

**POLITECNICO DI TORINO**

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**Master of Science Degree  
in Textile Engineering**

Master Thesis

**New hybrid sol-gel coating containing phytic acid as  
flame retardant system for cotton fabrics**



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## Abstract

In the present work, new hybrid sol-gel systems were designed and applied to cotton fabrics, in order to provide cotton with flame retardant features. In addition, the sol-gel system, obtained starting from an alkoxy precursor, namely tetraethoxysilane (TEOS), was modified by the addition of different amounts of phytic acid (PA), i.e. a by biomacromolecule rich in phosphorus. The first goal was to identify the TEOS-PA ratio that allowed achieving the best flame retardant properties, with the lowest total dry add-on on the fabrics. To this aim, different TEOS-PA sols were prepared and applied to cotton. In particular, it was found that a total dry add-on of 16 wt. % together with TEOS: PA ratio of 70:30 ensured self-extinction in both horizontal and vertical flame spread tests. Therefore, this formulation was further investigated in forced-combustion (i.e. cone calorimetry) tests, exposing the treated fabrics to an irradiative heat flux of 35 kW/m<sup>2</sup>. Untreated cotton and all the treated fabrics were thoroughly investigated as far as their morphology, thermal and thermo-oxidative stability are considered. Furthermore, the durability of the treated fabrics was assessed by means of washing cycles (4 cycles in distilled water at R.T.). It was found that the fabrics significantly lose their good fire performances, as a consequence of the partial washing out of the deposited hybrid coating. Finally, the coating deposition turned out to increase the stiffness of the fabrics, as assessed by tensile tests.

**KEYWORDS:** cotton, flame retardant, biomacromoleclues, phytic acid, TEOS, sol-gel treatment, washing durability, SEM analysis, thermal characterization.

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Author

Rozita Movaghar Zadeh

*“Patience is the key element of success”*

- Bill gates

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# Chapter 1: Introduction and Literature Review

## 1.1. Introduction

In the last century, polymeric materials and cellulosic textiles became one of the most universally used materials but also one of the most combustible. Cellulosic materials, like cotton, flax, hemp, show low fire resistance and burn easily. These materials at high temperature produce a wide range of volatile, organic compounds that are highly inflammable; exothermic oxidation of the volatiles occurs and the material burns.

A possible solution to enhance the level of fire safety of combustible materials is the use of flame retardant (FR) chemicals. They are not designed to hinder material from ignition but to minimize the rate of flame spread and to prevent sustained combustion. In the last decades, different FRs have been developed; these compounds may contain halogens (namely, chlorine and bromine), phosphorus, magnesium, nitrogen, aluminium, antimony, molybdenum, or recently developed nanofillers. In fact, halogen-based compounds are the most widely used FRs, but have been proved to be persistent, bioaccumulative, and/or environmentally toxic for animals and humans [1,2]. Recently, some studies have been carried out to develop possible alternatives solutions, represented by biomacromolecules like DNA and caseins. Thanks to their chemical structures and compositions, these biomacromolecules have shown effective flame retardant properties. In fact, it has been proved that, these phosphorus-based compounds can act in condensed phase by favoring the formation of stable aromatic char.

In this present study, new sol-gel coatings based on a novel green biomacromolecule (phytic acid) have been designed and applied to cotton fabrics in order to improve their flame retardant properties.

In this thesis, chapter 1 provides a general overview on cotton properties and on the sol-gel process, as well as introducing some biomacromolecules that have already been utilized in flame retardancy and finally describing the main analytical techniques used to characterize the treated fabrics in the present thesis work. Chapter 2 will detail the materials and methods used to perform the experiments. Chapter 3 will discuss the results obtained and finally, chapter 4 will report the main objectives achieved.

## 1.2. Cotton

Cotton can be considered as one of the most important commercial products of worldwide; it is generally recognized that, cotton is the most used cellulosic textile fiber in textile industry; due to the interesting and utilizable properties - comparable to synthetic fibers -such as comfort, softness, high absorbency of moisture, good color retention, machine washable and dry cleanable, good tensile strength as well as high wet strength and easily sewing and handling, Almost half of the world's requirement for textile fiber are met by cotton.

Cotton is a warm-weather plant that grows naturally in form of tree or shrub as an annual crop due to the commercial aims. In the both hemispheres it can be cultivated, mainly in North and South America, India, Asia, and Africa.

Naturally agricultural staple fiber "Cotton "originates as a single cell, elongated in the epidermis of the seed inside the boll. Once cotton plant becomes mature its boll will burst and leave the fibers (**Figure 1.1**). After 2 to 3 weeks the final length of fiber will generate.

Cotton bolls dehisce at maturity, leaving the fibers fully exposed to air and sunlight. The water content of the fiber decreases rapidly, by entering of the air to the open boll, the clean, white fiber will dry and soften ready for harvesting. Cotton production is very sufficient, in the sense that only ten percent or less of the weight is lost in subsequent processing to convert the raw cotton bolls (seed coat) into pure fiber.

Fibers (lint) are removed from the seeds mechanically by the "ginning" process. Then, a brushing-machine removes the linters.

The cotton linters are fine, silky fibers, which are traditionally used in the manufacture of paper and as a raw material in the production of high quality cellulose man-made fibers.



**Figure 1.1.** Mature cotton

### 1.3. Chemical composition of cotton

This paragraph describes the cotton fiber chemical composition and the relationship between fiber structure and cellulose synthesis, development of fiber and other chemical and structural feature (physical properties, thermal behavior.)

Cotton is known as purest source of cellulose once it has been processed to remove seeds (ginning) and traces of honeydew (a secretion from aphids), protein, vegetable matter, and other impurities (88-96% pure cellulose).

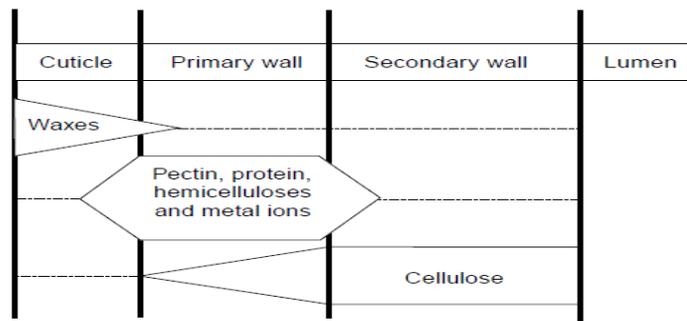
Cotton fiber is composed of primary wall, cuticle, secondary wall and lumen. Primary wall and cuticle contain nearly only 55% low molecular weight cellulose [3], conversely, secondary wall is the main cellulose source in nature.

Some studies have been shown that the inner microfibrils lattice of the cell wall (primary wall-cuticle), are arranged randomly and surrounded by a mixture of noncellulosic materials [4].

The noncellulosics are attributed to proteins (1.0–1.9%), wax (0.4–1.2%), organic acid, pectins (0.4–1.2%), sugars, inorganic salt (0.7–1.6%), and other nitrogen containing compound (0.5–8.0%) [5] , **Figure 1.2.**

These components in the cell wall give some advantages to the fiber surface, such as nonfibrillar appearance and also hydrophobic protection as well as lubricated fiber surface for further processing.

The cellulose content of cotton fiber can be increased up to 99% after removing naturally occurring noncellulosic materials by means of some special treatments such as scouring and bleaching. Another reason for cotton fiber purification (partial removal of waxy component) is that the uniform and quick absorbency of cotton fibers in many applications such as dye and finishing chemicals is essential, as they need to penetrate and access fiber's body; at variance, raw cotton exhibits slight water absorbency and water repellency due to these surface contaminants (specially waxes and pectins); therefore, the scouring process, during which hydrophobic waxes and dirt can be removed from fiber, is important. Other insoluble impurities such as proteins, pectins and ashes are solubilized and efficiently removed from cotton fiber in the alkaline scouring process.



**Figure 1.2.** Cellulosic and non- cellulosic materials in cotton fabric [6]

## 1.4. Cotton Structural Properties

### 1.4.1. Structure overview

The initial structure of a cotton fiber is determined by series processes referring to biosynthesis. The distinct steps involved in the development of cotton fiber cells are: initiation, elongation, secondary cell wall thickening and maturation and desiccation [7]. Elongation relates to the stage of structural development of cotton fiber during formation of primary wall. In the secondary cell wall thickening; cellulose synthesis will take place and during desiccation, formation of highly hydrogen-bonded structure occurs [8]. There are many factors that affect the structure, ranging from the weather before the fiber is harvested to processes in the industries.

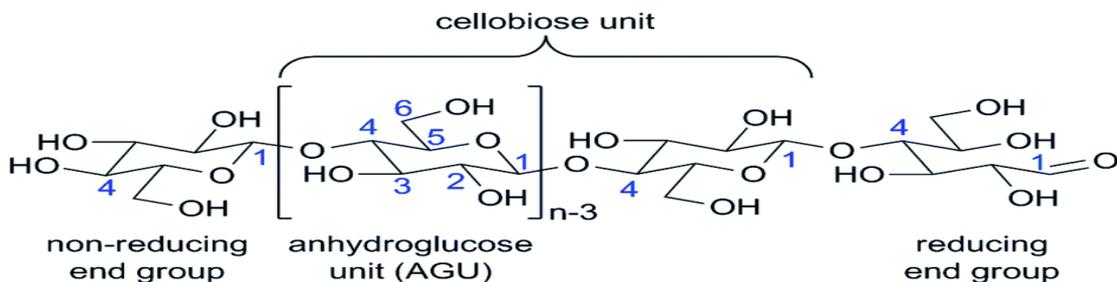
Cotton fibers are composed mainly of cellulose (around 95%), which is long-chain carbohydrate molecule, in the cell wall, multilayer structures of cellulose are composed of crystalline microfibrils.

For a comprehensive qualification about cotton fiber structure, a good knowledge about cellulose macromolecule is required (i.e. examining the structure and perfection of its crystalline arrays, the packing of these arrays (elementary fibrils) into microfibrils, and then the arrangement of these microfibrils in the primary and secondary cell walls).

### 1.4.2. Cellulose chemistry and structure

Cellulose is high molecular weight linear polymer, the cellulose structure can be defined as carbohydrate with D-glucopyranose repeating units, and these units that are covalently linked together via  $\beta$ -1, 4-glycosidic bonds. Cellulose of standard cotton has empirical formula  $H(C_6H_{10}O_5)_nOH$ , in which  $n$  is the number of repeating units in the range of 200 to  $\sim 10,000$ , with molecular weights of 32,400 and more than 1,600,000 respectively [9].

As shown in **Figure 1.3**, the structure of cellulose molecule is like a ribbon, which consists of covalently bonded six-membered rings, in which the hydroxyl groups are located out of the plane of the ribbon.



**Figure 1.3.** Molecular structure of cotton [10]

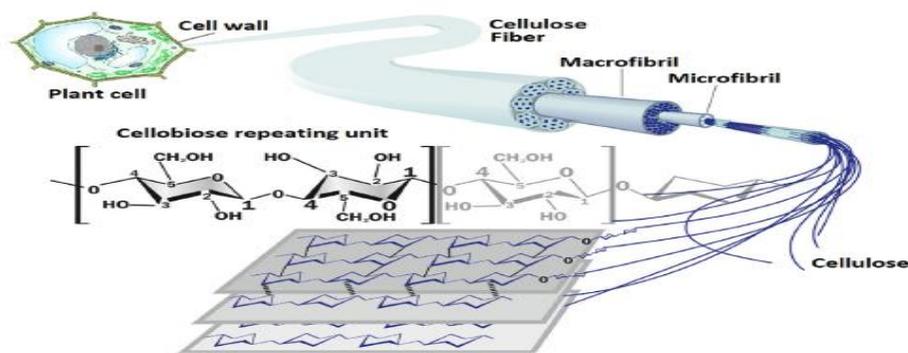
The hydroxyl groups present in cellulose macromolecules are responsible for the formation of hydrogen bonds with the oxygen atoms of the same or of an adjacent chain, which give rise to strong inter and intra-molecular hydrogen bonds. These inter and intra molecular hydrogen bonds are responsible for the cellulose structure. These hydrogen bonds allow the chains grouping together in highly ordered structures, resulting in various ordered crystalline arrangements. Structure order, symmetry and H-bonds are responsible for the high cellulose crystallinity.

The association of the cellulose chains by hydrophobic, intermolecular hydrogen bonds promotes the formation of microfibrils.

Since the chains are usually longer than the crystalline regions, they are thought to pass through several different crystalline regions, with areas of disorder in between. The inter-chain hydrogen bonds in the crystalline regions are strong, giving the resultant fibers good strength and insolubility in most solvents; they also prevent cellulose from melting.

The less ordered regions represent the amorphous domains: here the chains are further apart and more available for hydrogen bonding to other molecules, such as water. Most of the cellulose structure can absorb large amount of water, therefore cellulose swells but does not dissolve in water.

The proportionality of crystalline and amorphous domains varies in most of the cellulosic materials depending on origin or further treatments. **Figure 1.4** shows the organization of cellulose fiber [11].



**Figure 1.4.** Cellulose fiber and its organization [11]

## 1.5. Morphological organization of cotton fiber

### 1.5.1. Fiber development

#### 1.5.1.1. Nature of the fiber in close boll

Naturally agricultural staple fiber “Cotton “arise as a single biological cell, elongated in the seed coat’s epidermis inside the boll.

When the growth onset from the seed coat, the first part of the cell, primary wall in the model of thin tubular membrane is formed and in 2 to 3 weeks the final length of fiber is reached [12]. At this time, only the lumen, which has been surrounded by primary wall, is observed. On the outer surface of primary wall, a layer of waxy matter, cuticle appears. When the primary wall has been developed to reaches almost full length, the formation of secondary wall starts as result of deposition of nearly pure cellulose within the primary wall and it continues until the boll start to open. The secondary wall plays a major role in the fiber performance characteristics, as it is composed of nearly 95% total cellulose in the fiber. This secondary wall is established in the layers of fibrils, in which the number of layers demonstrates the number of growth days started after its deposition. These elementary fibrils lay down in highly oriented state and they align with an angle to the axis of fiber and helix around concentric layers, leading to high crystallinity in the fiber in the state of never dried (when the boll is still close) [13]. Fibrils layers, made of pure cellulose, are packed in the secondary wall; the wall development builds up the body and rigidity of the cotton fiber. The periodical changing in the direction of spirals throughout the fiber axis is characteristic for the fibrils and it is called reversals (**Figure 1.5** and **Figure 1.6**).



**Figure 1.5.** Reversals in fibrillar direction [13]

It is worthy to mention that in the never dried state of mature fiber, the interfibrillar slippage indicates that crystalline elementary fibrils are plasticized by water.

A different structure from primary and secondary wall, which is called, winding, exactly under primary wall has to be considered in the morphology of the cotton fiber.

During the growth period, the central channel of fiber, lumen, develops all over the fiber length, which is filled with cytoplasm.

### 1.5.1.2. Nature of the fiber in open boll

#### 1.5.1.2.1. Dehydration

The boll of cotton opens and fibers dehydrate and desiccate. The completely dehydration of fiber comprises the elimination of fluid from lumen and inter-molecular water contained in

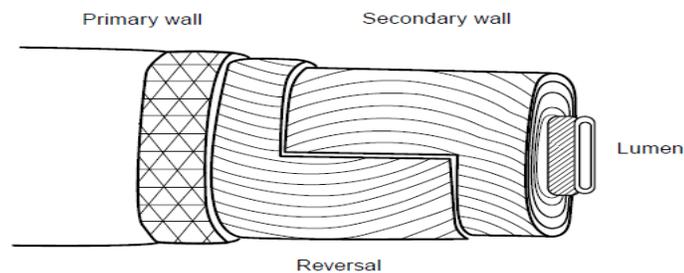
the cellulose. When the lumen loses its fluid, the fiber wall collapses leading to change into bean cross sectional shape, which in turn helps the spinning process of yarn. Cylindrical fiber wall collapses as a result of fluid loss in the lumen and cylindrical fibers changes to form twisted ribbon or convolution. As the wall thickness is different depending on variety and maturity of cotton fiber; this thickness strongly affects the number of the convolutions. Few convolutions for both thin and thick walled fiber and just medium thickness lead to plenty of convolutions. These twists reverse their direction periodically along the fiber, and this is linked to orientation of microfibrils in secondary wall, in which their organization is influenced by rigidity differentiation and H-bonding of microfibrils. This transition from cylindrical fiber to convolution form causes a decrease in cotton cellulose perfection and size of crystallite: this occurs as a reaction to stresses exerted by collapse of fiber wall [14].

When the intermolecular water is lost, the cellulose chains get closer together and the formation of intermolecular hydrogen bonds takes place between them. Before dehydration of the fibers, high porosity and mobility have been observed in the structure of matured cotton fiber [15].

As a result of these phenomena, some morphological variation occurs irreversibly: these changes specify the performance of fibers, such as the decrease in strain to break of the fiber and also the decrease in porosity and sorption properties of the dried fiber.

After fiber desiccation, decreasing in high intrinsic mobility of mature cotton fibers was observed as a consequence of irreversible hydrogen bonding between the fibrils.

Cotton fibers show variation in molecular packing densities; the highest densities correspond to tow curved ends at bean figure cross sections, therefore minimum availability to reagents.



**Figure 1.6.** Cotton structure [16]

All these features in the cotton morphology are important to determine the physical properties of cotton fiber.

## 1.6. Cotton fiber properties

### 1.6.1. Physical properties

#### 1.6.1.1. Maturity, dimension and density of the fiber

Cotton Maturity is an important parameter for evaluation of the quality of cotton fibers that can be used in manufacturing process. The maturity of cotton fiber is related to the development degree of secondary wall thickness. The proper explanation for maturity of cotton was given by Raes and Verschraege [17], who considered the relative wall thickness, according to their definition; “maturity is the thickness of the cell wall relative to the diameter or perimeter of fiber.”

The stiffness of cotton fibers is affected by maturity; therefore the maturity degree is an important parameter for prediction of textile properties. The best fibers for spinning process are those with a maturity degree of 2.0 to 3.0.

The fiber length varies with the type and quality, within the range 10 to 65 mm.

The fiber diameter ranges from 11 to 22  $\mu\text{m}$ .

The fiber linear density is the mass per unit length of fiber and is expressed in Tex (g/km).

#### 1.6.1.2. Fineness

Fiber fineness is evaluated as fiber linear density expressed in millitex ( $\mu\text{m}/\text{m}$ ), which is mass per unit length of fiber. Finer the fiber, finer the yarn has been obtained.

The practical range of fineness for U.S. upland cotton is about 125-225 millitex.

Usually the micronaire value is referred to evaluate fineness of cotton together with its suitability for spinning particular count of yarn; hence it combines fineness and maturity of cotton.

### 1.6.2. Mechanical properties

#### 1.6.2.1. Tensile strength

The tensile property of textile fibers is an important parameter, by which they can be selected for specified textile end-use applications.

Strength is the capacity or power to withstand an applied force; by referring to textile field it can be expressed as force or load required to break the fiber under specified conditions (Breaking strength) and it is a good indicator of fiber strength.

Breaking stress is a great criterion to indicate fiber strength, in which the breaking strength of materials is normalized to their cross section area. In the case of textiles, the better way is to consider mass rather than area, therefore it is expressed as force per mass per length of fiber; this term also refers to specific stress or tenacity.

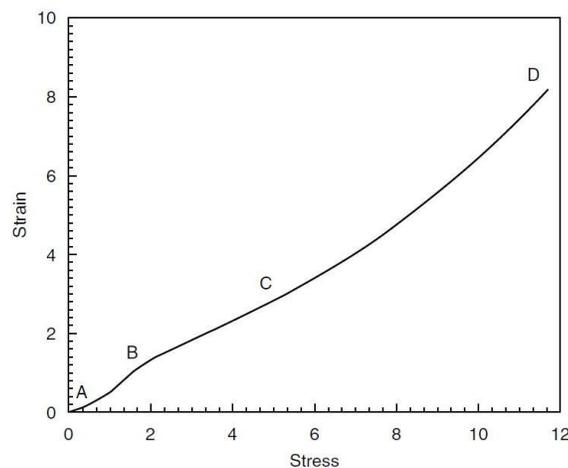
Considering the force in millinewtons and linear density of fibers in tex (1 Tex = 1 mg/m), the stress will be in mN/tex.

Tensile strength of single fibers varies from nearly 127.5 to 313.7 mN (Tex) [18]. Comparing cotton fiber to most of the other fibers, it gains strength when humidity increases. As temperature increases, the surface becomes smoother while fiber strength decreases.

For having prediction about yarn's strength, knowing the strength of raw cotton that is spun to yarn is necessary. The better way is to test bundles of parallel fibers.

### 1.6.2.2. Elongation, elasticity, stiffness

A common stress-strain curve for cotton is shown in **Figure 1.7** [19]. It illustrates the cotton response to the applied load until to the point of break, also allowing determining most of the parameters.



**Figure 1.7.** A typical stress–strain curve for cotton [13]

The term elongation refers to the capability of fiber to increase its length or to undergo deformation, before it breaks, while elasticity refers to capability of fibers to turn back to its original shape whenever the loading is removed.

Cotton fiber elongation is evaluated as percentage at the breaking point. 6-9 % values have been obtained for the cotton fiber elongation at break; they increase at high relative humidity up to 10% since water adsorption causes recline in interfibrillar cohesion as well as internal fiber stress. Elongation of fiber can be affected by swelling agents in the greater way than that by water.

The fiber elasticity is estimated according to two approaches: in one method the fiber is experienced the defined level of cyclic loading and fiber elastic recovery decreases from 0.9 to almost 0.4, which correspond to 1% elongation and elongation at break respectively. Therefore, after stretching cotton shows imperfect elasticity as it does not recover all the

elongation that it took during stretching. It is notable that this elastic property is evaluated with low rate of applied stresses.

It has been suggested that microfibrils with reverse pattern of spiral shape give a good opportunity to cotton fiber to acquire optimal strength, elongation and elasticity from linear chain of cellulose molecules [20]. Besides it has been proposed that the major part of breaks takes place close to reversal area [21, 22].

Stiffness of fiber can be evaluated by Young's modulus numerical value, and it is equal to the ratio of tensile stress per tensile strain ( $F.L/\Delta L.A$ ), in which  $\Delta L$  is the elongation parameter that can be calculated either at the beginning of elongation and referred to initial modulus or at the breaking point.

Cotton's Young modulus value varies, for example around 80 g/den for sea island cottons and this value decreases significantly for Asian cottons by around 40 g/den.

Hydrophilicity and porous feature of cotton fiber causes the swelling of the fibers in water liquid. This accessibility of pores to water molecules is not the same for the chemicals; therefore, chemical modification is an important issue to provide cotton fabric with such required properties as flame resistance, coloration.

### 1.6.3. Chemical properties of cotton

As already mentioned, cotton fibers are composed of 95% cellulose; therefore the chemical reactivity of cotton is equal to that of the cellulose polymer.

As considered before, 2-OH, 3-OH, and primary 6-OH sites on each anhydroglucose unit are responsible for association of chains of cellulose and formation of intermolecular hydrogen bonds, which cause the formation of a highly ordered crystalline structure. This crystalline structure of cotton fiber can be affected and changed to different polymorphs by means of some treatments.

As hydroxyls groups are involved in hydrogen bonding, they are not available for reaction with the chemical agents that can enter the internal pores of the cotton fiber. It has been suggested that swelling pretreatment and type of reagent influence the relative reactivity of the 2-OH, 3-OH, and primary 6-OH [13].

#### 1.6.3.1. Swelling

##### 1.6.3.1.1. Water

Cotton is hydrophilic (regain 8.5%) and mechanical properties improve when wet (-H bonds).

##### 1.6.3.1.2. Sodium hydroxide

One of the important swelling agents for cotton is an aqueous solution of sodium hydroxide. This treatment is called mercerization; the improvement of cotton properties by this technique has been widely investigated.

The term mercerization is referred to the process of converting native cellulose I to more stable cellulose II by means of concentrated sodium hydroxide that swells the native cellulose. This swelling is accomplished by reorganization of the cellulose chains and causes the change in cellulose structure from parallel to antiparallel sheets of chains, as they are still stabilized by inter-intra molecular hydrogen bonding. A significant reduction of the degree of crystallinity as well as an improvement in moisture regain ability has been proven for mercerized cotton fibers [23, 24].

The enhancement in the chemical reactivity, affinity of fiber to dye, tensile behavior, luster and smoothness appearance have been observed on mercerized treated cotton. Better result for strength properties and decreased elongation-at-break of fabric can be obtained if the treatment is applied under tension. The parameters that have to be considered in mercerizing fabrics are caustic concentration, contact time, temperature, squeezing pressure and washing condition. For mercerizing cotton, other chemical agents such as alkali metal hydroxides, lithium hydroxide and potassium hydroxide can be considered [13].

#### 1.6.3.2. Fire resistance

Cotton burns easily and it is considered as a combustible material and low fire resistance. In order to develop suitable flame retardants, it is important to know what physical changes as well as chemical reactions occur when cellulose burns.

As mentioned before, cellulose is composed of carbon and hydrogen that acts as fuel and oxygen, which supports the combustion, therefore cellulosic materials burn surely.

The burning process of cellulosic materials can be accompanied by a flame or glow by considering two distinctly different processes: flaming combustion and smoldering combustion.

Flame retardant textile refers to the fabric that does not support a flame after removing the ignition source. Glow resistance refers to the fabric that does not continue to burn by the smolder or glow mechanisms when the source of ignition has been removed.

It is useful to determine a number of terms before going into details of fire resistance and thermal behavior of cellulosic fabrics like cotton.

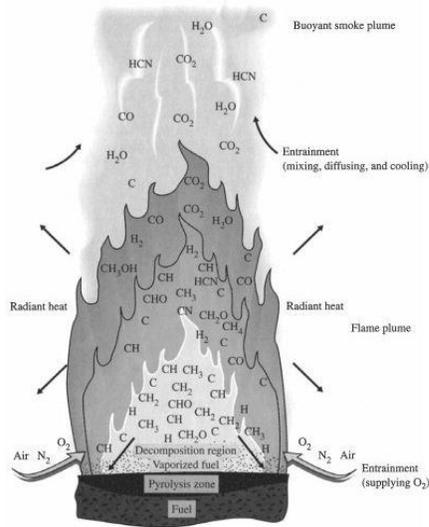
### **1.7. Flaming combustion and moldering combustion**

Flaming combustion and smoldering combustions are the two forms of fire. Hereinafter, the chemical mechanisms involved in each of these forms of fire will be described.

#### 1.7.1. Flaming combustion

This open-flame fire is the most usual type of combustion. In this chemical process, the gaseous state of fuel is essential to be able to react with an oxidizing species. It is gas to gas reaction, so, to get involved in the exothermic combustion reaction, it is important that the solid or liquid fuel undergo a change in the phase or a chemical change to become a gas first.

At least, 10% oxygen (as an oxidizer) must be present in the case of flaming fire occurrence. **Figure 1.8** illustrates the mechanism of flaming combustion [25].



**Figure 1.8.** Representation of flaming combustion [25]

### 1.7.2. Smoldering or glowing combustion

This type of combustion referred to direct oxidation of surface of the combustible solid and chars and other nonvolatile decomposition products, without the generation of flames; it is a solid to gas chemical reaction. Lower concentration of oxygen is required for sustainable glowing combustion. This usually occurs at temperatures lower than the ignition temperature of the substrate [26].

## 1.8. Theory of Combustion

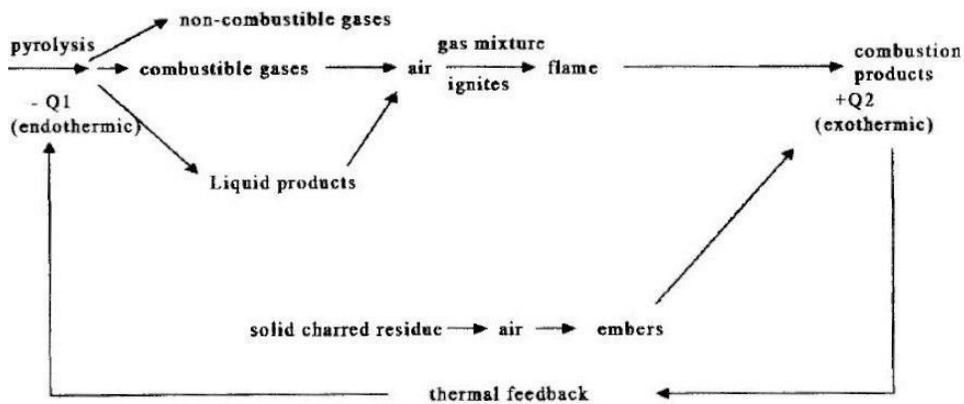
Combustion is described as a fast, exothermal redox chemical reaction. It is necessary that the fuel is heated at a temperature beyond the ignition temperature.

The sequence of processes is as follows: primary heating of the substrate and moisture releases, further heating, decomposition of substrate and formation of small, volatile organic compounds and their combustion and at the end char combustion.

The combustion of polymers is a process initiated by heating and endothermal decomposition. When the flammable gases are generated, they form the mixture with oxygen in the air and are ignited, hence promoting the propagation of flame (exothermic processes) and release of heat.

Heating and pyrolysis of polymers comprise endothermic processes; exothermic processes are initiated during ignition, which in turn, reinforces pyrolysis of the polymer through thermal

feedback. High Energy H and OH radicals provide support for the diffusion of flame. **Figure 1.9** shows the schematic behavior of polymer combustion.

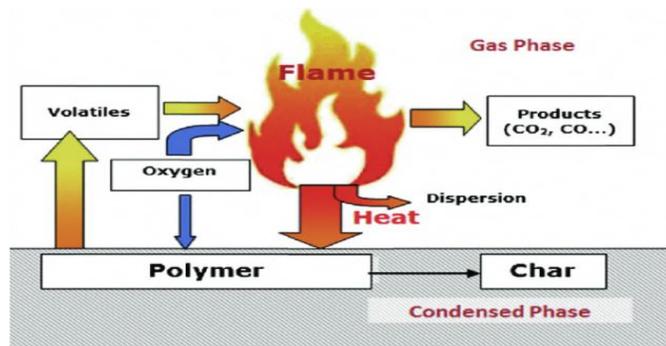


**Figure 1.9.** Exothermic and endothermic processes involved in polymer combustion [27]

### 1.8.1. Polymer combustion and fire loop

Textiles and polymer materials, which are mainly composed of organic compound, have been developed in usual and advance technologies and their usage is limited as they are flammable. In the studies of polymer combustion, it was discovered that physical and chemical phenomena are involved in this complex process. These phenomena occur between the gas and condensed phase, in which combustible volatiles are developed by polymer pyrolysis and then volatiles oxidation takes place as a combination with oxygen and thermal degradation products develop great amounts of heat.

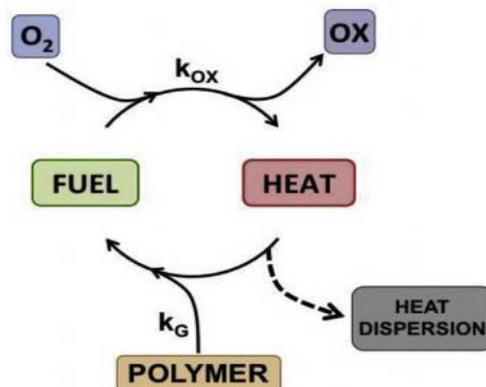
For a self-sustaining combustion cycle (**Figure 1.10**), adequate heat should be given to decompose the polymer and ignite the degradation products, and sufficient heat generated in the combustion has to be transferred back to the matter, which causes the further degradation and supporting the burning cycle. Different products from the fire can be obtained depending On the combustible species. In the case of polymers there is the production of carbon dioxide ( $\text{CO}_2$ ), carbon monoxide ( $\text{CO}$ ) and water vapor ( $\text{H}_2\text{O}$ ). The remaining solid residue is made of carbon ( $\text{C}$ ) and ash (oxidized metals) [28].



**Figure 1.10.** Polymer combustion cycle [29]

Another model to define polymers combustion is related to the kinetics involved between the two successive pyrolysis and oxidation reactions as they have a cyclic connection. Therefore, these two reactions influence each other. The rate of oxidation-combustion is affected by polymer pyrolysis as it produces volatile compounds. At same time, this oxidation-combustion affects pyrolysis via heat production during combustion reaction [30].

**Figure 1.11** illustrates this model of polymers combustion.



**Figure 1.11.** Fire cycle [31]

In the evaluation of efficient flame retardants for cotton, it is good to know the chemical reactions involved when cellulose burns. It is said that every polymeric material, before starting to ignite, experiences thermo-oxidation and then burning: therefore, it is essential to know what is its behavior upon thermal oxidation in order to design an efficient new flame retardant.

## 1.9. Thermal degradation or pyrolysis of cellulose

The most important parameters that affect the behavior of the cotton fiber upon heating are temperature, heating rate, availability of oxygen in the ambient atmosphere, existence of any material that accelerates or delays the degradation processes.

The ignition temperature, moisture content of the fiber, rate as well as the heat of products of combustion is the parameters that influence the burning behavior of cellulose [32-34].

Crystalline state and degree of polymerization (DP) of cellulose are other important factors that affect the flammability of the cotton: in particular, a higher crystallinity increases the ignition temperature due to the requirement of more energy for decomposing the crystalline structure.

Decreased pyrolysis also results from increased orientation or higher DP of cellulose.

Cotton, in the presence of oxygen and at elevated temperature (360-420 °C) can start to burn, either by flaming or smolder combustion.

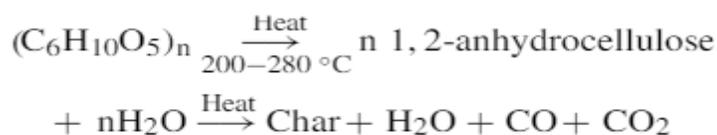
Combustion of cotton follows three major steps: ignition, propagation and afterglow. The ignition step is controlled by several factors, mainly: heat transfer to cotton fiber from the source of ignition, thermal degradation of cotton and reaction of the degradation products with oxygen [34]. When cotton fibers are heated in the range from 110 to 120 °C either in vacuum or air the absorbed moisture is partially removed.

In this range of temperature there is a bit change in DP, which slightly decreases and also the amount of carboxyl and carbonyl species increases to some extent while hydroxyl groups decrease.

When the temperature increases up to 150 °C, the loss in degree of polymerization as well as tensile strength of heated fiber in air is observed, while in vacuum or inert atmosphere these changes are quite limited.

The tensile strength is completely lost when the cotton fiber is heated above or at 200 °C while the oxygen is absent. Above this temperature, cellulose is ready for thermal decomposition and depolymerization is going to start.

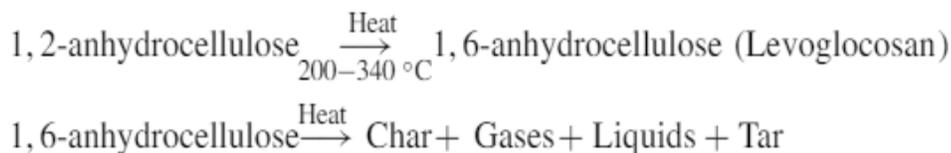
It has been suggested that in the pyrolysis of cellulose, two decomposition reactions occur, depending on temperature [35]. The first reaction occurs between 200 and 280 °C and anhydrocellulose is generated as cellulose loses water [35] **Figure1.12**.



**Figure 0.12.** Anhydrocellulose formation [36]

Elevated temperature further promotes the decomposition of this anhydrocellulose to several primary volatile compounds like aldehydes, alcohols and alkanes, flammable gases, methane, ethylene, carbon monoxide and non flammable gases, carbon dioxide, water vapour and char.

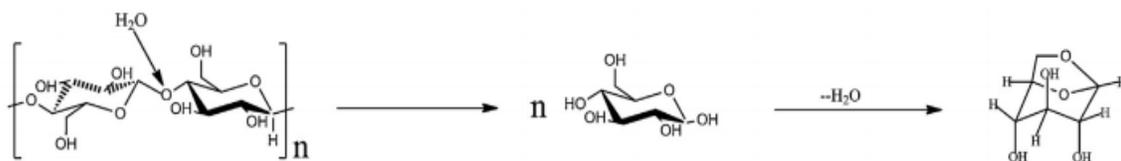
The second reaction involves the heterolytic bond scission or scission of glucosidic linkages; volatile products include anhydroglucoses (such as levoglucosans) that account for 5% of the cellulose weight **Figure1.13**. The mechanism that has been suggested for this step is characterized by chain-unzipping degradation [37].



**Figure 1.13.** Levoglucosans formation [36]

Methane, ethane, carbon monoxide are the combustible gases generated in this reaction; noncombustible gases comprise formaldehyde, carbon dioxide etc.

Levogluconan is the major important primary product in the cellulose pyrolysis [38-41], and it is an important intermediate for the formation of other products [42-47]. **Figure 1.14** shows the mechanism of levogluconan formation via glucose intermediate in cellulose pyrolysis). Irvine and Oldham claimed that levogluconan can be derived from glucose, which is formed during hydration of cellulose chain [48].



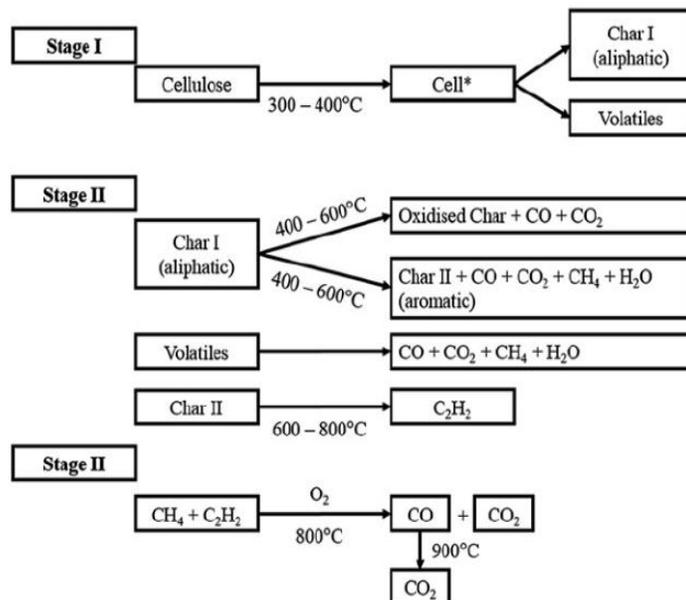
**Figure 1.14.** Mechanism of levoglucosan formation [49]

As a general view, Broido-Shafizade observed that, during the cellulose pyrolysis, cellulose decomposes first to active cellulose. No weight loss is observed in this step. Then depolymerization of active cellulose into volatiles occurs, notwithstanding that it can be polymerized to solid char.

Milosavljevic and Suuberg reported that cellulose primary pyrolysis is characterized by 218 kJ/mol activation energy [50], though this value was higher around 228 kJ/mol, as reported in another work [51].

The activation energy for the primary decomposition of cellulose according to Capart study is around 202 kJ/mol when cellulose pyrolysis is carried out in nitrogen.

The scheme shown in **Figure 1.15** illustrates the overall mechanisms and processes involved in cellulose pyrolysis [52-54].



**Figure 1.15.** Cellulose pyrolysis and char formation [55]

In the thermal degradation of cellulose in the case of flaming process when the combustible gases burn, the liquids are volatilizing, some fraction of these volatiles burn and a carbonaceous residue is formed by other fractions. At the end of the process, the remaining carbonaceous matter is transformed into ash as result of glowing and oxidizing reactions [56-58].

In air, the pyrolysis of cotton gives rise to the formation of levoglucosan.

## 1.10. Flame retardants

### 1.10.1. The meaning of flame retardants

Understanding the concept of “flame retardants” is important for giving label to materials that delay or extinguish flame under test conditions in a standard laboratory. The flame retardant definition proposed by the relevant ASTM terminology subcommittee is “a chemical which, when added to a combustible material, delays ignition and reduced flame spread of the resulting material when exposed to flame impingement” [59].

Flame retardants are defined as chemicals that inhibit or even suppress or slow down the combustion process as described before, by modifying the pyrolysis or oxidation reactions involved in the combustion. Some of the flame retardants, depending on their nature act via chemical mechanisms and some of them physically. Their mechanisms may operate in the condensed phase or in some cases in the gas phase, especially when radicals are trapped or also combustible gases are diluted by their actions.

As mentioned before, combustion process includes several steps; flame retardant additives can interfere with this process during a particular stage or stages, for instance during heating, decomposition or pyrolysis, ignition and flame propagation.

## 1.10.2. Flame retardant mode of action

### 1.10.2.1. Physical action

Physical actions of flame retardants are described as follows:

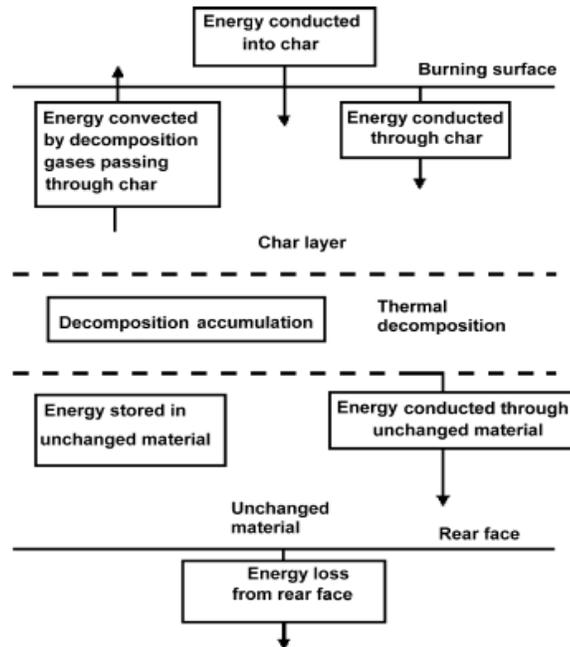
- By cooling; they modify the pyrolysis process as the endothermic decomposition of some additives consumes heat. This causes a decrease of temperature and the cooling of either the substrate or reaction medium to temperature below that necessary for sustaining the burning process. Hydrated tri-alumina at temperature around 200°C or magnesium hydroxide at around 300°C starts to release water vapor.
- By formation of solid or gaseous protective layers
- Dilution of fuel in solid and gas phases; upon decomposition, some flame retardants originate inert gases such as H<sub>2</sub>O, CO<sub>2</sub>, NH<sub>3</sub>, etc. which dilute the combustible gaseous mixture.

### 1.10.2.2. Chemical action

Chemical actions of flame retardants refer to chemical reactions that interfere with the burning processes and modify the fire process chemically. They may act in the condensed and gas phase. Flame retardants can interrupt the free radical mechanism of combustion process (inhibition of flame by radical trapping). The flame retardant additives can react with the free radicals that evolve during combustion process. Specific radicals such as Br or Cl are released by flame retardant in gas phase and react with highly reactive radicals like H and OH; as a consequence, less reactive molecules are formed.

Two kinds of chemical reactions by flame retardants in condensed phase can stop the combustion process: a char (carbonaceous) layer or intumescent protective layer can be formed by flame retardants on the surface of polymer or textile when it is exposed to a flame or a heat source. This char separates the condensed phase from gas phase and acts as a physical barrier. **Figure 1.16** demonstrates the mechanism of thermal transfer during combustion.

The second chemical mechanism that occurs with some flame retardants involves the speed up of polymer chains break; as a consequence, the polymer drips and thus moves away from the flame action zone.



**Figure 1.16.** Mechanism of thermal transfer during materials combustion [60]

Flame retardants can be classified into reactive and additive flame retardants.

Reactive flame retardants refer to those that are combined in the polymer chains; they can be chemically embedded into the polymer during polymer synthesis or by post-reaction process for instance via chemical grafting.

Additive flame retardants are those that can be incorporated into the polymer during the transformation process by physical means, but when the fire starts and temperature is high enough they react with polymer. Mineral fillers and hybrids belong to this category.

### 1.10.3. Mineral flame retardants

Among them, hydroxycarbonates (less widely used), metal hydroxides (mainly magnesium and aluminum), Borates (especially zinc borates) are widely used. These inorganic fillers have physical actions as they decompose endothermically and release non-combustible molecules, which dilute combustible gases; also a ceramic protective layer can be developed according to their action.

### 1.10.4. Halogenated flame retardants

The type of halogen highly affects the performance and effectiveness of flame retardants. Among the halogenated flame retardants, Iodine- and Fluorine-based compounds are not applicable; conversely, Bromine and Chlorine are widely used, as they can be easily released

during the combustion process. In fact, they have low bonding energy with carbon and take part in the free radical mechanism of the combustion process (react with highly reactive H and OH free radicals (**Figure 1.17**)), as discussed before.



**Figure 1.17.** Reaction of halogenated flame retardants with free-radical species [60]

Tetrabromobisphenol A (TBBPA), Polybrominated diphenyl ethers (PBDE), Hexabromocyclododecane (HBCD), tetrabromophthalic anhydride (TBPA) are the most common halogenated flame retardants.

### 1.10.5. Nitrogen-based flame retardants

Melamine is a thermally stable organic compound with a melting point around 345 °C and 76 wt. % content of nitrogen [61]. At temperature around 350°C sublimation of melamine takes place, followed by significant amount of energy absorption: therefore, temperature decreases. The decomposition of melamine at high temperature is followed by elimination of ammonia, which causes the dilution of combustible gases and also formation of melam, melem and melon, i.e. thermally stable condensates [62].

Melamine phosphate, melamine cyanurate and melamine pyrophosphate are melamine based salts; their action in the condensed phase is much higher than pure melamine because during heating these salts decompose, giving rise to the formation of a large fraction of re-formed melamine.

### 1.10.6. Silicon-based flame retardants

Silicas, silicones, organosilanes, silicates and silsesquioxanes are silicon-based compounds suitable for flame retardant purposes. They can be embedded into the polymer as fillers or in the form of copolymers.

High heat resistance silicones with great thermal stability release limited amounts of toxic gases during decomposition.

Silicones were employed as flame retardants for polycarbonate (PC) [63]. They can be easily dispersed in polycarbonate and during the combustion they migrate towards the surface to form a highly stable char as a result of the combination of polysiloxane and condensed aromatic compounds.

Referring to silica, the effect of silica gel pore volume on flame retardant properties of polypropylene has been investigated by Gilman et al. [62]. A significant reduction of heat release rate was observed when pore volume of silica was high.

The flame retardant behavior of silica, silica gel, fumed silica and fused silica has been studied and reported by Kashiwagi et al [64].

### 1.10.7. Phosphorus-based flame retardants

Phosphorus flame retardants are effective in condensed phase with oxygen containing polymers such as polyamide, polyester and cellulose [65]. Phosphorus-containing flame retardants are numerous as they can comprise many oxidation states. Phosphonates, phosphates, phosphines, phosphine oxides, phosphatase, phosphates and red phosphorus are widely used as phosphorus-based flame retardant products. They can be introduced into the polymer chain during its synthesis or can be used as additives; their action is in gas or/and condensed phase.

Thermal decomposition of oxygen-containing polymers treated with the phosphorus-based flame retardants involves the production of phosphoric acid and then the formation of pyrophosphate structures and water molecules from readily condensation of phosphoric acid. When water is released, the oxidizing gas phase becomes dilute. The carbon-carbon double bonds and carbocation formation (which at high temperature generate carbonized structure) occurs as a result of the dehydration reaction of the terminal alcohols catalyzed by phosphoric acid and pyrophosphoric acid. This carbonized layer known as char acts as an insulator the polymer as discussed before.

Another action of phosphorus-based flame retardants in gas phase is as scavengers of highly reactive  $H\cdot$  and  $OH\cdot$  radicals because, during thermal decomposition, they can also volatilize and form  $PO_2\cdot$ ,  $PO\cdot$  and  $HPO\cdot$  active radicals, which are more effective as combustion inhibitors than bromine and chlorine radicals [66].

The presence of oxygen or nitrogen in the polymer chain is important for the action of phosphorus-based flame retardants.

### 1.10.8. Inorganic phosphates

Ammonium polyphosphate (APP) is an example of inorganic phosphate compound. This inorganic salt of polyphosphoric acid and ammonia is a non-volatile and stable compound.

The char formation on polymer (containing oxygen and/or nitrogen) incorporated with APP during thermal degradation have been widely discussed in some studies [67-70].

### 1.10.9. Organic phosphorus-based compound

The main categories of organophosphorus compounds are phosphonates, phosphate esters, and phosphinates. They can be introduced to polymer as additives or as reactive monomers/oligomers.

Resorcinol bis (diphenyl phosphate) (RDP) and biphenyl A bis (diphenyl phosphate) (BDP) are two examples of oligomer phosphates. When they react with polycarbonate phenolic functions, during thermal degradation, they promote the char formation and polymer chains crosslinking (crosslinking of BDP and PC), as discussed in some studies [71, 72].

#### 1.10.10. Intumescent

Intumescence is one of the flame retardant mechanisms of materials that swell when exposed to heat source or fire, to form an expanded carbonized layer. This latter can act as insulating barrier to heat, also reducing fuel transfer and limiting the oxygen diffusion into the material [73,76].

The formulation of intumescent materials requires a carbonizing agent or char forming agent, an acid source that promotes the char formation, a blowing agent (foaming agent), which, during decomposition, releases gas and forms a swollen multicellular layer.

#### 1.10.11. Synergistic effect

The consequence of two compounds acting as flame retardants can be synergistic or additive or antagonistic. If the effect of two compounds acting together is simply the sum of the effect of two or more component measured independently, the effect known as an additive. Conversely, a synergistic effect is much greater than an additive effect.

### 1.11. Flame retardancy of cellulosic materials

Many publications have been studied about flame retardant finishes for cellulosic and especially for cotton fabrics [77-82].

Flame retardants for cellulosic materials can be classified according to some of their characteristics into:

- Inorganic or organic compounds.
- Flame retardants containing such elements as phosphorous, nitrogen, halogen, etc.
- Reactive or additive flame retardants.
- On the basis of the phases, in which the flame retardants act (condensed, gas), or on the basis of the mechanism of action (chemical or physical).
- On the chemical structure (i.e. bases, ethers, acids, esters, salts, oxides, hydroxides, etc.).
- On the basis of the durability of the flame retardant finishing.

### 1.11.1. Durability

The flame retardants that can be used for cotton by considering their resistance to laundry conditions are classified as non-durable, semi-durable and durable. Non-durable flame retardants refer to those that wash off instantly when immersed in water but may stand out dry cleaning. Semi-durable flame retardants are those that can resist to water-soaking and durable ones resist more than 50 washing cycle.

Some nondurable chemicals, which are employed for cellulose, are inorganic water soluble salts. They are more acceptable than inorganic acids and bases as the latter are intrinsically corrosive.

Examples of inorganic salts suitable for cellulose include diammonium and ammonium phosphates, ammonium sulfamate and urea phosphate.

These salts, upon heating decompose to acids, which in turn catalyze the dehydration and char forming reactions during the cellulose decomposition process.

Organophosphorus compounds are durable flame retardants. They can be incorporated into cellulose by chemical interaction or either can be polymerized within the fiber matrix. Most of the durable flame retardants contains phosphorus or/and nitrogen or halogen elements. N-hydroxymethyl (dimethyl phosphono) propionamide and tetrakis (hydroxymethyl) phosphonium salts such as chloride (THPC), sulfate (THPS), and oxalate are some known examples for this category.

Fyrol® and Fyroltex® are two durable treatments for cotton and cotton blends fibers. This phosphorus-containing oligomer can be cured on cotton with incorporation of ethyldihydroxyethyleneurea or trimethylolmelamine.

### 1.11.2. Additive or reactive flame retardants

Additive flame retardants for cellulosic material are those which can be deposited onto the surface on fibers with no chemical interactions.

NaCl, CaCl<sub>2</sub>, SbCl<sub>3</sub>, ZnCl<sub>2</sub>, NH<sub>4</sub>Cl, (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub>, (NH<sub>4</sub>)<sub>2</sub>HPO<sub>4</sub>, NaHCO<sub>3</sub> are inorganic salt examples for this group [83, 84]. They decrease the temperature of cellulose decomposition and promote the char formation.

Reactive flame retardants include those molecules that chemically react with cellulose, highly depending on the availability of hydroxyl groups on C-2, C-3 and primary C-6 of each glucopyranose repeating unit of cellulose, as they are involved in hydrogen bonding.

When hydrogen bonds are broken, it has been proven that C-6 hydroxyl group is more preferred for the reaction [85]. This reaction causes disruption of cellulose depolymerization during thermal degradation; therefore, it lowers the combustible gases production, at the same time increasing the char formation.

### 1.11.3. Flame retardants based on mechanism of action on cellulosic materials

#### 1.11.3.1. Physical action

Physical action involves formation of protective layer on fiber surface at high temperature close to fiber and retardants combustion temperature. Upon heating, inorganic salts with low melting point, melt and form a glassy layer on the fiber. This layer insulates fiber from oxygen and also traps the volatiles products of cellulose degradation. Boric acid-borax systems, phosphates, and polyphosphates, silicates are some examples.

Another physical action of flame retardants involves the development of inert or non-combustible gases such as  $\text{NH}_3$ ,  $\text{HCl}$ ,  $\text{CO}_2$ , and  $\text{SO}_2$ , which lead to the dilution of flammable gases evolved during cellulose pyrolysis. Examples of this type include ammonium halides, phosphates, sodium carbonate, sulfates and bicarbonate, zinc, calcium and magnesium chlorides, aluminum sulfate and ammonium sulfamate [86].

#### 1.11.3.2. Chemical action

The chemical action of flame retardants for cellulosic materials takes place in condensed and gas phase. Condensed phase chemical action of flame retardants can be explained according to Lewis acid mechanism. The acid promotes and catalyzes dehydration process of cellulose, hence favoring the char formation and minimizing the production of flammable gases and tars as the decomposition process of cellulose is changed. The phosphorus- and nitrogen-based flame retardants are more effective in this mode of action. The action of phosphorous-containing flame retardant will be discussed later.

When flame retardants are heated to combustion temperature, their chemical action in vapor phase involves the production of free radical terminators. This type of flame retardant during thermal degradation generates free radicals, which can react with free radicals such as  $\text{H}\cdot$ ,  $\text{OH}\cdot$  and  $\text{HO}_2\cdot$ , which are formed during oxidation of cellulose in the gas phase. Halogenated flame retardants are an example.

#### 1.11.4. Metallic Compounds

Metallic salts are mainly used to reduce the smoke produced during combustion and pyrolysis of flame retardant treated and untreated polymers. Many studies have been performed to show the effect of such metallic agents as titanium, antimony, and molybdenum.

Good flame retardant properties have been obtained with complexes of chemically reacted cellulose phosphate with metal ions such as chromium, manganese, zinc, copper, nickel, cobalt, zirconium, molybdenum [87].

### 1.11.5. Phosphorus element

Phosphorus containing flame retardants are mainly inorganic phosphates, organophosphates, insoluble ammonium phosphates and phosphonates, chlorophosphates and phosphines, phosphonium salts, phosphonates, and phosphine oxides.

Monoammonium orthophosphate ( $\text{NH}_4\text{H}_2\text{PO}_4$ ) and diammonium orthophosphate ( $(\text{NH}_4)_2\text{HPO}_4$ ) are non-reactive inorganic salts that can be used individually or mixed together. Ammonium phosphate mixed with ammonium bromide, borates and ammonium sulfamates are employed as effective commercially-available flame retardants [88].

#### 1.11.5.1. Reactive phosphate

$\text{H}_3\text{PO}_4$  or  $\text{POCl}_3$  are strong acids that cause phosphorylation of cellulose, which is effective for conferring flame retardancy to the cellulosic material; conversely, these strong acids degrade cotton: this drawback can be reduced by adding urea and formaldehyde.

Stabilized cellulose phosphates have been synthesized by Lewin [89].  $\text{POCl}_3$  with an organic solvent used for phosphorylation of cellulose and then sodium methoxide were used to treat dichlorocellulose. The resulting dimethyl ester of cellulose showed excellent durable flame retardant properties.

#### 1.11.5.2. Phosphorylamides

These type of flame retardants are referred to phosphoric acid derivatives, which contain - $\text{NH}_2$  (or  $\text{NHR}$  or  $\text{NRR}'$ ) groups replacing  $\text{OH}$  groups. Tris (aziridiny) phosphine oxide (APO) is an efficient flame retardant when combined with urea and ethylenediamine, phosphoric acid and urea. Due to the highly toxicity of APO, bis (aziridiny) chloro methyl Phosphine oxide has been proposed by Tesoro et al. [90]: in combination with ammonium dihydrogen phosphate this product confers durable flame retardant features to cotton.

### 1.11.6. The role of Nitrogen

Synergistic activity of nitrogen with phosphorus element for the flame retardancy of cellulose has been proven by Tesoro and coworkers.

They have claimed that with a constant level of phosphorus, by increasing the nitrogen level, the effect on flame retardancy is more than additive [91], but, at the same time, it highly depends on the chemical nature of nitrogenous compounds. Urea derivatives showed poor results while substituted melamine were more effective.

## 1.12. Influence of flame retardants on cellulose pyrolysis

### 1.12.1. Mode of action of phosphorus containing flame retardants on cellulose

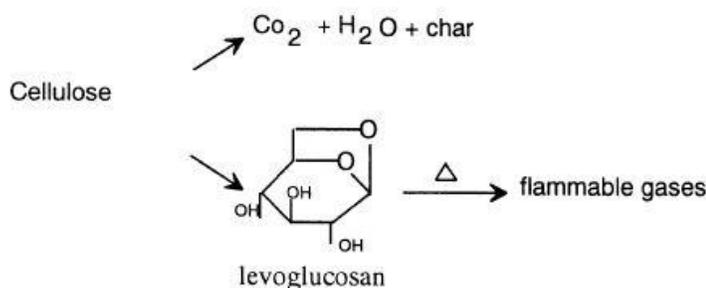
#### 1.12.1.1. Condensed Phase Mechanisms

In the thermal degradation of cellulose treated with flame retardants, the acid formation induced by the flame retardants in cellulose is essential, as it favors the dehydration and induces the char formation in the condensed phase; besides, it interferes with the formation of combustible volatiles.

Condensed phase mechanism of phosphorus-based flame retardants is more effective on polymers which contain hydroxyl groups like cellulose.

Thermal degradation of cellulose may occur according to two alternative paths .as it shows in **Figure 1.18**, one path leads to the formation of volatile combustible organic compounds from an intermediate which is known as levoglucosan. Another path (which can be canalized by acid) involves the formation of water and non-combustible carbonaceous char. Inorganic and organic phosphorus compounds according to their specific properties can change the decomposition chemistry of most polymers, as for cellulose.

Among many acids that can catalyze water and char formation reactions, phosphoric acid is considered the best as it is non-volatile and also at elevated temperature it produces polyphosphoric acid that is more capable to catalyze dehydration reaction. These acidic intermediates produced from the thermal decomposition of phosphorus compounds can react with the substrate and catalyze dehydration process and promote the char formation [92-94]. In fact, the action of phosphorous based flame retardant in cellulose is known as phosphorylation of cellulose and the water and carbonaceous char formation is a result of phosphorylated cellulose cleavage. Therefore, this protective layer coats the surface of the decomposing polymer and isolates it from the heat and oxygen.



**Figure 1.18.** Pyrolysis of cellulose [95]

### 1.12.1.2. Gas Phase Mechanisms

The phosphorus compounds can act in gas phase and their function is a flame inhibition through radical trapping. It has been shown that these compounds in the flame can decompose to smaller molecular species such as  $\text{PO}\cdot$ .

Scavenging of  $\text{H}\cdot$  radicals by phosphorous radicals is the proposed mechanism for phosphorus based flame retardants in gas phase; therefore, the combustion chain interrupts by this action.

Cullis et al. have studied the action of nitrogen and phosphorus in the gas phase. Phosphorus was introduced via direct phosphorylation and phosphorus-containing compounds (namely, tritolylphosphate and triphenyl phosphine oxide) were added to cotton fabric. The results showed that the phosphorus was lost at primary stages of decomposition in the thermal degradation of cotton: this finding can be interpreted by vapor phase action of such flame retardant species as  $\text{P}\cdot$  and  $\text{PO}\cdot$  radicals formed by Triphenyl phosphine oxide.

Referring to other cellulose substrates treated with phosphorus-containing compound, the action of phosphorus is predominantly in the condensed phase [96].

It has been shown and proven that some of the current commercially-available halogenated (especially pentabromodiphenyl ether, decabromodiphenyl ether and polychlorinated biphenyls) and some phosphorus-based flame retardants (Proban® and Pyrovatex®), which are very effective; at the same time they have potential to be bioaccumulative, environmentally harmful, carcinogenic and toxic. As concerns are increasing for these environmental and toxicological impacts, many studies and researches have been carried out to create new non-halogenated eco-friendly flame retardants suitable for cellulosic materials. The new products should fulfill the following issues [97]:

- Any new flame retardant should offer equivalent or superior ease of application.
- Any new flame retardant should not evolve formaldehyde during application or service.
- Any new flame retardant should support comparable textile service-life features including durability, comfort, tensile properties.
- Any new flame retardant should meet an overall comparable cost-effectiveness to those already exist and preferably be less costly
- Any new flame retardant should have equivalent or lower toxicity and environmental impact.

According to Lewin [98]:

- A new flame retardant should endure 50 hot alkaline laundries.
- Air permeability of the treated cotton should be maintained, as result of high deposition of the chemicals to provide flame retardants properties

- The tensile, burst and tear strength and abrasion resistance of treated cotton fabric should not be changed.

### **1.13. Toward the development of novel bio-based flame retardants for cotton**

In the last decade, many researches and studies have been done to develop novel environmentally-friendly flame retardants efficient enough to replace halogens or halogen derivatives.

As discussed before, some compounds containing phosphorus have been found suitable for cellulosic materials but still there are some disadvantages for recently developed halogen-free substituents. As an example, hydroxymethylphosphonium salts (Proban®) which represent commercially-available flame retardant, release formaldehyde upon heating and during life service. Recently, some research has been focused on selected biomacromolecules, which have intrinsically potentials in flame retardancy features.

To address these properties, caseins, whey proteins, hydrophobins, and deoxyribonucleic acid (DNA) so far have shown considerable potential to modify the fire behavior and resistance of materials like cotton, polyester and cotton/polyester blends as green flame retardants, simply by covering the surface of the substrate via impregnation/exhaustion or layer-by-layer depositions.

Despite many valuable advantages such as flame retardant effectiveness and low environmental impact, the availability and extraction of some of them at a large scale is still under investigation and limits their applications in the industry. Furthermore, the durability of treated fabric is still an issue to be solved.

Beside all the efforts, which have been done for developing eco-friendly flame retardant systems, nanotechnology has got most of the attention recently. Very thin layer of nanoparticles on the surface of the substrate can be created by different approaches and among them Layer by Layer assembly, adsorption (impregnation of fabric in a nanoparticle suspension), sol-gel and dual-cure techniques have been shown potential in the field of environmentally-friendly flame retardants.

#### **1.13.1. Fire retardant property imparted by protein-based biomacromolecules**

##### **1.13.1.1. Caseins and DNA biomacromolecules as novel green flame retardants**

###### **1.13.1.1.1. Caseins**

Caseins are a heterogeneous group of phosphoproteins and major protein groups in milk especially bovine milk. Recently, this phosphorus-rich protein has been found to be effective

for designing novel green flame retardant finishing for cotton fabrics. The latter have been treated by simply depositing these proteins from aqueous solutions.

The protein coated fabric has shown improvements in the fire retardant properties and thermal and thermo-oxidative stability.

#### 1.13.1.1.2. DNA

DNA can be extracted from herring sperm. The special structure of this biomacromolecule consists of two spiral chains of deoxyribonucleic acid, bonded together in a double helix.

The intrinsic characteristic of this biomacromolecule is to act as an intumescent flame retardant because of the presence of intumescent components in its structure such as phosphate groups, which produce phosphoric acid, deoxyribose units that act as blowing agents and carbon source, and ammonia that may be released from nitrogen-containing bases (adenine, thymine, guanine and cytosine).

### 1.14. The sol-gel process

The versatile solution process of sol-gel is usable to make advanced materials, such as organic-inorganic hybrids and ceramics. In general, according to sol-gel process, the solution system undergoes a transition from a liquid “sol” (mainly colloidal) into a solid “gel” phase. The precursors for “sol” preparation are mostly inorganic metal salts or metal organic compounds for example (semi)metal alkoxides (mainly tetraethoxysilane, tetramethoxysilane, titanium tetraisopropoxide, aluminium isopropoxide...). These chemicals are subjected to hydrolysis and condensation reactions and result into the formation of colloidal suspension (“Sol”) at or near room temperature, followed by the formation of organic-inorganic hybrid or entirely inorganic coatings, which can act as an insulator on polymer surface.

Several parameters can influence the structure of the resulting oxidic networks such as pH, nature of (semi)metal, as well as alkyl/alkoxide groups, temperature, reaction time and existence of co-solvents [99].

The sol-gel process has been utilized for various applications, such as composites, monoliths, powders grains and spheres, fibers, thin films and coatings, nanotechnology. Referring to textiles, the sol gel processes have been applied to confer multifunctional properties to textiles, as widely discussed in several studies [100-111].

Recently, the use of the sol-gel method has been investigated to impart flame retardant properties to textiles. The result of the formation of ceramic phase and sol-gel derived hybrid architecture on the fabric is to act as physical barrier for both heat and oxygen transfer during the exposure to a flame or a heat source; in addition, the sol-gel coating prevents the formation of volatile compounds that act as fuel for combustion and further textile degradation and somehow promotes the char formation [112]. Another effective action of this network is to absorb the heat from the environment.

At variance, the sol-gel coated fabrics are not able to provide a complete shielding effect because of the thin thickness of the fabric; furthermore, the action of the sol-gel coating alone is only in condensation phase, while for very effective flame retardant systems the action in vapor phase is essential. In order to obtain more effective flame retardants properties provided by sol-gel derived coatings, it is better to combine them with other flame retardant compounds for instance phosphorus-and/or nitrogen-containing, exploiting synergistic or joint effects.

Three forms of coating architectures can be derived from sol-gel: they include, inorganic, phosphorus-doped silica, hybrid organic–inorganic coatings.

Inorganic coating involves the pure deposition of oxidic phases, which have shown good results in the fire and combustion behavior of viscose, cotton, polyester and their blends. In particular, it is reported that TEOS and TMOS (tetramethylorthosilicate), as silica precursors, have shown better results in flame retardancy of cotton fabrics with respect to other alkoxy precursors. It is noteworthy that the good result in washing durability of cotton fabric treated is obtained when TMOS was used as precursor, under optimized sol-gel process conditions.

These pure sol-gel oxidic phases can show improvement in flame retardant features when active compounds such as phosphorus- and/or nitrogen-containing compounds are incorporated within the oxidic phase in joint or synergistic effects.

Recently, an effective thermal insulator system was designed as inorganic-organic hybrid derived sol-gel coating, employing dual-cure processes [113]. This coating showed significant improvements of fire and combustion behavior of cotton fabric and to some extent also the durability was enhanced.

These effective results obtained from sol-gel stimulated the researchers towards the development of novel green flame retardants systems. In this context, in the present study, a sol-gel process is exploited in order to synthesize organic-inorganic flame retardant hybrids based on phytic acid (PA-CPTS), able to confer and improve the fire behavior of the treated fabric.

The flame retardancy of cotton fabrics treated with PA embedded into a sol-gel coating has been investigated and in the next chapter the results will be discussed in details. TEOS was used as alkoxy precursor and phytic acid as phosphorus-containing compound.

## **1.15. Fire retardant property imparted by plant based bio-macromolecule**

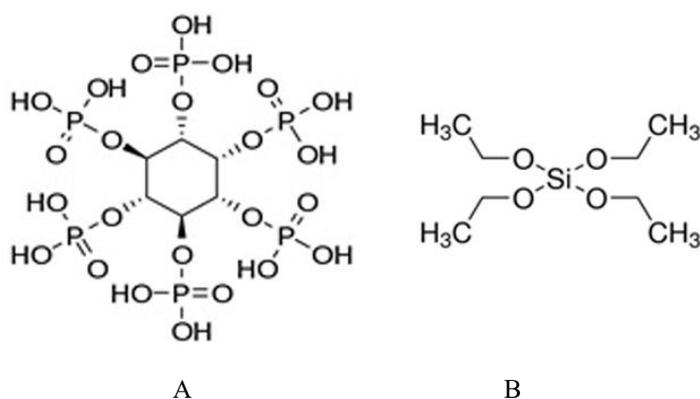
### **1.15.1. Phytic acid**

Phytic acid, naturally occurring compound, is considered as green macromolecule, which is one of the major storage forms of phosphorus-containing compounds; it is abundant in plant tissues such as soy beans, cereal grains and oil seeds. This eco-friendly, biocompatible and nontoxic organic phosphoric acid has been used in certain application; in particular, as flame

retardant it has been applied for various materials such as polylactic acid (PLA), nonwoven fabric (through pad-dry-cure technique), silk and wool and cotton fabrics.

In addition to the high phosphorous content (28 wt. % based on the molecular weight) of phytic acid, its special chemical structure (**Figure 1.19**) provides potential to be used as an effective flame retardant finishing agent for cellulosic materials.

Its structure consists of 6 phosphate groups, each bearing 2 hydroxyl groups; phosphorus can act in both gas and condensed phases and interfere in combustion process. It has been shown that hydroxyl group of phytic acid become reactive in water and then could attach and react with cellulose of cotton [114]. The water present in the starting phytic acid solution (50 wt. %) can be exploited for the hydrolysis reactions involved in sol-gel process, without further addition of water.



**Figure 1.19.**Chemical structure of Phytic acid (A) and TEOS (B)

## 1.16. Characterization techniques

The performance of flame retardant systems can be evaluated and assessed through several analytical and testing techniques. In order to develop and optimize new textile flame retardants, the assessment of the performance of flame retardant textiles plays an important role. The testing techniques and methods, which are normally used in both laboratory and industry in order to evaluate the fire behavior, are described as follows.

### 1.16.1. Laboratory fire testing

- The flame retardancy of the prepared samples can be assessed through flammability and forced combustion tests.
- The morphology and surface structure of the prepared samples as well as charring layer of residue and the related morphology can be observed using Scanning Electron Microscopy (SEM) .

- The chemical reactions/structure at solid/liquid interface can be investigated by Fourier transform infrared spectroscopy analysis (FTIR) with Attenuated total reflection (ATR) accessory, FTIR-ATR.
- The thermal and oxidative-thermal properties can be evaluated with thermogravimetric (TG) analysis performed in N<sub>2</sub> and air, respectively.
- The mechanical behavior and the tensile properties of treated samples can be evaluated by tensile tests.

#### 1.16.1.1. Scanning Electron Microscopy analysis – SEM

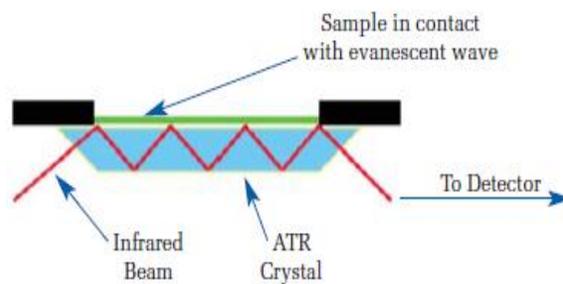
SEM produces electrons, which were spread over the sample. The electronic ray reacts with the sample, generating several types of signals. The intensity of the signals varies according to the sample size. The signals are collected by a detector and their output synchronized in a picture form.

#### 1.16.1.2. Fourier transforms infrared spectroscopy analysis (FTIR) with Attenuated total reflection (ATR) accessory - FT-ATR

FTIR spectroscopy is a practical analytical tool for identifying functional groups present in the material structures. In FTIR, infrared radiation passes through the sample. The bonds present within the functional groups absorb the radiation energy and vibrate with different frequencies (strong/weak), depending on the strength of the bonds. The energy absorption produces the peaks corresponding to vibration frequencies and a molecular fingerprint of the samples is generated. The sample fingerprint presents an IR transmission (absorbance) versus frequency curve to explain the molecular structure of the sample. Each molecule has a unique combination of bonds that produce peaks at specific frequencies. The size and shape of the peaks indicate the amount of materials present in the sample.

ATR is the common technique used in FTIR. ATR exploits a crystal (i.e. diamond, zinc selenite or germanium), through which the infrared beam passes and then it goes back down, which then sets up evanescent wave, when the infrared beam hits the surface of crystal. This evanescent wave scans the materials outside the crystal: therefore, if the sample gets in contact with the surface of the ATR crystal, the infrared light interacts with the sample as shown in **Figure 1.20**. Before placing the sample, the crystal area should be cleaned and then background should be collected. Once the sample has been placed, the pressure arm should be applied over crystal/sample.

Independent from the employed technique, the ATR spectra are usually recorded at wavelengths from 600 to 4000 cm<sup>-1</sup> with 4 cm<sup>-1</sup> resolution (for organic compounds), and 16 or 32 scans are recorded for each spectrum.



**Figure 1.20.** FTIR-ATR spectroscopy

### 1.16.1.3. Thermal stability

#### 1.16.1.3.1. Thermogravimetric analysis (TGA)

The thermal stability and thermal decomposition of textile materials is often evaluated by thermogravimetric analysis (TGA). Thermogravimetric analysis (TGA) is a technique for measuring changes in the mass of the sample that occur as the sample temperature changes according to a controlled temperature program ( $T(t)$ ). The program can be either isothermal ( $T(t) = \text{constant}$ ) or non-isothermal. The most regular non-isothermal program is the one, in which the temperature changes linearly by means of time; so that the heating rate ( $\beta$ ) is constant. The used device is called a thermos-balance (**Figure 1.21**), which is a combination of a delicate analytical balance with an electronically planned furnace. A characteristic temperature range of the instruments is from room temperature to 1000°C.

While the heating rates could be set up in the range from a fraction to hundreds °C/min, the most commonly used range is within 1 to 20°C/min. a TGA run could take in a single temperature program. The runs are carried out in controlled gaseous atmosphere that could be either static or dynamic. The gas can be either inert or reactive, for example nitrogen, oxygen, and argon or helium atmosphere.

In TGA, the observation of mass loss is the result of loss of a volatile component in thermal degradation. The weight loss is monitored in a specified atmosphere as a function of temperature and/or time to demonstrate thermal transition in the material and referred to loss of solvent and plasticizer in the case of polymers, water of hydration in the case of inorganic materials and at the end to the decomposition of materials, which leads to change of mass. The temperature of the sample is programmed. A non-oxidative degradation refers to apply heat to materials under an inert gas flow, while under air or oxygen flow oxidative degradation of samples occurs.

The outcome of TGA measurements is a thermogravimetric curve that could be obtainable in either integral (TG curve) or differential form (DTG curve). In the integral form, absolute mass in gram or relative in % of initial mass is plotted vs. time or temperature. The differential form is the derivative of the TG curve with respect to time that is plotted against time or temperature. In a DTG curve, upward and downward peaks respectively stand for mass gain and mass loss steps. DTG curves allow better identifying individual mass loss steps.



**Figure 1.21.** TGA 4000-Perkin Elmer

#### 1.16.1.4. Assessment of the fire behavior

##### 1.16.1.4.1. Cone calorimetry

Cone calorimetry is a rather new bench-scale test, which has been developed in the case of fire testing and research and operates according to the principle of oxygen consumption. The fire behavior of polymers and associate calorimetric analysis to mass loss measurements and also the mechanism of action of fire retardant can be investigated through cone calorimetry. A major range of fire properties can be monitored by cone calorimetry in a well-defined fire scenario. Ignition and subsequent flaming combustion can be evaluated by cone calorimetry.

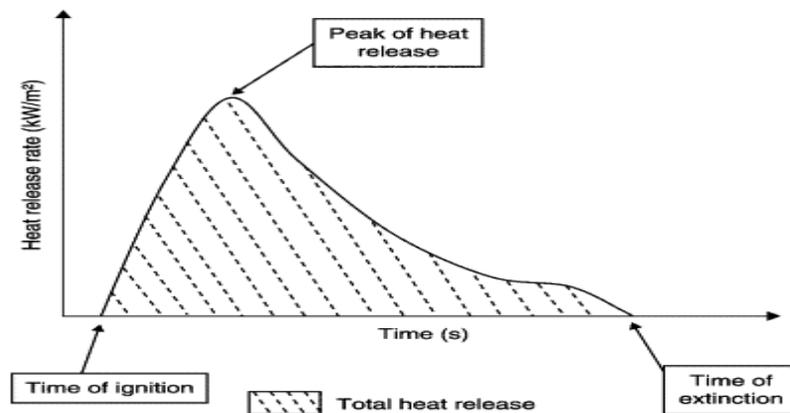
A temperature-controlled radiant heater imposes an extend irradiance (zero to above 100 kW/m<sup>2</sup>). The heat release rate of products can be evaluated by measuring the gas flow of combustion products and oxygen depletion, and at the same time mass loss is recorded.

The data attained from cone calorimetry test include:

- Heat release rate (HRR) expressed in kW/m<sup>2</sup>, i.e. the quantity of heat released per unit time and surface area.
- Peak HRR (PHRR), which is referred to the maximum value of heat release rate over time and this value, is mainly considered as an important parameter to evaluate the fire properties.

- Total heat release (THR), i.e. the integral of heat release rate with respect to time, expressed in  $\text{kJ/m}^2$ .
- Mass loss rate during combustion and experiment.
- Quantities of CO and CO<sub>2</sub> produced expressed in g/s and total smoke released (TSR), which are the result of incomplete combustion.
- Time to ignition (TTI), expressed in seconds; time of combustion or extinction (TOF) can be also characterized.

A typical HRR vs. time obtained from cone calorimetry tests is shown in **Figure 1.22**.

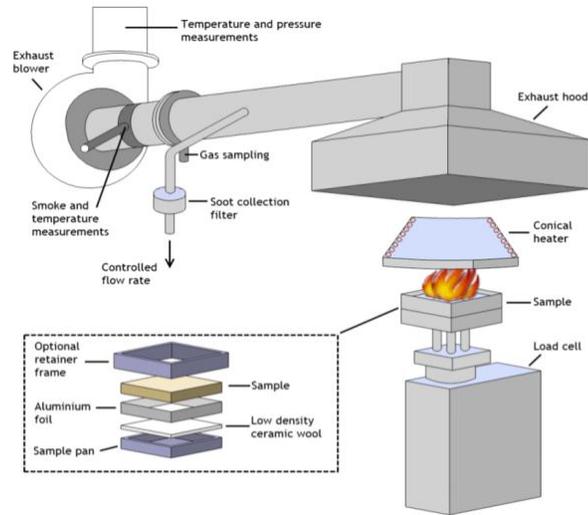


**Figure 1.22.** HRR vs. time curve

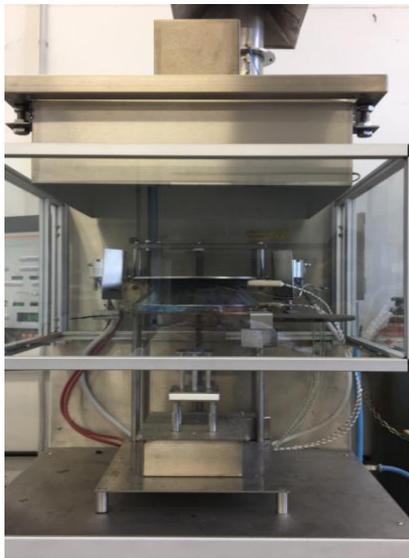
#### 1.16.1.4.1.1. Apparatus

The main parts of cone calorimeter device are illustrated in **Figure 1.23**. The weighted sample with specified dimensions is put in aluminum foil and placed in sample holder and maintained in the correct position with a metallic grid above the sample.

The cone shaped electrical heater heats the sample (**Figure 1.24**). The gases produced during pyrolysis are ignited by means of a spark; rate of heat release is assessed from oxygen reduction in the exhausted gases, therefore an accurate hood system is required.



**Figure 1.23.** Experimental set-up for a cone calorimetry test



**Figure 1.24.** Laboratory cone calorimeter

#### 1.16.1.4.2. UL-94 (vertical and horizontal flame spread tests)

Underwriter’s Laboratory UL-94 standard tests are widely used for evaluating the ease of ignition and flame spread of polymeric materials exposed to a small flame (controlled blue methane flame, around 25 mm long); there is no external heat flux as the flame ignition source is taken away after certain seconds.<sup>92</sup>

Two test protocols are involved in the UL-94 standard:

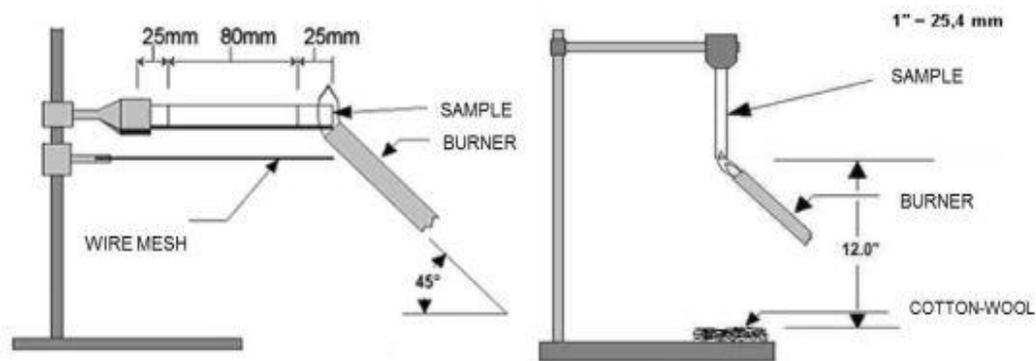
1. Horizontal burning tests, in which the rate of flame spread of samples is evaluated after tests. A sample (5 x10 cm) is fixed to a specimen support in horizontal position with 45° tilt over a Bunsen burner (hand-held); the flame (methane) should be applied to one end of sample for 3 and 10 seconds respectively. After removing the flame, if the sample continues to burn, the times for the sample to burn between the first 1 inch ( $t_1$ ) and 3 inch ( $t_2$ ) and the total time ( $t_{tot}$ ) for complete burning are recorded. Finally, burning rate (BR) can be calculated, as well as the final residue

2. Vertical burning tests (which are more severe), in which a specimen is put in vertical position and the same flame as horizontal test is applied to the bottom of the sample for 3 and 10 seconds and then it should be removed.

**Figure 1.25, Figure 1.26** and **Table 1.1** show the horizontal and vertical configurations involved in UL94 flammability tests.

Materials can be certified according to Underwriters Laboratory; UL rating increases from HB, to V-2, V-1 or V-0. The last represents the best fire retardant behavior.

The time is recorded during the tests and the burning time, the burning behavior and dripping of the sample can be evaluated during the test.



**Figure 1.25.** UL94 flammability tests

**Table 1.1.** UL94 apparatus

<p><b>Laboratory Fume Hood</b></p>	<p>At least inside volume of 0.5 m<sup>3</sup>, the observation can be done through chamber and should provide thermal circulation of air during burning. For safety, it is better this enclosure be equipped with an evacuation device. For example, an exhaust fans to remove combustion products which can be off during the test.</p>
<p><b>Laboratory burner</b></p>	<p>This contains a tube with inside diameter of 9.5 ±0.3 mm and length of 100 ±10 mm.</p>

<b>Ring Stands</b>	Which have clamps suit for horizontal and vertical positioning of sample and can be adjusted to different heights and angles.
<b>U-shaped metallic frame</b>	This metal support fixture is used when sample is not self-supporting.
<b>Gas supply</b>	Uniform gas flow of technical grade methane is supplied.
<b>Room or chamber conditions</b>	23 ±2°C and a relative humidity of 50% ±5.



**Figure 1.26.** Flammability test in horizontal and vertical configuration in lab

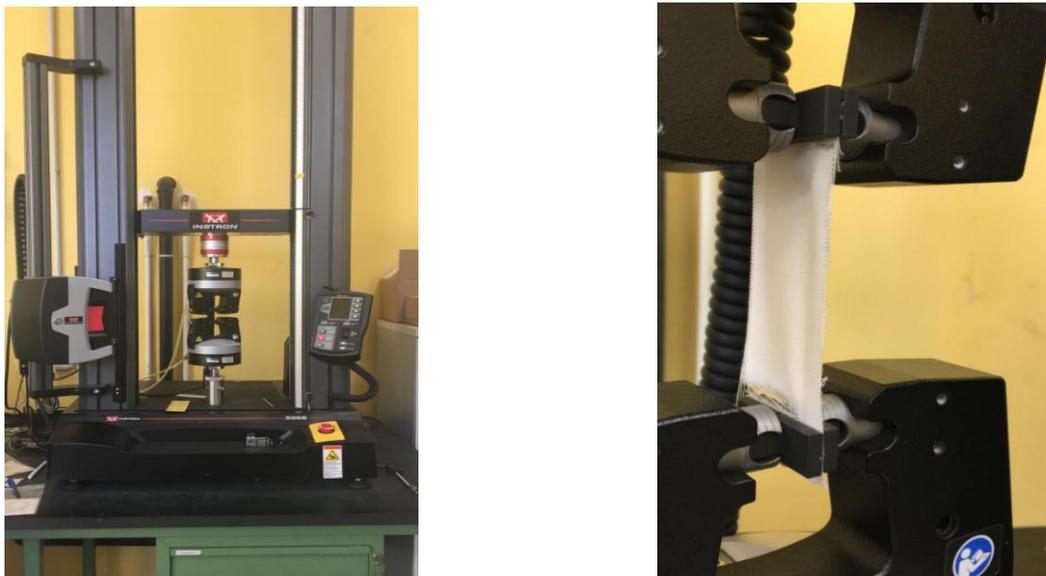
#### 1.16.1.5. Tensile tests

A tensile load is applied to the specimen by moving the crosshead up, as shown in **Figure 1.27**.

The applied load is measured by a load transducer (load cell), which is mounted in series with the specimen. Control system measures and displays an electrical signal that is converted from a load by the load cell. Load cells have the capability of being interchangeable with different capacities to provide a range of load measuring capabilities, which are limited only by the load frame at its maximum capacity.

Strain transducers can also measure strain.

A specific software program, designed for materials testing, controls the testing system. It has the ability to operate the system, collect and analyze test data, and set test parameters. Software online help provides detailed information on operating the system from the software.



**Figure 1.27.** Dynamometer

## **1.17. Washing fastness**

Durability of flame retardant system is one of the most important issues. Beside the flame retardant effectiveness, durability should also be considered. This means that after repeated washing the fire behavior should not change. Some commercially-available phosphorus-/nitrogen-based systems such as Proban®, Pyrovatex® and later Fyrol®, Fyroltex®, are well known to impart effective durability to cotton fabrics; conversely, they show some drawbacks referring to harmful impact of some chemicals included in their recipes on environment and human beings.

In the present study, washing durability of treated fabrics with sol-gel solutions was evaluated by washing the treated fabrics in distilled water at room temperature for 3 times. After washing treatment the fabrics were dried in oven at 80°C.

## Chapter 2: Materials and Methods

In this chapter, the materials will be introduced; besides, the methods and chemical treatment procedure will be discussed.

### 2.1. Materials

#### 2.1.1. Cotton fabric

Knitted pure cotton fabric ( $220 \text{ g/m}^2$  and 0.2 mm thick) was used as natural fabric and it was provided by Fratelli Ballezio S.r.l. (Torino, Italy).

#### 2.1.2. Phytic acid (PA)

Phytic acid (PA, 50 wt. % aqueous solution, molecular formula ( $\text{C}_6\text{H}_{18}\text{O}_{24}\text{P}_6$ )) was purchased from Sigma-Aldrich Corporation, USA and used as received.

#### 2.1.3. Tetraethyl orthosilicate (TEOS)

TEOS ( $\text{Si}(\text{OCH}_2\text{CH}_3)_4$ ; purity  $>99.0 \text{ wt. } \%$ ) was supplied by Tokyo chemical industry co.,LTD used as received.

#### 2.1.4. Dibutyltin Diacetate (DBTDA)

Dibutyltin Diacetate ( $\text{C}_{12}\text{H}_{24}\text{O}_4\text{Sn}$ ) was purchased from Aldrich Chemical Co. and used as condensation catalyst.

#### 2.1.5. Ethanol

Ethanol was purchased from Aldrich Chemical Co. and used as solvent.

### 2.2. Chemical treatment of cotton fabrics

Different types of sol-gel solutions were prepared with different phytic acid/TEOS ratios as shown in **table 2.1**. The results will be discussed in the next chapter.

#### 2.2.1. Preparation of the sol-gel solution

The sol-gel solution was prepared by mixing desired amounts of Phytic Acid (50 wt. % aqueous solution) and TEOS, adding one drop of Dibutyltin Diacetate as catalyst. The obtained mixture was stirred while ethanol was added slowly at room temperature. Thanks to the water content of phytic acid, the hydrolysis reaction involved in sol-gel process does not require further addition of water. Another important factor is that, usually in the sol-gel

process, the addition of acids such as HCl is required; in the designed system, the acidic character of phytic acid was exploited.

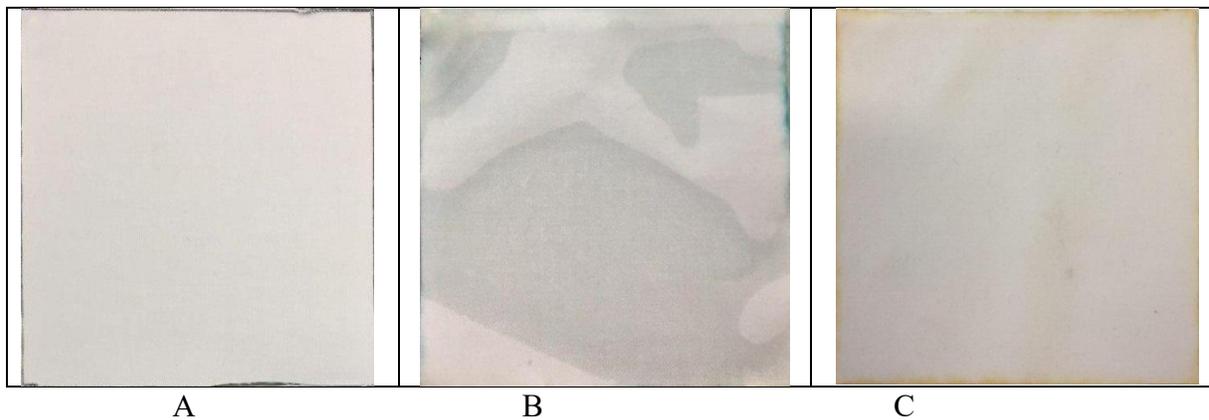
### 2.2.2. Sol-gel treatment

Cotton fabrics were cut into square pieces (10x10 cm), weighted and then impregnated with the solution. The impregnated fabrics were put on a glass support and dried to a constant weight in the oven at 80°C for 30 min: during this time the evaporation of water and the sol-gel reactions take place. This was witnessed by the colour change of the fabrics as shown in **Figure 2.1** and then modified cotton fabric was weighted quickly. After that, total dry solids add-on on the cotton samples (the weight gain (A), wt. %) was determined by weighing each sample before (Wi) and after the impregnation with the solution and the subsequent thermal treatment (Wf). The weight gain of the treated fabric was calculated using the following formula:

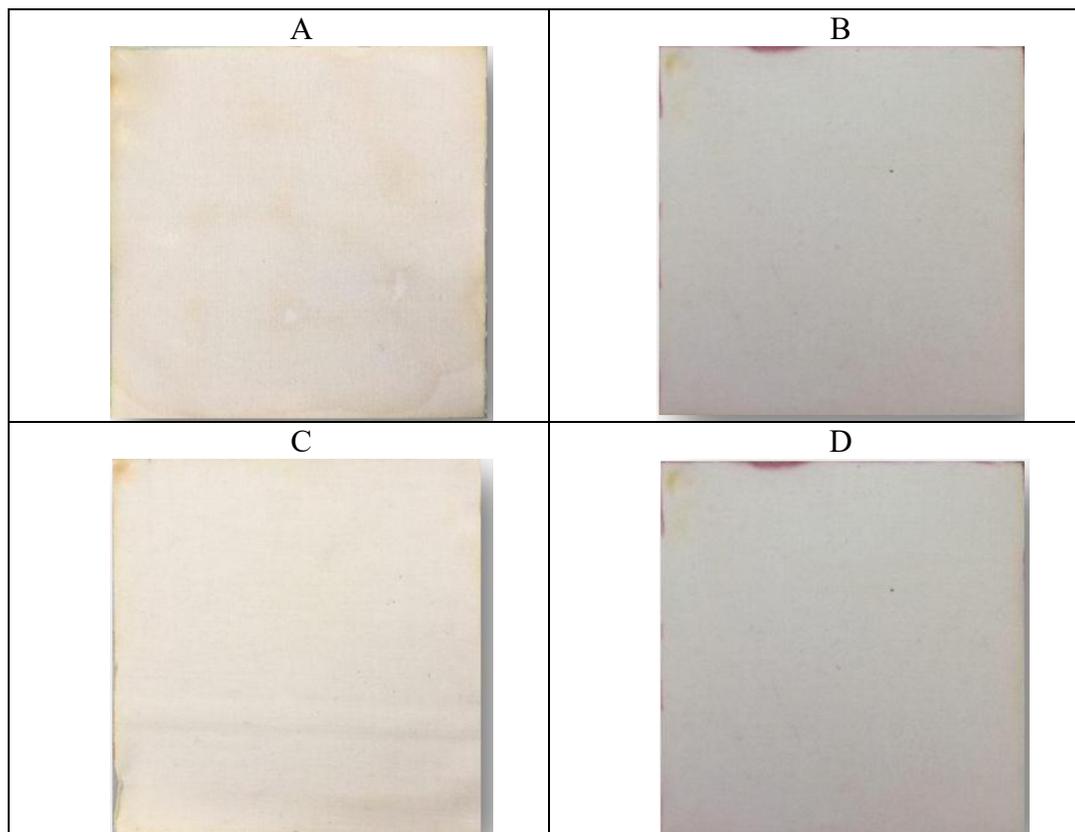
$$A = \frac{Wf - Wi}{Wf} * 100$$

**Table 2.1.** Composition (wt. %) of the treated cotton fabrics investigated

Phytic acid %	TEOS %	SAMPLE CODE	Total add-on wt. % (A)	Phytic acid wt. %
50	50	COT+SOL (50/50)	30	10
			24	8
			21	7
			19	6
60	40	COT+SOL (60/40)	23	10
			19	8
			17	7
			14	6
40	60	COT+SOL (40/60)	40	10
			32	8
			28	7
			24	6
70	30	COT+SOL (70/30)	19	10
			15	8
			13	7
			12	6



**Figure 2.1.** A. untreated cotton. B. impregnated (wet) cotton, C. dried treated cotton fabric



**Figure 2.2.** Cotton modified with sol-gel solution. A. COT+SOL (50/50), B. COT+SOL (60/40), C. COT+SOL (40/60), D. COT+SOL (70/30). All the treated fabrics contain 8.5 wt. % of PA.

## 2.3. Washing treatments

For evaluating the washing fastness of the system, impregnated fabrics were washed in a baker with distilled water for 3 minutes and then were dried to a constant weight in oven (temperature: 80°C). The procedure was repeated four times.

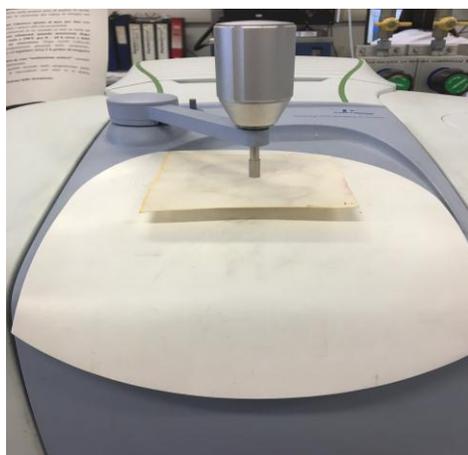
## 2.4. Characterization technique

### 2.4.1. Field-Emission Scanning Electron Microscopy (FESEM)

The morphology of treated and untreated cotton fabrics has been investigated using FESEM (ZEISS, MERLIN), equipped with an x-ray probe (INCA Energy Oxford) which was utilized for performing elemental analysis. Cotton fabrics were cut and metallized with platinum (thickness of the layer: 5 nm)

### 2.4.2. Fourier Transform Infrared; FTIR-ATR spectroscopy analysis

A Perkin Elmer Spectrum 100 spectrometer equipped with an attenuated total reflection (ATR) accessory (**Figure 2.3**) was used to obtain the FT-IR spectra of untreated and treated cotton. The FTIR spectra were recorded at wavelengths from 700 to 4000  $\text{cm}^{-1}$  with 4  $\text{cm}^{-1}$  resolution. The apparatus was set to scan each sample for 16 times. A background spectrum was also obtained.



**Figure 2.3.** FTIR-ATR Spectrophotometer

### 2.4.3. Tensile tests

The mechanical properties were evaluated using an Instron 5566 tensile tester (**Figure 2.4**). The dimensions of the samples were 70x30x0, 25 mm. Untreated and modified cotton fabrics either before or after washing, were tested.



**Figure 2.4.** Instron 5566 series

#### 2.4.4. Thermogravimetric Analysis

The thermal and thermo-oxidative stability of the fabrics was evaluated by thermogravimetric (TG) analyses in air and in nitrogen, respectively, from 50 to 700°C with a heating rate of 20°C/min. A TAQ500 analyzer (TA Instrument Inc., Waters LLC, USA) was used, placing the samples (approximately 8 mg) in open alumina pans, in inert or oxidative atmosphere (gas flow: 35 ml/min).

#### 2.4.5. Characterization of the fire behavior

The combustion behavior and the flame retardants properties of the treated samples were evaluated by cone calorimeter and UL94.

##### 2.4.5.1. UL 94 tests

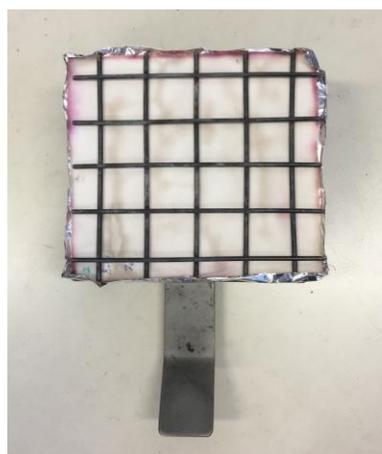
Flammability tests in horizontal and vertical configuration were carried out by applying a methane flame for 3 second on the short side of the specimens (5 x10 cm). For horizontal tests, cotton fabrics were clamped in a U-shaped metallic frame, tilted 45° with respect to the plane containing the frame, while, for vertical tests, the fabrics were placed vertically (**Figure 2.5**). Total burning time, burning rate (calculated as the ratio between the length of the burnt cotton and the burning time) and final residue (%) were evaluated.



**Figure 2.5.** UL94 burning test (in horizontal configuration)

#### 2.4.5.2. Cone calorimetry tests

To simulate the behaviour of the samples in a real fire scenario, cone calorimetry tests were performed according to the ISO 5660 standard. Square specimens (10x10 cm) were irradiated with a heat flux of  $35 \text{ kW/m}^2$  in horizontal configuration. The cotton fabrics were placed on a sample holder and maintained in the correct position using a metallic grid (**Figure 2.6**). For each formulation, the test was repeated three times.



A



B

**Figure 2.6.** A. sample placed on a sample holder with metallic grid. B. cone calorimeter

## Chapter 3: Results and Discussion

The first goal of this work was to identify the TEOS: PA ratio (**Table 3.1**) that allowed achieving the best flame retardants properties, with the lowest total dry add-on on the fabrics.

**Table 3.1.** Composition (wt. %) of the different system investigated

<b>SAMPLE CODE</b>	<b>wt. % PA</b>	<b>wt. % TEOS</b>
<b>COT+SOL(50/50)</b>	50	50
<b>COT+SOL(60/40)</b>	60	40
<b>COT+SOL(40/60)</b>	40	60
<b>COT+SOL(70/30)</b>	70	30

The morphology, the thermal and oxidative-thermal stability, and the mechanical properties of the untreated and treated cotton fabrics will be discussed and the experimental data obtained will be analyzed.

### 3.1. Washing durability

First of all, washing durability of the treated cotton was studied. The data presented in the **Tables 3.2-3.5** show that major part of the deposited coating, in case of COT+SOL(50/50), COT+SOL(60/50), COT+SOL(70/30), is lost after the first washing treatment. Cotton impregnated with a higher percentage of TEOS (COT+SOL (40/60)) showed a lower weight loss (i.e. 54 %). To compare these data, the washing treatment has been applied only to the samples treated with 8, 5 wt. % PA.

The remaining part of the solution is well incorporated in the cotton fabrics; in fact, the subsequent washing did not further extract the coating.

**Table 2.2.** COT+SOL (50/50) after 3 washing cycles

<b>Washing cycle</b>	<b>Weight loss (%)</b>
1	85
2	1
3	1

**Table 3.3.** COT+SOL (60/40) after 3 washing cycles

<b>Washing cycle</b>	<b>Weight loss (%)</b>
1	79
2	1
3	1

**Table 3.4.** COT+SOL (40/60) after 3 washing cycles

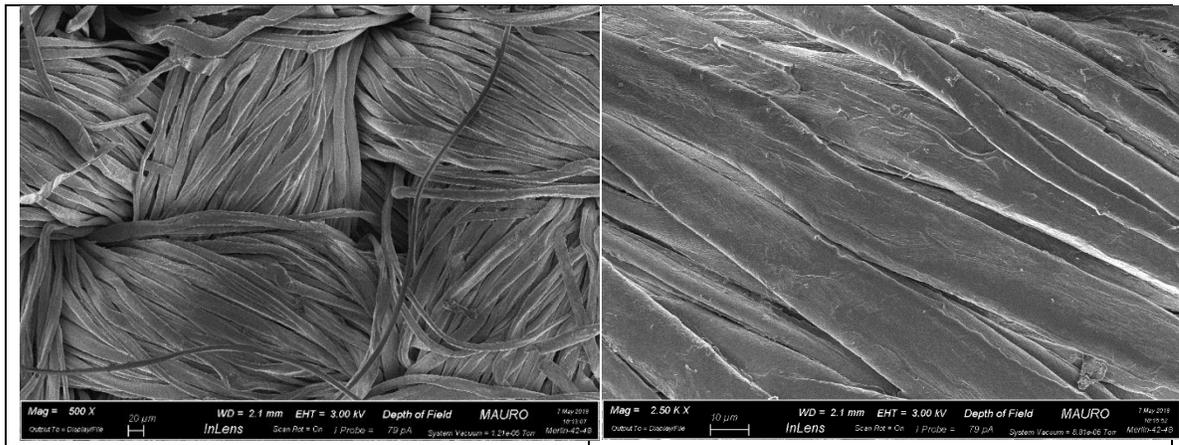
<b>Washing cycle</b>	<b>Weight loss (%)</b>
1	50
2	4
3	4

**Table 3.5.** COT+SOL (70/30) after 3 washing cycles

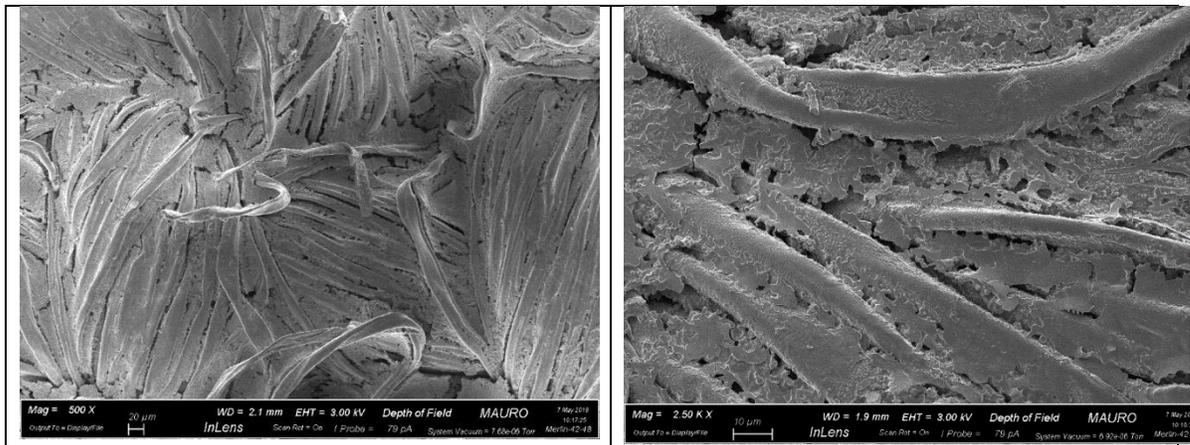
<b>Washing cycle</b>	<b>Weight loss (%)</b>
1	76
2	6
3	6

### 3.2. Morphological Analysis

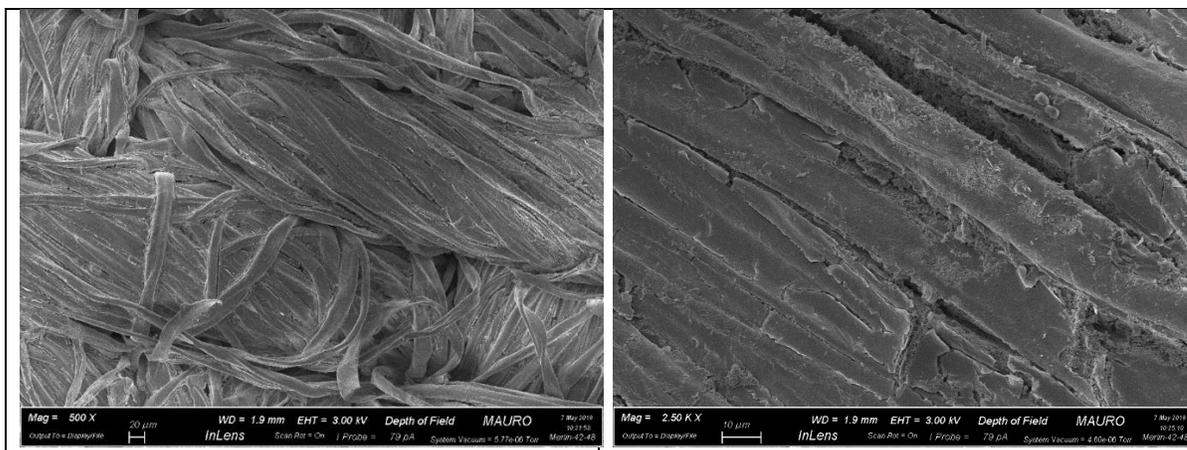
FESEM observations have been performed in order to assess the morphology of the cotton fibers before and after the sol-gel treatments. Untreated cotton shows the characteristic smooth texture (**Figure 3.1**), while for the treated cotton (**Figures 3.2** and **Figure 3.3**); the fibers increase their roughness, because their surface is covered by the sol-gel coating. Besides, the coating is still present even after the fabrics has undergone the washing cycles. These findings clearly demonstrate that the sol-gel coatings, the fabrics have been treated with, are at least partially anchored to the textile.



**Figure 3.1.** FESEM images of untreated cotton



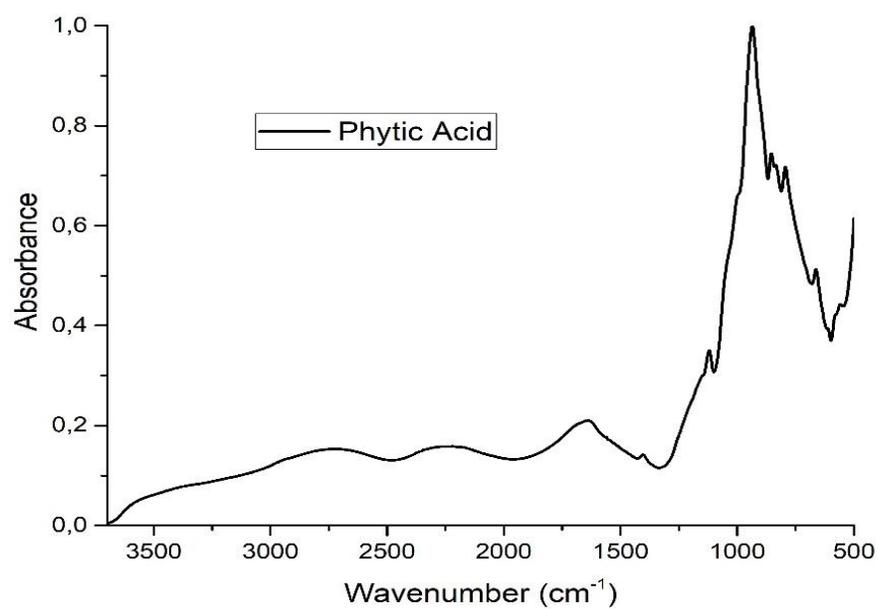
**Figure 3.2.** FESEM images of cotton impregnated with solution (COT+SOL (70/30), 8.5 wt. % PA add on)



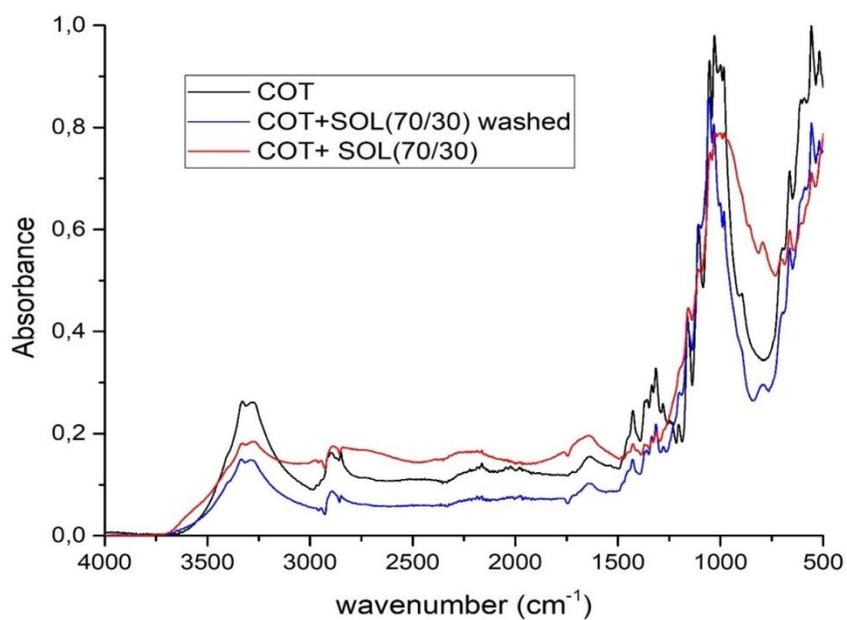
**Figure 3.3.** FESEM images of cotton impregnated with solution (COT+SOL (70/30), 8.5 wt. % PA add on) and then washed

### 3.3. FT-IR ATR spectroscopy

The effectiveness of the deposition of the sol-gel coatings on the cotton fabrics has been assessed through FTIR-ATR spectroscopy. **Figure 3.5** shows the typical ATR spectra of cotton and sol-gel treated cotton, before and after washing. The typical peaks of cellulose are well detectable in untreated cotton (namely:  $\nu(\text{OH})$  at ca. 3300,  $\nu(\text{CH}_2)$  at 2900,  $\delta(\text{OH})$  at 1640,  $\delta(\text{CH}_2)$  at 1425,  $\delta(\text{CH})$  at 1370,  $\delta(\text{OH})$  at 1310,  $\nu(\text{C}-\text{C})$  at 1020, and  $\delta(\text{OH})$  at 894  $\text{cm}^{-1}$ ). In the ATR spectra of pure phytic acid (**Figure 3.4**) three characteristic peaks located at 1650, 1060 and 980  $\text{cm}^{-1}$  and corresponding to stretching vibration of P=O and asymmetric and symmetric stretching of P-O-C are present. The ATR spectrum of treated cotton still shows the presence of some typical vibrational modes of cellulose but these signals are less intense and defined because of the presence the sol-gel coating (**Figure 3.5**). Furthermore, the treated cotton shows the presence of a peak at 790  $\text{cm}^{-1}$  (**Figure 3.5**) corresponding to symmetrical stretching of Si-O-Si. This evidence confirms the effective presence of the sol-gel derived ceramic phase incorporated in the cotton structure.



**Figure 3.4.** ATR spectrum of pure PA



**Figure 3.5.** ATR spectrum of COT, COT+SOL (70/30), COT+SOL (70/30) washed

### 3.4. Thermogravimetric analysis

TGA has been used to evaluate the thermal and thermo-oxidative stability of the untreated and treated cotton fabrics.  $T_{ONSET}$ , the maximum weight loss temperatures ( $T_{max1}$  and  $T_{max2}$ ), the residue at the maximum weight loss temperature and the final residue at 700°C are shown in **Table 3.6**.

The presence of phytic acid on cotton fabric induces several changes in the thermal stability (**Table 3.6**).

**Table 3.6.** Thermal and thermo-oxidative stability of the treated cotton fabrics

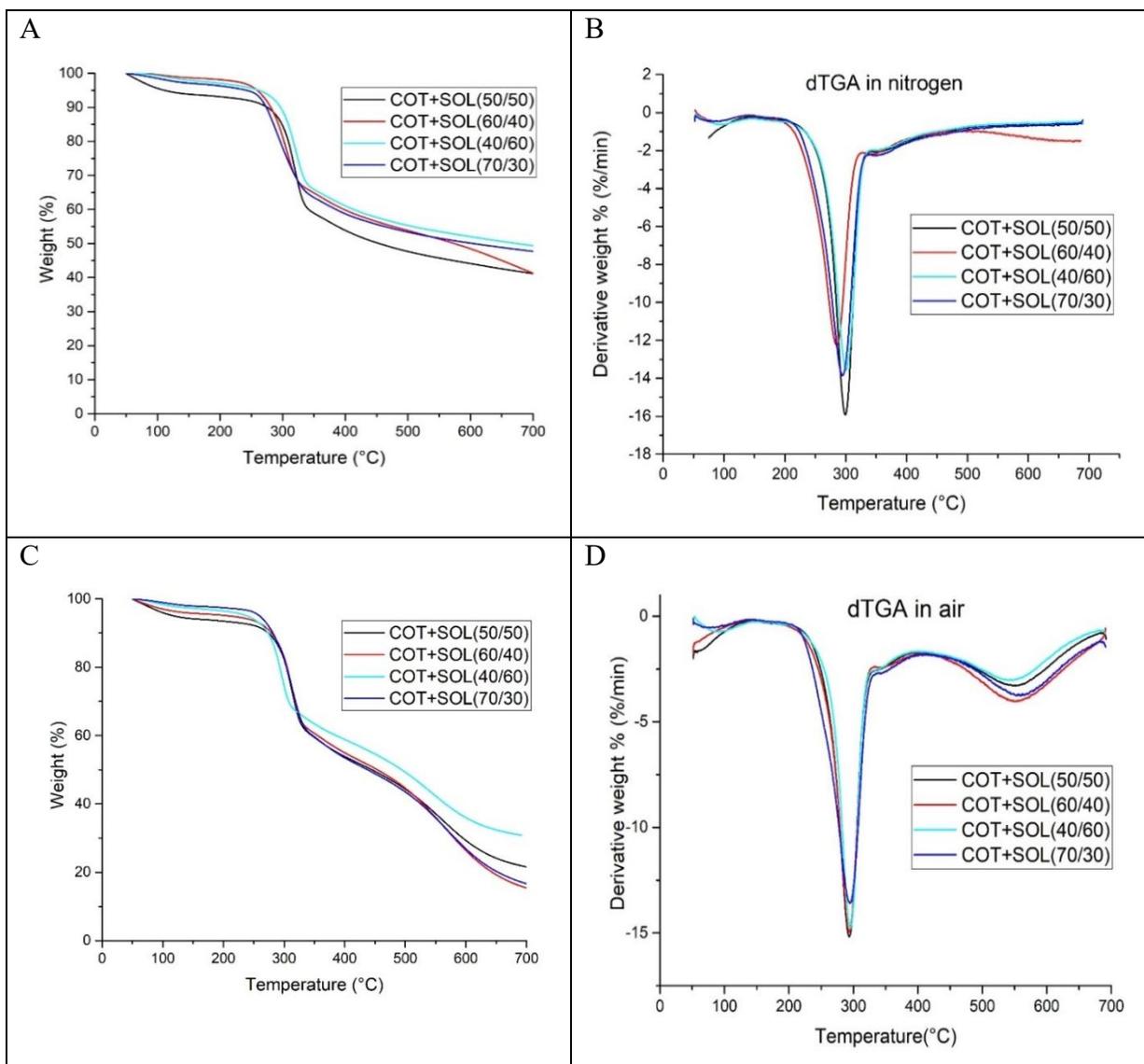
<b>Atmosphere: nitrogen</b>						
<b>Sample code</b>	<b><math>T_{ONSET}</math> (°C)</b>	<b><math>T_{max1}</math> (°C)</b>	<b>Residue@ <math>T_{max1}</math></b>		<b>Residue@700°C</b>	
			<b>(%)</b>		<b>(%)</b>	
<b>COT</b>	358	386	48,3		3,8	
<b>COT+SOL (50/50)</b>	277	299	70,7		40,7	
<b>COT+SOL (60/40)</b>	253	284	78,3		41,3	
<b>COT+SOL (40/60)</b>	276	300	76,9		49,3	
<b>COT+SOL (70/30)</b>	264	295	74,4		41,1	
<b>Atmosphere: air</b>						
<b>Sample code</b>	<b><math>T_{ONSET}</math> (°C)</b>	<b><math>T_{max1}</math> (°C)</b>	<b>Residue@ <math>T_{max1}</math> (%)</b>	<b><math>T_{max2}</math> (°C)</b>	<b>Residue@ <math>T_{max2}</math> (%)</b>	<b>Residue @ 700°C (%)</b>
<b>COT</b>	350	368	53	514	7,3	3,5
<b>COT+SOL (50/50)</b>	268	294	71,7	551	34,8	21,5
<b>COT+SOL (60/40)</b>	265	291	76	551	32,7	15,4
<b>COT+SOL (40/60)</b>	271	294	78,3	542	43,7	30,8
<b>COT+SOL (70/30)</b>	261	294	72,8	557	32,5	16,6

The TG and dTG plots in **Figures 3.10-3.13** clearly show some differences in thermal behavior between COT, COT+SOL (70/30) and COT+SOL (70/30) washed.

In inert atmosphere (nitrogen), the decomposition of the untreated cotton takes place according to a single main degradation step; the degradation onset occurs at about 358°C and the maximum degradation rate is observed at 386°C (**Table 3.7**). The sol gel coating is responsible for an anticipation of the cellulose decomposition temperature as revealed by  $T_{\max}$  and  $T_{\text{ONSET}}$ . In fact, in case of COT,  $T_{\max}$  and  $T_{\text{ONSET}}$  are 386 and 358 °C respectively, while for COT+SOL (70/30) are 295 and 264 °C. This effect can be attributed to the activation of the coating prior to the decomposition of cellulosic matrix. In doing so, the flame retardant coating promotes the formation of a stable residue (char), able to act as a thermal barrier. As a consequence, the final residue is dramatically higher for COT+SOL (70/30) (41,1%), if compared with COT (3,8%).

In air, decomposition usually occurs by three steps. The first (300-400°C) involves two competitive pathways, which produce aliphatic char and volatile products; during the second step (400-800°C), some char converts to an aromatic form, producing CO and CO<sub>2</sub> as a consequence of simultaneous carbonization and char oxidation. The third step (at ca. 800°C), the char and hydrocarbon species are further oxidized mainly to CO<sub>2</sub> and CO. In this work, two decomposition peaks (**Table 3.7**, at 368 and 514°C) are observable for untreated cotton (**Figure. 3.13**). The presence of flame retardant coating anticipates the decomposition ( $T_{\text{ONSET}}$ ) and the maximum weight loss ( $T_{\max1}$ ) but favors the formation of stable char as revealed by  $T_{\max2}$  and the final residues (**Table 3.7**).

The treated fabrics do not show significant differences in thermal and thermo-oxidative parameters (**Table 3.6, Figure 3.6**). COT+SOL (50/50), COT+SOL (60/40), COT+SOL (40/60), COT+SOL (70/30) show similar results in terms of  $T_{\text{ONSET}}$ ,  $T_{\max1}$ ,  $T_{\max2}$  in both nitrogen and air (**Table 3.6**).

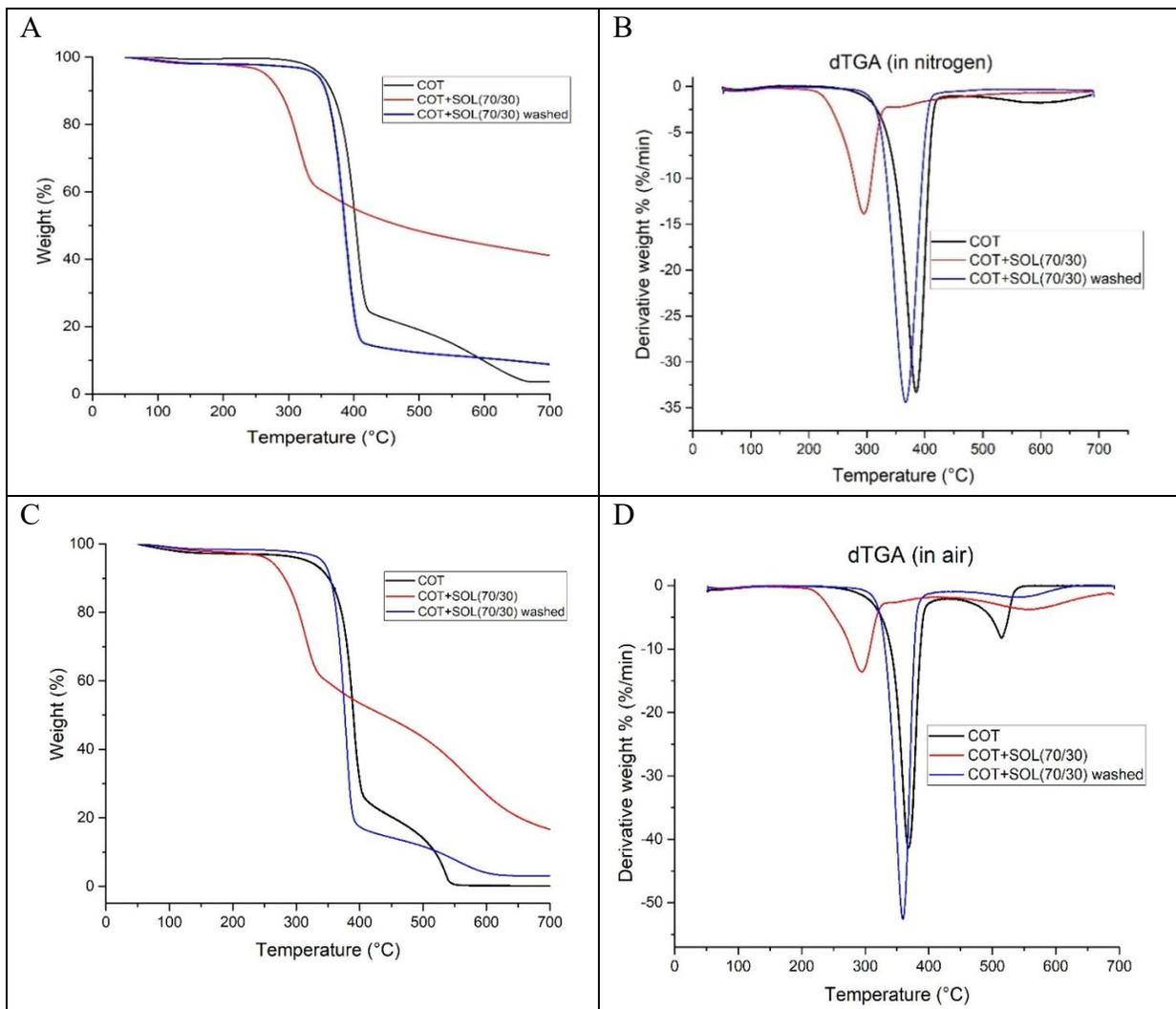


**Figure 3.6.** TG and dTG curves of treated cotton fabrics. TG of treated cotton fabrics in  $N_2$  (A) and air (C) and dTG of treated cotton fabrics in  $N_2$  (B) and air (D)

After washing treatment, as discussed before, a significant part of the sol-gel coating is lost. This evidence is also proven by TGA analysis in nitrogen and air (**Figure 3.7**). However, “COT+SOL(70/30) washed” still exhibits a higher thermal stability and final residue (**Table 3.7**) when compared with untreated cotton. This evidence confirms that a part of sol-gel coating is still present in the cotton structure.

**Table 3.7.** Thermal and thermo-oxidative stability of cotton (COT), treated cotton fabrics and treated cotton fabrics after washing

<b>Atmosphere: nitrogen</b>						
<b>Sample code</b>	<b>T<sub>ONSET</sub> (°C)</b>	<b>T<sub>max1</sub> (°C)</b>	<b>Residue@T<sub>max1</sub> (%)</b>		<b>Residue@700°C (%)</b>	
<b>COT</b>	358	386	48,3		3,8	
<b>COT+SOL(70/30)</b>	264	295	74,4		41,1	
<b>COT+SOL(70/30) washed</b>	344	366	51,9		8,8	
<b>Atmosphere: air</b>						
<b>Sample code</b>	<b>T<sub>ONSET</sub> (°C)</b>	<b>T<sub>max1</sub> (°C)</b>	<b>Residue @T<sub>max1</sub> (%)</b>	<b>T<sub>max2</sub> (°C)</b>	<b>Residue@ T<sub>max2</sub> (%)</b>	<b>Residue @ 700°C (%)</b>
<b>COT</b>	350	368	53,0	514	7,3	0
<b>COT+SOL(70/30)</b>	261	294	72,8	557	32,5	16,6
<b>COT+SOL(70/30) washed</b>	342	359	45,7	/	/	3,3



**Figure 3.7.** TG and dTG curves of COT, COT+SOL(70/30), COT+SOL(70/30) washed. TG curves in N<sub>2</sub> (A) and air (C) atmosphere and dTG in N<sub>2</sub> (B) and air (D)

### 3.5. Fire behavior

#### 3.5.1. UL 94 (horizontal and vertical configuration)

The flame retardant properties of treated and untreated cotton have been evaluated by horizontal and vertical flame spread tests. The rate of flame spread (BR) and final residue (%) of all the samples were evaluated by means of horizontal flame spread tests: the results are collected in **table 3.8**. **Figures 3.8** and **Figure 3.9** show the residues after the tests.

The burning rate (BR, mm/s) was calculated according to the following equation:

$$BR = \frac{\text{char length}[mm]}{\text{burning time}(s)}$$

**Table 3.8** collects the results of UL-94 tests (in both configurations) of cotton fabric treated with sol-gel solutions. Untreated cotton, irrespective of the configuration (vertical or horizontal) adopted for the flammability test completely burns after the application of the methane flame (**Table 3.9**).

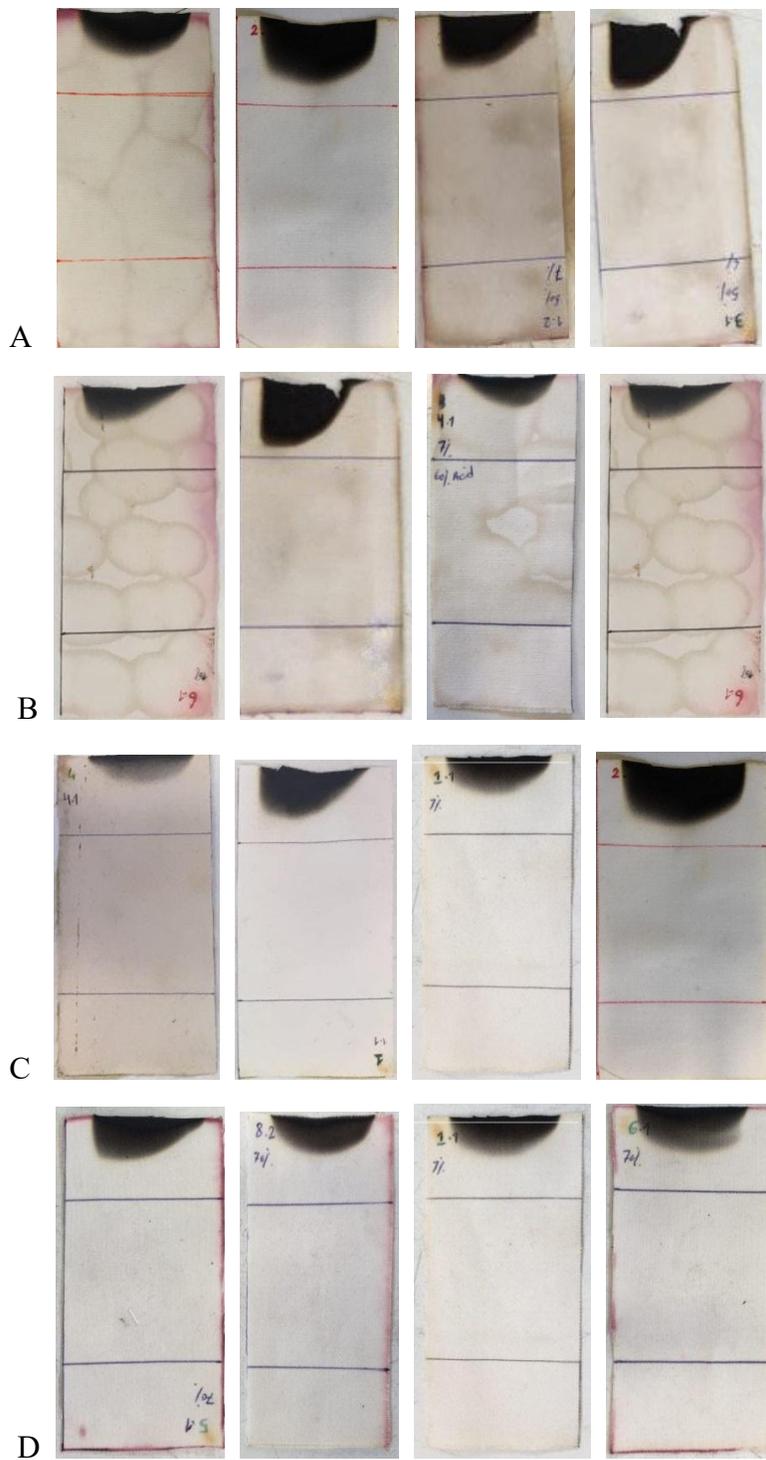
To better understand the flame retardant properties, solutions with a different ratio between PA and TEOS were prepared. The preliminary burning tests show that the best flame retardant properties correspond to the cotton fabrics impregnated with a solution with 70% PA and 30% TEOS (**Table 3.8**). By maintaining this ratio constant, different amounts of solution have been added to cotton fabrics in order to define the minimum amount of solution necessary to achieve self-extinction (in both configurations). The results, in vertical and horizontal configuration, have shown that 16% total add on is the minimum add-on necessary for reaching self-extinction.

Therefore, the cone calorimetry tests were performed using this sol (16% total add on, 8,5% PA).

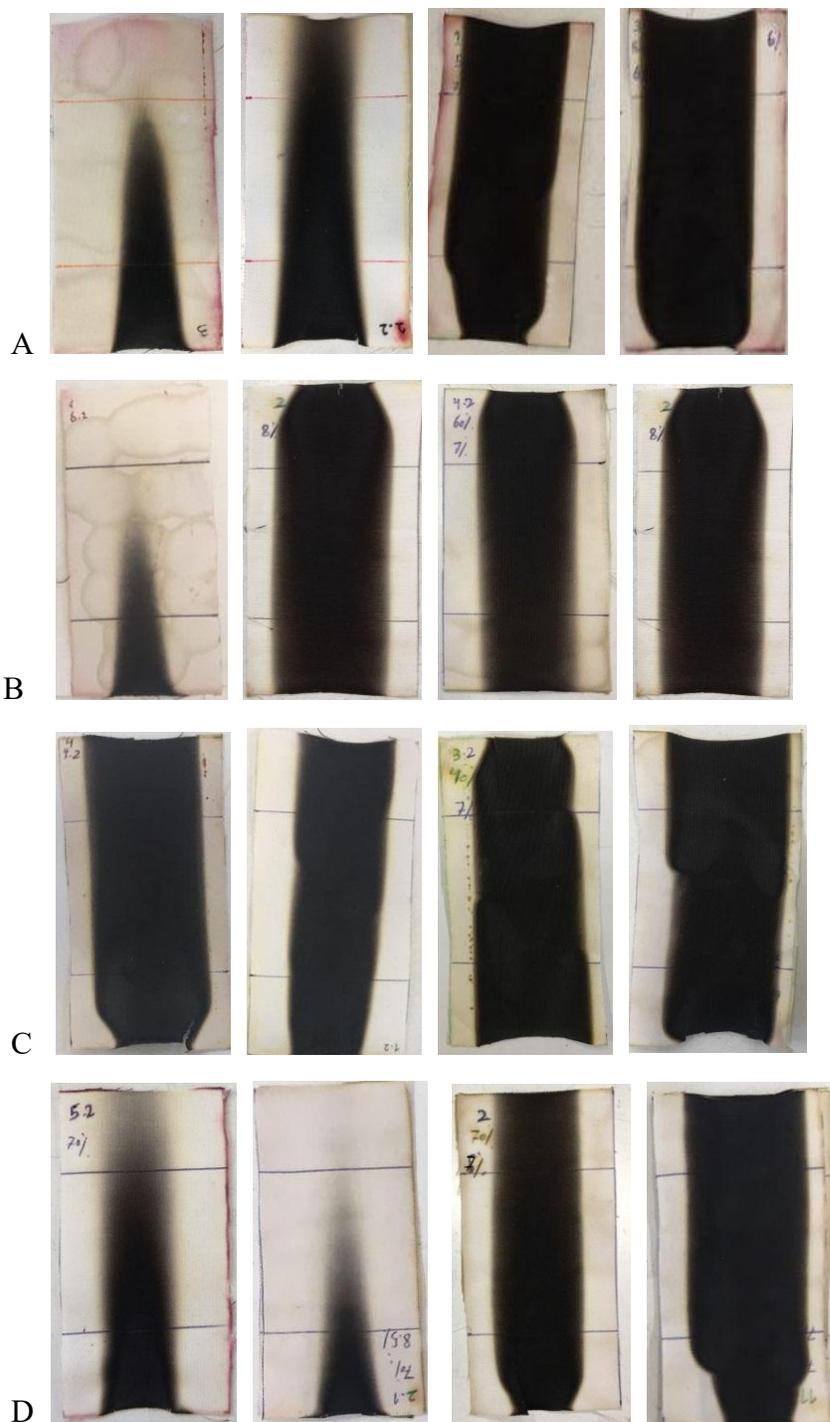
**Table 3.8.** Horizontal and vertical flame spread tests performed on treated samples

Horizontal flame spread tests				
SAMPLE	PA content (%)	Total dry add-on (%)	SELF-EXTINCTION	Residue (%)
COT+SOL (50/50)	10	30	YES	96
	8	24	YES	95
	7	21	YES	95
	6	19	YES	95
COT+SOL (60/40)	10	23	YES	97
	8	19	YES	96
	7	17	YES	96
	6	14	YES	95

<b>Horizontal flame spread tests</b>				
<b>SAMPLE</b>	<b>PA content (%)</b>	<b>Total dry add-on (%)</b>	<b>SELF-EXTINCTION</b>	<b>Residue (%)</b>
<b>COT+SOL(40/60)</b>	10	40	<b>YES</b>	89
	8	32	<b>YES</b>	87
	7	28	<b>YES</b>	86
	6	24	<b>YES</b>	85
<b>COT+SOL(70/30)</b>	10	19	<b>YES</b>	94
	8.5	16	<b>YES</b>	93
	7	13	<b>YES</b>	93
	6	12	<b>YES</b>	95
<b>Vertical flame spread tests</b>				
<b>COT+SOL(50/50)</b>	10	30	<b>YES</b>	92
	8	24	<b>YES</b>	88
	7	21	<b>NO</b>	63
	6	19	<b>NO</b>	56
<b>COT+SOL(60/40)</b>	10	23	<b>YES</b>	96
	8	19	<b>NO</b>	68
	7	17	<b>NO</b>	55
	6	14	<b>NO</b>	56
<b>COT+SOL(40/60)</b>	10	40	<b>NO</b>	77
	8	32	<b>NO</b>	74
	7	28	<b>NO</b>	60
	6	24	<b>NO</b>	55
<b>COT+SOL(70/30)</b>	10	19	<b>YES</b>	86
	8.5	16	<b>YES</b>	91
	7	13	<b>NO</b>	67
	6	12	<b>NO</b>	58



**Figure 3.8.** Residues after horizontal flame spread tests. A. COT+SOL(50/50), B. COT+SOL(60/40), C. COT+SOL(40/60), D. COT+SOL(70/30).each rows contained 10, 8, 7, 6 wt.% phytic acid.



**Figure 3.9.** Residues after vertical flame spread tests. A. COT+SOL(50/50), B. COT+SOL(60/40), C. COT+SOL(40/60), D. COT+SOL(70/30), each rows contained 10, 8, 7, 6 wt.% phytic acid

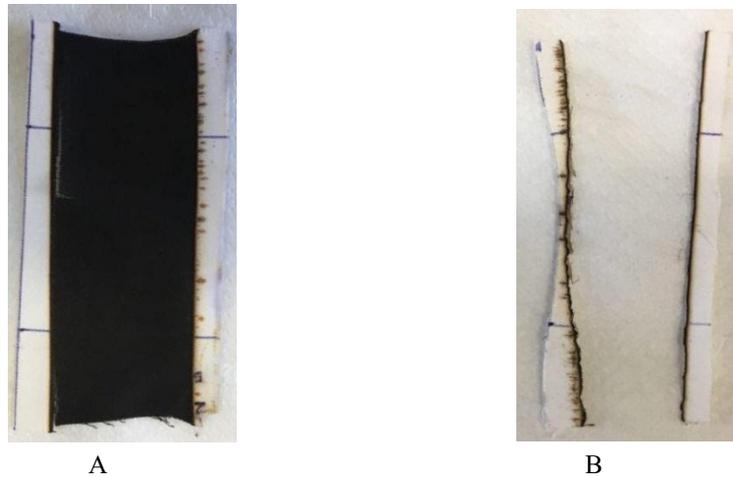
After washing (**Table 3.9**), cotton fabrics lose self-extinction but still burned slower with respect to untreated cotton; furthermore, the final residue was higher (**Table 3.9**).

In addition, it is possible to observe that, although the fibers are slightly consumed (**Figure 3.10.A**) by the fire, the texture of the fabric is still maintained and the residue is coherent.

The data presented in **table 3.9** shows that a higher total add-on (PA and TEOS solution) correspond to a lower burning rate and higher residue left. The best results were obtained for COT+SOL (40/60) that contains the highest amount of TEOS in comparison with the other systems.

**Table 3.9.** Horizontal flame spread tests performed on treated samples after washing

<b>Horizontal test</b>							
<b>SAMPLE</b>	<b>PA add-on (%)</b>	<b>Total add-on (%)</b>	<b>T1 (s)</b>	<b>T2 (s)</b>	<b>Ttot (s)</b>	<b>Burning rate (mm/s)</b>	<b>Residue Left (%)</b>
<b>COT</b>	/	/	12	40	63	1,58	0
<b>COT+SOL (50/50)</b>	10	30	18	58	91	1,09	25
	8	24	12	44	80	1,25	18
	7	21	16	46	74	1,35	24
	6	19	14	44	71	1,40	19
<b>COT+SOL (60/40)</b>	10	23	9	35	70	1,43	26
	8	19	16	47	72	1,39	15
	7	17	14	45	74	1,35	13
	6	14	16	47	74	1,35	10
<b>COT+SOL (40/60)</b>	10	40	15	57	96	1,04	38
	8	33	13	44	78	1,28	35
	7	28	15	55	79	1,26	25
	6	24	15	52	84	1,19	18
<b>COT+SOL (70/30)</b>	10	19	16	46	72	1,39	16
	8.5	16	14	45	72	1,39	15
	7	13	10	42	66	1,51	12
	6	12	11	42	63	1,59	11



**Figure 3.10.** A. COT+SOL (70/30) washed, B. untreated cotton after flammability

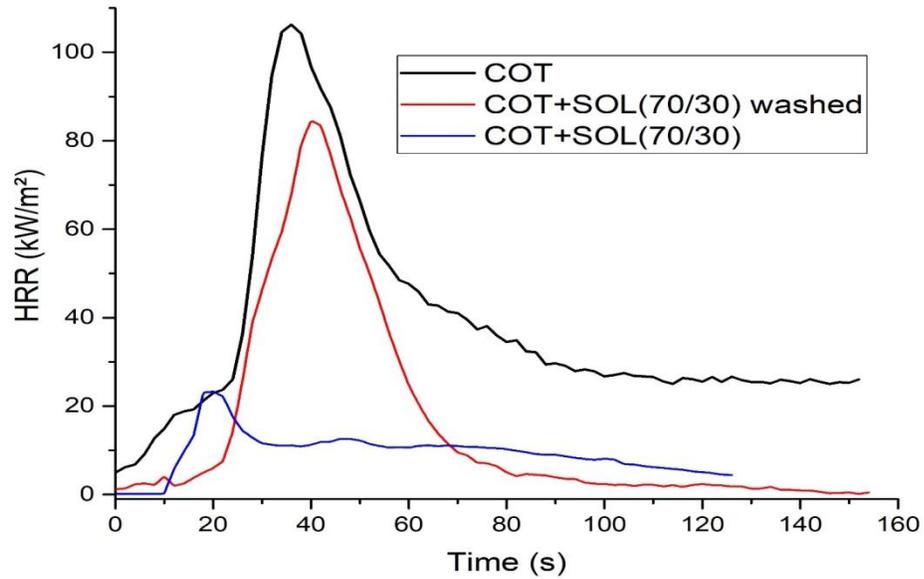
### 3.5.2. Cone calorimetry tests

To simulate a realistic fire behavior of the treated and untreated cotton fabrics, cone calorimetry test has been performed. The results are collected in **Tables 3.10** and **3.11**.

The Heat Release Rate (HRR) curves vs. time shown in **Figure 3.11** indicate that HRR peak of COT is higher than COT+ SOL and COT+SOL (WASH). Although the ignitability increased in case of treated cotton, HRR, HRR peak and THR values are significantly lower with respect to untreated cotton (**Table 3.10**). Furthermore, the untreated cotton completely burns (0% residue), while for COT+SOL the residue is much higher (25,8%). HRR, HRR peak and THR values are higher for COT+SOL washed sample, because of the partial removal of the sol-gel coating; however, the thermal parameters are still lower as compared to untreated cotton.

**Table 3.10.** The combustion data for treated and untreated cotton fabrics

Sample	Time to ignition (s)	HRR (kW/m <sup>2</sup> )	HRR peak (kW/m <sup>2</sup> )	Time to peak (s)	THR (MJ/m <sup>2</sup> )	Residue (%)
COT	19	15,6	106,4	38	2,01	0
COT+SOL(70/30)	13	10,0	26,9	19	1,21	25,8
COT+SOL (70/30) washed	22	10,7	92,9	44	2,56	16

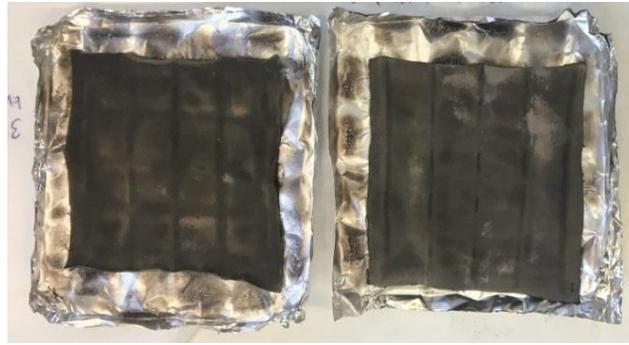


**Figure 3.11.** HRR vs. time for COT, COT+SOL (70/30), COT+SOL (70/30) washed

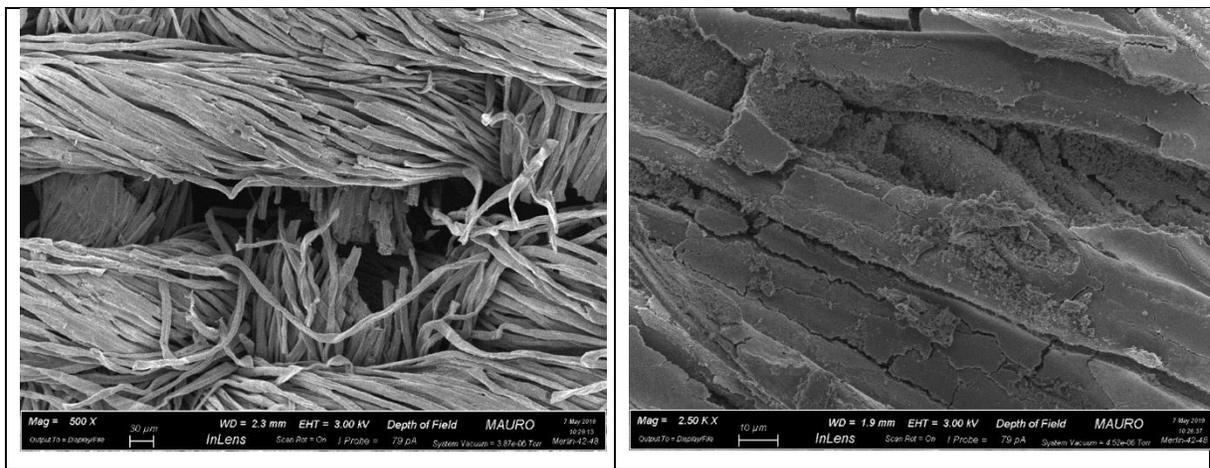
As already observed in flammability tests, the sol-gel coating, exerting some protection on the underlying cotton, is able to favor the formation of coherent and thick residues, which maintain the fabric texture, as shown in **Figures 3.12** and **3.13**. FESEM analyses performed on the residues after cone calorimetry test, shown in **Figures 3.14** and **3.15**, confirm these findings. Furthermore, it is possible to observe on the surface the presence of “bubbles” (**Figure 3.15**) as a consequence of the intumescent character of the deposited coatings.



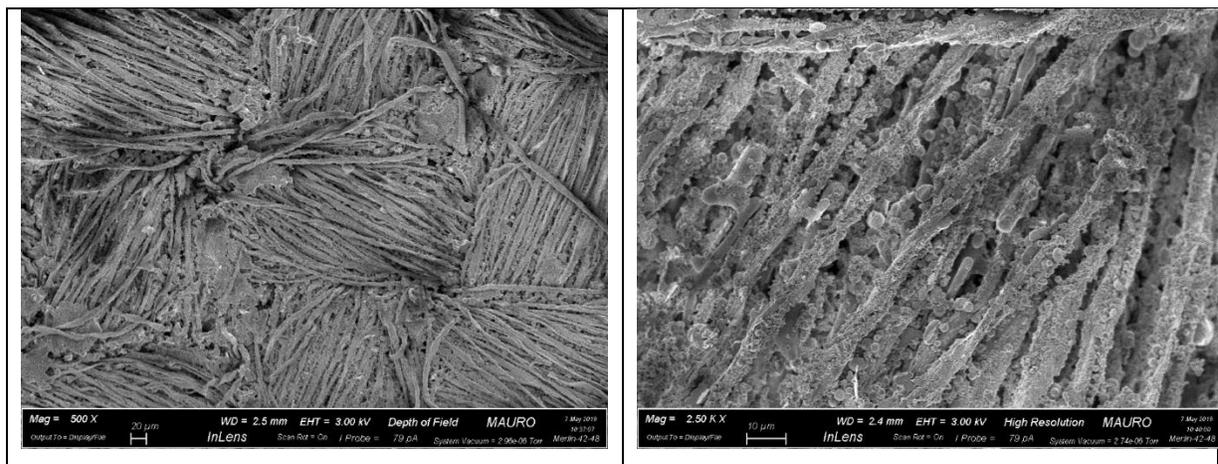
**Figure 3.12.** Residue of COT+SOL (70/30) after cone calorimetry test



**Figure 3.13.** Residue of “COT+SOL (70/30) washed” after cone calorimetry test



**Figure 3.14.** SEM images of cotton impregnated with solution after cone calorimetry test



**Figure 3.15.** SEM images of cotton impregnated with solution and then washed, after cone calorimetry test

Another important ability that the designed sol-gel coatings should possess refers to the reduction of the smoke release (TSR). As reported in **table 3.11**, the value for untreated cotton is 29.8 (m<sup>2</sup>/m<sup>2</sup>) while, in the presence of the sol-gel coating, this value decreased to 16.3 m<sup>2</sup>.

Finally, the CO/CO<sub>2</sub> ratios, as reported in **Table 3.11**, increase in case of treated cotton if compared with the untreated counterpart. This evidence indicates that the action of flame retardant (sol-gel coating) is mainly in condensed phase and is able to favors the formation of a stable char.

**Table 3.11.** Smoke parameters of treated and untreated cotton fabrics

SAMPLE	Total smoke release (m <sup>2</sup> /m <sup>2</sup> )	Total smoke production (m <sup>2</sup> )	Specific extinction area (m <sup>2</sup> /kg)	Mean CO yield (kg/kg)	Mean CO <sub>2</sub> yield (kg/kg)	CO/ CO <sub>2</sub>
COT	29, 80	0, 1	47, 78	0, 0001	0, 0068	0.02
COT+SOL(70/30)	16, 3	0, 17	70, 96	0,001	0, 0077	0.12
COT+SOL (70/30) washed	16, 8	0, 1	66, 91	0, 15	0, 48	0.31

### 3.6. Tensile Tests

The results of tensile tests performed on untreated cotton, sol-gel treated cotton before and after washing are reported in **table 3.12**.

Young Moduli of COT+SOL (70/30) significantly increased (134, 8 MPa) with respect to untreated cotton (33, 9 MPa). This evidence shows that cotton fabric after sol-gel impregnation become stiffer. Furthermore, it is worthy to note that this value dramatically decrease when treated fabric is subjected to washing, as a consequence of the partial removal of the sol-gel coating.

**Table 3.12.** Young moduli of COT, COT+SOL (70/30), COT+SOL (70/30) after washing

Sample	Young Moduli (MPa)
COT	33,9 ± 2,5
COT+SOL(70/30)	134,8 ± 10
COT+SOL(70/30) washed	35,3 ± 11,2

## 4. Conclusions

In the present work, new hybrid sol-gel systems (containing phytic acid and TEOS) were designed and applied to cotton fabrics in order to study the thermal stability and flame retardant properties.

FESEM images and FTIR-ATR spectra confirmed the effective deposition of the sol-gel on the cellulosic substrate. Different TEOS/PA sols were prepared and applied to cotton; it was found that a total dry add-on of 16% wt. together with TEOS:PA ratio of 70:30 ensured self-extinction in both horizontal and vertical flame spread tests.

The sol-gel sols turned out to anticipate the thermal and thermo-oxidative degradation of the cotton, favoring, at the same time, the formation of a stable residue (char), able to act as a thermal shield, as revealed by the high residues at the end of thermogravimetric analyses.

Cone calorimetry tests revealed, once again, that the sol-gel coatings anticipate the ignition of the samples, but, at the same time, are able to reduce HRR and HRR peak, and to increase the final residues.

The thermal and thermo-oxidative and flame retardant properties were partially lost after washing treatments as a consequence of the partial washing out of the deposited hybrid coating. This evidence represents a significant limitation in the use of cotton fabrics treated with sol-gel coatings, because the washing fastness is very often required in the textile field.

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