

# THERMAL DEGRADING AND FLAME RETARDING STUDIES OF MODIFIED COTTON

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## INTRODUCTION

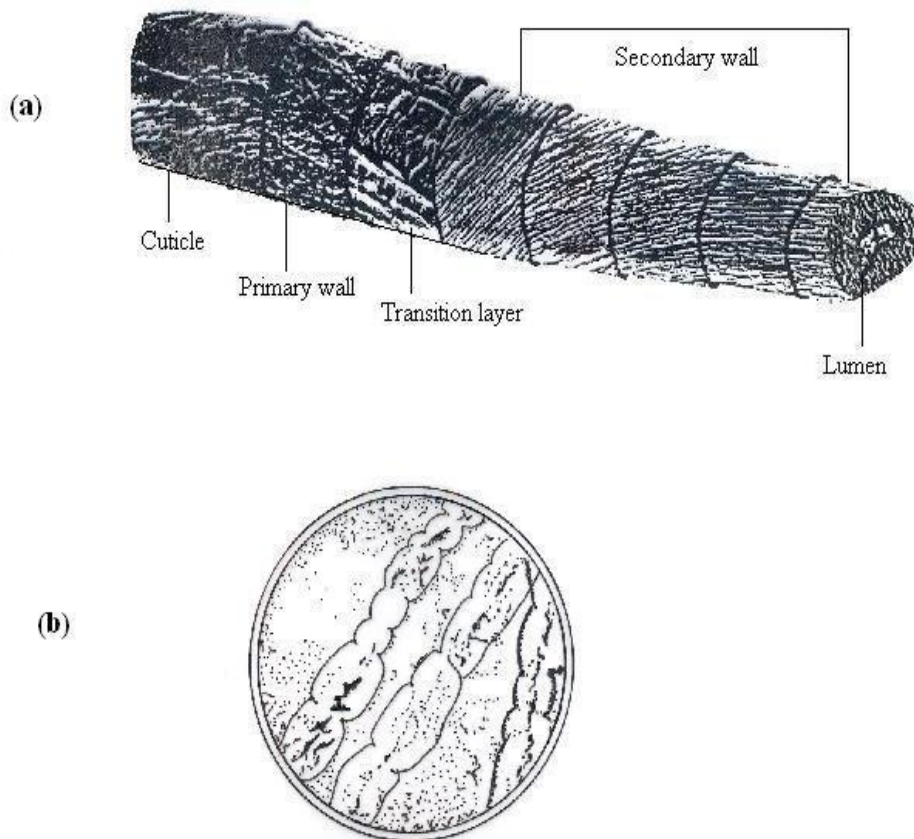
Cotton is the most important natural textile fibre used to produce apparel, home furnishings and industrial products. Worldwide about 38% of the fibre consumed in 2004 was cotton. As cotton contains 90-95% of cellulose, so it is essential to know about the basic material. Cotton is a plant of genus *Gossypium hirsutum* and belongs to the natural order of the Malvales. It grows in subtropical climate. India is one of largest producer of cotton besides America, Egypt and China. In 2004-05, about 35% of world's cotton production was biotech cotton (*Bacillus thuringiensis*, Bt) and within five years, world biotech cotton production could be rose to 50 %. In recent years there has been a renewed interest in naturally colored or pigmented cotton which has existed for over 5000 years. Presently, it is grown in China, Peru and Israel.

## PHYSICAL STRUCTURE OF COTTON FIBRE

Cotton fibre has elongated some what cylindrical shape. With the help of different staining and microscopic examinations it is clearly found that cotton is made up of four different sections (Fig. 1.1a). A thin layer of mostly non-cellulosic component on the surface of the fibre which is about 100 nm thick, made up of wax as a main component is present which is called as a cuticle. It is the outermost wall. Cuticle encloses another wall made up of cellulose and about 100-200 nm thick. This is called as a primary wall. This wall forms an envelope for the protoplasmic solution. The secondary wall constitutes the bulk of the cellulosic component. It is the main storage of cellulose as its thickness is 4000 nm. Primary and secondary walls together form a thread like structure called as fibrils. At last there is a cavity called as lumen. It is filled by the dried cell sap and has a lining of thin film of residual protein matter. Before drying, this lumen represents one fourth to half of the total cross sectional area. After collapse the lumen area is about 1/10 of cross sectional area. Cotton fibre swells up in Schweitzer's reagent which is a solution of copper hydroxide in ammonia. The cuticle and inner lining of lumen are insoluble in this solution. However, bulk area swells up. It can be clearly seen through microscope (Fig 1.1b). The constricted portions are those where the insoluble layers are present i.e. cuticle and swollen region are where the cellulose has expanded and forced its way through cuticle. In a fully ripened mature cotton fibre there are about 200-300 convolutions per inch.

## CHEMICAL COMPOSITION OF RAW COTTON

Raw cotton fibre, after ginning and mechanical cleaning, is approximately 95 % cellulose (% dry weight). The noncellulosic constituents of the fibre are located in the cuticle, primary cell wall and in the lumen. The noncellulosic constituents include proteins & other nitrogen containing compounds (1.3%), wax (0.6%), pectic substances (0.9%), organic acids (0.8%), sugars (0.3%), inorganic salts (1.2%) and pigments (0.8%). Cotton fibre and its primary wall both contain proteins, peptides and amino acids. Variation in these constituents arises due to difference in fibre maturity, variety of cotton and environmental conditions like soil, climate etc.



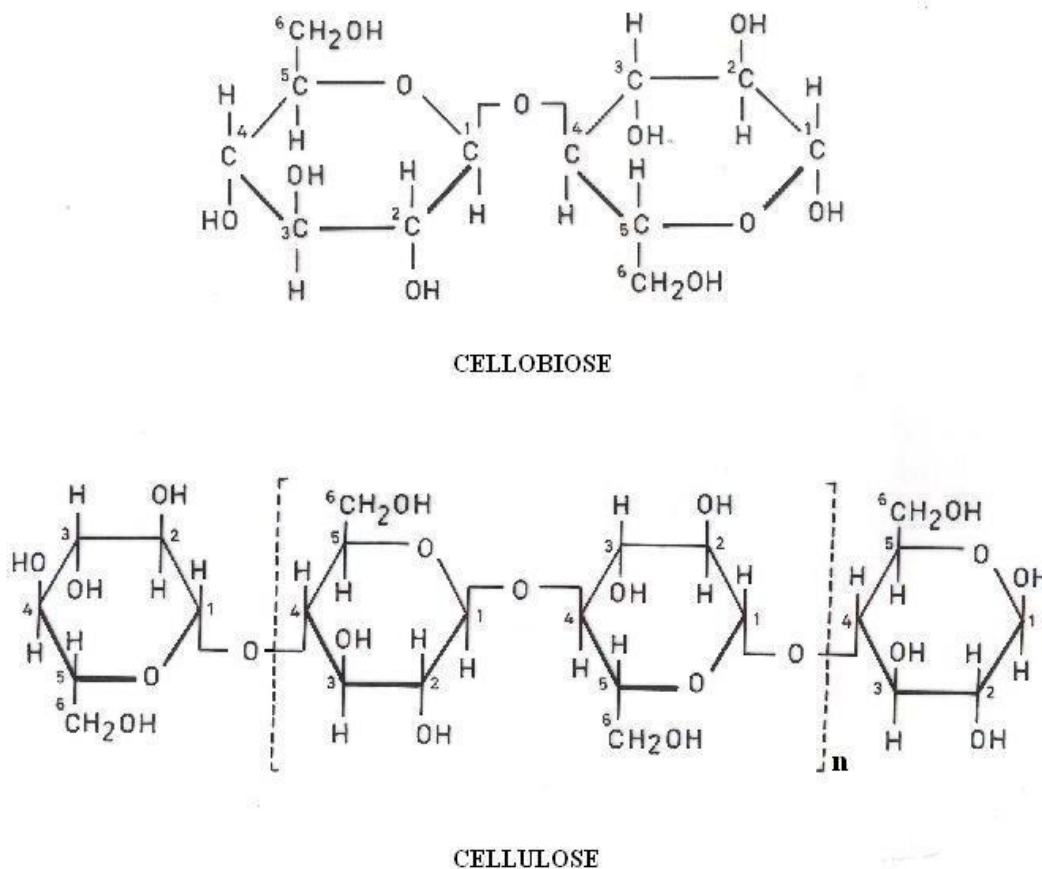
**Fig. 1.1** (a) Overview of the layered structure of cotton fibre,  
(b) Globular swelling of cotton.

## CELLULOSE MOLECULE

The cellulose is a carbohydrate having empirical formula of  $(C_6H_{10}O_5)_n$  where  $n$  is the degree of polymerization. Cellulose is a 1-4 linked linear polymer of  $\beta$ -D-glucopyranose (Fig 1.2) as evidenced from degradation of hydrolysis, oxidation and other chemical reactions. These monomers are linked together by elimination of one molecule of water between the hydroxyl groups attached to the number 1 carbon atom of one glucose molecule and the number 4 carbon atom of another. Repetitions of these condensations during biosynthesis lead to the unbranched polymer chains. In cotton fibre, the molecular chain length i.e. degree of polymerization (DP) may be higher than 20,000 monomeric D-glucopyranosyl units corresponding to a molecular weight of 3,240,000. The monomers are often referred to as anhydroglucose units or glucose residues. It is often stated that the repeating unit of cellulose is a cellobiose residue composed of two glucose residues. This acknowledges that cellulose and cellobiose both have  $\beta$ -(1-4)-glucosidic linkages and the cellulose chain has twofold screw-axis symmetry in a crystalline form.

The cotton fibre strength is influenced by the structural organization of cellulose chain. Molecular weight of a polymer is one of the most important influences on its physical properties. For polymers, higher molecular weight and narrower molecular weight distributions are positively correlated with increased strength. Marx-Figini fractionated various cellulose derivatives and determined their molecular weights and distributions. Her work for cotton fibre showed that secondary wall cellulose has a much larger molecular weight than primary wall cellulose.

The cellulose molecule has a screw axis, each glucose unit being at right angles to the previous one. Free rotation about C-O-C link does not occur owing to steric effect. Due to this and close packing of atoms, a rigid chain molecule is formed. These long chains form hydrogen bonds and this cellulose has 3-D network and in turn produces strong fibres having great rigidity.



**Fig. 1.2** Structure of cellobiose and cellulose.

## THERMAL DEGRADATION OF COTTON CELLULOSE

Thermal degradation of cellulose mainly proceeds through two types of reactions. (i) At low temperature i.e. below 250 °C, there is a gradual degradation which includes depolymerization, hydrolysis, oxidation, dehydration and decarboxylation. (ii) At higher temperature i.e. above 250 °C, there is rapid volatilization accompanied by the formation of laevoglucosan, leaving charred material. Bradbury et al proposed a precursor step in which activated cellulose is formed which undergoes further decomposition.

### Reactions at low temperature

It is difficult to differentiate the ageing of cellulose and thermal degradation at low temperature. At low temperature, the degree of polymerization is decreased due to thermal

degradation. During degradation, H<sub>2</sub>O, CO<sub>2</sub> and CO gases are evolved and carbonyl and carboxyl groups are formed. The formation of carbonyl and carboxyl groups and evolution of gases is greatly influenced by the presence of oxygen. At heating mainly three reactions take place. (i) Hydrolysis at certain of the glucoside linkages and at bonds which have become sensitive to hydrolysis due to oxidation reactions at C2 or C3 atoms, (ii) Oxidation of the C1 atom leading to the formation of a carboxyl group in addition to the C6 atom. Oxidation may also convert secondary alcoholic groups into ketonic groups resulting in higher sensitivity to hydrolysis, and (iii) Decarboxylation of the carboxyl groups in the various positions.

### Reactions at higher Temperature

Pyrolysis of cellulose produces the gases such as CH<sub>4</sub>, CO, CO<sub>2</sub>, a spate of volatiles products usually obtained as an aqueous distillate laced with intractable tars and a carbonaceous residue. The major product in the tar is considered to be laevoglucosan (1,6-anhydro-β-D-glucopyranose). Many other products of the decomposition have been detected in small quantities e.g. aldehyde, ketone, organic acid, 5-hydroxymethyl furfuraldehyde, polynuclear hydrocarbons etc. The yields of the various products depend on the source of cellulose and the rate of heating.

## PREPARATION OF CELLULOSE DERIVATIVES USING CELLULOSE POWDER

### Preparation of diethylphosphoramidous chloride

To 29.1 mL of PCl<sub>3</sub> (1/3 mol) was added 69.2 mL of diethylamine (2/3 mol) dropwise in 250 mL three necked round bottom flask with continuous stirring under dry nitrogen atmosphere at ice cold temperature for three hours. The reaction mixture was then stirred for an additional 3 hours under nitrogen atmosphere while the system warms slowly to room temperature. The reaction mixture was then distilled under nitrogen and diethylphosphoramidous dichloride was collected at 178-179 °C.

### Preparation of cellulose diethylamino phosphinate (CEAP)

Cellulose diethylaminophosphinate was prepared by treating 4.86 g (0.03 mol of an anhydroglucose unit of cellulose) of swollen cellulose with 13.1 mL (0.09 mol) of diethylphosphoramidous dichloride at 90 °C for 4 h in 100 mL of pyridine as solvent under constant stirring. Cellulose was swollen in 100 mL pyridine for 12 h before the reaction. The product obtained was filtered, washed first with pyridine and then thoroughly by distilled water. Finally the product was dried at room temperature in air and then dried over P<sub>2</sub>O<sub>5</sub>. Similarly cotton fibre was also treated with diethylphosphoramidous dichloride for morphological studies.

## **PREPARATION OF CELLULOSE DERIVATIVES USING COTTON FABRIC**

### **Cellulose phosphate (CP)**

Cellulose phosphate was prepared by treating 4.86 g (0.03 mol of an anhydroglucose unit of cellulose) of swallowed cotton fabric with 8.2 mL (0.09 mol) of  $\text{POCl}_3$  at  $90^\circ\text{C}$  for 4 h in 100 mL of pyridine as solvent under constant stirring. The phosphorylated cotton fabric was washed first with pyridine and then thoroughly by distilled water. Finally it was dried at room temperature in air and then dried over  $\text{P}_2\text{O}_5$ .

### **COATING OF COTTON FABRIC SAMPLES**

#### **Coating with intumescent containing ammonium polyphosphate, melamine and sorbitol**

Intumescent formulation was prepared containing components ammonium polyphosphate (APP), sorbitol, and melamine in ratio 3:1:1 wt/wt<sup>17</sup> of cotton fabric (total approximate 30 % wt/wt of cotton fabric). Zydex – 7600, the acrylic resin (20 % wt/wt of cotton fabric) was used for coating the intumescent formulation on cotton fabric of area density,  $140\text{ g/m}^2$ . The intumescent formulation was prepared by mixing evenly in pastel and mortar in the form of paste of desired consistency using water as a solvent. This formulation in the paste form was coated on cotton fabric with simple knife-blade technique, giving approximate 45 % add on weight on the cotton fabric substrate. Similarly all the samples of phosphorylated cotton fabric were coated. Each coated fabric was placed in an oven to dry at  $80^\circ\text{C}$  at 3 h and then cured at  $125^\circ\text{C}$  for 5 minutes in oven. The area density of coated fabric samples was found in the range  $200\text{-}205\text{ g/m}^2$ .

### **SUMMARY**

Polymers in general and cotton textiles particularly find many uses and add significantly to the quality of modern day life. However it must be acknowledged that it carries with it an increased fire hazard, since most of the natural and synthetic polymers including cotton are flammable. This problem becomes more serious today because of the present living phenomenon of great number of people in confined space of considerable height. The field of flame retardancy of polymers has significantly developed and expanded during last two decades. But there are doubts about the general use of halogenated compounds as flame retardants (FRs) because of environmental contamination from highly toxic combustion products released during fires and waste incineration from halogenated FR system. Therefore, there exists a need for new and more effective environmentally benign approaches with a permanent effect that reduces flammability with minimum change to the physicochemical properties.

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