CHAPTER VI
SUMMARY AND CONCLUSIONS
Cotton fibres present in the unopened cotton bolls are known as 'Never-dried' or 'Undried' cotton fibres. These fibres are full of moisture and possess considerable plasticity. The fibres are tubular and give circular cross-sections. After reaching full maturity, cotton boll bursts open. The never-dried fibres thus exposed begin to lose their shape as drying continues. The fibres shrink in length and width and become ribbon-shaped. Convolutions are formed along the longitudinal direction during drying. The number of convolutions per unit length of fibre depends upon the type of cotton and conditions of drying. The bulk density of the fibres is increased after drying due to considerable reduction of cell-wall porosity. Intermolecular hydrogen bonds between the adjacent cellulose chains are formed in increasing number as drying continues. The bond energies depend upon the conditions of drying and molecular arrangement of cellulose chains. All the above-mentioned changes which take place after drying of never-dried cotton fibres produce changes in mechanical, physical and chemical properties of cotton fibres. Considerable confusion exists regarding the molecular organization of cellulose in never-dried cotton. Also, no conclusive data are available from the existing literature to decide which
of the conditions of drying produce better properties in the cotton fibres. The present work is concerned with the investigations on the structure of cellulose in the developing cotton fibres, accessibility of never-dried cotton fibres to reagents such as dyes, resins and esterifying agent and effect of these reagents on the morphology and structure of cotton fibres.

(i) Fine Structure, Accessibility and Swelling of Never-dried Cotton

Equatorial X-ray diffraction study was carried out on never-dried and dried cotton fibres at different stages of growth. Accessibility of never-dried and nature-dried cottons was measured by water retention measurements. The effect of various solvents of different polarity such as benzene, THF, DMSO, DMF, pyridine and morpholine on the fine structure and porosity was investigated by means of X-ray diffraction and, water retention and glycerol retention measurements. Decrystallization of both cottons with NaOH was also studied.

Results showed that crystallization of cellulose in cotton takes place simultaneously with the deposition of cellulose. Both, crystallinity and crystallite width increase gradually with the increasing age of the fibre and finally level off. Drying of never-dried fibre increases the crystallization of cellulose but only to a marginal extent. Thus, the earlier finding that cellulose in the
never-dried cotton is fully amorphous has been refuted in the present study by direct X-ray diffraction study. It is conclusively proved that although, there is considerable lamellar and fibrillar aggregation upon drying of never-dried fibres, very little molecular crystallization of cellulose takes place. Water retention measurements showed never-dried cotton to be highly accessible in comparison with nature-dried cotton. Porosity measurements indicate that never-dried cotton is highly porous and drying results in a considerable loss in porosity. Properties of solvents used for solvent exchange drying such as polarity, capacity to form hydrogen bonds or interact with cellulose, etc., have considerable effect on porosity and fine structure of the dried fibres. In general, drying from nonpolar solvents results into lesser collapse of the structure. An important finding in the NaOH-decrystallization study is that phase transformation from cellulose I to cellulose II is complete in never-dried cotton whereas in nature-dried cotton, there is residual 10% cellulose I. This has been attributed to higher structural porosity of never-dried cotton.

(ii) Equilibrium Direct Dye Adsorption

Equilibrium adsorption on fully mature never-dried and nature-dried cotonns was carried out with two direct dyes, Chlorazol Sky Blue FF and Chrysophenine G. Thermodynamic parameters were evaluated. Equilibrium adsorption
of Chlorazol Sky Blue FF was carried out on cotton fibres at different stages of growth and various solvent exchange-dried samples. Adsorbed dye from various dyed samples was extracted with 25% aqueous pyridine. Heat of wetting measurements were made on various dyed never-dried and nature-dried samples. These studies show that never-dried cotton is more accessible to direct dyes as compared to nature-dried cotton. Adsorption on never-dried cotton was found to be 1.5 to 2 times more than that on nature-dried cotton. The affinity values, heats of adsorption and entropy values for adsorption on never-dried cotton were found to be slightly lower than those for nature-dried cotton. This was attributed to the high exchange energy of dyeing due to the presence of water held by strong forces with cellulose. Inaccessible zones develop within the cellulose structure simultaneously with cellulose deposition. This results in the decreasing accessibility of never-dried cotton with increasing age of cotton. Inaccessible zones further increase upon drying of never-dried cotton. This again reduces the accessibility of cotton. It was found that accessibility of cotton depends on the polarity and other properties of solvent used for solvent exchange drying. Never-dried cotton dried from nonpolar solvent was highly accessible to direct dyes. Heat of wetting measurements indicated that in dyed never-dried and nature-dried fibres the dye molecules blocked the
sites for water adsorption after adsorption of $15 \times 10^{-3}$ moles/kg of dye on the fibre had taken place.

(iii) Sorption of Textile Finishing Agents on Never-dried Cotton

Reactivity of never-dried cotton towards some of the textile finishing agents in comparison to nature-dried cotton was examined. Equilibrium reactions with reactive dyes and formaldehyde, and initial chemisorption with DMEU and DMPU were carried out. Rates of acetylation were also examined.

Reactivity of never-dried cotton towards reactive dyes and formaldehyde was found to be the same as that of nature-dried cotton, whereas initial chemisorption of DMEU and DMPU was 1.5 times more on never-dried cotton than on nature-dried cotton.

Rates and extents of acetylation were found to be the nearly equal for both cottons. Acetylation is a non-swelling type reaction occurring on the fibrillar surface. Reaction with reactive dye is a specific one taking place at the points of structural dislocations. In other words, it is directly related to the noncrystalline portion in the fibre. The dependence of reaction extent with crystallinity was also observed in the study of reactive dyeing as a function of growth. Crosslinking with formaldehyde is an intrafibrillar reaction and proceeds independently of the morphology of fibre. The chemisorption of DMEU and DMPU, on the other hand, was carried out only for
15 minutes. Here, rate of diffusion of reagent molecules into the fibre structure becomes an important factor. Never-dried cotton shows higher reactivity on account of higher rate of diffusion due to its large structural porosity. Polymolecular adsorption also may not be ruled out.

All these observations suggest that although considerable fibrillar aggregation takes place upon drying of never-dried cotton, large fibrillar surface area develops upon re-wetting with water. Availability of this surface area to reagents depends upon several factors like size of the reagent molecule, nature of the reaction, selective accessibility of the hydroxyl groups of cotton, molecular weight of the reagent, affinity of the reagent for cotton etc. In the above reactions, slightly higher reactivity of never-dried cotton corresponding to its lower crystallinity value was expected. However, due to retarding action of strongly held water in never-dried cotton this was not observable.

(iv) Morphological and Mechanical Properties of the Treated Never-dried and Nature-dried Cotton Fibres

Morphological and mechanical properties of never-dried and nature-dried cottons treated with various reagents were examined. In optical microscopic examination of cross-sections of fibres, it was observed that circularity of the cross-sectional shape in the case of cotton treated in