TEXTILE TECHNOLOGY

Implications of Surface Chemistry on Cotton Fiber Processing

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ABSTRACT

Increasing speeds of cotton yarn production in the textile mill have made it necessary to development complementary methods to traditional measurements of physical fiber properties, such as length and strength, as predictors of yarn spinning efficiency. With the goal of investigating possible complementary measures to address this problem, this research attempts to quantify the pectin, wax, glucose, and surface electrolyte components of the cotton fiber in order to develop a chemistry-based methodology to elucidate currently unknown factors involved in yarn spinning efficiency. The amount of each component was measured for 21 cotton samples, and the results are correlated with micronaire-normalized frictional measurements based on draft force and fiber-to-fiber friction. Results indicate that inter-fiber friction decreases primarily as a function of increasing pectin and soluble salt components on the cotton fiber surface. Variations in wax content do not appear to significantly affect inter-fiber friction relative to the effects produced by variations in pectin and salt content. These are important observations not only from the standpoint of being able to set fiber processing equipment parameters based on chemical measurements, but it also raises the possibility of breeding cotton to produce desirable spinning characteristics based on the level of surface chemical components developed during the fiber growth period. This research provides results on samples from the first year (crop year 2001) of a 5-year, leading commercial cultivars study performed by ARS. Further information obtained in subsequent crop years will be used to expand the current database.

In recent years, improvements in production technology for cotton yarn have led to great increases in production rates. One consequence of these improvements is that the standard high volume instrumentation (HVI) measurements of fiber properties, such as length, strength, and uniformity, are no longer able to satisfactorily predict yarn-spinning efficiency (El Mogahzy et al., 1997). Spinning performance is affected by the surface characteristics of cotton fibers (El Moghazy et al., 1998). Several factors contribute to the surface frictional forces between fibers, including fiber morphology (convolutions), geometric features (length, fineness), and static electrical forces. In addition, the surface of the fiber is comprised of a primary cell wall composed chiefly of pectin and hemicellulose and a cuticle composed of waxes, as well as metabolic residues including electrolytes and sugars. Since these outer surface components are in direct contact with neighboring fibers, their physical dimension and chemical compositions may have a much larger impact upon spinning performance than is reflected by their low overall abundance relative to cellulose. The quantity of calcium present in the fiber has been correlated with decreased fiber-to-fiber and fiber-to-metal friction (Brushwood, 2001). Calcium in cotton fiber, which serves to cross-link pectin polymers, is associated with the primary cell wall (Wartelle et al., 1995), so increased pectin content is indirectly correlated with decreasing fiber friction.

In order to elucidate some of the factors involved in spinning performance, it is necessary to further characterize the surface chemical constituents of cotton. Surface frictional properties are potentially directly correlated with quantities of surface chemical constituents. One factor affecting the quantity of pectins, waxes, and metabolic residues relative to the whole fiber is maturity. Maturity is a function of the proportion of secondary cell wall relative to the fiber perimeter. For cottons exhibiting similar perimeters, micronaire effectively measures the degree to which the secondary cell wall has been established, so it is used as a measure of maturity. The secondary cell wall is comprised nearly exclusively of cellulose and accounts for approximately 95% (w/w) of the raw cotton fiber (Meinert and Delmer, 1977). Because growth of the secondary wall is initiated following the establishment of the primary cell wall and cu-

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ticle (Hartzell-Lawson and Hsieh, 2000; Seagull et al., 2000), the proportions of chemical components comprising the primary cell wall and the cuticle are expected to decrease as the fiber matures and the micronaire value increases. This has been observed in the case of wax (Cui et al., 2002; Gamble, 2003), pectin (Gamble, 2003), and metabolic residues (Gamble, 2003). The purpose of this research was to examine the dependence of micronaire-normalized inter-fiber frictional measurements upon levels of pectin, wax, glucose, and electrolytes. Any correlation established between inter-fiber friction and surface chemistry can potentially be used to optimize textile processing equipment, as well as in the manipulation of genetic characteristics to produce desirable spinning performances.

MATERIALS AND METHODS

Cotton Samples. For this study, 21 upland cotton (*Gossypium hirsutum* L.) samples (Table 1) with a wide range of genetic diversity and micronaire from different growing regions were chosen. All samples were conditioned at 65% relative humidity and 21°C, and values for all of the measured chemical components are reported relative to the weight of the conditioned fiber.

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

Pectin content. Pectin content of the cotton fiber was determined by enzymatic degradation and subsequent analysis of galacturonic acid, the primary

Table 1. Physical and chemical fiber properties of 21 cotton samples distinguished according to genetic cultivar and growing location

Cultivar (location) [y]	Micronaire (μg in^{-1} x 2.54)	RotorRing fiber-fiber friction (J)	Draft force (N)	Galacturonic acid fraction (x1000)	Wax fraction (x1000)	Conductivity ($\mu\Omega^{-1}$ cm^{-1})	Glucose fraction (x1000)
FM832(T)	2.89	21998 a [z]	2.136 cd	7.25 a-b	6.45 b	1025 a	2.82 c
PM2800(T)	3.44	18646 cd	1.914 d-g	6.96 a-d	5.53 cd	963 b	1.82 d
PM2200(T)	3.38	18416 cd	1.598 g-i	7.14 a-c	5.73 cd	967 b	1.65 de
FM819(T)	3.15	19573 c	2.238 a-d	7.12 a-c	6.01 b-d	900 c	3.83 a
FM989(T)	3.05	19576 c	2.149 b-d	7.06 a-c	7.08 a	1000 ab	3.12 b
FM958(T)	3.24	18835 cd	2.354 a-c	6.49 de	5.89 b-d	990 ab	2.67 c
FM966(T)	3.20	18234 cd	2.136 cd	6.64 c-e	6.02 bc	980 ab	2.87 c
PM2326(T)	3.78	15072 fg	1.611 g-i	6.83 a-d	4.54 e	990 ab	1.87 d
DP491(G)	4.06	17641 de	2.069 c-f	6.46 de	3.83 f	692 de	1.63 de
PHY355(G)	4.76	15092 fg	1.446 hi	6.16 ef	4.91 e	650 ef	1.03 f
FM966(G)	4.35	17919 d	1.744 f-h	5.26 g	4.77 e	642 ef	1.73 d
DP(G)	4.28	17611 de	1.780 e-h	6.69 b-e	5.70 cd	625 fg	1.40 e
FM832(G)	4.04	19568 c	2.077 c-e	6.18 ef	4.40 ef	625 fg	0.93 fg
SG747(G)	4.75	14603 gh	1.380 i	6.20 ef	4.32 ef	742 d	1.75 d
DP(M)	4.55	16289 ef	1.967 d-f	5.67 f	3.84 f	500 i	0.53 hi
PHY355(M)	4.80	14374 gh	1.566 hi	6.23 de	4.41 ef	717 d	0.90 fg
FM832(M)	3.97	21683 b	2.479 ab	3.76 i	4.15 ef	350 k	0.28 i
DP491(M)	4.05	19529 c	2.496 a	4.36 h	5.65 cd	408 j	0.73 gh
FM966(M)	4.53	17680 de	2.229 a-d	4.90 g	3.75 f	550 hi	0.55 h
SG747(M)	4.98	14424 gh	1.388 i	4.22 hi	3.07 g	583 gh	0.72 gh
PM1218(M)	5.56	13372 h	1.388 i	5.00 g	2.89 g	600 f-h	0.48 hi

[y] **Location: T = Texas, G = Georgia, M = Mississippi.**

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

byproduct of enzymatic degradation. Six replicate analyses were performed on each of the 21 cotton samples. Enzyme treatments of cotton samples consisted of adding 10 μL of pectinase (Sigma Chemical Co.; St. Louis, MO) to a 0.10 g cotton sample in 10 ml of a pH 4.0 buffer solution. After adding 0.01 g of EDTA, the sample was heated at 50°C for 18 hours, at which point no further degradation occurs. For galacturonic acid analysis, high performance anion exchange chromatography (HPAEC) was performed on the resultant suspensions with a Dionex DX-500 (Dionex Corp.; Sunnyvale, CA) using pulsed amperometric detection and two Dionex Carbopac PA-1 (4 x 250 mm) columns connected in series, preceded by a Dionex PA-1 guard column. Solutions were automatically filtered using Dionex Polyvial Filtercaps on the 0.5 ml sample vials. Elution was carried out at 0.75 ml/min using 200 mM NaOH as the mobile phase and a sigmoidal gradient of 0 to 500 mM NaOAc. Galacturonic acid content is reported as the fraction (w/w) present on the conditioned fiber.

Conductivity and glucose measurements. Cotton samples were extracted using 20 ml deionized water per gram of cotton, and six replicates were performed for each of the 21 cotton samples. Each sample was agitated with a glass rod in order to promote wetting of the cotton surface. The wetted sample was allowed to stand for 15 min before being wrung out. The resulting extract was then subjected to conductivity measurements and glucose measurements. Conductivity measurements, reported in microsiemens per centimeter ($\mu\Omega^{-1}$ cm^{-1}), were performed on a Model EP conductivity meter (Myron L Co.; Carlsbad, CA). Glucose measurements, reported as the fraction (w/w) present on the fiber, were performed using a Model 2700 Bioanalyzer (Yellow Springs Instrument, Inc.; Yellow Springs, OH) equipped with a glucose oxidase membrane.

Wax content. Wax content, reported as the fraction (w/w) present on the conditioned fiber, was determined by Soxhlet extraction. Six replicates were performed for each of the 21 cotton samples. Extractions were performed using trichloroethylene as a solvent on 2.5-g samples of cotton. The resultant solutions were evaporated to dryness at 105°C, which left a wax residue that was subsequently weighed.

Fiber-to-fiber friction measurements. Duplicate slivers (4.96 g/m) for each of the 21 cotton samples were evaluated for drafting force on a Draft Force–Evenness Tester (McAlister et al., 2003).

The drafting force, measured in newtons (N), is a measure of the force required to parallelize the assembled fibers. The measurement was determined by deflection of one pair of rollers in a two pair draft zone, and was calibrated using weights to determine the force required to cause a given deflection of the roller pair.

Four replicates for each of the 21 cotton samples were evaluated for fiber-to-fiber friction using the RotorRing 580 (Spinlab; Knoxville, TN). Slivers in this case were approximately 14.75 g/m and results are reported in joules (J).

Equations. All of the equations presented have been derived by the author for this research.

Statistics. All linear regressions were performed using SigmaPlot 8.0 (SPSS Science; Chicago, IL). Multivariate analyses and 1-way ANOVA were performed using SigmaStat 3.0 (SPSS Science; Chicago, IL).

RESULTS AND DISCUSSION

Results for frictional and chemical measurements on the 21 cotton samples are presented in Table 1. Pectin, wax, and glucose content are indicated as unit-less fractions of the total fiber weight. In effect, the measurements are normalized to provide single fiber quantities of these components. Soluble salt content is measured by the conductivity of the 20 ml water extract from 1.0 g of cotton. Because there is a mixture of salts on the inner and outer surface of the fiber, this measurement cannot be readily converted to units of mass in order to arrive at a unit-less fraction. Previous work indicates that the primary electrolyte present on the fiber surface is potassium malate (Dhindsa et al., 1975). Assuming that potassium malate is the dominant electrolyte present, then a calibration of conductivity versus known potassium malate concentrations can be accomplished. The results of this calibration indicate that an approximately linear relationship exists between conductivity and concentration within the observed ranges (Figure 1). The fraction of potassium malate present on the surface of the cotton fiber is therefore directly proportional to the conductivity of the extract. Having substantiated this proportionality, the conductivity measurement obtained under the condition that 1.0 g of each cotton sample is extracted into 20 ml of water can be considered to be proportional to the electrolyte fraction on individual fibers.
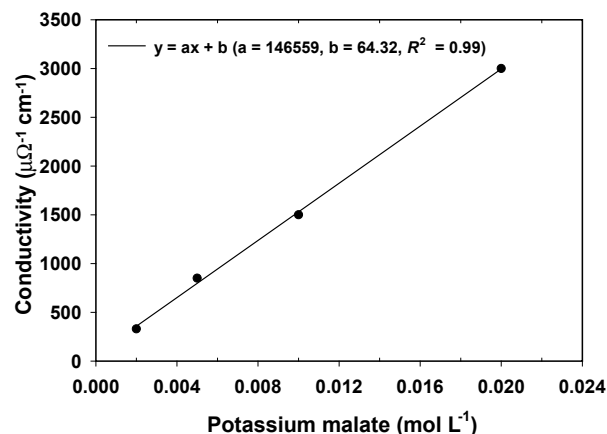
Figure 1. Relationship between conductivity of the solution and the potassium malate concentration.

Frictional measurements are measured in newtons (N) in the case of draft force and in joules (J) for fiber-to-fiber friction, as measured by the RotorRing, for a given weight of fibers. In order to normalize these data to account for the frictional properties of individual fibers, as opposed to the entire sliver, the relationship between the linear density of the fiber bundle and the linear density of the individual fibers in the bundle are transformed. In the case of the draft force measurement, slivers exhibiting identical linear densities (49,992 µg/cm) for each cotton sample were tested. The number of individual fibers in a cross section of the sliver can be estimated by

$$\text{\# fibers} = D_s / D_f \qquad (1)$$

where D_s is the linear density of the sliver and D_f is the linear density of the individual fibers. Us-

ing micronaire in units of [(µg/cm) x (2.54)], as a measure of individual fiber linear density, equation 1 becomes

$$\text{\# fibers} = 126{,}980 / M \qquad (2)$$

where M indicates micronaire. In order to ascertain the draft force per individual fiber, the draft force measurement made on the sliver is divided by the number of fibers in a cross-sectional area of the sliver

$$F_{s,df} / \text{\# fibers} = F_{f,df} \qquad (3)$$

where $F_{s,df}$ is the measured draft force of the sliver and $F_{f,df}$ is the calculated draft force of an individual fiber in the sliver. Substituting equation 2 into equation 3, then

$$F_{f,df} = (F_{s,df})(M) / 126{,}980 \qquad (4a)$$

A similar relationship is tentatively presumed for the case of fiber-to-fiber friction as measured by the RotorRing, except that a sliver approximately 3x than that used in the draft force measurement is used. In this case we obtain

$$F_{f,rr} = (F_{s,rr})(M) / 375{,}000 \qquad (4b)$$

where $F_{s,rr}$ is the fiber-to-fiber friction measured by the RotorRing on the sliver and $F_{f,rr}$ is the resultant calculated fiber-fiber friction of an individual fiber in the sliver. Equations 4a and 4b provide a basis for comparison of the quantities of various chemical constituents found on the surface of cotton fiber with the inter-fiber frictional properties of individual fibers. Results of these comparisons from linear regression are shown in Table 2.

Table 2. Coefficients of determination (R^2) between physical and chemical fiber properties

	Mic	$F_{s,df}$	$F_{f,df}$	$F_{s,rr}$	$F_{f,rr}$	Pectin	Wax	Salts	Glucose
Mic	1	0.36	0.10	0.60	0.34	0.30	0.71	0.48	0.61
$F_{s,df}$		1	0.30	0.69	0.02	0.05	0.20	0.00	0.00
$F_{f,df}$			1	0.04	0.63	0.66	0.14	0.65	0.34
$F_{s,rr}$				1	0.00	0.00	0.41	0.02	0.14
$F_{f,rr}$					1	0.68	0.29	0.88	0.61
Pectin						1	0.28	0.74	0.55
Wax							1	0.39	0.57
Salts								1	0.69
Glucose									1

With header "Physical and chemical property [z]" spanning columns.

[z] $F_{s,df}$ = force (N) required to parallelize an assembly of fibers (4.96 g/m sliver) using the Draft Force-Evenness Tester. $F_{f,df}$ = force (N) required to parallelize a single fiber within a sliver, calculated using the equation, $F_{f,df} = (F_{s,df})(micronaire)/126{,}980$. $F_{s,rr}$ = energy (J) required to open an assembly of fibers (14.75 g/m sliver) using the RotorRing. $F_{f,rr}$ = energy (J) required to open a single fiber within a sliver, calculated using the equation, $F_{f,rr} = (F_{s,rr})(micronaire)/375{,}000$.

The inter-fiber frictional force, as measured on the sliver by draft force ($F_{s,df}$) and RotorRing ($F_{s,rr}$), show no significant correlation with any components of the matrix other than each other ($R^2 = 0.69$). Individual fiber friction, as calculated from equation 4a for draft force ($F_{f,df}$) and equation 4b for rotorring ($F_{f,rr}$), show significant correlations with pectin content (Fig. 2 and 3), soluble salt content (Fig. 4 and 5), and to a lesser extent with glucose and wax contents (not shown). A multilinear regression using $F_{f,df}$ as the dependent variable and the four chemical components as independent variables results in multicollinearity among the independent variables. If wax and glucose are eliminated, the regression indicates that $F_{f,df}$ can be predicted solely by the soluble salt component as measured by conductivity ($P = 0.032$). Multilinear regression using $F_{f,rr}$ as the dependent variable gives a similar result. These

results, however, must be interpreted in light of the multicollinearity present among the supposed independent variables.

The fact that each chemical component measured exhibits a significant correlation with all of the other components indicates that any one of these, or a combination thereof, may be responsible for the frictional behavior observed. At the least, these components correlate with single fiber frictional behavior, indicating their potential utility as predictors of inter-fiber friction. Direct evidence of the role of soluble surface components, including salts and sugars, in the frictional behavior of fibers is obtained by removal of these components through water extraction and subsequent determination of the change in frictional behavior resulting from this removal. This was performed for the sample FM832(M), which exhibits low values for both soluble salts and glucose,
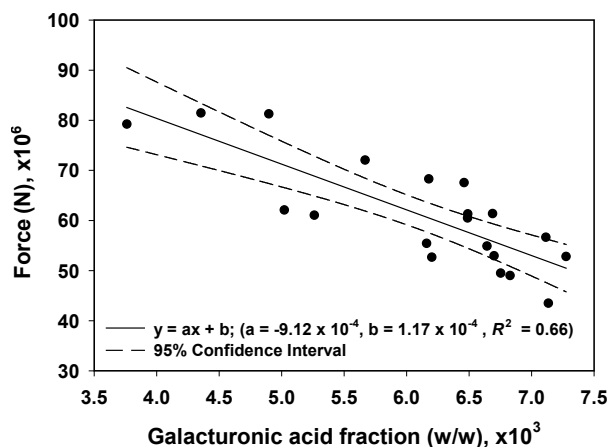

Figure 2. Relationship between the force required to parallelize a single fiber using the Draft Force-Evenness Tester and the galacturonic acid fraction present on the fiber.
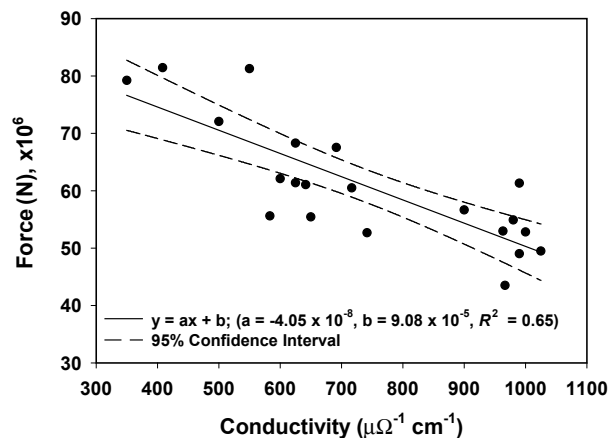

Figure 4. Reltionship between force required to parallelize a single fiber using the Draft Force-Evenness Tester and the conductivity of a 20 ml water extract of 1.0 g of fiber.
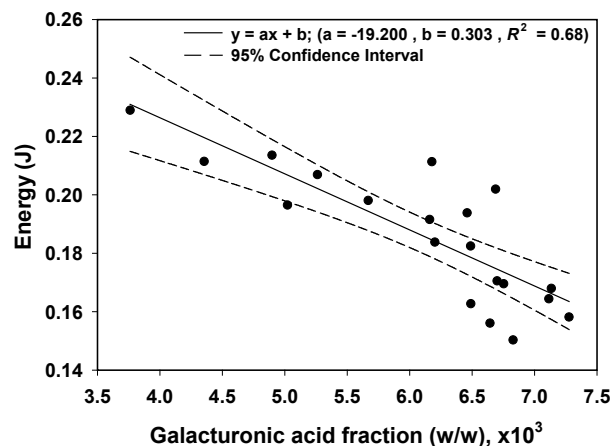

Figure 3. Relationship between the energy required to open a single fiber using the RotorRing and the galacturonic acid fraction present on the fiber.
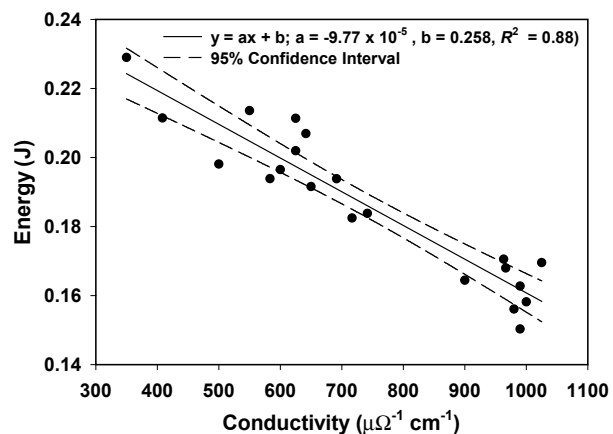

Figure 5. Relationship between the energy required to open a single fiber using the RotorRing and the conductivity of a 20 ml water extract of 1.0 g of fiber.

and FM832(T), which exhibits high values for these same components. Each sample was extracted with deionized water until no measurable salts or sugars remained. Upon subsequent measurement of fiber-to-fiber friction via the RotorRing, no significant change in inter-fiber friction was observed for either sample upon washing [FM832(T); 21,998 ± 2040 J before washing, 21,523 ± 2260 J after washing : FM832(M); 21,683 ± 548 J before washing, 21,871 ± 1510 J after washing]. Therefore, the strong correlations observed between the dependent variable $F_{f,rr}$ and the independent variables, soluble salts and glucose, appear to be indirectly caused by co-linearity of these two independent variables with one or more other variables, which are the true sources of inter-fiber frictional behavior.

It has been previously demonstrated that total removal of the wax component leads to a substantial increase in inter-fiber friction, as measured using a West Point cohesion tester (Cui et al., 2002). This same study further indicated that the natural wax content showed a very low correlation ($R^2 = 0.01$) with fiber cohesion. Results from the present study indicate that wax content has a low, albeit non-negligible, correlation with single fiber friction as measured by the Draft Force tester and the RotorRing ($F_{f,df}$ and $F_{f,rr}$, respectively). The pectin component exhibits a much stronger correlation with single fiber friction than does wax (Table 2), but direct observation of the effect of the pectin layer on single fiber friction is not easily achieved due to the fact that it cannot be removed from the cotton fiber without concomitant changes to other components of the fiber, including soluble salts, glucose, and waxes. Selective removal of pectin requires digestion in a water solution of pectin specific enzymes, but salts and sugars will be simultaneously removed by dissolution. Since these components have been demonstrated to play no role in fiber-to-fiber friction, this simultaneous loss is of little consequence. More problematic is the effect upon the waxy cuticle, which is in direct contact with the outer surface of the pectin layer. Loss of the pectin layer leads to detachment of the waxy cuticle, and any ensuing frictional measurements will be affected. Experimental methods designed to address the difficulty of directly observing the role of the pectin component in inter-fiber frictional behavior are currently under evaluation.

CONCLUSIONS

Electrolytes and sugars present on the surface of cotton fiber, as well as pectin present in the primary cell wall, exhibit significant correlations with single fiber friction, and surface wax shows a substantially weaker correlation. Removal of the surface electrolytes and sugars by water washing the fibers does not result in a significant change in frictional behavior, and it is concluded that these components do not play a significant role in inter-fiber friction. Of the four chemical components measured in this study, increasing pectin content appears to be the most strongly associated with decreasing inter-fiber friction, while increasing wax content has a smaller but significant correlation. Methodologies to selectively decrease pectin content without affecting the wax component are currently under evaluation in order to provide direct evidence for the role of pectin in inter-fiber friction. In addition, other variables are being evaluated for their effect upon fiber friction. One such variable is fiber convolution, or crimp. It has been demonstrated that fiber crimp increases as a function of increasing fiber linear density or micronaire, and by extension, fiber maturity (Foulk et al., 2002). It has also been demonstrated that concomitant decreases in pectin, wax, salt, and sugar contents are exhibited with increasing fiber linear density (Gamble, 2003). A correlation is thus inferred between fiber crimp and the chemical constituents present on the outer surface of the fiber, and investigation of this inference is the goal of continuing research in this laboratory. This work reflects results on samples from the first year (crop year 2001) of a 5-year, leading commercial cultivars study performed by ARS, and additional data obtained in subsequent crop years will be used to expand the current data base.

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