alcohol was perceived as a high-temperature char-forming agent when deposited as bicomponent composite nanoparticles in combinations with casein (i.e., char-forming and blowing agent) on cotton fabrics that were capable to produce intumescent char operating as a thermal barrier and retard the flame propagation.

- The thermal resistance/insulation behavior (i.e., thermal protective performance), of casein-alkaline/acidic, casein-ammonium polyphosphate, and casein/polyvinyl alcohol finished cotton fabrics, was found to improve. The transmitted heat flux density and heat transmission factor were discerned to shift towards lower values for finished cotton fabrics as compared to that of control cotton fabric manifesting as protection against radiant heat as well as enhanced thermal protection phenomenon subjecting on treatments of cotton fabrics with casein alone or casein-based synergistic/hybrid systems.

Physiological comfort and mechanical properties

- As flame retardant textile finishing comprises the loss of physiological comfort and mechanical properties of textile fabrics. It is due to the reason, that at an industrial/production scale, the flame retardant chemicals/materials/finishes are usually applied to textile fabrics through traditional padding and coating methods and generally in higher amounts to attain the desired flame retardancy level. After application on fabrics, through impregnation or coating, the flame retardant chemicals/materials/finishes penetrate and/or coat the fibers/yarns, and then bind/crosslink the fibers/yarns, resulting in the blockage of inter- and intra- fiber/yarn interstices, and consequently the loss of physiological comfort and mechanical properties.
- The treatments of cotton fabrics with casein coatings through traditional methods were evinced to forfeit their physiological comfort and mechanical properties normally at higher add-on values of casein that were typically effective to induce higher flame retardancy accompanying slower flame propagation and greater amount of intumescent char residues.
- The treatments of cotton fabrics with casein-based nanoparticles through modernized electrospraying technique were recognized to establish an adequate viable balance between their thermal characteristics and flame retardant behavior, and, physiological comfort and mechanical properties.

Washing durability performance

- The casein coatings on casein finished cotton fabrics were not resistant and/or less durable to washing treatments even in mild conditions washings; i.e., at low temperatures for short cycles and with and/or without using any detergent.
- Washing durability was effectuated through post-treatments of casein treated cotton fabrics using certain suitable less toxic and/or environmentally friendly chemical agents conforming to different crosslinking/binding systems (such as phenols, aldehydes, carboxylic acids, resins, silanes).

The essence of this research work study is the possible potential flame retardant attributes provided by the bio-treatments/bio-applications along with their safety and environmental aspects. This appears to represent a robust starting point of ecological and economic interests for the development of flame retardant alternatives, which can replace partially/fully and affirm flame/fire rendition comparable to traditional/conventional environmentally-dangerous high-performing halogen-based or phosphorus-based synthetic flame chemicals/materials/finishes for textile materials. Significant achieved results as described above have clearly demonstrated that it is possible to expatiate techno-chemical features of casein protein toward the development of efficient green and eco-friendly flame retardant systems for cotton fabrics. Correspondingly, cotton fabrics finished with casein and casein-based synergistic/hybrid systems can be utilized in apparel/clothing, home furnishings, technical textiles, etc. The potentiality of biomass-based (bio-based, i.e., biopolymers; biomacromolecules) natural products in the field of flame retardants and/or flame retardancy is quite high although almost all discussed approaches in existent literature related to the subject matter still require more deep explorations. At present, there are certain limitations related to the development of efficient flame retardants based on all biopolymers comprising casein protein. However, the possibility of adjusting these green technologies to a large scale (semi-pilot, pilot, or industrial) is still under evaluation, depending on the cost-effectiveness of biopolymers. But there is no doubt about its potential and suitability to mature and commercialize this emerging technology for imparting flame retardancy to textile substrates, which can find application in various niche areas.

Even though bio-based natural materials/products have been studied and researched considerably in the recent decade still need to be further. This does not exclude the near future exploitation of biologically derived chemical treatments, or at least, of chemicals with a low environmental impact, which could make biopolymers more effectively efficient and durable than today. The ideas, experiments, results data, and deductions generated as part of this research work study have added to the knowledge domain that could be useful to define future work directions and provide insightful references for researchers. The probable potential of this research can be realized by pursuing to conduct further studies. Further research work studies may be devoted to exploring certain possible solutions for limitations keeping in mind that an acceptable balance between green features of naturally occurring biopolymers including casein protein and the use of other thermally stable and flame retardant synergistic/hybrid chemicals/materials/products (such as metal oxide and hydroxide, metal nanoparticles, carbon and silicon nanoparticles, graphene and graphene oxide, nano clays and fillers, nanoclays, etc.) for enhancing its flame retardant features for different kind of textile fabrics as well as for textile and/or polymer composites, films, and membranes.

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LIST OF PUBLICATIONS

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