Part I

The structure and properties of cotton

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Chemical structure and properties of cotton

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1.1 Introduction

Cotton fibers are the purest form of cellulose, nature's most abundant polymer. Nearly 90% of the cotton fibers are cellulose. All plants consist of cellulose, but to varying extents. Bast fibers, such as flax, jute, ramie and kenaf, from the stalks of the plants are about three-quarters cellulose. Wood, both coniferous and deciduous, contains 40–50% cellulose, whereas other plant species or parts contain much less cellulose. The cellulose in cotton fibers is also of the highest molecular weight among all plant fibers and highest structural order, i.e., highly crystalline, oriented and fibrillar. Cotton, with this high quantity and structural order of the most abundant natural polymer, is, not surprisingly, viewed as a premier fiber and biomass.

This chapter focuses on the chemical structure of cotton fibers and its structural relationship to cellulose synthesis, fiber development and dehydration as well as other chemical and structural aspects (physical properties, dyeing and finishing) not dealt with in the following chapters. Cotton fiber cells are developed in four overlapping but distinct stages of initiation, elongation, secondary cell wall thickening and maturation and desiccation (Naithani *et al.*, 1982). Structural development and properties of cotton fibers during the primary wall formation (elongation) and secondary wall thickening (cellulose synthesis) as well as during desiccation (transition from mobile to highly hydrogen-bonded structure) are detailed.

1.2 Chemistry

1.2.1 Chemical composition

Cotton fibers are composed of mostly α-cellulose (88.0–96.5%) (Goldwaith and Guthrie, 1954). The noncellulosics are located either on the outer layers (cuticle and primary cell wall) or inside the lumens of the fibers whereas the secondary cell wall is purely cellulose. The specific chemical compositions

of cotton fibers vary by their varieties, growing environments (soil, water, temperature, pest, etc.) and maturity. The noncellulosics include proteins (1.0–1.9%), waxes (0.4–1.2%), pectins (0.4–1.2%), inorganics (0.7–1.6%), and other (0.5–8.0%) substances. In less developed or immature fibers, the non-cellulosic contents are much higher.

The primary cell walls of cotton fibers contain less than 30% cellulose, noncellulosic polymers, neutral sugars, uronic acid, and various proteins (Huwyler *et al.*, 1979; Meinert and Delmer, 1977). The cellulose in the primary cell walls has lower molecular weight, with the degree of polymerization (DP) between 2,000 and 6,000 and their distributions are broader (Goring and Timell, 1962; Hessler *et al.*, 1948). The secondary wall of the cotton fiber is nearly 100% cellulose. The DP of the cellulose in the secondary wall is about 14,000, and the molecular weight distribution is more uniform (Figini, 1982). The high molecular weight cellulose characteristic of mature cotton has been detected in fibers as young as eight days old. In the later stage of elongation or 10–18 days following initiation, the higher molecular weight cellulose decreases while the lower-molecular weight cell wall components increase, possibly from hydrolysis (Timpa and Triplett, 1993). Between the ages of 30 and 45 days, the DPs estimated from intrinsic viscosities of fibers have been shown to remain constant (Nelson and Mares, 1965).

Of the non-cellulosic components in the cotton fibers, the waxes and pectins are most responsible for the hydrophobicity or low water wettability of raw cotton fibers. The term 'cotton waxes' has been used to encompass all lipid compounds found on cotton fiber surfaces including waxes, fats, and resins (Freytag and Donze, 1983). True waxes are esters, including gossypyl carnaubate, gossypyl gossypate, and montanyl montanate. Alcohols and higher fatty acids, hydrocarbons, aldehydes, glycerides, sterols, acyl components, resins, cutin, and suberin are also found in the wax portion of the cuticle in varying quantities. Pectins are composed primarily of poly(β-1,4-polygalacturonic acid) and rhamose to make up the rhamnogalacturonan backbone (Heredia *et al.*, 1993). The side chains are composed of arabinose, galactose, 2-*O*-methylfucose, 2-*O*-methylxylose and apiose. Eighty-five percent of the polygalacturonic acid groups are methylated leading to a highly hydrophobic substance. Proteins are located primarily in the lumen, but small amounts of hydroxyproline rich proteins are present on the fiber surface (Darvill *et al.*, 1980). The far lower extents of the non-cellulosics than cellulose make their detection in mature cotton fibers challenging. Extraction and reaction techniques are often employed to separate the non-cellulosic cell wall components for characterization. These procedures, however, tend to disrupt their organization and possibly alter their chemical compositions.

The amounts of the noncellulosic components change during fiber elongation and the transition from primary to secondary wall, but discrepancies remain

in the exact quantities of these changes. Some of the protein constituents (enzymatic, structural or regulatory) are unique to cotton fiber cells and have been found to be developmentally regulated (Meinert and Delmer, 1977). The non-cellulosic constituents in developing cotton fibers through the onset of secondary cell wall synthesis can be clearly identified by analytical techniques, including FTIR/ATR, DSC, TGA, and pyrolysis-GC/MS methods (Hartzell-Lawson and Hsieh, 2000). The waxy compounds in developing fibers up to 17 days old are detected by their melting endotherms in the DSC. Pectins can be detected by FTIR in the 14-day-old as well as the mature fibers. FTIR/ATR measurements indicated the presence of proteins in developing fibers up to 16 dpa. The presence of proteins can be measured by FTIR/STR methods in up to 16-day-old fibers and by pyrolysis-GC/MS in up to 14-day-old fibers. Only pyrolysis-GC/MS could detect the presence of the non-cellulosic compounds in 27-days-old fibers. The detection of the non-cellulosics diminished as the proportion of cellulose rapidly increased at the onset of secondary cell wall synthesis. The presence of hydrophobic compounds on the surfaces of cotton fibers of all ages and their removal by alkaline scouring are easily determined by their water contact angles.

Among the inorganic substances, the presence of phosphorus in the form of organic and inorganic compounds is of importance to the scouring process used to prepare fibers for dyeing. These phosphorus compounds are soluble in hot water, but become insoluble in the presence of alkali earth metals. The use of hard water, therefore, can precipitate alkali earth metal phosphates on the fibers instead of eliminating them (Hornuff and Richter, 1964).

1.2.2 Cellulose chemistry and reactions

Cotton cellulose is highly crystalline and oriented. α-cellulose is distinct in its long and rigid molecular structure. The β-1,4-D(+)-glucopyranose building blocks in long cellulose chain are linked by 1,4-glucodic bonds. The steric effects prevent free rotation of the anhydrogluco-pyranose C-O-C link. Each anhydroglucose contains three hydroxyl groups, one primary on C-6 and two secondary on C-2 and C-3. The abundant hydroxyl groups and the chain conformation allow extensive inter-molecular and intra-molecular hydrogen bonding to further enhance the rigidity of the cellulose structure.

Chemical reactions and heating effects on cotton cellulose depends on the supermolecular structure as well as the activity of the C-2, C-3 and C-6 hydroxyl groups. Heat or reactions begin in the more accessible amorphous regions and the surfaces of crystalline domains. Chemical reactivity of the cellulose hydroxyl groups follows those of aliphatic hydroxyl groups, i.e., higher for the C-6 primary than the secondary on the C-2 and C-3. Etherification and esterification are the two main categories of reactions. Esterification reactions, such as nitration, acetylation, phosporylation, and sulfation, are

usually carried out under acidic conditions. Etherification, on the other hand, is favored in an alkaline medium.

Cellulose is readily attacked by oxidizing agents, such as hypochlorites, chlorous, chloric, and perchloric acids, peroxides, dichromates, permanganates, periodic acid, periodate salts, and nitrogen tetroxide (Bikales and Segal, 1971). Most oxidizing agents are not selective in the way they react with the primary and secondary hydroxyl groups. Oxidation of cellulose can lead to two products, reducing and acidic oxycellulose. In reducing oxycellulose, the hydroxyl groups are converted to carbonyl groups or aldehydes, whereas in acidic oxycellulose, the hydroxyl groups are oxidized to carboxyl groups or acids. The oxycellulose can be further oxidized to acidic oxycellulose. Reducing oxycellulose is more sensitive to alkaline media and the chain lengths are often reduced. Periodic acid and periodate salts break the anhydroglucose ring between C-2 and C-3, converting the two secondary hydroxyl to aldehydes which can be further oxidized to carboxyl groups. Nitrogen tetraoxide reacts specifically with the primary hydroxyl groups on C-6, oxidizing it to carboxyl group directly or to polyglucuronic acid, an oxycellulose.

1.2.3 Heating effects

Heating generally causes dehydration and decomposition of cellulose. These reactions are influenced by the presence of other compounds as well as the temperature and rate of heating. Dehydration reactions are favored in the presence of acid catalysts whereas depolymerization reactions are favored by alkaline catalysis. Heating at lower temperatures favors dehydration and enhances subsequent char formation (Shafizadeh, 1975). Higher temperature heating causes rapid volatilization via the formation of laevoglucosan, forming more gaseous combustible products. Greater dehydration also reduces the yield of laevoglucosan and subsequently lowers the volatile species. Therefore, acid catalysts are of special importance to impart flame retardancy to cellulose.

Heating cotton cellulose up to 120 °C drives off moisture without affecting strength. Heating to a higher 150 °C has been shown to reduce solution viscosity, indicative of lowered molecular weight, and tensile strength (Shafizadeh, 1985). Between 200 °C and 300 °C, volatile products and liquid pyrolyzate, mainly 1,6-anhydro-β-D-glucopyranose, commonly known as levoglucosan, evolve. At 450 °C, only char remains. Of total pyrolytic products, 20% is the gaseous phase (CO, CO_2, CH_4), 65% is the liquid phase (of which 80% is levoglucosan) and 15% is the char. The heating rate can affect the amount of char formation (Shafizadeh, 1985). Heating below 250 °C affects only the amorphous regions since no change in the crystalline structure has been found. The crystalline structure of cellulose has been shown to be lower when heated at 250 °C to 270 °C, and then disappear on further heating to

300 °C. Highly crystalline cellulose has been shown to decompose at higher temperatures, for instance 380 °C (Bikales and Segal, 1971).

Blocking the primary hydroxyl groups of cellulose prevents depolymerization, thus reducing production of volatiles. The reduction of flammable gases is accompanied by more complete intra-ring and inter-ring dehydration, giving rise to keto-enol tautomers and ethermic linkages, respectively. The carbonyl groups so formed can participate in a variety of reactions, leading to cross-linking, thus increasing char formation as well as carbon dioxide. The packing density of cellulose also affects the extent of levoglucosan formation. Lowered crystallinity in cotton by either mercerization or liquid ammonia leads to a higher yield of levoglucosan formation (Shafizadeh, 1985). Mono- and difunctional radicals are formed by the cleavage of glucoside linkages, and these radicals in turn give rise to volatile products and levoglucosan.

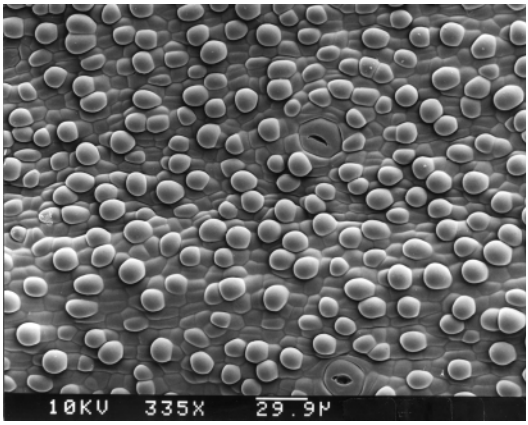
1.3 Fiber development

1.3.1 Fiber structures during cell growth

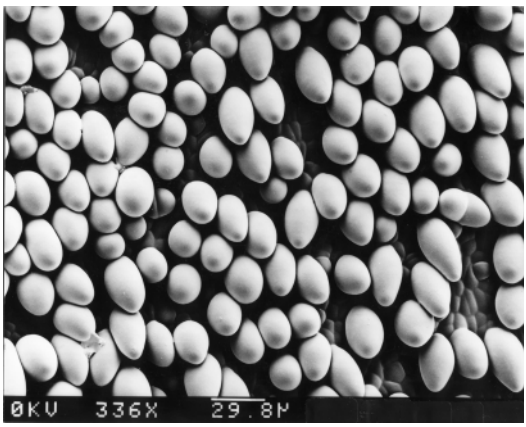
The structure of cotton fibers can be viewed along the fiber axis and across the fiber section. Current understanding of cotton fiber structure has been mainly from investigation of the matured fibers in their dried state. Although the biochemical nature of cotton cell structure, particularly during early cell growth, has been extensively studied, the development macrostructure of the main constituent of the fiber, cellulose, is not as well understood.

Cotton fibers are the largest (longest) single cells in nature. The fibers are single-celled outgrowths from individual epidermal cells on the outer integument of the ovules in the cotton fruit. About one in four epidermal cells differentiates into fiber cells beginning at one day before to two days after anthesis (flowering) (Graves and Stewart, 1988). Four overlapping but distinct stages are involved in cotton fiber development: initiation, elongation, secondary-wall thickening, and maturation (Naithani *et al.*, 1982). The initiation of fibers begins from the epidermal cells on the ovule surface (Fig. 1.1(a)) followed by the elongation and formation of the primary cell wall. Elongation of the primordial fiber cells starts on the day of anthesis by spherical expansion above the ovular surface (Figs 1.1(b) and 1.1(c)) and continues for 16 to 20 days. The cell elongation orients initially against the micropylar end of the ovule, then become spiral after two to three days. The primary cell walls continue to elongate until reaching the final fiber lengths of 22 to 35 mm in about 20 to 25 days. This primary cell wall is very thin (0.2 to 0.4 μm) and extensible.

Secondary wall synthesis starts around 15 to 22 days past anthesis (dpa) and continues for 30 to 40 days. The cellulose formation is about 130 ng/mm



(a)



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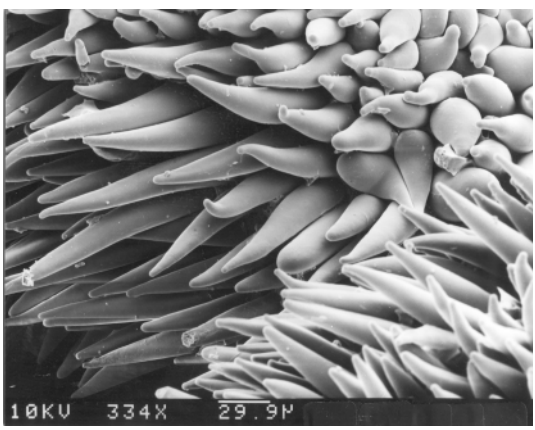


(c)

1.1 Scanning electron micrographs of seed with the initiation (a) 0 dpa of fibers and the beginning of elongation (b) 1 dpa; (c) 2 dpa. Provided by J. Jernstedt, University of California, Davis.

during secondary wall formation as compared to 2 ng/mm during primary wall development (Meinert and Delmer, 1977). Fiber maturation is evident by desiccation of the fiber and collapse of the cylindrical cell into a flattened, twisted ribbon beginning 45 to 60 dpa. Most cotton fibers have aspect ratios, or length-to-width ratios, in the 1,000 to 3,000 range. However, some matured fibers can reach up to 4,000 times in length of their diameters. Both fiber length and secondary wall thickness are increased with higher potassium supply during growth (Cassman *et al.*, 1990).

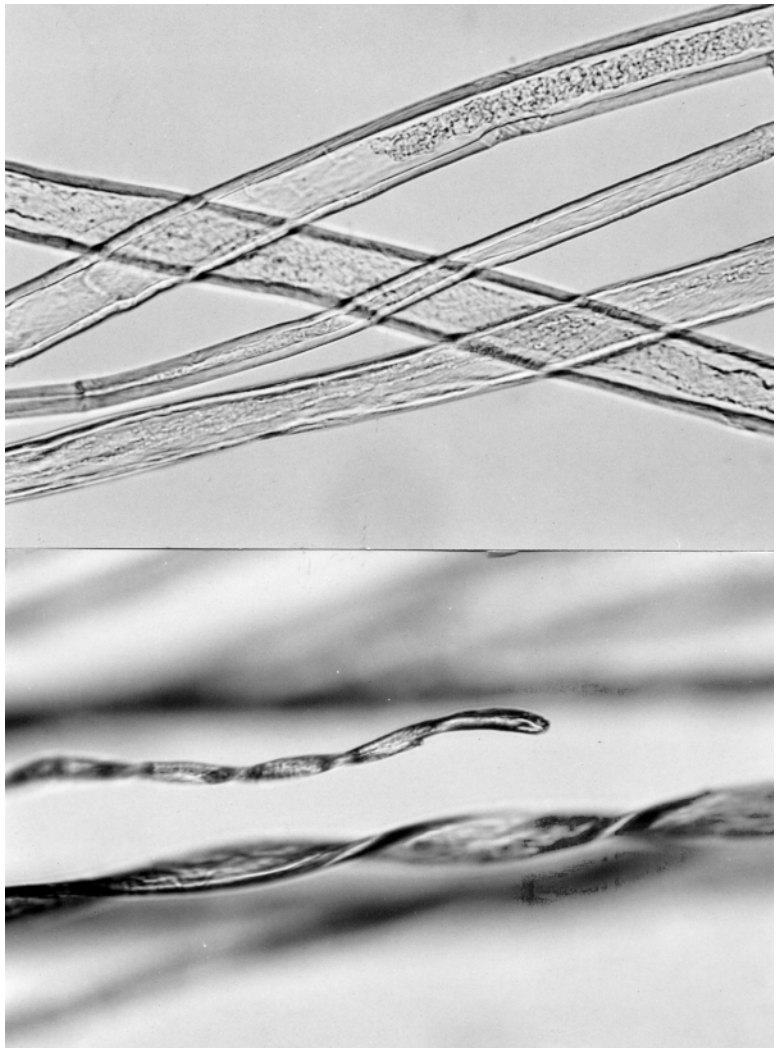
1.3.2 Desiccation and dehydration

The fully hydrated cylindrical fibers are cylindrical under light microscopy (Fig. 1.2(a)). Drying of the fibers involves the removal of fluids from the lumens and inter-molecular water in the cellulose. The fluid loss from the lumens causes the cylindrical fibers to collapse to form twists or convolutions (Fig. 1.2(b)). The loss of intermolecular water allows the cellulose chains to come closer together and form intermolecular hydrogen-bonds. Prior to ball dehiscence and fiber desiccation, matured cotton fibers have been shown to exhibit high intrinsic mobility and porosity in their structure (Ingram *et al.*, 1974). The accessibility of water in fiber structure in the hydrated state is higher than after desiccation.

The collapse of cell walls and hydrogen bond formation cause irreversible morphological changes including structural heterogeneity, decreasing porosity, and sorption capacity in the fibers (Stone and Scallan, 1965). These changes increase molecular strains and reduce chain mobility, and may have an influence on properties essential to strength and dyeing/finishing processes. As these irreversible changes determine the utility of fibers, understanding of the structural changes from desiccation is essential to fiber quality research.

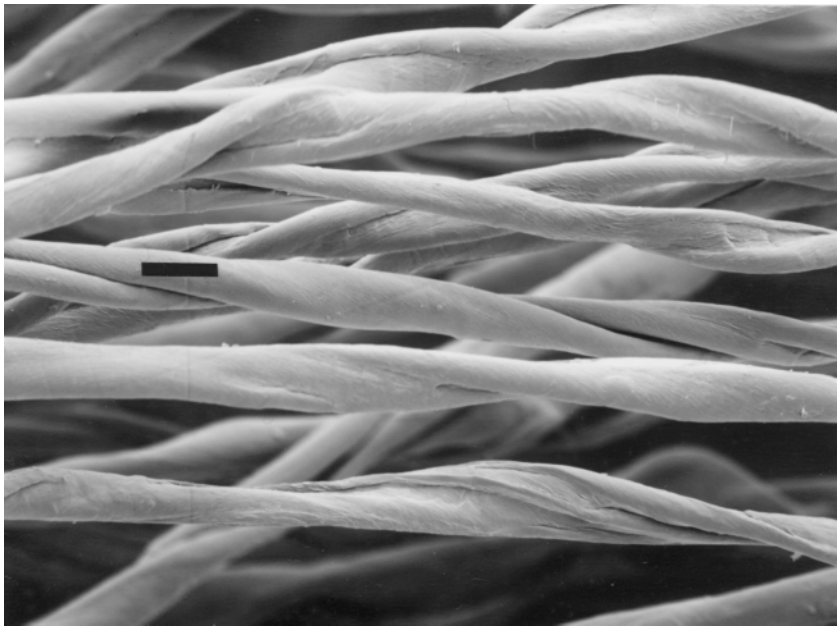
The matured fibers dry into flat twisted ribbon forms (Fig. 1.3). The twist or convolution directions reverse frequently along the fibers. The number of twists in cotton fibers varies between 3.9 and 6.5 per mm (Warwicker *et al.*, 1966) and the spiral reversal changes one to three times per mm length (Rebenfeld, 1977). The convolution angle has been shown to be variety dependent (Peterlin and Ingram, 1970). Differences in reversal frequency have been observed among different species and varieties of cotton, between lint and fuzz on the same ovule, and along a single fiber (Balls, 1928).

The reversals in cotton fibers are related to the orientation of the secondary wall microfibrils whose organization is critically important to fiber strength. The orientation angles and shifts of microfibrils along the fiber axis change with cell-development stages and have been related to the cellular organization of the cortical microtubule during cotton fiber development (Seagull, 1986, 1992; Yatsu and Jacks, 1981). At the beginning of fiber development, i.e., 1 dpa, cortical microtubules have a random orientation. During the transition



1.2 Light micrographs of fully hydrated fibers (top) and dried fibers (bottom).

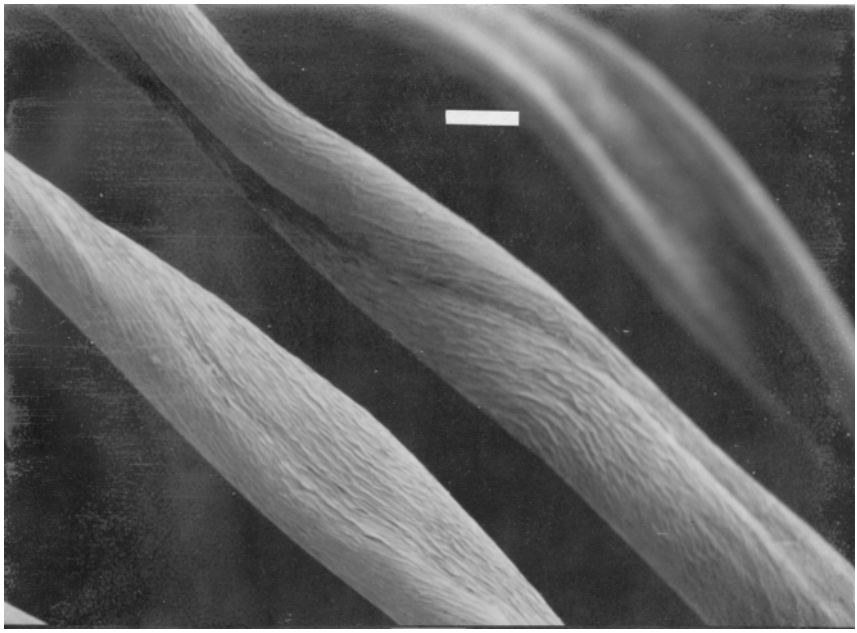
between initiation and elongation, i.e., 2–3 dpa, a shallow pitched helical orientation of 75–80° is developed. Such angles, which are nearly perpendicular to the fiber axis, are maintained throughout primary wall synthesis. An abrupt shift in orientation to a steeply pitched helical pattern occurs between the primary and secondary wall synthesis. As secondary cell walls thicken, the angles reduce further. In early secondary wall synthesis, there is a four-fold increase in the number of microtubules. The fibrillar orientation reverses along the fiber periodically. The mechanism which regulates the synchronized shifts in microtubule orientation is not yet understood.



1.3 Scanning electron micrographs of mature fibers (bar=18.9).

The concomitant shifts in orientations of microtubules and microfibrils indicate a strong relationship between the two. However, differing degrees of variability between these two populations suggest other factors may modify the order imparted by the microtubules. During secondary wall synthesis, microfibrils exhibit variability in orientation or undulations. Inter-fibril hydrogen bonding and differential rigidity of microtubules and microfibrils have been suggested as possible factors influencing the final microfibril organization.

The spiral fibrillar structure can be observed on the surface of mature fibers underneath the primary wall (Fig. 1.4). Parallel ridges and grooves are seen at 20–30° angles to the fiber axis. Scouring exposes the fibrils of the primary and secondary walls. Neither soaking in water nor slack mercerization removes surface roughness (deGruy *et al.*, 1973; Muller and Rollins, 1972; Tripp *et al.*, 1957). However, stretching a swollen fiber can smooth the surface and make residual ridges more parallel to the fiber axis secondary walls. The less developed cotton fibers have thinner secondary cell walls and contain less cellulose. They appear flattened with little or no twist as seen in the SEM of Fig. 1.5. These fibers tend to become entangled into matted fibrous clusters, called neps, causing problems in mechanical processing and dyeing of cotton products. They cannot be dyed to shades as dark as mature fibers. Their flat surfaces also reflect more light and give them a lighter color. Immature fibers can cause white specks, the light spots on a dyed

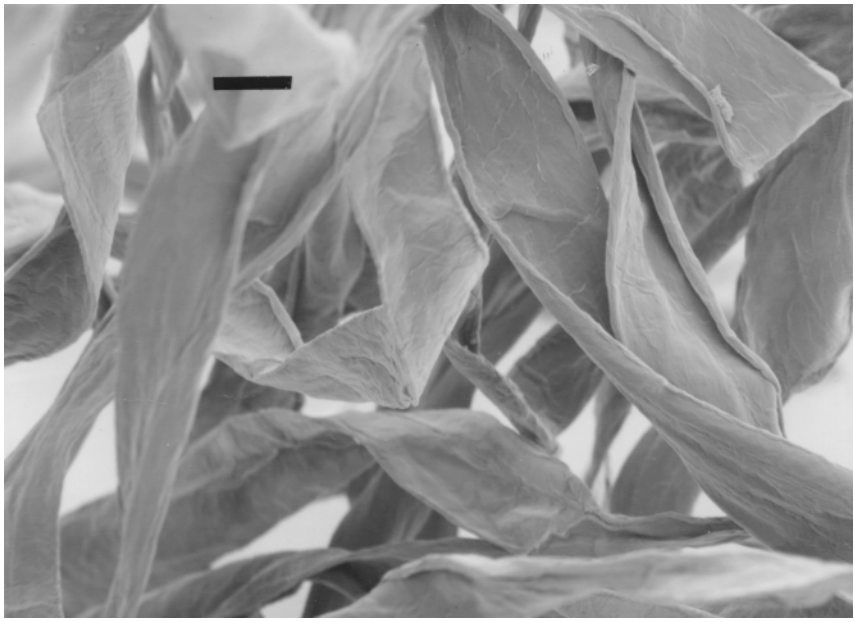


1.4 The cellulose fibrils orient at an angle to the fiber axis and spiral around the concentric layers. The fibril angle reverses every so often. The fibrillar structure and the reversal of outer most cellulose layer can be observed on the fiber surface through the primary wall on these 34-dpa fibers (bar = 10.3).

fabric that either have an absence of color or appear lighter than the rest of the fabric.

The molecular packing densities along the fiber, particularly near the spiral reversals, are believed to vary. The packing of fibrils at the reversals is denser (Patel *et al*., 1990). The adjacent fibrillar structures are less densely packed and often have different dimensions (fineness). Therefore, these adjacent regions are believed to be the weak points on the fiber rather than the reversals themselves. It has also been suggested that the reversals may be growth points in the fibers (Raes *et al*., 1968). However, this has not been confirmed by others.

The dried cotton fibers have a bean-shaped cross-section. The bilateral structure is thought to originate from the asymmetry of mechanical forces in the fibers during drying. Heterogeneity of molecular packing in cotton fibers has been demonstrated by ultramicrotomy, histochemical staining, and accessibility to reagents (Naithani *et al*., 1982; Basra and Malik, 1984; Meinert and Delmer, 1977). The two highly curved ends of the bean-shaped cross-section have the highest molecular packing density and least accessibility to reagents. The structure of the convex part is less dense and more accessible.



1.5 Immature fibers have much thinner secondary cells or less cellulose. Collapse of the immature fibers leads to flattening with little or no twist as seen in this 21-dpa fiber (bar = 17.4).

The concave section of the cross-section is the most accessible and most reactive portion of the fibers. The higher density and parallel membranes in the curved extremes and convex parts are thought to result from radial compressive forces, whereas the concave portion of the cross-section is subject to tangential compressive forces. The sections between the curved ends and concave parts are denoted as neutral zones which are by far the most accessible. These differential structures in the cotton cross-section have been confirmed by enzymatic attacks (Kassenback, 1970).

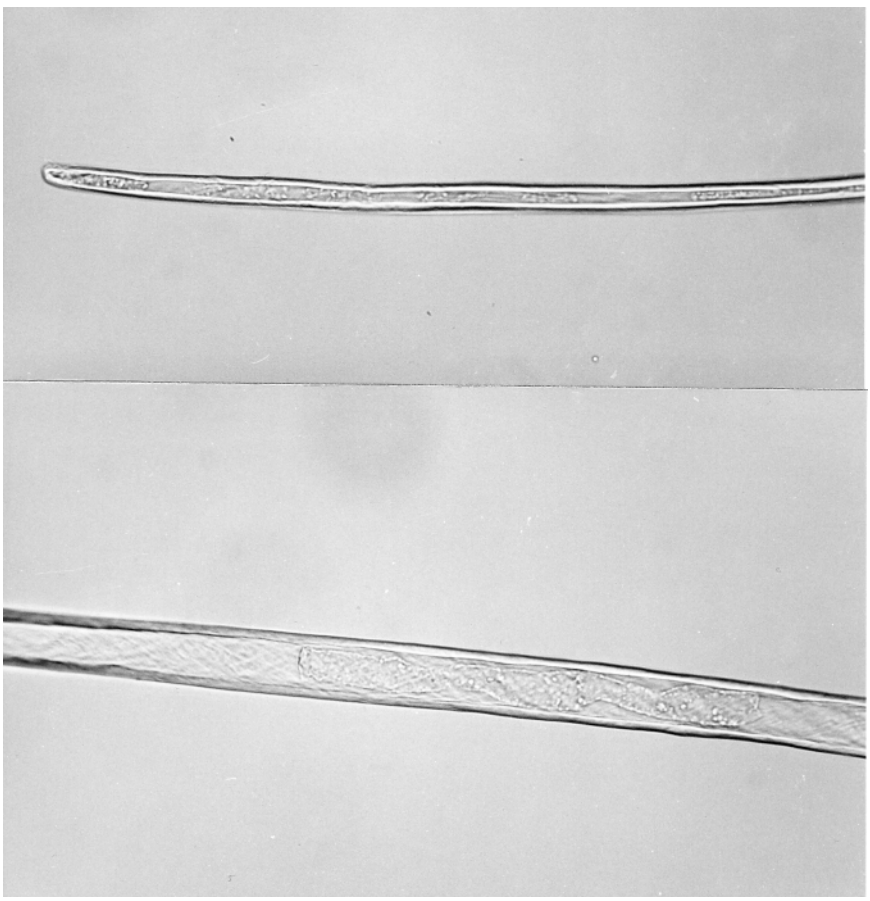
1.3.3 Structural variations

Cotton seed fibers include the long lint and short fuzz fibers, both epidermal hairs on the cotton ovules or seeds. Fuzz fibers are initiated 4 to 10 dpa in successive waves of initiation (Beasley, 1977). Fiber quality traits, i.e, length, fineness, and strength, are determined by both the genetic and environmental variables. Both fiber fineness and fiber length are genetic characteristics. Fiber fineness has been shown to be developed at the base of the fibers by about 2 dpa (Fryxell, 1963; Kulshreshtha *et al.*, 1973a). Fiber length is determined during the elongation stage, i.e., during the first 20 to 25 dpa.

Fibers on a single ovule initiate and mature at different times (Stewart, 1975) and boll development on a single plant depends on the positions on

plants (Jenkins *et al*., 1990). On an ovule, fibers initiate first near the chalazal end, then down toward the micropylar end. Seeds located near the middle of a locule have the longest fibers whereas those near the basal location have thickest secondary cell wall (Davidonis and Hinojosa, 1994). On a single ovule, fibers in the micropylar region have thicker cell walls than those in the chalazal end. Bolls located closer to the main stem are favored in the allocation of nutrients (Jenkins *et al*., 1990). Temperatures lower than optimal reduce both fiber length and cell wall thickness (Gibson, 1986; Haigler *et al*., 1991). Seasonal effects of secondary wall development have been demonstrated on summer-grown versus autumn-grown fibers (Goynes *et al*., 1995).

It has been shown that fibers taper toward thinner tip ends. Using light microscopy, we have observed that about 15% of fiber length from the tip has smaller dimensions on fully developed SJ-2 fibers (Fig. 1.6). As much as



1.6 Light microscopy of a hydrated fiber showing thinner tip than the rest of the fiber.

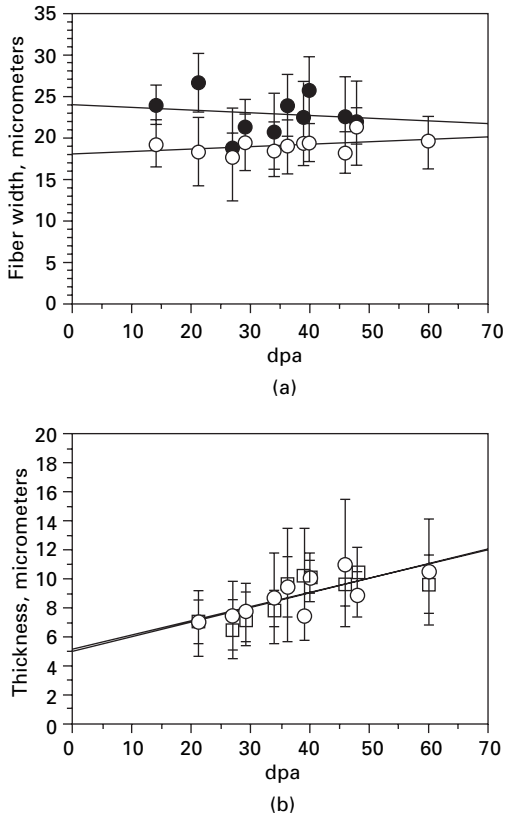
one-third of fiber length has been reported on Delta 61 fibers (Boylston *et al.*, 1993). Fibers shrink in proportion to the amount of cellulose present in the cell wall. The perimeter of less mature fibers (thinner cell wall) is larger than that of a more mature (thicker cell wall) fiber. The thinner cell wall is found nearer the fiber tip than the rest of the fiber. Fiber fineness directly determines yarn fineness. Although as few as 30 fibers can be spun into yarns in ring spinning, approximately 100 fibers in the yarn cross-section are usually the lower limit. Therefore, reduction in fiber fineness is the only way to achieve fine yarns within the limit of spinning processes.

Fiber maturity is a growth characteristic. The definition of fiber maturity is the proportion of cotton cell wall thickness compared to the maximum wall thickness when growth is completed. Therefore, maturity represents the development of the secondary cell wall and the maturity level can be complicated by both developmental and environmental factors.

1.3.4 Twist and convolution

The formation of twists or convolution occurs when the fully hydrated cylindrical fibers collapse from the loss of fluids and drying upon maturation and boll opening or as previously shown during light microscopy observation (Fig. 1.2). On developing SJ-2 fibers, typical twists were observed on 28-dpa fibers whereas 21 dpa fibers tend to roll and fold onto themselves (Fig. 1.5). The lateral dimensions of convoluted fibers are characterized by their ribbon or 'fiber width' (widest portion) and 'twist thickness' (thinnest portion). The fiber widths decrease from drying (Fig. 1.7(a)). The twist thicknesses increase with fiber development, from approximately 6.5 μm at 21 dpa to 10.5 μm at 40 dpa and maturity (Fig. 1.7(b)). The twist frequency or the lengths between twists have been found to be highly irregular along an individual fiber as well as among fibers. The lengths between twists have been grouped into 'short' and 'long'. At 21 dpa, the average short and long lengths between twists are 110 μm and 240 μm, respectively. As fibers developed, long lengths reduce by nearly one-half to 130 μm. Short twist lengths, on the other hand, show only a slight decrease with fiber development to about 90 μm. Upon drying, fiber widths between the long twists are reduced slightly but not significantly than those of the hydrated fibers. Fiber widths between the long twists are slightly higher than those between the short twists, but these differences diminish with fiber development.

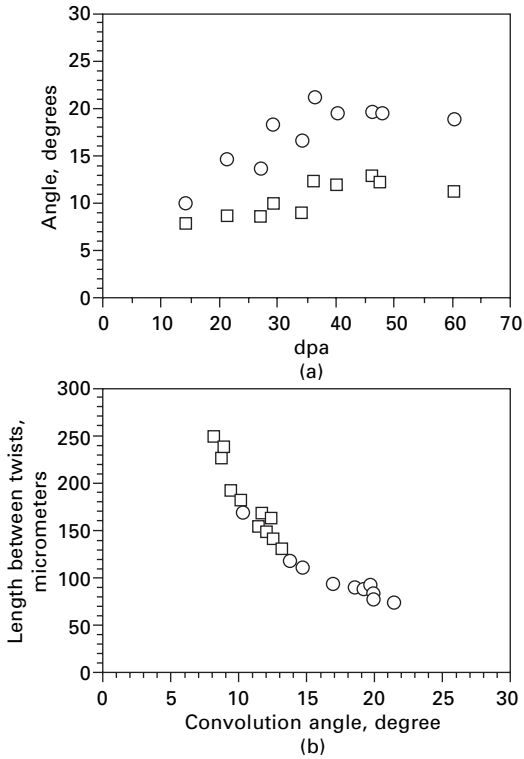
The twist thicknesses increase slightly between 20 and 36 dpa and then become level, but the twist thicknesses remain similar between the long and short twists. Using the average W and L values, the convolution angle (θ) of the twist is calculated as $\theta = \tan^{-1}(2W/L)$. A distinct increasing trend with development to about 40 dpa has been observed on the convolution angles of the long twists whereas only a slight increase is observed on the short twists



1.7 Fiber dimensions at varying developmental stages of *G. hirsutum* (SJ-2), (a) Fiber width: ● hydrated, y = 24.0 – 0.034x, r = 0.16; ○ dried short twists, y = 18.1 – 0.03x, r = 0.41. (b) Twist thickness: □ long twists, y = 5.0 + 0.10x, r = 0.77, ○ short twists, y = 5.1 – 0.10x, r = 0.78.

during the same period (Fig. 1.8a). This trend is expected from the fiber width and twist length data. The lengths between twists lowered with increasing convolution angles (Fig. 1.8(b)). The insignificant changes in convolution angles after 36 dpa indicate insignificant changes in both the twist length and width, coinciding with the little change in the linear density or cell wall mass. These findings show that twist characteristics are closely associated with secondary cell wall thickness and thus are excellent indicators of fiber maturity within a given variety of cotton.

As the spiral reversals occur less frequently (1 to 3 times per mm as reported by Rebenfeld, 1977) than the convolution (3.9 to 6.5 twists per mm by Warwicker *et al.*, 1966), the lateral alignment of the fibrillar reversals in the concentric cellulose layers and the ultimate twists in the dried fibers appear to be related. Twists are formed from cell collapsing and the numbers of twists increase with fiber maturity or with increasing secondary cell wall



1.8 Convolution or twist characteristics of developing *G. hirsutum* (SJ-2) fibers (□ long, ○ short): (a) angles; (b) relationship between lengths and angles.

thickness. Upon drying, lateral dimensions of the fibers reduce. The spiral reversals of the cellulose fibrils are where buckling most likely occurs in each layer. As secondary cell wall thickens, the probability of the reversals in the concentric layers overlapping at a given point across the fiber increases, leading to twists. It appears that when a threshold level of overlapped reversals is reached, stress from buckling leads to twist formation. Whether the twist or the span between two twists is where the reversals overlapped is unclear. How the reversals in the concentric layers related to the varying packing density or accessible regions in the fiber cross-section is also an important question.

1.4 Fiber strength

1.4.1 Single fiber strength

The strength of cotton fibers is attributed to the rigidity of the cellulosic chains, the highly fibrillar and crystalline structure, and the extensive

intermolecular and intramolecular hydrogen-bonding. Varietal link to fiber strength has been well documented by bundle strength, such as that generated by the Stelometer and the high volume instrument (HVI) in recent years. Much less is known about the strength of developing cotton fibers. Kulshreshtha *et al.* (1973a) have shown that the Stelometer bundle strength increases gradually with fiber growth between 30 and 70 dpa. The youngest age, in that case, is about two weeks into, or about half way through, the secondary cell wall development. However, bundle strength has been shown not to be sensitive to strength variability.

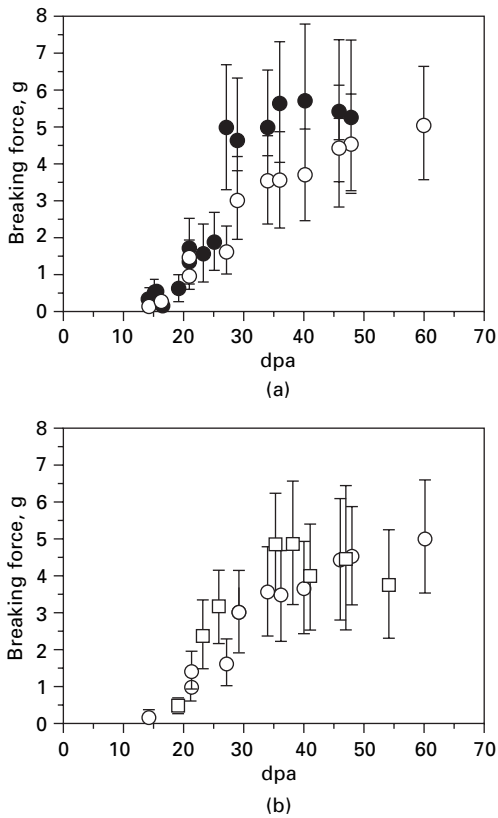
How fiber strength is developed during growth and is related with genotypical traits has been confirmed by single fiber tensile measurements. The major challenges in single fiber measurements are the selection and the quantity of fibers to represent each specific population. Single fiber tensile measurements using a standard tensile tester and fiber sampling protocols were evaluated in an exploratory study (Hsieh, 1994) and subsequent extensive data collection (Hsieh *et al.*, 1995).

Tensile measurements of both hydrated (as early as 15 dpa) and dried fibers were made using either an Instron tensile tester (1122 TM) equipped with standard pneumatic and rubber-faced grips or a Mantis single fiber tester. A 3.2 mm-gauge length was used with both methods. A 50-mm/min strain rate was employed on the Instron whereas the strain rate on the Mantis was 60 mm/min. All measurements were performed at a constant temperature of 70 °F and a 65% relative humidity. The much higher rate of measurement on the Mantis instrument has enabled collections of much larger number of single fiber strength data (Hsieh *et al.*, 1995, 1997; Hsieh 1999; Hsieh and Wang 2000; Hu and Hsieh, 1996, 1997a, 1998; Liu *et al.*, 2001, 2005). As a Mantis single fiber tensile instrument is not readily available but is employed in most work cited in the following sections, it is worth mentioning the difference from the Instron measurements. The breaking forces measured by the Mantis instrument appear to be slightly higher than those by the Instron whereas the opposite is observed with the breaking elongation values (Hsieh *et al.*, 1997). On the Mantis, fibers are positioned manually. The instrument automatically straightens, clamps down, and exerts a preload on individual fibers. Single fiber measurements conducted on the Instron tensile instrument required extensive handling to prepare each fiber in a paper holder (Hsieh *et al.*, 1995). The extra fiber handling on the Instron is believed to be the cause of the lower strength. The absence of preload when preparing fibers for measurement using the Instron explains the higher breaking elongation values.

A standardized fiber selection and sampling approach for developing cotton has been established. It starts with tagging the flowers on the day of flowering (anthesis). Green bolls aged 14 days post anthesis (dpa) to 50 dpa and opened bolls can be sampled from first-position (closest to the main stem) between the fourth and the twelfth fruiting branches. Sources of fiber development

variations can be minimized by using the fibers from the medial section of the ovules and the middle ovules from each boll. Furthermore, the middle sections of fibers are measured as they are stronger than the fiber sections closer to the basal or the tip ends at all stages of fiber development. The verification of this approach is briefly summarized in the following section.

The forces required to break hydrated and dried single Maxxa fibers increase with fiber development (Fig. 1.9(a)), with hydrated fibers being stronger. The breaking elongation values are higher for the dried fibers, leading to similar work to break between the hydrated and dried fibers. The breaking forces of the dried fibers appear to increase at a higher rate between 20 and 30 dpa than in the later stages. The decreasing forces and increasing strain at break from the hydrated state to the dry state may be explained by the increased convolution angles resulting from cell collapsing and dehydration. The effects between branches from branch four to twelve on single fiber strength are negligible (Fig. 1.9(b)).



1.9 Single fiber breaking forces of developing *G. hirsutum* (SJ-2) cotton: (a) ● hydrated, ○ dried; (b) ○ random first-boll position from 6 plants, □ first-boll position from single plant.

The cotton ovules or seeds are shaped like inverted teardrops, with the round and pointed ends being the chalazal and micropylar regions of the seeds, respectively. For *G. hirsutum* (Maxxa), the medial fibers and the micropylar fibers have similar breaking force and fiber widths (Table 1.1) (Hsieh *et al*., 1997). Fibers from the chalazal ends were narrowest and had lower linear densities whereas those from the micropylar end have higher linear densities, indicating thicker secondary cell walls. Therefore, the medial fibers have the higher tenacities, while those from the chalazal and micropylar ends being lower and similar. Similar observations have been made on Texas Marker 1, another *G. hirsutum* variety and Pima S7 (*G. barbadense*) as well (Hsieh *et al*., 2000). These findings confirmed the medial seed region fiber selection.

Fibers from five varieties representing four cultivated cotton species (*G. herbeceum*, *G. arboreum, G. hirsutum, G. barbadense*) were studied for effects of seed position on fiber strength (Liu *et al*., 2001). With the exception of *G. arboreum*, breaking forces, toughness and linear density are highly dependent on the seed positions in the locule, and the dependence is especially high for *G. herbeceum* and *G. barbadense*. Fibers from seeds located closer to the main stem have higher breaking forces and linear density, indicating their association to the distribution of nutrition resources. These findings confirmed that the mid-ovule fibers represent the population.

The relationships between single fiber tensile properties and fiber lengths also vary among these cotton species (Liu *et al*., 2001). The breaking forces and tenacities are independent of fiber lengths for *G. barbadense*, whereas positive fiber-length dependence is observed with *G. herbaceum*, *G. arboreum*

Table 1.1 Properties of plant-matured fibers* from three seed locations of *G. hirsutum* (Maxxa)

Properties/seed location	Chalazal	Medial	Micropylar
Force to break (g)	3.13	5.47	6.16
CV (%)	24	19	13
Breaking elongation(%)	7.4	7.6	7.6
CV (%)	16	10	10
Work to break (μJ)	4.2	6.9	7.5
CV (%)	33	23	15
Linear density (tex)	0.132	0.197	0.259
CV (%)	13	10	9
Tenacity (g/tex)	23.7	27.8	23.9
CV (%)	21	16	14
Ribbon width (μm)	13.9	15.6	16.2
CV (%)	2	3	4

* Tensile properties and ribbon widths were from a total of 750 measurements on fibers sampled from 15 ovules of five first-position plant-matured bolls. Linear density data were calculated from 45 measurements of 100-fiber bundles, nine each, from the same five bolls.

and a negative trend is found with the Maxxa variety of *G. hirsutum*. For *G. herbaceum*, *G. arboreum*, longer fibers have higher breaking forces whereas the opposite is found in Maxxa. The single fiber breaking elongation decreases with increasing fiber lengths for all except for *G. barbadense*. Overall variations of single fiber tensile properties are associated more strongly with the seed positions in the locule than with the fiber lengths. Among these five cultivars, the single fiber strength of Pima S7 is highest, with *G. hirsutum* varieties being second, *G. herbaceum* the third and *G. arboreum* the lowest (Table 1.2). The cell wall mass as indicated by the linear density (LD) follows the same order, except that *G. herbaceum* is the highest due mostly to its high fiber widths.

The distributions of breaking forces and elongation of single fibers from these five cultivated cotton varieties show significantly different range and distribution patterns and appear to be highly dependent on genotypes (Liu *et al.*, 2005). Within each cultivar, fibers of varying lengths have similar distributions in their breaking forces and elongation. This lack of relationship with fiber length suggests that these fiber tensile properties may be independent of length development, i.e., during elongation of primary cell wall through the early state of secondary cell wall synthesis. Single fiber breaking force and elongation were positively correlated ($r = 0.259$ to 0.443) for all five varieties, with Pima having the highest correlation coefficient.

The mass of seed fibers (fiber and seed) and fibers as in linear density have both shown to be reliable indicators for the stage of fiber development. The seed fiber weights increase linearly with fiber development. With developing fibers, the strength and seed fiber weight relationship is similar to that of the strength-dpa relationship. Therefore, it is quite conceivable that fiber strength may be projected from seed fiber weight throughout the secondary cell wall synthesis stage when such strength-seed fiber weight correlations have been established. The linear densities of the developing fibers also increase with fiber development, most significantly during the first 10–14 days of secondary cell wall synthesis. The linear density to age relationship varies with the varieties, indicating the rate of cellulose synthesis and how single fibers gain strength during the early part of secondary cell develop to be variety dependent.

Generally, the forces to break single fibers increased significantly during the fourth week of fiber development. Beyond 30 dpa, neither linear densities nor single fiber tenacities showed any changes. Data on *G. hirsutum* varieties have shown that fibers at about 21–24 dpa exhibit significant strength. This is at the onset of the secondary wall formation where fiber elongation is nearly completed. Using estimated linear densities for SJ-2 fibers at 14 to 16 dpa, the breaking tenacities of dried fibers are estimated to be 21.5 and 31.3 g/tex, respectively (Hsieh *et al.*, 1995). The primary cell wall appears to contribute toward two-thirds or more of the fiber strength. These fiber strength

Table 1.2 Tenacity (gf/tex) and linear density (mtex) of fibers from middle seeds in locule*

	G. herbaceum African-51		*G. arboreum* Asian 163		*G. hirsutum* Maxxa		TM-1		*G. barbadense* Pima S7	
	tenacity	LD	tenacity	LD	tenacity	LD	tenacity	LD	tenacity	LD
Mean	44.6	213	37.3	274	41.2	180	39.1	185	55.9	150
CV (%)	7.3	11.9	5.7	3.2	2.8	5.7	3.1	4.0	6.2	7.4
r	0.77	0.99†	–0.70	0.82	0.64	0.96†	0.43	0.89†	0.80	0.95†

* Twenty first-position plant-mature bolls from ten plants of each variety were harvested five to seven days after boll opening. Three bolls with weights closest to the average boll weight (BW) of the 20 collected were used.

† Denotes different correlation coefficients of the linear regression between fiber tensile properties and seed positions in locule at a 5% significance level.

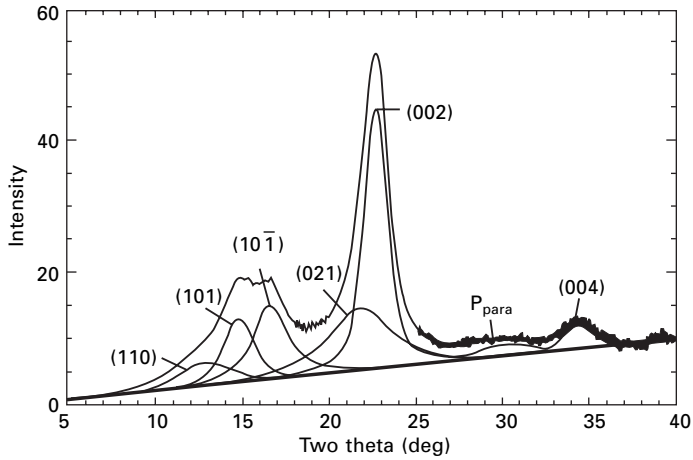
estimations are consistent with the report on 14 dpa *G. hirsutum* Delta Pine 61 fibers whose breaking tenacity was slightly more than half of the fibers that were 49 dpa (Hebert, 1993). Both the breaking forces and fiber mass or linear densities continue to increase throughout the first 36–40 days of fiber development. Therefore, the secondary wall thickening continues to contribute to the single fiber breaking force. However, the breaking tenacities of single fibers appear to reach the maximal level when the fibers are about 21 to 24 dpa.

1.4.2 Crystalline structure of cellulose

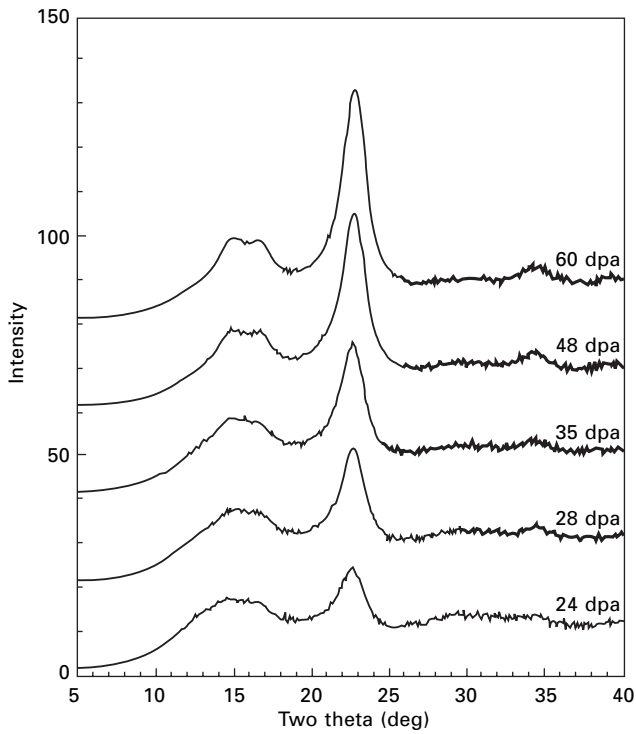
The fine structure of cotton cellulose has been most widely investigated by wide-angle X-ray diffraction, a well-developed and powerful tool for discerning structural organization of polymer solids. The structural studies of cotton cellulose have been extensively reported, mainly on field grown matured cotton and those treated in urea and sodium hydroxide (Khalifa *et al.*, 1991). The formation of primary and secondary cell walls in cotton fibers is distinct and of relatively long duration, allowing studies of crystalline structure at specific stages of fiber development. The crystalline structure of developing *G. hirsutum* cotton fibers (Hu and Hsieh, 1996, 1997a; Hsieh *et al.*, 1997) has been detailed using wide-angle X-ray diffraction and a multi-peak resolution method previously developed (Hindeleh *et al.*, 1980). In this method, the total scatter was resolved into peaks over a non-crystalline scatter background, where crystallinity is the ratio of the summation of all resolved peaks to the total scatter as detailed in our previous paper (Hu and Hsieh, 1996). Crystallite dimensions normal to the hkl planes were calculated following peak broadening corrections caused by structural broadening ($\delta\beta$) and instrumental broadening. The apparent crystallite sizes of the 101, $10\bar{1}$ and 002 reflection planes was based on the Sherrer equation.

A typically resolved X-ray diffraction spectrum of 60-dap Maxxa cotton fibers is illustrated in Fig. 1.10. The multiple peak resolution method yields seven peaks from the WAXD spectrum collected between 5° and 40°. The four peaks located near 2θ angles of 14.7°, 16.6°, 22.7° and 34.4° are characteristic of the 101, $10\bar{1}$, 002 and 040 reflections of cellulose I, respectively, and are used for structural analysis and comparison.

The cellulose **I** crystalline structure is clearly evident near the onset of secondary cell wall formation, or 21 dpa (Fig. 1.11). The cellulose **I** crystalline structure has been confirmed on dried SJ-2 and Maxxa cotton fibers at varying developmental stages and remains unchanged during secondary cell wall biosynthesis and at maturity (Hsieh *et al.*, 1997). The degree of crystallinity doubled from the beginning to the end of the secondary cell wall formation, i.e., from about 30% at 21 dpa to 60% at 60 dpa. The most significant increase in crystallinity, i.e., from 30% to 55%, is observed between 21 and



1.10 Typical wide-angle X-ray diffraction pattern of matured cotton fibers.



1.11 Crystallite dimensions of developing *G. hirsutum* (Maxxa) cotton fibers.

34 dpa. The extensive data on several Acala varieties grown under well-controlled green-house conditions show that significant crystallinity is attained during the first half of the secondary cell wall development. One early report also showed increased crystallinity with fiber development of a field-grown Indian cotton variety (Kulshreshtha *et al.*, 1973b). The stage studied was in the later stages of secondary cell wall development (35 to 65 dpa).

Both *G. barbedense* and *G. hirsutum* series of developing cotton fibers show increased overall crystallinity and apparent crystallite sizes with fiber development (Table 1.3) (Hsieh *et al.*, 2000). The most significant increases in L_{101}, $L_{10\bar{1}}$, and crystallinity occur between 20 dpa and 35 dpa, corresponding to the first two weeks of cellulose synthesis or the fourth and fifth weeks of overall fiber development. Fiber development beyond five weeks does not contribute to any change in crystallite dimensions nor cyrstallinity. This is consistent with the leveling of tenacities at the later stage of fiber development. These are consistent with others' findings that the lateral apparent crystallite sizes and their orientation increase during the cellulose biosynthesis (Nelson and Mares, 1965).

Structural studies of native celluloses have also included the use of high-resolution CP/MAS ^{13}C NMR (Atalla and VanderHart, 1984; VanderHart and Atalla, 1984, 1987). Native celluloses have been classified into two families: that of algal-bacterial cellulose, where the cellulose is rich in the I_α phase, and that of cotton-ramie-wood cellulose, where the I_β phase is dominant. Infra-red spectroscopy is another solid-state technique that can be used to distinguish the structures of these two families of celluloses (Michell, 1990). The Fourier transfer infra-red spectroscopy (FTIR), another structural characterization tool, was employed to elucidate the crystalline structure of a series of highly crystalline celluloses (Sugiyama *et al.*, 1991). The absorption

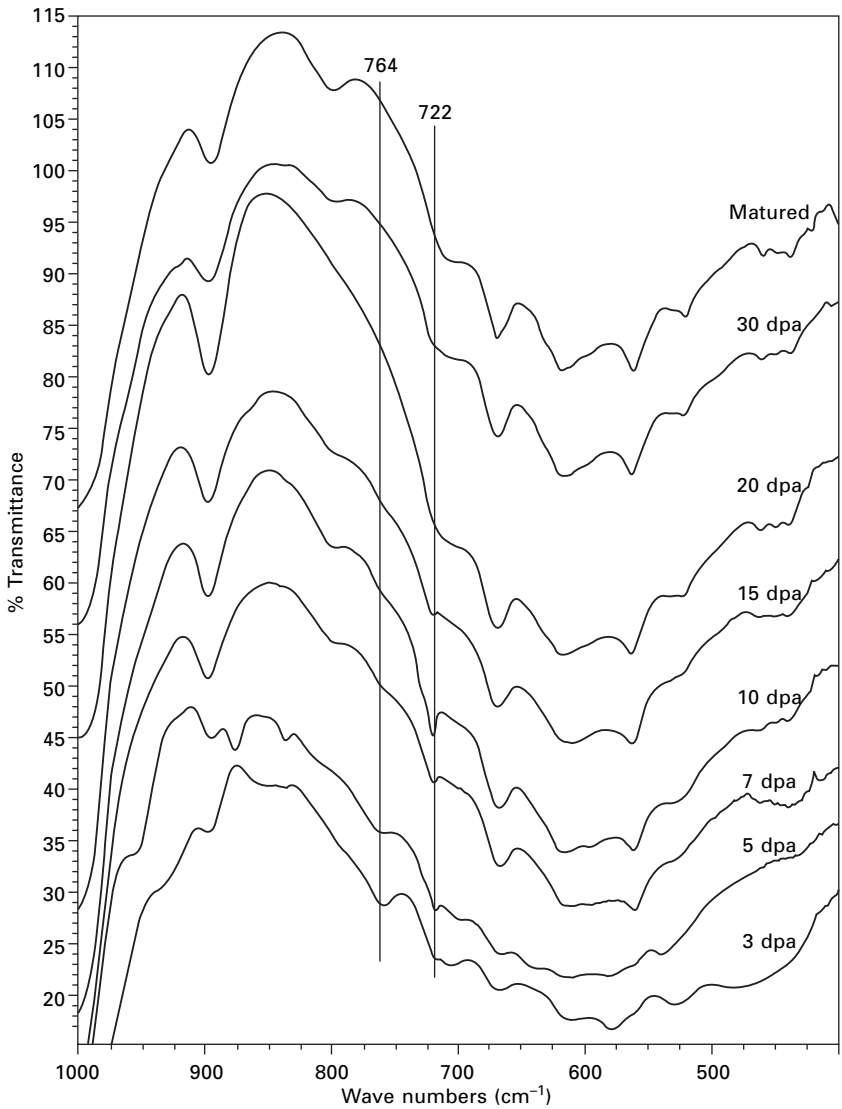
Table 1.3 Crystallite size (L, angstrom) and crystallinity (X, %) of developing *G. hirsutum* (Texas Marker 1) and *G. barbedense* (Pima S7) cotton fibers*

	20 dpa	28 dpa	35 dpa	42 dpa	Mature
G. hirsutum (Texas Marker 1)					
L_{101}	22.2	27.2	37.8	40.1	37.7
$L_{10\bar{1}}$	22.3	27.1	36.0	39.5	37.5
L_{002}	41.3	41.2	41.9	44.4	43.6
X	23	37	52	54	46
G. barbedense (Pima S7)					
L_{101}	26.9	35.2	43.6	43.9	45.7
$L_{10\bar{1}}$	22.1	30.9	34.8	34.6	35.7
L_{002}	37.7	40.7	41.4	41.2	42.3
X	23	48	55	56	60

* Fibers for each stage of development were sampled from five first-position bolls randomly sampled from nine plants.

bands at 3240 and 750 cm^{-1} corresponding to the I_α phase and those near 3270 cm^{-1} and 710 cm^{-1} corresponding to the I_β phase were reported.

The FTIR spectra of developing cotton fibers exhibit absorption bands at 764 cm^{-1} and 722 cm^{-1}, characteristic of I_α and I_β phases of the cellulose crystalline structure, respectively (Fig. 1.12) (Hu and Hsieh, 1997b). The 764 cm^{-1} band intensity was highest in the 3-dpa fibers, indicating rich I_α phase in fibers at the beginning of elongation. While the 764 cm^{-1} peak



1.12 FTIR of developing *G. hirsutum* (Maxxa) cotton fibers.

intensities decreased rapidly from 3 dpa to 10 dpa, the 722 cm^{-1} band, also observed in the spectrum of 3-dpa fibers, increased markedly. Only a trace of the 764 cm^{-1} band was observed in the spectrum of 15-dpa fibers. The FTIR spectra clearly showed that the I_α and I_β phases coexist at the beginning of fiber elongation. The I_β phase increases markedly from 3 dpa to 10 dpa and becomes predominant at the onset of the secondary wall synthesis, i.e., 15 dpa, the onset of secondary cell wall synthesis. These results indicate that the crystalline components in developing cotton fibers change from the coexistence of the I_α and I_β phases at 3 dpa to a predominantly I_β phase at 15 dpa.

The interesting questions brought by the FTIR results of developing fibers are the origin in the biphasic character and their conversion of cotton fibers. The I_α phase was previously thought to be from the built-in strains during cellulose biosynthesis whereas the I_β phase was from crystallization in an entirely strain-free environment. The strong relationship between I_β/I_α ratio and fiber elongation by our FTIR suggest that such a relationship may be related to the changes in turgor pressure during fiber elongation. Other factors, such as interactions among cellulose chains, the arrangement of Tcs (cellulose-synthesizing terminal enzyme complexes), and the affinity of other polysaccharides for cellulose, may also affect the biphasic character and their conversion, but their effects are not clearly understood at this point.

The IR spectra of 20-dpa, 30-dpa, and matured samples only showed the band at 722 cm^{-1}, while the band at 764 cm^{-1} disappeared, indicating the absence of the I_α phase during the secondary cell wall synthesis and in the matured cotton fibers. This is consistent with the common knowledge of cellulose structure from higher plants. The I_β phase becomes more dominant with increasing cellulose biosynthesis in the primary cell wall. Only the I_β phase was found in the secondary wall and matured cotton fibers. The question that remains to be answered is whether the formation of the I_α phase has stopped or the triclinic I_α phase is metastable and is later converted to the stable monoclinic I_β phase during the secondary cell wall synthesis.

The evidence is clear that cotton fibers exhibit only cellulose I crystalline structure during the entire fiber biosynthesis. Contrary to few reports, neither X-ray, solid-state NMR nor FTIR provides any evidence of other cellulose structure, i.e., II, III or IV. The primary cell walls of cotton fibers contain crystalline cellulose whose degree of crystallinity is lower than that of the secondary cell wall (Hsieh *et al.*, 1997). In contrast to solid-state NMR spectroscopy and X-ray diffraction, infra-red spectroscopic methods require much smaller quantities of materials, a particular advantage for studying cotton fibers at early stages of development where fiber mass is very limited. The studies of the I_α and I_β phases in the primary and secondary walls and their polymorph changes during cell wall synthesis help to discern the *in vivo* mechanism for cellulose biosynthesis and crystallization.

1.4.3 Strength and crystalline structure relationship

Positive relationships between bundle strength by the Stelometer and crystallinity (53% to 69%) have been reported on matured fibers from eight Egyptian cottons (Hindeleh, 1980). However, the relationships between strength and crystallinity may not be easily compared among studies. One reason is that the extents of crystallinity of matured cottons range from 50% to nearly 100% depending on the measurement techniques. The differences resulting from the methods of crystallinity determination are further complicated by the inevitable variations among cotton fibers due to a combination of varietal and environmental factors.

One intriguing question about the development of strength in cotton fibers is the structural contributing factors. Although positive relationship between the Stelometer bundle tenacities and crystallinity has been shown (Hindeleh, 1980), information on strength-crystallinity relationship on developing fibers is limited. Our work has shown positive relationships between single fiber breaking forces and overall crystallinity among developing fibers from the SJ-2 and Maxxa varieties (Hsieh *et al.*, 1997). With increasing crystallinity from 30% to 58%, the forces to break Maxxa fibers increase more than those for the SJ-2 fibers. In other words, single fiber breaking forces are higher for Maxxa fibers than SJ-2 fibers when compared at the same crystallinity. Crystallinity of the Maxxa fibers is lower than SJ-2 with the same amount of cellulose. The positive relationship between single fiber breaking force and crystallinity may be variety dependent.

In general, the overall crystallinity, apparent crystallite sizes, and single fiber breaking forces of fibers increase with fiber development (Hsieh *et al.*, 1997). The patterns by which these crystalline structure parameters and properties vary with age are different between these two varieties. The breaking forces of the developing Maxxa fibers increase more with crystallinity (between 30 and 50%) than those of the SJ-2 counterparts. The increasing patterns in crystallite dimensions were different between the two varieties, resulting in different breaking force-crystallite dimension relationships. The most significant differences between SJ-2 and Maxxa are in their breaking relationships with the 101- and 002 crystallite dimensions. Therefore, the dependency of single fiber breaking force on crystallite sizes is obviously different for these two varieties.

Although the overall crystallinity and apparent crystallite sizes increase with fiber development, the unit cell sizes decrease slightly and thus the crystal densities increase with fiber development. Among the crystal lattice planes, the alignment of the glucosidic rings in respect to the 002 planes improves most significantly with fiber cell development. The crystallinity and crystal density of SJ-2 fibers are higher than those of Maxxa fibers during the fifth and sixth weeks of fiber development. The 002 and 101

crystallite dimensions of Maxxa fibers, on the other hand, are larger than those of the SJ-2 fibers. These increases coincide with the largest increase in forces to break single fibers.

Within each variety, positive relationships are observed between single fiber breaking forces and the overall crystallinity as well as between single fiber breaking force and crystallite size. However, the relationships between tenacities and crystallinity are different between these two varieties. The single fiber breaking tenacities of the SJ-2 cotton fibers do not appear to vary from 21 dpa to maturity. For the Maxxa cotton fibers, however, breaking tenacities appear to be positively related to fiber development or thickening of the secondary cell wall. Additionally, negatively relationships have been observed between breaking tenacities and crystal densities for both varieties. The increased crystallinity and crystallite sizes and perfection offer only partial explanation to the strength development of cotton fibers. Although some preliminary observation regarding the tenacity-age relationships and varietal differences in tenacity-structure relationship of developing fibers have been made, additional data collection and analysis are necessary to fully establish these relationships. Furthermore, structural parameters such as fibril orientation and residual stress may play key roles in cotton fiber strength and should be considered in future work.

1.5 Conclusion

Cotton fibers are nature's purest form of cellulose, composing about 90% of α-cellulose. The non-cellulosics are located on the outer layers or inside the lumens of the fibers whereas the secondary cell wall is purely cellulose. Both the structure and compositions of the cellulose and noncellulosics depend on the variety and the growing conditions. The cellulose fibrils spiral in the concentric cell wall layers at decreasing angle toward the center of the fiber. The spirals reverse along the fiber length and cause the cylindrical cells to collapse into the twisted ribbon fibers upon drying.

Cotton cellulose consists of β-1,4-D(+)-glucopyranose that repeats thousands of times. The very long chain that is limited in rotational freedom about the anhydrogluco-pyranose C-O-C link leads to a rigid and highly crystalline structure. The abundant hydroxyl groups, one C-6 primary and two C-2 and C-3 secondary on each anhydroglucose unit, allow extensive inter-molecular and intra-molecular hydrogen bonding to further enhance the cellulose structure for strength. These hydroxyl groups are also critical chemical characteristics of cotton fibers as they bond water and are responsible for the chemical reactivity such as in chemical modification, dyeing and finishing.

All three main fiber quality parameters, i.e., length, fineness and strength, have been linked to genotypes as well as growing conditions. The length and fineness of fibers are determined in the early stages of cell growth and

development. Fiber length is determined during the elongation stage, i.e., during the first 20 to 25 days past anthesis (dpa). The final thickness of fiber cells is developed at the base of the fibers by about 2 dpa. How cotton fibers gain strength has much to do with both primary wall formation (elongation) and secondary wall thickening (cellulose synthesis) as well as during desiccation (transition from mobile to highly hydrogen-bonded structure).

Ultimate fiber tensile properties were reached in the 30 dpa fibers and further fiber development contributed to thicker cell wall, thus fiber mass or lint turnout, but not the intrinsic fiber strength. For *G. hirsutum* varieties, the single fiber breaking forces increase most significantly during the fourth week of fiber development. The forces required to break single fibers are similar among varieties through the end of the fourth week of cell development. Beyond 30 dpa, both the single fiber breaking forces and tenacities differentiate among cultivars due partly to the differences in their linear densities and seed fiber weights at the same developmental stages. The cellulose **I** crystalline structure is clearly evident at 21 dpa and remains unchanged throughout fiber development. The overall crystallinity and the apparent crystallite sizes increase with fiber development for all varieties. Within each variety, the single fiber breaking forces are positively related to both the overall crystallinity and crystallite sizes. At the same developmental stages, Maxxa fibers have larger crystal sizes but lower crystallinity and lower crystal density than the SJ-2 fibers.

Although positive relationships between single fiber breaking forces and the overall crystallinity as well as between single fiber breaking force and crystallite size have been observed in both *G. hirsutum* and *G. barbedense* varieties, the relationships between tenacities and crystalline structure parameters are different between these two varieties. The tenacity-age relationships and varietal differences in tenacity-structure relationships remain to be further clarified. Additionally, experimentally determined fiber strengths are far from those predicted theoretically. Better understanding of the structural factors for cotton fiber strength will help to explain these discrepancies, and to improve strength.

1.6 Acknowledgements

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2

Physical structure and properties of cotton

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2.1 Introduction

Cotton was the dominant fibre of the 20th century. Now it is only exceeded in volume by polyester – and this position is achieved without the diversity of form and physical properties of polyester fibres. Partly the dominance of cotton textiles is due to the economics of production, distribution and manufacture, but it also results from the combination of structure and physical properties that is the subject of this chapter. Cotton first entered Western markets in the form of expensive fine fabrics, such as muslin and lawn, but by the end of the 19th century its properties made it a material of universal usage, sometimes as the best fibre for the purpose and sometimes as a cheaper alternative. Now cotton needs the properties that give a market for high quality, since polyester has captured much of the cheaper end of the market, as well as providing premium types for higher quality fabrics.

Section 2.2 will describe the structure and dimensions from the molecular to the whole-fibre level, which give rise to the physical properties. The absorption of moisture (section 2.3) has a major effect on properties as well as swelling the fibre. The mechanical properties (section 2.4) are the most important of the physical properties and are determined by structural features at all levels. Other properties, electrical, optical, thermal and frictional, are covered in section 2.5. Finally, the relevance of the extensive research in the middle of the 20th century will be mentioned, followed by a consideration of the future role of cotton and the effect of genetic engineering.

2.2 Cotton morphology

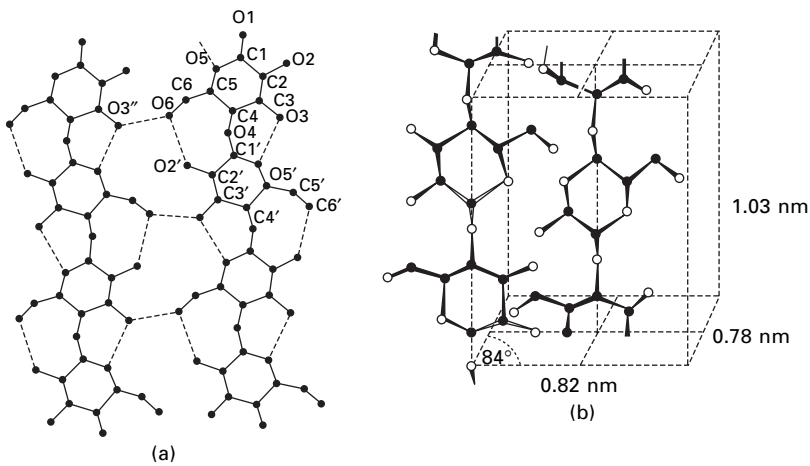
2.2.1 The cellulose molecule and crystalline fibrils

There is an abundant and sometimes contradictory literature on the formation of cellulose and its crystallisation. The following account summarises the features that are important to understand physical properties, but the numerical

values, although certainly close to the real values, should not be taken as explicitly authoritative.

From a physical viewpoint the cellulose molecule, described in Chapter 1, is a ribbon-like structure of linked six-membered rings with hydroxyl groups projecting out in the plane of the ribbon. The covalently bonded chain-molecule is further stiffened by internal hydrogen bonds, which, as shown in Fig. 2.1(a), parallel the oxygen bridges between the rings. In tension, the molecule has high modulus and high strength, and it has high rigidity for bending in the plane; but it can easily twist or bend out of the plane. As discussed by Rouselle (2002), exact determination of molecular weight (MW) is difficult, because of the problems of dissolving cellulose. The use of a new solvent after a pre-(mercerisation) swelling treatment of cotton print cloth shows a distribution of molecular weights with a peak at 2×10^5 and most values between 10^4 and 5×10^6; the peak value corresponds to a chain length of about 0.5 μm with a molecular aspect ratio of about 1000:1. Timpa and Ramey (1994) report higher values of MW.

Cellulose crystallises with lattices in which hydrogen bonds between hydroxyl groups link the molecules into sheets, Fig. 2.1(a); between the sheets, there are weaker van der Waals forces. Natural cellulose fibres, including cotton, have a crystal lattice known as cellulose I, which differs from cellulose II in cellulose regenerated from solution or treated with a strong swelling



2.1 (a) Assembly of cellulose molecules in a sheet. C1, O1, etc., are positions of carbon and oxygen atoms; hydrogen atoms complete the valencies; hydrogen bonds are shown by dotted lines. From French (1985). (b) A schematic view of the crystal lattice of cellulose I, adapted from the drawing by Meyer and Misch (1937), which had anti-parallel chains. Hydrogen bonded sheets are in the plane of the paper. The sheets in the middle of the cell are staggered with respect to those on the front and back faces.

agent. The classical X-ray diffraction studies of Meyer and Misch (1937) proposed a unit cell for cellulose I, with 1.03 nm for two repeats along the chain axis, 0.835 nm for spacing between neighbouring chains in the sheets, and 0.79 nm between two equivalent sheets, which are separated by a staggered sheet of anti-parallel chains. Only small variations in the size of the unit cells have been proposed by other workers. However, the question of whether the chains were parallel or anti-parallel was controversial. Sarko and Muggli (1974) made a more detailed study of *Valonia* cellulose. They found that the chains were all aligned in the same direction in the cellulose I lattice. Since there were no differences from the pattern for cotton and ramie, except those attributable to the larger crystallite size in *Valonia*, they inferred that the cotton crystal lattice had the same cellulose I lattice, containing staggered sheets of parallel chains. There are minor differences in unit cells proposed around the same time by other studies (French, 1985). Figure 2.1(b), which is a modification of the Meyer and Misch lattice, shows the features essential to an understanding of the role of crystalline cellulose in cotton. Unlike the monomeric glucose molecules, the crystals do not dissolve in water, but can be disrupted by caustic soda and some solvents.

In growing cells, cellulose is synthesised by the condensation of glucose molecules at enzyme complexes, each of which generates 30 cellulose molecules. These naturally lie in the same direction and crystallise into long microfibrils, which are about 7 nm in width. In this sense, natural cellulose can be regarded as virtually 100% crystalline. The evidence, from moisture absorption, density, X-ray diffraction and other techniques, that cotton is about 2/3 crystalline can be explained by the imperfect packing of the microfibrils, which are normally separated by absorbed water. X-ray diffraction of ground cotton fibres gives crystallinity values of 92.6 to 94.7% (Timpa and Ramey, 1994).

2.2.2 Multi-wall helical assembly

Large numbers of cotton fibres grow from each seed within the cotton boll. Each fibre is a single plant cell, which first grows to its full length and diameter by forming a primary wall. The primary wall is reported to have a 'basket-weave orientation or alignment of the fibrils' (Hebert, 1993). X-ray diffraction of fibres removed at two weeks post-anthesis (after flowering), which consist solely of the primary wall, have a crystalline index of 30%, and a calculated fibril diameter of 2.98 nm, contrasted with 70% and 4.22 nm for mature fibres at seven weeks post-anthesis (Boylston and Hebert, 1995). Studies of changes in crystalline structure during fiber development are reported by Hsieh *et al*. (1997) and Hu and Hsieh (2001).

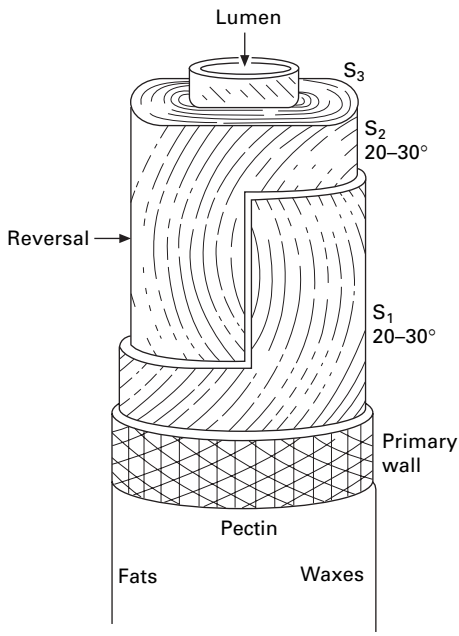
Then a secondary wall is formed in daily growth rings inside the tube, leaving a small lumen at the centre when the cotton is mature and the boll

opens. Goynes *et al*. (1995) report SEM and TEM studies of the development of the secondary wall in field and greenhouse grown cotton at different numbers of days post-anthesis. In mature fibres, the secondary wall comprises about 94% of the fibre material and thus dominates the mechanical properties. Immature cottons, resulting from premature opening of the boll, due to frost disease or application of plant hormone, are thin-walled tubes. The fibre surface consists of a waxy cuticle, which is removed by wet processing. Studies of changes in crystalline structure during fibre development are reported by Hsieh *et al*. (1997) and Hu and Hsieh (2001).

An impression of the overall structure of the cotton fibre is shown in Fig. 2.2. In the secondary wall the microfibrils are laid down in helical layers on the inside of the tube, with helix angles changing from around 35° in the outer layers to 20° in the inner layers (Hebert *et al*., 1970; Morosoff and Ingram, 1970). At intervals along the cell walls, there are reversals between left-handed to right-handed helices. In a scanning electron micrograph, the reversals can be seen on the fibre surface.

2.2.3 Collapse and convolutions

When the fibre dries, the hollow tube collapses a characteristic shape Kassenbeck (1970) pointed out that different parts of the collapsed fibre,

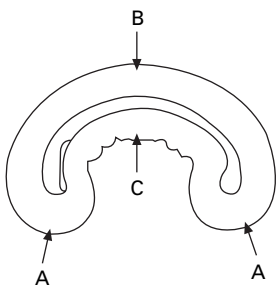


2.2 Representation of the structure of a cotton fibre. From Jeffries *et al.* (1969).

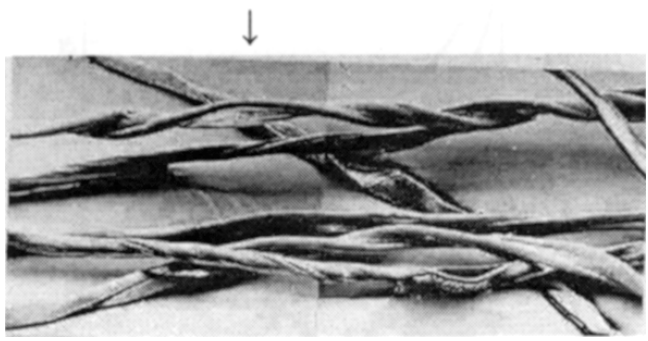
shown in Fig. 2.3, differed in structure. This can be demonstrated by collapsing a roll of adhesive tape. In regions C and N, the structure opens up and is more easily susceptible to chemical attack. In region A, the structure is tightened and, in B, there is little change.

The collapsed fibre is convoluted, as shown in Fig. 2.4. By comparison with the collapse of a twisted rubber tube, Hearle and Sparrow (1979a) showed that this was a natural consequence of the collapse of a helical structure. At intervals along the fibre, there are changes between left-handed and right-handed convolutions. Hearle and Sparrow (1979a) also showed that a cotton fibre without convolutions could be produced by tensioning a wet fibre and then allowing it to dry under tension.

The changes in structure on drying cause cotton fibres to develop crimp, a periodic kinkiness or waviness along the length of the fibre. Foulk and McAlister (2002), in an extensive study of dimensions and properties of three American upland cottons with different finenesses, each divided into seven length groups, used an opto-electrical sensor to measure crimp and report values from 11 to 13 crimps/cm.



2.3 Cotton fibre cross-section. Diagrammatic representation by Kassenbeck (1970) showing regions with differences in structure.



2.4 Convolutions of a cotton fibre. Note reversal of twisting of convolution at ↓. From Hearle and Sparrow (1979a).

2.2.4 Fibre dimensions and density

Linear density equals mass per unit length, expressed in g/km, which is termed tex.

Cotton fibres range in dimensions from superfine Sea Island cottons with a length of 5 cm and a linear density of 1 dtex to coarse Asiatic cottons of 1.5 cm and 3 dtex. This corresponds to mean linear thicknesses of 10 to 20 μm. Most of the world's crop will be in the middle of the range. The maturity can be defined as the ratio of the area of the cell wall to the area of a circle with the same perimeter, which is equivalent to an uncollapsed fibre, and typically has values around 0.85 for mature fibres. An excess of immature fibres with values less than 0.5 is undesirable. Length, fineness and maturity and their variabilities are important measures of fibre quality, which is covered in Chapter 3. The density of the cell wall of cotton is 1.55 g/cm^3 when dry, 1.52 g/cm^3 at 65% rh and 1.38 g/cm^3 when wet. The effective density will be lower when the lumen is taken into account.

2.2.5 Mercerised and resin-treated cottons

In mercerising treatments in caustic soda or other reagents, the cotton fibre swells and de-swells. The resulting fibres are more nearly circular in cross-section and more lustrous in appearance. During mercerisation, the crystalline structure is disrupted, without complete loss of fibre integrity, to a degree sufficient for recrystallisation to occur in the form of cellulose II with anti-parallel chains. The cellulose II lattice is also found if cotton, or other sources of cellulose, is dissolved and regenerated. The degree of disorder in mercerised cotton as indicated by X-ray diffraction is 49% compared with 29% for unmercerised cotton (Warwicker *et al.*, 1966). The fibrillar structure is probably less well defined and there may be substantial regions of amorphous structure, in contrast to the wholly crystalline fibrillar structure of unmercerised cotton. In resin-treated cottons, the hydroxyl groups on neighbouring fibrils are permanently joined by the covalent groups of the resin.

2.3 Moisture absorption

2.3.1 RH-regain relations

In the recommended terminology regain – or moisture regain – is the ratio of mass of absorbed water to oven-dry mass of fibre. Moisture content is the ratio of mass of absorbed water to the total fibre mass. Both quantities are usually quoted as percentages (Denton and Daniels, 2002).

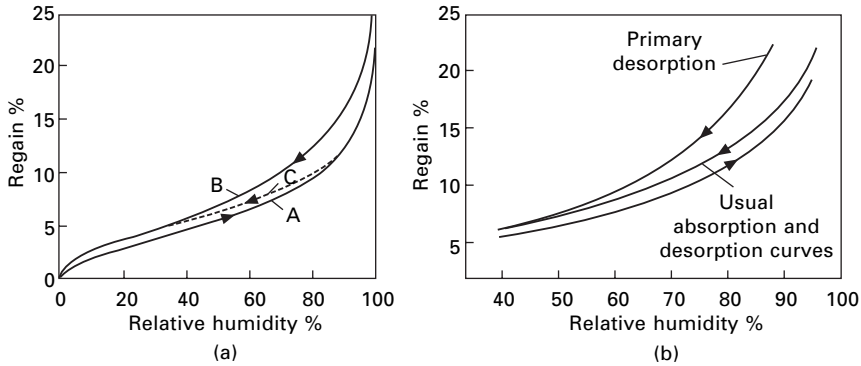
As cotton fibres grow, the plant cells have a high concentration of water.

When the boll opens, the fibres lose water to equilibrate with the ambient humidity. The amount of absorbed water then rises and falls with changes in humidity. The maximum absorption at 100% rh or in water never reaches the original value, so that some studies are carried out on never-dried fibres.

The rate of absorption and desorption of water with change of humidity is very fast for an isolated fibre. For fibre assemblies, the changes are much slower and involve interaction between the rate of diffusion of water molecules and the evolution and transmission of heat of sorption. Experimental and theoretical studies by Henry (1939) and others are summarised by Morton and Hearle (1993). Changes are carried on two waves with a final exponential approach to equilibrium. A standard half-change period of 12 hours applies to a slab of cotton fibres 2.5 cm thick, with a density of 0.5 g/cm^3 when dry, at a regain of 7% and a temperature of 18 °C. Ninety-nine per cent of the total change is completed in 14 times the half-change value (one week). The time increases linearly with (volume/ surface area)^2; it increases with package density from 1/6 of standard value at 0.09 g/cm^3 to 1.33 times at 0.7 g/cm^3; it falls from six times the standard value for zero regain, to a minimum of 2/3 at 4% and then rises to five times at 14% regain; it falls from 2.4 times the standard value at 5 °C to 0.4 times at 30 °C. Due to hysteresis, the equilibrium regain is higher when humidity is increased than when humidity is decreased.

Figure 2.5(a) shows a typical rh-regain curve (Urquhart and Eckersall, 1930). Enough time was allowed for equilibrium to be reached at each humidity. The lower curve is for absorption from the dry state; the upper curve is for desorption from 100% rh; the dotted line shows desorption from an intermediate value. As Ashpole (1952) showed for viscose rayon, there are difficulties in making measurements close to 100% rh and the true saturation values may be higher than shown in Fig. 2.5(a). Preston and Nimkar (1952) found that suction of a wet cotton yarn to minus 30 cm of mercury gave a retained regain of 52%, and of 48% after centrifuging at 1000 g for five minutes; however, there is a question of how much water is held by capillary forces and how much is absorbed within the fibre. Figure 2.5(b) shows how the primary desorption curve of cotton from the boll is at a higher regain level down to 40% rh.

Urquhart and Williams (1924) showed that up to about 85% rh, the regain of cotton at a given humidity decreases with rise of temperature from 50 to 110 °C. The reduction increases from 0.9% at 20% rh to 1.8% at 70% rh. At 85% rh, the curves cross over and there is a higher regain at higher temperatures. In a standard atmosphere of 65% rh and 20 °C, the absorption regain of cotton is 7–8%. Hysteresis increases the desorption value by 0.9%. The recommended allowance for calculating the mass of fibre in commercial transactions is 8.5%.



2.5 (a) Typical regain-rh curve for cotton (soda-boiled). *A*: absorption. *B*: desorption. *C*: intermediate. (b) Primary desorption curve for cotton taken from the boll. From Urquhart and Eckersall (1930).

2.3.2 Heat of sorption

> The [differential] heat of sorption is the heat evolved when one gram of water is absorbed by an infinite mass of material at a given humidity. The heat of wetting [integral heat of sorption] is the heat evolved when a specimen of material, which has a mass of one gram when dry, is completely wetted out.

Table 2.1 gives values of the heat of sorption of cotton, which decreases rapidly from a high value for dry cotton as the starting humidity increases. The upper row are measured values for absorption of liquid water; the lower row is corrected by adding the latent heat of vaporisation of water, 2.45 kJ/g. Values of heat of sorption from the dry state ranging from 1.19 to 1.33 kJ/g have been reported for three different types of cotton (Morton and Hearle, 1993). The corresponding heats of wetting from the dry state ranged from 46.1 to 47.3 kJ/g; other data for various types and methods ranged from 41 to 54 kJ/g (Morton and Hearle, 1993).

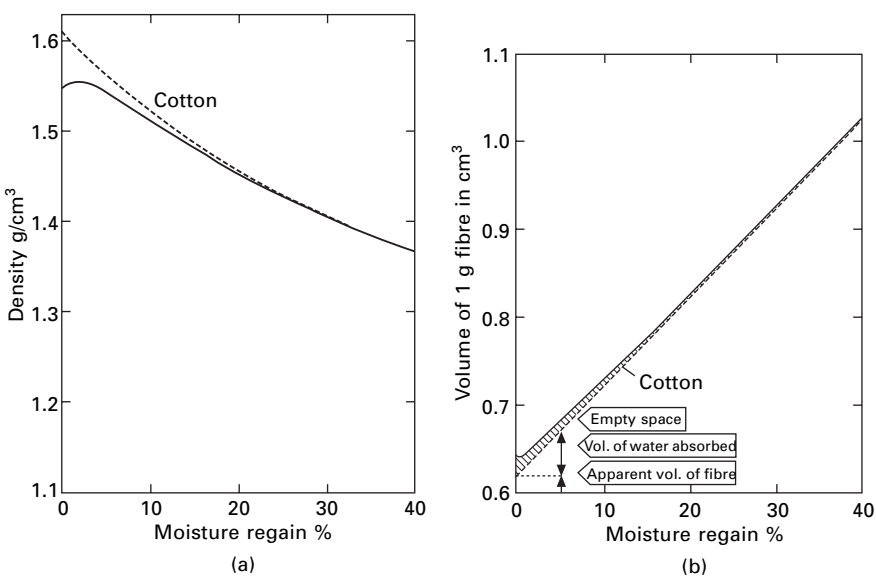
Table 2.1 Variation of heat of sorption of Sea Island cotton with humidity. From Guthrie (1949)

	Relative humidity %				
	0	15	30	45	60
Heat of sorption from liquid water kJ/g	1.24	0.50	0.39	0.32	0.29
Heat of sorption from water vapour kJ/g	3.69	2.95	2.84	2.77	2.74

2.3.3 Swelling

Figure 2.6(a) shows the change of density of cotton with change of regain; in Fig. 2.6(b), this is converted into change in specific volume. Initially from the dry state, there is an increase of density due to water molecules occupying 'empty space' within the fibre. The density is a maximum at about 2% regain, and then decreases since the density of water is less than that of fibre. Above 20% regain, the volume increase equals the equivalent volume of liquid water.

The swelling of cotton fibres is predominantly in the transverse direction. Meredith (1953) states that, in going from the dry to the wet state, the increase in length is 1.2% but the increase in diameter is 14%. However, these quantities are difficult to measure because of the lumen, the cross-sectional shape of cotton fibres, and changes in helix angles and twist angle of convolutions as a result of swelling. Preston and Nimkar (1949) checked values from different sources and found values for diameter swelling from dry to wet of 23, 20 and 7%, with area swellings of 42, 41 and 21%. Ibbett and Hsieh (2001) report a diameter swelling of 10–15% with a length contraction of 0–0.5%. The data in Fig. 2.6(b) would give a maximum volume swelling of 63%. This is compatible with a regain of 40%, but implies that the increase of area or length of the fibre material, excluding the lumen, must be greater than indicated by the above values.



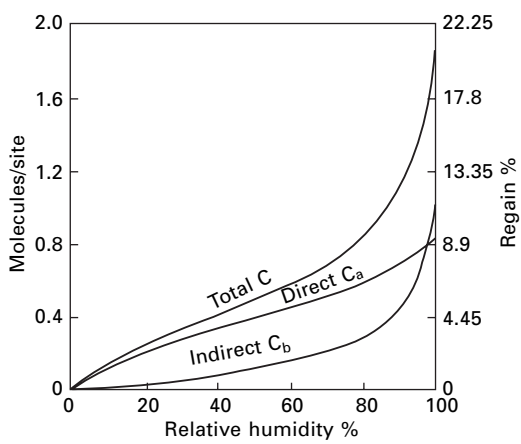
2.6 (a) Change of cotton fibre density with regain. Dotted line is density from mixture law for fibre and water based on high regain values. (b) Recalculated as change of volume. From Meredith (1953).

2.3.4 Structural changes and theoretical models

In the completely dry state, hydrogen bonds will form between those hydroxyl groups that are not already linked within crystalline regions. With the view of the structure described in section 2.2.1, the available hydroxyl groups will be on the surface of the crystalline fibrils. As humidity is increased, water will be attracted to accessible hydroxyl groups. There will be an equilibrium between the free energy of the cellulose/water mixture and the free energy of the water vapour in the atmosphere.

The first water molecules to be absorbed will be directly attached to hydroxyl groups. Later absorption may be on remaining available hydroxyl groups or form secondary layers attached to already absorbed water molecules. As indicated in section 2.3.3, the direct absorption results in more efficient molecular packing and gives an initial increase in density. The later absorption just adds the same volume as that of liquid water. The heat of sorption, as noted in section 2.3.2, is also higher for the initial absorption. At very high humidities, some water will be held by capillary forces. Experimental results suggest that this is significant only above 99% rh, which would correspond to a pore size of 110 nm (Morton and Hearle, 1993).

There have been a number of theories that explain the shape of the regain-rh curve in terms of multilayer absorption. Peirce (1929) presented a simple mechanistic argument. He assumed that there was an equal probability of an added water molecule being absorbed by unoccupied sites and already occupied sites. The experimental regain-rh curve then divides between directly and indirectly absorbed water as shown in Fig. 2.7. If C is the total number of absorbed water molecules per absorption site, which is divided into C_a directly absorbed and C_b indirectly absorbed, the resulting partition is:



2.7 Division between directly and indirectly absorbed water according to Peirce (1929).

$$C_a = 1 - \exp(-C) \quad C_b = C - 1 + \exp(-C) \qquad 2.1$$

He then showed that the torsional rigidity of cotton fibres decreased linearly with C_a, the amount of directly absorbed water.

Peirce postulated that the directly absorbed water, which is more firmly bonded, will make only a small contribution to the vapour pressure p. The indirectly absorbed water is the main controlling factor, with a vapour pressure given by (saturation vapour pressure $p_0 \times$ fraction of sites occupied by indirectly absorbed water). In order to fit experimental data, it was necessary to introduce an arbitrary factor ($1/\beta$), which represented the fraction of sites that were accessible to secondary absorption. Peirce justified this by suggesting that one indirectly absorbed water molecule blocks off a number of sites. This leads to the expression:

$$p/p_0 = 1 - \exp(-\beta\, C_b) \qquad 2.2$$

With the addition of a contribution from directly absorbed water reduced by a factor K, the assumption that only a fraction γ of hydroxyl groups are effective in absorption, substitution of the fractional regain r, and taking account of the molecular weights of water and cellulose per hydroxyl group, this gives the following dependence of rh on regain:

$$p/p_0 = 1 - [1 - K(1 - \exp(-3\gamma\, r)]$$
$$\exp\{-\beta\, [\exp(-3\gamma\, r) - 1 + 3\gamma\, r)]\} \qquad 2.3$$

Peirce found a good agreement with an experimental rh-regain relation with $\gamma = 1/3$, $K = 0.4$ and $(1/\beta) = 0.185$.

In several other theoretical treatments, which are discussed by Morton and Hearle (1993), corrections are needed at low or high humidities. Good agreement with experiment is found by Hailwood and Horrobin (1946), who treat the directly absorbed water molecule as a hydrate attached to particular units of the cellulose molecule and the indirectly absorbed water as forming an ideal solid solution.

A different approach to moisture absorption, which was developed by Barkas (1949) in relation to wood, is also relevant to cotton. Barkas, based on the analogy with osmotic pressure, considers that water is absorbed until the stresses generated by swelling prevent more water flowing into the fibres. He used a thermodynamic cycle to derive a differential equation relating directional swelling to directional stresses and moisture absorption. An alternative derivation, which includes a relation between absorption and fibre tension, is given by Hearle (1957); the prediction agreed with absorption by regenerated cellulose fibres under tension as measured by Treloar (1953).

On a purely molecular approach, hysteresis in moisture absorption is explained as a tendency for the structure to resist change in absorption and desorption:

cross-links breaking; water attaching
dry structure with →→→→→→→→→→→→→ wet structure with
many cross-links ←←←←←←←←←←←← few cross-links
water coming off; cross-links forming

In terms of swelling stresses, hysteresis in moisture absorption results from mechanical hysteresis, which is covered in section 2.4.1.

2.4 Mechanical properties

2.4.1 Tensile stress-strain relations

For fibres, tensions are best normalised on a mass basis. Specific stress is given in N/tex. On an area basis, conventional stress in GPa equals (specific stress in N/tex × density in g/cm^3). Tenacity is specific stress at break. Modulus is the slope of the specific stress vs. strain curve.

Meredith (1945a) made an extensive study of the tensile properties of cottons available in the middle of the 20th century, which showed the wide range of values in different cottons. Table 2.2 gives data for the strongest, weakest and intermediate strength types. The weaker cottons, such as those grown in India, will now have been replaced by improved varieties. Tensile properties of modern cottons are included in the chapter on fibre quality. Cotton falls in the category of weaker and less extensible general textile fibres. The toughness (work of rupture) values are low, in comparison with many other textile fibres. Generally longer and finer fibres show greater tenacity, which is a measure of strength, and modulus, which is a measure of stiffness. Within a given sample of cotton, Morlier *et al.* (1951) found a rise in tenacity for fibres in increasing length array groups. Timpa and Ramey (1994) found an increase of strength, measured in four laboratories according to HVI standards, from 0.2 to 0.3 N/tex with increasing length from 21.2 mm

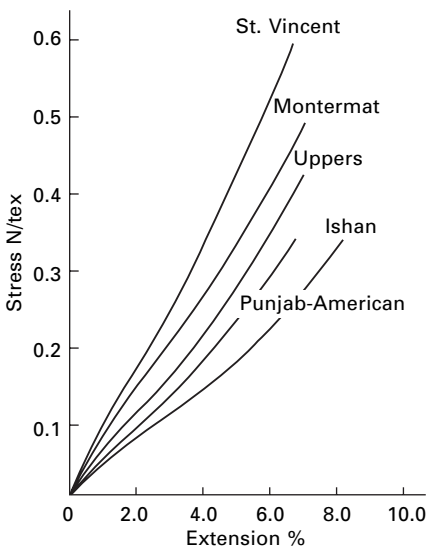
Table 2.2 Tensile properties of cotton at 65% rh, 20 °C. From Meredith's (1945a) set of tests (1 cm test length; 0.9 (N/tex)/min; 50 tests per sample)

	Fineness dtex	Initial modulus N/tex	Tenacity N/tex	Work of rupture mN/tex	Breaking extension %
St Vincent, Sea Island	1.00	7.3	0.452	15.0	6.80
Uppers, American	1.84	5.0	0.323	10.7	7.10
Bengals, Indian	3.24	3.9	0.185	5.0	5.60

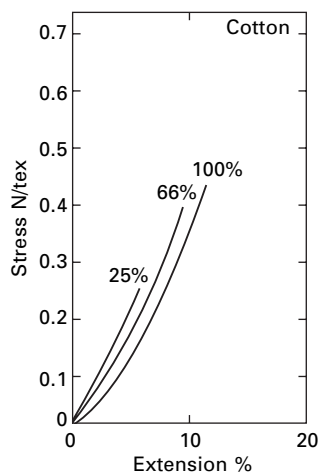
(staple length code: 26) to 32 mm (code: 40); they also found a significant increase of strength with molecular weight, albeit with considerable scatter. Foulk and McAlister (2002) report an extensive study of the tensile properties of cottons with three micronaire values, each subdivided into seven length groups. Meredith (1946) found a correlation between tenacity and birefringence with an increase from 0.2 N/tex at a birefringence of 0.04 to 0.37 N/tex at 0.05. In a later paper Meredith (1951) showed correlation with X-ray orientation angle, which correlates with convolution angle.

Figure 2.8 shows stress-strain curves for various cottons as measured by Sparrow (1973). Stress-strain curves of cotton at increasing humidities, Fig. 2.9, show a reduction of stiffness, but, unlike most fibres, an increase of strength. A technical bulletin from Du Pont (1958) shows stress-strain curves of cotton, both in air and wet, decreasing in stiffness and strength with increase of temperature.

Within a given sample of cotton, there is considerable variability in test results. Liu *et al*. (2005) give histograms of break force and break elongation for five cottons; coefficients of variation are from 37 to 45% for break force and 30 to 44% for break elongation. Hu and Hsieh (1998) give histograms for cotton fibre toughness (work of rupture) with coefficients of variation of 51 to 56% in skewed distribution with a long tail of high values. Variability between fibres leads to lower values of bundle strength than the average of single-fibre strengths. Variability along the test length has a major effect on measured strengths due to the weak-link effect. Table 2.3 shows values



2.8 Stress-strain curves for various cottons, from Sparrow (1973).



2.9 Effect of humidity on stress-strain curves of cotton at 20 °C. From Meredith (1953).

Table 2.3 Effect of test length and variability on tenacity in N/tex tests by Meredith (1946)

	Tenacity 1 cm	Standard deviation 1 cm	Coefficient of variation %	Tenacity 1 mm	Tenacity ratio % (1 cm/1 mm)
St Vincent	0.473	0.136	28.7	0.609	78
Sakel	0.405	0.180	44.4	0.535	76
Uppers	0.288	0.136	47.2	0.477	60
Ishan	0.324	0.093	28.7	0.446	73

obtained by Meredith (1946) for lengths of 1 cm and 1 mm in single-fibre tests. Although the result for Sakel cotton is anomalous, the general trend is for the loss in strength from 1 mm to 1 cm test length to increase with the coefficient of variation of the tenacity test. Data on the reduction of bundle strength with test length for various cottons is given by Brown (1954) and Taylor (1994).

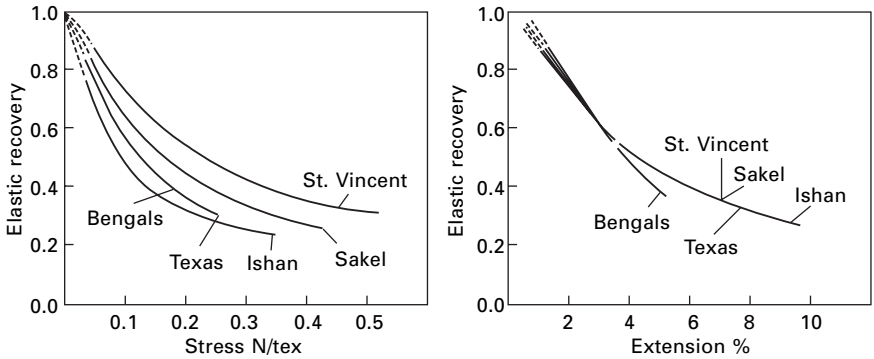
Research at University of California, Davis, has studied the change of strength and structure during fibre development in greenhouse-grown Acala cottons (Hsieh *et al*., 1995, 1997), *G. hirsutum* and *G. barbadense* (Hsieh *et al*., 2000), among ovule locations and along fibre lengths (Hsieh and Wang, 2000), and effects of dehydration (Hu and Hsieh, 2001). A study on mature fibres examined the association with seed position and fibre length (Liu *et al*., 2001).

Hebert (1993) reported that the strength of an immature fibre with only primary wall was one-sixth that of a mature fibre, which is dominated by the thicker secondary wall. The tenacity was just over half that of the mature fibre, reflecting the basket-weave orientation of fibrils in the secondary wall.

2.4.2 Elastic recovery

Even under constant test conditions for a particular cotton fibre, there is not a single-valued relation between stress and strain. In tests to successively higher strains, the recovery curve falls below the elongation curve and the unrecovered extension at zero stress increases with the increase in maximum stress and strain. Figure 2.10 shows the dependence of elastic recovery, which is the ratio of recovered to total extension, as functions of imposed strain and stress respectively. Cyclic tests between strains will show a characteristic hysteresis loop.

The ‘permanent’ extension left after elongation when dry is reduced or eliminated when the fibre is wetted out due to swelling recovery. This effect is related to the glass transition temperature discussed in section 2.5.3. The increased stiffness and strength and reduced break extension after cotton has

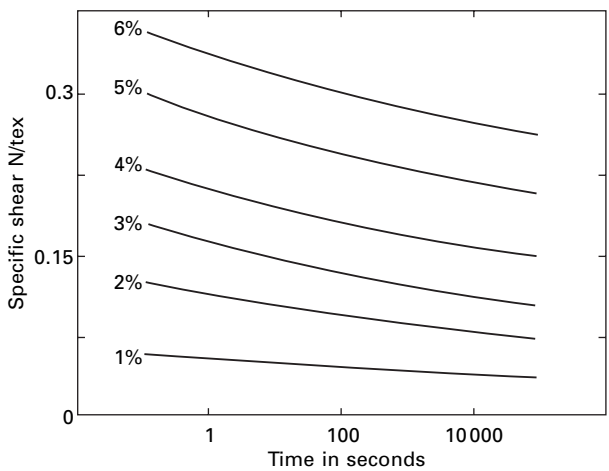


2.10 Elastic recovery of cottons plotted against stress and strain. From Meredith (1945b).

been wetted and dried under tension is discussed in connection with the influence of convolutions in section 2.4.4 (see Table 2.3).

2.4.3 Time effects

Time also affects the behaviour. Figure 2.11 shows the stress relaxation of cotton held at constant length. Roughly the stress decreases by 7% for every tenfold increase in time. Creep in fibres held under tension is the complementary effect. Tests by Collins (1924) and Steinberger (1936) showed that parts of extension-time plots were linear with log(time) though the slope changed somewhat irregularly. In tensile tests, stress levels at given strains rise with



2.11 Stress relaxation of cotton from different extensions at 65% rh, 20 °C, from Meredith (1954).

rate of extension. Meredith (1953) reports that strength of cotton decreases with time according to the equation:

$$F_1 - F_2 = 0.088 \log_{10}(t_2/t_1) \qquad 2.4$$

where F_1 and F_2 are breaking loads after times t_1 and t_2 under load.

2.4.4 Directional effects

There is only limited published data on the twisting and bending properties of cotton. For a linear-elastic rod, the flexural rigidity (bending moment per unit curvature) is proportional to the fourth power of the radius and, in terms of linear density T, specific modulus E and density ρ in consistent units, equals $(\eta ET^2/4\pi\rho)$ where η is a shape factor, which is dependent on distance from the neutral plane and is 1 for a circle. In order to eliminate the direct effect of linear density, a specific flexural rigidity in units of tex and g/cm^3 as $[(\eta E/4\pi\rho) \times 10^{-3}]$ N mm^2/tex^2 is used. Owen (1965), using a double-pendulum method, found a specific flexural rigidity for cotton of 0.53 mN mm^2/tex^2. There are complications:

- It is difficult to determine η for cotton, because of the irregular shape of the fibre.
- Due to the ribbon-like form, cotton fibres will tend to twist in such a way as to bend perpendicularly to the greater width.
- Although there is no specific information for cotton, oriented molecular structures yield more easily in compression than in tension. Consequently the neutral plane moves towards the inside of a bend and, when this yielding occurs, the bending stiffness falls below that given by the linear-elastic case.

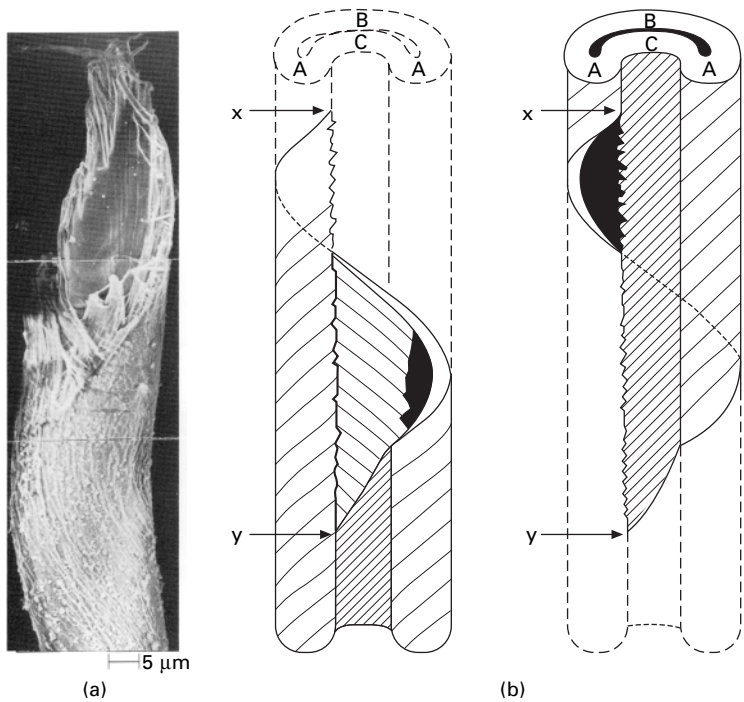
Another effect of bending is that loop and knot strengths are less than those for straight fibres. Bohringer and Schieber (1948) found that knot strength of cotton was 91% of tensile strength.

At low twist levels, torsional rigidity follows similar relations to flexural rigidity, except that shear modulus replaces tensile modulus and the shape factor ε is dependent on distance from the centre of the fibre. Owen (1965), using a double-pendulum method, found a specific torsional rigidity of 0.16 mN mm^2/tex^2 for cotton. The ratio of shear modulus to tensile modulus is given by Morton and Hearle (1993) as 0.27. At high twist levels, the increase in length of the outer levels of the fibre means that there is a large influence of tensile modulus on torsional rigidity. The breaking twist angle for cotton was found by Koch (1949) to be 34 to 37°. Dent and Hearle (1960) found that the strength of cotton fibres twisted at constant length fell from 0.34 N/tex at zero twist to near zero at a twist factor of 110 tex$^{1/2}$/cm. There was a corresponding contraction in fibre length and reduction in breaking extension.

By testing fibre bundles in shear, Finlayson (1947) estimated that the shear strength of cotton was 35% of the tensile strength. Maxwell *et al.* (2003) used atomic force microscopy to determine the hardness of the secondary wall of cotton. Penetration into a cross-section increased markedly above 70% r.h. They interpreted the reduction in hardness as being due to a glass transition.

2.4.5 Fracture and fatigue

The form of tensile fracture of cotton fibres depends on the state of the fibre (Hearle and Sparrow, 1971, 1979d). At 65% rh, the form is shown in Fig. 2.12(a), which is diagrammatically drawn in Fig. 2.12(b). Similar forms are found in mercerised cotton. Some reports have suggested that the reversal is a point of weakness, where break occurs. A closer study indicates that breaks are adjacent to reversals. The form of break is a consequence of the changes due to collapse of the fibre on drying, which were discussed in section 2.2.3 and illustrated in Fig. 2.4. There is a line of weakness at the boundary between zones A and C, which is where break starts. Under tension, there is an untwisting at reversal points, as further discussed in section 2.4.6, which

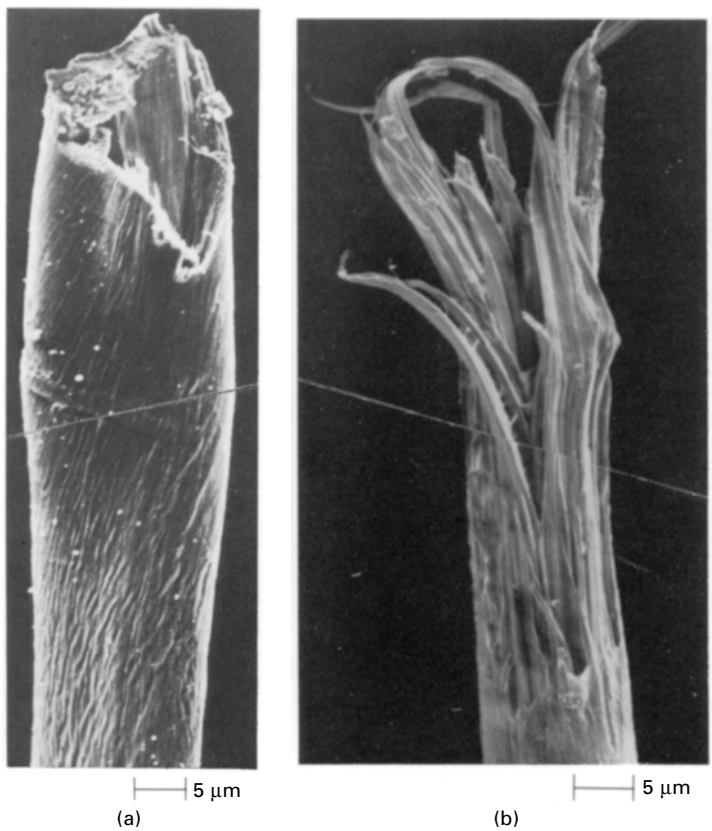


2.12 (a) Scanning electron micrograph of break of cotton. (b) Schematic of form of break of cotton. From Hearle *et al.* (1998).

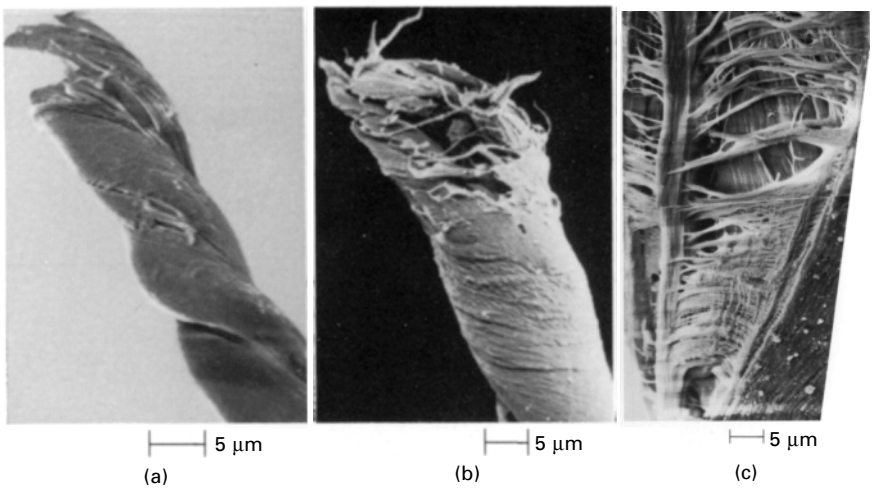
gives rise to shear stresses. A crack develops and runs round the fibre following the lower bonding between fibrils until it reaches the line of weakness and tears across zone C.

In resin-treated cotton at 65% rh, Fig. 2.13(a), and in raw cotton at zero humidity, there is a granular break, which is typical of fibres with a fibrillar structure. The axial splitting of Fig. 2.12 is resisted due to the stronger inter-fibrillar bonding between fibrils by covalent bonds in the treated fibre and hydrogen bonds in the dry fibre. The boding is weaker in wet resin-treated cotton, which shows breaks similar to Fig. 2.12. For wet raw cotton, the links between fibrils are weaker still. There is no cooperative effect and the fibrils break individually, Fig. 2.13(b).

Twist breaks of cotton show axial splitting with a sharp tear-off at the end, Fig. 2.14(a), (b). Tensile fatigue (Hearle and Sparrow, 1979c) results in extensive splitting between fibrils before failure, Fig. 2.14(c). Biaxial rotation fatigue gave failure with considerable splitting, but tests give a large scatter



2.13 (a) Break of resin-treated cotton at 65% rh. (b) Break of wet mercerised cotton. From Hearle *et al.* (1998).



2.14 (a) Twist break of raw cotton. (b) Twist break of mercerised cotton. (c) Axial splitting due to tensile fatigue. From Hearle *et al.* (1998).

of lifetimes due to the concentration of the test on a short fibre length and complications from the shape of cotton fibres and the reversals along their length. Chauhan *et al*. (1980) report distributions for lifetimes in flex fatigue in bending over a bar. SEM views of wear for a range of products (Hearle *et al*. 1998) show that the common form of damage is multiple splitting. The cause of the splitting is twisting and bending as a result of the forces exerted on fabrics in use or in laundering. It eventually leads to wearing of holes in the fabric or to weakness that allows the fabric to be easily torn.

2.4.6 Structural mechanics

The moderately high strength and extensibility of cotton, which make it a good textile fibre, is a result of a number of structural features. The treatment in this section follows a model by Hearle and Sparrow (1979b). The easiest mode of extension of a cotton fibre results from untwisting of the convolutions. Timoshenko (1957) gives an expression for the contraction of a thin rectangular strip on twisting. The converse of this, which was confirmed by Hearle and Sparrow (1979a) with tests of a nylon strip heat-set in a twisted form, is that a ribbon of width b and twist φ would extend by ε_c, equal to $(\varphi^2 b^2/24)$, when fully untwisted. In terms of convolution angle ω_0, the extension is $(\tan^2 \omega_0)/6$. Cotton fibres have varying ω_0 along their length, unequal lengths of S and Z twist, some fibres more circular than others, and some fibres in a wrapped-ribbon instead of twisted form. The ideal expression is replaced by ε_c equals $(X \tan^2 \omega_0)$, where X takes account of the anomalies. Although there

is considerable scatter in extensions, values of X between 0.5 and 1 give agreement with experiment.

The role of convolutions is supported by two observations (Hearle and Sparrow, 1979a). First, when a cotton fibre was extended in a scanning electron microscope, the convolutions are gradually removed. The ribbon was partially untwisted at 3.8% extension and fully untwisted at 6.8%; break was at 7.4%. Second, when wet cotton fibres were tensioned at two grams for five minutes and then held while being allowed to dry, optical microscopy showed that the convolutions had been removed; they are set in an extended state, which would be released on wetting. The stress-strain curves of these fibres showed less curvature, with a mean modulus about three times higher. Table 2.4 compares mean properties before and after the treatment.

The above discussion does not introduce the effect of stress in pulling out convolutions. When the convolution angle is reduced from ω_0 to ω, the strain ε is $X(\tan^2 \omega_0 - \tan^2 \omega)$. An approximate energy analysis by Hearle and Sparrow (1979b) then gives the following expression for stress f at increasing values of extension ε:

$$f = K\{[\tan \omega_0/(\tan^2 \omega_0 - \varepsilon/X)^{1/2}] - 1\} \qquad 2.5$$

where $K = (g\ A\ S/\pi\ b^2\ X)$ and g is a shape factor, A is area of cross-section, and S is shear modulus. Data on fibre dimensions and torsional properties indicate a value for K of 180 MPa, but values can be expected to vary widely for different cottons. Plots of stress against deconvolution strain with K = 200 and $\omega = 14°$ are markedly concave upwards. The curves become more concave with decreasing values of K and increasing values of ω.

The second influence on the extensibility of cotton is the basic helical arrangement of the fibrils. The simplest approximation indicates that the helix angle reduces the strain in fibrils by $\cos^2 \theta$ and the contribution to stress by $\cos^2 \theta$. Stiffness and strength would be proportional to the mean value of $\cos^4 \theta$. In cotton, the helix angle changes little from a value of 22° with distance from the centre of the fibre; this would give a reduction of 0.74 compared to a fibre with axially oriented fibrils.

Table 2.4 Properties of three fibre types before and after wetting and drying under tension. From Sparrow (1973)

Fibre type	Permanent extension %	Break extension %		Break load g	
		Before	After	Before	After
Deltapine	11.4	11.1	3.6	4.7	6.8
Menoufi	7.0	8.2	4.9	5.7	8.4
Acala 1517	5.8	7.0	3.5	4.6	7.4

A more exact analysis follows the mechanics of twisted yarn mechanics (Hearle, 1980; Thwaites, 1980). For small strains, geometrical analysis shows that fibril extension ε_f is given in terms of fibre extension ε by:

$$\varepsilon_f = \varepsilon\,(\cos^2\theta - \sigma\sin^2\theta) \qquad 2.6$$

Lateral contraction reduces the extension and consequently the Poisson's ratio σ, which is probably close to 0.5, is introduced in eqn 2.6. Furthermore, the change in helix angle leads to shear. (In twisted yarn mechanics, this is ignored because it is assumed that fibres can slide past one another, but within a cotton fibre the fibrils are hydrogen-bonded together.) The shear strain β is given by:

$$\beta = -\varepsilon\,(1 + \sigma)\,(\sin\theta\cos\theta) \qquad 2.7$$

Hence the total strain energy U per unit volume (or mass if specific quantities are used) is given by:

$$U = {}^1/_2\,\varepsilon^2\,[E_f\,(\cos^2\theta - \sigma\sin^2\theta)^2 + S_f\,(1 + \sigma)^2\,(\sin\theta\cos\theta)^2] \qquad 2.8$$

Differentiation gives stress f as a function of strain ε.

However, there is another important difference from treatments of yarn mechanics. Rotation at the reversal points will reduce the helix angle and cause extension. The system is thus equivalent to a twisted yarn that is free to untwist under tension. The fractional rotation is put equal to $(-\gamma\varepsilon)$. This leads to changes in the expression for tensile and shear strains. The full energy expression is given by[1]:

$$U = {}^1/_2\,\varepsilon^2\,\{E_f\,[\cos^2\theta - (\gamma + \sigma)\sin^2\theta]^2 + S_f\,(1 + \gamma + \sigma)^2\,(\sin\theta\cos\theta)^2\} \qquad 2.9$$

The value of γ, determined by energy minimisation, $[\mathrm{d}U/\mathrm{d}\gamma = 0]$, is given by:

$$\gamma = [(E_f - S_f)\cos^2\theta/(E_f\sin^2\theta + S_f\cos^2\theta)] - {}^1/_2 \qquad 2.10$$

Substitution shows that the fibre modulus E, which is the term in { } in eqn 2.9, is given by:

$$E = E_f\,S_f\cos^2\theta/(E_f\sin^2\theta + S_f\cos^2\theta) \qquad 2.11$$

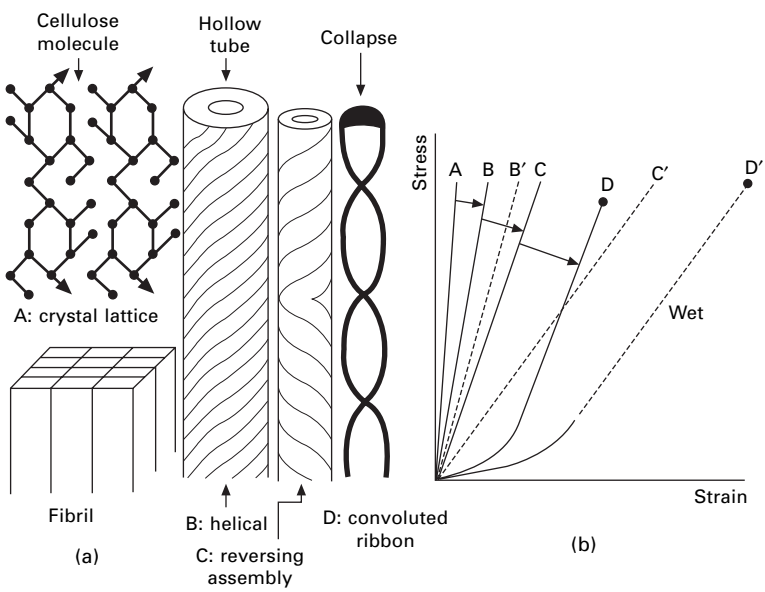
The final input to the prediction of the stress-strain curve of cotton consists of the values of the tensile modulus, E_f, of the fibrils, which will depend on covalent bonding along cellulose crystals, and the shear modulus S_f, which will depend on intermolecular bonding. Treloar (1960) calculated E_f to be

[1]The full analysis by Hearle and Sparrow (1979b) includes a volume energy term, but energy minimisation shows surprisingly that the extension is at constant volume with $\sigma = {}^1/_2$.

57 GPa, and Jawson *et al*. (1968) calculated values between 36 and 67.2 MPa for S_f. Taking the higher value for S_f, eqn 2.11 gives a modulus of 24 GPa for an unconvoluted fibre with a helix angle of 22°. This agrees well with extrapolation of Meredith's (1946) experimental data to zero convolution angle. If we take a typical value of 5 N/tex, which is equivalent to 7.5 GPa, and multiply it by the threefold increase from untreated cotton to cotton tensioned wet and dried, we have a value of 22.5 GPa.

The above discussion relates to dry fibres in which there will be fairly strong hydrogen-bonding between fibrils. In wet cotton, absorbed water will lower the shear modulus. This reduces the resistance to untwisting of convolutions and lowers the shear modulus acting in both the extension of the helical structure and the rotation at reversals.

There are many uncertainties resulting from the complexity of variability, shape and internal structure of cotton, but the treatment outlined here explains the mechanisms involved in the extension of cotton fibres in terms of a reasonable quantitative model. This is summarised in Fig. 2.15 in the reverse order to the above presentation. The modulus of the crystal lattice in the fibrils (A) gives the line A, which is then lowered due to the helical structure (B) and the reversals (C). The convolutions (D) bring in the nonlinearity. For wet fibres the lower shear modulus shifts the lines to B′, C′, D′.



2.15 (a) Structural features of cotton, which determine the tensile properties. (b) Stress-strain plots. Line A is for extension of crystal lattice, lowered to B due to helical structure, to C by untwisting of reversals and to D by pulling out convolutions. The dotted lines are for wet cotton. From Hearle (1991).

The increase in strength with increase of moisture content is due to the release of internal stresses as the hydrogen-bonding is weakened and to the ability to pull the structure into a more highly oriented form without generating stress concentrations. The existence of internal stresses is confirmed by Perel (1990), who found that the apparent crystallite size in the (0,0,1) direction increased from measurements at 20% rh to those at 90% rh.

2.5 Other physical properties

2.5.1 Electrical properties

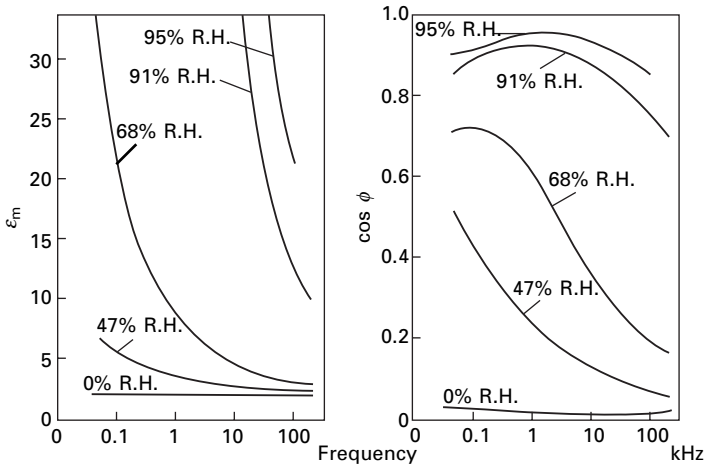
For many fibres, static electrification is the electrical property of most concern but, as shown below, the electrical conductivity of cotton is high enough to dissipate the charge rapidly except at extremely low humidities. Static electricity is not a problem for cotton. For moisture-absorbing fibres such as cotton, conductivity is by movement of charged ions. Salts, which are naturally present in the fibre, increase their degree of dissociation with increase in dielectric constant, thus increasing the number of ions available to transport electric charges. Hearle (1953d) showed that this led to the following relation between electric resistance R and dielectric constant (permittivity) κ:

$$\log R = a/\kappa + b \qquad 2.12$$

where a is proportional to the energy of dissociation with $\kappa = 1$ and inversely proportional to temperature, and b depends on the concentration and valency of available ions.

The above relation fits experimental data well except at very high humidities, when dissociation is complete. Interestingly, salts with bivalent ions do not dissociate so easily and consequently replacement by calcium sulphate increases the resistance. A more detailed account of experimental and theoretical aspects of dielectric properties, resistance and static electrification of fibres is given in Morton and Hearle (1993).

In practice, it is only possible to measure the dielectric properties of an assembly of fibres, which is a mixture with air. Hearle (1954) made measurements on cotton yarns wound on a cone. An outer cone was pressed on to give a packing factor of about 45%. Figure 2.16 shows values of the dielectric constant ε_m and power factor $\cos \varphi$ of the air-cotton mixture. At the lower frequencies, there is a rapid rise in dielectric constant, which is alternatively termed *relative permittivity*, and power factor with humidity. The changes are not as great at lower frequencies. The dielectric constant decreases with frequency and this trend continues in other experiments at frequencies in the megacycle range (Hearle, 1956). Except for some data at low humidity and low frequency, power factor decreases with increase of frequency. When plotted against moisture content M, dielectric constant



2.16 Dielectric properties of cotton yarns between cones at a packing factor of 45%. From Hearle (1954).

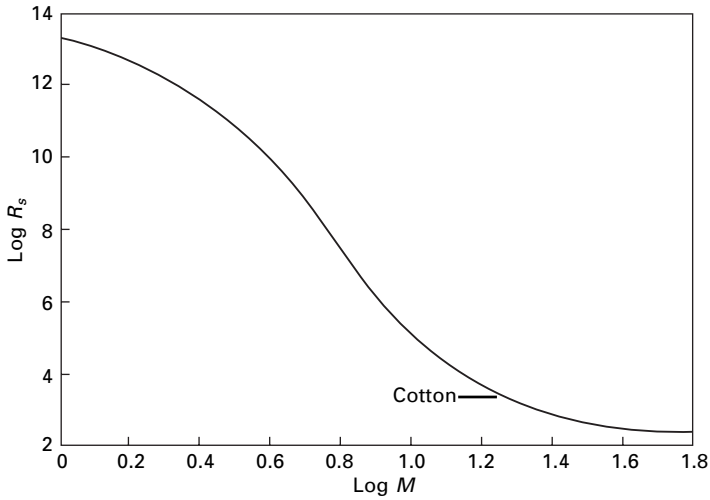
rises rapidly above M = 4% and power factor shows a sigmoidal relation similar to that found for electrical conductivity.

Electrical conductivity was measured by Hearle (1953a) on multiple ends of yarn held between bulldog clips. The results were presented in terms of 'mass specific resistance', which in consistent units equals the conventional specific resistance in (ohm m) multiplied by density in kg/m^3. In practice, values of R_s are expressed in ohm g/cm^2. Figure 2.17 shows the change of resistance with moisture content. The use of a log-log scale is partly because of the many orders of magnitude of change of resistance and partly because, over the important middle range between 30% and 90% rh, there is a linear relation between log R_s and log M. With constants n and K, this gives the equation:

$$\log R_s = -n \log M + \log K \quad \text{or} \quad R_s M^n = K \qquad 2.13$$

If M is expressed as a percentage, the values for cotton are n = 11.4 and log K = 16.7. The high value of the index n reflects the great effect of moisture on electrical resistance, as dissociation of ions increases exponentially in its dependence on dielectric constant.

Cotton shows a linear decrease in log R_s with relative humidity from a specific resistance of 10^{11} ohm g/cm^2 at 10% rh to 10^6 ohm g/cm^2 at 80% rh. Static electrification becomes a serious problem only for values > 10^{10} ohm g/cm^2 (about 30% rh for cotton), so, in this context of high voltages and low charges, cotton is a 'good conductor'. However, the resistance is high enough for cotton to be an effective insulator. Until the middle of the 20th century, when better plastic insulators became available, electric wires were commonly wrapped in cotton, though steps were taken to increase resistance by reducing ion content.



2.17 Change of mass specific resistance Rs of cotton with moisture content M%. Note that M = 7% (65% rh) is at log M = 0.85, close to the middle of the graph. The maximum value of 1.8 is at M = 63%: a high moisture content with water molecules effectively free. From Hearle (1953a).

Purification of cotton can increase resistance by five times; addition of salts lowers resistance, for example by 180 times for 10% of added potassium chloride (Hearle, 1953a). The electrical resistance of cotton decreases about 100 times between 20 °C and 80 °C (Hearle, 1953b). The electrical conductivity of cotton is non-linear, increasing rapidly for voltages below 50 V; this and other complicating factors are reported by Hearle (1953c).

2.5.2 Optical properties

Fundamentally, optical properties are electrical properties at very high frequencies. Refractive index is a measure of polarisability and depends on the orientation of polarisable groups, mainly the –OH groups, in the cellulose molecules. Birefringence is the difference between axial refractive index n_1 and transverse refractive index n_2. The calculated isotropic refractive index is n_{iso}. Table 2.5 gives values of refractive indices measured by Meredith (1946). The calculated isotropic refractive index is n_{iso}. The birefringence decreases with increase in spiral angle, but as discussed in section 2.2.3 this is an average value of the fibril helix angles increased by the effect of convolutions, which cause the main difference between cotton fibre types. The increase in birefringence is due to decreases in n_1. The small scatter of values of n_2 and n_{iso} is probably due to experimental error.

Measurements of regenerated cellulose by Hermans (1949) showed that, after a small increase from 0 to 5% regain, n_2 decreased from 1.534 to 1.508

Table 2.5 Refractive indices and birefringence of cotton related to spiral angle (Meredith, 1946)

Cotton type	Refractive indices			Birefringence	Spiral angle θ
	n_1	n_2	n_{iso}		
St Vincent	1.581	1.530	1.556	0.052	27°
Giza	1.579	1.530	1.554	0.049	29°
Sakel	1.580	1.532	1.556	0.048	29°
Montserrat	1.578	1.529	1.553	0.049	30°
Punj-Amer	1.577	1.530	1.553	0.047	31°
Uppers	1.576	1.530	1.554	0.046	32°
Uganda	1.576	1.532	1.554	0.044	32°
Memphis	1.575	1.532	1.554	0.044	33°
Texas	1.575	1.532	1.554	0.044	33°
Tanguis	1.575	1.530	1.554	0.044	34°
Brazilian	1.574	1.531	1.552	0.044	34°
Oomras	1.574	1.532	1.552	0.043	34°
Bengals	1.574	1.531	1.551	0.043	34°

at 20% regain with little change in birefringence. A similar reduction in n_2 with increased moisture absorption would be expected in cotton, but the birefringence will be affected by the change in helical structure and convolutions due to swelling.

The lustre of cotton fibres is strongly influenced by their ellipticity, *a/b* where *a* and *b* represent equatorial and polar fibre x-section radii respectively Adderley (1924) examined ten cotton types and found that the lustre in arbitrary units ranged from 5.7 for an American cotton with $a/b = 3.07$ to 10.7 for a Sea Island cotton with $a/b = 1.91$. The correlation was not perfect for intermediate values and this may be due to differences in convolutions. A rounder mercerised cotton with $a/b = 1.47$ gave a lustre of 13.9.

2.5.3 Thermal properties

Values for various thermal properties of cotton are reported in the literature. The specific heat of dry cotton is 1.21 J g^{-1} K^{-1} (Magee *et al.*, 1947). However, as discussed in section 2.3.2, the effective specific heat of cotton will be dominated by the heat of absorption as the moisture content changes with temperature. The thermal conductivity of a pad of cotton with a bulk density of 0.5 g/cm^3, i.e., a packing factor of 1/3, is 71 mW m^{-1} K^{-1} (Rees, 1946), which is 2.8 times that of still air. The coefficient of expansion of cotton is 4×10^{-4} K^{-1} (Morton and Hearle, 1993). Cotton does not melt, but decomposes by charring with loss of water at about 200 °C with increased burning to carbon dioxide at higher temperatures. Illingworth (1953) reported that at 100 °C cotton lost 8% of its strength after 20 days and 32% after 80 days; at 130 °C, the losses were 62% and 90%.

As in all polymers, there are secondary transitions, which may be called glass-to-rubber transitions, at temperatures below the notional melting-point when thermal vibrations would disrupt the crystals if decomposition had not intervened. Increase of temperature causes a drop in elastic modulus and a peak in the dissipation factor tan δ. For dry cotton, Meredith (1969) found that tan δ in dynamic bending tests on mercerised cotton was a minimum at about 40 °C. Tan δ was increasing towards one peak at less than –50 °C, which would be due to the loss of rotational and flexural mobility in some covalent bonds, most likely the oxygen bridges, in amorphous regions of mercerised cotton. The effect may not be present in more perfectly crystalline, unmercerised cotton. Going to higher temperatures, there is a small shoulder at about 125 °C and continuing rise to what would be a peak above 170 °C. This change is ascribed to increased mobility at hydrogen bonds. A similar effect was found by van der Meer (1970, 1974) for viscose rayon, who also observed that the peak fell below 0 °C when the fibre was wet. Increased mobility and a low transition temperature would also be expected in wet cotton. The change from above to below the transition temperature when cotton dries is a cause of creasing and wrinkling after laundering.

2.5.4 Friction

The frictional properties of fibres are determined by the state of the fibre surface. In raw cotton there are natural waxes on the surface that may be removed by washing and bleaching. Other finishes may be added to improve processing or to enhance performance in use. Furthermore, the simple laws of friction are not obeyed; the coefficient of friction varies with normal load, form and area of contact, and speed and direction of rubbing. Reported values of coefficient of friction thus vary widely. Table 2.6 gives typical values for the coefficient of friction μ of cotton.

Buckle and Pollitt (1948) measured friction for a coarse grey (unbleached) cotton yarn over stainless steel of radius 0.75 in (19 mm) at standard conditions of 79 yd/min (72 m/min), 25 g initial tension, 70 °F (21 °C) and 65% rh.

Table 2.6 Values for coefficient of friction μ of cotton

System	μ	Reference
Cotton on cotton		
Crossed fibres	0.29, 0.57	Mercer and Makinson (1947)
Parallel fibres	0.22	Morton and Hearle (1993)
Cotton passing over guides		
Hard steel	0.29	Buckle and Pollitt (1948)
Porcelain	0.32	Buckle and Pollitt (1948)
Fibre pulley	0.23	Buckle and Pollitt (1948)
Ceramic	0.24	Buckle and Pollitt (1948)

Increasing speed increased the coefficient of friction from 0.159 at 1.9 yd/min (1.7 m/min) to 0.279 at 120 yd/min (110 m/min). On a finer cotton yarn at 67 yd/min (61 m/min), the coefficient of friction fell from 0.30 at 25 g initial tension to 0.245 at 250 g.

Morrow (1931) found that the coefficient of friction of cotton on steel increases from 0.24 at 0% regain to 0.36 at 11% regain. This can be explained by the increased softening of the fibre, which leads to more intimate contact. Theory indicates that frictional force is proportional to shear strength × area of contact. If contact results from plastic yielding this leads to proportionality to (normal load)^n, where n is between 0.5 and 0.75 depending on the contact geometry. El Mogahzy and Broughton (1993) describe experimental and theoretical studies of the effect of number of contacts in fibre/fibre and fibre/metal contacts. In general, one can say that the coefficient of friction of cotton is highly dependent on the state of the fibre and the test conditions.

2.6 Sources of further information

The great period for the study of cotton structure and properties started around 1920 with the formation of the British Cotton Industry Research Association, which grew to several hundred staff. Later the Textile Research Institute was founded in the USA and the United States Department of Agriculture did a great deal of work on cotton in their New Orleans laboratory. Other laboratories in Europe and India were also active. The National Cotton Council in USA and the International Institute for Cotton in Europe supported research. This period of major research activity ended by about 1980.

Consequently, the major source of information on physical structure and properties of cotton is found in research papers from this early period, particularly those in the *Journal of The Textile Institute* and the *Textile Research Journal*. Books from the same period are another source of information, notably *Matthews' Textile Fibers* (Mauersberger, 1954), Meredith's (1956) *The Mechanical Properties of Textile Fibres* and the chapter by Bailey *et al.* (1963) in *Fibre Structure.* More specialised books are *Moisture in Textiles* (Hearle and Peters, 1960) and *Friction in Textiles* (Howell *et al.*, 1959). More general aspects of physical structure and properties are covered in *Physical Properties of Textile Fibres* (Morton and Hearle, 1993). The review by Warwicker *et al.* (1966), of which about a quarter is directly relevant to this chapter, contains 1484 references.

Finally, one should mention a pioneer in the field, the botanist, W. L. Balls who, after working on cotton growing in Egypt, became research director of a UK spinning company; his *Studies of Quality in Cotton* (1928) still provides valuable insights and information.

2.7 Future trends

The physical structure and properties of cotton have been thoroughly researched. Experimental studies will continue to characterise the properties of particular cottons depending on their type and growth location and conditions. The major new feature is the advent of genetic engineering. To date, this has been used to improve yields and resistance to pests. It has not been used, so far as I know, to modify fibre properties – and conventional breeding has been limited to the more obvious characteristics of length, fineness, colour and strength.

Genetic engineering gives the opportunity to design cottons with properties optimised for particular markets, including new features with special market opportunities. However, if molecular biologists are not to introduce genes at random, it will be necessary to develop a thorough understanding of the sequence: genes → growth of fibre → fibre structure → fibre properties → performance in processing and use. In the context of this chapter, the need is to convert the generic analysis described in section 2.4.6 into a model that can input the structural differences between different cottons. The model would be validated by measurements on current cottons and then used to explore new variants. The model would also need to be developed to include other properties that influence performance, particularly bending and twisting of fibres. The effects of moisture absorption and chemical treatments on structure and properties would also have to be covered. This is a challenging research opportunity, but should be possible with current computer power.

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3
Cotton fibre quality

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3.1 Introduction

Measures of cotton fibre quality may be described by any of, or in relation to, the chemical and/or physical properties described in Chapters 1 and 2. The reason for attributing value to cotton is to gain premiums (or discounts) from the market on the basis of that cotton's suitability for particular end-uses. In fact it can be said that cotton fibre quality is the utility particular cotton achieves in the textile processes involved in its conversion to the final product. Traditionally, the most desirable cotton (*Gossypium spp.*) is said to be as white as snow, as strong as steel, as fine as silk and as long as wool.[1] As well as this, spinners also demand that the fibre be inexpensive.[2] This chapter discusses the fibre properties defined and valued by the textile industry; how these properties are currently measured, and the limitations of the test methods applied to measure each property. For the most part the fibre properties discussed in this chapter are closely linked to the physical and chemical properties already discussed in Chapters 1 and 2, however each of the parameters discussed in this chapter has a large effect on yarn and fabric quality and processing efficiency, and as such, are be used routinely in combination with other parameters to predict the expected quality of the yarn or fabric and the efficiency with which it is produced.

Fibre quality properties, e.g. length, strength, fineness and colour have always been important in determining the value of cotton fibre. These properties and others are measured soon after the cotton is ginned to determine the market value of the cotton, and to reward (or discount) growers for the quality they have grown. Until 50 years ago a sample of cotton taken from the ginned bale was classed against physical cotton standards by a human cotton classer. Comparison with physical standards, whether those of the United States Department of Agriculture (USDA) Agricultural Marketing Service (AMS), to which there are over 20 signatory cotton associations from around the world, or other national country standards, is still the predominant method for measuring the value of cotton fibre. However, there

is currently active organization from within the international cotton industry to promote objective test measurement of important fibre parameters.[3]

The stimulus to determine cotton fibre quality by more accurate and precise objective means is not only based on technical considerations of predicting spinning efficiency and product quality from measured fibre properties more accurately; it is also based on the cost and risk of using cotton as a natural raw material. Raw material costs in a spinning mill comprise up to 65% of mill operating costs. Further, the advocacy for objective testing is also about competition in the world short-staple fibre market and keeping cotton competitive with synthetic fibres such as polyester, which are less variable in nature and more predictable in terms of processing behavior.

For the three short-staple spinning systems used by the cotton textile industry today, i.e. ring-spinning, rotor (or open-end) spinning and air-jet spinning, the fibre properties listed in Table 3.1 are considered especially important. In combination, the listed parameters describe fibres that are sufficiently flexible to accommodate the continuous arrangement and bending of fibers during drafting and consolidation; and which also have optimum surface adhesion to allow smooth drafting.

3.1.1 Cotton classing

Subjective classing by hand and eye with the help of physical reference standards has been the predominant method of grading cotton fibre quality since cotton trading began. Establishment of formal cotton classification standards occurred in the United States after the 1907 International Cotton Congress at a time when the commercial trade of raw cotton and fabrics made from cotton yarns reached significant volumes.[4] Even at the time it was recognized that cotton destined for the manufacture of textiles for household and clothing products, demanded the development of measurements for predicting yarn and fabric attributes. The first cotton classification standards for fibre colour and length grades were established in 1909 by the USDA. The standards for colour were, at first, based on physical samples that exhibited a range of colour. Cotton fibre length was judged by a human cotton classer using a manual technique that involved pulling fibres away from small bundles into a spread of fibres from which the fibre length, or staple length as it is still known, could be determined.

Table 3.1 Major fibre parameters of importance in short-staple spinning systems

Importance rank	Ring	Rotor (open-end)	Air-jet (inc. MVS)
1	Length	Strength	Length
2	Strength	Fineness	Trash
3	Fineness	Length	Fineness
4		Trash	Strength

A Universal Cotton Standards Agreement was established in 1923 between the USDA and 23 other cotton associations from 21 countries.[4] Since this time other cotton nations have developed their own official cotton standards and descriptions, e.g. the Tanzanian Cotton Board (TCB) has developed physical standards based on colour, trash and preparation, good preparation of which is essentially the smooth appearance of the fibre after combing in the lint cleaning process. The USDA Universal Cotton Standards now cover strength, length, uniformity index, micronaire, colour grade, and procedures used to achieve agreement.

3.1.2 Development of instrument test methods

Anderson[5] defined three distinct phases in the development of fibre measurement methods; the first being subjectively based hand and eye perceptions, the second phase from 1920 to 1948, which utilized direct, more objective tests, e.g. microscopes, scales and comb sorters, and the third phase from 1950 to 1970, which arose from industry demand for quicker objective test methods. The high volume instrument (HVI) lines used today (Fig. 3.1) evolved during this period as textile mills installed high-speed manufacturing equipment that places additional stresses on the raw fibres. These instrument-based methods, which except for strength measurements made using a strain gauge, measured fibre properties indirectly via light meters, air-flow meters, pressure gauges and capacitors.

The second and third phases defined by Anderson[5] are actually less distinct as the Fibrograph and Micronaire, two instruments still used today to assess fibre quality, were developed during the 1940s. After 1980, increases in computing power and the development of digital sensors and robotic systems enabled a cotton sample to be measured for multiple properties in less than a minute. Today, one HVI line measures 825 samples for length, length uniformity, short fibre content (SFC), strength, extension, micronaire and colour in a seven-hour, 20-minute shift.[6] Since 1980 there has also been the development of test instruments to measure other important fibre properties such as stickiness, fineness and maturity, and the distribution of fibre properties such as length and trash.

3.2 Length properties

Cotton fibre length is probably the most significant fibre property because it directly affects irregularity of fibre assemblies and longer lengths contribute to the tenacity of yarn via increased frictional forces with adjacent fibres. The presence of short fibre in cotton causes appreciable increases in processing wastes, excessively uneven fibre assemblies, less efficient spinning, and weaker yarns. Cotton is the shortest commercial textile fibre and as such a

3.1 Modern high volume instrument (HVI) lines (photo courtesy of Australian Classing Services, Wee Waa, Australia).

premium is typically paid for long fibre. However, no premium is paid for cotton with good uniformity of length, but nor is a discount applied to cotton with high SFC.

Fibre length is a genetic trait and varies considerably across different cotton species and varieties. Length and length distribution are also affected by agronomic and environmental factors during fibre development, and mechanical processes at and after harvest. Gin damage to fibre length is known to be dependent upon variety, seed moisture, temperature (applied in the gin) and field exposure.[7–9] The distribution pattern of length in hand-harvested and hand-ginned samples is markedly different from samples that have been mechanically harvested and ginned; two processes that result in the breakage of fibres. Cotton that is mechanically harvested and ginned is likely to have an extended tail of shorter fibres or even an additional peak, bi-modal distribution, at shorter lengths.

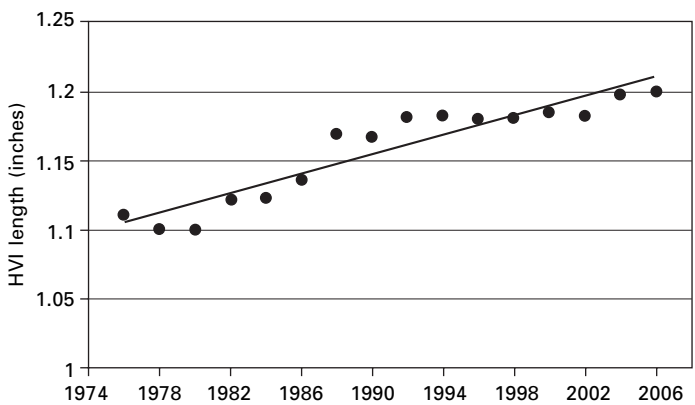
Fibres from a single seed reveal different distribution patterns depending on the region of the cotton-seed that the fibre is taken from. Delanghe[10] found markedly different patterns in fibres taken from the micropylar (upper pointed end), middle and chalazal (bottom rounded end) regions of the cotton-seed, whilst Vincke *et al.*[11] found mean fibre lengths were shortest in the micropylar region of *Gossipyium hirsutum*, *G. barbadense* and *G. arboreum* cottons. Bradow and Davidonis[1] and May[12] reviewed the environmental and genetic factors respectively that effect length and other fibre parameters.

The selected studies they reviewed showed length to be affected by temperature,[13–16] water supply[17,18] and light.[19] Selective plant breeding has resulted in increases in 'staple' length[20] (Fig. 3.2).

Upland cotton varieties (*G. hirsutum*), which represent 90% of the world's cotton production have staple lengths typically ranging from 1 (25.4 mm) to $1^1/_8$ inches (28.6 mm). Fibre lengths of Upland cotton have increased over the last 20 to 30 years with new Upland varieties extending this range currently to $1^1/_4$ inches (32 mm). Pima-type cotton (*G. barbadense*), which includes 'Sea Island' and 'Egyptian' long staple (LS) and extra-long staple (ELS) type cotton and represents around 8% of the world's production, are longer and finer than Upland cotton. The staple length of *G. barbadense* cottons typically ranges from $1^1/_4$ (32 mm) to 2 inches (50.8 mm). Fibre from other cotton plant species such as *G. Arboreum* and *G. Herbaceum* is produced in small quantities (< 2%), and typically have very short, coarse fibre with staple lengths ranging only to 1 inch (25.4 mm).

3.2.1 Measuring fibre length

Fibre length is defined usually as the upper-half mean length (UHML) or 2.5% span length (2.5%SL) from a Fibrogram beard. Both measures coincide in a roundabout way with the classer's staple. Historically, fibre length is measured in inches (in 1/32-inch divisions) although conversion into millimetres is now common. There are various methods of measuring fibre length. Length can be measured simply by aligning the end length of a fibre against a ruler and noting its length. However, this approach is tedious and cotton fibres in any sample vary considerably in their length such that measuring a representative sample in this way is impractical. In the past cotton classers were trained to evaluate 'staple' length by measuring the length of a paralleled bunch of fibres



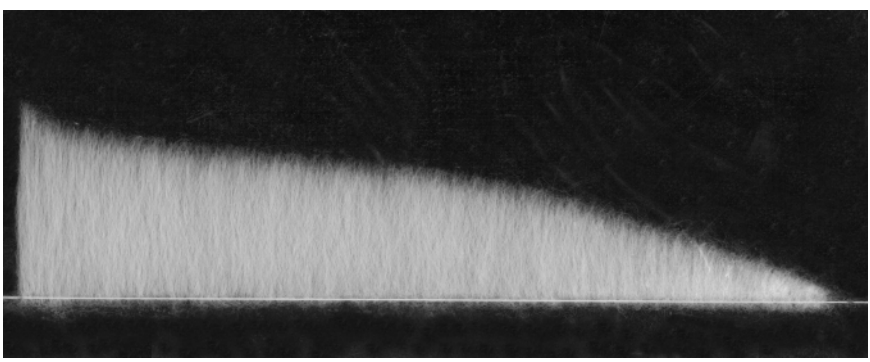
3.2 Improvement in Upland HVI staple length (UHML) [20].

against one of their digits. The Textile Institute definition of staple length noted that 'the staple length corresponds very closely to the modal or most frequent length of the fibres when measured in a straightened condition'.[21]

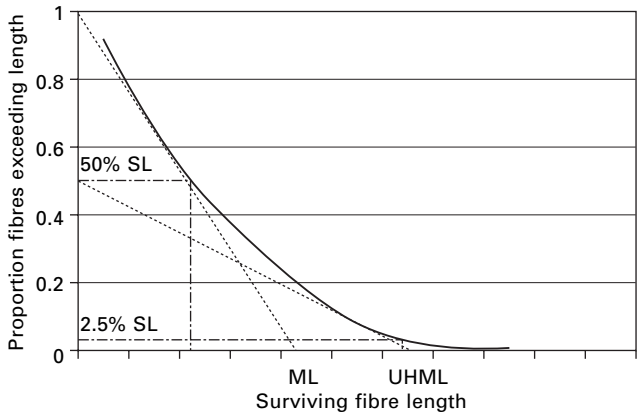
Accurate determination of fibre length can be achieved using fibre arrays or staple diagrams (Fig. 3.3) produced using a comb-sorter apparatus. The diagrams can be used to define upper staple lengths such as the upper-quartile length (UQL), which is the length of the shortest fibre in the upper quarter of the length distribution by weight, and other length parameters such as mean length, 'effective' length and SFC.[22,23] Comb-sorter apparatus uses a series of hinged combs separated at 1/8-inch intervals, to align, separate and allow the withdrawal and description of weight-length or number-length groups from a sample.

Whilst comb-sorter methods are accurate they are unacceptably expensive in terms of operator cost, too slow and too imprecise for routine testing for commercial trading purposes. To this end the Fibrograph Tester instrument was developed in the early 1940s by Hertel.[24] Initially used as a stand-alone instrument it was later incorporated into HVI lines. Test specimens are fibre beards prepared either manually for stand-alone and older HVI instruments, or automatically from a bale sample by newer HVI units. The fibre beard is held in a comb that is inserted into the instrument and scanned by a light source. The variation in density (light intensity) of the different lengths of fibre is recorded and reproduced in the form of a length-frequency curve called a Fibrogram (Fig. 3.4). Interpretation of the Fibrogram takes into account the comb gauge length, i.e., the depth of the comb at which fibres are held (0.25 inch).

Two different kinds of fibre length measurement can be generated from a Fibrogram; mean lengths and span lengths. Mean lengths, e.g. UHML, which is the mean length by numbers of the longer half (50%) of the fibre by weight,[25] and the mean length (ML) are more commonly used since they



3.3 Comb-sorter staple array of ginned cotton (CSIRO Textile and Fibre Technology, Belmont, Australia).



3.4 Fibrogram showing position of mean (ML and UHML) and span length (2.5% SL and 50% SL) measurements.

relate the mean of percentages of fibres represented in the Fibrogram. Span lengths, which came about as a result of a technical shortcoming in the ability of the first digital Fibrograph to graphically run a tangent to the Fibrogram, represent fibre extension distances, e.g. the 2.5%SL represents the distance the longest 2.5% of fibres extend from the comb.

Proponents of the Fibrograph make the point that the fibre beard scanned to produce the Fibrogram expresses a fibre length distribution comparable to the situation, during the processing of fibre into yarn, at any instant of time, of fibres caught and protruding from draft rollers or aprons. It is this relationship, some say, which makes the Fibrogram information superior to comb-sorter arrays. However, others note that fibres held in the Fibrograph comb are less parallel in arrangement than fibres found in sliver and yarn assemblies. Further, fibres in the comb are caught randomly along their length and there is a high probability, dependent upon fibre length, that the ends protruding from the comb represent the same fibre curled around one or two teeth of the comb. Much work has been undertaken in the past to relate comb-sorter measurements to Fibrogram measurements in order to provide calibration material for the Fibrograph. However, although significant correlations have been obtained on some data sets,[26] the relationships between the two are never perfect since the fibre assemblies are never the same and each measures or senses different parameters.[5] Further, specimen selection for Fibrograph analysis tends to be length and weight biased, i.e. longer fibres tend to be selected by the Fibrosampler comb and in describing length on weight basis the heavier longer fibres are accentuated in the distribution.

Other currently used methods for measuring fibre length include the Uster Advanced Fibre Information System (AFIS) length and diameter module, which yields information on single fibre length and is able to build and

report length by number and by weight distributions. The AFIS is also calibrated to measure fineness and maturity, neps and trash and dust. Measurement is based on detecting the amount of light that is scattered and occluded by a fibre or particle as it is transported by air through a beam of near-infra-red light. When the fibre or particle impinges on the beam the electro-optical sensor records two signals, i.e. scattered and occluded light. A computer program analyzes the signals and presents mean and distribution data on the particular parameter. The AFIS takes a 0.5 gram sample of fibre hand-drawn into a 25 cm sliver. Test time is around three minutes including sample preparation, which limits the test to laboratory analyses rather than commercial testing. Further, results are influenced by operator technique in preparing samples.

Cotton length measurements using the Peyer Almeter AL-101 system are less frequently reported. This instrument, a version of which is widely used to test wool fibre length, is less common in cotton testing because of speed and sample preparation issues. The measurement is based on a scanning light measurement like the Fibrograph but is able to return a staple diagram by number on the basis that the fibre ends of the sample are aligned during the test. Using an estimate of the sample weight allows the AL-101 to calculate length characteristics according to three length distribution types; unbiased distributions by number, weight-biased and a length-weight span length distribution.[27] The Premier aQura is a new cotton test instrument that automates sample preparation and measures length from an end aligned sample in the same way as the AL-101.

3.2.2 Length uniformity

Length uniformity is generally defined as either the uniformity index[27] (UNI), which is the ratio between the ML and the UHML expressed as a percentage, or the uniformity ratio (UNR), which is the ratio generally between the 2.5%SL and the 50%SL.[28] Table 3.2 lists the descriptive designations given to HVI generated values of uniformity index by the USDA AMS.[29] Inter-laboratory coefficients of variation (CV) for UNI are good; across a range of different cottons tested as part of the Bremen Round Trials between 2003 and 2005, inter-lab CVs ranged between 0.67% and 1.09%.[30]

3.2.3 Short fibre content

The most common definition of short fibre content (SFC) is the proportion by weight of fibre shorter than one half inch (12.7 mm). The value is of concern to textile manufacturers because it relates directly to the amount of waste extracted in combing and cotton with high values has a detrimental effect on the quality of yarn and fabric.[31–33] Short fibre content measured by

Table 3.2 USDA descriptive designation for HVI uniformity index values

Descriptive designation	HVI uniformity index
Very high	Above 85
High	83 to 85
Average	80 to 82
Low	77 to 79
Very low	Below 77

the HVI is referred to as short fibre index (SFI) and is the most widely used value to describe SFC in a sample, even though short fibres are not actually measured directly by the HVI Fibrograph, nor can the instrument be calibrated. Typical SFI values vary from 4–12% in ginned lint and are much lower in un-ginned lint. Precision is generally poor by comparison with test methods for other properties. Inter-laboratory CVs for SFI across a range of different cottons tested as part of the Bremen Round Trials between 2003 and 2005 ranged between 15.8% and 24%.[30]

Accuracy of the measure of HVI SFI is debatable. Calibration and selection of appropriate predictors are the main issues. In the past, SFI has been calculated from Fibrogram data using first-order algorithms that used measures such as 2.5%SL and 50%SL and the 2.5%SL and the uniformity index[34] as independent variables. More recently SFI in HVI lines has been predicted using second-order algorithms containing HVI length and uniformity index[35] (see eqn 3.1). The author notes that because these length measures are functions of the fibre-length distribution they will work well only for cotton exposed to similar picking and gin practices. Currently, a SFI value determined by an algorithm, which calculates the fibre array curve from the Fibrogram, is being tested. From this a weight-based length distribution is derived from which the percentage of short fibres at one-half inch is calculated. The mathematical basis for the conversion algorithms is described in reviews by Woo[36] and Zeidman and Batra.[37] The relationship between SFI measured this way and SFC measured by the AFIS is reasonable with a correlation of 0.96 quoted for a series of standard cottons with different staple lengths.[38]

$$Z = a + bX + cX + dX^2 + eY^2 + fXY \qquad 3.1$$

where
Z = predicted short fibre index,
X = HVI length,
Y = Uniformity Index,
a = 384.3966, b = –120.3791, c = –6.7003, d = 12.4901, e = 0.02957 and f = 1.0306

As well as the issue of repeatability in the SFC measurement, much debate is currently centred on the definition of SFC; the view held is that the one-half inch definition is inadequate given that spinning machinery is largely adjusted to accommodate the proportion of longer fibres, synonymous with the standard measures of staple length. The argument for changing the one-half inch benchmark is that for a given amount of fibre damage short-staple cotton will show a higher percentage of short fibres than longer staple cotton. One inch staple fibre is not necessarily unfortunate if processing equipment, i.e. draft zones have been set up for this length fibre. Short fibre content is therefore a relative number that should be minimized as a proportion of the measured long or effective length so that problems associated with uncontrolled fibres can be avoided. Heap[39] proposed a measure of relative SFC, defined as the percentage of fibres by weight shorter than one-half of the staple length (or UHML).

Kearny-Robert *et al.*[40] proposed and illustrated the concept of the broken fibre content (BFC), which they propose would be a more accurate measure of SFC, since the term allows for separation of inherent SFC from 'phenotypic' SFC. El-Moghazy and Krifa[41] define the length utilization efficiency (LUE) expressed as the ratio between the percentage of fibres longer than an upper threshold, of nominally one inch, and those shorter than a lower threshold, nominally a half inch, although its value at these thresholds had yet to be determined.

3.3 Transverse properties

Cotton fibres are single elongated plant cells and their growth from the cotton seed epidermis is determined largely by the environmental conditions. A mature fibre is defined as one that has achieved an acceptable degree of cell wall thickening relative to the perimeter of its cross-section. Conversely, an immature cotton fibre is one that has little or no cell wall thickening. The perimeter by itself, and which is largely genetically determined, defines the intrinsic or biological fineness of a cotton fibre, although cotton fibre fineness is nearly always expressed in terms of linear density, defined as the mass per unit length. Units are usually given in tex (grams per km) or more usually for fibres, millitex (milligrams per km). The average linear density depends on both perimeter and the degree of wall thickening (maturity). Intrinsically fine cottons of small perimeter can give lower values or mass per unit length than coarse cottons of large perimeter. For a constant perimeter mature fibres have a higher degree of wall thickening.

Both properties are regarded as important; both define the number of fibres required in a yarn cross-section, a number which has significant effects on yarn quality and processing efficiency. Both also have significant effects on fibre lustre and degree of dye uptake. Immature fibres are associated with

the formation of small fibre entanglements called neps, irregularities in processed fibre assemblies including finished yarns, non-uniform dyeing of fabrics and decreased processing efficiency. Good reviews on test methods to the 1980s, which remain largely relevant today, and the importance of fineness and maturity to the spinner include those by Ramey[42] and Lord and Heap.[44]

3.3.1 Measurement of fibre maturity

Whilst it is easy to define fibre maturity, measurement is more difficult. Limitations of the test methods currently available are slow test times making large numbers of measurements impractical and/or the test methods measure fibre parameters not solely related to fibre maturity, e.g. Micronaire measures specific surface area by the air pressure differential across a weighed plug of randomly distributed fibres. Maturity can also be expressed as the absolute wall thickness or wall area measured directly from microscope images of transverse sections (Fig. 3.5). However, because average wall thickness tends to increase with increasing perimeter, it is an unsuitable measure for comparing levels of maturity between different cottons. Moreover, the process of sectioning cotton fibres and measuring their cross-sectional area is a process fraught with experimental and sampling type errors.

3.5 Cross-sections of cotton fibres embedded in methyl-butyl methacrylate resin showing cell wall and lumen (CSIRO Textile and Fibre Technology, Belmont, Australia).

It is proposed[43,44] that the most satisfactory expression of maturity is one that measures maturity independently of differences in intrinsic fineness. Thus the degree of thickening (notated θ) is defined as the ratio of the cross-section area of the fibre wall (A_w) to the area of a circle of the same perimeter (P) as the fibre cross-section (see eqn 3.2).

$$\theta = 4\pi A_w/P^2 \qquad 3.2$$

The ratio is equal to unity for a completely solid circular fibre and becomes smaller for fibres with less wall development. Mature cottons have average θ in excess of 0.60 whilst particularly immature cottons have average θ values of less than 0.30. In all cottons there will be a wide distribution of θ values, e.g. a sample of mature cotton will contain fibres with θ values ranging from 0.15 through to 0.96.[45] Ratios of other cross-sectional and longitudinal geometric measurements have also been used to express maturity although θ remains the preferred and most used measure.

3.3.2 Measurement of fibre fineness

The Micronaire is the most widely used test method for obtaining estimates of cotton fibre fineness. The test measures the resistance offered by a weighed plug of fibres to a metered airflow. The change in the rate of airflow or pressure is correlated with measurements of linear density although it is now understood that the change in airflow is dependent upon specific surface area. The test was incorporated into HVI lines from the beginning of their development and has been changed to improve test time and precision from the earlier laboratory bench-top instrument of the late 1940s, which took a couple of minutes to measure a well blended and conditioned sample of 50 grains (3.24 grams) in weight. The HVI version now takes a 10 gram sample of raw, unblended but conditioned fibre from the bale sample and completes the test in seconds. The scale on the Micronaire is marked in micrograms per inch, which is based on an observed linear relationship between air permeability and linear density for a range of cotton samples of similar maturity. Subsequent testing of immature cotton produced results that varied significantly from actual weight per unit inch determinations. Further studies showed the relationship between Micronaire and fibre weight was curvilinear and that changes in fibre maturity produced concomitant variations in Micronaire readings.[46] Equation 3.3 shows the relationship between Micronaire (X) and the linear density (H) and maturity (M), measured as maturity ratio,[56] determined in ref. 46:

$$MH = 3.86X^2 + 18.16X + 13 \qquad 3.3$$

Despite these shortcomings the Micronaire test is still widely accepted on the basis that the usefulness of other expressions for cotton fibre fineness,

including perimeter, diameter or ribbon width, cross-sectional area and standard fibre weight, is also hindered by inter-relationships that exist between them and other parameters such as maturity and the density of the fibre. Inter-laboratory CVs for Micronaire across a range of different cottons tested as part of the Bremen Round Trials between 2003 and 2005 ranged between 1.7% and 3.2%.[30] Table 3.3 lists the typical range of Micronaire values found in Upland cotton together with comments on the type of cotton they represent from a market viewpoint and the range of premiums and discounts applied to particular values. The Micronaire scale is nominally calibrated from 2.3 μg/inch to 8.0 g/inch,[47] and suffers from significant error at either end of the scale. An alternative scale exists for Pima-style cotton.[48]

3.3.3 Methods for separating fibre maturity and fineness

The need to separate the widely used Micronaire into its fineness and maturity components is of particular importance to producers of fine, mature cotton which can be wrongfully discounted because low Micronaire values are taken as indicating immaturity. For example, there is cotton grown in the 3.3 to 3.7 range in Table 3.3 that is actually fine and mature and therefore should have a premium rather than a discount applied.

The International Textile Manufacturers Federation (ITMF) Working Group on Fineness and Maturity advocates that any instrument measure of fibre maturity should give results that vary directly with θ.[44] However, whilst theoretically more accurate, this direct method suffers from significant experimental error due to the fine detail involved in preparing fibres for measurement and the limited number of fibres that can be practically measured. The same issue applies to Standard Methods for determining fibre linear density.[51] These issues have limited the measurement and application of reference method values to only a few laboratories around the world and left fineness and maturity measurement to indirect methods such as Micronaire, the Uster AFIS and the 'Shirley' Fineness and Maturity Tester (FMT), a

Table 3.3 Micronaire values for Upland Cotton

Micronaire (μg/inch)	Comments	Discounts applied (points* per pound [49, 50])
< 3.2	Significantly immature	400 to 1400 pts off
3.3–3.7	Immature	200 to 500 pts off
3.8–4.5	Fine and mature fibre for fine to medium count yarn	50 pts on for 3.8 to 4.2 range
4.6–4.9	Coarse fibre for coarse count yarn	
> 5.0	Significantly coarse	250 to 700 pts off

* 100 points = 1 US cent.

double compression airflow instrument that relates the pressure differential for air metered at two flow rates between a plug of fibres compressed to two volumes.[52]

Over the last twenty years a number of methods different from those already discussed have been investigated for their potential to measure fibre fineness and maturity separately. Near-infra-red reflectance (NIR) spectroscopy was investigated extensively for measuring fibre fineness and maturity because the speeds that can be applied in measurement and sample preparation suit inclusion in HVI lines. However, the method largely measures the physical scattering of light from the specimen, a response that correlates very well with Micronaire and other descriptions of surface area. A thorough review of published work on its application to measuring cotton fineness and maturity has been written by Montalvo and Von Hoven.[53] Other more recent and promising investigations have focused on automating already standard direct methods utilizing high-speed digital cameras and image analysis to measure fineness and maturity. Two such methods are the Commonwealth Scientific Industrial Research Organisation (CSIRO) SiroMat,[54,55] which measures maturity based on the interference colours transmitted by fibres under crossed polars,[56] and the CSIRO Cottonscan,[55,57] which measures the length of a weighed bundle of fibre snippets suspended in a liquid as they pass through an optical cell.

3.4 Tensile properties

The ability of cotton to withstand tensile force is fundamentally important in the processing of cotton. Yarn strength correlates highly with fibre strength, and good tensile strength specific to fibre fineness, is an important factor in resisting damage through the gin, particularly through the lint cleaner.[58] A minimum tensile strength exists for base grade cotton with large discounts for fibre with values below this level. Table 3.4 lists the descriptive designations given to HVI measured values of tenacity by the USDA AMS.[29] Much of the world's exported cotton exceeds these tenacity values. However, no premiums are paid for high tenacity values although improved tensile properties remain a primary objective for cotton plant breeders.

3.4.1 Tensile measurement

The fundamental aspects of tensile strength testing are explained in depth in Chapter 2. To recap, the maximum resistance to stretching forces developed during a tensile test in which the fibre or fibre bundle is broken is called the breaking load, and is measured in terms of grams (or pounds) weight. In order to compare cotton fibres of different fineness the breaking load is normalized by dividing it by the fineness of the fibre measured in terms of

Table 3.4 USDA descriptive designation for HVI tenacity values

Descriptive designation	HVI tenacity (grams per tex)
Very weak	< 20
Weak	21 to 23
Average	24 to 26
Strong	27 to 29
Very strong	> 30

linear density. Tenacity is a useful parameter for describing fibre quality because different cotton varieties and growths can be compared directly with each other and with values for the subsequent yarn or fabric.

Rapid measurement of fibre tenacity and breaking extension is currently realized through HVI measurement of these properties. The current HVI instrument that measures tensile properties evolved from laboratory bench fibre bundle test method instruments like the Pressley Tester and later the Stelometer. In both, a flat bundle of fibres is prepared and the ends fixed between two clamps. A controlled rate of load is applied; in the Pressley Tester by the application of a beam-lever mechanism, and later in the Stelometer by a dashpot controlled pendulum assembly, which improved reproducibility over the Pressley Tester and added the measurement of breaking extension. The broken fibre bundle is weighed using a micro-balance and the result expressed as the average tenacity of that bundle. Average single fibre test results correlate reasonably well with bundle test results, with differences attributable to fibre interaction within the fibre bundle and subsequent effects on the 'weak-link' theory, particularly at small to zero gauge lengths.[59] Table 3.5 from ref. 59 lists the tenacity measured on a Pima cotton tested in single fibre and fibre bundle forms over a series of gauge lengths. The drop in tenacity values is attributed to a 'weak-link' effect in both situations.

Bundle tests measure the tensile properties of the weakest and least extensible fibres included in the bundle. Suh *et al.*[60] pointed out that a typical bundle strength test measures only 1/25,000,000th of the fibres in a bale. The use of small, flat bundles of aligned cotton fibres expedites accurate measurement that could be obtained only through exhaustive sampling and testing of thousands of single fibres. However, the methods of bundle preparation and the gauge length at which they are broken have significant effects on the end result. Residual crimp adversely affects the bundle force measurement in HVI lines. If a bundle is not flat then not all fibres will contribute directly to the load applied. The same is true if fibres are not 100% extended between the jaws by brushing.[61] Fibre specimens prepared by automatic samplers were more representative of cotton lint than specimens prepared for strength tests by conventional methods.[62] Further, the gauge length at which fibres

Table 3.5 Pima cotton stress properties at different gauge lengths using different tensile tests

Nominal gauge length	Tenacity (gf/tex)	
	Single fibre	Flat bundle
0-inch	52.23	40.67
1/8-inch	42.92	27.9
3/16-inch	39.61	25.26
$^1/_4$-inch	37.65	23.41

are broken introduces an inverse length bias on the test, particularly if a sample has a high SFC.

Use of laboratory bench bundle testers is diminishing and most tensile values reported today are generated using HVI lines. Inter-laboratory CV results for fibre strength across a range of different cottons tested as part of the Bremen Round Trials between 2003 and 2005 ranged between 3.6 and 5.1%.[30] Aside from increased speed, due to faster equilibrating strain gauges and the development of high-speed measurements of specimen linear density using light, the success of the HVI strength measurement has arisen from the change in specimen loading to a constant rate of extension rather than a constant rate, which eliminated force measuring errors caused by hardware accelerations.[63] Godbey *et al.*[64] varied the extension rate of the clamping jaws in an HVI over a wide range, and showed tensile strength increased with rates of extension at moderately high speeds and then declined at near-ballistic speeds of load. Since the measurements of specimen linear density do not provide sufficient accuracy, strength calibrations are performed by testing calibration cottons whose bundle strength value has been established. The strength values of calibration cottons are established by testing them on other HVI systems, calibrated with calibration test cottons.

3.4.2 Extension

As well as average tenacity, breaking extension, which is also termed extensibility and elongation is also measured, although the value of this parameter in the market is less understood. No premium or discount is paid on the basis of this property and only a small number of high-end spinning mills appear to pay attention to this property.[2] Little or no attention is paid also to the continuous record of load versus extension although it is likely that plant breeders will take an interest in new varieties that withstand higher breaking loads but which reportedly have lower breaking extensions.

3.5 Colour

Objective measurements of cotton fibre colour are defined in terms of the Nickerson-Hunter colour diagram, which describes colour in three planes; reflectance (Rd), red/green (a) and yellow/blue (+b). The red/green plane is not used because the range of values across physical cotton standards is relatively small and its exclusion simplified the colour classification. The Nickerson-Hunter diagram scale runs from 40 to 85 for Rd values, although the calibrated range of the two photo-sensors in the colorimeter of HVI lines, using physical colour tiles, is from 60 to 90 and from 5 to 15 for yellowness values, with a calibrated range of 7 to 11. The colour of cotton lint has always played a major part in assessing fibre value although for much of the base grade export cotton, e.g. USDA colour grade 31 traded each year, colour becomes largely irrelevant after blending in the spinning mill where cotton of colour grades 31 and higher are very similar to each other in terms of processing ability.

The USA and many other cotton-producing nations use USDA classing colour grade to describe the colour of cotton. Under this system colour is related to physical 'universal' cotton standards, which have names and a number identity. In the 1960s the 'Universal' standards were overlaid by a XY plot of Rd versus +b values to enable comparison between objective measurements using a colorimeter and subjective assessment of colour. The USDA colour grades are listed in Table 3.6[29] with typical ranges of Rd and +b values applicable to each grade. These colour grades refer only to Upland (*G. hirsutum*) cottons, which represent the bulk of the world crop. *Gossypium barbadense* have a creamier yellow appearance and are distinctly different in terms of Rd and +b ranges. Discolorations due to dust, contamination, rain damage, ultraviolet radiation, insect secretions, heat and microbial blooms attract different descriptions, e.g. colour grade 32 relates to a middling grade cotton with light spot. More recently, in the name of objectivity, the USDA AMS have required that colour grade be assessed entirely by objective measurement using the colorimeter operated within the standard HVI line.

Table 3.6 USDA Colour grades and corresponding Rd and +b values

Classer USDA grade		Colorimeter Rd	+b
Good middling	11	80–82	8.2–11.2
Strict middling	21	78–81	7.8–10.2
Middling	31	75–79	7.0–9.8
Strict low middling	41	71–78	5.8–9.0
Low middling	51	66–74	5.2–8.4
Strict good ordinary	61	60–67	5.0–8.6
Good ordinary	71	54–62	5.0–8.0

3.6 Impurities in cotton

3.6.1 Trash

Trash particles or visible foreign matter (VFM) in cotton are typically plant parts that are incorporated into the seed-cotton during harvest and then broken down into smaller pieces during mechanical ginning. Chief components are pieces of stem, bract, bark, seed-coat fragments, motes (whole immature seeds) and leaf. Trash accounts for 1–5% by weight of baled cotton with the amount and type of trash reflected in the leaf and colour classing grade of particular cotton.

The need to determine the amount and type of trash in a particular cotton fibre is based on the effort required to clean it, the adverse effects on yarn quality and process efficiency and the realized yield of fibre, in particular raw cotton. Whilst larger particles of cotton fruit and leaf trash affect the classer's leaf grade they are easier to remove during processes in the spinning mill. The presence of bark and grass is a more serious problem because their fibrous nature makes these contaminants difficult to separate from the cotton fibre. Bark or grass spun into yarn and then knitted or woven into fabric, results in costly claims to the seller of the yarn or fabric. As a result the presence of bark and grass in the classer's sample attracts heavy discounts at classing. Pepper trash, which comprises very small particles of plant matter and dust, is more difficult to 'see' and even though by weight represents a small proportion of the bale, creates large problems in rotor spinning. The sensitivity to rotor spinning of small trash and dust particles has led to the development of instruments that measure the different aspects of trash content; the Uster AFIS Trash and Dust module separates and measures the amount of trash and dust by number and by weight; the Micro-Dust and Trash Analyzer (MDTA3), which has had several manufacturers, separates trash and dust particle fractions via a series of filters, allowing expression of a weight-based measure.

Trash content in a particular cotton is still largely determined by subjective assessment against physical and descriptive grades. Determination by instrument is either too slow, e.g. gravimetric based methods, or too imprecise, e.g. optical (scanner) methods utilized in current HVI lines. The USDA ARS has been investigating the latter methods since the late 1970s when Barker and Lyons[65] used a TV monitor to capture images to measure trash. Research over the last 20 years on the application of scanning devices (TV and video cameras were followed by digital cameras and scanners) for measuring trash has focused on the spectral contribution of colour and trash particles, gaining consistent illumination and contrast in samples to ensure accurate thresholding of scanned images, measuring the effects of pixel resolution and thus trash particle edge definition and calibration of image shape to define the type of trash 'seen' by the analysis.[66]

In 1992 USDA cotton grades were separated into colour and leaf grades. Table 3.7 lists the percentage area of trash, i.e. the percentage area of sample scanned covered by leaf particles, in USDA physical standards scanned by the HVI Trashmeter (of 1992)[66] with the USDA Classer's Leaf Grade scale. A new set of six glass-covered physical samples covering a similar range of trash areas is currently in use in 2006, however, inter-laboratory CVs for the HVI Trashmeter units are still too high[30] and are outside USDA prescribed performance specifications.

3.6.2 Neps

Neps occur in all ginned cotton but hardly at all in unpicked seed-cotton. Neps are fibre entanglements that have a hard central knot that is detectable. Harvesting, ginning (particularly lint cleaning), opening, cleaning, carding and combing in the mill are mechanical processes that affect the amount of nep found in cotton. The propensity for cotton to nep is dependent upon its fibre properties, particularly its fineness and maturity, and the level of biological contamination, e.g. seed coat fragments, bark and stickness. Numerous articles have been published on the conditions for the formation of neps and their deleterious effects on yarn and fabric appearance. Notable among these is the early defining work by Pearson,[67–69] the review of research by Mangialardi[70] and the more recent review of the subject at large by Van der Sluijs and Hunter.[71]

The formation of a nep usually centres around some sort of catching device around which fibres collect and become entangled. Three types of nep are defined throughout the literature; mechanical neps, biological or shiny neps and seed-coat fragment neps. In mechanical neps, the nep nucleus comprises folded immature or fine fibre, although mature fibres are also found. Similarly, trash particles including seed-coat fragments and stick, leaf and bark pieces may contribute to the formation of a nep. In some cases the contents of the fibre lumen (the fibre cell protoplasm) can escape causing fibres to stick together with the cohering fibres becoming the nucleus to

Table 3.7 HVI trashmeter area versus USDA leaf grade

Percent area	Classer's leaf grade
0.08	1
0.12	2
0.18	3
0.34	4
0.55	5
0.86	6
1.56	7

form a biological nep. Other naturally occurring 'cements' such as the exudates from insects (see stickiness) or the cotton flower can also act to coalesce fibres and create neps. Mechanical processes involved in taking fibre to the yarn stage also influence the extent to which neps are formed although neps formed from overly aggressive processing are not necessarily correlated with the above fibre properties.

Mechanical neps

The formation of mechanical neps is dependent on two factors; the properties of the fibre that enable it to resist collapse and buckling when frictional and direct forces are applied and the type and degree of mechanical processing exerting force on the fibre. Properties that affect the degree of nep formation include fibre immaturity, fineness (micronaire), low strength, length (in relation to the aspect ratio), high and low wax content and resistance to bending and twisting. Dever *et al.*[58] found nep formation was influenced and inversely related to fibre maturity and directly related to the trash content of cotton. The combination of long-staple length and fibre fineness was conducive to nep formation during mechanical manipulation. Together with non-lint content, these fibre properties predicted nep formation better than any single fibre property. Alon and Alexander[72] suggested that processing fibres produces neps through a stress build-up and sudden realease mechanism, which induces buckling along the fibre length. The propensity for a fibre to buckle is strongly correlated with fibre properties such as maturity, fineness and length. Marth *et al.*[73] found an inverse logarithmic relationship between neps in card sliver and Micronaire values. Fibre with micronaire values less than 3 had more than four times the number of neps greater than fibre with Micronaire values greater than 3.5.

The number of mechanical neps found in cotton has been surveyed many times by workers through each stage of processing from the boll through ginning to the spinning mill.[71] Typical nep numbers found at each stage of mechanically harvested and ginned cotton through to the mill are listed in Table 3.8. Although there is no discount applied to cotton on the basis of its measured nep content most spinning mills prefer fibre with low nep numbers. A value of 250 neps per gram, as measured by the AFIS nep instrument, is often nominated as a maximum value.

Biological neps

Unlike mechanical neps, the nuclei of biological or shiny neps are not formed as a result of a mechanical process. They are found in the opened cotton boll and are thought to form when sticky fluid from the cell protoplasm leaks onto fibres causing them to stick together. It has been noted that the fibres in

Table 3.8 Mechanical neps found through each stage of production and processing

Process	AFIS neps per gram
Field	
Boll	30
Harvest	90
Gin	
Pre-clean	115
Pre-gin	140
Pre-lint cleaner no. 1	210
Pre-lint cleaner no. 2	290
Bale	300
Pre-card	400
Card sliver	90
1st Draw passage	80
Comber lap	60
Comber sliver	20

these neps are usually dead or very immature and are stuck together in a parallel arrangement.[74,75] This suggests that these neps are formed when the boll ripening process is interrupted by insect attack, extreme weather or the premature application of a harvest aid. When these fibres are processed they do not separate from the cemented clump, although the clump may be broken into smaller particles. The clumps tend to be larger prior to ginning and are broken down into smaller particles during ginning and other mechanical processes. The concern for weavers and knitters is that these neps survive processing and show up as white and light-coloured un-dyed specks on finished fabric.[76]

Measurement of neps

When cotton was assessed largely by hand and eye, high levels of nep in the bale or classing sample would indicate that the cotton was likely to be immature. However, subjective assessment of nep levels is unable to be any more than an indicator of potential problems in later processing. There are several methods for measuring the number of neps in loose fibre or mechanically prepared fibre webs. Some involve counting neps directly while more recent methods utilize electro-optical signals and/or digital cameras to measure the number and also the size and shape of neps in a sample. Methods for measuring neps in loose fibre can be divided into four general groups.

1. Manual assessment, where neps in cotton are counted in thin webs prepared by a carding machine or by hand; such methods have become less practical as speeds of other fibre test methods have increased. Further, there is

always difficulty in obtaining reproducible results when the counting is conducted by different operators.

2. Gravimetric assessment, where dust, trash and neps are mechanically separated in a trash separator and weighed; the difficulty with this approach is that neps are not separated from other trash and non-lint particles. There is also the question of whether the opening process in the separator also contributes to the formation of neps.
3. Electro-optical assessment is used in the AFIS Nep Module to assess the number, size and shape profile of neps that pass through a beam of near infra-red light. The voltage/time wave forms produced are proportional to the amount of light scattered and occluded by the object. Individual neps produce a characteristic spike wave form, which is much greater in amplitude and period than the wave forms for individual fibres. A series of threshold voltage levels indicate the size and shape of the nep, which allows neps to be categorized into two categories, fibre (or mechanical) neps and seed-coat fragments.[77,78]
4. Digital cameras are currently used in two commercial instruments that measure neps via analysis of web images. The Truetzschler Nep Control (NCT) uses a digital camera to record the condition of the fibre web being doffed in a cotton card. It continuously records the number and type of neps; fibrous and seed-coat fragment neps, in the fibre web. Good correlations ($r = 0.98$) have been observed between NCT results and the AFIS nep results.[79] The recently developed Lintronic Fibre Contamination Tester (FCT) works in a similar manner to the NCT. The instrument automatically prepares a web from a sample of raw fibre, which is then photographed by a digital camera. The image is then analysed for neps.

Measurement of biological or shiny neps using any of the above methods is difficult because of their small size. Conversion of fibre into woven and dyed sateen fabric is required for accurate counts of these neps. Against moderately dark, dyed backgrounds these neps contrast as white specks and can be counted manually or by image analysis. Knitted fabric can be used also although nep counts are lower as a proportion of the neps are hidden in the knit structure.

3.6.3 Stickiness

Sticky cotton is a major concern for spinning mills. Physiological plant sugars in immature fibres, contaminants from crushed seed and seed coat fragments, grease, oil and pesticide residues are all potential sources of stickiness. However, these are insignificant compared with contamination of cotton from the exudates of the silverleaf whitefly (*Bemisia tabaci*) and the

cotton aphid (*Aphis gossypii*).[80] The sugar exudates from these insects lead to significant problems in the spinning mill including a build-up of residues on textile machinery, which results in irregularities and stoppages in sliver and yarn production. Even at low to moderately contaminated levels, sugar residues build up, decreasing productivity and quality, and forcing the spinner to increase the frequency of cleaning schedules.[81] A reputation for stickiness has a negative impact on sales, exports and price for cotton from regions suspected of having stickiness. Reductions in the market value of lint due to stickiness are applied regionally and indiscriminately. In Arizona, perceptions regarding stickiness lead to 563-point (5.63 US cents)/lb discounts relative to Californian cotton.[82]

The major sugars excreted by *A. gossypii* are melezitose, sucrose, glucose and fructose while for *B. tabaci*, there is the additional sugar, trehalulose. Analysis by Hendrix *et al.*[83] of cotton aphid and silverleaf whitefly exudates showed that around 40% of the total sugar exuded by the aphid was melezitose, while the silverleaf whitefly exudate consisted of around 40% trehalulose plus about 17% melezitose. The two sugars that contribute most to cotton stickiness problems in spinning mills are trehalulose (a disaccharide) and melezitose (a trisaccharide).

Measurement of stickiness

There are a range of test methods currently used to assess stickiness in cotton. Test methods can be divided into two types: either counting methods whereby sticky spots that arise from heating a thin card web of the suspected cotton compressed against a heated plate for a certain time are counted, or chemical analyses whereby the sugars are extracted and identified according to colour changes, spectroscopy or chromatography. The main limitations of these are speed and, except for high-performance liquid chromatography (HPLC) and forms of spectroscopy, which are not widely used in routine analyses, the inability of the test methods to distinguish between types of sugar, particularly with regards to concentrations of the sugar trehalulose, which is difficult to collect because of its low melting point and high hygroscopicity. Recent work has shown that whitefly exudate caused more trouble in the mill than the cotton aphid exudate.[81]

Specific test methods for measuring cotton stickiness (spots) include the Sticky Cotton Thermodetector (SCT) developed by the Center de Co-operation Internationale Recherché Agronomique pour le Development (CIRAD), the High Speed Stickiness Detector (H2SD), which is a high speed version of the original SCT developed also by CIRAD and the Lintronics Fiber Contamination Tester (FCT) developed by Lintronics. Agreement between test method results, and between laboratories for the same test method are typically poor[84] although the methods are reasonable at ranking sticky cotton samples consistently.

3.6.4 Contamination

Contamination, even from a single foreign fibre, can lead to the downgrading of yarn, fabric or garments or even the total rejection of an entire batch. In 2002 the ITMF reported[85] that claims due to contamination amounted to between 1.4 and 3.2% of total sales of cotton and blended yarns. Most contamination arises from impurities being incorporated into the bale as a result of human interaction during harvesting, ginning and baling. The ITMF Cotton Contamination Survey of 2005[86] again showed a rise in the level of contamination in raw cotton from the last several surveys, which are sent to spinning mills every two years. Fibrous contamination from plants, e.g. bark and grass, human hair and materials such woven polypropylene, woven polyethylene, dyed cotton yarn and jute constitute the worse type of contamination for spinners because of the difficulties in removing them from cotton fibre. As a result of the increased incidence of contamination spinning mills are forced to use detection sensors and clearing devices throughout the mill, although there are limitations to what these sensors can 'see' with small contaminants incorporated into yarn or fabric, that are still objectionable to the human eye, e.g. < 1 mm, being difficult to see and remove. One mill currently employs the unique option of manually removing contamination from every bale purchased for contamination-sensitive products, i.e. light coloured weaves and yarn sales.[87] In doing this they are able to provide objective data on the level of contamination found in the growths they use. Table 3.9 lists the percentage of bales delivered from selected countries that contained extraneous (non-plant) contamination. In these data a single foreign fibre found in a bale establishes the bale as being contaminated.

Table 3.9 Percentage of bales from selected growths with extraneous contamination measured manually

Origin	1999/2000	2004/2005	
	Average	Average	Range
Australia	14	20	10 to 30
China	20	23	15 to 30
Brazil	35	27	15 to 35
USA SJV	28	28	20 to 45
USA Memphis	23	32	30 to 60
West Africa	58	66	62 to 80
Uzbekistan	84	86	80 to 95
India	94	92	87 to100
Zimbabwe	–	93	75 to 100
Pakistan	100	97	95 to 100
Syria	100	100	100

3.7 Moisture

Regain and moisture content are terms used interchangeably to refer to the mass of water as a percentage of the fibre mass. The correct terminology is defined in Chapter 2. The commercial regain of cotton is 8.5% although this level is practically unachievable in new cotton under normal ambient conditions. As per descriptions given in Chapter 2 regains in excess of 7.5% indicates wet cotton. The rate of diffusion between absorption and desorption is relatively quick and cotton will readily equilibrate to ambient conditions dependent upon temperature and packing density of the cotton sample. Under ambient conditions in temperate climes moisture levels in bales of cotton typically range from 3.5% to 6.5% moisture.

Moisture is important in fibre testing because of its effect on the physical properties of cotton particularly tensile properties and other expressions normalized for weight. Fibre crimp, compressability and torsional rotation are also affected by high humidity. The fibre strength (tenacity) of cotton conditioned at 55% relative humidity (RH) was 25.8 g/tex and this increased to 29.1 g/tex after conditioning at 75% RH.[88] Moisture content increases with trash content and fibre yellowness.[89] Much work has been aimed at adjusting HVI tensile measurements for conditions in the laboratory at the time of testing.[90] Under ideal standard laboratory conditions and conditioning fibre samples passively for 48 hours, or by following prescribed rapid conditioning protocols, these adjustments do not need to be made. However, maintaining and exposing cotton to standard conditions is a large cost and so new methods that adjust measurements to allow or correct for moisture are attractive. Taylor[90] investigated four methods for measuring moisture in HVI systems including capacitance, two conductivity methods and NIR. All were compared to weight loss by oven drying, which remains the standard test for determining moisture.[91] Near infra-red reflectance spectroscopy was the most accurate method of the four tested.

3.8 Wax content

Cotton wax is essential for the efficient processing of cotton fibre into spun yarn. It provides a lubricating layer that reduces fibre-to-metal friction and therefore fibre breakage during mechanical processing. The downside is that this layer also acts as an impermeable barrier to the entry of water and dye molecules into the fibre. For successful even dyeing this barrier must be removed by scouring and/or bleaching.

Cotton wax is the lipid material extracted from cotton by an organic solvent. Sugars are co-extracted with most solvents and it is necessary to separate the wax lipids from these sugars for quantitative wax analysis. The most common method for determination of the wax content of cotton was

developed by Conrad in 1944.[92] This method involves extraction of the fibre with hot ethanol, which is claimed to extract more wax, more quickly than other solvents, followed by a back extraction with chloroform and water. The sugars and non-waxy constituents remain dissolved in the water fraction while the wax passes into the chloroform layer, which is separated and then evaporated off to leave the wax component. Generally between 0.6% and 1% wax by weight of fibre is obtained by the Conrad method. The chemical composition of the wax is complex and contains a number of lipid classes including wax alkanes, fatty acids, fatty alcohols, plant steroids and mono, di and triglycerides.[93–96]

Only a limited amount of work in establishing the quantitative and qualitative differences in wax content among different cotton samples to the varietal and/or environmental background of the plant has been published. Most of these studies[97–99] found that the chemical components of wax from different varieties and species were very similar. However, in two circumstances Marsh *et al.*[98] and Gordon *et al.*[99] cottons with waxes that were significantly different in content were found. Marsh *et al.*[98] found wax from cotton exposed to weathering had a lower melting point, and higher wax content as measured by the Conrad method, whilst Gordon *et al.*[99] found some low Micronaire cotton in the set examined had much higher concentrations of hydrocarbon or alkane waxes. High concentrations of this wax were not found on all low-Micronaire cotton samples tested and the tentative conclusion was made that the relationship became manifest after the particular cotton had suffered heat and water stress during growth. The strong relationship between the amount of wax extracted from the fibre and the surface area per unit weight of fibre, determined by airflow methods such as the Micronaire is also revealed in these and other studies.[100,101] Table 3.10 lists the correlations for the relationships between the wax extracted and the surface area per unit weight of the fibre as quoted in the literature.

Table 3.10 Relationship between percentage wax (%EW) by the Conrad method and specific surface area by various test methods

Reference	Surface area measurement	Micronaire range	%EW range	No. of samples	Correlation coefficient
98	Arealometer	2.17–3.92[2]	0.19–0.95	74	0.94
100	Micronaire	3.62–4.95	0.52–0.72	36	–0.79
101	Micronaire[1]	3.62–4.95	0.52–0.72	33	–0.82
99	Micronaire	3.8–4.8	0.29–1.05	29	–0.42

1. Micronaire values calculated from AFIS fineness and maturity ratio measurements.
2. Specific surface area values measured using the Arealometer (cm^2/mg).

3.9 Microbial attack

The term 'cavitoma' was coined in the 1950s to describe cotton damaged by micro-organisms such as cellulolytic bacteria and fungi. All cotton contains populations of micro-organisms that increase if the right conditions for their growth are applied. The condition was noted in the 1950s in the mid-south and eastern growth areas of the USA during some wet years. Moisture and warmth are the chief criteria required to propel micro-organism populations. Moisture levels in excess of 9% are the minimum required for growth of the micro-organisms.[102]

Perkins and Brushwood[103] provide the most recent review of the conditions and fibre effects associated with micro-organisms and test methods to identify their presence. Acute infection by cellulolytic micro-organisms results in alkaline pH, low sugar content, colour change, poor appearance, low strength and increased wet-out. The tests for cavitomic infection tend to be qualitative tests based around pH indicator tests, and exposure of the sample to UV light to view any fluorescent spots associated with growth of some fungi. Spinning mills using a pH indicator spray will sometimes rate the degree of staining that occurs after spraying the cavitomic cotton. Infected fibres can also be examined under a microscope. Examination of cavitomic fibres under a light microscope can reveal fungal hyphae and fractures in the surface of the fibre. Swelling cavitomic fibres in concentrated sodium hydroxide will cause differential swelling at fracture points along the length of the fibre. Allen *et al.*[104] found good agreements between laboratories examining cavitomic cotton, induced in the field, on the basis of pH determinations and reasonable agreements between laboratories using a method involving microscopic analysis of fibres in sodium hydroxide.

3.10 Future trends

Cotton fibre quality is dependent upon progress in understanding and modifying the genetic and environmental influences on the cotton plant, particularly at the point of fibre development. In the future fibre quality will be defined by the expression of fibre properties in transgenic cotton varieties (see Chapter 4) and through better control of agronomic, water and nutritional variables. The fibre from these plants will likely be longer, finer and stronger, and may have new attributes such as colour or increased extension.

Measurement of fibre quality in industrial countries, e.g. the USA, will occur in the gin rather than at classing laboratories. According to Ghorashi,[6] the future fibre testing system will be implemented in the gin (see Chapter 6). The testing will be fully automated and installed in line with the process flow of the gin. The system of the future will have remote monitoring, calibration and will measure all pertinent fibre qualities a multiplicity of

times. For agricultural based countries the proportion of cotton classed by HVI lines will increase.

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