Australian Government
Cotton Research and Development Corporation

FINAL REPORT 2016

For Public Release

Part 1 - Summary Details

Please use your TAB key to complete Parts 1 & 2.

CRDC Project Number: CMSE1201

Project Title: The Glass Transition Temperature of Cotton

Project Commencement Date: 07/2012 **Project Completion Date:** 09/16

CRDC Research Program: Value Chain

Part 2 – Contact Details

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Date Submitted: ______________

Part 3 – Final Report

(The points below are to be used as a guideline when completing your final report.)

Background

1. Outline the background to the project.

Excerpt from Chapter 1 (please refer to chapter for full details): The glass transition temperature (T_g) is the thermal transition at which point a polymer goes from a firm glassy state to a more pliable form. Finding this transition temperature in cotton, or better still, a reliable and reproducible method of measuring T_g, is being studied with the aim of improving the processing of the raw product into usable cotton fibre and yarn.

Objectives

2. List the project objectives and the extent to which these have been achieved, with reference to the Milestones and Performance indicators.

Objective 1: *Detailed literature review and analysis on cotton cellulose Tg and crystallinity and the relationship of these characteristics to the mechanical behaviour of the fibre.*
Literature survey was completed and techniques suitable for measuring the Tg of cellulose were determined. See Chapters 1 & 2 for detailed review, Section 2.4 outlines previous works by other authors.

Objective 2: *Survey a range of physical chemistry techniques for their applicability in measuring the Tg of raw cotton fibres.*
A range of cotton samples were characterised and ranked on the basis of their moisture content, crystallinity and glass transition. Chapter 3 outlines the basic characterisation of the three standard samples selected (cotton, Tencel and viscose) including moisture content and crystallinity; while Chapters 4 & 5 discuss the methodologies and results of the techniques trialled for measuring Tg. Dynamic mechanical analysis (DMA), freezing point differential scanning calorimetry (DSC) on saturated samples, dynamic vapour sorption (DVS) and pycnometry gave the most consistent results and concurred well with one another.

Objective 3: *Originally: Measure effects of Tg on the mechanical and processing properties of cotton fibres. Updated to: Compare measured Tg results with established cotton processing guidelines (determined by empirical studies) and investigate whether there are changes in Tg in cottons with varying developmental maturity.*
DMA was determined as the most suitable method for studying the Tg in cotton. Using this method mature samples of Coker 315 and Sicot 74BRF were compared and samples of Sicot 74BRF of differing maturity were compared. It was shown that there was no identifiable difference in the Tg between samples. The conditions at with the Tg in cellulose occurs was then compared to the current cotton processing methods and it was found that optimum processing conditions sit just at the lowest point of the T_g range or even slightly below it. See Chapters 1, 6 & 7 for further details.

Methods

3. Detail the methodology and justify the methodology used. Include any discoveries in methods that may benefit other related research.

Please refer to Chapters 4 and 5 of thesis for the primary methodologies use in this project.

Results

4. Detail and discuss the results for each objective including the statistical analysis of results.

Please refer to Chapters 4 and 5 of thesis for the results obtain during this study.

Outcomes

5. Describe how the project's outputs will contribute to the planned outcomes identified in the project application. Describe the planned outcomes achieved to date.

Excerpt from Chapter 7: There have been numerous empirical studies on cotton which demonstrate the need for moisture within the fibre during all facets of post-harvest processing. This study has identified the T_g of cotton cellulose and used this information to clarify the role of T_g in resilience during processing. It was found that the empirically assessed moisture content, humidity and/or temperatures recommended for highest quality output, appear to sit just at the lowest point of the T_g range or even slightly below it. In a physical sense, what this means is that the polymer chain, cellulose, within the fibre is only just beginning to move more freely, improving only slightly its ability to deform and recover. This however appears to be enough to improve the resilience of the fibre.

6. Please describe any:-

a) technical advances achieved (eg commercially significant developments, patents applied for or granted licenses, etc.);

Not applicable

b) other information developed from research (eg discoveries in methodology, equipment design, etc.); and

Pycnometer method of determining Tg, though further research is needed to determine the validity of the method. See Section 5.4 for further details.

c) required changes to the Intellectual Property register.

No changes required

Conclusion

7. Provide an assessment of the likely impact of the results and conclusions of the research project for the cotton industry. What are the take home messages?

Excerpt from Chapter 1: "From the farm gate onward, cotton undergoes a number of processing steps to bring the fibre to market. Many of these processes require exerting force on the fibre, leaving it vulnerable to damage. [Previous] empirical studies have shown that changes in moisture content and temperature during these processes affect the overall fibre quality. An example of this is ginning. It is known from empirical studies that best performance of the gin, and fibre preservation are achieved at 6-7% moisture content and around 20ºC, yet [prior to this investigation] little [was] known about the functional characteristics of cotton as a polymer." Measurement of the glass transition give new insight into the ideal moisture and temperature conditions under which to process cotton, to achieve optimum resilience. Fine tuning of these processes will not only allow for a high quality end product but will likely reduce the inputs needed to deliver it.

Extension Opportunities

8. Detail a plan for the activities or other steps that may be taken:

(a) to further develop or to exploit the project technology.

This work has potential to reduce input costs involved in ginning and other down-stream processing, as well as improve fibre resilience, boosting productivity and quality, and reducing environmental impact. Therefore, this knowledge could be used to refining the power and water usage inputs and improve quality outputs in all post-harvest processes.

(b) for the future presentation and dissemination of the project outcomes.

Major outcomes will be published in peer reviewed journals. Likely article titles include: "Dynamical mechanical analysis of cotton and regenerated celluloses", "Differential scanning calorimetry of cellulose" and "Pycnometry: An alternative method for measuring the glass transition".

(c) for future research.

In extension to this body of work the following areas should be considered for further study:

- Duplication of the DVS method on samples of both early and late developmental maturity (low and high DPA)
- Further DMA studies on the Tg of cotton which encapsulates different cotton species rather than just different varieties of the same species (*G. hirsutum*)
- Further DMA studies to compare difference in the absolute modulus in samples of differing maturity and source
- DSC freezing point studies on samples of different varieties and developmental maturity
- Repetition of the AFM method, both dry and wet on low crystallinity or amorphous cellulose
- Further explore methods of generating amorphous cellulose that allows repetition of these methods for measuring T_g

9. A. List the publications arising from the research project and/or a publication plan. (NB: Where possible, please provide a copy of any publication/s)

Future publication plans are as listed in Section 8b of this document. Current publications include:

C. Denham, M. Huson, S. Gordon, X. Wang **The Glass Transition of Cotton**
Proceedings of the 13th Asian Textile Conference vol.2 pp. 634-638.

M. Huson and C. Denham **Chapter 3: The Glass Transition of Cotton**, in S. Gordon & N. Abidi (Eds) *Cotton Fibres: Characteristics, Uses and Performance.* New York: Nova Publishers. Submitted 21st Sept 2016

B. Have you developed any online resources and what is the website address?

Not applicable

Part 4 – Final Report Executive Summary

Provide a one page Summary of your research that is not commercial in confidence, and that can be published on the World Wide Web. Explain the main outcomes of the research and provide contact details for more information. It is important that the Executive Summary highlights concisely the key outputs from the project and, when they are adopted, what this will mean to the cotton industry.

This research was initiated to clarify understanding of the glass transition behaviour of cotton cellulose. The work was supported by the Cotton Research and Development Corporation (CRDC) and was undertaken with the aim of producing data which could thenceforth be used to manage current post-harvest cotton processing methods, nominally ginning but also spinning mill processing, and in turn improve the productivity and performance of the Australian cotton industry.

Up to this point there have been several studies reporting on the glass transition of cellulose. While individually many of these show convincing results, as a collective the results lacked sufficient clarity to draw any definitive conclusions and therefore warranted further investigation. Work was done to determine whether the glass transition of cellulose could indeed be measured, in both the wet and dry state, on samples of cotton, Tencel and viscose. The techniques used to try and measure the glass transition included: differential scanning calorimetry (DSC), dynamic mechanical analysis (DMA), atomic force microscopy (AFM), dynamic vapour sorption (DVS), pycnometry and inverse gas chromatography (iGC).

DSC was used to study the heat flow through cellulose samples with changing temperature under various moisture conditions. Samples were run through many DSC cycles at fast and slow heating and cooling rates (over 700 in total), in both standard and modulated fashion, yet very few positive results were found. DSC was also used to study the freezing water content and temperature in saturated samples. Using Pierlot's (1999) freezing point method for measuring the glass transition (in wool), it was determined that at a moisture content of 15.8% in cotton, 23.7% in Tencel and 22.2% in viscose, the samples showed a glass transition at approximately -1ºC. These tests showed that the experimental results for these samples, particularly cotton, concurred well with the data in papers by Sakabe et al. (1987) and Ur'yash et al. (2010).

DMA allow for the study of mechanical changes within cellulose samples under changing moisture conditions at different temperatures. Testing singles fibres, it was found that there was a significant decrease in modulus of the samples at high humidity, and the onset of this critical humidity decreased as temperature was increased. This drop and levelling off of modulus was shown to occur in cotton and viscose at 60ºC (6.9%MC / 12.4%MC), 70ºC (6.4%MC / 12.0%MC) and 80ºC (5.2%MC / 10.7%MC), and 70ºC (13.1%MC) and 80ºC (12.2%MC) in Tencel. The onset of critical humidity was then extrapolated for the lower temperature cycles using superposition of all cycles.

Dynamic vapour sorption, like DMA, relied on the application of moisture, rather than heat to measure the transition. These results concurred reasonably well with the data collected using DMA and freezing-point transitions on DSC, although the transition occurred at slightly lower moisture content. Pycnometry again relied on changes in moisture to measure Tg. Originally used to measure the density and calculate the crystallinity of samples, this technique showed significate changes in volume upon moisture loss, which were not equivalent to the water volume lost. Assume this to be a consequence of the glass to rubber transition, it was investigated at various temperatures. The results in cotton also made a very close comparison with those measured using DMA, if a little higher in moisture content. Inverse gas chromatography (iGC) was found to have a working range (temperature and moisture) too small to allow for measurement of Tg in cellulose and was therefore discontinued. While AFM has failed to show any convincing results to date.

Individual tests, while generally positive, do not clarify the results currently published in the literature. However, when considered together, the results are strongly in favour of the existence of a glass transition in cellulose. The results gathered in this thesis not only provide a measure of the glass transition at a variety of moisture contents, but also enable the identification of differences between the results of various techniques and between cellulose types. This study has also considered the role of T_g in resilience during processing. It was found that the empirically assessed moisture content, humidity and/or temperatures recommended for highest quality output, appear to sit just at the lowest point of the T_g range or even slightly below it. In a physical sense, what this means is that the polymer chain, cellulose, within the fibre is only just beginning to move more freely, improving only slightly its ability to deform and recover. This however appears to be enough to improve the resilience of the fibre.