

I
INTRODUCTION

I. INTRODUCTION

I.1. GENERAL

Fibres are characterized by flexibility, fineness and high ratio of length to thickness. Fibres may be classified according to their origin into two groups :

- (i) natural and (ii) man made.

Natural fibres can be grouped as vegetable, animal and mineral.

Vegetable fibres can be further classified as :

- (i) seed fibres, e.g. cotton, kapok, etc; (ii) bast fibres, e.g. flax, hemp, ramie, jute etc; (iii) leaf fibres, e.g. sisal, manila, hemp (abaca), etc; and (iv) wood fibres which have not been separated as fibres. Seed and bast fibres are referred to as soft vegetable fibres, while leaf fibres are referred to as hard fibres. Vegetable fibres are cellulosic materials.

Man made fibres can be classified into three groups as :

- (i) regenerated fibres, e.g. viscose, rayon, etc; (ii) mineral or inorganic fibres, e.g. glass fibres, etc; and (iii) fibres of synthetic polymers such as polyamides, polyesters, polyolefins, polyurethanes, etc.

Cellulose is a polymer biosynthesized in nature in the plant kingdom. It forms the basis for several industries such as pulp, paper and allied products, cotton textiles, regenerated fibres such as viscose, rayon, cuprammonium rayon, etc, cellulose derivatives such as cellulose acetate, cellulose nitrate, carboxy-methyl cellulose, hydroxy ethyl cellulose, methyl and ethyl celluloses, cellulose acetate butyrate, cellulose acetate phthalate, etc.

In most of the applications, cellulose is used in a more or less pure form.

In the natural state, cellulose is associated with noncellulosic materials such as lignin, hemicelluloses, pectins, tannins, resins, fats, waxes, colouring agents, etc.

Properties of fibres depend, in general, on their composition and structure. Properties such as elasticity, dyeability, flammability, soiling, static build-up, wrinkle recovery, strength, etc, can be altered by chemical modifications namely derivatizing, crosslinking and grafting.

In this study, cotton cellulose has been used for chemical modifications by the above three processes. Before considering the actual processes and the modifications brought about by them, it is relevant to discuss the structure and properties of these fibres which provide necessary background for the modifications.

I.2 CHEMISTRY AND STRUCTURE OF COTTON FIBRES

2(a) GENERAL STRUCTURE

The cotton fibre is a single cell that grows as a seed hair on a plant belonging to the genus "Gossypium". Raw cotton is 88-95 % cellulose. The non-cellulosic substances such as pectins, waxes, proteins and ash are present in the outer layer and lumen. Cotton purified by scouring and bleaching is 99 % cellulose. Cellulose is a natural high polymer and its building blocks are anhydroglucose units. Structurally, cellulose is a β (1 \rightarrow 4) linked condensation polymer of glucose (Fig.I.1). The β configuration of the glycosidic bond in cellulose differentiates it from another natural condensation polymer of glucose, namely starch which has a α (1 \rightarrow 4) inter unit linkage (Fig.I.2). The difference in chemical structure between the two polymers accounts for major differences in their physicochemical properties.

An average value for the number of glucose units in the chain molecule is designated as degree of polymerization (D.P.). The determination of D.P.

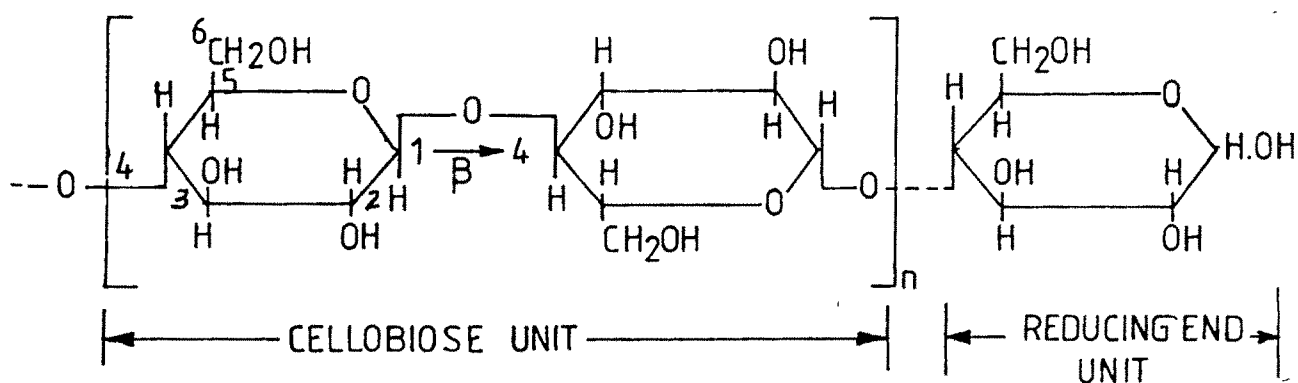


FIG.I.1 CELLULOSE MOLECULE

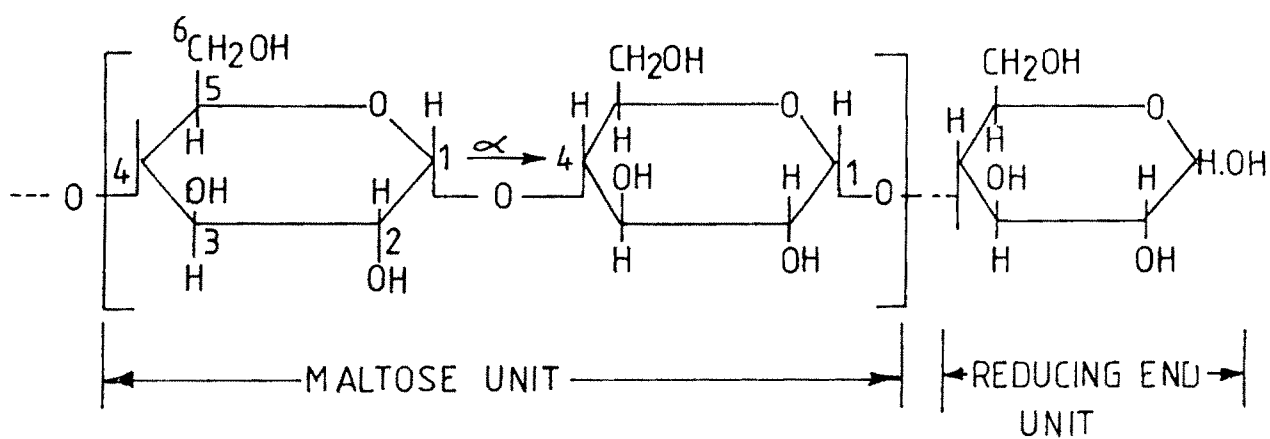


FIG.I.2 STARCH MOLECULE

of cellulose in industry is usually carried out by measuring its viscosity in selected solvents. In cotton cellulose, the D.P. is estimated to be about 5000 (1).

Conformational analysis (2) shows that anhydroglucose in the chair form (Fig.I.3) unites through (1 \rightarrow 4) β linkage to give a thread like structure. The spacial arrangement of the chains involves interlinking through hydrogen bonding.

2(b) REACTIVE GROUPS OF CELLULOSE

There are two reactive groups or functions in the cellulose molecule. The principal one is the hydroxyl group of which there are three in each glucose unit, the primary located at C-6 position and two secondary hydroxyls located at C-2 and C-3 positions respectively (Fig.I.1). The hydroxyl groups in cellulose undergo reactions typical of simple alcohols, such as oxidation, esterification, etherification, crosslinking, etc. However, the reactivity of cellulose hydroxyls is much less than that of alcholic hydroxyls. This is primarily because of the heterogeneous nature of several cellulose reactions wherein the availability of hydroxyl groups for reaction is restricted by the crystalline character of cellulose. In homogeneous reactions, all the hydroxyls become available but the reaction rates are slow because of the restricted mobility of polymer molecules.

Other reactive group in the cellulose molecule is the glycosidic group or the inter unit linkage (Fig.I.1). Being an acetal linkage, it can be easily cleaved by acids, especially mineral acids. The cleavage results in a shortening of the cellulose chain. Glycosidic cleavage can also be brought about by alkali which, however, needs much more drastic conditions compared to acids. Certain specific enzymes can hydrolyse cellulose. Depolymerization of cellulose can also be induced by heat.

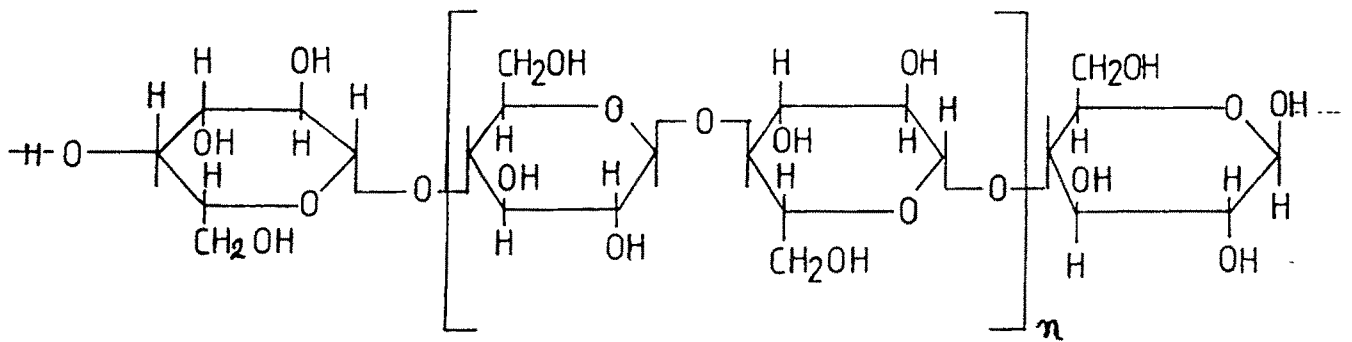
2(c) MICROSCOPIC STRUCTURE

Microscopically, cotton fibre appears like a flattened convoluted ribbon. The cross section of the dried fibre is bean shaped. The structure of cotton can be represented schematically as consisting of cuticle, primary wall, secondary wall and lumen (Fig.I.3).

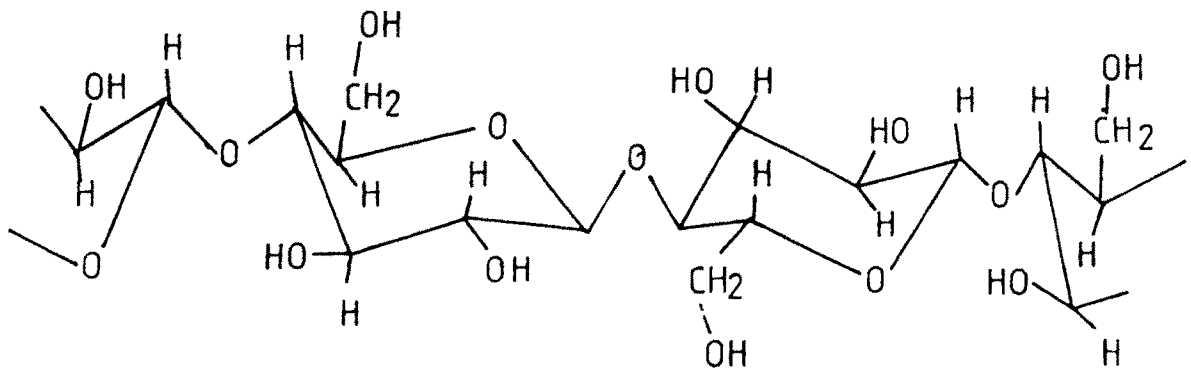
Cuticle is the outermost membrane of cotton fibre which contains pectins and waxes and can be regarded as non-cellulosic. Primary wall is the first cellulose layer. Roelofsen (3), Tripp and coworkers (4) and Ramnathan (5) indicated that two types of fibrils running parallel and transverse to the fibre axis make the network structure. The outermost layer of secondary wall is called the " S_1 layer". The fibrils in this layer are oriented in the opposite direction to those of the next inner layer of secondary wall in the " S_2 layer". These fibrils form a helix round the fibre axis at a helix angle of 30-45° with frequent reversals in the direction of helix (6). Lumen contains pectins, waxes and degenerated protoplasm.

2(d) CRYSTAL STRUCTURE

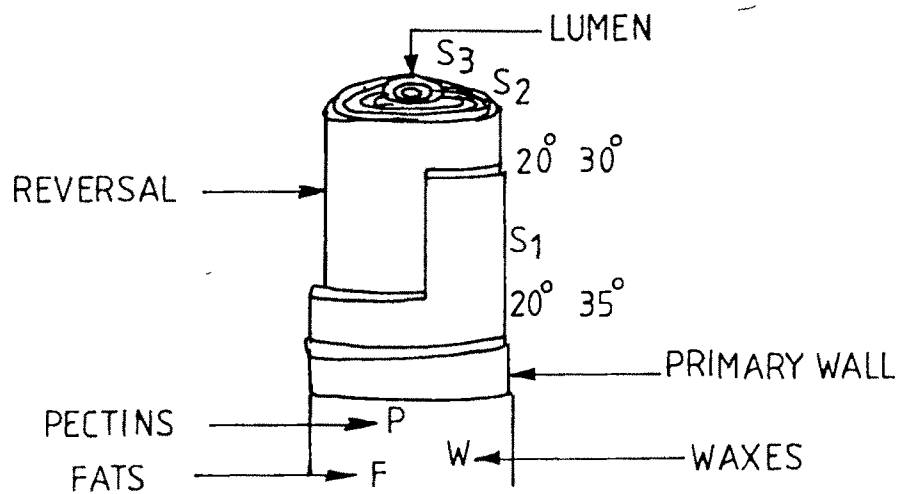
Herzog and Jancke (7a) were the first to show with the help of X-rays that cotton is crystalline. The structure of cellulose in cotton fibrils (Fig.I.4) was considered as basic three dimensional structure. The basic or the unit cell shows all the properties of a crystal lattice. Each unit cell contains four anhydroglucose residues, which are held firmly together by main valence linkages (1 \rightarrow 4 β glycosidic linkages), hydrogen bonds and vander Waals forces. Cellulose I is the crystalline cellulose occurring in nature. An important lattice modification of cellulose I is cellulose II produced by intracrystalline swelling such as mercerization. Two more lattice modifications of cellulose, cellulose III & cellulose IV are also known. The unit cell of different celluloses belongs to the monoclinic system differing only in the parameters of unit cell. Thus, from X-ray and IR spectral



CHEMICAL STRUCTURE OF CELLULOSE CHAIN

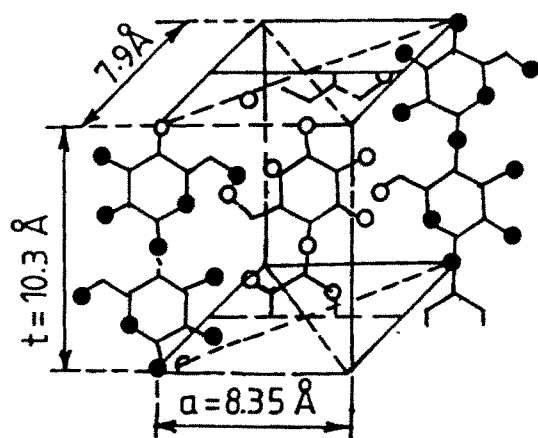


CONFORMATIONAL STRUCTURE OF CELLULOSE CHAIN

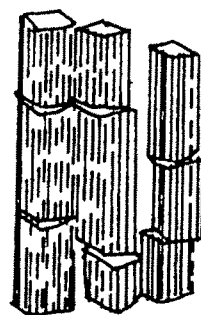
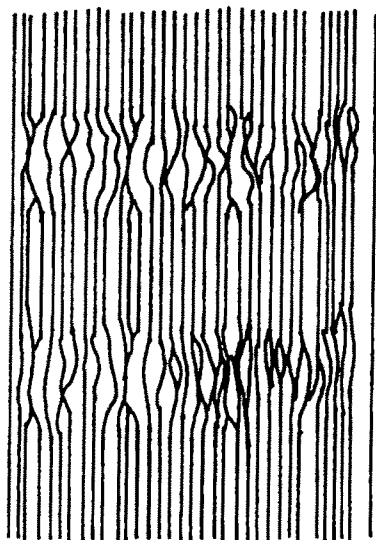


MORPHOLOGICAL STRUCTURE OF THE COTTON FIBRE

FIG I.3



UNIT CELL OF CELLULOSE

SCHEMATIC MODEL THE TWISTING
AND TILLING OF CRYSTALLITIES IN
THE SECONDARY WALL FIBRILS
OF COTTON

FRINGED MICELLE STRUCTURE



FRINGED FIBRIL STRUCTURE

FIG.I.4

studies (8), It was found that cellulose chains are held together by vander Waals forces, intermolecular hydrogen bonds between hydroxyl at C-6 and the bridge oxygen of the adjacent molecular chain and intramolecular hydrogen bonding between adjacent anhydroglucose rings resulting into a strong hydrogen bonded network structure with unit cell repeating itself to build polycrystalline aggregates.

2(e) FINE STRUCTURE

According to the present concept of the structure of cellulose, the long chains of anhydroglucose units are arranged in bundles parallel to the length of the chain. These bundles are called "micelles". Within each micelle, there are closely packed crystalline or ordered regions and loosely distributed disordered regions. Thus, the parallel cellulose chains are tightly packed at some places due to strong hydrogen bonds. These regions are well ordered and give sharp X-ray patterns. The loosely arranged portions called amorphous regions are responsible for swelling of cellulose in water and other solvents.

Kratky (7b) and Frey-Wyssling (7c) proposed a structure known as fringed-micellar structure (Fig.I.4) in which cellulose chains much longer than crystallites are visualised as passing through several crystalline and amorphous regions. The crystallite boundaries are not sharply defined but gradually merge into the less ordered amorphous regions.

Hearle (9) modified the 'fringed-miscellar' theory and proposed a 'fringed-fibrillar' theory in which the micelles are replaced by fibrils. This concept combines the essential feature of fringed micelles within those of fibrils in a structure (Fig.I.4) in which molecules pass continuously through fringed crystalline fibrils and non-crystalline regions between the fibrils. Here the crystalline regions are regarded as continuous 'fringed-fibrils' composed of molecules diverging from the fibrils at different positions along their length. The fringed fibrillar theory is widely accepted and it represents

the idea of continuous structure of Staudinger and important features of 'fringedmiceller' theory. It discards only the concept of micells of limited length.

Manley (10) proposed a model of cellulose as a possible structure in which he suggests that microfibrils do not contain amorphous regions. According to him, cellulose chains are folded to form a crystalline ribbon (35°A thick) which, in turn, is helically wound to give a somewhat open spring-like structure. Chemical reactions are known to occur on the surface of these fibrils. This concept, however, has not been widely accepted.

The physical structure of cellulose can be changed by swelling and regeneration. Cellulose can be swollen in a suitable swelling agent and partially deswollen by removal of the swelling agent. Practically, there is no change in the chemical structure of the fibre but there are considerable changes in the physical fine structure resulting in enhancement of fibre strength, lusture and reactivity. In regeneration, the native cellulose is treated to render it soluble and then regenerated from the solution. The process is the basis of rayon and cellophane manufacture, gives rise to a transformation of the structure from cellulose I lattice to cellulose II lattice, and results in a corresponding modification of the physical structure.

I.3 MODIFICATION OF CHEMICAL STRUCTURE

The chemical structure of cellulose can be changed in three ways by chemical methods :

- (i) by reaction of cellulose hydroxyls, whereby the cellulose molecules are altered through introduction of bulky side groups either by an etherification reaction or by an esterification reaction;
- (ii) by reacting cellulose with difunctional compounds whereby crosslinking and resinification would take place thereby stabilizing its structure

and imparting crease resistance, shrink resistance, etc., to the cellulose fibres and

- (iii) by preparing a branched cellulose or what is called graft copolymer of cellulose. The process represents a means of modifying the cellulose molecule through the creation of branches of synthetic polymers that impart certain desirable properties without destroying the intensive properties of cellulose.

Esterification, crosslinking and grafting (branching) are now considered.

I.4 ESTERIFICATION

Cellulose esters, namely cellulose nitrate and cellulose acetate constitute the oldest man made plastics. Various organic esters of cellulose have been reviewed by Coheen (11) and Turner (12). The primary hydroxyl group is intrinsically more reactive in esterification process than secondary ones.

Cellulose reacts with acid anhydrides and acid chlorides to form esters. First reported organic ester of cellulose was cellulose acetate prepared by Schutzenberger in 1865 by heating cotton with acetic anhydride at 180°C until cotton dissolved. The product was soluble in alcohol.

Franchimont, in 1879, prepared cellulose ester at lower temperature with the aid of sulfuric acid catalyst. In 1903, Miler prepared partially hydrolyzed cellulose acetate and fully acetylated esters previously prepared as acetone soluble derivatives and chloroform soluble derivatives respectively.

The reactivity of cellulose with organic acid or anhydride decreases with increasing carbon chain. Esters of monobasic acids containing upto four carbon atoms (i.e. lower esters) are prepared with little difficulty by the acid anhydride reaction, but the synthesis of higher esters by this method is usually unsatisfactory. Esters higher than butyrates are often prepared by the reaction of cellulose with an acid chloride in pyridine.

Chloroacetic anhydride (13) and trifluoro acetic anhydride (14) have been used as impellents (drive-in agents) in esterification with acids having very long substituents. Eight different partial esters of cellulose in fabric form having approximately the same acyl content were prepared by using trifluoroacetic anhydride impellent procedure (15) and evaluated. There is a progressive loss in each property with increasing molecular size of the ester group.

The introduction of organic acids of longer aliphatic chains changes the properties of the resulting esters towards those influenced by the organic substituent (16). Softness of the ester and solubility in various organic liquids increases and moisture sorption decreases with increase in chain length of the substituent. Esterification velocity and degree of substitution decrease as well.

In 1965, Campbell and Francis (17) prepared crosslinked cellulose diester in presence of trifluoroacetic anhydride which showed that only malonic acid reacted readily in the $C_3 - C_5$ range while in the $C_6 - C_{22}$ range all the acids reacted readily, the reactivity decreasing with increasing chain length. At a constant degree of crosslinking, the crease recovery increased with increasing chain length.

Ueno and Kogyo (18) observed some cellulose degradation in rapid trifluoroacetylation of cellulose diacetate. Decrease in the degree of polymerization of cellulose was also observed in the rapid acetylation of powdered cellulose and Egyptian cotton by acetic acid-trifluoroacetic anhydride mixture in chloroform (19).

Berni and Benerito (20) used trifluoroacetic anhydride and acid chloride in DMF and prepared cellulose esters of long chain monobasic acids like oleic acid, palmitic acid and stearic acid. Later they (21) prepared esterified cellulosic textiles with unsaturated long chain fatty acids like oleic acid, phenyl-stearic acid, undecanoic acid, etc in the presence of trifluoroacetic

anhydride using controlled cellulose-acid anhydride ratios. The product showed improved dry crease recovery.

Rowland and Brannan (22) studied the effect of ionic substituent at low degree of substitution on wrinkle recovery angles of crosslinked esterified cotton.

Mixed esters of cellulose with α - β unsaturated carboxylic acid were prepared in presence of acetic acid and trifluoroacetic anhydride (23). Unsymmetrical anhydrides $\text{RCO}_2\text{COCF}_3$, were the active intermediate species. The partial esters of cellulose namely oleates, sorbates, cinnamates, coumarates, phthalates, crotonates, maleates, etc have been prepared (24).

Crosslinked cellulose ester was prepared using succinic anhydride and nonaqueous medium (25). Crosslinked cellulose derivatives were prepared by Bullock and coworkers (26) using acetylene carboxylic acid. The fabric had improved dye affinity and wrinkle resistance and was useful as ion exchange material and in wash wear garments.

Polycarboxylic acid-modified cellulose fibres were prepared by Rowland and coworkers (27). The treated cloth had enhanced wet and dry wrinkle resistance and crease retention and retained its original suppleness.

Polycarboxylic acid-modified cellulose esters were prepared using their partial salts. Cellulose reacted also with salts of dicarboxylic acids such as maleic acid, citric acid, etc by dry curing process (28). Cellulose polycarboxylcarboxylates were also prepared by reaction of cotton with polycarboxylic acid (29).

Thomas (30) carried out partial esterification of cellulose with carboxylic acids giving cellulose benzoate, adipate and succinate. The above crosslinked cellulose caused increase in crease recovery, and decrease in strength and abrasion resistance.

Cellulose was esterified with carbonic carboxylic anhydride (31) for improved dry crease recovery but it resulted in lowering of tensile and tear strengths.

Cellulose acid phthalate (32) was prepared by rapid esterification of cellulose with dicarboxylic acid anhydride. Lupton and Lougalin (33) found that cotton readily dyeable with cationic dyes was prepared by esterification with phthalic anhydride.

Tris N, N bis (hydroxy methyl) carbamic acid ester (34) was also used as a textile modifying agent.

Chipalkatti and Desai (35) obtained cellulose textiles with high wet and dry crease recovery and high abrasion and tear resistance by treating them with a $C_{14} - C_{18}$ acid ester of a 1,3 - dihalo - 2 propanol or 2,3 dihalo-1-propanol and aqueous alkali in the slack condition and with a cross-linking resin in the stretch condition. Hussain and coworkers (36) studied the reaction of the stearyl ester of 1-3-dichloropropan - 2 - ol with cellulose in presence of aqueous sodium hydroxide and its reaction with the improvement in flex resistance of the treated cotton fabrics.

Low molecular weight esters of cellulose were also prepared by Iwami and coworkers (37) using cellulose acetate heated with saturated or unsaturated organic acids in the presence of cation exchange resin.

The swellability and solubility of partially substituted cellulose esters with bifunctional compounds were studied (38). Mixed cellulose esters of 2 - 3 - and 4 - Carbon acid are readily prepared from suitable mixtures of acids and anhydrides. Cellulose acetate propionate and cellulose acetate butyrate are manufactured commercially and used in large quantities.

Chemically modified cellulose acetate and some new types of cellulose esters of mixed acids such as cellulose acetate sorbate and cellulose acetate oleate and mercury derivatives of cellulose acetate were studied by Rogovin (39).

Cellulose acetate maleate was prepared and its properties were studied by Sabirov and Aikhodzhaev (40). Akhararkhodzhaeva and Elisseva (41) prepared secondary mixed cellulose esters using sorbic acid or oleic acid. They measured the hydrolysis rates of acetate, sorbate and oleate ester groups.

Cellulose tosylate, cellulose pyruvate, cellulose tosyl propiolate and cellulose methoxy acrylate were also prepared and their structures and properties were studied (42). Cellulose acrylic - acetic mixed acid esters were prepared using acetic acid, acetic anhydride and acrylic acid (43).

Ratovskaya and Shkol'nik (44) synthesized cellulose acetate succinate using succinic anhydride. Alimardanov and coworkers (45) synthesized cross-linked mixed unsaturated cellulose acetate ester using acid anhydrides like acrylic anhydride and maleic anhydride and crosslinked in presence of radical initiators.

Malm & Coworkers (46) prepared organosoluble esters from propionate through palmitate by the acid chloride - pyridine procedure. Stanonis and King (47) used pyridine-acid chloride procedure without additional solvent.

In 1960, Benerito and coworkers (48) prepared partial perfluoro esters of cellulose by reacting perfluoro octanoyl chloride with cotton fabric in presence of pyridine. Partial esters of cellulose, varying in the degree of substitution from 0.02 to 0.58, were obtained. The use of essentially homogeneous solution of acid chloride resulted in a product that retained properties of the original cotton and showed, in addition, oil and water repellency and durability to dry cleaning and aqueous launderings in presence of neutral detergents.

In 1961, Matschat (49) pointed out that the esterification of cotton fabric with stearoyl chloride imparted rather high dry crease recovery to the fabric. Mckelvey and coworkers (50) pointed out that the unsaturated C_{18} acid chloride (oleoyl) at a similar degree of substitution (DS: 0.12, equivalent to having about 4 % of the hydroxyl groups reacted) is more effective than the saturated C_{18} acid chloride (stearoyl) in this regard.

They also found that above 60°C the presence of an acid scavenger such as pyridine in the reaction medium was necessary to prevent extensive damage from acid to the fabric. The esterification reaction for obtaining durable water repellency for textiles has been reviewed by Baird (51).

In 1963, Riemschneider and Sickfeld (52) esterified cotton cellulose with several acid chlorides at 80°C in presence of varying amounts of pyridine. They observed that the average degree of polymerization of the final product diminished rapidly as the amount of pyridine decreased.

Robbins and Perkins (53) studied the reaction of acyl chlorides with aminized cotton and unreacted control cotton at room temperature. They observed higher reactivity for aminized cotton than for the control cotton. Stearoyl and terphthaloyl chlorides were most effective in this respect.

Alimardanov and coworkers (45) synthesized a crosslinked unsaturated cellulose acetate ester by the reaction of cellulose acetate with acyl chloride like methacryloyl chloride in presence of pyridine.

Mixed cellulose esters of oleic, linoleic and linolenic acids were synthesized (54) by the interaction of cellulose with acid chlorides of these acids in presence of base and by the reaction of cellulose with acid anhydrides in presence of acid catalyst.

Crosslinked heterocyclic esters of cellulose were prepared by Singh and Arthur (Jr.) (55). Cellulose was esterified with 5-bromo-2-furoyl chloride, 5-bromo-2-thionyl chloride or 5-bromo-2-thiophene acryloyl chloride and crosslinked with 1,3-bis (4-pyridyl) propane to give fabric with improved crease recovery.

Sircar and Stannonis (56) proposed a possible mechanism for the side reaction of cotton cellulose with propionyl chloride. Cellulose propionyl propionate was formed as a side product.

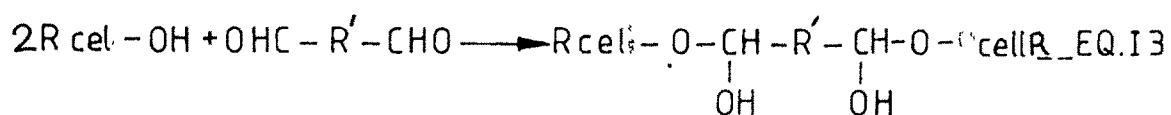
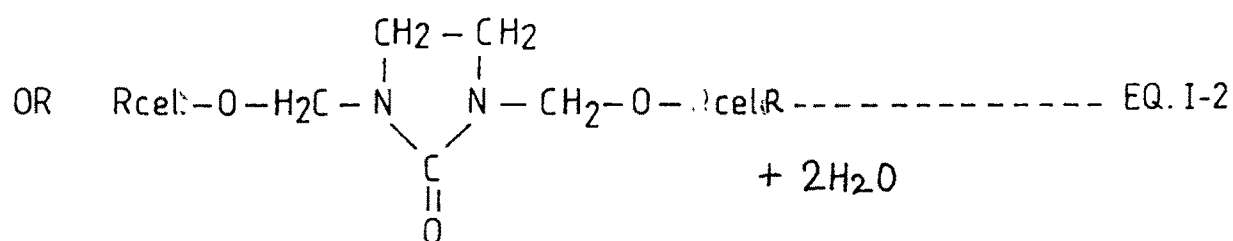
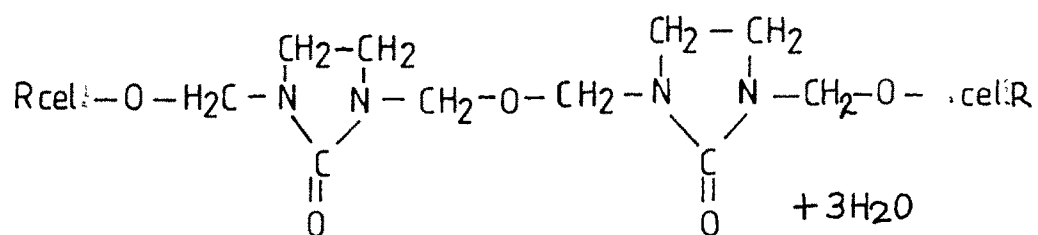
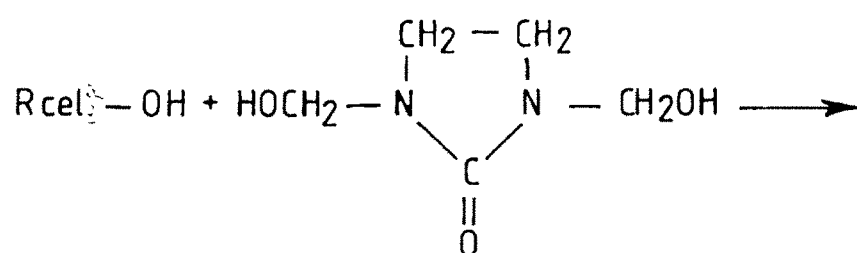
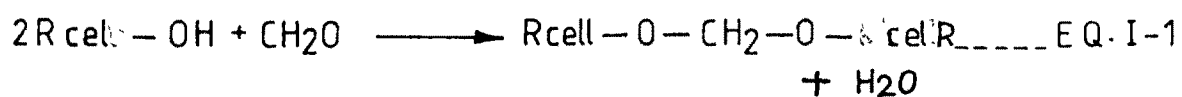
I.5 ACETAL CROSSLINKING

It was not until 1948 that improvements in wrinkle resistance were related to crosslinking (57). It is generally believed that one crosslink per four to five anhydroglucose units is desirable; however, the question of optimum degree of crosslinking is still controversial. Nevertheless, treatments of cellulosic materials, particularly cotton and rayon, with difunctional reagents capable of reaction with hydroxyl groups have been extremely important commercially and theoretically. Crosslinked esters are considered in the previous section; crosslinked acetals are considered in this section.

Formals : Formaldehyde was the first material used to crosslink cellulose (eq.I.1). Catalysis by strong acids is necessary to achieve appreciable rates of reaction. The methylene linkages formed are fairly stable to both acid and alkaline hydrolysis. O' Brien and van Loo (58) considered that a considerable fraction of formaldehyde was involved in intramolecular bonding. Formaldehyde alone is not often used in modern treatments of cellulosic fibres because of its deleterious effect on the strength of fabrics. However, a commercial crosslinked rayon (59) based on formaldehyde finishes has been reviewed by Mazzeno and coworkers (60).

The use of Lewis acid as a catalyst for crosslinking cellulose with formaldehyde at a pH between 5 and 10 was patented (61). Crosslinking with gaseous formaldehyde (62) or diethyl formal in presence of mineral acids (63) was studied. Also described was the use of formaldehyde to crosslink a cellulose fabric that was heated with an acrylamide containing at least one hydrogen linked to nitrogen (64).

The change of crosslink length with formaldehyde as a condition of application was suggested (65). Later work (59) confirmed that the majority of crosslinks with certain rayons consisted of low molecular-weight polyoxymethylene chains.



Urea-formaldehyde combinations have been employed to crosslink cellulose but the simple derivatives, such as dimethylolurea, $\text{HOCH}_2\text{NHCONHCH}_2\text{OH}$, have strong tendency to react with themselves as well as with the cellulose. Apparently, a large proportion of the urea-formaldehyde and melamine-formaldehyde resins used became thermosetting within the cellulosic substrate rather than actually causing much crosslinking. Since 1949, so-called "reactant resins" have been used which would not in themselves form thermosetting resins. These difunctional reactants are believed to be efficient in crosslinking cellulose. One of the first few to be utilized was the bis-methylol derivative of cyclic ethylene urea, which reacts with cellulose to form methylene crosslinking (Eq.I.2).

With respect to crease resistance of cotton fabrics, the optimum effect is reached with the use of 11% of the reagent which corresponds to one methylol group per cellobiose unit as only 40 % of the cellobiose is accessible. Other similar compounds such as "dimethylol tetramethylene urea" have been used. A related tetrafunctional reagent called "tetramethylol acetylene diurea" (Fig.I.5) is derived from urea and glyoxal. It has a stronger tendency to combine with the fibre than with itself. Bis methylol derivatives of monoamides, particularly formamide, have been found to crosslink cellulose (66).

On the basis of theoretical considerations relating to hydrolytic stability of the $\text{RCell-O-CH}_2\text{NHCO-}$ linkage, $(\text{HOCH}_2\text{NHCOCH}_2\text{CH}_2)_3\text{N}$, Tris (N-methylol-2-carbamoylethyl) amine, was suggested as a crosslinking agent for cotton (67) and was found to give a highly durable finish.

Other aldehydes :- The possibility of acetal formation has led to the utilization of dialdehydes as crosslinking agents for cellulose. Glyoxal, the simplest dialdehyde, has been tested and the commercial availability of glutaraldehyde

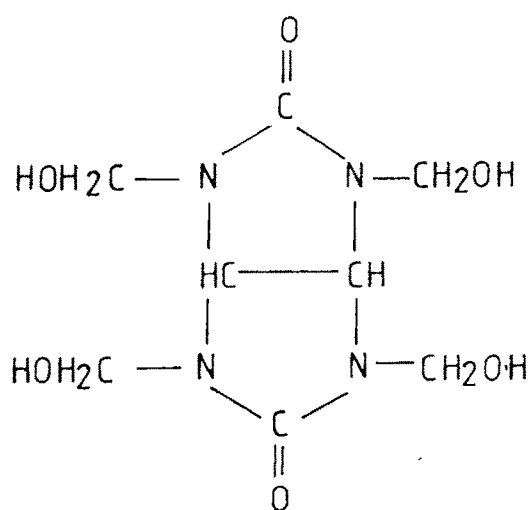
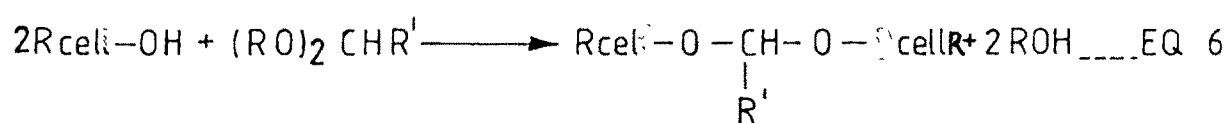
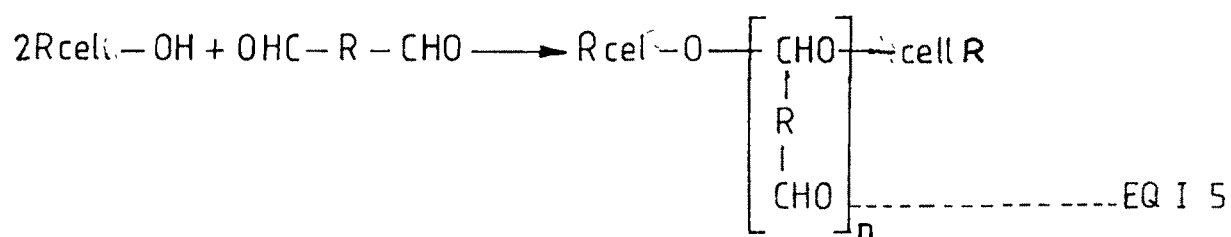
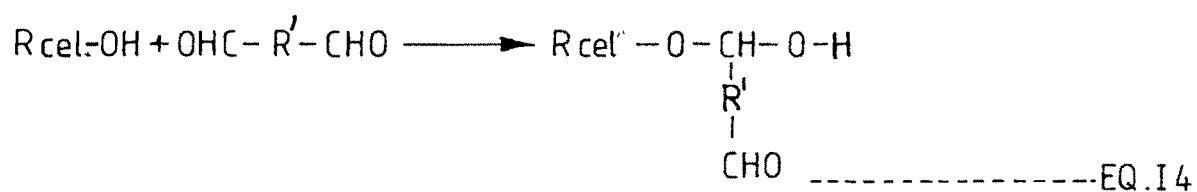


FIG. I.5

and α -hydroxyadipaldehyde led to their examination as crosslinking agents for cellulose. It was reported (68) that glutaraldehyde gave better results. The simplest reaction of a dialdehyde may be depicted as in (eq.I.3). Other reactions that may occur are shown in (eq.I.4) and (eq.I.5). Combinations of all three equations may occur. Involvement of both aldehydes offers the advantage of being relatively nonvolatile, but hemiacetal bonds, unlike acetal bonds are unstable to both acid and alkaline hydrolysis. Formals and acetals have been applied to cellulose with acid catalysts to induce crosslinking by transacetalization (eq.I.6).

Acid catalysts and swelling agents

Chance and Leonard (69) treated cotton fabrics with formaldehyde in presence of HCl and CaCl_2 and found that temperature, time and concentrations of formaldehyde and catalysts affected the wrinkle resistance and reaction rate. Chance and Perkins (70) also treated cotton fabric in partially swollen condition with formaldehyde in acid using aluminium chloride or zinc fluoroborate. Reaction rate was much slower in presence of acetic acid than in presence of HCl . They observed no improvement in wrinkle recovery with zinc fluoroborate.

Arceneauv (71) crosslinked cotton with formaldehyde in presence of hydrochloric acid and observed that the fabric had improved wrinkle resistance and wash wear properties but its strength decreased as crease recovery angle increased.

Datye (72) treated unmodified, modified and dyed cellulose with formaldehyde. He concluded that the reaction was dependent on the concentrations of formaldehyde and calcium chloride but, independent of the concentration of hydrochloric acid. Same author (72) treated mercerized cellulosic fibre under tension and without tension and observed that fibre crystallinity, moisture regain, susceptibility to oxidation and uptake of dye varied with the combined formaldehyde values.

Bredereck and Dolmetsch (73) examined the resin finished cotton under the electron microscope and confirmed that crosslinking between the lamellae of cotton was responsible for improved crease recovery. They also crosslinked cotton in swollen condition using swelling agent and differentiated between intercrystalline and intracrystalline swelling.

Mehta and coworkers (74) found that favourable location of crosslinks in the fine structure of cellulose was associated with good crease recovery of fabric swollen with urea and treated with formaldehyde vapor and dried in a stretched condition.

Menon and coworkers (75) crosslinked cotton with urea and formaldehyde in slack condition and observed free shrinkage in cotton. They also treated yarn with dimethylol ethylene urea and studied elongation percentage of finished fabric.

Singh (76) reviewed the mechanism of improved recovery achieved on resin treatment of cellulose textiles. He discussed deposition theory and crosslink theory. Dorset (77) reviewed vapor treatment of cotton fabrics with silanes, epichlorohydrin and formaldehyde. McCartney (78) reviewed the reaction of phenol (or amine) and formaldehyde with cellulose and discussed their influence on elasticity, flexural strength, shrinkage, abrasion resistance and crease recovery in comparison to the effect of urea-formaldehyde treatment.

Chemical bonding and reaction rates of wrinkle resistant finishes on cotton were studied by O' Brien and van Loo (79). They studied wrinkle resistance improvement as a function of time and concentration of trimethylol amine, dimethylol ethylene urea and biglycidyl ether.

Roff(80) studied the reaction of cotton and viscose rayon with formaldehyde. He observed that uptake of formaldehyde increased on adding salts and nitrogenous compounds like urea or melamine.

Wehner and Zollinger (81) showed that reaction rate of formaldehyde crosslinked cellulose containing sulfuric acid, acetic acid and water was maximum at pad bath water content of 30%. They observed that water content did not affect the loss of physical properties but wash wear ratings and wet crease recovery increased and dry crease recovery decreased with increasing pad bath water content.

Heinisch and coworkers (82) studied the chemical structure of cross-linked cotton with immersion of fabric in formaldehyde, acetic acid, hydrochloric acid and water. They found that long crosslink increased the wet recovery and short chain length improved the resiliency of the conditioned fabric.

Gilbert and Smith (83) studied degradation of formaldehyde modified cellulose in presence of acid catalyst under aqueous and non-aqueous conditions. They determined tear strength, break strength, crease recovery, functional group content and chain length of the samples.

Liljemark and coworkers (84) carried out crosslinking of cotton fabric at different degrees of swelling and observed effects of crosslinking on its properties. They used formaldehyde and dimethylol dihydroxy ethylene urea. They studied properties at different moisture regain and found good crease recovery with hydrochloric acid at 4-5% moisture regain during reaction.

Pierce (Jr.) and Frick (Jr.) (85) treated cotton print cloth with formaldehyde in phosphoric acid as swelling agent and observed high wet crease recovery and moisture absorptivity, low dry crease recovery, uniform intralamellar crosslinks and little crystallinity and lattice type changes.

Joarder and coworkers (86) carried out uncatalyzed vapor phase crosslinking reaction of cotton cellulose with paraformaldehyde and the same reaction in presence of boric acid as catalyst. They found differences in bound formaldehyde, reaction time and crease recovery of the fabric.

Melikuzieva and Tashpulatov (87) studied the physicochemical properties of cotton fibre and rayon modified with formaldehyde in the vapor phase in the presence of hydrochloric acid. They observed that an increase the number of crosslinks decreased the solubility and swelling degree of both the fibres. Degree of order and fibre strength also decreased but satisfactory crease resistance was observed.

Evans (88) treated bleached mercerized cotton poplin with formaldehyde and sulfuric acid of different concentrations and studied its minimum ironing property.

Frick (Jr.) (89) crosslinked the fibre by soaking it in a solution of formaldehyde and acid. He observed that peripheral crosslinking was less effective in improving wrinkle resistance than uniform crosslinking.

Modi and Mehta (90) crosslinked cellulose with formaldehyde in dry and wet condition. They observed that in wet condition, fixation of formaldehyde on cellulose increased with an increase in acidity of bath. They also observed that wet and dry crease recoveries increased when the fabric was crosslinked in dry condition.

Guthrie (91) studied the length of oxymethylene bridges (crosslinks) introduced into cotton cellulose when it was treated with formaldehyde by various processes.

Segal and Timpa (92) studied the effect of formaldehyde crosslinking of cotton on the chain length of the cellulose molecule. They observed that changes in the fabric could be attributed to acid hydrolysis caused by the acid catalyst used in the treatment.

Jain (93) studied the effects of crosslinking on strength and wrinkle resistance in cotton. He found that loss in tensile strength was related to crease recovery increase.

King (94) padded cellulose fabric at room temperature with formaldehyde, magnesium chloride and water. He observed improvement in tensile strength, dry crease recovery angle, shrinkage percent for warp and filling. He used the process for improvement of finishing qualities.

Gonzalès and Guthrie (95) studied reaction of cotton cellulose with glyoxal and a variety of acids, amides, polyamides, dyes, hydroxy compounds and magnesium chloride. They found that wrinkle recoveries were affected.

Frick (Jr.) (96) discussed the reaction of crosslinking agents, including methylol ureas, methylol melamines, methylol derivatives of cyclic ureas, methylol carbamates and other crosslinking agents and correlated strength loss to crosslinking. Frick (Jr.) and Gautreaux (97) crosslinked cotton at low temperature with N,N dimethylol ethylene urea in presence of zinc nitrate and observed that the specimens cured at lower temperature had higher strength. Frick (Jr.) and coworkers (98.) also applied crosslinking agent to cotton fabric from organic solvent and studied the properties.

Mckelvey and coworkers (99.) improved the resiliency of cotton fabric by treating it with an aqueous solution of sodium silicate, sodium azide sodium sulfite or calcium chloride prior to crosslinking the fibres with epichlorohydrin in presence of OH donating catalyst.

Hobart (100) crosslinked cotton cellulose with N-methylol acrylamide in successive acid-catalyzed and base catalyzed steps. He confirmed occurrence of crosslinking with development of Cu-ene insolubility and wrinkle recovery. He observed that hydrolisis did not lower the crease ratings of any of the samples.

Harper (Jr.) and coworkers (101) studied the crosslinking of cotton and polyester blended cotton textiles with dimethylol dihydroxy ethylene urea in presence of a hydroxy acid catalyst. They observed moderate improvement in the overall fabric strength. It provided grafted carboxy groups that decreased the wet crease recovery but improved the soil release, dyeability and whitening of the cellulose.

Keceroovsky and Buchar (102) investigated the structural modification of yarn and the structural parameters of fibres were correlated with mechanical and viscoelastic properties of fibres and yarns modified after crosslinking with dimethylol ethylene urea in presence of magnesium chloride. They observed that the modification caused an increase in orientation and in the amorphous phase and a decrease in the length of crystallites.

Andrews and coworkers (103) crosslinked cotton fabric with dimethylol ethylene urea and polyvinyl alcohol and showed that stress recovery increased with crosslinking, that tensile strength and elongation at break decreased with crosslinking and that modulus increased with fibre stretch during crosslinking.

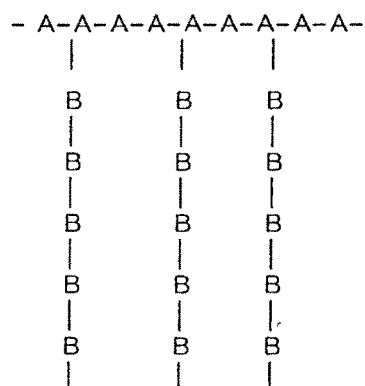
Tetsuo (104) grafted cotton fabrics with acrylamide and crosslinked by different methods. He crosslinked the fabric (i) in the vapor phase with paraformaldehyde in presence of ammonium chloride (ii) by pad dry cure method in presence of ammonium chloride after N-methylation of the grafted fabric and (iii) by pad-dry-cure method in presence of formaldehyde and ammonium chloride after N-methylation of the grafted fabric. He observed that methods (ii) and (iii) gave fabrics with superior dry and wet wrinkle resistance and with better retention of strength. Same author (104) grafted cotton fabric with acrylamide and crosslinked with formaldehyde in the vapor phase. He observed that wet and dry crease recoveries were markedly improved by grafting with acrylamide and by crosslinking respectively. He also observed that tensile strength of grafted cotton fabric decreased with increasing degree of crosslinking.

Soiling and soil removal studies of some modified crosslinked cottons were done by Beninate and coworkers (105). They treated cotton with dimethylol ethylene urea or triazine crosslinking formulation and found improved wet soil resistance of and soil removal from finished fabrics.

Effects of moisture and temperature on the crease recovery of cotton fabric and blended fabrics containing cotton were studied by Mclasen and coworkers (106). They crosslinked cotton with dimethylol ethylene urea.

I.6 GRAFTING :

Grafting is a reaction by which a polymer is attached through covalent linkage, as a pendant to the backbone of another. Chemically it is polymerization of a given kind of monomer in the presence of an already formed polymer. The branched polymer is popularly known as graft copolymer and can be represented as :



The sequence of 'A' units in the graft copolymer is referred to as the backbone, and branches (pendant groups) of 'B' as the grafts. The backbone may be homopolymeric or copolymeric with pendant groups of either type.

Graft copolymers possess some of the properties of both backbone polymer and the graft polymer. Thus, grafting is a suitable technique for modifying existing polymers. However, grafting can not greatly modify the properties of the existing backbone polymer since only a few linkages are involved. Rather, it is a technique for adding the properties of one polymer to those of another polymer without significantly affecting the properties of the main backbone polymer. Fibres thus modified can be regarded as new textile materials.

Basically the idea of grafting vinyl monomers to cellulose was conceived to produce a structure which will combine the good qualities of both. The process envisaged was to polymerize a vinyl monomer in the presence of cellulose

under conditions that will promote covalent bonding between the cellulose chain and the synthetic polymer chain. Usually, the homopolymer can be easily extracted out of the cellulose structure by solvents. While a grafted polymer cannot be removed by solvent extraction of the modified cellulose, it does not necessarily establish that a covalent bond is formed between the synthetic polymer and cellulose. Whether this bond is present or not in the graft copolymer, it may be assumed that there is intimate association between the two to resist their separation by common fractionation procedures.

There are three major methods known for the preparation of graft copolymers : (i) Chain transfer, (ii) Chemical initiation and (iii) Physical methods of initiation.

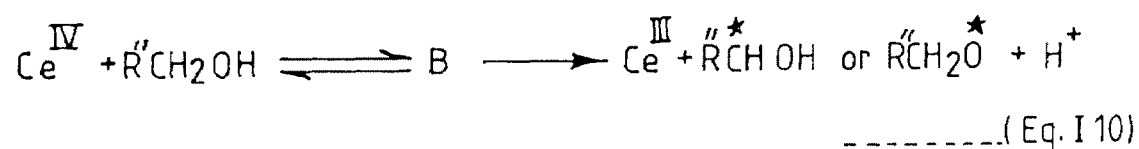
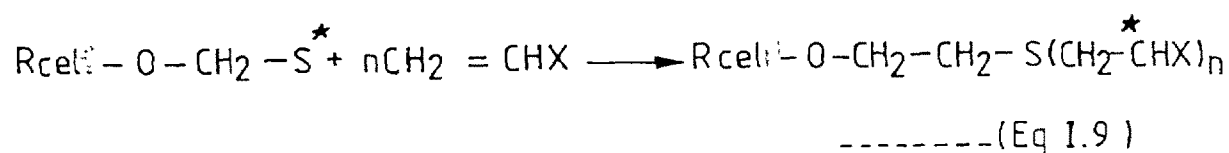
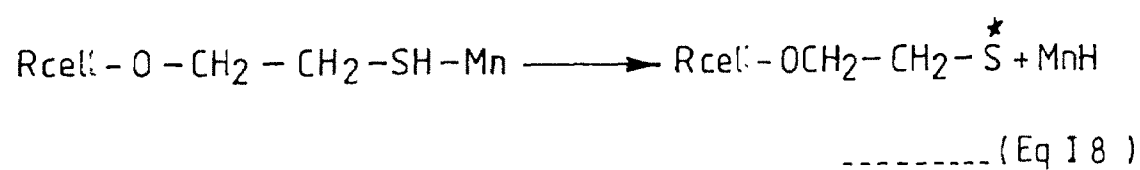
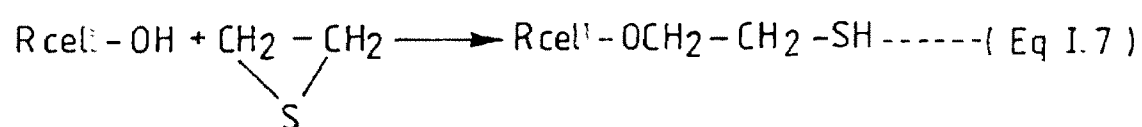
(i) Chain transfer

Growing polymer radicals are capable of abstracting hydrogen atoms from various compounds. Transfer reaction may take place between the growing chain and the initiator, monomer, solvent, polymer or another growing chain. Chain transfer reaction is by far the most common method used for the preparation of grafted copolymers. Graft copolymer is always formed in admixture with homopolymer.

Grafting onto cellulose by chain transfer techniques has been reported. Machell and Richards (107) reported that cellulose being a poor transfer system, the efficiency of grafting is quite low. The efficiency can be increased by introducing certain groups with large transfer constant (108), e.g. mercapto (-SH) groups introduced into cellulose enhance hydrogen abstraction by the growing radical (eq.I-7,8,9). The main difficulty of transfer method is that, the process takes place at random along the polymer chain, and no control over the number of branches per molecule is possible. Furthermore, the graft is formed in admixture with homopolymer.

(ii) Chemical initiation system

Some of the commonly used chemical systems for initiating grafting



via free radicals formed on the cellulose backbone are listed in (Fig.I.6).

(a) Persulfate Initiation.

Grafting on cellulose has been achieved through initiation by persulphate ions. Some experiments were carried out with cotton and acrylonitrile by Hydel and coworkers (109), but they did not investigate whether real grafting occurred and referred to the process as deposition and coating onto cotton. Kulkarni and Mehta (110) strongly supported the postulate of a graft formation of polyacrylonitrile with cellulose using potassium persulphate.

(b) Redox system

Potassium persulphate - Sodium thiosulphate redox system has been used by Kulkarni and coworkers (111) for the preparation of cellulose acrylonitrile graft copolymers. They have reported that pretreatment with thiosulphate and a trace of copper sulphate reduced the induction period, accelerated the grafting reaction and decreased homopolymer formation, giving higher graft yields.

It has been claimed (112) that the reaction between H_2O_2 and Fe^{++} in the presence of cellulose and a vinyl monomer produces a graft copolymer.

(c) Initiation by ceric ion

Mino and Kaizerman (113) proposed mechanism for initiation of graft polymerization (eq.I.10), where B represents a ceric - alcohol complex and RCHOH^* or RCH_2O^* free radicals produced from the alcohol. Thus, when cellulose was used as a reducing agent, the formation of homopolymer was greatly suppressed and high graft yields were obtained. They also showed that, in absence of alcohol, little or no initiation of the vinyl monomer takes place. On account of its ease of application, this system has gained considerable importance in grafting reaction (114-122). Terasake and Terakasi (123),

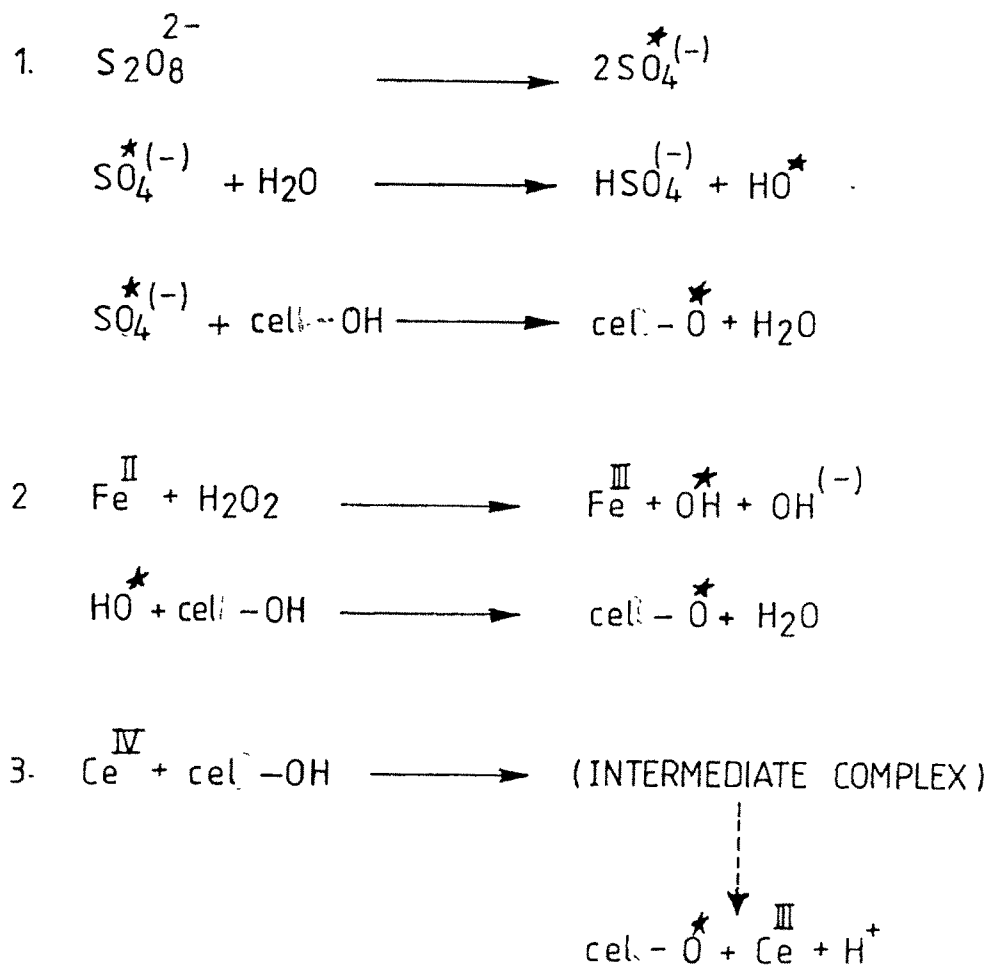


FIG I-6

Cumberbirch and Holker (122) and Arthur and coworkers (124) postulated bond cleavage in cellulose during grafting initiated by Ce^{IV} .

Kulkarni and Mehta (125) studied the oxidation of cellulose by Ce^{IV} , and showed that, in the initial stage of oxidation, the reaction proceeded very rapidly due to formation of Ce^{IV} cellulose complex and oxidation of the hemiacetal groups of cellulose. Thereafter, oxidation of the secondary hydroxyl group at C-2 occurs without the $\text{C}_2 - \text{C}_3$ bond cleavage. The glycol bond cleavage takes place at high Ce^{IV} concentration and on prolonged oxidation of cellulose. Hebeish and coworkers (126) strongly support the above postulation on the basis of kinetic studies of grafting of vinyl monomers on modified cottons. Hebeish and Mehta (127) studied the effect of accessibility of cellulose on the graft yields using the ceric ion-cellulose system.

Grafting of various vinyl monomers and their binary mixtures on cellulose using this redox system was investigated (121).

(iii) Physical Methods for initiation

Radiation Initiation

Although the method is convenient to apply in the laboratory, has general applicability to a variety of substrates, and has received remarkable attention throughout the world, little commercial use has been made of this technique.

Radiation graft copolymerization may be initiated by two techniques. In one, the substrate is irradiated separately before being brought into contact with the monomer and the formation of polymer is termed "preirradiation graft polymerization". Alternatively, the substrate may be placed in a monomer solution or vapor and the whole system is irradiated; this leads to simultaneous or mutual radiation grafting. In general, the latter method leads to much larger amounts of polymer being grafted to the substrate.

Stannett and Hofman (128) reviewed the application of radiation techniques in the textile industry and showed that gamma radiation yields

essentially uniform distribution of initiation sites. Irradiation with high-energy electrons (β rays) produces essentially the same effect.

A general discussion of the effect of radiation on polymers was given by Gilbert and Stannett (129). They reported that most natural polymers appeared to degrade on irradiation rather than form crosslinks and that this effect increased with dose rate for a given dose.

The preirradiation technique of polymer initiation suffers from the disadvantage that oxygen must be carefully excluded from the system and that relatively high radiation doses are required to bring about reasonable amount of polymer graft. There is, however, one attractive advantage in that if the substrate is irradiated alone, before the introduction of the monomer, the only initiating sites present during polymerization are on the backbone chain of the substrate. Thus very little homopolymer is formed. Simultaneous grafting of polymer to a substrate has an immediate advantage over preirradiation grafting in that much higher polymer add-ons may be achieved and usually at a much lower irradiation dose.

Dilli and Garnett (130) studied the simultaneous grafting of a number of monomers onto cellulose and found that total doses less than 1 Mrad were effective in producing grafts of 50 to 100% w/w whereas preirradiation grafting using doses in excess of 1 Mrad seldom results in more than 25% w/w of grafted polymer.

Armstrong and Rutherford (131) developed a techniques of applying the monomer from the vapor phase. Water, methanol and acetic acid vapors accelerated the rate of addition of vinyl monomers to cellulosic materials, and polyacrylonitrile to cotton and wool textile fibres. Undoubtedly the swelling of the substrate by these additives assists the monomer to diffuse to the interior and, therefore, accelerates diffusion controlled reaction. Armstrong and Rutherford also pointed out that, even with monomer within a cellulose

substrate, no polymerization occurred without the addition of a sensitizer. It was not necessary for the sensitizer to be present during the radiation step if polymerization was initiated by preirradiation.

In general, the grafting on a non-swollen substrate will restrict the polymer to the substrate surface, whereas a swollen substrate permits homogeneous distribution of the polymer. If the substrate is insufficiently swollen so that polymerization is diffusion controlled, there will be a distribution of polymer concentration from the surface to the center of the substrate. Similarly, if the polymerization is carried out before the swelling agent has time to penetrate far into the substrate, the grafting will only occur in the swollen portions near the surface.

Another variation due to Hargreaves (132) is to irradiate only the monomer to be grafted and not the substrate. This avoids degradation of the substrate which may be associated with ionizing irradiation and could have particular relevance to cotton which appears to be more sensitive to radiation than other forms of cellulose such as wood, paper, and viscose.

Graft copolymerization of acrylonitrile, methylacrylate, styrene, methyl methacrylate and vinyl acetate on cellulose was carried out using ceric ammonium nitrate as initiator (133) and distribution of grafted copolymer in cellulose was measured. The yield of the graft copolymer increased with increased concentration of the catalyst, nitric acid and the monomer in general. It was found that the degree of iodine absorption and the change of cellulose fibre diameter increased with the increase in the degree of grafting.

Salsbury and Coworkers (134) studied the grafting process of cotton fabric web using ceric ammonium sulfate, acrylonitrile-water azeotrope was used for grafting on web. The treated fabric showed outstanding resistance to degradation by microorganisms and no loss of strength after 6 week burial in soil.

Livshits and Ragovin (135) synthesized a graft copolymer of cellulose with polyacrylonitrile in presence of tetravalent ceric salts at 0° and 5° in Ar or air stream. They discussed the effect of several factors on the grafting rate and the quantity of grafted polyacrylonitrile. They (136) also developed a new method for graft copolymerization of acrylonitrile without the formation of homopolymer. They have used oxidation-reduction system containing Mn(III) pyrophosphate as oxidizing agent and free macroradicals as reducing agent. Degree of grafting was determined.

Grafting of vinyl monomers onto various fibres via free radical mechanism in the absence of an initiator was studied by Imoto and coworkers (137).

They grafted methacrylic acid onto cellulose fibres. He used neutral emulsifier such as poly (oxyethylene) phenyl ether as accelerator.

Purification and configurational structure of cellulose acrylonitrile graft copolymer with ceric ammonium nitrate as initiating agent was studied by Chou and coworkers (138).

Gulina and coworkers (139) synthesized cellulose polyacrylonitrile graft copolymers in the presence of the redox system. (Cellulose- Fe^{++} - H_2O_2). They developed a method of grafting for the determination of the polymerization coefficient of polyacrylonitrile grafted on cellulose and of the conversion degree of cellulose during this reaction. Optimum conditions for the grafting of acrylonitrile with cellulose using Fenton's reagent as initiator were determined by Vlasta and coworkers (140).

Composition and structure of cellulose - polyacrylonitrile graft copolymers obtained by Mn(IV) initiator in gaseous phase were described by Egon and Rainer (141). They studied the degree of polymerization of a few selected samples and observed considerable expansion of fibre structure during grafting.

Reactivity to grafting of cotton fibres with polyacrylonitrile prepared from pre activated fibres was studied by Razikov and coworkers (142). They observed that the treatment with sodium hydroxide rendered the fibres more reactive to grafting.

Properties of modified cellulose were also studied by Dimov and Pavlov (143). They prepared graft copolymers of cellulose with acrylonitrile using redox system cellulose xanthate - H_2O_2 . They observed degradation of cellulose during grafting. Mechanical strength increased with increasing percentage of grafting.

Structure and properties of cellulose and its derivatives were studied by Morin and coworkers (144). They synthesized cellulose graft copolymers using vapours of the monomers in the presence of ammonium persulfate and the effects of initiation conditions on polymerization degree of grafted polyacrylonitrile and on conversion degree of cellulose were studied.

Iichiro and coworkers (145) carried out graft polymerization of acrylonitrile onto cellulose in presence of cerium diammonium hexanitrate initiator, zinc chloride and acetic acid and the effects of different parameters on the polymerization rate and the degree of grafting were studied.

Kurlyankina and coworkers (146) prepared cellulose graft copolymers with acrylonitrile and acrylamide in presence of cobalt(III) salts. He found that there was no significant degradation of cellulose and no large amount of homopolymer was formed.

Rao and Kapur (147) developed a method for quantitative estimation of the extent of grafting on cellulose. They have synthesized acrylonitrile grafted cellulose using ceric salt as initiator and found that 20% increase in weight highly improved resistance to microorganisms.

Kamogawa and Sekiya (148) prepared the copolymer of acrylamide and cotton using ceric salt. This grafted fabric was further treated to prepare

methyolated grafted fabric by immersing in formaldehyde. They found that methyolated grafted fabrics showed good crease resistance but poor strength.

Narita and coworkers (149) studied the mechanism of grafting of acrylamide on cellulose using ceric ion as initiator. They carried out the reaction in air and nitrogen but difference in reaction mechanism was hardly recognised.

Graft copolymers of cellulose with acrylamide were studied by Neimo and Sihotla (150). They suggested that block copolymer was formed.

Tetsuo (109) grafted polyacrylamide onto cotton fabrics and the grafted fabrics were crosslinked with formaldehyde to study their wrinkle resistance in dry and wet states. Dry crease recovery was improved by crosslinking and tensile strength of grafted warp yarn decreased with increasing degree of crosslinking.

Vilanderberg and coworkers (151) studied the mechanism of grafted polymerization of cellulose in presence of iron (II) - H_2O_2 system.

Tetsuo (108) grafted the cotton fabrics with acrylamide and further crosslinked with paraformaldehyde in presence of ammonium chloride. By this method, they found superior dry and wet crease resistance with better retention of strength.

Mehta (152) studied the properties of cotton fabrics grafted with acrylamide in presence of ceric ammonium nitrate and treated with sodium hypochlorite. They found that it acquired high wet wrinkle recovery and flex abrasion resistance without significant loss in break strength. Khristov and coworkers (153) synthesized graft copolymer of cellulose with polyacrylamide in presence of potassium persulfate and optimum conditions of grafting were determined.

Structure and properties of cellulose and its derivatives were investigated by Kozlova and coworkers (154). They synthesized graft copolymers

of cellulose with poly (acrylic acid) and poly (methacrylic acid) and observed that the introduction of - COOH group increased the hygroscopicity of cotton fabrics. They also observed that cellulosic fabric containing 4 to 6 % of polyacrylic acid has a much greater resistance towards microbial attack and high cation exchange capacity.

Khun and coworkers (155) modified cellulosic fibres with polymerizable substances like acrylic acid and methacrylic acid. They found that tensile strength and crease recovery were not affected.

Mal'tseva and coworkers (156) synthesized graft copolymers of cellulose and poly (acrylic acid) using $\text{Fe-H}_2\text{O}_2$ oxidation - reduction system. He observed that the system $\text{Fe(III)/H}_2\text{O}_2$ gave similar results with less weakening of the cellulose fabric strength.

Properties of acrylic acid grafted cotton fabrics were also studied by Waichiro and coworkers (157). They observed that the fibres had improved affinity for basic or cationic dyes. Washfastness of basic dyed grafted fabrics was low and soiling resistance of the fibres was inferior to that of nongrafted fibres.

Rowland (158) polymerized and fixed carboxyl containing vinyl monomers on fibrous substrates. He used several combinations of vinyl monomers to provide antistatic properties, soil resistance, hydrophilicity and durable press finish to textiles.

Effects of grafting cellulose with methyl methacrylate by different methods were discussed by Ernest and coworkers (159). They observed that grafting with poly (methyl methacrylate) improved the resistance to degradation by microorganism.

1.7 WATER SORPTION

Cotton textiles contain hydrophilic hydroxylic groups and hence these cellulosic materials would sorb water and swell. Esterification or acetalization of the hydroxylic group will reduce the capacity of the material to sorb water thereby affecting water swelling and water repellency.

The swellability and solubility of partially substituted esters cross-linked with formaldehyde were studied by Petropalovskii and coworkers (38). Water repellency of partially esterified cotton fabrics was studied by Benerito and coworkers (48) and Baird (51). Decrease in the solubility and swelling degree of fibres on formalization was observed by Molikuzieva and Tashpulatov (87). Rowland (158) used several combinations of vinyl monomers for grafting onto fibres for modifying hydrophilicity of fibres.

Water sorption in cellulose block graft polymers has been related to the crystallinity of blocks, block size, etc. (160). Sorption of moisture by cotton fabric treated with sodium hydroxide or ammonia was investigated by Barkhuyan and Rensbury (161).

Grafting of cellulose and cellulose acetate fibres with vinyl fluoride, hexafluoropropylene, etc. imparted water repellency to the fibres (162).

Sorption of methanol by cellulose styrene graft copolymers or blends decreased with increasing styrene content, presumably due to build-up of hydrophobic groups (163).

Hydrophilicity of cellulose was expressed as the equilibrium sorbed water content (a) at a given temperature (T) and relative humidity (Ψ) (164). Young and Nelson's equations have been applied to the sorption of water vapour by cellulosic materials (165). Heat of wetting (ΔH) of cellulosic materials is directly proportional to their surface area calculated from water

vapour sorption isotherm (166). NMR studies showed that molecular mobility of water sorbed by hemicellulose increased with increasing moisture content (167).

The sorption of NaCl and CaCl_2 from aq. and aq. ethanolic solutions increased with increasing ethanol concentration and is related to the donor-acceptor interaction between ions and OH groups of alcohol (168).

I.8 PRESENT WORK

In recent years considerable work is being carried out on chemical modification of cotton fibres. Yastu, Calamari and Benerito (169) have studied X-Ray diffractograms of Cellulose I, Cellulose II, Cellulose III and Cellulose IV formed by treatment of natural cellulose with alkali, liquor ammonia and ethylene diamine. Correlations between sweat and clothing have been considered by Gwosdow et al (170). Frick (Jr) (171) suggested from scanning electron micrographs that layer expansion of cotton is observed on treatment with DMDHEU. Formaldehyde release in formal finishes has been studied by Turner (172).

In our laboratories considerable work has been carried out on different types of polymers. Thus work has been carried out on coordination polymers (173), semiconducting and pyrolysed chelate polymers (174), chelating polymers (175), ion-exchange resins and redox polymers (176), ionomers (177), swelling of hydrophilic polymers (178), etc. In continuation of such studies, we considered the chemical

modification of cotton fibres grown in Gujarat by esterification, formalation, grafting, etc. Such studies can help in developing some techniques and/or identifying some product which may have commercial viability. Hence it was planned,

- (1) to prepare (a) anhydrides from various acids, such as adipic acid, fumaric acid, sebacic acid, cinnamic acid, etc. and (b) acid chlorides from various acids such as adipic acid, sebacic acid, fumaric acid, acrylic acid, methacrylic acid, linear alkyl benzene sulphonic acid, etc,
- (2) to esterify the cotton fibres and fabrics with acid anhydrides and acid chlorides,
- (3) to study their IR spectra, TG analysis, SE micrographs, Crease recovery, diameter, etc,
- (4) to modify cotton fabrics with polyvinyl alcohol (PVA) and formaldehyde, paraformaldehyde, butyraldehyde etc. and resinify the products in presence of resorcinol, melamine, etc,
- (5) to study the formalized and resinified cotton fabrics by determining their % add-on, break-strength, crease recovery, etc,
- (6) to copolymerize cotton fibres and fabrics with various vinyl monomers such as acrylonitrile, acrylamide, methyl methacrylate, methacrylic acid, vinyl acetate, etc,
- (7) to study the properties of grafted fabrics and fibres, such as % add-on, crease recovery, diameter, etc,

- (8) to study water sorption characteristics of some of the modified fabrics.

The experiments carried out and results obtained are presented and discussed in the following page.