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Thermogravimetric analysis of developing cotton fibers

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ABSTRACT

In this research, thermogravimetric analysis (TGA) was used to investigate the structural changes that occur during cotton fiber development starting at 10 days post-anthesis (dpa). The percent weight losses attributed to water, non-cellulosic materials, and cellulose macromolecules were calculated from the thermograms. Valuable information was obtained related to the composition of the cell wall and the timing of the transition between the primary cell wall and the secondary cell wall. The results indicated that the two cultivars investigated (TX19 and TX55) exhibited different structural evolution. The transition phase between the primary cell wall and the secondary cell wall occurs between 17 and 18 dpa in fibers from the TX19 cultivar, while this transition occurs between 21 and 24 dpa for fibers from the TX55 cultivar. These conclusions are in agreement with the results obtained with Fourier transform infrared spectroscopy.

1. Introduction

The cell wall of cotton fiber has been documented to undergo significant structural and compositional changes during its growth and development [1–5]. The developmental process of the cotton fibers is divided into five major overlapping phases: differentiation, initiation, polar elongation, secondary cell wall deposition, and maturation [6]. Fiber initiation, which commences at anthesis (0 days post-anthesis = 0 dpa), signals the onset of fiber morphogenesis. Several studies have reported that the transition period between 16 and 21 dpa represents a major developmental change: from the end of the primary cell wall formation to the initiation of the secondary cell wall synthesis [2–4]. During this period, important structural changes occur which lead essentially to the deposition of cellulose macromolecules ($\beta(1 \rightarrow 4)$ glucopyranose) to form secondary cell wall, which is composed of nearly 100% cellulose [7].

Different techniques have been used to study the changes occurring during the different phases of fiber development (from initiation until full maturation). These techniques were based essentially on the analysis of cell wall extracts by chromatographic methods [1–5]. In previous work, we reported on the use of Fourier transform infrared spectroscopy (FTIR) and thermogravimetric analysis (TGA) to investigate the structural changes that occur as a function of developmental programming of cotton fibers (*Gossypium hirsutum* L.) [8]. FTIR and TGA analyses were performed on intact cotton fibers harvested at different stages of development (10, 14, 17, 20, 36, 50, and 61 dpa). The examination of the FTIR spectra showed the presence of non-cellulosic compounds (wax, protein, hemicelluloses, pectic substances, amino acids, etc.) at 10, 14, 17, and 20 dpa. However, at 36 dpa the vibration corresponding to non-cellulosic compounds disappeared. It was concluded that the transition between the primary cell wall synthesis and the secondary cell wall synthesis occurs at or around 20 dpa for both cultivars. The results obtained with thermogravimetric analysis supported this finding. However, because the fibers were harvested with a relatively large time intervals (17, 20, and 36 dpa), it was not possible to bring out cultivar differences.

Therefore, we repeated the same study with narrow time intervals, i.e. 10, 14, 17, 18, 19, 20, 21, 24, 27, 30, 36, 46, and 56 dpa [9]. The results of this study demonstrated that the evolution of the FTIR integrated intensities for specific vibration bands located at 1733 cm^{-1} (C=O stretching originating from esters, fatty acids, or amides), 1534 cm^{-1} (NH_2 deformation corresponding to proteins or amino acids), and 1627 cm^{-1} (O–H bending vibration of adsorbed water molecules) could be used as indicators for the switch of emphasis from the primary cell wall synthesis to the secondary cell wall synthesis [9]. In addition, TX19 and TX55 cultivars were found to exhibit different behaviors. In fibers from TX19 cultivar, the transition phase between the primary cell wall and the secondary cell wall occurs between 17 and 18 dpa. However, in fibers from TX55 cultivar, this transition occurs between 21 and 24 dpa. This finding is extremely important because a few day differences in the initiation of the secondary cell wall synthesis could have a large impact on fiber maturity at the end of the growing season. Fiber maturity is probably the most important fiber property because low maturity

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fibers tend to be weak. Weak fibers tend to break during processing, which leads to poor yearn quality and ultimately to poor quality fabrics with lower dye affinity.

The purpose of this work is to analyze the evolution of the thermal properties of developing cotton fibers using thermogravimetric analysis to strengthen the conclusions reported in a previous work using FTIR [9].

2. Experimental

2.1. Materials

For this study, 2 replications (10 plants each) of two cotton cultivars (*Gossypium hirsutum* L. cv. TX19 and TX55) were planted in a greenhouse with day/night cycles varying from 13/11 to 11/13 h and day/night temperatures of about 31/24 °C. Plants were grown in 20 l (5 gallons) pots of Sungrow SB 300 potting mix that had been amended with Peters 15-9-12 slow release fertilizer prior to potting. Plants were watered as needed. On the day of flowering (0 dpa), individual flowers were tagged, and 14 developing bolls per cultivar and per replication were harvested at 10, 14, 17, 18, 19, 20, 21, 24, 27, 30, 36, 46, and 56 dpa. The pericarp was immediately removed (excised with scalpel) and isolated ovules were transferred to cryogenic vials and stored in a Cryobiological Storage System filled with liquid nitrogen for analyses. Each replication was tested independently.

2.2. Sample dehydration

An established dehydration procedure for frozen samples was carried out as previously described [8,10,11]. The dehydration procedure consists of washing the hydrated sample (previously rinsed with water to remove soluble sugars) with acidified 2,2-dimethoxypropane (one drop of HCl in 50 ml of 2,2-dimethoxypropane), followed by five exchanges for 15 min each in 100% acetone. In a slightly acidic solution, 2,2-dimethoxypropane is instantly hydrolyzed by water to form methanol and acetone [10,12].

2.3. Thermogravimetric analysis

Thermogravimetric analysis (TGA) of fiber samples was performed using the Pyris1TGA equipped with a 20-sample autosampler (PerkinElmer Shelton, CT). Thermograms were recorded between 37 and 600 °C with a heating rate of 10 °C/min in a flow of nitrogen at 20 ml/min. Cotton lint samples were conditioned in a laboratory maintained at 65 ± 2% relative humidity and 21 ± 1 °C for at least 48 h. Then, sub-samples were rolled into small balls (between 1.5 and 2 mg) by hand (wearing latex gloves to avoid moisture transfer), and then placed in the sample pan. Three replications were performed from each developmental stage to produce a total of 6 tests per dpa (3 replications × 2 greenhouse replications). The Pyris software was used to calculate the first derivatives of the thermograms (DTG) and to calculate the percent weight loss for each sample.

2.4. Cellulose content determination

Cellulose content of developing cotton fibers was determined using the anthrone method [13]. The anthrone, a tricyclic hydrocarbon ($C_{14}H_{10}O$), is generally used for cellulose assay and calorimetric determination of carbohydrates. This method consists of adding anthrone solution (0.05–0.20%) in concentrated sulfuric acid to an aqueous solution of cotton fibers (previously digested by sulfuric acid). The absorbance of the green color of the solution is measured using a UV–vis spectrophotometer (LAMDA 650, PerkinElmer) at 625 nm and is proportional to the cellulose content of the sample. It should be pointed out that the cotton fibers were not subjected to any treatment to remove non-cellulosic materials (pectins, proteins, etc.).

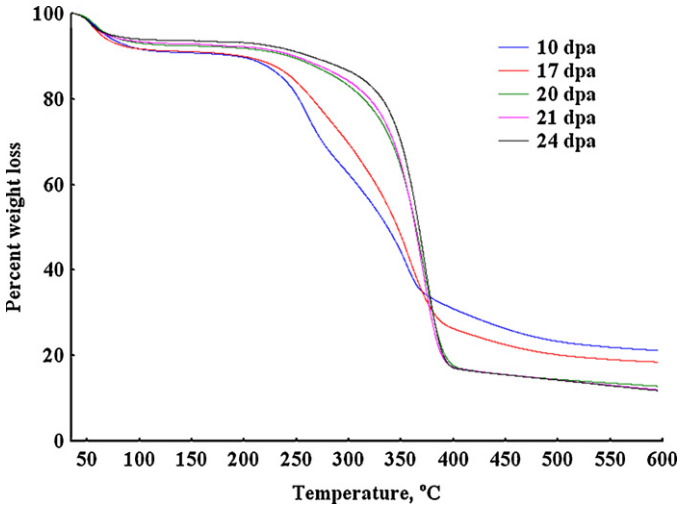

Fig. 1. Thermograms of representative developing cotton fibers from TX19 cultivar (*Gossypium hirsutum* L. cv.) at 10, 17, 20, 21, and 24 dpa.

2.5. Statistical analysis

Statistical analysis of the data was performed using Statistica Software (StatSoft Inc, Tulsa). Factorial ANOVA (analysis of variance) was performed to test any statistically significant effects and the mean separation was determined according to Newman–Keuls tests (with $\alpha = 5\%$).

3. Results and discussion

In previous work, we investigated the relationships between cotton fiber physical properties – micronaire, maturity, and fineness – and the fiber thermal properties as determined by thermogravimetric analysis [14]. The High Volume Instruments (Uster, TN) and the Advanced Fiber Information System (Uster, TN) were used to determine fibers micronaire, maturity ratio, and fineness. The thermograms of cotton fibers were divided into three regions of thermal decomposition: region I was located between 37 and 150 °C, region II was located between 225 and 425 °C, and region III was comprised between 425 and 600 °C. Complete decomposition of the fibers occurred at 600 °C. The results showed significant effects of fineness and maturity indicators on the weight loss and the peak temperature in the region 225–425 °C. High micronaires (coarse or very mature fibers), high maturity ratios, and low standard fineness values were associated with low weight losses. However, high weight losses are associated with high primary cell wall areas per unit mass (low maturity).

TGA was performed on fibers harvested at different stages of development from both cultivars as detailed in Section 2. The objective of this analysis was to elucidate the structural changes during the different phases of fiber development and to confirm the conclusions of the FTIR study [9]. Figs. 1 and 2 show representative thermograms of cotton fiber samples from TX19 and TX55 cultivars respectively harvested at various stages of development: 10, 17, 20, 21, and 24 dpa. Three major weight loss regions are observed in these thermograms. The first weight loss occurred between 37 and 150 °C, the second weight loss occurred between 150 and 400 °C, and the third weight loss occurred between 400 and 600 °C.

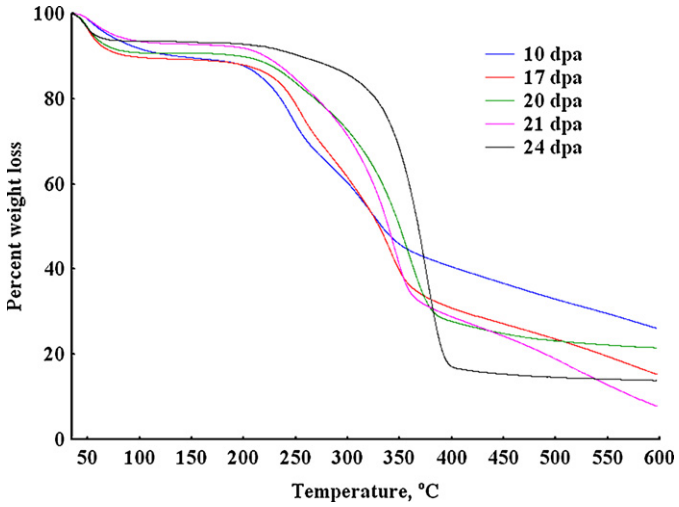

Fig. 2. Thermograms of representative developing cotton fibers from TX55 cultivar (*Gossypium hirsutum* L. cv.) at 10, 17, 20, 21, and 24 dpa.

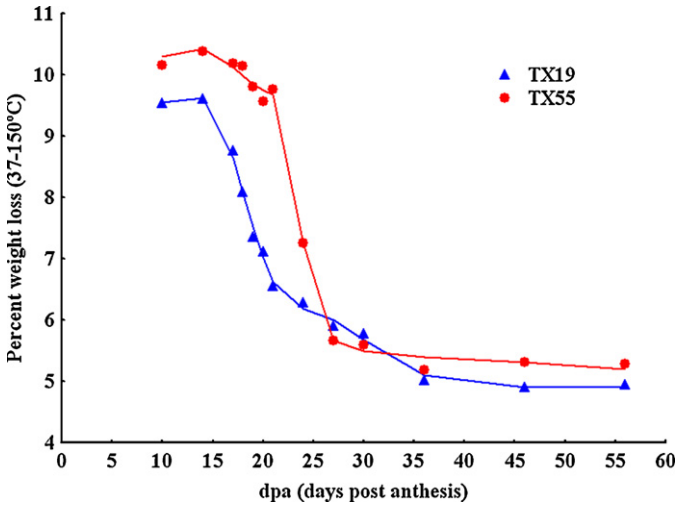

Fig. 3. Thermogravimetric analysis: percent weight loss between 37 and 150 °C versus dpa (days post-anthesis).

The percent weight loss in the region 37–150 °C was calculated and reported in Fig. 3, for both cultivars as a function of dpa. The weight loss in this region is primarily attributed to the adsorbed water molecules [8]. Some non-cellulosic compounds having low decomposition temperatures may also contribute to the weigh loss in this region (e.g. some wax components) [15]. The statistical analysis (analysis of variance) showed a significant effect of the developmental stage (dpa) and the cultivar on the percent weight loss as well as a significant interaction cultivar × dpa (Table 1). For fibers from TX19 cultivar, the percent weight loss decreased continuously from 9.54% for fibers at 10 dpa to around 5.02% for fibers at 36 dpa. However, for fibers from TX55 cultivar the percent weight loss did not show any significant change between 10 and 21 dpa (∼10.16%). It starts decreasing at 24 dpa. It is important to point out that both cultivars exhibited the same weight loss starting at 30 dpa.

The evolution of the percent weight loss between 150 and 400 °C is shown in Fig. 4 for both cultivars. The weight loss in this region is attributed to the decomposition of non-cellulosic materials and cellulose macromolecules [15]. The statistical analysis showed a significant effect of the developmental stage and the cultivar as well as a significant interaction cultivar × dpa (Table 2). For fibers from

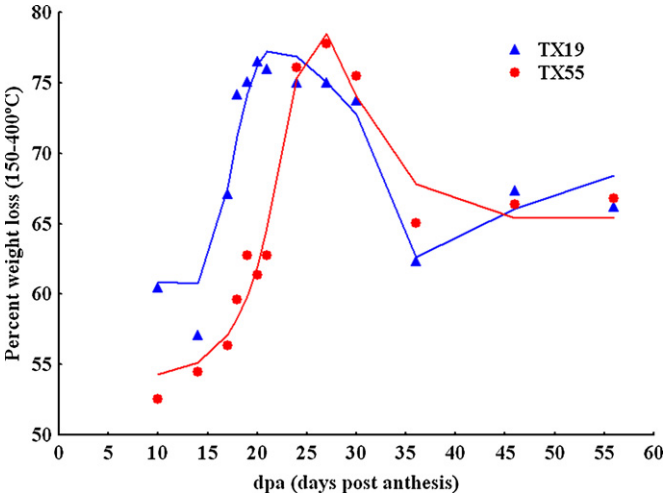

Fig. 4. Thermogravimetric analysis: percent weight loss between 150 and 400 °C versus days post-anthesis (dpa).

Table 1
Variance analysis: effect of developmental stage (days post-anthesis) and cultivars on the percent weight loss in the region 37–150 °C.

Parameter	df	*F*	Probability	TX19: % weight loss¥ (37–150 °C)	TX55: % weight loss¥ (37–150 °C)
Intercept	1	13532.66	0.000001		
Cultivar	1	75.06	0.000001		
dpa	12	69.13	0.000001		
10				9.54 a	10.16 a
14				9.61 a	10.39 a
17				8.76 b	10.18 a
18				8.10 c	10.14 a
19				7.35 d	9.81 a
20				7.12 de	9.56 a
21				6.55 ef	9.76 a
24				6.28 fg	7.25 d
27				5.90 fgh	5.67 ghi
30				5.80 fghi	5.60 ghi
36				5.02 hi	5.20 hi
46				4.90 i	5.31 hi
56				4.95 i	5.30 hi
Cultivar × dpa	12	5.76	0.000094		
Error	26				

df, degrees of freedom; *F*, variance ratio.
¥ Values not followed by the same letter are significantly different with $\alpha = 5\%$ (according to Newman–Keuls tests).

Table 2
Variance analysis: effect of developmental stage (days post-anthesis) and cultivars on the percent weight loss in the region 150–400 °C.

Parameter	df	*F*	Probability	TX19: % weight loss[¥] (150–400 °C)	TX55: % weight loss[¥] (150–400 °C)
Intercept	1	47517.19	0.000001		
Cultivar	1	73.27	0.000001		
dpa	12	34.36	0.000001		
10				60.50 bcd	52.52 e
14				57.10 cde	54.45 de
17				67.06 b	56.36 cde
18				74.15 a	59.59 bcd
19				75.10 a	72.73 bc
20				76.50 a	61.36 bc
21				76.00 a	62.74 bc
24				75.00 a	76.10 a
27				75.00 a	77.75 a
30				74.00 a	75.48 a
36				62.33 bc	65.06 b
46				67.31 b	66.36 b
56				66.15 b	66.80 b
Cultivar × dpa	12		0.000001		
Error	26				

df, degrees of freedom; *F*, variance ratio.
[¥] Values not followed by the same letter are significantly different with $\alpha = 5\%$ (according to Newman–Keuls tests).

TX19 cultivar, the percent weight loss increased from 60.50% for fibers at 10 dpa to 76.50% for fibers at 20 dpa and starts decreasing thereafter. For fibers at 36 dpa, the percent weight loss dropped to 62.33%. However, for fibers from TX55 cultivar, a gradual increase of the percent weight loss is observed between 10 dpa (52.52%) and 27 dpa (77.75%). For fibers at 36 dpa, the percent weight loss dropped to 65.06%. No significant changes in the percent weight loss are noticed between cultivars for fibers older than 36 dpa. The increase of the percent weight loss during fiber development could be attributed to the increase of cellulose content as the secondary cell wall develops. This is illustrated by the evolution of the cellulose content during the fiber development for both cultivars (Figs. 5 and 6). As shown in these charts, for both cultivars the cellulose content increases from around 10.3% (at 10 dpa) to more than 80% (at 30 dpa). This increase of cellulose content is associated with an increase in the percent weight loss as determined with thermogravimetric analysis.

To further explain the changes in the percent weight loss of developing cotton fibers, we plotted the integrated intensities of the FTIR peak 1733 cm^{-1} (C═O stretching, attributed to esters, fatty acids, or amides) and 1534 cm^{-1} (NH_2 deformation attributed to proteins or aminoacids) as a function of dpa. The FTIR data were obtained on the same sample and were reported in a previous work [9]. For both cultivars, the increase of the percent weight loss in the region 150–400 °C is associated with a decrease of the integrated intensities I_{1733} and I_{1534}, thus, in the relative amount of non-cellulosic compounds (Figs. 7 and 8). Because the cellulose content remains constant after 36 dpa, the drop in the percent weight loss after 25 dpa (Figs. 5 and 6) in the region 150–400 °C is associated with the drop in the amount of non-cellulosic materials. These results are in agreement with previous work in which changes in biochemical composition of the cell wall of the cotton fiber during development were studied [2]. The authors reported that the percent by weight of neutral sugars decreased from 25% at 10 dpa to 4% at 29 dpa. A decrease was also reported for the uronic acids (from 22% at 10 dpa to 2% at 22 dpa) and proteins (from 22% at 10 dpa to 3% at 18 dpa). Furthermore, previous research reported that cell walls of elongating cotton fibers contained large amounts of galacturonans (acidic polymers) and β-glucans (β-1,3-glucans) [4]. It showed that the extractable amounts of these compounds increased as fibers grew during the elongation phase (up to 20 dpa) and decreased thereafter [4]. Therefore, the increase of the percent

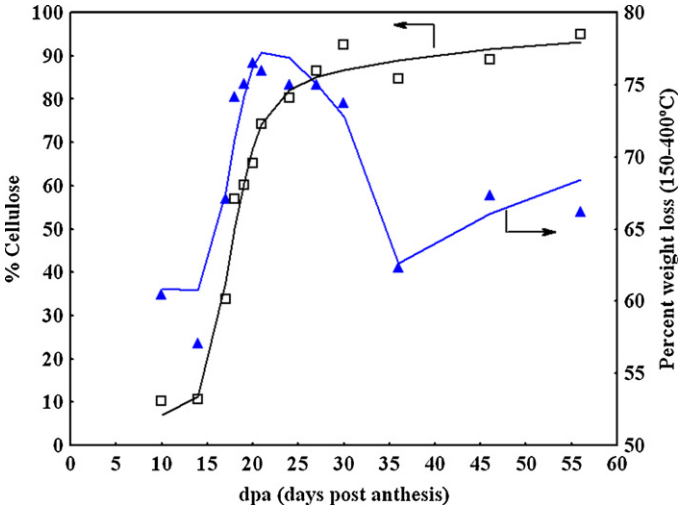

Fig. 5. Percent weight loss in the region 150–400 °C vs. percent of cellulose for fibers from TX19 cultivar (*Gossypium hirsutum* L. cv.).

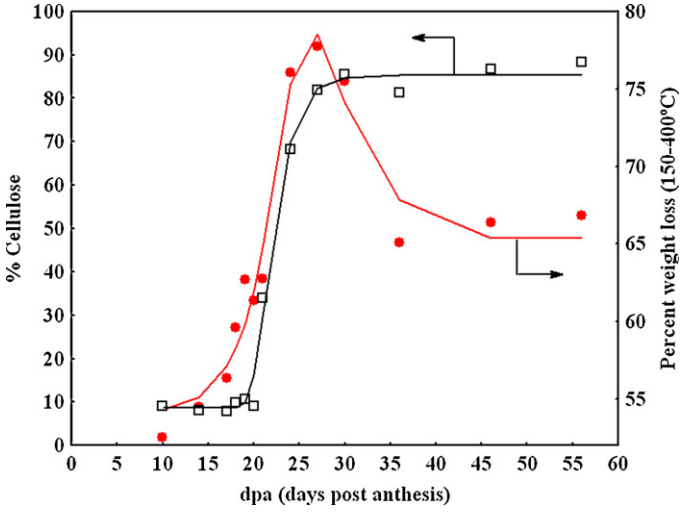

Fig. 6. Percent weight loss in the region 150–400 °C vs. percent of cellulose for fibers from TX55 cultivar (*Gossypium hirsutum* L. cv.).

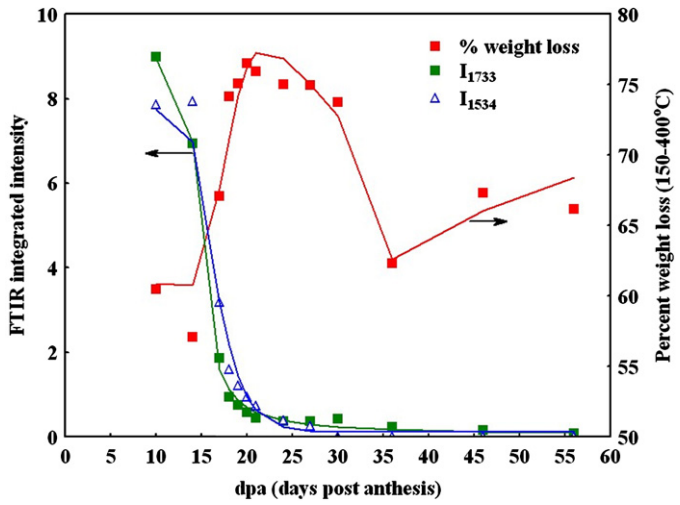

Fig. 7. FTIR integrated intensities (I_{1733} and I_{1534}) vs. percent weight loss in the region 150–400 °C for fibers from TX19 cultivar (*Gossypium hirsutum* L. cv.).

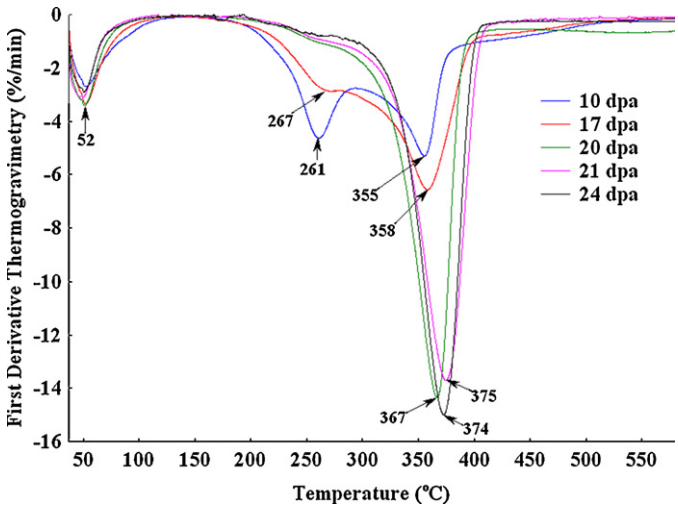

Fig. 9. First derivative thermogravimetry of developing cotton fibers from TX19 cultivar (*Gossypium hirsutum* L. cv.).

weight loss could be associated with the elongation phase. However, the maximum weight loss could be associated with the end of the elongation phase and the beginning of the wall thickening stage (secondary cell wall formation). For TX19 cultivar, this peak is reached around 18 dpa. However, for TX55 this peak is reached around 24 dpa.

It is important to point out that, both TGA and FTIR measurements were performed on intact fibers (no cell wall extractions were performed). These two independent analytical measurements revealed the occurrence of important structural changes during the cotton fiber development.

First derivatives of thermograms of developing fibers were calculated to highlight the inflection points that indicate thermal transitions. As an illustration, Figs. 9 and 10 show the first derivatives of thermograms of fibers at 10, 17, 20, 21 and 24 dpa from TX 19 and TX55 cultivars, respectively. For fibers from TX19 cultivar, three major transitions are observed at 10 and 14 dpa. The first transition occurring at 52 °C is attributed to the loss of adsorbed water, the second transition at 261 °C is attributed to the loss of non-cellulosic compounds, and the third transition around 355 °C is attributed to the decomposition of cellulose macromolecules. As fibers develop, the second transition is noticed only as a small shoulder (shifted to 267 °C) in the thermograms of fibers at 17 dpa from TX 19 cultivar, and it disappeared completely at 18 dpa. For fibers from TX55 cultivar, the same three transitions are observed with a very important difference: the second transition disappeared at 21 dpa.

The temperature of decomposition of cellulose (third peak) was calculated from the first derivatives of the thermograms for fibers at different developmental stages. The analysis of variance (Table 3) shows significant effect of the fiber development stage on the temperature of decomposition of cellulose as well as a significant interaction cultivar × dpa. For fiber from TX19 cultivar, the temperature of decomposition increases from 346.00 °C for fibers at 10 dpa to 368.27 °C for fibers at 27 dpa. For fiber from TX55 cultivar, the temperature of decomposition increases from 342.30 °C for fibers at 10 dpa to 374.00 °C for fibers at 27 dpa. At 10 dpa, the cellulose content in the fibers is less than 20% and increases sharply during fiber development to reach ~95% at full maturity. This increase in cellulose content is accompanied with an increase in the percentage of crystallinity (structural organization of the cellulose macromolecules). To support, this hypothesis, X-ray diffraction is being performed on these samples and will be reported in the near future. According to the literature, it was reported that the degree

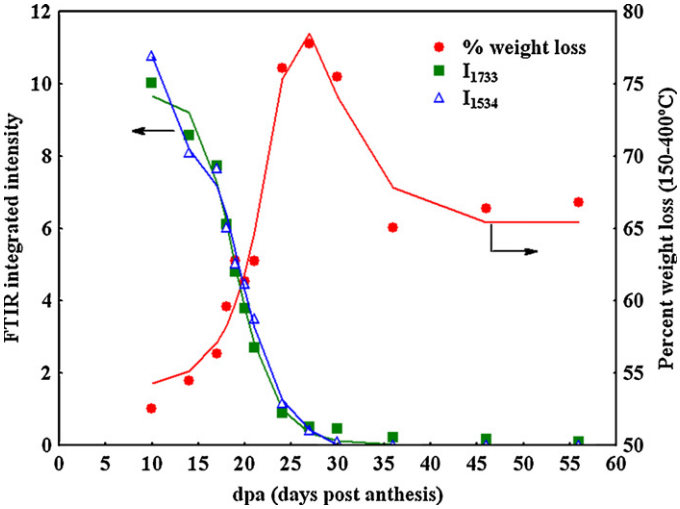

Fig. 8. FTIR integrated intensities (I_{1733} and I_{1534}) vs. percent weight loss in the region 150–400 °C for fibers from TX55 cultivar (*Gossypium hirsutum* L. cv.).

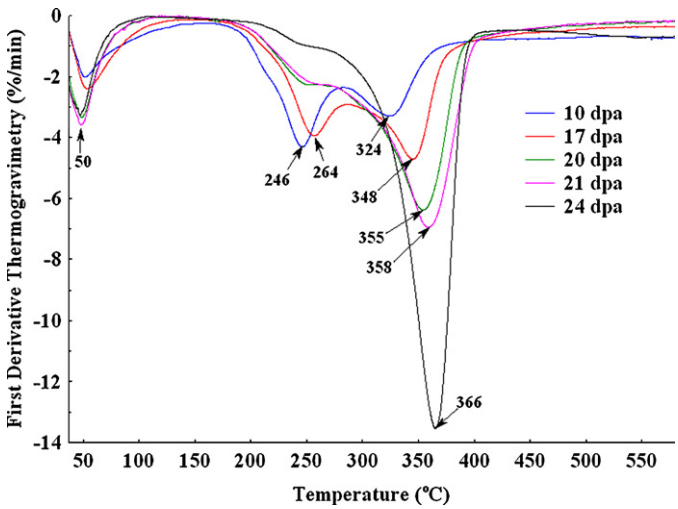

Fig. 10. First derivative thermogravimetry of developing cotton fibers from TX55 cultivar (*Gossypium hirsutum* L. cv.).

Table 3
Variance analysis: effect of developmental stage (days post-anthesis) and cultivars on the peak temperature in the region 325–400 °C.

Parameter	df	*F*	Probability	TX19: peak temperature (°C)[¥]	TX55: peak temperature (°C)[¥]
Intercept	1	209192.0	0.000001		
Cultivar	1	22.7	0.000063		
dpa	12	9.4	0.000001		
10				346.00 def	342.30 f
14				349.43 cdef	345.20 ef
17				360.40 abcdef	343.03 f
18				369.42 abc	343.00 f
19				368.10 abc	353.10 abcdef
20				371.00 abc	356.45 abcdef
21				368.30 abc	353.00 abcdef
24				368.33 abc	372.30 ab
27				368.27 abc	374.00 a
30				366.00 abcd	366.40 abcd
36				351.00 bcdef	345.00 ef
46				364.33 abcde	360.00 abcdef
56				360.00 abcdef	362.00 abcdef
Cultivar × dpa	12	2.9	0.011453		
Error	26				

df, degrees of freedom; *F*, variance ratio.
[¥] Values not followed by the same letter are significantly different with $\alpha = 5\%$ (according to Newman–Keuls tests).

of crystallinity of Maxxa Acala fibers increases steadily from 38 to 57% between 24 and 60 dpa [16].

4. Conclusions

Thermogravimetric analysis was used to investigate the structural changes that occur during cotton fiber development starting 10 days post-anthesis. The evolution of the percent weight loss attributed to water, non-cellulosic materials, and cellulose macromolecules provided valuable information related to the composition of the cell wall. The results indicated that the two cultivars investigated (TX19 and TX55) exhibited different structural evolution. The transition phase between the primary cell wall and the secondary cell wall occurs between 17 and 18 dpa in fibers from TX19 cultivar, while this transition occurs between 21 and 24 dpa for fibers from TX55 cultivar. These results are in agreement with previously reported results of the FTIR study of fiber development. Our results indicated that the two cultivars appear to mature at different rates. This finding is extremely important in the selection of the genotype because a few days difference in the initiation of the SCW synthesis could have a large impact on fiber maturity at the end of the growing season. Fiber maturity is probably the most important fiber property because low maturity fibers tend to be weak. Weak fibers tend to break during processing, which leads to poor yarn quality and ultimately to poor quality fabrics with lower dye affinity.

Acknowledgments

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