

1802 The Relationship Between Maillard Reaction Product Formation and the Strength of Griege Yarns Subjected to Accelerated Ageing Conditions

Dr. Gary Gamble , USDA ARS CQRS, Clemson, SC

Previous work examining the effect of ageing on cotton fiber surface chemical and HVI properties, yarn processing performance, and yarn quality showed that cotton bales stored for extended periods exhibit significant changes in a number of these variables including primarily surface sugar content, HVI +b color grade, and yarn strength. The present study attempts to further elucidate the relationship between these three variables by subjecting pre-spun yarns to accelerated ageing conditions. A single variety of cotton was spun into yarn and subjected to a series of thermal and dehydration treatments. The resultant yarns as well as a control which was not subjected to treatment were subsequently analyzed for glucose, pH, conductivity, moisture, UV-vis absorption, fluorescence, and yarn strength. Results suggest that ageing of griege cotton yarns results in an increase in Maillard-type browning reaction products, consistent with changes observed in +b. The amount of these reaction products correlates with loss of yarn strength. These results are discussed in terms of changes in surface morphology of the fiber resulting from a temperature dependent reaction mechanism.

Introduction

Previous work conducted at the Cotton Quality Research Station has demonstrated that cotton stored in bale form for 2 years exhibits changes in a number of chemical and physical fiber properties as well as a decrease in resultant yarn strength (Gamble 2007a). The chemical properties examined included moisture content, pH, wax content, conductivity, and glucose content. Of these, only moisture content and glucose content exhibited significant changes. Moisture content decreased from 6.97% to 6.59%, while glucose content decreased from 0.15% to 0.04%. A decrease in pH from 6.88 to 6.36 was also observed, though this was not significant under the conditions of the statistical model. Concomitantly, +b was the only HVI variable which exhibited a significant change, increasing from 9.07 to 11.61 as a result of storage. HVI length, strength, uniformity and Rd were unchanged. Yarns produced from both the new crop cotton and duplicate bales stored for two years were evaluated for opening waste, strength (Statimat-M), elongation, thick places and thin places. Of these yarn variables, only strength exhibited a significant difference as a result of bale aging, decreasing from 17.54 g/tex to 16.13 g/tex. Taken together, these results appear to indicate that the chemical changes occurring as a result of ageing do not impact fiber strength as indicated by HVI, but may be responsible for the observed decrease in yarn strength. The fact that fiber strength is unaffected by ageing while yarn strength is suggests that a fiber surface phenomenon is responsible for the observed loss in yarn strength, because a component of yarn strength involves fiber-to-fiber friction interactions. The nature of this postulated change in fiber surface morphology may involve any one or all of the surface chemical constituents, including waxes, pectins, proteins, or any soluble sugars or salts present on the surface. The present work is an attempt to resolve whether the observed changes in +b and glucose content are directly related, to what extent they are responsible for changes in yarn strength, or if they may be used as possible indicators of yarn quality for marketing purposes. Identical yarns were subjected to two different elevated temperatures for a period of 72 hours, and an additional yarn sample was subjected to a dehydrating environment for the same period. The effect of these treatments is to accelerate the ageing process. Following these treatments, the yarns were

reconditioned at 65% RH and 25C and subsequently tested for yarn strength, moisture content, glucose content, pH, absorbance at 360 nm, and fluorescence intensity at 393 nm.

Materials and Methods

Yarn Processing

A single upland cotton variety was processed through the Truetzschler Opening and Cleaning line (American Truetzschler Inc., Charlotte, NC) and card to produce a 70 grain sliver at 150 lbs/hour. All fiber was processed through the following sequence: blending hoppers in a Fiber Controls Synchromatic Blending System (M & M Electric Service Inc., Gastonia, NC), Axi-Flo cleaner (American Truetzschler Inc., Charlotte, NC), GBRA blending hopper (American Truetzschler Inc., Charlotte, NC), a RN cleaner (American Truetzschler Inc., Charlotte, NC), RST cleaner (American Truetzschler Inc., Charlotte, NC), DUSTEX fine dust remover (American Truetzschler Inc., Charlotte, NC), chute fed Saco Lowell card (Saco Lowell Inc., Easley, SC), Rieter RSB draw frame (Rieter Corp., Spartanburg, SC), Zinser 660 roving frame (Saurer, Inc., Charlotte, NC), and Zinser 321 ring spinning frame (Saurer, Inc., Charlotte, NC). All roving sliver was prepared using the same spindle and run on the same spindle of the ring spinning frame into 20/1 yarns at a spindle speed of 16,500 RPM, a front roll speed of 260 RPM, and a 4.1 TM.

Heat Treatments

2 sets of yarn samples of 3 replicate spindles each were subjected to heating at 70 C and 105 C for 72 hours in a forced draft convection oven.

Dehydration Treatment

An additional set of yarn samples of three replicate spindles was subjected to dehydrating conditions (RH = 13%) in a closed vessel containing CaCl₂ for 72 hours.

Yarn Tensile Testing

The Statimat-M (Zellweger Uster, Knoxville, TN) was used for yarn strength measurements. Each spindle was subjected to 200 single end breaks. Tensile properties of yarn were determined using standard test methods (ASTM, 1994). Moisture Determination

Duplicate moisture determinations on the cotton samples before and after ageing were performed according to standard test methods (ASTM 2001). Conductivity, pH and Glucose Measurements

Cotton samples were extracted using 20 ml deionized water per gram of cotton, with three replicates performed for each of the cotton samples. Each sample was agitated with a glass rod in order to promote wetting of the cotton surface. The resultant wetted sample was allowed to sit for 15 minutes before being wrung out. The resulting extract was then subjected to pH and glucose measurements. Measurements for pH were performed on a Orion Model 310 pH meter. Glucose measurements, reported as ppm present in solution, were performed using a Yellow Springs Instrument Co. Model 2700 Bioanalyzer (YSI, Inc., Yellow Springs, OH) equipped with a glucose oxidase membrane.

UV-vis and Fluorescence

UV-vis absorbance spectra were collected on a Beckman DU-7 spectrometer. Fluorescence spectra (320–750 nm) were acquired using a Fluorolog3-121 (Jobin-Yvon Spex, Edison, NJ) with 300 nm excitation. The exit slit of the excitation monochromator and the entrance slit of the emission monochromator were set at 2 nm bandwidth, and spectra were acquired using a 0.5 s integration time.

Results and Discussion

Results of chemical, spectroscopic, and yarn strength measurements as a function of different accelerated ageing temperature and dehydration conditions are presented in Table 1. Each of the measured variables exhibits significant differences between each of the treatments. Moisture content of the yarn samples after treatment and subsequent reconditioning does not appear to correlate significantly with yarn strength, as seen in Figure 1. The decrease in glucose content in response to treatment conditions indicates that glucose is degraded by a thermally activated process, and furthermore that this process possibly involves a dehydration reaction mechanism as indicated by the fact that yarn stored in a desiccating environment at 25 C shows a decrease relative to the control. In addition to the observed decreases in glucose content, pH is also observed to experience a decrease as a function of temperature and dehydrating conditions. The relationship between glucose content and pH is shown in Figure 2. The strong linear relationship indicates the possibility that a Maillard type reaction is responsible for the observed changes in both glucose and pH, since it has been demonstrated (Ajandouz et al., 2001) that the Maillard reaction, which involves a thermally activated condensation reaction between reducing sugars such as glucose and amino acids, concomitantly leads to a decrease in pH. The fact that the yarn samples held in a desiccating environment experience decreases in glucose and pH without additional heat suggests that the reaction is also activated by a dehydrating condition, since the reaction is a condensation reaction resulting in the loss of a water molecule. Such a mechanism has been previously reported (Koster and Leopold, 1988). In order to substantiate the tentative conclusion that the yellowing of cotton may be due to formation of Maillard reaction products, the water extracts were additionally analyzed for fluorescence intensity, since Maillard reaction products are known to exhibit fluorescence in the range 380–440 nm (Matiacevich et al., 2005). Figure 3 shows the relationship between fluorescence intensity of the water extract at 393 nm and glucose concentration. The strong correlation observed is further evidence that the yellowness of cotton lint is due in part to Maillard type reaction products.

When glucose content is compared with yarn strength (Figure 4) a clear correlation is seen, though it is non-linear. A non-linear relationship is also observed (not shown) when fluorescence intensity is compared with yarn strength. By comparison, when the absorbance (360 nm) of the water extract is compared with yarn strength, as seen in Figure 5, a strong linear relationship is observed. Figure 6 is a comparison of fluorescence intensity vs. absorbance, and the non-linear relationship indicates that absorbance increases at a faster rate than fluorescence, the possible explanation being that other browning reactions, i.e. caramelization, are occurring which do not result in fluorescent products. Additionally, the non-linear relation seen in Figure 4 may be due to the fact that other non-reducing sugars, primarily fructose, also react to form browning reaction products. The linear relationship seen in Figure 5 shows clear evidence that the creation of browning reaction products due to thermal mechanisms is highly correlated with the concomitant decrease in yarn strength. It is not evident that the chemical changes due to the Maillard reaction should have a direct effect upon yarn strength. Most of the sugars and amino acids involved in this reaction are

presumably present primarily in the lumen, and therefore would not be expected to have an effect upon outer surface properties. Previous work has demonstrated, though, that sugars present on the outer surface of the fiber lead to increased yarn strength via a hydrogen bonding mechanism (Gamble 2007b). Further work must be undertaken in order to determine whether the browning reactions observed occur on the outer fiber surface, or solely in the lumen. Regardless of whether the browning reactions have a direct effect upon yarn strength, however, it appears from the present evidence that they may be useful as predictors of yarn quality, specifically yarn strength.

References

Ajandouz, E.H., Tchiakpe, L.S., Ore, F.D., Benajiba, A., and A. Puigserver. 2001. Effects of pH on Caramelization and Maillard Reaction Kinetics in Fructose-Lysine Model Systems. *J. Food Sci.*, 66(7): 926-931.

American Society for Testing and Materials (ASTM). 1994. Standard test method for tensile properties of yarn by single strand method (D-2256). *In Annual Book of Standards, Section 7.01, Textiles*. ASTM International, West Conshohocken, PA.

American Society for Testing and Materials (ASTM). 2001. Standard test method for moisture in cotton by oven drying (D2495-01). *In Annual Book of ASTM Standards*. Vol. 07.01. ASTM, West Conshohocken, PA.

Gamble, G.R. 2007a. The Effect of Bale Ageing on Cotton Fiber Chemistry, Processing Performance and Yarn Quality. *J. Cot. Sci.*, in print.

Gamble, G.R. 2007b. The Effect of Fiber Surface Sugar Content on Yarn Properties.

Proc. Beltwide Cotton Conf., New Orleans, LA.

Koster, K.L, and C. Leopold. 1988. Sugars and Desiccation Tolerance in Seeds. *Plant Physiol.* 88: 829-832.

Matiacevich, S.B., Santagapita, P.R., and M.P. Buera. 2005. Fluorescence from the maillard reaction and its Potential Applications in Food Science. *Critical Reviews in Food Science*. 45: 483-495.

Table 1. Yarn chemical, spectroscopic and yarn strength properties as a function of treatment conditions.

<i>Sample Treatment</i>	<i>Glucose (ppm)</i>	<i>pH</i>	<i>Moisture (% w/w)</i>	<i>Absorbance ($\lambda = 360 \text{ nm}$)</i>	<i>Fluorescence Intensity ($\lambda = 393 \text{ nm}$)</i>	<i>Yarn Strength (g/tex)</i>
Control	66.2 a	6.54 a	6.25 b	0.142 d	11 d	14.34 a
Desiccated	53.5 b	6.40 b	6.28 a	0.156 c	12 c	14.26 b
70 C heat	35.2 c	6.18 c	5.69 d	0.214 b	16 b	13.99 c
105 C heat	5.5 d	5.98 d	5.92 c	0.472 a	20 a	12.92 d

Figures

Figure 1. Moisture content vs. strength of the treated yarns.

Figure 2. Glucose content vs. pH of a water extract of the treated yarns.

Figure 3. Glucose content vs. fluorescent intensity of a water extract of the treated yarns.

Figure 4. Glucose content of a water extract vs. strength of the treated yarns.

Figure 5. Absorbance of a water extract vs. strength of the treated yarns.

Figure 6. Fluorescent intensity vs. absorbance of a water extract of the treated yarns.

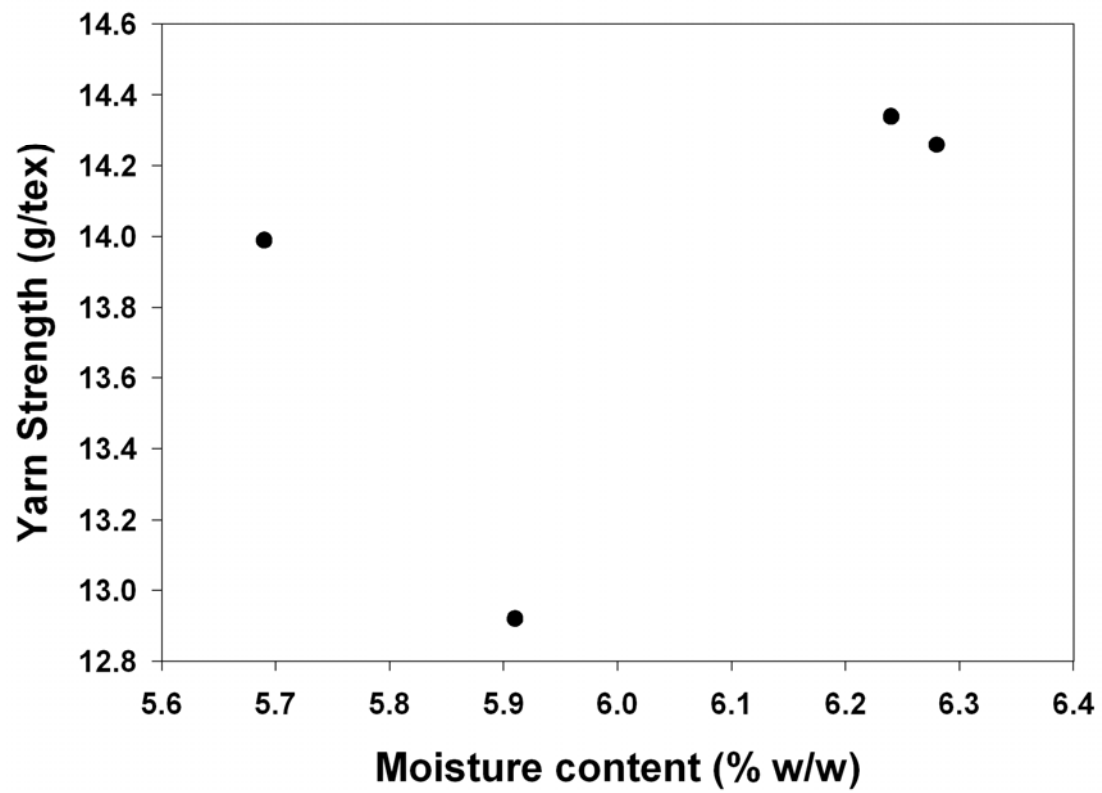


Figure 1

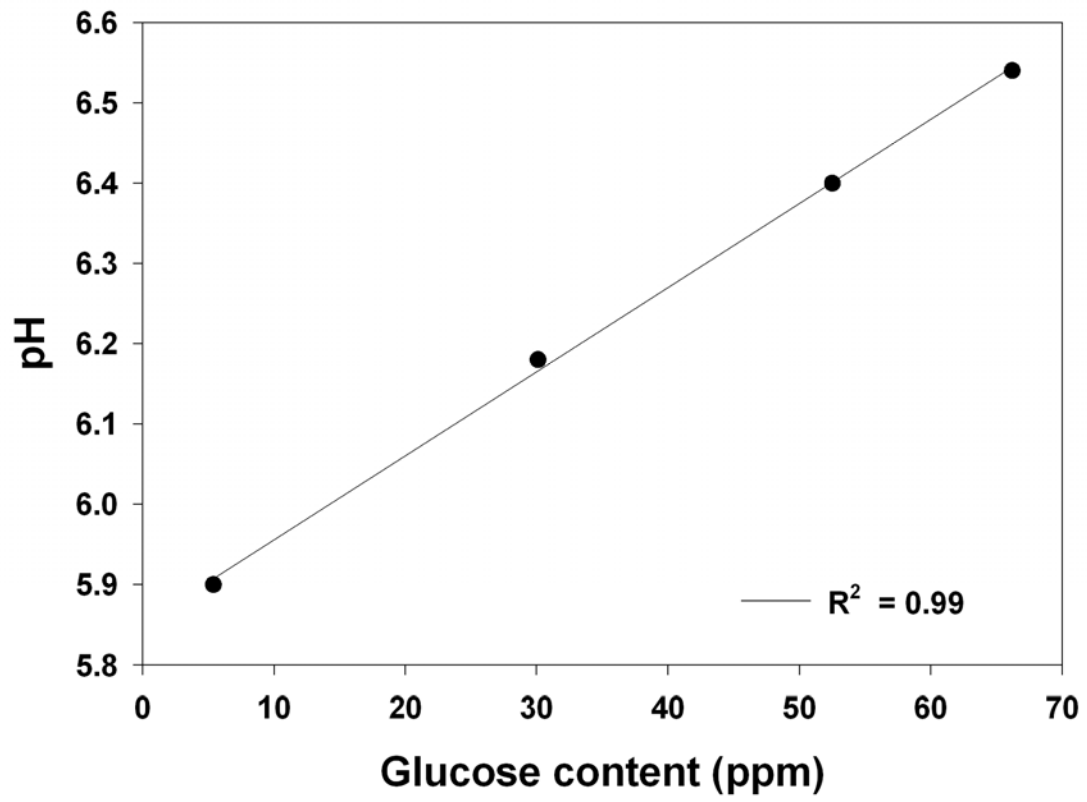


Figure 2

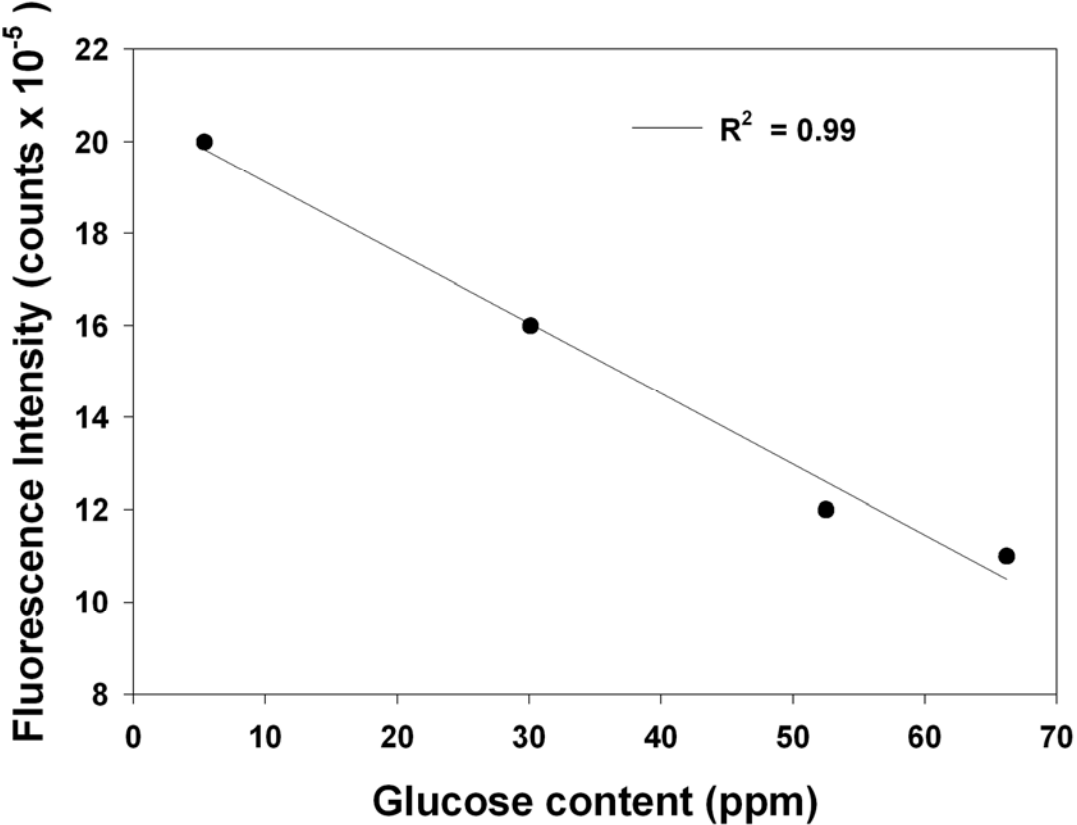


Figure 3

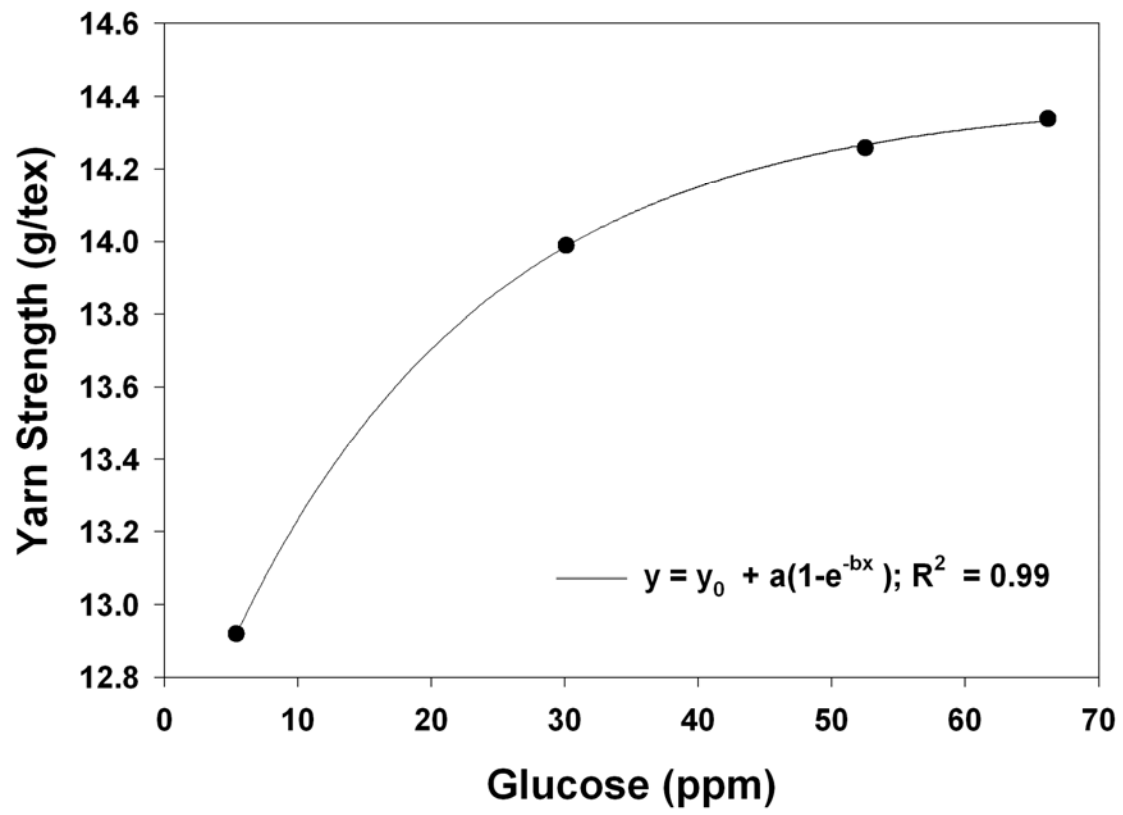


Figure 4

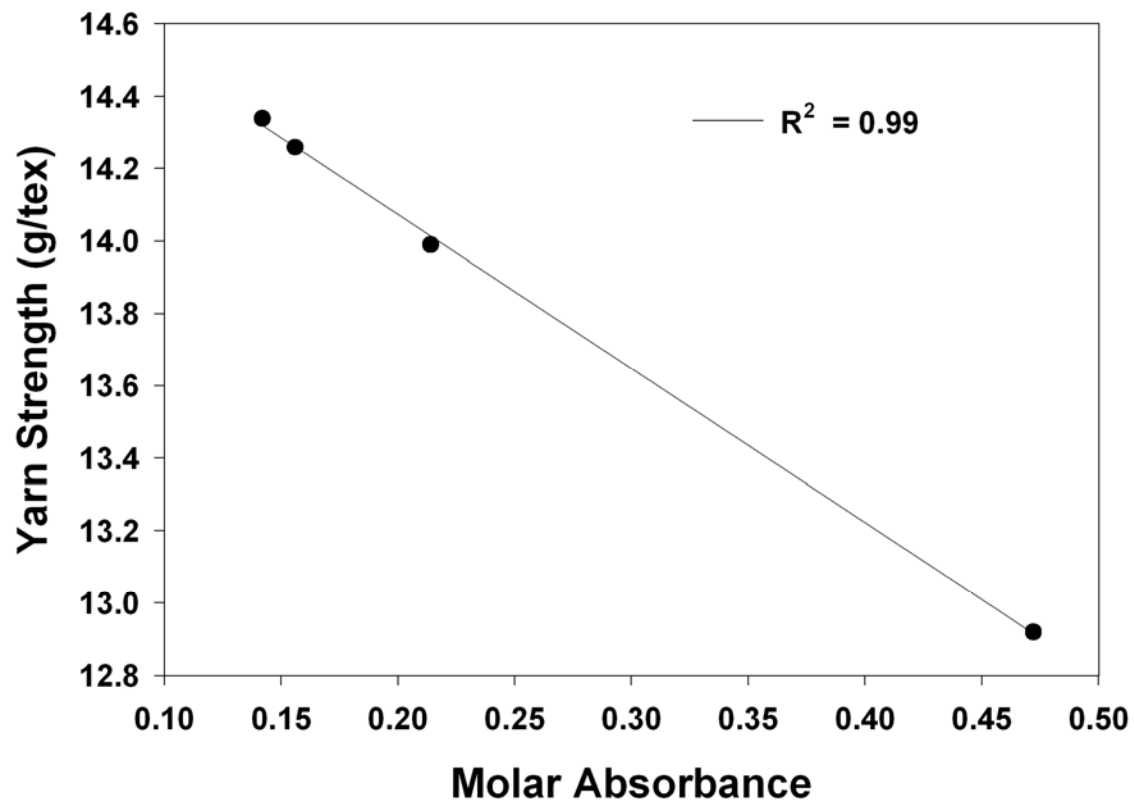


Figure 5

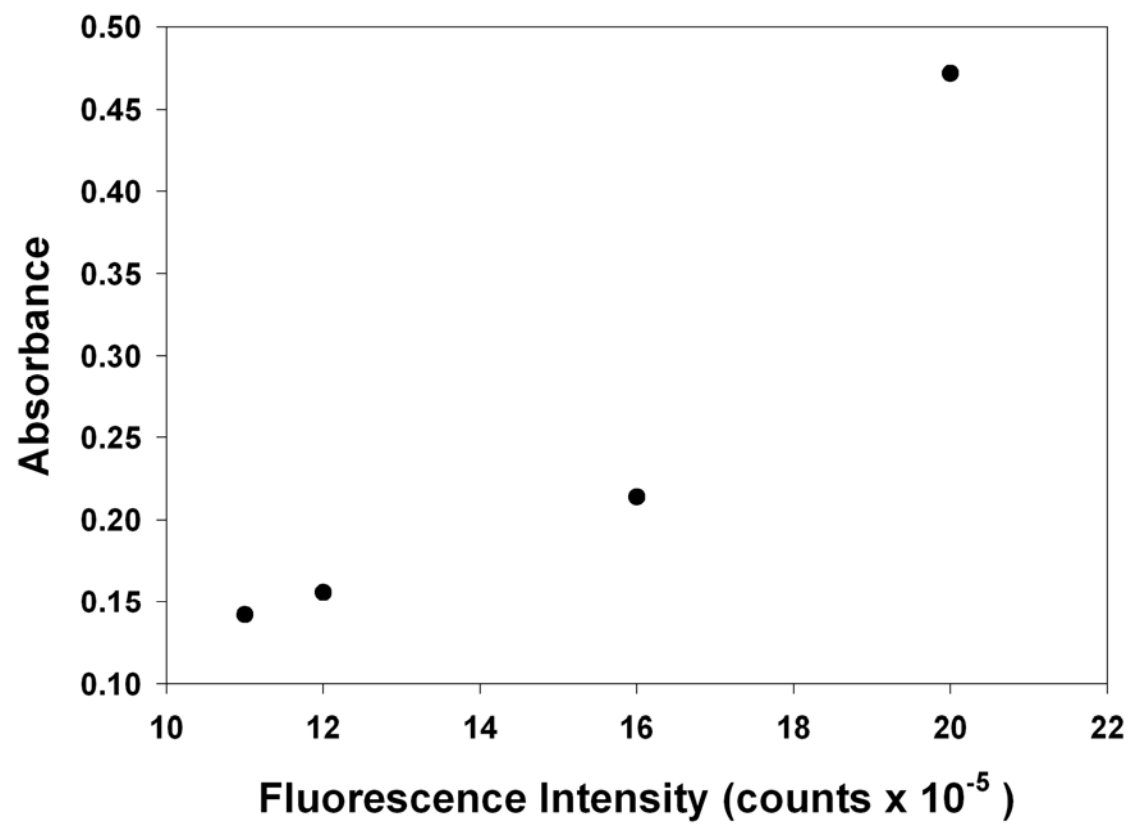


Figure 6