2007 Beltwide Cotton Conferences, New Orleans, Louisiana, January 9-12, 2007

ON THE USE OF THERMOGRAVIMETRIC ANALYSIS TO STUDY COTTON FIBERS (*)

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Abstract

Thermal analysis of cotton fiber showed the presence of three regions of thermal decomposition, between 37ºC and 150ºC for region I, between 225ºC and 425ºC for region II, and between 425ºC and 600ºC for region III. Complete decomposition of the fiber occurred at 600ºC. The results showed significant effects of the fineness/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 fineness values are associated with low weight losses. High weight losses are associated with high primary cell wall areas per unit mass. Differences in weight loss between two cottons with different maturities allowed estimating the primary cell wall width.

Introduction

Raw cotton fibers consist of 95% cellulose I (β-1,4-D-anhydroglycopyranose)) (Lewin and Pearce, 1998). The major portion of the non-cellulosic compounds is located primarily in the cuticle and the primary cell wall and contains wax, pectic substances, organic acids, sugars, and ash-producing organic salts (Hartzell-Lawson and Hsieh, 2000). After chemical processing of cotton fibers (scouring and bleaching), virtually all these non-cellulosic materials are removed and the cellulose content of the cotton fibers is over 99%. It has been reported that the primary cell wall, which is less than 0.5 µm thick, consists of about 50% cellulose (Maxwell et al., 2003). Therefore, two cotton fibers samples 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 measuring the weight loss as a function of the temperature using Thermogravimetric analysis (TGA).

In this work, we utilize the TGA to record the weight loss of cotton fibers having a variety of maturities and fineness values. At constant fiber perimeter, immature cotton fibers have more primary cell wall for a given mass than mature cotton; therefore, the weight loss is expected to be negatively correlated to cotton fiber maturity.

Materials and Methods

Eighty carded cotton fiber samples were selected based on their distinct physical properties. The cotton samples were tested on High Volume Instrument (HVI), with 10 length and strength measurements and 4 micronaire measurements. They were also tested on the Advanced Fiber Information System (AFIS), with 5 replications of 3,000 fibers. The AFIS results (maturity ratio and standard fineness) have been calibrated using image analysis results as reported by Hequet et al. (2006). The fiber properties range from very immature and weak fibers (maturity ratio = 0.51, and strength = 24.4 cN/tex) to very mature and strong fibers (maturity ratio = 1.07, and strength = 33.4 cN/tex).

Thermogravimetric analysis of the fiber samples was performed using the Pyris 1 TGA equipped with an autosampler for automatic testing of 20 samples. The thermograms were recorded between 37ºC and 600ºC with a heating rate of 10ºC/min in a flow of nitrogen at 20 ml/min.

The cotton lint samples were rolled into small balls (between 1.5 mg and 2 mg) by hand (wearing 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 percent weight loss for each sample.

Results and Discussion

Figure 1 shows a representative thermogram of a cotton fiber sample having a micronaire of 4.8, HVI strength of 28.5 cN/tex, and a calibrated AFIS maturity ratio of 0.909. This thermogram is divided into three regions. The initial weight loss (region I) is located between 37ºC and 150ºC and is followed by a plateau region before the major weight loss occurs in region II, located between 225ºC and 425ºC. Finally, the region III is located between 425ºC and 600ºC. The first derivative of this thermogram (DTG), also illustrated in Figure 1, clearly reveals the inflection points. Three peaks located at 48ºC (peak I), 359ºC (peak II), and 521ºC (peak III) are observed. Faughey et al., who generated the thermal spectra of flax fibers, observed two such peaks for flax (Faughery et al., 2000). The primary peak (revealing cellulose decomposition) occurred between 240ºC and 400ºC, while another minor peak occurred between 400ºC to 520ºC.

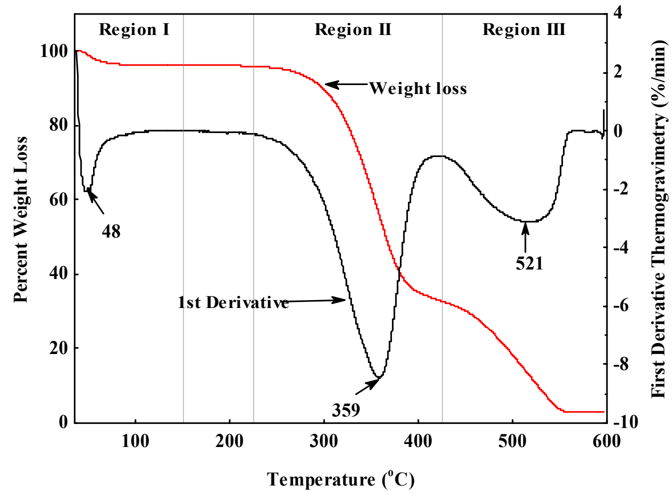

Figure 1. TGA thermogram of a representative cotton fiber with the corresponding derivative.

The thermograms of the eighty cotton samples were analyzed. The percent 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-value = 21, p-value = 0.000001) and region III (df = 79, F-value = 1.92, p-value = 0.000274).

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

There was no statistical significance to the relationship between percent weight loss in region I (37-150ºC) and the AFIS maturity ratio because of the combination of a high CV% and a very narrow dynamic range. Neither was there any significant relationship between weight loss and either micronaire or standard fineness in region I.

Figure 2 shows a significant negative linear relationship between the micronaire and the percent weight loss in the region II ($WL_{225\text{-}425}$ = 74.60 - 2.13 micronaire, R^2 = 0.425).

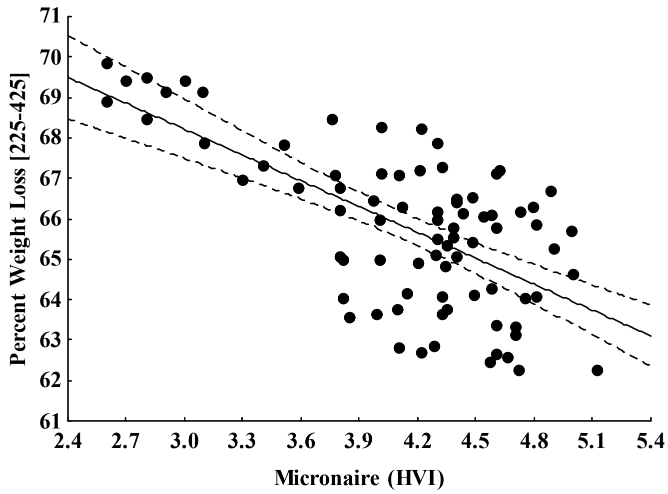

Figure 2. Percent weight loss in the region II [225°C - 425°C] vs. Micronaire.

Fiber maturity ratio is a measure of the relative amount of the cellulose in the fiber cross-section. The maturity ratio (M) as determined with the AFIS versus the weight loss in region II is shown in Figure 3. A significant negative linear relationship is obtained ($WL_{225\text{-}425} = 77.68 - 14.45$ M, $R^2 = 0.683$).

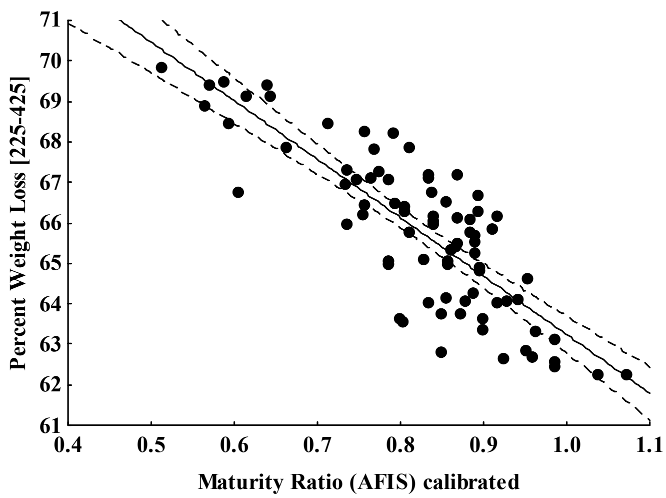

Figure 3. Percent weight loss in the region in region II [225°C - 425°C] vs. Maturity Ratio.

Fineness and standard fineness AFIS data were used to estimate the surface area per unit mass. An excellent negative relationship between maturity ratio and the estimated surface area per unit mass (Estimated Surface Area = 594.8 – 322.44 M, $R^2 = 0.925$) was found. Logically, very immature fibers develop large surface area per unit of mass, which is essentially primary cell wall because of the poorly developed secondary cell wall of very immature fibers. Therefore, the amount of the non-cellulosic materials per unit mass is higher for immature fiber than for mature fibers. This results in higher weight loss in region II for immature cottons.

Fiber standard fineness determined by the AFIS is positively correlated to the percent weight loss as follows (Figure 4): $WL_{225\text{-}425} = 24.27 + 0.32\ Hs - 0.0006\ Hs^2$, $R^2 = 0.719$.

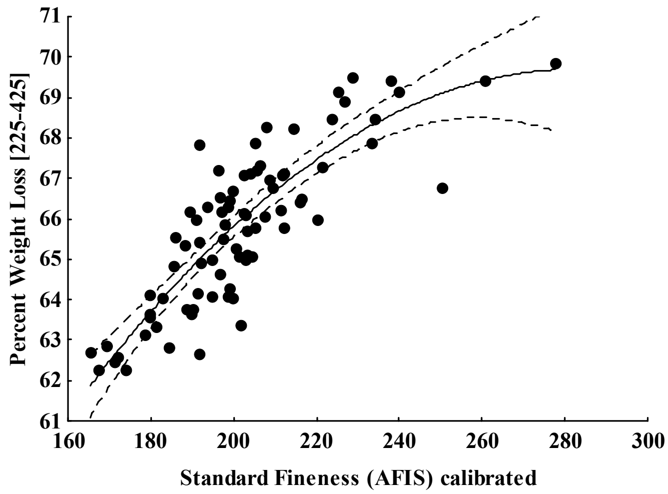

Figure 4. Percent weight loss in the region II [225°C - 425°C] vs. Standard Fineness.

This result is somewhat counter-intuitive because, all other things being equal, a decrease in the fiber standard fineness (smaller diameter fibers) would seem to be associated with increased fiber surface area per unit weight. The explanation is found in the fact that a strong positive correlation exists between standard fineness and maturity ratio for this set of cottons. It is well documented in the bibliography that smaller fiber diameter have the tendency to be more mature. (Hequet et al., 2006).

As hypothesized earlier, since two cotton fiber samples having different maturities contain different proportions of primary cell walls (different degree of the secondary cell wall development for a given fiber perimeter), the difference in the weight loss observed could be directly related to the amount of the primary cell wall per unit mass. To explain the differences in percent weight loss in region II [225-425], we selected 2 cotton fibers having distinct characteristics, as shown in Table 1.

Table 3. Fiber properties of two selected cotton fibers.

	Cotton 3625	**Cotton 3143**
Mean Length by Number (mm)	16.2	19.9
Perimeter (µm)	63.1	49.9
Theta (θ=MR/0.577)	0.2984	0.618
Weight loss (%)	69.9	62.2
AFIS Fineness (H)	142.0	186.4

The number of fibers per mg, is given by: N = 100000/(H*L), where H is the fiber fineness and L is the mean fiber length in cm. Thus, $N_{3625} = 435$ and $N_{3143} = 270$.

If we assume that cotton fibers have a cylindrical shape of length L, and a perimeter P that could be estimated with Hs, then the Estimated Fiber Surface Area per mg is EFSA = LxPxN, where N is the number of fibers per mg. 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 is $\Delta = EFSA_{3625} - EFSA_{3143} = 444.7 – 268.1 = 176.6$ mm^2. From the TGA measurements, the difference in percent weight loss in region II between cotton 3625 and 3143 is 7.61%. Therefore, we could hypothesize that an area of 176.6 mm^2 of primary wall corresponds a weight of 0.0761 mg. From this, we can deduce the primary cell wall width (PCW), PCW = $0.0761/(176.6*\rho_{pc})$, where ρ_{pc} is the primary cell wall density. To calculate the ρ_{pc} we used the values reported by Pierce et al. (1940). For an extremely immature cotton, the authors reported the following values: θ = 0.177, cell wall area $A_w = 23.8$ µm^2 and fineness H = 40 mtex. In these conditions, this cotton is essentially composed of primary cell wall. From all these values we can estimate the density of the primary cell wall (ρ_{pc}= H/A_w = 1.14 g/cm^3).

Taking the density of the primary cell-wall equal to 1.14 g/cm^3, we can calculate the primary cell-wall thickness corresponding to this weight loss as equal to PCW = 0.378 µm. This result is consistent with PCW values previously reported in the literature. Indeed, Ryser reported that during fiber elongation, the width of the primary cell wall ranges between 0.2 and 0.4 µm (Ryser, 1999). Maxwell et al. reported that the thickness of the primary wall is less than 0.5 µm and is composed of 50% cellulose, with pectin, waxes, and proteins making up the remainder (Maxwell et al., 2003).

Conclusions

To our knowledge this is the first study that attempts to estimate the primary cell wall width using Thermogravimetric analysis of the cotton fibers. In addition to being an interesting theoretical exercise, these results show that Thermogravimetric analysis has the potential of being an important tool for a better understanding of cell wall development. Further investigations are ongoing in order to determine the implication of the fiber microstructure (crystallinity, crystallite size, fibril orientation, degree of polymerization) on the thermal decomposition of the cellulose macromolecules.

** Adapted from a paper published in the Journal of Applied Polymer Science December 2006. Entitled "Thermogravimetric Analysis of Cotton Fibers: Relationship with Maturity and Fineness" (available at http://www.interscience.wiley.com).*

Acknowledgment

This research was supported by Cotton Incorporated and the International Cotton Research Center/USDA.

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