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THE RELATIONSHIP BETWEEN FIBER MATURITY AND MOISTURE CONTENT

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Abstract

Moisture and micronaire measurements were performed on 21 cotton samples exhibiting a range in genetic diversity and growing locations. A comparison of these results indicates that moisture content increases as a function of decreasing micronaire, suggesting a concomitant decrease in cellulose crystallinity. Determination of crystallinity indices by FTIR spectroscopy proved unable to distinguish between the upper and lower limit moisture samples due to the relative insensitivity of the method.

Introduction

The subject of moisture content has received a considerable amount of attention (Hu et al. 2001; Bhama Iyer et al. 1991) as regards the developmental aspects of the cotton fiber. Cotton fibers in unopened green bolls, referred to as never-dried fibers, develop in four distinct stages: (1) initiation, (2) elongation, (3) secondary wall thickening, and (4) maturation (Naithani et al 1982). Secondary wall thickening occurs as cellulose chains are laid down inwardly from the primary cell wall, and the cellulose chains thus formed assemble into fiber bundles exhibiting a helical arrangement. The direction of twist of this helix may change intermittently, and the points at which this occurs are called reversals. As the fiber matures, the cellulose chains comprising these bundles undergo a process of inter-fibril hydrogen bonding, or crystallization. In order for hydrogen bonding between fibrils to take place, water must be removed from the hydroxyl sites at which this bonding occurs. The process of secondary wall formation takes place in an environment containing ample free water, but when the mature cotton boll opens, an abrupt dehydration occurs which results in the tubular cell taking on the appearance of a twisted ribbon with a kidney-shaped cross section. Several reports (Bhama Iyer et al. 1991; Morosoff 1974; Hirai et al. 1990) have addressed the effect this dehydration has on the structural characteristics of the cellulose, though the results of these studies are often conflicting.

The distinctions between the 4 stages of fiber growth are not always clearly delineated. For example, it has been demonstrated (Meinert et al. 1977) that secondary wall formation overlaps the fiber elongation stage. Similarly, the process of fiber maturation may have some overlap with secondary wall formation. The result of this overlap is that when the boll opens and dehydration commences, the fibers may not have attained their full potential for secondary wall formation nor maturation, including the process of cellulose crystallization. This being the case, then fully matured fibers may potentially exhibit a greater degree of cellulose crystallization.

Materials and Methods

Cotton Samples

For this study, a total of 21 upland cotton (*Gossypium hirsutum)* samples (Table 1) exhibiting a wide range of genetic diversity, micronaire, and growing regions were chosen.

Moisture Determination

Duplicate moisture determinations on the 21 cotton samples were performed according to standard test methods (ASTM 2001).

Micronaire

Micronaire was measured by high volume instrumentation (HVI) according to standard test methods (ASTM 1997).

Mid-Infrared Spectroscopy

Duplicate infrared spectra for each cotton sample analyzed were obtained using a DuraSamplIR (SensIR Technologies, Danbury, CT) attenuated total reflectance (ATR) device in an Excalibur FTS 3000 (Digilab, Randolph, MA) Fourier transform infrared (FTIR) bench. Mats of cotton fiber were placed on the surface of the diamond ATR crystal and pressure applied to insure full contact of the fibers with the diamond surface. Spectra were obtained at a resolution of 4 cm^{-1} over 7111 scan points, covering the range of 4000 – 600 cm^{-1}. No apodization or baseline correction functions were applied. The peak centered at 1427 cm^{-1} was integrated between 1444 cm^{-1} and 1392 cm^{-1}, and the peak centered at 901 cm^{-1} was integrated between 917 cm^{-1} and 863 cm^{-1}.

Statistics

All non-linear regressions were performed using SigmaPlot 8.0 (SPSS Science, Chicago IL). 1 way ANOVA were performed using SigmaStat 3.0 (SPSS Science, Chicago IL).

Results and Discussion

Results of micronaire and moisture measurements are presented in Table 1. A comparison of cotton fiber moisture content with micronaire for the 21 cotton samples is shown in Figure 1. The results indicate that increasing micronaire leads to a decrease in fiber moisture content, though the correlation is clearly non-linear. In order to model this behavior, it is tentatively assumed that the decrease in moisture content obeys a first order rate with respect to the concentration of water present in the secondary wall tissue,

$$R = k[H_2O] \qquad (1)$$

where R is the rate (mic^{-1}), k is the first order rate constant (mic^{-1}), and $[H_2O]$ is the weight fraction (unitless) of water present in the cellulose matrix. Further, this rate can be alternatively defined as

$$R = d[H_2O] / dm \qquad (2)$$

Where dm represents an incremental change in micronaire, and $d[H_2O]$ an incremental change in water fraction. Combining (1) and (2) followed by integration results in

$$[H_2O] = [H_2O]_o e^{-km} \qquad (3)$$

where m is the micronaire value, and $[H_2O]_o$ is the weight fraction of water present in the secondary cell wall at the limit m = 0. Because the moisture content of cotton appears to reach a minimum non-zero value as m approaches infinity, an additional term is required:

$$[H_2O] = [H_2O]_\infty + [H_2O]_o e^{-km} \qquad (4)$$

where $[H_2O]_\infty$ denotes the minimum limit of the weight fraction of water in the cotton fiber secondary wall at $m = \infty$. When the data in Figure 1 is fit to Equation (4), the resulting curve, shown in Figure 1, provides a convincing correlation of moisture content with micronaire. At a theoretical micronaire of 0, the resulting y intercept becomes

$$[H_2O]_\infty + [H_2O]_o = 0.2224$$

describing the maximum fraction of water attainable. This number is close to the theoretical value of 0.2327 expected if there were no hydrogen bonding between the cellulose microfibrils in the cotton fiber. In this situation, the glucose units comprising the cellulose chains each have three available hydroxyl sites for hydrogen bonding with water. Assuming all of these sites are occupied, the limiting fraction of water is reached. The model described by Equation (4) indicates that the cellulose microfibrils in lower micronaire cottons have not attained a maximum level of crystallization, a process requiring the removal of water molecules from the hydrogen bonding sites on cellulose.

In order to determine whether the crystallinity is a function of micronaire, an attempt was made to measure the crystallinity indices of two samples, FM832(M) and FM832(T), which exhibit the minimum and maximum, respectively, of moisture content in the sample set. The crystallinity index is essentially a measure of the fraction of –OH groups hydrogen bonded in a regular crystalline manner. A measure of the crystallinity index of raw cotton (O'Connor et al. 1958) based on the ratio of IR absorptivities at 901 cm^{-1} and 1427 cm^{-1} was used. It has been previously determined (O'Connor et al. 1958) that the band at 1427 cm^{-1} decreased or disappeared as cotton is decrystallized by mechanical (ball mill) or chemical (ethylamine swelling) means. Concomitantly, the band at 901 cm^{-1} increased in intensity as crystallinity decreased. The crystallinity index is defined here as

$$I_x = A_{1427}/A_{901} \qquad (5)$$

A comparison of I_x for the two samples FM832(T) ($I_x = 0.957 \pm 0.019$), and FM832(M) ($I_x = 0.919 \pm 0.048$), which displayed the highest and lowest moisture contents in the sample set, respectively, indicates that no significant statistical difference exists. This observation, however, is inconclusive given that the actual difference in moisture fractions between the two samples is 0.005. This translates to a theoretical difference in I_x of 0.03 between the two samples, which is comparable to the observed standard deviation in the measurement. Given this, the primary conclusion reached is that the FTIR method is unsuitable for

measuring differences in I_x, given its relatively low sensitivity. Other methods for determination of I_x, including solid-state nuclear magnetic resonance and X-ray crystallography, are currently being evaluated in order to address this difficulty.

References

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Table 1. Fiber properties of 21 cotton samples distinguished according to genetic variety and growing location.

Variety (Location)[Z]	Micronaire (μg in^{-1})	Moisture Fraction
FM832(T)	2.89	0.0720 a
PM2800(T)	3.44	0.0688 e,f,g
PM2200(T)	3.38	0.0693 d,e,f
FM819(T)	3.15	0.0707 b,c
FM989(T)	3.05	0.0713 a,b
FM958(T)	3.24	0.0701 c,d
FM966(T)	3.20	0.0698 c,d,e
PM2326(T)	3.78	0.0692 d,e,f
DP491(G)	4.06	0.0680 g,h,i
PHY355(G)	4.76	0.0670 i
FM966(G)	4.35	0.0677 h,i
DP(G)	4.28	0.0675 h,i
FM832(G)	4.04	0.0673 h,i
SG747(G)	4.75	0.0672 h,i
DP(M)	4.55	0.0675 h,i
PHY355(M)	4.80	0.0683 f,g,h
FM832(M)	3.97	0.0670 I
DP491(M)	4.05	0.0683 f,g,h
FM966(M)	4.53	0.0678 g,h,i
SG747(M)	4.98	0.0670 i
PM1218(M)	5.56	0.0693 d,e,f

[Z] Location: T = Texas, G = Georgia, M = Mississippi

[Y] Means within a column followed by the same letter are not significantly different according to Duncan's Multiple Range test ($P \leq 0.05$).

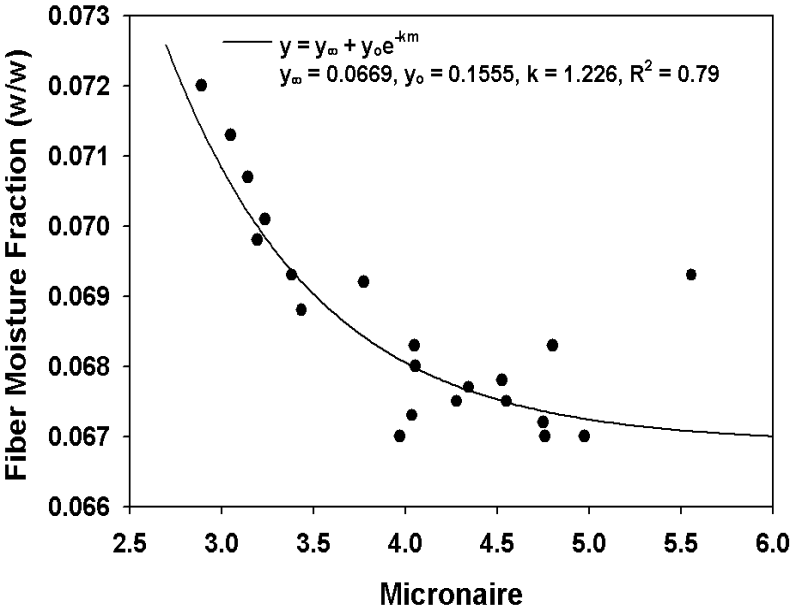

Figure 1. Comparison of fiber moisture fraction (w/w) as a function of micronaire.