Thermogravimetric Analysis of Cotton Fibers: Relationships with Maturity and Fineness

Noureddine Abidi, Eric Hequet, Dean Ethridge

International Textile Center, Texas Tech University, Lubbock, Texas 79409

Received 20 February 2006; accepted 30 March 2006
DOI 10.1002/app.24465
Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: In this study, we investigated the relationships between the thermal properties versus maturity and fineness (*H*) of 80 selected cotton fiber samples. The instrument measurements for maturity and *H* were (1) micronaire as determined with a high-volume instrument, (2) maturity ratio and *H* as determined with an advanced fiber information system, and (3) gravimetric *H* as determined by the cut-and-weigh method. Three regions of thermal decomposition were observed between 37 and 150°C for region I, between 225 and 425°C for region II, and between 425 and 600°C for region III. Complete decomposition of the fiber occurred at 600°C. The results showed significant effects of the *H*/maturity indicators on the weight loss and the peak temperatures in regions II and III. High micronaires (coarse or very mature fibers), high maturity ratios, and low standard *H* values were associated with low weight losses. However, high weight losses were associated with high primary cell wall areas per unit mass. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 103: 3476–3482, 2007

Key words: fibers; pyrolysis; thermal properties; thermogravimetric analysis (TGA)

INTRODUCTION

There is universal interest in the measurement of cotton fiber quality, that is, in the measurement of properties of the fibers that are useful to predict performance as an industrial raw material. Also, significant efforts are being made to develop, through breeding and biotechnology, new cotton varieties that provide superior fiber properties. The missing link in these efforts is a scientific understanding of the relationships between the desired properties and the fiber structure/morphology. The dominant tools used today are high-volume instrument (HVIs) and advanced fiber information systems (AFIS's). These instruments provide information on length, strength, maturity, fineness (*H*), and color of the lint. Although this information is necessary, it is not sufficient to provide answers about structure/morphology that are needed for new breakthroughs.

The effect of maturity on the dye uptake is well known and constitutes the basis of the Goldthwait test.[1] Similarly, it is known that fine and mature fibers make it possible to spin a finer yarn. However, maturity and *H* of cotton fibers are also essential qualitative characteristics if one wants to better understand the propensity to break fibers when they are subjected to stress. It is intuitively obvious to hypothesize that immature fibers (having a thin, poorly developed secondary wall) will be fragile. Thus, they are likely to break during multiple mechanical stresses involved in transforming the fibers from field to yarn. These generate short fibers and neps (entanglements of fibers), which result in yarn defects and decreased productivity.

Raw cotton fibers consist essentially of 95% cellulose I (β-1,4-D-anhydroglycopyranose).[2] The major portion of the noncellulosic compounds is located primarily in the cuticle and primary cell wall and contains wax, pectic substances, organic acids, sugars, and ash-producing organic salts.[3] After cotton fibers are chemically processed (by scouring and bleaching), virtually all of these noncellulosic materials are removed, and the cellulose content of the cotton fibers is over 99%. It was reported that the primary cell wall, which is less than 0.5 μm thick, consists of around 50% cellulose.[4] Therefore, two cotton fibers that are identical except for having different maturities (i.e., different degrees of secondary cell wall development) have different quantities of primary cell wall per unit of mass. Consequently, it should be possible to estimate the amount of the primary cell wall per unit mass by the measurement of the weight loss as a function of the temperature with thermogravimetric analysis (TGA).

TGA is one of the most commonly used thermal techniques for the characterization of both inorganic and organic materials, including polymers (e.g., cellulose). It provides quantitative results regarding the loss of weight of a sample as a function of increasing

Correspondence to: N. Abidi (n.abidi@ttu.edu).
Contract grant sponsor: Cotton Incorporated and The International Cotton Research Center/USDA.

temperatures. It was observed previously that the major weight loss of the developing cotton fibers occurs between 130 and 380°C.[3] Moreover, TGA measurements provide basic information about the thermal properties of the material and its composition. Derivative thermogravimetry (DTG) can be used to investigate differences between thermograms. This technique was used, for example, to elucidate differences in flax fibers and to determine their *H*.[5]

Cellulose can be classified as a polymer of moderate thermal stability. Cellulose undergoes rapid chemical decomposition at temperatures between 250 and 350°C.[6] The complexity of the thermal degradation of cellulose results from the large number of parallel and consecutive steps of the reaction. The predominant reaction route changes as the temperature increases and as the ambient atmosphere evolves; this, hence, influences the degradation process. Also, the structure of the cellulose sample may affect the process of thermal degradation.[6]

Studies with TGA have shown that different steps are involved in the thermal degradation of cellulose. At temperatures below 200°C, the weight loss noticed is due primarily to the loss of adsorbed water. At temperatures above 200°C, thermal decomposition and depolymerization occurs.[2] Between 250 and 290°C, primary volatile decomposition releases CO_2, CO, and H_2O. It was proposed that this stage consists of random chain scission in the low-order regions of the cellulose followed by relaxation of the broken chains and dehydration, decarboxylation, or decarbonylation of anhydroglucose units. At temperatures between 290 and 310°C, the volatile products include anhydroglucoses (1,6-anhydro-β-d-glucopyranose, 1,6-anhydro-β-d-glucofuranose, and 1,4:3,6-dianhydro-α-d-glucopyranose).[2] At temperatures between 310 and 350°C, the volatile products include, in addition to the volatile products mentioned in the previous stages, products formed by dehydration of the anhydroglucoses (5-hydroxymethyl-2-furfural, 2-furyl hydroxymethyl ketone, and levoglucosenone).

In this study, we used TGA to record the weight loss of cotton fibers having a variety of maturities and *H* values. At a constant fiber perimeter (*P*), immature cotton fibers have more primary cell wall for a given mass than mature cotton; therefore, weight loss was expected to be negatively correlated to cotton fiber maturity.

EXPERIMENTAL

Materials

We selected 80 cotton fiber samples on the basis of their distinct physical properties. The cotton samples were first carded to remove the trash (visible and invisible foreign matter, e.g., leaf fragments, dust). This process also helped to homogenize the samples. The cotton samples were tested on a HVI (HVI 900A, Uster, Knoxville, TN) with 10 length and strength measurements and four micronaire measurements. They were also tested on an AFIS (Uster, Knoxville, TN) with five replications of 3000 fibers. The AFIS results [maturity ratio (MR) and standard fineness (H_s)] were calibrated with image analysis results reported by Hequet et al.[7] Table I summarizes the minimum and maximum values of the physical properties of the cotton samples selected for this study. The fiber properties ranged from very immature and weak fibers (MR = 0.51 and strength = 24.4 cN/tex) to very mature and strong fibers (MR = 1.07 and strength = 33.4 cN/tex).

Gravimetric *H* determination

Gravimetric fineness was determined by the cut-and-weigh method (H-C&W), also known as *Lord's method.* This method consists of one forming a parallel fiber bundle, cutting a 1-cm section in the median portion, weighing the cut fibers, and counting the number of fibers.[8] The method used in this research differed slightly from Lord's method; the bundle of fibers was combed parallel, secured in stelometer clamps, and then cut.[9] The bundle was released from the clamp and weighed, and then, the fibers were counted. Six bundles were selected for each sample. The cut-and-weigh method introduces a bias into the measurements because the sample taken is not independent of the fiber length. Only fibers longer than the width of the stelometer clamps (11.74 mm) were evaluated. Prakash and Ilengar[10] reported that Lord's method of measuring the gravimetric *H* gave results 8 to 10% higher than the weighing of the whole fibers. Measuring the length and weighing each individual fiber on a large set of samples is impractical; therefore, we chose the cut-and-weigh method despite the bias it introduces.

TGA

TGA of the fiber samples was performed with a Pyris 1 thermogravimetric analyzer (PerkinElmer, Shelton,

TABLE I
Fiber Properties (Minimum and Maximum) of Selected Cotton Fibers

	Minimum	Maximum
HVI		
Upper half mean length (mm)	24.4	30.0
Micronaire (index)	2.60	5.12
Strength (cN/tex)	24.1	33.4
AFIS		
Calibrated MR (index)	0.51	1.07
Calibrated H_s (mtex)	165	278

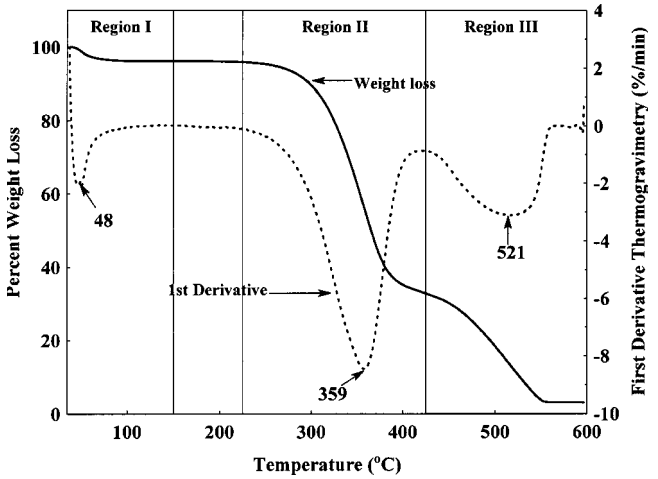

Figure 1 TGA thermogram of a representative cotton fiber with the corresponding derivative.

CT) equipped with an autosampler for automatic testing of 20 samples. The thermograms were recorded between 37 and 600°C at a heating rate of 10°C/min in a flow of nitrogen at 20 mL/min.

The cotton lint samples were rolled into small balls (1.5–2 mg) by hand (we wore latex gloves to avoid moisture transfer) and then placed on the sample pan. Three replications were performed for each cotton sample. The Pyris software was used to calculate the first derivatives of the thermograms (DTG) and to determine the percentage weight loss for each sample.

RESULTS AND DISCUSSION

Figure 1 shows a representative thermogram of a cotton fiber sample with a micronaire of 4.8, a strength of 28.5 cN/tex, and a calibrated MR of 0.909. This thermogram was divided into three regions. The initial weight loss (region I) was located between 37 and 150°C and was followed by a plateau region before the major weight loss occurred in region II, located between 225 and 425°C. Finally, region III was located between 425 and 600°C. The first derivative of this thermogram (DTG), also illustrated in Figure 1, clearly revealed the inflection points. Three peaks located at 48°C (peak I), 359°C (peak II), and 521°C (peak III) were observed. Faughey et al.,[5] who generated the thermal spectra of flax fibers, observed two such peaks for flax. The primary peak (revealing cellulose decomposition) occurred between 240 and 400°C, with another, minor peak occurring between 400 to 520°C.

The thermograms of the 80 cotton samples were analyzed. The percentage of weight loss in each region and the peak temperatures were determined. The statistical analysis (analysis of variance) showed a significant effect of the cotton type on the weight loss in both region II ($df = 79$, $F = 21$, $p = 0.000001$) and region III ($df = 79$, $F = 1.92$, $p = 0.000274$). In region II, the minimum percentage of weight loss averaged 62.3%, whereas the maximum averaged 69.9% (Table II). In region III, the minimum percentage of weight loss averaged 22.1%, whereas the maximum averaged 30.0%. Furthermore, significant effects of the cotton fiber type on the peak temperatures in region II ($df = 79$, F = 19, $p = 0.000001$) and region III ($df = 79$, $F = 6.3$, $p = 0.000001$) were noticed. In region II, the minimum peak temperature was around 350.6°C, and the maximum was around 369.3°C. In region III, the minimum peak temperature was around 496.2°C, and the maximum was around 566.6°C (Table II). The average within-sample coefficients of variation (CV%'s) are also listed in this table. The average CV% was very low (~1%) for the percentage weight loss in region II ($WL_{225–425}$), but it was high for regions I and III (12.0 and 7.3%, respectively). The peak temperatures appeared to be less variable with CVs of 4.3, 0.5, and 1.9 for regions I, II, and III, respectively. For the 80 cotton samples, the average intrasample CV% for the measurements of MR, H, and H_s as measured with the AFIS were 1.04, 1.06, and 0.90, respectively. There is a consensus within the textile industry that the intrasample CV% of cotton fiber properties is generally between 1 and 5%. This was also the case for the weight loss measurements with TGA in region II and for the peak temperatures in all of the regions but not for the weight losses in regions I and III.

Cotton fiber weight losses in regions I, II, and III were correlated to calibrated MR and calibrated H_s as determined by the AFIS and to micronaire as determined by HVI. We selected these fiber properties because they provide indirect measurement of cellulose deposition within the cotton fibers (fiber maturity).

TABLE II
Average, Minimum, and Maximum Peak Temperatures and Average CV% of the Peak Temperatures and Percentage Weight Loss in the Different Regions

	Peak temperature (°C)			Percentage weight loss		
	Region I	Region II	Region III	Region I	Region II	Region III
Average	47.9	359.7	528.0	4.2	65.8	26.1
Minimum	45.1	350.6	496.2	3.3	62.3	22.1
Maximum	53.2	369.3	566.6	5.1	69.9	30.0
Average CV%	4.3	0.5	1.9	12.0	1.0	7.3

The summary data in Table II reveal that in region I, the observed weight loss variations were very small (ranging from 3.3 to 5.1%) and quite variable (intrasample CV% = 12%). With the combination of a high CV% and a very narrow dynamic range in region I, it was not surprising that there was no statistical significance in the relationship between percentage weight loss and the AFIS MR (Fig. 2), neither was there any significance between weight loss and either micronaire or H_s in region I.

As previously noted, the weight loss in thermal region I was primarily associated with the loss of adsorbed water. In cotton fibers, this adsorption is a function of bonding between H—O—H and the —OH in the cellulose macromolecules.

Cotton fiber micronaire is defined as a function of H and MR. It is based on the measurement of an air flow that passes through a porous plug of cotton fibers. The definition of fiber H in cotton does not relate directly to P. Indeed, fiber H (expressed in millitex) is the weight in milligrams of 1000 meters of fibers. Therefore, a fine fiber may have a small P and a high MR. Conversely, a fine fiber may have a large P and a low MR (which implies a large lumen in the fiber). In a similar manner, high micronaire readings indicate coarse fibers (high weight per unit length), whereas low micronaire readings indicate fine fibers (low weight per unit length). The micronaire was measured by HVI. Figure 3 shows a significant negative linear relationship between the micronaire and $WL_{225–425}$ ($WL_{225–425}$ = 74.60 − 2.13 Micronaire, R^2 = 0.425). Worley and al.[11] estimated that the relationship between the micronaire scale and the fiber surface area per volume (A) was

$$A(\mathrm{mm}^2/\mathrm{mm}^3) = 1904.8 + 169.32\mathrm{Micronaire} - 1047.4(\mathrm{Micronaire})^{0.5}$$

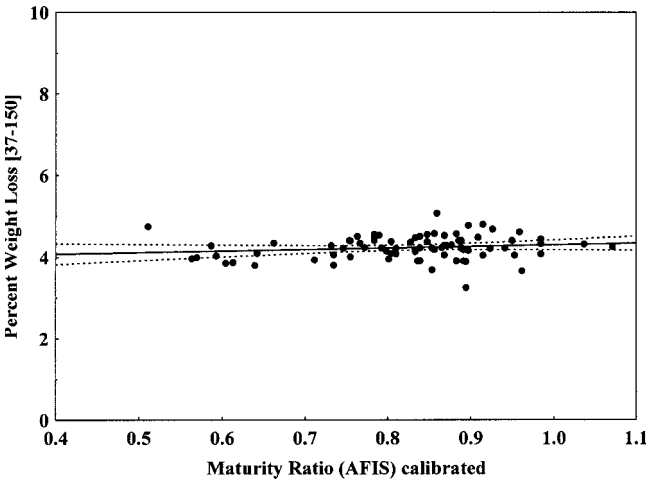

Figure 2 Percentage weight loss in the region 37–150°C versus MR.

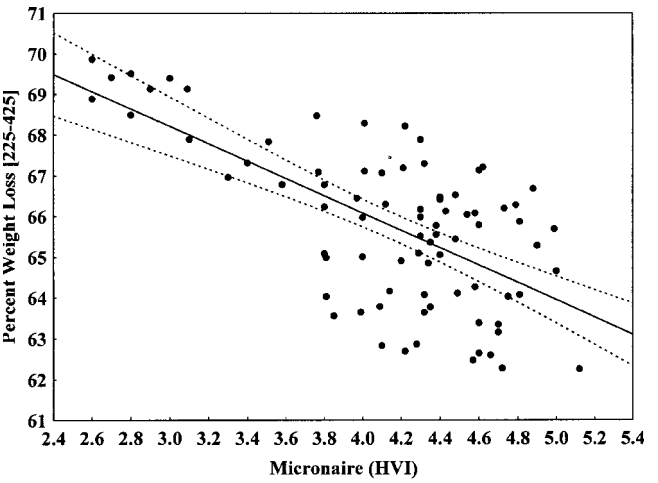

Figure 3 $WL_{225–425}$ versus micronaire.

Therefore, a high surface area of fibers is associated with a low micronaire (finer fibers), and the quantity of noncellulosic compounds should increase with decreasing micronaire readings. Thus, we hypothesized that the observed increase in the weight loss ($WL_{225–425}$) with decreasing micronaire readings meant that in addition to the pyrolysis reactions of the cellulose macromolecules, the decomposition of noncellulosic compounds also took place in region II. An examination of the relationship between H-C&W and $WL_{225–425}$ could confirm this hypothesis. Figure 4 shows that there was no significant correlation between these two parameters. Indeed, H-C&W provided a direct measurement of the weight for a given length of fibers. With cellulose being largely dominant in cotton fibers (>95% of pure cellulose), the fiber weight for a given length could be considered equivalent to a quantity of cellulose for a given length. Therefore, this lack of correlation probably meant that the weight loss differences between cot-

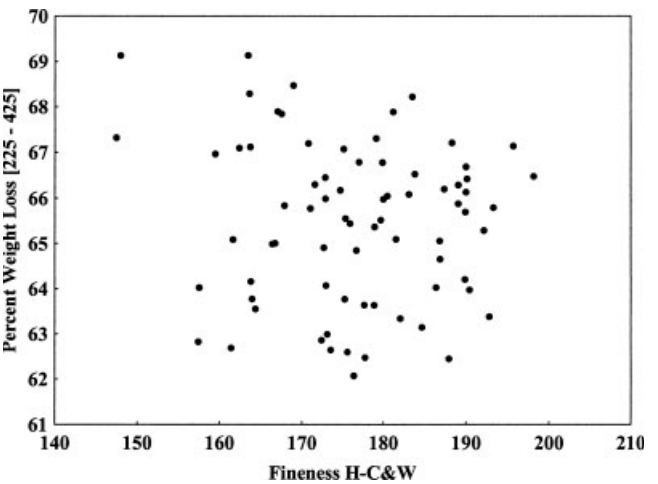

Figure 4 $WL_{225–425}$ versus H BSM.

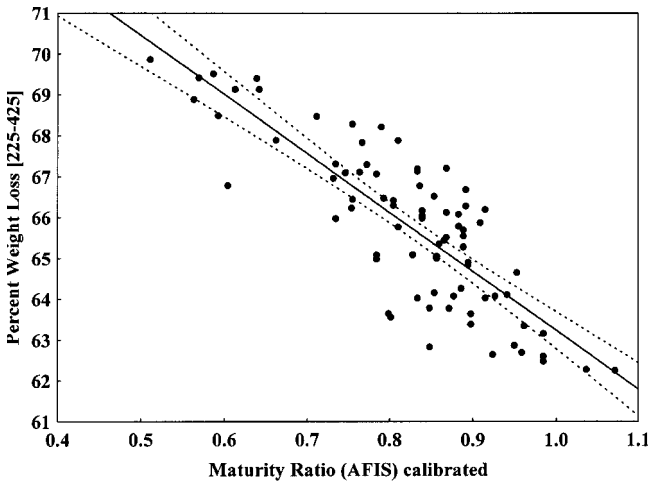

Figure 5 $WL_{225–425}$ versus MR.

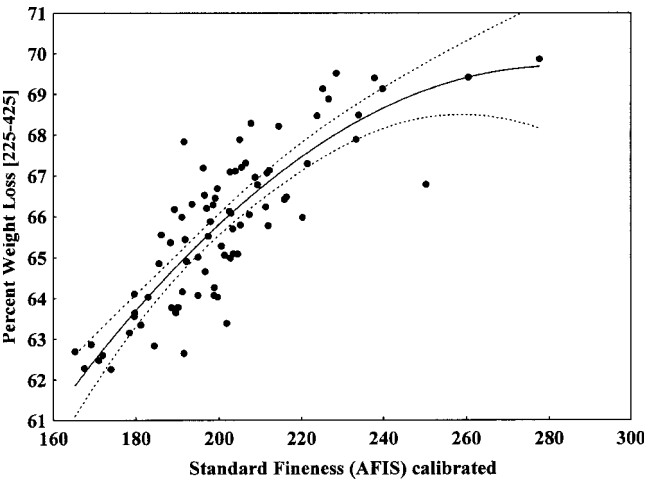

Figure 7 $WL_{225–425}$ versus H_s.

tons observed in this region were not directly related to the amount of cellulose but to the noncellulosic compounds mainly present in and on the primary cell wall.

Fiber MR is a measurement of the relative amount of the cellulose in the fiber cross-section. The values are dimensionless numbers and range between 0.5 and 1.2. MR as determined with the AFIS (MR) versus $WL_{225–425}$ is shown in Figure 5. A significant negative linear relationship was obtained ($WL_{225–425} = 77.68 - 14.45MR$, $R^2 = 0.683$). H and H_s AFIS data were used to estimate the surface area per unit mass (SA). Figure 6 shows an excellent negative relationship between MR and the estimated surface area (Estimated Surface Area $= 594.8 - 322.44MR$, $R^2 = 0.925$). Thus, consistent with the results for low micronaire, immature fibers developed a large SA, which was essentially primary cell wall. Therefore, the amount of the noncellulosic materials was higher, which resulted in higher weight loss in this region.

Cotton fiber H_s is defined as the mass per 1000 meters of fibers having a MR of 1. Therefore, H_s can be expressed as a function of P as follows:

$$H_s = 0.577P^2\rho/4\pi$$

where ρ is the cell wall density.[7]

Fiber H_s determined by the AFIS was positively correlated to the percentage weight loss as follows (Fig. 7): $WL_{225–425} = 24.27 + 0.32H_s - 0.0006{H_s}^2$, $R^2 = 0.719$. This result was somewhat counterintuitive because, all other things being equal, a decrease in the fiber H_s (smaller diameter fibers) would seem to be associated with increased fiber surface area per unit weight. The explanation was found in the fact that a strong positive correlation existed between H_s and MR. It is well documented in the literature that smaller fiber diameters have a tendency to be more mature.[7] Figure 8 confirms this observation by showing a positive correlation between H_s and MR on our set of samples

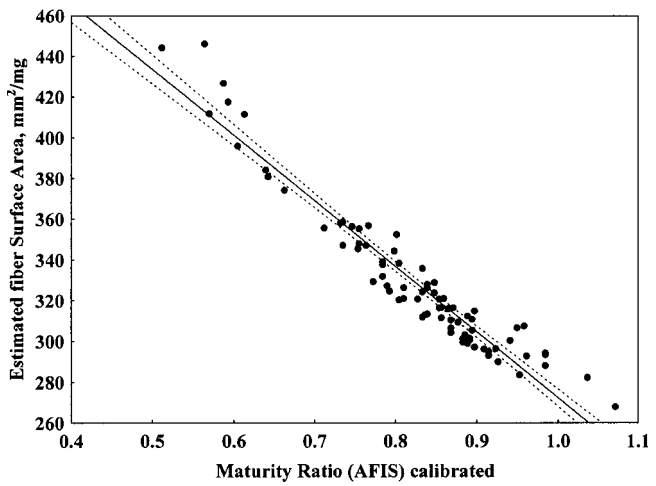

Figure 6 EFSA versus MR.

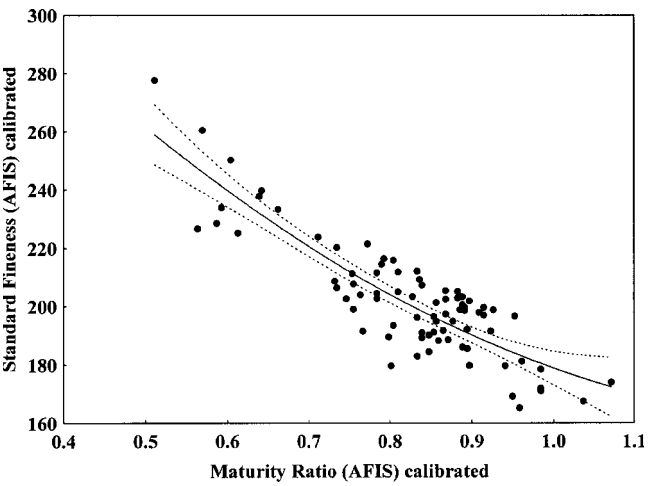

Figure 8 H_s versus MR.

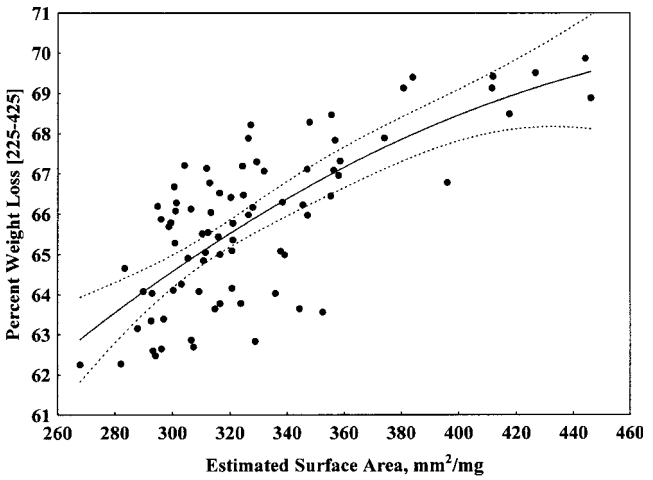

Figure 9 $WL_{225–425}$ versus estimated surface area.

($H_s = 409.67 - 361.52MR + 130.68MR^2$, $R^2 = 0.761$). Therefore, it was necessary to estimate the surface area for a given weight with AFIS H and AFIS P derived from AFIS H_s.

Figure 9 shows the relationship between $WL_{225–425}$ and the estimated SA. As expected, the correlation was positive:

$$WL_{225–425} = 40.16 + 0.113SA - 0.0001SA^2, R^2 = 0.528$$

Faughey et al.[5] found similar results for flax fibers. They showed that high weight loss of the flax fibers (64–66%) was characteristic of finer fibers compared with a lower weight loss (58–61%), which was associated with coarser fibers.[5] In this case, for flax fibers having no lumen, fine fibers meant high SAs.

As hypothesized earlier, because two cotton fibers with different maturities contain different proportions of primary cell walls (different degrees of the secondary cell wall development for a given P), the difference in the weight loss observed could be directly related to the amount of the primary cell wall per unit mass. The secondary cell wall is composed almost entirely of cellulose; therefore, no significant differences were expected in the weight losses of the secondary cell wall for two cotton samples with the same amount of cellulose.

To explain the differences in $WL_{225–425}$, we selected two cotton fibers with distinct characteristics, as shown in Table III. AFIS H for these two cottons were $H_{3625} = 142$ and $H_{3143} = 186.4$.

The number of fibers per milligram (N) is given by

$$N = 100,000/HL$$

where H is the fiber fineness and L is the mean fiber length by number (cm). Thus, $N_{3625} = 435$ and $N_{3143} = 270$.

If we assumed that the cotton fiber had a cylindrical shape of L and P that could be estimated with H_s (see previous discussion), the estimated fiber surface area (EFSA) per milligram was

$$EFSA = LPN$$

For cotton 3625, $EFSA_{3625} = 444.7$ mm^2/mg, and for cotton 3143, $EFSA_{3143} = 268.1$ mm^2/mg. The EFSA difference between the two cottons was $\Delta = EFSA_{3625} - EFSA_{3143} = 444.7 - 268.1 = 176.6$ mm^2/mg. From the TGA measurements, the difference in $WL_{225–425}$ between cotton 3625 and 3143 was 7.61%. Therefore, we hypothesized that an area of 176.6 mm^2/mg would correspond to a weight of 0.0761 g. From this, we deduced the primary cell wall width (PCW):

$$PCW = 0.0761/176.6\rho_{PC}$$

where ρ_{PC} is the primary cell wall density. To calculate ρ_{PC}, we used the values reported by Pierce and Lord.[12] For an extremely immature cotton, the authors reported the following values: $\theta = 0.177$, cell wall area (A_w) = 23.8 μm^2, and $H = 40$ mtex. In these conditions, this cotton is essentially composed of primary cell wall. From all these values, we could estimate ρ_{PC}:

$$\rho_{PC} = H/A_w = 1.14 \text{ g/cm}^3$$

Taking a density of the primary cell wall equal to 1.14, we calculated the primary cell wall thickness corresponding to this weight loss as PCW = 0.378 μm. This result was consistent with PCW values previously reported in the literature. Ryser[13] reported that during fiber elongation, the width of the primary cell wall ranged between 0.2 and 0.4 μm. Maxwell et al.[4] reported that the thickness of the primary wall was less than 0.5 μm and was composed of 50% cellulose, with pectin, waxes, and proteins making up the remainder.

The implication of the results obtained here was that $WL_{225–425}$ was closely related to the quantity of primary cell wall per unit mass. However, the relationship obtained was not perfect, so it was quite likely that the significant effects of the cotton type on the weight loss and on the peak temperatures could have involved other structural parameters that may have contributed to the pyrolysis decomposition of cellulose macromolecules. Such parameters could include, among others, fiber crystallinity, crystallite

TABLE III
Fiber Properties of Two Selected Cotton Fibers

	Cotton 3625	Cotton 3143
Mean length by number (mm)	16.2	19.9
P (μm)	63.1	49.9
θ (MR/0.577)[7]	0.2984	0.618
Weight loss (%)	69.9	62.2

size, fibril orientation, degree of polymerization, and molecular weight distribution. Most of these parameters are directly or indirectly related to cotton fiber maturity and, therefore, to cellulose deposition. Modorsky et al.[14,15] showed that rayon decomposed faster than cotton and suggested that this behavior might have been due to the low degree of polymerization of rayon. Further investigations are ongoing, aimed at examining of the implication of the structural parameters (crystallinity, crystallite orientation, etc.) on the percentage weight loss of the cotton fiber.

CONCLUSIONS

To our knowledge, this is the first study that attempted to estimate the primary cell wall with TGA of the cotton fibers. In addition to being an interesting theoretical exercise, these results show that TGA has potential as an important tool for a better understanding of cell wall development.

In this study, we investigated the relationships between three important cotton fiber physical properties, micronaire, maturity, and *H*, and fiber thermal properties as determined by TGA. The results show significant effects of the cotton fiber type on the percentage weight loss and the decomposition temperatures of the cellulose in the temperature region 225–425°C. In this region, good correlations were established between the weight loss and the quantity of primary cell wall per unit mass. Differences in weight loss between two cottons with different maturities allowed us to estimate the PCW that was in agreement with the existing literature.

Further investigations are ongoing to determine the implication of the fiber microstructure (crystallinity, crystallite size, fibril orientation, degree of polymerization) on the thermal decomposition of the cellulose macromolecules.

References

1. Goldthwait, C. F.; Smith, H. O.; Barnett; M. P. Textile World, July 1947, p 105.
2. Handbook of Fiber Chemistry; Lewin, M.; Pearce, E. M., Eds.; Marcel Dekker: New York, 1998.
3. Hartzell-Lawson, M.; Hsieh, Y.-L. Text Res J 2000, 70, 810.
4. Maxwell, J. M.; Gordon, S. G.; Huson, M. G. Text Res J 2003, 73, 1005.
5. Faughey, G. H.; Sharma, S. S.; Mccall, R. D. J Appl Polym Sci 2000, 75, 508.
6. Comprehensive Cellulose Chemistry: Volume 1. Fundamentals and Analytical Methods; Klemn, D.; Philipp, B.; Heinze, T.; Heinze, J.; Wagenknecht, W., Eds.; Wiley-VCH: Weinheim, 1998.
7. Hequet, E.; Wyatt, B.; Abidi, N.; Thibodeaux, D. Text Res J, 2006, 76, 576.
8. Pierce, F. T.; Lord, E. J Text Inst 1939, 30, T173.
9. Standard Method for Breaking Strength and Elongation for Cotton Fibers; ASTM D 1445; American Society for Testing and Materials: West Conshohocken, PA, 2001.
10. Prakash, S.; Ilengar, M. Text Res J 1965, 35, 90.
11. Worley, S., Jr.; Krowicki, R. S.; Cox, E. L. Text Res J 1975, 45, 326.
12. Pierce, F. T.; Lord, E. Shirley Institute Memoirs; Shirley Institute Didsbury: Manchester, England, 1939–1940; Vol. XVII, p 25.
13. Ryser, U. In Cotton Fibers, Development, Quality Improvement, and Textile Processing; Basra, A. S., Ed.; Food Products: Binghamton, NY, 1999; Chapter 1, p 1.
14. Madorsky, S. L.; Hart, V. E.; Straus, S. J Res Natl Bur Stand Res Pap 1956, 56, 2685.
15. Madorsky, S. L.; Hart, V. E.; Straus, S. J. Res Natl Bur Stand Res Pap 1958, 60, 2853.