The Glass Transition of Cotton

by

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Submitted in fulfilment of the requirements for the degree of

Doctor of Philosophy

Deakin University
September, 2016
I am the author of the thesis entitled

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submitted for the degree of Doctor of Philosophy (Engineering)

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Abstract

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. Like all polymers, the glass transition is a property which is key to understanding the characteristics and performance of cellulose. Cellulose is the world’s most abundant biopolymer and it is found in its purest form in cotton. 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. Empirical studies have shown that changes in moisture content and temperature during these processes affect the overall fibre quality. There have also been 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.

With the support of the Cotton Research and Development Corporation (CRDC), this work was undertaken to improve the understanding of the glass transition behaviour of cotton and regenerated cellulose. This knowledge is important for identifying optimum temperature and moisture conditions 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.

The primary objective of this thesis was to determine whether or not cotton cellulose has a glass transition and if it could be reliably measured. Successful measurement of a reduction in modulus in DMA; calculation of $T_g$ at the point of freezing, using DSC to measure the colligative effect of cotton in water; and measurement of mass change with the addition of water using DVS, have all indicated that cellulose does in fact go through a glass transition, and is measureable. 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.
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COTTON, CELLULOSE AND OTHER POLYMERS

Cellulose, the most abundant biopolymer on the planet, is the backbone of all plant life and is found in its purest natural form in cotton. As a result, humans have utilised this resource to make products ranging from pharmaceuticals, to money, to explosives (as nitrocellulose) and textiles. Like all polymers, the glass transition is a property which is key to understanding the characteristics and performance of cellulose. 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.

From the farm gate onward, cotton undergoes a number of processing steps (discussed in section 1.4) to bring the fibre to market. Many of these processes require exerting force on the fibre, leaving it vulnerable to damage. 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 (Anthony 2006) that best performance of the gin, and fibre preservation are achieved at 6-7% moisture content and around 20°C, yet little is known about the functional characteristics of cotton as a polymer. It is believed that measurement of the glass transition temperature will allow for further understanding and fine tuning of these processes.

The following thesis will cover the fundamentals of cotton plant and fibre development, polymer characteristics and post-harvest cotton processing (Chapter 1); before moving on to discuss techniques used to measure the $T_g$ of polymers and how these have previously been applied to cellulose (Chapter 2). Three key samples will then be characterised using various techniques (Chapter 3) and used to identify standard (Chapter 4) and alternative (Chapter 5) methods capable of measuring the $T_g$ of cellulose. Characterisation of two cotton varieties of varying maturity will then follow, with the aim of identifying any difference in the $T_g$ between samples (Chapter
6). A summary of results and recommendations for future work will then conclude this dissertation (Chapter 7).

1.1 COTTON GROWTH AND STRUCTURE

1.1.1 PLANT AND FIBRE DEVELOPMENT

Cotton fibre or “lint” is produced by the elongation of individual epidermal cells of the cotton plant ovule (seed). From the time of seed plantation, it takes approximately four to six weeks for the seed to germinate and grow into a fruit producing plant. Once a plant has reached sufficient maturity, flower buds (called squares) form, and begin to produce white or pale yellow flowers. Cotton, being a self-fertilising plant, then turns from white to a reddish colour, upon pollination, very soon after opening. Within a week of opening, the flower petals dry and fall away revealing the cotton fruit or “boll”. In optimum conditions, a single cotton plant may produce up to thirty fruits. Figure 1.1 illustrates the cycle from planting to fruit growth (and on to harvest) with reference to the typical production time.

![Cotton plant growth chart](image)

*Figure 1.1: Cotton plant growth chart*

The typical growth cycle of a cotton plant from the time of planting to harvest (National Cotton Council of America and The Cotton Foundation n.d.).

From the time of flowering or “anthesis”, the production of cotton fibres begins on the ovules within the boll (see Figure 1.2). It is on the day of anthesis (or slightly before) that initiation begins (Stewart 1975). Initiation is a short lived period which sees the start of the elongation of approximately one in four of the ovular epidermal...
cells. This initiation is stimulated by the presence of hormones and growth regulators, such as gibberellic acid and auxin, which have also been shown to contribute throughout the subsequent stages of fibre development (Mauney and Stewart 1986).

Elongation, as the name suggests, is the lengthening of these initiated cells up to 22-35 mm in length, allowing a single cell to reach a length as much as four thousand times its final width (Hsieh 2007). This length of fibre gives cotton the honour of having one of the longest single cell structures in nature. Elongation will generally cease at around 25 days post anthesis (DPA). Toward the end of elongation, around 15-22 DPA, lint cells begin the process of depositing layer upon layer of cellulose, forming the secondary cell wall. This cellulose biosynthesis expands the thickness of the cell wall from approximately 0.2-0.4 µm (Ryser 1999), which is the thickness of the primary cell wall alone, up to approximately 8-10 µm (Ryser 1999) as the secondary wall develops. Together the walls of the collapsed cell produce a total mature fibre width in the region of 16-20 µm.

![Figure 1.2: Cotton fibre development](image)

*Figure 1.2: Cotton fibre development*

Phases of growth of cotton on the ovule, including the expected time frame (DPA) for each stage of development (adapted from Chen and Guan 2011).
Maturation of the cotton fibres occurs at around day fifty post anthesis (National Cotton Council of America et al. n.d.). At this time these fibres have not only completed growing, but have also become desiccated. It is at this time that the boll opens revealing multiple fluffy white balls of cotton, containing (depending on the variety) as many as forty-five seeds each (Oosterhuis, Stewart et al. 1994). Individually, the fibres are relatively easily detached from the cotton seed, at just over 18mN (Boykin 2012). Microscopically they appear kidney shaped across their breadth (see Figure 1.3), due to the dehydration of the protoplasm and subsequent collapse of the hollow lumen. Fibres also demonstrate alternating twists, with the direction relating to the orientation of cellulose microfibrils (see Figure 6.2a) in that region. Changes in twist direction or “reversals”, indicate a corresponding directional change of the cellulose microfibrils in that area of the cotton fibre cell wall.

Unlike the twisted cord-like structure of the mature fibres, immature cotton fibres appear very flat and ribbon-like (see Figure 6.2c), showing little to no twisting along their length, due to the lack of cellulose thickening in the secondary wall. A lack of maturity in cotton yield can cause problems in downstream processing, as immature fibres are prone to tangle, causing “neps”. The smooth flat surface and thin cellulose layer of immature cotton also result in greater reflectivity than that of mature cotton, making it appear lighter in colour when dyed in the same way.

There are a number of factors which may affect the growth of the cotton plant itself, the fruit it produces and eventually the overall yield and quality of the fibre harvested. Factors such as competition with weeds for resources and attack by insects and other pests are important, however the key aspects involved in the production of mature, high quality fibres are primarily environmental and nutritional.

Water availability is high on the list of essential resources. This may seem obvious as it is a requirement of all living things; however beyond mere survival, cotton requires access to water to be able to maintain turgor pressure within the growing fibres to promote elongation (Bange 2012). Without this pressure, elongation of the fibre is suppressed and maximum fibre length cannot be achieved.
Plant nutrition also plays a role in cell growth, not only by maintaining a healthy plant, but by assisting to sustain the turgor pressure of cells (potassium is particularly important for this). Temperature and light also contribute to the nutrition of the plant, by the production of carbohydrates through photosynthesis (Bange 2012). Access to plenty of carbohydrates during cellulose biosynthesis is particularly necessary, as it is the raw material required for cellulose production. A loss of foliage during cellulose biosynthesis would have a similar detrimental effect as low light and temperature conditions, all of which would result in a lack of carbohydrate production and consequently less secondary wall thickening.

The other factor which is worth consideration with regard to obtaining maximum yield potential, is the choice of cotton variety. Firstly, the plant variety chosen should be capable of growing under conditions which reflect the environment in which a farmer is operating. For instance, there are some varieties which mature in a shorter space of time than others; these may be a better choice in regions that have a shorter growing season than standard cotton varieties (Cotton Seed Distributors 2012). While some cotton varieties have improved disease resistance over others, which is likely to make them a better choice for growing in a disease-prone area. Many modern varieties also contain genetic modifications which confer specific disease and/or herbicide resistance (Bourland 2011). Ultimately it is a balancing act, choosing plants which are likely to do well in a given area and produce high quality, yield and profit.

1.1.2 COTTON FIBRE STRUCTURE

The cotton fibre is made up of three distinguishable elements. These are the cuticle, the cell wall and the lumen. The cuticle is a layer which surrounds the fibre. It consists of waxes and other materials which perform the function of waterproofing and generally protecting the fibre from the elements.

The lumen of a cotton fibre is a hollow within the centre of the fibre which once contained the cytoplasm and all the organelles necessary for energy production and cell growth prior to maturation. Once fibre cells reach maturity however, they no
longer need to maintain metabolism for energy production, becoming more or less ‘structural’ in nature. This means that a mature cotton fibre is fundamentally a ‘dead’ cell, void of the intracellular fluid which supported the cytoplasmic contents and made it a living cell. Figure 1.3 shows a mature cotton fibre which has (naturally) dehydrated and appears flat and roughly kidney shaped.

The cell wall of a cotton fibre makes up the largest fraction (by weight) of the fibre, and is considered to have two parts: the primary cell wall and the secondary cell wall. The primary wall of cotton lies below the cuticle and can be best described as having a ‘basket weave’ (Hearle 2007) or mesh-like formation, due to the criss-crossed orientation of the cellulose microfibrils. As the name suggests, the primary wall is present from the first development of the fibre cell and continues to grow throughout the period of elongation. It consists predominantly of cellulose, hemicellulose and pectins which together not only form the initial structure of the cell, but also allow it to grow and expand as the secondary wall is laid down within. Electron microscopy studies carried out by Willison and Brown (1977) support this description of microfibril orientation and cell growth. They showed that the microfibrils in the external part of the primary wall align parallel to the length of the fibre, while in the innermost region of the primary wall they run at approximately 90° to the length, suggesting that the outer part of the wall was constructed first and elongated with the fibre.

Following primary wall growth, the secondary wall begins to develop at approximately 15 to 22 DPA. The winding layer is the first layer of the secondary wall, sitting adjacent to the primary wall and is often referred to separately due to its unique structure. Despite the fact that the winding layer closely resembles the primary wall, displaying a woven mat of cellulose microfibrils, it actually has the same chemistry as, and is therefore considered part of, the secondary wall (Rollins 1945, Wakelyn, Bertoniere et al. 2006, Willison et al. 1977).

The subsequent thickness of the secondary wall then develops over the next 25 days, increasing to around 4 µm, forty times (Rjiba, Nardin et al. 2010) the thickness of the
primary wall (0.1 µm), as seen in Figure 1.3. The secondary wall accounts for over 90% of the entire cell mass; it is made up of cellulose of significantly greater relative molecular weight and percentage crystallinity than the rest of the cell (Wakelyn et al. 2006). In a similar fashion to the winding layer of the secondary wall, layers also emerge within the remainder of the secondary wall and are thought to develop as a result of varying growth rates through the diurnal light/heat cycle (Flint 1950). Also, changes in direction of the secondary wall microfibrils are responsible for the reversals (in twist) seen in the mature cotton fibre.

Figure 1.3: Cotton fibre structure
The longitudinal (a) and transverse (b) structure of a typical mature cotton fibre (adapted from Rjiba et al. 2010).

1.1.3 THE CHEMICAL STRUCTURE OF COTTON
Cellulose is a polymer made up of many glucose subunits (residues), in a straight (non-branching) chain of (1,4)-ß-D-glucan, shown in Figure 1.4. This straight chain configuration is supported by the rigid cyclic structure of the glucose residues (Meyers, Chen et al. 2008).

Figure 1.4: Glucose and cellulose structure
To the left the structure of ß-D-glucose which is the precursor material used to form cellulose, shown to the right (adapted from Klemm, Schumann et al. (2001).

Chains are synthesised by the cellulose synthase (CESA) proteins embedded in bundles of thirty-six within the plasma membrane of the cell (Figure 1.5). These
bundles allow the individual chains to come together and form a single cellulose microfibril (Doblin, Pettolino et al. 2010) held together by hydrogen bonds.

![Figure 1.5: Cellulose microfibril synthesis units](image)

Cellulose synthase complexes are grouped together in rosettes, and produce (1,4) β-D-glucan chains which bundle together to form cellulose microfibrils (Cosgrove 2005).

The average number of subunits (‘n’ in Figure 1.4), otherwise known as the degree of polymerisation, varies between cellulose products, but is usually in excess of ten thousand residues for the secondary wall of cotton and around half this for the primary wall (Hessler, Merola et al. 1948).

Hydrogen bonds form between aligned chains, establishing a lattice, which resembles the β-sheets of proteins (Meyers et al. 2008). These sheets may then stack atop one another, held together by van der Waals forces, forming the “tertiary” crystalline structure. Between the crystalline regions are disordered or “amorphous” regions in which the cellulose chains are able to rotate about bonds within the backbone, allowing them to relax into a low energy state. It is the energy of this movement which the author endeavours to study. The current understanding of cotton cellulose is that it is a semi-crystalline material, which may exist in a state anywhere between highly amorphous and highly crystalline. Mature cotton is quoted as having a crystallinity between 46 - 91% (Wakelyn et al. 2006), which develops from very low (<10%) crystallinity just after initiation to near mature crystallinity by 20 DPA (Lee, Kafle et al. 2015, Pettolino 2013).
1.2 THE BEHAVIOUR OF POLYMERS

1.2.1 BASICS PRINCIPLES

A polymer is, by definition, a molecule made up of many repeating subunits or “monomers”. These subunits may be arranged in a number of configurations from a one dimensional chain-like structure, to branched or cross-linked structures (for instance) which then form more complex three dimensional networks.

Polymerisation is the process of linking together these monomers and it occurs by two primary mechanisms, these are addition polymerisation and condensation polymerisation (seen in Figure 1.6).

\[ \text{Addition polymerisation} \quad \text{Condensation polymerisation} \]

![Figure 1.6: Polymerisation mechanisms](image)

The two primary mechanisms of polymerisation are illustrated here by the addition polymerisation of ethylene monomers to form polyethylene, and condensation polymerisation of glucose molecules to form cellulose (adapted from Stamm 1964, Klemm, Schumann et al. 2001 and Bailey Training n.d.).

Addition polymerisation occurs between monomers which contain double bonds or rings which may be broken in order to form a bond with another monomer, and is initiated by the presence of free-radicals. Condensation polymerisation on the other hand occurs between monomers that contain functional end groups, which can react to form a chain of molecules while also producing by-products such as water. In the case of cellulose, polymerisation occurs as a result of a condensation polymerisation reaction.
A polymer may be anywhere from completely amorphous to 99% crystalline (semi-crystalline). A semi-crystalline material is one which readily forms in a matrix or lattice like structure. Often the structure of this type of material is held together by hydrogen bonds and/or van der Waals force (as seen in cellulose), which make it stable and reasonably immobile. Regular packing into a crystalline structure is energetically favourable and will occur whenever possible; because of this, polymers with regular structure and small side-groups such as polyethylene (shown in Figure 1.6) tend to be more highly crystalline than polymers which have an irregular structure or containing bulky side-groups. These lower density non-crystalline regions are known as amorphous.

Amorphous materials do not form matrices of highly interconnected molecules; this gives them a more ‘free flowing’ nature allowing for greater molecular movement. This movement occurs predominantly as a result of rotation about bonds, particularly in the polymer backbone. It is an increase in this movement which occurs at \( T_g \) and identified by a change in the properties of the material. Some movement can also be attributed to the sliding of polymer chains along one another, though complete sliding of chains would require the addition of further energy (heat) to disentangle the polymer chains and side-chains. Bending and stretching of bonds and movement in molecular side-chains may also occur prior to \( T_g \), these are known as \( T_\gamma \) and \( T_\beta \) transitions.

1.2.2 THERMAL BEHAVIOUR
Polymers may exhibit a range of different behaviours when exposed to variations in temperature or pressure. Changes at these temperatures describe kinetic and heat capacity changes within the material. The most common of these behaviours are listed below.

**Decomposition** is an irreversible chemical process which generally occurs at high a temperature. Decomposition occurs as a result of chain scission and may cause samples to appear burnt or charred on inspection.
Cross-linking, sometimes known as curing, is another irreversible process that refers to the formation of bridges in the form of covalent bonds between polymer chains. These bonds are stronger than the hydrogen bonds and van der Waals forces which hold together crystallised polymer. Cross-linking, which is used to strengthen rubber (for example) is unlikely to be a factor in this study.

Crystallisation is the aggregation of polymer chains on cooling, into ordered lattices, which minimise their energy. Crystallisation of a material depends on the ability of polymer chains to line up in close proximity to one another and adequate time for this organisation to occur. If a polymer is cooled rapidly, “quenched”, it may avoid crystallisation and cool in an amorphous state.

Melting is a function of the crystalline regions of a polymer. These regions melt when the energy of molecular movement overcomes the forces which hold together the crystalline lattice. Consequently, if a material has no crystalline regions there will be no melt observed.

The Glass Transition Temperature ($T_g$) is the temperature at which a polymer goes from being a rigid glass-like substance into a more malleable rubber-like state. The glass transition occurs within the amorphous regions of polymers and is best described by Seyler (1994) as “…a passage between short range vibrational processes in the glassy solid and long-range translational and rotational processes in the rubber/liquid state within a finite temperature interval.” On a molecular level, this translates to an increased ability for the molecule to move within its confines; hence, the key to understanding $T_g$ is to recognise that it is directly related to the ability of the polymer to move about the bonds within its backbone. A polymer’s molecular structure therefore plays a significant role in determining its glass transition temperature.

Along the backbone of the molecule, structures such as double bonds and ring formations increase the rigidity of the polymer; while bulky side-chains may act as physical barriers to backbone rotation. A polymer with a rigid backbone (Kevlar $T_g <$
580°C) and/or large pendant molecule (polystyrene $T_g = 95°C$) would be expected to have a much higher $T_g$ than a simpler straight chain polymer, for example polyethylene ($T_g = -120°C$). Other factors such as plasticisation, crystallinity, hydrogen bonding and molecular weight can also influence the value of $T_g$. These factors, along with experimental parameters effecting $T_g$, will be covered in the following sections.

1.2.3 PHYSICAL AGEING

Physical ageing is a reduction in free volume which occurs in the amorphous region of glassy polymers. This should not be confused with chemical ageing which refers to a chemical change in the material such as oxidation or crosslinking (as noted in Section 1.2.2). Physical ageing involves the settling or relaxation of the polymer towards equilibrium over time, into a more compact and lower energy state. This occurs at temperatures below the material’s glass transition temperature, and the rate of relaxation depends on the proximity between $T_g$ and the temperature at which the polymer is held. The closer the temperature is held to the $T_g$, the faster this relaxation will occur.

This loss of entropy (and very small amounts of heat) over time, means that ageing can affect the thermal properties of an amorphous material. It does this by increasing the energy required to move a material through its glass transition temperature due to the higher degree of “packing” associated with an aged polymer. The increase in packing of an aged polymer not only increases the amount of energy required to induce motion in the polymer, it also affects other measureable properties. For example, the tighter packing seen in aged specimens may cause changes in optical and mechanical properties of materials, changes in the dielectric properties of the polymer and possibly alter the gas diffusivity, swelling and solubility properties also. Understanding this, physical ageing can be used to confirm the existence of $T_g$, if ageing can be induced. Significant studies in the area of ageing carried out by Struik (1978) and others (Hodge 1995, Hutchinson 1995, Noel, Parker et al. 2005) support the use of ageing to indicate the presence of $T_g$. Seyler (1994) however suggests that ageing may not necessarily occur at the same temperature as a material’s glass
transition, concluding that ageing is an unreliable indicator of $T_g$. This seems unlikely given that both relate to the same “low temperature” entropic and volume effects, although Struik (1978) did account for such possibilities describing semi-crystalline polymers as having amorphous regions with varying mobility, translating into potential variation of the glass transition and ageing of these polymers.

1.3 POLYMERIC FACTORS EFFECTING THE MEASUREMENT OF $T_g$

There are a number of factors which influence both the measurement of $T_g$ and the value of $T_g$. Many of these factors are specific to the method used to measure the transition, and will therefore be covered in later sections. The degree of hydrogen bonding, ease of rotation around bonds within the polymer backbone, molecular weight and molecular side-chains are all polymeric factors which affect $T_g$. These factors are expected to remain reasonably constant between cellulose samples, however the degree of crystallinity and moisture content of samples are important and will need to be considered throughout.

1.3.1 THE INVOLVEMENT OF CRYSTALLINITY

Crystallinity in polymers refers to ordered regions held in place by hydrogen bonds and van der Waals forces. While crystalline regions do exhibit thermal transitions during crystallisation and melting, they do not directly affect the glass transition temperature of a polymer. However, it is important to know the crystallinity of these polymer samples for a number of reasons. Firstly, knowledge of the crystallinity of a polymer can help to give an idea of the degree of difficulty involved in finding its glass transition temperature, due to the restriction in movement which crystals will impose. This means, the higher the crystallinity, the less amorphous area available for movement to occur in, and the lower the intensity of the property changes that occur at $T_g$. Restriction of polymer movement not only dilutes the measurable response to $T_g$ but also has the potential to increase the glass transition temperature of polymers and cause it to appear over a broader temperature range (Atkinson, Hay et al. 2002, Hay 1995). This makes some testing methods, such as differential scanning calorimetry (DSC), less sensitive to the change.
Arguably the most important reason for knowing the crystallinity of a sample, though, is to understand the effect of a plasticiser on the sample. When a plasticiser such as water, is applied to a sample, it only takes effect in the amorphous regions of the polymer. As a result, a high crystalline polymer sample (with low amorphous content) is going to need less water to reach the same percentage plasticiser content than a polymer sample of low crystallinity.

1.3.2 PLASTICISATION

A plasticiser is, in essence, a substance which internally lubricates a polymer and aids in the free movement of the polymer molecule and its side chains. It is important to consider the influence of plasticisers, as they have the ability to vary the thermal properties of a polymer, specifically the glass transition temperature. The reason behind this change in thermal properties of a polymer is the increase in free volume provided by the plasticiser. Referring back to the description of \(T_g\) (page 11), it is clear that an increase in the molecular movement of a polymer is going to translate into a drop in temperature at which the glass transition of the plasticised polymer occurs. Water acts as a plasticiser for cellulose.

Many compounds have the ability to absorb moisture, adsorb moisture or a mixture of the two. Absorption of moisture is the transfer of volume (absorbate) into volume (absorbent) by permeation or dissolution; while adsorption refers to the moisture (adsorbate) which accumulates on the surface of the adsorbent. In this thesis, sorption will refer to the presence of water within the sample. The general understanding of water sorption in cellulose is that it occurs predominantly within the amorphous regions of the material. Mihranyan’s (2004) work supports this description of sorption in cellulose demonstrating that there is a decrease in the total moisture content (MC), with an increase in the crystallinity of cellulose.

The moisture sorption ability of cellulose is therefore an important consideration when measuring \(T_g\) and needs to be accounted for during experimentation. Moisture sorption isotherms are graphical representations of the relationship between relative humidity and the equilibrium moisture content of a material. Generally speaking,
they form a sigmoidal shaped graph (Figure 1.7), which allows the reader to determine the likely moisture content at a given relative humidity (RH).

Figure 1.7: Cellulose moisture sorption isotherms
Moisture sorption isotherms of cotton (CF), Tencel® (TF) and viscose (VF). Arrows indicate sorption (upward) and desorption (downward) of moisture (adapted from Hill 2009, Okubayashi, Griesser et al. 2005).

At lower relative humidity, there is a rapid sorption of water suggestive of monolayer and polylayer adsorption, which sees water associating with the polar –OH molecules of the cellulose, both in the amorphous regions and on the surface of crystallites (Wertz, Bédué et al. 2010). The graph then levels out as these sites become saturated. The later increase in water content, at high relative humidity, is thought to be due to accumulation of water in pores opened by swelling of the cellulose at lower relative humidities (Wertz et al. 2010). While this is possible, the model determined by Vrentas and Vrentas (1991) for predicting moisture sorption and desorption (fitting it to a polycarbonate – carbon dioxide system) is more likely. Their model explains the levelling off of the moisture content at low relative humidity as the sample approaching saturation below $T_g$. Once it goes through its glass transition then it becomes more mobile allowing for greater sorption of water, therefore linking the upturning change in sorption to $T_g$. This model has since been substantiated in
pharmaceutical (Hancock and Zografi 1993), textile (Pierlot 1999) and food (Jin, van der Sman et al. 2011, Oliver and Meinders 2011, Van Der Sman and Meinders 2013) – water systems.

The difference in moisture content on sorption of water from the dry state and desorption of water from the wet state is known as hysteresis. Accumulation of moisture in the amorphous regions of cellulose alone does not explain the hysteresis effects seen in moisture sorption isotherms. A number of theories have been put forward to explain moisture sorption hysteresis in cellulose, including liquid/solid contact angle (Cassie and Baxter 1944, Chen, Amirfazli et al. 2013), the presence of atmospheric gasses in the material (Hamm and Patrick 1936, Walker, Campbell et al. 1937) and contribution of heat of wetting (Stamm 1964). Mihranyan (2004) observed that at humidities above 76% RH, some samples of high crystallinity showed an increase in moisture content, thought to be a result of water accumulation in the porous network of these samples. The swelling of the material exposes previously unreachable –OH sites for monolayer sorption and opens up microcapillaries in which moisture can collect. However the most accepted hypothesis explaining this trend is a change in the mechanical/elastic properties of the cellulose on the addition of moisture, due to swelling (Ceylan, van Landuyt et al. 2012, Ioelovich and Leykin 2011, Mihranyan et al. 2004). This is supported by the findings of Hill (2009) and Okubayashi, Griesser et al. (2004) who noted that an increase in experimental temperature resulted in a reduction in hysteresis. These findings suggested that extending the rubbery region of the moisture sorption isotherm to a lower relative humidity improves the moisture uptake (on wetting) and reduces the size of the hysteresis loop. The speed of desorption has also been shown to be affected by the size of the desorption step (Mackay and Downes 1969), occurring faster when the step change is greater.

There are numerous mathematical models which have been developed to aid in determining the amount of plasticiser required to bring about a desired glass transition (Couchman and Karasz 1978, Fox Jr and Flory 1950, Gordon and Taylor 1952, Kaelble 1971, Kelley and Bueche 1961, Pochan, Beatty et al. 1979, Schneider
1989). Hancock et al. (1993) studied the relationship between a number of these models and applied them to a variety of polymer samples. They found that while the Gordon-Taylor/Kelley-Bueche models fit most of the samples tested, they were unable to resolve \( T_g \) and moisture content for the cellulose/water system without first accounting for the degree of crystallinity, and in turn the (water containing) amorphous content of the sample. For this reason crystallinity of plasticised polymers must always be taken into account.

Salmen and Back (1977)'s earlier paper also accounted for the degree of crystallinity, finding that the “Kaelble approach” to plasticisation worked well to explain the effect of water on cellulose \( T_g \), despite overlooking the effect of polar molecules (-OH groups) and temperature change on the cohesion parameter. Szczesniak (2008) agreed with the findings of Salmen et al. (1977), observing that the Kaelble approach has merit for estimating the \( T_g \) of cellulose and going so far as to say that it may be useful in determining the crystallinity of cellulose (and other materials) from the measured \( T_g \) and moisture content. The methods were however found to be ultimately very similar, varying only by the definition of the constant in each calculation.

As part of the current study, a simplified version of the Gordon-Taylor/Kelley-Bueche models has been used, in the form of the Fox equation (Katkov and Levine 2004), to graphically model the expected \( T_g \) for known sample crystallinity and moisture content (Figure 1.8). The Fox equation (shown here),

\[
\frac{1}{T_g} = \frac{w_1}{T_{g1}} + \frac{w_2}{T_{g2}}
\]

calculates the \( T_g \) of a ‘mixture’ by accounting for the \( T_g \) of the individual components, \( T_{g1} \) (cellulose \( T_g = 220^\circ C – Kargin 1960 \)) and \( T_{g2} \) (water \( T_g = -137^\circ C – Capaccioli 2011 \)), with reference to the weight fraction of each \((w_1 \text{ and } w_2)\). To reference the crystalline content of the sample using the Fox equation, with \( C_c \) describing the cellulose crystallinity, and assuming \( w_2 = 1 - w_1 \), the following equation can be used to calculate the \( T_g \) of a sample with known water content and crystallinity:
\[ T_g = \frac{T_{g1} \times T_{g2}}{1 - \left( \frac{w_2}{1 - C_c} + w_2 C_c \right) T_{g2}} + \left( \frac{w_2}{1 - C_c} + w_2 \right) C_c T_{g1} \]

This equation was used to establish a functional temperature range in which to run samples, so as to observe the glass transition. For example, a sample of 75% crystallinity would be expected to have a \( T_g \) around 60°C if it contained 5% water. However, the same sample with a water content of 15% would have a much lower expected \( T_g \), of around -40°C. Experimental data is also plotted in this format on successive pages as a means of comparing results.

Figure 1.8: Fox equation – graph

Using the Fox equation, this graph was made to give an estimate of the \( T_g \) for cellulose samples of known crystallinity and water content.

Plasticisation is a useful ally in the study of \( T_g \). Lowering of the \( T_g \) is particularly useful in studying polymers, such as cotton, where the glass transition of a “dry” (or unplasticised) sample may be difficult to reach due to degradation at high temperature, and reduces the need for high temperature experiments. Also, alteration of the plasticiser content (such as by varying relative humidity when using water as a plasticiser) can move the measured temperature of \( T_g \) by degrees, relative to the amount added. This technique of altering plasticiser content will be used as a confirmation of \( T_g \).
1.4 WHY IS IT IMPORTANT TO KNOW THE $T_g$ OF COTTON?

Scientifically, it is important to know the glass transition of cellulose because it is our most abundant and highly utilised biopolymer, and many properties of all semi-crystalline and amorphous polymers change at $T_g$. Industrially, knowledge of the $T_g$ of cotton has the potential to improve the durability of cotton fibres during post-harvest processing.

Unlike the empirical studies used previously, which have shown dry cotton to be brittle and easily broken during processing, this project aims to understand a fundamental fibre property, the $T_g$. Doing so has the potential to not only improve the robustness of the fibres, but also improve the performance of current cotton processing methods. Optimisation of processing performance would have a two-fold benefit of reducing damage to cotton fibres and lower processing costs, and would ultimately translate to higher revenue for producers.

The following paragraphs outline the progress of cotton from farm to fabric. Many of the fibre processing phases involve stress being put on the cotton fibre, increasing the potential for breakage. Work has been done (Byler 2006, McAlister III, Chun et al. 2005, Pillay 1963, Pillay 1971) to establish how changes in moisture and temperature affect processing, but it is hypothesised that knowledge of the polymeric properties of cotton cellulose is the key in judging the best moisture and temperature conditions in which to process cotton. There is also evidence to support claims that maintenance of strength is cumulative throughout all steps of processing (Byler 2006).

GROWING

Please refer to section 1.1.1 for a detailed review of cotton fibre development. Measurement of cotton’s $T_g$ is unlikely to have much of an impact on the way that cotton is grown.
**Picking**

Modern cotton pickers (Figure 1.9) used in Australia use a system of rotating spindles and doffers to remove cotton lint and seed from the plant. According to Cotton Australia (2012) and Cotton Inc. (nd) picking should occur at less than 12% moisture content to prevent downgraded fibre quality due to microbial action and to ensure seed MC is at or below 12% for best ginning efficiency. Seed cotton with a moisture content of between 9% and 12% at harvest is likely to be more flexible and will therefore be somewhat protected from breakage during picking. Cotton fibres picked at moisture contents above 12% are not only more susceptible to microbial degradation, they are also more at risk of self-combustion due to heat production during fermentation, while awaiting ginning.

![Figure 1.9 Picking zone of John Deere 7760 cotton picker](image)

*Figure 1.9 Picking zone of John Deere 7760 cotton picker*

Spindles catch the cotton as plants move through the picking zone of the vehicle. Doffers then remove the cotton from the spindles, where it is drawn away by blowers to the collecting chamber.

**Ginning**

The next step in bringing cotton to the market is ginning. Ginning is a process of removing the seed from the cotton fibre, while also removing contaminants such as extraneous plant material from the fibre (Figure 1.10). This is the process in which most fibre breakage occurs. Ginning is the primary target for using knowledge of cotton’s $T_g$ to improve fibre robustness, potentially translating to greater fibre quality.
and yield. Empirical studies have established targets for cotton moisture contents for minimum breakage, yet understanding of the $T_g$ may allow for refinement of the process.

Figure 1.10: Ginning
Ginning removes cotton lint fibre from the seed and most of the trash from the fibre. Australian cotton often also undergoes lint clean prior to and after passing through the gin stand. Adapted from Gordon, Horne et al. 2007, McGraw-Hill Higher Education 2000).

Field baled cotton is removed from its wrapping and blown toward the gin through pre-cleaning and drying units (if necessary). Once the cotton reaches the gin, ideally at a moisture content of 6-7% (Anthony 2006), though it is often lower in Australian gins (Krajewski and Gordon 2010), and typically at temperatures above 20°C, it will become part of the seed roll. This is then raked by a saw which detaches the lint from the seed. It has been found that fibres containing less than 5% moisture are cleaner at the end of ginning and contain less trash, but are more brittle resulting in higher short fibre and nep counts (Anthony 2006). Dry cotton is also more prone to damage from overheating, can cause blockages within the gin due to static electricity and is harder to compress, resulting in low bale weights.
On the other hand, ginning at a higher moisture content, of 11-15%, reduces the force required to separate fibre from seed (Byler 2006) but interferes with the ginning process by forming tight twists in seed cotton or creating wads of fibre that can block the gin. As with picking, ginning and baling at high moisture contents also increases the risk of discolouration (7.5% plus) due to the presence of microbes.

Overall it is something of a balancing act to find the correct temperature and moisture content at which to gin cotton to achieve high quality clean fibre in a reasonable timeframe and minimal cost (Figure 1.11).

![Figure 1.11: The influence of fibre moisture content on ginning performance](image)

Ginning performance and fibre quality is strongly connected to fibre moisture content. Best results are achieved when a fibre quality can be maintained with minimum trash content (Anthony 2006).

**CARDING AND SPINNING**

Once cotton has been ginned it is sent to the mill. Turning a bale of cotton from the gin into yarn is a two stage process. The first step is carding (Figure 1.12). A card uses a system of rollers covered in small teeth to comb the fibres and remove any residual trash. The cotton is released from the card as a soft rope of aligned fibres known as a sliver. The sliver can then be fed into the spinning machine (Figure 1.13) where it is drawn through multiple rollers and twisted into a fine yarn. Once spun, the yarn can then be woven or knitted into fabric.
Within the card it has been found that cool damp conditions are best for maintaining fibre length. McAlister III et al. (2005) showed this, with a reduction in fibre breakage while carding by increasing the relative humidity and reducing the temperature from 20°C and 55% RH to 16°C and 75% RH. These results were of particular benefit when the fibres were then spun using vortex or ring spinning methods which require longer fibre lengths (than rotor spinning).

Studies focusing on spinning have shown similar results. Results by Pillay (1971) showed cotton to have greatest yarn strength when spun at high relative humidity of 75% RH at 21°C, with greatest uniformity being achieved at 65% RH regardless of the temperature. At room temperature, this puts the moisture content of the cotton within the same range as mentioned for optimum ginning, 6-7%. Operating at this humidity has also been shown to reduce static charging which interferes with spinning (Dyson, Iredale et al. 1974). On the other hand Pillay (1971) also found that the converse was true for yarn elongation, which was highest when spinning was carried out at low humidity (34%).

Figure 1.12: Carding
The cotton card removes further trash after ginning and forms a rope of cotton known as the ‘sliver’ (Textinfo 2011).

Figure 1.13: Spinning
Sliver is twisted into yarn after being drawn through multiple rollers (Anthony, Clapp et al. nd).
Dyeing and finishing is the last stage in the production of cotton for textiles and can be applied to either a continuous length of fabric through solution or to spools of yarn. Dye stuffs are more readily taken up above a polymer’s $T_g$ (Aspland 1993, Koh 2011) which means dyeing often requires elevated temperatures to improve dye uptake. Generally, dye baths are run at temperatures around 90°C (Taylor 2000), well in excess of cotton’s expected $T_g$ for saturated sample (as modelled using the Fox equation). Knowledge of cotton’s $T_g$ has the potential to optimise production efficiency and reduce processing costs, as it will be possible to lower dye bath temperature to just above $T_g$.

1.5 SUMMARY

Cotton is one of the purest forms of the world’s most abundant biopolymer cellulose, and while there has been significant empirical research into the best conditions for processing cotton, researchers are still divided as to whether cotton cellulose goes through a glass transition. With a background into the growth habits and chemical structure of cotton and an understanding of the behaviour of polymers, this thesis will go on to discuss the methods of measuring $T_g$ before using these methods to measure the glass transition in cotton and regenerated cellulose products.
Knowledge of the glass transition temperature of polymers is very important, as many properties change as a polymer goes through its $T_g$. These properties include: heat capacity, specific volume, modulus, refractive index, conductivity and diffusion (Collins, Bareš et al. 1973, Cowie 1973). As $T_g$ is critical for understanding changes in the physical characteristics of polymers, any method that measures these changes may be used to determine the temperature of the transition.

One point necessary to consider when measuring $T_g$, is that the transition occurs over a range of temperatures. It is, however, conventional to assign a single value to the glass transition, most commonly the onset or midpoint of the change, although other points such as offset are also occasionally used (Seyler 1994). The measured $T_g$ will also vary marginally depending on the method used and the rate at which a sample is measured. This is mainly due to the viscoelastic nature of polymers, which causes them to be rate dependant. For the following studies, unless otherwise stated, the onset of the temperature range will be assigned as $T_g$ of the samples tested.

Physical ageing (see Section 1.2.3) will also need to be accounted for in the following experiments, particularly in the case of differential scanning calorimetry. While this may be useful in identifying weak transitions (as is likely to be seen in cellulose), cyclic heating and cooling can be used to anneal the sample. This will erase any ageing effects, giving the sample a known thermal history and removing any endothermic effects which may mask $T_g$.

This chapter will describe both standard and alternative methods for measuring $T_g$. It will then go on to discuss the instrumental factors affecting the measurement of $T_g$ and review the literature pertaining to the measurement of $T_g$ in cellulose.

### 2.1 Standard Methods of Measuring Glass Transition Temperature

There are two prominent methods which are commonly used in the characterisation of thermo-mechanical material properties; these are calorimetric and mechanical analyses. Differential scanning calorimetry (DSC) is used most commonly to study the
thermal properties of polymers and has the advantage that, if sealed pans are used, constant moisture content can be maintained during heating. Dynamic mechanical analysis (DMA) is more often used to look at the tensile and mechanical properties of materials as a function of temperature, but is also suitable for studying thermal properties of polymers as it can be ramped through varying temperatures (like DSC) and humidity levels. This method is more sensitive than DSC as the modulus can change at $T_g$ by approximately three orders of magnitude (Collins et al. 1973). It is however much harder to maintain a constant environment in DMA experiments than in DSC experiments.

### 2.1.1 Differential Scanning Calorimetry

Differential scanning calorimetry (DSC) is a method which measures the transfer of heat into (endothermic) and out of (exothermic) a sample. It is used to determine the point(s) at which there is a change in the thermal properties of a substance. This may be a phase change, such as the transformation of solid to a liquid phase (melting), but it maybe also be a more subtle, second order change as demonstrated by the softening of a solid through its glass transition. DSC is typically used to determine material properties such as melting point, the degree and temperature of crystallisation, specific heat capacity, thermal stability, purity and reaction kinetics.

Since its introduction in the early 1960’s (Schick 2009) DSC has become a popular tool for studying thermal transitions in many materials, particularly polymers. This is primarily due to the simplicity of the technique, but also relates to the fact that calorimetry can be used universally to measure heat produced or consumed by both physical changes and chemical reactions. In the area of materials science, a thermal event shown on a DSC may be translated directly into a physical change in a test material.

The technique works on the principle of tracking the amount of energy needed to heat or cool a pan containing a sample at a predetermined rate (eg. 10°C/min). Changes in heat absorbed (endothermic) or emitted (exothermic) by the sample are
reported relative to a reference pan, which is generally empty but may also contain an inert material.

The heat flow can be measured in two ways, the first is through power compensation. This method utilises individual furnaces for the sample and the reference pans. These are heated such that the temperature of each remains the same, and the power consumed by each furnace is recorded. Any difference in power required to keep the temperature equal can be used to calculate the heat flow within the sample.

The other method, which was used in the experiments performed in this study is heat-flux (Figure 2.1). This method uses thermosensitive platforms to record and compare the temperature of the sample ($T_S$) and an empty reference ($T_R$) pans placed in a single furnace. The $T_{\text{zero}}$ sensor ($T_C$) within the furnace measures the absolute temperature of the furnace ($T_C$) and is used to account for any heat leakage which may be present in the cell.

![Figure 2.1: TA Instruments discovery DSC internal schematic](image)

The main image shows the main functional assembly of the instrument used in the following experiments. Insets expand the measuring platforms, illustrating $T_{\text{zero}}$ sensor apparatus and represents the configuration of the thermocouple. Heat flow is determined by the difference between the heat flux into the sample and reference platforms, plotted as a function of the furnace temperature (adapted from Yen-Shan 2012).
The heat flow in the sample is then calculated with reference to the calibrated thermal resistance and heat capacities. The tabulated data can then be represented graphically to visualise the flow of heat between the sample and chamber. Figure 2.2 shows an idealised graph of the five most commonly studied thermal transitions in polymers. $T_g$ is detected as an endothermic step change in the heat flow of the sample as the temperature is ramped through the glass transition of the sample.

![Figure 2.2: Thermal transitions in differential scanning calorimetry](image)

An idealised graphical representation of a heating DSC trace showing typical thermal transitions (adapted from Yen-Shan 2012).

The use of heat capacity as a method of determining $T_g$ is affected by a number of sample and method based factors, as listed in Tables I and II in section 2.2, but it is particularly susceptible to ambiguous results due to overlapping thermal events. One method for getting around this issue, is the use of modulated DSC (MDSC), which has a slow overall heating rate, but a faster ‘point to point’ (peak to trough) sigmoidal rate. This approach involves the heating of the sample in a sinusoidal mode. From this, the kinetic or “non-reversing” heat flow can be determined by subtraction of heat capacity or “reversing” heat flow from the total heat flow. In this way reversing thermal events, incorporating $T_g$ can be separated from non-reversing thermal events such as physical ageing, which manifests as a small endothermic peak associated with $T_g$ on heating, usually towards the end of the range.
2.1.2 DYNAMIC MECHANICAL ANALYSIS (DMA)

Dynamic mechanical analysis (DMA) is a method of determining the physical characteristics of a material, particularly polymers, using a number of techniques which put “stress” on the material under either varying temperature or moisture conditions. A number of different modes of deformation may be used to test a given sample, these include bending, compressing and putting the sample under tension. Often the stress is applied in an oscillating fashion, with the amplitude and phase of the responding sample deformation being measured. This allows the viscoelastic properties of the sample, such as modulus and damping to be obtained. Most DMA instruments are capable of making these measurements as a function of temperature and frequency and in some cases humidity. This allows the measurement of thermal properties of the sample, such as the glass transition temperature.

DMA can be traced back to the early 1900’s with Poynting’s (1909) work studying the lengthening of steel wire exposed to oscillatory force. From this time, many have used oscillating force to study materials and a number of reviews of the technique have been written. DMA is now routinely utilised by industry to analyse the mechanical and curing properties of materials, and to predict the performance of said materials over their lifetime (Menard 2008).

An oscillating stress (or strain) is used in DMA to displace the sample mounted between a moveable and a stationary clamp. This results in a strain (or stress) within the sample and potentially displacement of the sample which can be measured through the moveable clamp (Figure 2.3) by an attached optical encoder. This is most often done while ramping the temperature and/or humidity, but frequency and stress/strain sweeps are also possible. Changes in the sample in response to the forces applied are monitored throughout testing.

A number of different clamping arrangements may be employed to measure the properties of a polymer subject to shear, compression or tension forces. The fibre samples examined in this study will be measured under tension. Given the variety of
methods available when using DMA, it is unsurprising that there are also many sample types which may be tested, including powders, fibres and films.

The dynamic modulus, measured by the DMA, is made up of two parts: stress and strain. Together they describe the specific properties of viscoelastic polymers. The stiffness or storage modulus ($E'$), the viscosity or loss modulus ($E''$) and damping or tan delta ($\tan \delta$).

A purely elastic polymer would be in phase ($0^\circ$) with the oscillating force and would show a high relative storage modulus as it is disposed to store applied energy. On the other hand, a purely viscous polymer would have a high relative loss modulus and be completely out of phase ($90^\circ$) with the applied oscillating force, as energy is lost as heat. This means that the storage modulus is a measure of the amount of energy which can be stored by a sample, and can then be released as the stress is removed; while the loss modulus is the measure of dissipated energy. Most polymers lie somewhere in the middle of these two extremes, giving a phase displacement equalling $\delta$. This can be seen in Figure 2.4. $\tan \delta$, is a ratio of these two moduli.
The glass transition temperature of cotton

Figure 2.4: Elastic, viscous and viscoelastic responses to force applied by DMA
This image shows the theoretical change in phase observed when measuring the response to force applied by DMA in purely elastic, purely viscous and viscoelastic samples (adapted from TA Instruments 2010).

These viscoelastic moduli and damping properties are often used to measure the $T_g$ of polymers. Below $T_g$ polymers exist in a stiff, high modulus state, due to the low level of molecular movement. On the other hand, a polymer above its $T_g$ is more mobile and has a much lower modulus. In most synthetic polymers this difference in modulus equates to around three orders of magnitude (as shown in Figure 2.5). The glass transition is marked by a drop in storage modulus denoting a loss in sample rigidity, followed closely by a peak in loss modulus as segmental motion within the backbone of the polymer increases.

Figure 2.5: The glass transition temperature in dynamic mechanical analysis
An idealised graphical representation of a DMA trace showing changes in storage modulus ($E'$), loss modulus ($E''$) and Tan $\delta$ (adapted from TA Instruments 2010).

The most common measure of $T_g$ however is Tan delta. Tan $\delta$ marks the centre-point of the ‘leathery’ transition region as the dissipation potential of the material (related
to $E''$) reaches a maximum as its elasticity returns to an equilibrium and is again more able to store energy ($E'$). The Tan $\delta$ peak can however be reduced by molecular constraints, such as crystalline regions, which restrict molecular motion and reduce the dissipation response displayed by the loss modulus. Figure 2.5 shows DMA trace that would be expected for a synthetic polymer as it passes through its glass transition.

The conditions required to run a specific test are best determined using a (constant) strain sweep. This is done by applying force at a set rate until the sample yields, allowing for the determination of the stress and strain range of linear viscoelastic behaviour, used for evaluating the storage and loss properties of viscoelastic polymers. In this range the dynamic processes which allow the sample to move are at equilibrium, meaning that the sample is able to fully recover from an applied force within this range. The later non-linear region of the stress–strain curve gives information about yield stress and the failure properties (breaking strength and elongation) of a polymer. It is necessary to note however that, although the stress-strain curve gives information about the behaviour of the polymer, the results collected cannot be directly applied to a dynamic test. This is because the sample is not under constant strain and therefore does not take into account the frequency dependence of viscoelastic polymers (Menard 2008). Frequency dependence of a polymer relates to its free volume. Any movement in a polymer requires it to flex and rotate around its backbone and pendant molecules, which requires time. As the frequency of a force applied to a polymer is increased, there is less time allowed for the movement of the polymer chain and as a consequence, it becomes (or appears to become) stiffer. As such, the parameters gathered from a constant stress/strain sweep when used at high frequency may cause the sample to break. Frequency dependence can also have the effect of increasing the measured $T_g$ of polymers.

The primary advantage of using DMA over other methods to determine $T_g$ is its ability to detect very low intensity transitions. Not only is DMA able to detect glass transitions where other methods cannot (Kilburn, Bamford et al. 2002, Sakurai, Maegawa et al. 2000, Suryanegara, Nakagaito et al. 2009), such as in samples that
are highly crystalline or crosslinked, it also has the potential to detect transitions such as beta transitions (due to rotation and bending of sidechains below $T_g$) and crystalline slippage prior to melting (Perkins Elmer Inc. 2008). In industry DMA is often used for polymer cure and other optimisation studies.

There are also a number of disadvantages of using DMA to detect $T_g$, such as instrument compliance, sample geometry and temperature accuracy. However, following careful instrument calibration, the aspects most likely to affect the measurement of $T_g$ in this study are limited to temperature and humidity gradients, and clamping effects. Assuming the same clamping technique is used for all samples, clamping effects should be minimal. The small size of the samples used in this study should negate the effects of temperature and humidity gradients, but there may be a chance that the size of the clamps relative to the sample may affect the measurement of temperature if the clamps act as a heat sink. The main disadvantage to using DMA in this study is accurate measurement of sample size, particularly when using fibre arrays. The diameter of single fibres may be measured using electron microscopy or a Vibroscope, but this becomes impractical when using arrays in excess of one hundred fibres. Though this is not ideal, it is the temperature and/or RH at which softening occurs that is of greatest significance in these experiments and will still allow for the examination of modulus of fibres, relative to one another.

2.2 ALTERNATIVE METHODS OF MEASURING GLASS TRANSITION TEMPERATURE

While DSC and DMA are commonly used to determine $T_g$, there are many properties other than heat flow and modulus which change in this temperature range. Other less common methods, such as pycnometry, scanning probe microscopy (SPM) and dynamic vapour sorption (DVS) may also be used to characterise $T_g$, using material properties such as volume, elastic modulus and the rate of moisture sorption.

2.2.1 INVERSE GAS CHROMATOGRAPHY (IGC)

Gas chromatography is a technique which is used to separate a complex solution into its various fractions. The technique involves injecting a sample (mobile phase), which can be vaporised, into the head of a packed column, which depending on the packing
(stationary phase) can separate the fractions of the mobile phase by size and/or chemical interactions.

Inverse gas chromatography (iGC) works in a similar way to standard gas chromatography, however unlike standard chromatography, where the sample is carried as a vapour through a known solid phase, the column in iGC is packed with the sample material and probe molecules are passed through the sample. It may be used to determine surface properties such as surface energy of a sample, surface heterogeneity, work of cohesion or adhesion and heat of sorption on most solid or semi-solid samples which can be packed in a glass column. Bulk properties such as diffusion and solubility parameters, degree of crosslinking and, of interest in this project, phase transitions (Braun and Gillot 1976, Surana, Randall et al. 2003) may also be measured by iGC (Surface Measurement Systems Ltd nd).

Inverse GC measures the volume of carrier gas required to elute a vaporised probe from a column packed with sample, against the volume of carrier gas required to elute a non-retainable reference probe (usually methane) (Surface Measurement Systems Ltd 2013), and the time taken to elute both probe and reference probe. Figure 2.6 compares the two chromatographic methods.

![Analytical Gas Chromatography vs. Inverse Gas Chromatography](image)

Figure 2.6: Standard chromatography versus inverse gas chromatography
Analytical gas chromatography is used to separate components of gaseous samples from one another by means of a standard solid phase, while in inverse gas chromatography the retention time of a single gas probe is used to study the properties of a solid (or semi-solid) packed into the chromatography column (Surface Measurement Systems Ltd n.d.).
Upon exiting the end of the column the gas is picked up by a detector, often a flame ionisation detector (FID), and the elution time of the reference probe and the net retention volume of the carrier gas is established. The net retention time of the probe \( t_N \) is calculated by subtracting the retention time of the reference probe \( t_0 \) from the measured retention time of the probe \( t_R \), while the retention volume is given by the area beneath the peak. A typical elution peak for iGC is shown in Figure 2.7, with the comparison of \( t_N \), \( t_0 \) and \( t_R \) (inset).

\[
 t_{\text{com}} = \frac{t_i - t_f}{2}
\]

Where \( t_i \) and \( t_f \) are the initial and final peak times, respectively (Sen 2005).

To determine the glass transition of a polymer using iGC requires multiple injections of the selected probe over a range of temperatures, within the suspected region of the transition. As the temperature of the column is increased to the \( T_g \), there is a higher degree of molecular motion within the polymer, which allows the probe vapour greater accessibility to the bulk of the material (Surface Measurement...
As a result, the retention time, and the volume of carrier gas required to move the probe through the column will increase. In other words, below $T_g$ the retention volume is a reflection of probe sorption on the surface of the polymer, while above $T_g$ the retention volume provides information on both surface adsorption and bulk absorption (Voelkel, Strzemiecka et al. 2009).

The natural log of calculated net retention volume ($V_n$), with respect to temperature can then be plotted against the inverse of the temperature to demonstrate the state of non-equilibrium sorption that occurs during $T_g$ (Figure 2.8). Using this technique, the onset of the glass transition is taken as the point of inflection at the beginning of the non-equilibrium sorption region (Nastasović and Onjia 2008).

![Figure 2.8: Non-equilibrium sorption in iGC](image)

The start of non-equilibrium sorption can be used to determine $T_g$, as the samples molecular mobility increases, allowing the probe to penetrate into the sample rather than merely adsorbing onto its surface (Surface Measurement Systems Ltd 2013).

Although the iGC is by no means traditionally used to measure the $T_g$ of polymers, it has the advantage of being a sensitive way of measuring the transition in polymers that may be difficult to measure by other means. In the case of cellulose, the expected increase in molecular motion brought about by increasing temperature and humidity will allow penetration of the probe molecule into the amorphous regions, indicating $T_g$. Unfortunately, increasing the humidity of the column to plasticise the cellulose in this way then reduces the temperature window available to the instrument for measurement (see Figure 2.13, page 43). For this reason the
temperature and humidity conditions for measuring the $T_g$ of cellulose will need to be carefully chosen.

### 2.2.2 ATOMIC FORCE MICROSCOPY (AFM)

Atomic force microscopy (AFM) uses a fine probe to chart the surface of a sample, or analyse its properties. It was invented by Binnig, Quate et al. (1986), after earlier work done by the group on a scanning tunnelling microscope (STM). The initial STM work made it possible for the first time to image materials at atomic resolution, however it was only able to work on conductive and semi-conductive systems. Replacing the current detecting tip of the STM with a tip at the end of a cantilever, allowed contact force to be used in the feedback loop instead of the tunnelling current thus allowing imaging of non-conductive materials. An additional advantage of moving to a force based system meant that it was possible to expand from topographical imaging into more quantitative techniques which are able to make measurement of properties such as the sample hardness, elastic modulus, attraction or repulsion forces and surface friction. This makes it a useful tool for studying the softening of plasticised (moist) cotton fibres (Maxwell, Gordon et al. 2003). AFM also has the advantage of making it possible to assess a sample in different environments, such as in the presence of humidity or at increased temperature.

An atomic force microscope is made up of two distinct units, a piezoelectric scanner and a detection system, as shown in Figure 2.9. The piezoelectric scanner, to which the AFM probe is attached, allows movement of the probe laterally and vertically, in x, y and z planes. The detection system is made up of a laser source aimed at the cantilever, and a quadrant photodiode array which detects deflection of the cantilever. An electric feedback loop within the instrument (Figure 2.9), attached to the scanner, is used to maintain a constant deflection of the cantilever and hence force between sample and probe.

There are two primary imaging modes in which AFM can be run, these are contact mode, and intermittent contact or tapping mode. Contact mode relies on the probe being in constant contact with the sample surface and is primarily used on hard
samples which are able to resist potential damage from the probe. Contact mode enables both topographic and frictional imaging, using set point deflection (in the z plane) and torsional deflection (in the x,y plane) respectively. Intermittent contact mode or tapping mode is performed with an oscillating cantilever which, as the name suggests, taps on the surface of the sample. Tapping mode has the advantage of not causing damage to the surface of the sample as can happen with contact mode. It also reduces the likelihood of interference by surface contaminants, such as water.

**Figure 2.9: AFM system set-up and feedback loop**

The AFM photodetector picks up movement of the cantilever as the tip scans the surface of the sample, from changes in the reflected laser light. The feedback loop allows the piezo to react to excess movement in the z-plane by lifting or dropping the cantilever (adapted from Bruker Corporation 2010 and Institute of Physics 2015).

The interaction between probe and sample is best described using a force curve (Figure 2.10). This curve can be broken into two main parts, extension of the piezo toward the sample (shown in blue) and retraction away from it (orange). Prior to extension toward the sample, the cantilever is at rest and the tip has no contact with the surface of the sample. As the piezo approaches the sample (Figure 2.10 a-b), attractive forces may act upon the tip, drawing it onto the surface of the sample with a ‘snap’ and bending the cantilever toward the sample (Figure 2.10 b-c). As the piezo
continues to extend toward the sample, the tip is pressed onto/into the surface of the sample and the cantilever begins to deflect away from the sample (Figure 2.10 c-d). Once the instrument detects that the set force parameter (or trigger) has been reached, the piezo will begin to retract away from the sample. During retraction the cantilever deflection will reduce, pass through its resting position (Figure 2.10 e) and again be deflected toward the sample (Figure 2.10 e-f) due to surface adhesion. The cantilever will continue to deflect toward the surface of the sample until the tip breaks free of the surface (Figure 2.10 f-g), at this point the cantilever will return again to its resting position.

![Figure 2.10: AFM force curve structure](image)

Points a-d (blue) illustrate the forces exerted on the cantilever as it approaches the surface of the sample, while points d-h (yellow) depict the deflection of the cantilever as it is retracted away from the sample (adapted from Leite, Bueno et al. 2012).

Such force curves provide information on the adhesion strength of the fibre surface, the influence of attractive or repulsive forces and the sample stiffness. The force exerted on the sample during this cycle is best described by Hooke’s law:

\[
\text{Force} = k \times \Delta x
\]

Where, the force applied to the cantilever is equal to the product of \( k \), the spring constant of the cantilever and \( \Delta x \), the cantilever displacement. Force-volume mode can be used to collect a matrix of force curves and for each curve the penetration of...
the tip into the sample can be measured. This penetration is a measure of the stiffness of the sample which can then be used to calculate modulus. These changes in stiffness will be used to detect the glass transition in cellulose. Absolute modulus of fibres, however, are not the primary target of this work. The principal interest is in the temperature and/or relative humidity at which the fibres soften.

### 2.2.3 Dynamic Vapour Sorption (DVS)

Developed in 1994 by Surface Management Systems, the Dynamic Vapour Sorption (DVS) instrument was designed as an automated means of determining the moisture sorption characteristics of hygroscopic materials. The instrument uses computer controlled flow of dry and saturated carrier gasses (Figure 2.11) to control the relative humidity. Moisture uptake or elimination is determined by using ultra-microbalances to measure changes in mass of the sample and reference pans. This means, changes in the mass of a sample may be precisely monitored, particularly when the equilibration time is high.

![DVS system set-up](image)

*Figure 2.11: DVS system set-up*  
Computer controlled relative humidity and ultra-microbalances are used to determine moisture uptake or elimination by changes in mass of sample (Burnett, Garcia et al. 2012).

Isotherms are normally generated under isothermal conditions by incremental increase in the relative humidity, allowing the sample to reach equilibrium at each step. Once the cycle is complete the relative change in the mass of the sample can
be plotted against the relative humidity (partial pressure) of the system to produce moisture sorption isotherms, such as those seen in Figure 1.7 (page 15).

This technique may also be used to indicate the change from surface adsorption to bulk absorption. Burnett, Thielmann et al. (2004) showed (in lactose) that continuous ramping of relative humidity produces an inflection on a graph of change in mass against time (Figure 2.12) as relative humidity increased. This change from adsorption of moisture to the surface of the material, to absorption of moisture into the bulk of the material, is thought to be associated with the material softening thereby indicating the region of \( T_g \) (Burnett et al. 2004). The likelihood of this inflection functioning as an indicator of \( T_g \) is supported by its dependence on the rate of increase of relative humidity (Burnett et al. 2004) and its shift to lower relative humidity as the test temperature increases (Li 2010).

![Figure 2.12: \( T_g \) determination using DVS – Change in mass versus time](image)

Changes in sorption of water in spray-dried lactose at 25°C (Burnett et al. 2004).

This effect can also be seen in the moisture sorption isotherms (Wang, Yang et al. 2012), as discussed in Chapter 1. However due to the high crystallinity of the samples in this study, it is likely to be more difficult to determine \( T_g \) using sample isotherms than using the method outlined by Burnett et al. (2004) (Yuan, Carter et al. 2011).
2.3 INSTRUMENTAL FACTORS EFFECTING THE MEASUREMENT OF T\textsubscript{g}

As discussed in Section 1.3, there are a number of factors which impact the measurement of the T\textsubscript{g}. These can occur both as a result of the sample and instrumental influences. Table I reiterates the sample specific factors which relate to T\textsubscript{g}. Most of these relate to the molecular configuration of the polymer, and while T\textsubscript{ß} transitions in molecular sidechains may be hard to differentiate from T\textsubscript{g}, it is really only the degree of crystallinity that is going to affect the ability to measure T\textsubscript{g}, as discussed in Chapter 1.

Table I: Sample specific factors affecting the measurement of T\textsubscript{g}
This table outlines the effect of sample specific factors, such as increasing molecular weight (assigned with “↑”) on measurement of T\textsubscript{g}. Sensitivity in this case reflects the ability of the instrument to define a change in the measured parameter.

<table>
<thead>
<tr>
<th>Factors effecting measurement of T\textsubscript{g}</th>
<th>T\textsubscript{g}</th>
<th>S</th>
<th>R</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecular weight ↑</td>
<td>↑</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hydrogen bonds ↑</td>
<td>↑</td>
<td>↑</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Rotation about bonds on backbone ↑</td>
<td>↓</td>
<td></td>
<td></td>
<td>Eg. absence of C=C bonds</td>
</tr>
<tr>
<td>Side chains (number/size) ↑</td>
<td>↑</td>
<td>↑</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Crystallinity / Particulate fillers ↑</td>
<td>↓</td>
<td></td>
<td></td>
<td>Can ↑↑ T\textsubscript{g} in DMA</td>
</tr>
<tr>
<td>Plasticiser ↑</td>
<td>↓</td>
<td>↑</td>
<td></td>
<td>Reduces instrument temp range</td>
</tr>
</tbody>
</table>

T\textsubscript{g} = glass transition, S = sensitivity, R = resolution

In DSC, samples of higher crystallinity show a smaller, broader step change than at lower crystallinity. This effectively weakens the transition, making it harder to differentiate from the baseline measurement. Similarly, crystallinity reduces the change in storage modulus seen in DMA, however unlike DSC the change should still be distinguishable from any background noise. The reduction in storage modulus becomes a problem when the polymer also displays a T\textsubscript{ß} which may be of similar magnitude to the suppressed T\textsubscript{g}. It is also possible in DMA that a highly crystalline polymer may appear to have a higher T\textsubscript{g}, than measured using other methods (Menczel, Judovits et al. 2008). In iGC, high crystallinity has the potential to reduce the available surface area for penetration of probe, however this is likely to be circumvented by running the system at infinite dilution.
From Table I it is evident that the primary factors affecting $T_g$ are related to the molecular mobility of the sample, with crystallinity and plasticiser content being the most prominent factors in this study. In the case of synthetic polymers one of the techniques which is commonly used to reduce crystallinity, is to heat the sample above its melting point and then rapidly cool or “quench” the sample. Doing this retards crystallisation, enhancing the transition through the increase in amorphous material. However, use of this technique on cellulose would be very difficult, as the melting point of cellulose lies beyond its decomposition temperature. Schroeter and Felix (2005) have shown it is possible to melt a small sample of cellulose with a mixture of pressure, mechanical shear and laser radiation, but use of this technique can only produce very small samples (around 0.6 mg) with a rim of degradation around the edges, therefore it is unlikely to be useful.

Plasticiser (in this case water) content is also known to affect the temperature at which the $T_g$ is measured (see Chapter 1). What makes the use of this parameter difficult, however, is the working range of the instruments when moist samples are used. Figure 2.13 shows the humidity and temperature range at which each of these instruments works.

![Figure 2.13: Instrumental working range under humid conditions](image)

The area coloured on the graph for each instrument indicates the working humidity of each instrument with respect to temperature.
In addition to sample factors which can affect the measurement of $T_g$, there are also instrumental factors which can influence the result obtained when measuring the glass transition temperature. These are related to both the properties measured by each instrument and set parameters. Table II outlines the instrumental parameters which influence $T_g$, specific to the method used.

**Table II: Instrument specific factors affecting the measurement of $T_g$**

This table outlines the effect of increasing instrument specific factors, such as increasing pan mass (assigned with “↑”) on the measurement of $T_g$. Sensitivity reflects the ability of the instrument to define a change in the measured sample property.

<table>
<thead>
<tr>
<th>Factors effecting $T_g$ measurement</th>
<th>$T_g$</th>
<th>N</th>
<th>S</th>
<th>R</th>
<th>B</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>DSC</strong></td>
<td></td>
<td></td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sample size ↑</td>
<td>↓</td>
<td>↑</td>
<td>↓</td>
<td></td>
<td>↓</td>
<td></td>
</tr>
<tr>
<td>Heating rate ↑</td>
<td>↑</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Gas purge rate ↑</td>
<td>↑</td>
<td>↑</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Purge gas nitrogen</td>
<td>↑</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Wide temperature range</td>
</tr>
<tr>
<td>Purge gas air</td>
<td>↑</td>
<td>↓</td>
<td></td>
<td></td>
<td></td>
<td>Potential degradation</td>
</tr>
<tr>
<td>Reference pan mass ↑</td>
<td>↓</td>
<td></td>
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<td></td>
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<tr>
<td><strong>DMA</strong></td>
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<td></td>
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<tr>
<td>Sample size ↑</td>
<td>↑</td>
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<tr>
<td>Orientation</td>
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<tr>
<td>Heating rate ↑</td>
<td>↑</td>
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<tr>
<td>Frequency ↑</td>
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<td></td>
<td>↔ &amp; ↓ $E'$ slope and Tan δ peak</td>
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<tr>
<td>Gas purge rate ↑</td>
<td>↑</td>
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<td></td>
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<tr>
<td>Purge gas nitrogen</td>
<td>↑</td>
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<tr>
<td>Purge gas air</td>
<td>↑</td>
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<tr>
<td><strong>iGC</strong></td>
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<td>Sample size ↑</td>
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<td>Gas purge rate ↑</td>
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<tr>
<td>Purge gas nitrogen/helium</td>
<td>↑</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>May ↑ pressure gradient</td>
</tr>
<tr>
<td>Purge gas hydrogen</td>
<td>↑</td>
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<td></td>
<td></td>
<td></td>
<td>Low pressure gradient</td>
</tr>
<tr>
<td>Surface coverage ↑</td>
<td>↑</td>
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<td></td>
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<tr>
<td><strong>DVS</strong></td>
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<tr>
<td>Sample size ↑</td>
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$N =$ noise, $S =$ sensitivity, $R =$ resolution, $B =$ baseline curvature, $E =$ elution time
While there is a great deal of published work on the determination of the glass transition temperature of synthetic polymers, there are few studies available which investigate cellulose and specifically cotton cellulose. Of these, most focused on microcrystalline cellulose and cellulose derivatives (Ford 1999, Goring 1963, Hancock and Zografi 1994, Kargin, Kozlov et al. 1960, Picker and Hoag 2002, Szcześniak, Rachoki et al. 2008, Ur'yash, Larina et al. 2010, Yano, Hatakeyama et al. al. 1976) as often used in the pharmaceutical industry, paper pulping (Back and Didriksson 1969, Baldwin and Goring 1968, Goring 1963, Ogiwara, Kubota et al. 1970, Paes, Sun et al. 2010, Salmén 1979, Salmén and Back 1977, Salmén and Back 1978, Takamura 1968) and to a lesser extent, on cotton (Bryant and Walter 1959, Maxwell and Huson 2002, Ogiwara et al. 1970, Paes et al. 2010). A paper written by Kargin et al. (1960) established that the glass transition of solvent doped cellulose could be measured using a mechanical deformation method. These measurements were carried out at a range of solvent concentrations and a solvent free (unplasticised) $T_g$ of 220°C was obtained by extrapolation. While the figure of 220°C is widely accepted as the dry $T_g$ of cellulose, the range in which a dry $T_g$ has been reported is 200°C to 240°C (Alfthan, de Ruvo et al. 1973, Back et al. 1969, Baldwin et al. 1968, Kargin et al. 1960, Paes et al. 2010, Salmén et al. 1977, Salmén et al. 1978, Takamura 1968, Yano et al. 1976). Others have claimed it as being up to 377°C (Bryant et al. 1959), 174°C (Picker et al. 2002) and even as low as 80°C (Ranganathaiah 2002). Ranganathaiah’s (2002) dry $T_g$ of 80°C is fairly unlikely given that monomeric and dimeric (celllobiose) glucose molecules have glass transitions of 37°C and 77°C respectively. However, it is possible that a second DSC endotherm shown in this paper as decomposition, at 213°C, may in fact be a $T_g$.

Outside these papers, most authors have reported glass transitions in cellulose as a function of moisture content. Tokita (1956) was among these using a torsional pendulum technique to measure both moist and dry viscose. While the dry data is significantly lower than that measured by Kargin et al. (1960), at 81°C, the moist results showed a drop in measured $T_g$ with an increase in moisture content, as shown
in synthetic polymers. Another early paper written by Goring (1963), used a mechanical method on unplasticised cellulose, using a plunger system to allow the measurement of sample “collapse” as heat was applied. He found that unlike lignin and hemicelluloses, cellulose did not demonstrate a clear \( T_g \) upon the addition of heat, but showed general softening in the sample as water was added. Ogiwara et al. (1970) followed this paper, seven years later, using NMR to study the boundary temperature of cellulose as water become bound. In doing so the authors found that the boundary temperature of cellulose decreased as moisture content increased. Their results, shown in Figure 2.14 (with others) follow the model established using the Fox equation. Salmen and Back (1980) also show reasonably consistent results using tensile testing to determine modulus on paper pulp (Kraft sack) and cotton linters. Using the midpoint of the drop in modulus, they recorded values of 64°C at 6.4% MC down to -25°C at 14% MC, again following the expected trend for a polymer with increasing moisture content.

After this point, most studies of \( T_g \) in cellulose were carried out using DSC, with mixed results. Szcześniak et al. (2008) showed good results (Figure 2.14), demonstrating clear (though small) transitions in microcrystalline cellulose (MCC), in both the heating and cooling DSC runs. Increase in the moisture content in these experiments also saw a drop in the measured \( T_g \). Of some concern is the reporting of exothermic transitions as \( T_g \) in the cooling cycle of the samples containing 5.3% and 15% moisture content. However, though these results may be questionable graphically, the changes seen on cooling are strongly supported by the data shown on heating.

Picker et al. (2002) also reported a drop in the measured \( T_g \) as moisture was added (results not shown). However unlike Szcześniak et al. (2008) who’s results were generated at a heating rate of 5°Cmin\(^{-1}\), Picker et al. (2002) used standard DSC with fast heating rates of 60°Cmin\(^{-1}\) and modulated DSC, to report multiple transitions in each of their samples. Though they did not pinpoint a single reason for there being multiple transitions, they suggested it may be an artefact resulting from chemical processes used to produce the MCC or the existence of multiple phases within the material structure. Though it is still controversial, more recent work by Paes (2010),
using DMA to measure \( T_g \) in ball milled wood cellulose, indicates that the observation by Picker et al. (2002), of multiple glass transitions may be plausible. They have suggested that this may occur as a result of a “restricted mobility amorphous fraction”. Paes (2010) was however, unable to discern \( T_g \) using DSC.

Work by Batzer and Kreibich (1981) and Hancock et al. (1994) again confirmed transitions within cellulose by the addition water, using DSC (Figure 2.14). However, the moisture content of the wettest samples of 60% and 37% (consecutively) in these papers are highly unlikely considering moisture sorption isotherms give \( \approx 25\% \)MC at best.

Figure 2.14: Fox equation graph with reported glass transitions for cellulose
The predicted \( T_g \) for cellulose as calculated using the Fox equation, as discussed in Section 1.3.2, overlaid with \( T_g \) results as reported in the literature. Where necessary, results were converted to moisture content.

Alternative methods have been used along the way in an effort to determine \( T_g \). The DSC work of Sakabe, Ito et al. (1987) was demonstrated by Pierlot (1999) as showing potential for determining the “freezing” point \( T_g \) of cellulose. Using the results this way revealed a transition within samples containing 15-16.5\% MC at the point of freezing (Figure 2.14) and were supported by the data collected by Ur’yash et al. (2010). This method will be discussed further in Chapter 4. Using similar principles to Goring’s (1963) work using sample softening to study \( T_g \) and following from work
done on wool, Maxwell et al. (2002) used SPM to study the softening of cotton fibre with the addition of moisture. They found that the cotton appears to go through a transition at 10% MC under ambient conditions (Figure 2.14). While there are no issues with the data collated by these authors, these methods only generated single data points.

### 2.5 SUMMARY

Despite the fact that there are multiple authors who claim to have good results, evaluation of the literature currently available regarding the $T_g$ of cellulose reveals that while several techniques have been used for its measurement, few people have succeeded in establishing a strong, clear signal. Of greater concern however, is the lack of consistency between results.

This is particularly evident when the results are plotted against the expected result for $T_g$ as calculated using the Fox equation (Figure 2.14). An example of this can be seen as 16% MC, marked in Figure 2.14. Along this line there are three points which it crosses and several more that are very close; together these point span a temperature range of 193°C. Even taking into account variation in the source of the cellulose (i.e. MCC versus cotton fibre), differences in crystalline content and the array of different methods to measure transitions, it is very hard to reconcile such a gap. Further work is therefore needed to find a reliable and reproducible method of measuring the $T_g$ of cellulose, principally cotton.
3 SAMPLE CHARACTERISATION

As a means for looking at the basic characteristics of each of the samples, a number of tests were applied to determine the density, crystallinity, water content and the surface architecture. The techniques used to do this were scanning electron microscopy (SEM), pycnometry, x-ray diffraction and Karl Fischer titration.

3.1 STANDARD SAMPLES

Along with cotton, samples of Tencel® and viscose fibre have been used to study the T_g of cellulose. Although all these products are elementally the same, differences in the source of the cellulose and the way it is grown and/or processed, result in products which differ in properties such as purity and crystallinity.

Mature cotton fibres have a very high cellulose content, but they are not entirely pure, having approximately 88-96% cellulose content (Goldwaith and Guthrie 1954) with the remaining 4-12% made up of waxes, pectins and other non-cellulosic products. Cotton also has the added complexity of variation in the cellulose microfibril structure between its primary and secondary walls. An ideal sample for glass transition analysis, as previously mentioned, would possess low crystallinity (therefore being highly amorphous), high purity and consistent composition. It is for this reason that a variety of cellulosic products have been chosen for this project. It is hoped that the investigation of other cellulose samples will aid evaluation and modelling of the glass transition in cotton.

As discussed in the previous chapters, cotton undergoes very little change from field to fabric. Tencel® and viscose on the other hand are both derived from wood cellulose and undergo a process that involves dissolving and extruding wood pulp to form a fibre structure.

While the methods of processing Tencel® and viscose are similar overall, they differ in the chemicals used in dissolution and recovery. This gives the two fibres the same chemical make-up but slightly different attributes as far as regain, crystallinity and
strength are concerned. It is these attributes that will be discussed in the following pages.

Viscose is produced by dispersing the cellulose feedstock (usually wood, but cotton and bamboo among others are also used) in a mixture of sodium hydroxide and carbon disulphide (Figure 3.1). This solution is then extruded into a sulphuric acid bath where the strand hardens into fibres. These fibres can then be bleached and washed to whiten the fibre and remove chemical residues. The disadvantage of this process is not only its high environmental cost, but also its negative impact in terms of energy use and potential waste products.

The production of Tencel® on the other hand is somewhat more straightforward (Figure 3.2), owing to the absence of the degassing step, and the use of less chemicals. Tencel® is produced by dissolving cellulose feedstock in N-Methylmorpholine N-oxide (NMMO). The dissolved cellulose is then extruded into a water bath where the cellulose precipitates and forms fibre. Another advantage Tencel® has over viscose is that the cellulose has only been dissolved in the NMMO, not broken down in solution and rebuilt as the viscose is.
3.2 FIBRE MORPHOLOGY

3.2.1 SCANNING ELECTRON MICROSCOPY (SEM)

Electron microscopy was developed in 1931, by Ernst Ruska and Max Knoll in 1932 (Ruska 1987), as a means of improving upon the resolution of light microscopy (around 200 nm). This was done by using electrons, which are capable of travelling at much shorter wavelengths (of 1.23 nm at 1 eV) than photons of light (approximately 400–700 nm) and improved the resolution to approximately 0.2 nm. Consequently, scanning electron microscopy is the ‘subatomic’ equivalent of the dissecting light microscope and can be used to examine the surface morphology of a specimen.

Examination of samples by SEM is achieved by passing a fine electron beam back and forth, over the metal coated surface of a specimen. Backscattering and secondary electrons liberated from the sample surface are then picked up using a detector and displayed in an image format.

MATERIALS AND METHODS

Cross sectional images of fibres were achieved by inserting parallel fibres longitudinally into 10 mm lengths of heat shrink tubing. The tubing was then shrunk using a heat gun and sectioned into ~3 mm lengths. Tubes were mounted vertically onto aluminium SEM sample holders. Longitudinal images were taken of fibres mounted onto SEM sample holders using conductive carbon tape. Mounted samples
were coated with approximately 2 nm of Pt/Pd using a Cressington 208HRD coater. Images were produced under high vacuum using a FEI Phenom desktop SEM. The surface morphology was examined along the length of 3-5 fibres per sample and representative images were taken. Fibre diameter measurements were made from a single transverse section image of each fibre type containing a minimum of 150 measureable fibres. ImageJ analysis software was used to determine the mean Feret diameter of each fibre. Feret diameter is determined by measuring the fibre diameter (D) in multiple directions between two parallel tangential lines (Figure 3.3) and averaging the result.

Samples used for SEM studies are: CF – cotton fibre (supplied by P Henry, CSIRO), TF – Tencel® fibre (Lenzing), VF – viscose fibre (supplied by M Pate, CSIRO).

RESULTS AND DISCUSSION

SEM has been used on these samples to look at the surface morphology and estimate the shape and diameter of cotton, Tencel® and viscose fibres. Using image analysis software (ImageJ), the cross-sectional images were made binary and image transformations were used to separate fibres. Fibres still connected after transformation were separated manually using Photoshop Touch. The counting function in ImageJ was then used to count and measure the mean Feret diameter of fibres; discounting those overlapping the edge of the image.

Cotton fibre is approximately kidney shaped in cross-section, although the shape is irregular from fibre to fibre (Figure 3.4d). Some variation in fibre diameter is expected in cotton due to its natural variation in development. Image analysis was used and determined a 19 μm mean (Feret) diameter for cotton fibres, with a standard deviation of 5.4 μm. Longitudinally (Figure 3.4a) fibres clearly demonstrate microfibrils along the surface which change in direction with fibre reversals (not shown), concurring with the current literature (Hsieh 2007).
Tencel® fibre is shown transversely to have a quite spherical cross-section and reasonably high uniformity in both shape and size (Figure 3.4e). Image analysis determined the mean diameter of the fibres as 20 μm with a standard deviation of 4.6 μm. Surface images of Tencel® (Figure 3.4b) show an almost completely straight fibre with a somewhat smooth surface, displaying only a relatively small amount of surface irregularity.

Viscose fibre, unlike Tencel®, appeared much less uniform in shape when viewed transversely (Figure 3.4f), appearing lobular in shape. Fibre diameter remained fairly regular with a mean diameter of 17 μm and standard deviation of 3.8 μm. The surface of the viscose (Figure 3.4c) was also quite different to that of the Tencel®, displaying a rough and slightly pock-marked surface with deep channels running along the length of the fibre. Unlike cotton the diameters for Tencel® and viscose are determined by the extrusion parameters, rather than naturally during fibre growth. Fibre shape may have a minor influence on the rate of moisture uptake in each fibre type, but is unlikely to have a significant impact on the measurement of $T_g$. 

Figure 3.4: Scanning electron micrographs of cotton, Tencel® and viscose
Surface and transverse section images of cotton (a & d), Tencel® (b & e) and viscose (c & f) taken using scanning electron microscopy.
3.2.2 COTTONSCOPE

The Cottonscope was developed in 2010, combining two technologies which individually measured fibre fineness and maturity into a single instrument (Gordon, Naylor et al. 2012). This instrument uses a camera to capture coloured microscopic images of fibres within an aqueous solution, illuminated using polarised red and green light. Image analysis software then discerns fibre maturity based on a fibre’s birefringence colour (Gordon and Phair 2005) under cross-polarised light (red is mature, while dark or shadowy signifies immature) and the average fineness or linear density (H) of the fibre, using the equation:

\[
H = \frac{m}{V} \frac{v}{l}
\]

Where \( m \) is the total mass cell of snippets (see method), \( V \) is the total suspension volume, \( v \) is the measured sub-set volume and \( l \) is the measured length of fibre (Abbott, Higgerson et al. 2010).

MATERIALS AND METHODS

All fineness (linear density) and maturity studies were carried out on a BSC Electronics Cottonscope and analysed using Cottonscope software v2.14. Samples were conditioned at 20°C ±2°C and 65% RH ±2% for at least 72hrs prior to testing. Under the same conditions a guillotine was used to cut the fibres into 0.7 mm snippets and 20 mg of sample was added to the Cottonscope bowl and allowed to mix in the 0.4% Teric solution for 20 seconds prior to commencing the test. Weighed sample was added to the Cottonscope bowl and allowed to mix in the 0.4% Teric solution for 20 seconds prior to commencing the test. Each test was set to measure 20000 snippets with the exclusion of those under 2 µm and over 80 µm to avoid measuring non-fibre particles and large clumps. Two specimen from each sample were tested in triplicate.

Samples used for Cottonscope studies are: CF – cotton fibre (supplied by P Henry, CSIRO), TF – Tencel® fibre (Lenzing), VF – viscose fibre (supplied by M Pate, CSIRO).
RESULTS AND DISCUSSION

Standard Cottonscope testing procedures require 50 mg of sample per test. Due to the small volumes of some samples, a preliminary experiment was performed using cotton of known fineness and maturity to determine the effect of decreased mass on the test results (Figure 3.5). The samples used were: Sicala350B, 31105 and GM39 cottons. These mass tests showed change of approximately 3% in width, less than 1% in birefringent (BF) maturity ratio (not shown) when comparing 20 mg to 50 mg samples. While it is possible that the trend-line calculations could be used to correct results gained using 20 mg samples, the minimal size of the error and the comparative nature of the following tests (including results in Chapter 6) do not require this accuracy. Fibre fineness however showed a slightly large change of approximately 7.5%, and may be corrected for comparison with literature data (where noted).

![Figure 3.5: Cottonscope measurement variance with change in sample mass](image)

Results for three lab standard cottons, Sicala350B (red), 31105 (green) and GM39 (blue), used to determine variation in fineness and width results as sample mass decreases.

Following this initial experiment, 20 mg samples of cotton, Tencel® and viscose were run in the Cottonscope and the following results collected (Figure 3.6). The standard deviation between samples was found to be negligible (<2% for all tests accept for the MRBF of Tencel®, at 2.8%), error bars were therefore deemed unnecessary.
These results show a close similarity between cotton and viscose in all attributes, and a striking contrast between these fibres and the Tencel®. This is particularly obvious for the birefringent (MRBF) ‘maturity’ of Tencel® which appears very low. Although this (Tencel®) result has little tangible meaning as ‘maturity’, what it does show is a clear difference between the two regenerated cellulose types, likely due to a high degree of crystallite uniformity within the Tencel® (Coulsey and Smith 1996). The width of each sample measured using this method of 15 μm, 23 μm and 15 μm for cotton, Tencel® and viscose respectively concurs roughly with the diameter results as measured using electron microscopy (of 19 μm, 20 μm and 17 μm). The fibre diameter figures also concur with the figures as quoted in the literature of 16-20 μm for cotton (Ryser 1999), 10-30 μm for Tencel® (Schuster, Aldred et al. 2003) and 6-30 μm for viscose (Roggenstein 2011). CF was also measured as having micronaire of 4.4 using Cottonscope.

![Figure 3.6: Fineness and fibre width using Cottonscope](image-url)

Figure 3.6: Fineness and fibre width using Cottonscope
Fineness and width results for cotton, Tencel® and viscose using Cottonscope

As a means of checking the birefringence result given by the Cottonscope, particularly with respect to Tencel®, these three samples were investigated using polarised light microscopy, as used by Gordon and Phair (2005) to improve the contrast of the transmitted light.

The images in Figure 3.7 show that cotton and viscose have similar hues of predominantly yellow and green. Yellow and green colours are seen in mature cottons when using this method (Gordon and Phair 2005). Magenta and blue hues
as seen primarily in the Tencel® sample, are indicators of low maturity when seen in cotton. This is due to the high degree of uniformity of microfibril/crystallite alignment within the sample (Coulsey and Smith 1996).

In viscose the yellow/green colouration under polarised light is most likely the result of a lack of polymer/crystallite orientation, but it may also be related to the core-sheath structure of the fibre (not present in Tencel®). Edwards and Langley (1981) have also shown that the thickness of the cellulose through which light must travel has an effect on the interference colour seen, however the thickness of cellophane film used in their work was larger than the fibres widths seen in these experiments, and the results cannot be easily compared. This effect was not seen by Coulsey and Smith (1996) when working on Tencel® 2-11 µm.

![Figure 3.7: Polarising microscopic photographs of cotton, Tencel® and viscose](image)

Cotton, Tencel® and viscose as visualised using a Leica DM-LSP polarising microscope with a full-wave plate, and captured using Luminoptic DigiRetina 16 MPixel camera using ICS software.

Understanding the interference colouration in cotton is more difficult. It is known that the thickness of the fibre wall has some impact on the colouration, showing yellow/green in mature cotton and blue/magenta in immature cotton (Gordon and Phair 2005). Remembering the fibrils within the fibre are more highly aligned in mature fibres than immature ones (see Section 1.1.3), the result conflicts with that seen in viscose. However, Edwards and Langley (1981) also showed that films of aligned polymer direction displayed yellow/green interference colours seen when
crossed at 90°, analogous to the two alternate planes of aligned cellulose that light must travel through in a single mature cotton fibre, as accounted for by Meredith (1946).

Overall, the polarising microscope results concur with the graphical data showing maturity ratio in Figure 3.6. Though numerically the MR results for Tencel® and viscose have little meaning, they indicated a variation in the interference colour under polarising light, which, along with the polarising images gave some insight into the polymer alignment within the fibres.

3.3 CRYS TAL IN NITY / DENSITY

3.3.1 PYCNOMETRY

Pycnometry is a method of studying the density of a material. The difference between the density of packing between crystalline (more dense) and amorphous (less dense) regions with a polymer, means that this method may also be used to calculate sample crystallinity.

Density (ρ) is a measure of the degree of packing of a material, defined by the volume (v) and mass (m) of a sample, as shown in the equation:

$$\rho = \frac{m (g)}{v (cm^3)}$$

Within the instrument (Figure 3.8), the sample chamber (of known volume) contains the sample cup and sits alongside the “expansion chamber” (also of known volume). While sealed, pressurised gas enters the sample chamber through a fill valve, pressurising the chamber to a specified pressure (by user). The fill valve is then closed and the pressure (P₁) is recorded. A second valve is then opened between the sample and expansion chamber, allowing the pressurised gas to spread between the two chambers. Once the pressure (P₂) is recorded the gas can be expelled through a final venting valve. From these measurements the volume (V) of the sample chamber can be calculated using the ‘ideal gas law’, which states that PV = nRT, where n is the number of moles of gas, R is the ideal gas constant and T is the temperature of the
system. Since $n$ and $T$ remain constant when the gas is allowed to expand from the sample cell (cel) into the expansion chamber (exp), $P_1(V_{cel} - V_s) = P_2(V_{exp} + V_{cel} - V_s)$ from which the volume of the sample ($s$) can be calculated using the equation:

$$V_s = V_{cel} - \frac{V_{exp}}{P_1/P_2 - 1}$$

The density of the sample is then calculated using this sample volume and the known mass of the sample.

![Figure 3.8: Micromeritics AccuPyc II 1340 pycnometer internal schematic](image)

This schematic, taken directly from the Micromeritics FoamPyc software (Micromeritics Instrument Corporation 2011), shows the internal layout of the pressurised chambers (sample chamber – with lid – to the left) and venting system.

Accurate measurement of the displacement volume relies on accurate calibration of the chambers. National Institute of Standards and Technology (NIST - USA) traceable calibration spheres allow the volume of both the sample and expansion chambers to be calculated.

In order to obtain an absolute value of crystallinity using density, the density values for fully amorphous ($\rho_a$) and totally crystalline ($\rho_c$) forms of that material must be known as well as the plasticiser content if this is present in the sample. According to Mishra (2000) the percentage crystallinity (by weight) of a dry (unplasticised) sample may be calculated from sample density ($\rho_s$) using the equation:

$$\%\ Crystallinity = \frac{\rho_c(\rho_s - \rho_a)}{\rho_s(\rho_c - \rho_a)} \times 100$$
In the case of cellulose the density values occur within a range for fully amorphous and completely crystalline samples, an average of the range for each will be taken and the values quoted as 1.36 gcm$^{-3}$ and 1.59 gcm$^{-3}$ respectively (Sun 2005, Derecskei and Derecskei-Kovacs 2006). A complicating factor, however, is the water content of the cellulose samples. Most of the water will be removed prior to the test by the application of dry heat, but tightly bound water molecules associated with the samples may be difficult to remove. If the sample is not completely dry, then the volume of water remaining in the samples needs to be accurately measured. The aim of this set of experiments is to use the measurement of density to rank various cellulose samples in order of their crystallinity.

**MATERIALS AND METHODS**

All density studies were carried out with a Micromeritics AccuPyc II 1340 pycnometer, running at 25°C and using AR grade bottled helium as purge gas at a pressure of 19.5 psi. Sample mass was measured directly prior to testing and again at the conclusion of the run. The 1cm$^3$ sample cup was used for all measurements, holding a mass of around 150-350 mg (depending on the sample type).

Samples used for density tests are: CF – cotton fibre (supplied by P Henry, CSIRO), TF – Tencel® fibre (Lenzing), VF – viscose fibre (supplied by M Pate, CSIRO).

Samples were dried by placing the sample in an oven at 105°C overnight. On removal from the oven, samples were cooled in a desiccator containing silica gel and then rapidly transferred into the aluminium pycnometer cup. The cup was then placed back into the oven for 15 mins to remove any moisture picked up on transfer into the cup. The sample and cup were then cooled again over silica gel. Sample and cup were then weighed and placed directly into the instrument.

**RESULTS AND DISCUSSION**

Dry samples of cotton, Tencel® and viscose were tested in the pycnometer and over the course of 100 cycles the sample density was determined. Due to instrument equilibration over the first (approximately 50 cycles), the average sample density as
collected over the last 40 cycles of the run was used to calculate the fibre’s cellulosic crystallinity (equation on page 59). The calculated cellulosic crystallinity of each sample is listed in Table III.

Table III: Density and calculated crystallinity of dry cellulosic samples

<table>
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<th>Fibre</th>
<th>Measured Density (g cm⁻³)</th>
<th>Crystallinity (%)</th>
</tr>
</thead>
<tbody>
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<td>CF</td>
<td>1.538</td>
<td>80</td>
</tr>
<tr>
<td>TF</td>
<td>1.517</td>
<td>72</td>
</tr>
<tr>
<td>VF</td>
<td>1.500</td>
<td>65</td>
</tr>
</tbody>
</table>

The density values are consistent with the literature which quotes values for the density of dry cellulose of 1.50-1.55 g cm⁻³ (Hearle and Morton 2008). The order of crystallinity calculated from density is also consistent with the literature, listing cotton, Tencel® and viscose from most to least crystalline. This, along with the sorption isotherms in Section 1.4, supports the literature which suggests that chemical processing methods, as used on Tencel® and viscose result in a reduction in crystallinity. This type of chemical treatment would also have the effect of increasing the purity of the cellulose within the fibre. It is worth noting that although impurities such as lignin and pectin, which are of lower density than cellulose, are present in cotton, they are unlikely to impact heavily the calculation of crystallinity in mature fibres due to their minimal overall content within the fibre (Pettolino 2013).

3.3.2 X-RAY DIFFRACTION (XRD)

X-ray diffraction is used to determine the size and shape of crystallite structures by measuring the distance between atomic planes. This technique makes it possible to study these planes, due to the short wavelength of x-rays which are of similar magnitude as the spacing between crystal layers (approximately 0.1 nm), as indicated by ‘d’ in Figure 3.9a.

X-rays are produced when electrons move between shells within metal. This excitation and reaction occur within an x-ray tube that emits the rays towards a lead screen, which in turn reduces the emitted x-rays into a beam focused on the sample. Once the x-rays come into contact with the sample, the layered crystalline structure within the sample will scatter the rays in all directions (including back towards the source) depending on the angle of the crystallites within (Figure 3.9a). The diffracted
rays and the residual incident beam are then detected using a photographic plate. A single crystal will give only a limited amount of data, however a large number of randomly orientated crystals will form a pattern which can be considered as a sample fingerprint. This can be displayed graphically as shown in Figure 3.9b.

Figure 3.9: The anatomy of x-ray diffraction
A focused beam of x-rays become scattered as they come into contact with various layers of crystal within a sample (A). The degree of x-ray scatter at each angle can then be plotted graphically (B) and used to determine the crystalline structure of the sample (adapted from Chomet 1993, Fawcett, Crowder et al. 2013, Loye 2013).

MATeRIALS AND METHODS
All x-ray diffraction studies were carried out on a Panalytical X’Pert³ MRD (XL). The Cu x-ray source was operated at 40kV and 30mA. Fibre samples were mounted onto zero background plates using double sided tape and secured within the instrument. Scans were obtained from 10 to 40 degrees 2θ in 0.02 degree steps, at 5sec intervals.

Samples used for XRD testing are: CF – cotton fibre (supplied by P Henry, CSIRO), TF – Tencel® fibre (Lenzing), VF – viscose fibre (supplied by M Pate, CSIRO).
RESULTS AND DISCUSSION

Samples of cotton, Tencel® and viscose were bombarded with x-rays and the subsequent diffraction of the incident rays analysed to determine the crystallinity of the samples. Figure 3.10 shows the raw data collected for each sample.

The raw data was analysed using the Gaussian deconvolution method (Teeäär, Serimaa et al. 1987, Park, Baker et al. 2010) in Origin Pro software, after running a baseline correction. This method was used to separate the amorphous peak from those of the crystalline regions and was chosen in preference to the peak height method (Segal, Creely et al. 1959), which has been shown to overestimate sample crystallinity (Park, Baker et al. 2010). The ratio of the area of crystalline peaks compared to the total area could then be used to determine the percentage crystallinity of each sample. Figure 3.11 gives an example of the deconvolution carried out on cotton and tabulates (Table IV) the resultant crystallinity for all three samples.

![Figure 3.10: X-ray diffraction data for cotton, Tencel® and viscose (background corrected)](image)

X-ray diffraction pattern intensity graph for cotton (CF), Tencel® and viscose.

**Table IV: Peak area calculated from XRD data**

Area calculated for each of the peaks isolated using a Gaussian deconvolution, on cotton XRD data. Deconvolution peaks shown (labelled) in Figure 3.11.

<table>
<thead>
<tr>
<th>Peak</th>
<th>Area</th>
<th>St. Err.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Crystalline</td>
<td>716</td>
</tr>
<tr>
<td>2</td>
<td>Crystalline</td>
<td>438</td>
</tr>
<tr>
<td>3</td>
<td>Amorphous</td>
<td>1185</td>
</tr>
<tr>
<td>4</td>
<td>Crystalline</td>
<td>1347</td>
</tr>
<tr>
<td>5</td>
<td>Crystalline</td>
<td>226</td>
</tr>
</tbody>
</table>
Comparison of the data obtained using XRD to the results calculated using the dry density of each fibre type agrees well with the order of samples crystallinity, suggesting that calculation of the crystallinity of samples from the dry density is indeed a valid method of determining crystalline content in cellulose. There is however a difference in the calculated crystallinity between the methods (lower in XRD), of approximately 12.5% in cotton and viscose and 15.5% in Tencel®. In comparison to the literature, the XRD crystallinity data appears to be within the accepted range. Various authors have the crystallinity of cotton at 58-89% (Hermans and Weidinger 1948, Segal, Nelson et al. 1951, Segal, Creely et al. 1959, Patil and Radhakrishnan 1966, Teeäär, Serimaa et al. 1987, Buschle-Diller, Zeronian et al. 1994, Hu and Hsieh 1996, Gümüskaya, Usta et al. 2003), Tencel® at 34-80% (Udomkichdecha and Chiarakorn 2001, Colom and Carrillo 2002, Kreze and Malej 2003, Nostro, Fratoni et al. 2003, Gindl and Keckes 2006, Xu, Lu et al. 2006) and viscose at 16-76% (Hermans and Weidinger 1948, Hindeleh and Johnson 1974, Buschle-Diller, Zeronian et al. 1994, Colom and Carrillo 2002, Kreze and Malej 2003, Gindl and Keckes 2006, Xu, Lu et al. 2006, Rojo, Alonso et al. 2013) with medians of this data calculated to be 71%, 67% and 49% respectively.

Figure 3.11: Peak deconvolution of cotton XRD data
Gaussian deconvolution of cotton XRD data, showing the peak numbers as referred to in Table IV. The curve fitting was shown to have an $R^2$ of 0.995.
3.4 WATER CONTENT

3.4.1 KARL FISCHER TITRATION (KFT)

Karl Fischer titration (KFT) is a method of selectively determining the water content within a given sample. Unlike the measurement of mass loss on drying, which cannot differentiate between the loss of water and other volatiles, the titration reaction used in Karl Fischer utilises water, giving the reaction high specificity. In a methanolic solution (alcohols may vary depending on sample) the reaction is as follows:

\[ \text{H}_2\text{O} + \text{I}_2 + [\text{RNH}]^+\text{SO}_3\text{CH}_3^- + 2\text{RN} \rightarrow [\text{RNH}]^+\text{SO}_4\text{CH}_3^- + 2[\text{RNH}]^+\text{I}^- \]

Where \( RN \) is a base, commonly imidazole (early methods used pyridine). Water content can be determined by two methods: volumetric or coulometric (Figure 3.12) analysis.

**Figure 3.12: Coulometric Karl Fischer titration schematic**

The sample is heated within the oven to liberate any water molecules within the sample. This water vapour is then carried to the titration cell by dry carrier gas (nitrogen) and titrated with iodine solution. The endpoint is determined by a platinum measuring electrode (adapted from Mettler Toledo 2011).

In volumetric KFT, the reaction occurs as iodine is added (directly) by burette. As this happens, the \( \text{I}_2 \) is reduced to the iodide anion when it reacts with sulphur dioxide in a strong redox reaction. This method is best for larger samples and those with high
estimated water content (Metrohm ref). For samples with an estimated water content of less than 200 mg (down to 10 μg), coulometric KFT is recommended. Coulometric analysis utilises the same strong redox reaction as volumetric analysis, however the coulometric method produces iodide from iodine at a platinum anode when an electrical current is applied. Iodine, in both cases, is consumed at a rate of 1 mole per mole of water.

Both volumetric and coulometry methods, use a dual-prong platinum electrode (measuring electrode) to monitor the electrical current within the titration cell and determine the end point of the titration. In contrast to the standard “dead-stop” method of determining end points in titrations, the water within the reaction cell suppresses the electric potential until the water is consumed and I₂ is in excess. At this point the current increases to a maximum and the titration is complete. A typical titration curve is shown in Figure 3.13.

![Figure 3.13: Biamperometrically indicated titration curve for Karl Fischer titration](image)

Using the concept of the “dead-stop” method in reverse, the platinum measuring electrode detects the point at which water is no-longer in excess as a maximum in current (Bruttel and Schlink n.d.).

As well as being highly specific towards the measurement of water, KFT also has the advantages of being a fast and high precision test. The precision is however limited to some extent by the accuracy of measuring the sample mass. The two main disadvantages of KFT are interference by side reactions within the anolyte (or titrant) solution and “drift”. Side reactions cause inaccurate KFT when they release water or consume iodine. In many cases specialised anolytes may be used to suppress these side reactions. Due to the inert nature of the sample being tested, side reactions are unlikely to be of significance in this project. Drift on the other-hand cannot be
removed as it occurs as a result of ambient humidity. Drift is minimised through the use of dry carrier gas, molecular sieves, sealed reaction vessels and ‘dry-run’ calculation of the drift (calibration) at the beginning of each run.

One other point necessary to consider when running a Karl Fischer titration is the efficiency of water extraction from the sample, specifically solid samples. Solid samples often have water trapped within their bulk, which may simply sit in capillaries and voids or may be securely bound. To release these bound water molecules, homogenisation, solvent extraction and the application of heat are commonly used to help release trapped water. An extraction oven (analogous to that shown in Figure 3.12) will be used in the experiments of this study to extract water from the cellulosic fibres.

The aim of using KFT was to determine the water content of samples before and after testing using other techniques (such as pycnometry) and to determine the water content of samples before drying and after both oven and freeze-drying.

**Materials and Methods**

All water content measurements were carried out using a Metrohm 852 coulometer (with diaphragm) with an 874 oven sample processor. Standard ‘Hydranal Coulomat CG’ and oven specific reagent ‘Hydranal Coulomat AG Oven’ were used for all tests. Samples were weighed and sealed in 6 ml vials with Teflon coated silicone/aluminum septum caps prior to testing. Control vials were taken on each separate day that vials were sealed, to account for the ambient humidity within the laboratory. The instrument was set to heat samples to 150°C and dry nitrogen was used as a carrier gas to deliver the liberated water to the reaction vessel. The reaction endpoint was set as 50 mV. Each sample was run in triplicate.

Samples were oven dried and conditioned at 33%, 59%, 76%, 85% and 97% relative humidity (RH) in chambers containing saturated salt solutions; magnesium chloride, sodium chloride, potassium chloride and potassium sulphate (consecutive order). Conditioning occurred for a minimum of 70 hours. Oven dried samples were dried as discussed in Section 3.2.1.

RESULTS AND DISCUSSION

Cotton, Tencel® and viscose were oven dried and conditioned at a variety of humidities, and measured using KFT in order to study changes in moisture uptake. Oven dried samples of each fibre were also tested to determine the residual water content.

The results shown in Figure 3.14 indicate that Tencel® is able to take up the greatest volume of water, followed by viscose and cotton, which is consistent with the moisture sorption isotherms given in Chapter 1.

![Figure 3.14: Experimental water sorption values for cotton, Tencel® and viscose](image)

*Figure 3.14: Experimental water sorption values for cotton, Tencel® and viscose*

Average water content results for each fibre type are shown. Tabulated data in Appendix 1.

When compared with these isotherms however, the water content measured after equilibration at varying humidity appears slightly low. This effect is more pronounced in the regenerated celluloses, Tencel® and viscose, and is likely to be due to both the...
difference in method used to measure moisture content and RH equilibration at a slightly different temperature. It is also worth noting that all fibre types contain approximately 2-3% residual moisture content after drying at 105°C overnight. This may have consequences for the measurement of $T_g$ discussed in later chapters.

### 3.4.2 Dynamic Vapour Sorption

Dynamic vapour sorption, as discussed in Chapter 2, can be used to determine the $T_g$ of samples by way of critical RH. However it is most commonly used to determine the moisture sorption isotherms of hygroscopic materials, by measuring change in mass of the sample while increasing the humidity in a stepwise fashion.

#### Method

All samples were sent to Imperial College, London and were tested by J. Yamazaki under the supervision of Dr D. Williams. Samples were tested using a Surface Measurement Systems - Dynamic Vapour Sorption Advantage instrument, using nitrogen carrier gas. Tests were carried out at 25°C, on a sample size of approximately 20 mg, dried in-situ for at least 5 hours prior to sorption studies, using a flow of dry air. For cotton, humidity was then increased stepwise at a rate of 5%RH every two hours, up to 95%RH and then back down to dry conditions. Due to time restrictions for Tencel® and viscose, humidity was increased continuously at a rate of 5%RH per hour up to 90%RH and then back down to dry conditions. Cotton was also tested using the continuous sorption method and the difference in the sorption isotherm obtained using the two different methods was used to correct the sorption isotherms of Tencel® and viscose.

Samples used for DVS tests were: CF – cotton fibre (supplied by P Henry, CSIRO), TF – Tencel® fibre (Lenzing), VF – viscose fibre (supplied by M Pate, CSIRO).

#### Results

Results of a stepwise increase in humidity for cotton are shown in Figure 3.15. The continuous humidity increase runs for all samples can be found seen Figure 5.6 (cotton runs are shown together in Appendix 2). Once collected, these results were plotted as moisture content against relative humidity, rather than time, to determine
the moisture sorption isotherms for each sample. Though the use of two methods is not ideal, comparison of the results obtained on cotton shows reasonable agreement between methods on desorption, up to 75% RH, with an error of 6% at 90% RH. Absorption was more greatly affected showing low MC throughout with a median error of 7.5% (see Appendix 2). Using this error (calculated at 5% RH intervals), Tencel® and viscose isotherms were corrected. Moisture content values for Tencel® and viscose at 95% RH were also estimated by extending polynomial trend lines fitted to each curve. The moisture sorption isotherms for cotton, Tencel® and viscose, determined using DVS are shown in Figure 3.16.

![Figure 3.15: Moisture content of cotton with changing humidity as measured using DVS](image)

Moisture content is shown in blue for cotton. As relative humidity (red) is incrementally increased, the moisture content in cotton quickly increases and settles to equilibrium. The reverse happens on decreasing humidity.

The results shown in Figure 3.16 appear to be reasonably consistent with the literature values, at 90% relative humidity, of 24%, 22% and 15% for Tencel®, viscose and cotton, shown in Figure 1.7 (Mihranyan, Llagostera et al. 2004, Okubayashi, Griesser et al. 2004, Okubayashi, Griesser et al. 2005, Hill 2009). Cotton appears slightly low, which may be a result of the sample not being allowed to reach equilibrium before the humidity was increased, as can be seen at high humidity in
Figure 3.15, while a small error is expected in the Tencel® and viscose results due to the correction for difference in method. Tencel® and viscose take up more water than cotton with values at 95% RH of 25% and 22.5% and 14% respectively compared to 14% for cotton. Tencel® also appears to have a slightly higher measured hysteresis than shown in the literature.

Figure 3.16: Moisture sorption isotherms for cotton, Tencel® and viscose – measured using DVS

Moisture sorption isotherms for cotton (blue), Tencel® (purple) and viscose (green) measured stepwise at 5%RH every 2 hrs for cotton and 5%RH/hr for Tencel® and viscose (corrected).

There was some concern that the faster rate of moisture increase used in the testing of Tencel® and viscose would mean that the samples would not have had sufficient time to equilibrate at each humidity and would therefore result in an overall lower measure of moisture content. However, comparison between the step-wise (Figure 3.15) and continuous ramping procedures used on cotton (Figure 5.6), along with the comparison of the corrected measured isotherms with the literature values for Tencel® and viscose were used to establish confidence in these results. The reduced moisture content of these results may therefore have occurred as a result of insufficient drying of the samples at the beginning of the DVS cycle. It is also likely, with both the measured data and that found in the literature, that the samples
contain slightly more moisture than measured in this test, based on the low
temperature drying conditions and compared with the residual moisture content
measured in each sample using KFT.

3.5 SUMMARY OF RESULTS

Cotton, Tencel® and viscose have been tested using a number of methods, as a means
of characterising the samples, primarily in terms of size, crystallinity and moisture
content. This was done to gain some understanding of the samples prior to using
them to identify the $T_g$ of cellulose. Table V outlines these results.

Where more than one method has been used to determine a value/property the
results are reasonable, at least in determining the order of the different fibre types.
The average diameter of cotton fibres measured using SEM and Cottonscope, differs
by approximately 4 μm, giving an overall average diameter for cotton of 17 μm, which
fits well with the literature (Ryser 1999). Averages of 21 μm and 16 μm for Tencel®
and viscose, also agree with the literature, though these diameters are determined
by the extrusion parameters, rather than naturally as is the case for cotton.

<table>
<thead>
<tr>
<th>Instrument</th>
<th>Measure</th>
<th>Cotton</th>
<th>Tencel®</th>
<th>Viscose</th>
</tr>
</thead>
<tbody>
<tr>
<td>SEM</td>
<td>Feret’s diameter</td>
<td>19 μm</td>
<td>20 μm</td>
<td>17 μm</td>
</tr>
<tr>
<td>Cottonscope</td>
<td>Width</td>
<td>15 μm</td>
<td>23 μm</td>
<td>15 μm</td>
</tr>
<tr>
<td></td>
<td>BF maturity</td>
<td>0.84</td>
<td>0.16</td>
<td>0.83</td>
</tr>
<tr>
<td>Pycnometer</td>
<td>Density (g cm$^{-3}$)</td>
<td>1.54</td>
<td>1.52</td>
<td>1.50</td>
</tr>
<tr>
<td></td>
<td>Calc. crystallinity</td>
<td>80%</td>
<td>71%</td>
<td>65%</td>
</tr>
<tr>
<td>XRD</td>
<td>Crystallinity</td>
<td>70%</td>
<td>60%</td>
<td>57%</td>
</tr>
<tr>
<td>KFT</td>
<td>&quot;Dry&quot; MC</td>
<td>2.6%</td>
<td>3.3%</td>
<td>2.5%</td>
</tr>
<tr>
<td></td>
<td>97% RH MC</td>
<td>15.2%</td>
<td>17.3%</td>
<td>16.0%</td>
</tr>
<tr>
<td>DVS</td>
<td>95% RH MC</td>
<td>14%</td>
<td>23%</td>
<td>21%</td>
</tr>
</tbody>
</table>

The birefringent maturity, while having little meaning for samples other than cotton,
revealed a difference in the molecular configuration of Tencel® in comparison to
cotton and viscose. Further examination of the samples by polarising light
microscopy confirmed the Cottonscope results and indicates that there is a higher
degree of uniformity in the polymer/crystallite orientation in Tencel® than the other
two samples.
Pycnometry was used, initially to identify the density of the samples. The results are in reasonable agreement with figures in the literature of 1.55 (Gordon and Hsieh 2007), 1.5 (Männer, Ivanoff et al. 2011) and 1.52 (Hearle and Morton 2008) for dry cotton, Tencel® and viscose. These results were then used to estimate the crystallinity of the samples using the equation on page 59. Comparison of the calculated crystallinity from density and the XRD result showed that while there was a 12.5-15.5% difference in the calculated crystallinities, the order of most to least crystalline was consistent: cotton, Tencel®, viscose.

Studies of the “dry” moisture content of these samples, clearly show that all three contain residual moisture content, of around 3%, after oven drying overnight. This is an important point and may go some way to explaining the degree of variation in $T_g$ figures quoted in the literature results for dry cellulose. It will therefore be important to take this into account when trying to measure the dry $T_g$ in cotton.

The maximum equilibrium MC values for cotton, Tencel® and viscose conditioned at 95% and 97% RH are a little more difficult to understand. Both methods show increased moisture content for regenerated cellulose compared to cotton, which is consistent with higher density and crystallinity shown in cotton. However, Tencel® having a higher moisture content than viscose is at odds with both its higher density and crystallinity. The moisture sorption isotherms measured using DVS do, however, agree well with literature values (Okubayashi, Griesser et al. 2005, Hill 2009), while the values obtained using KFT on Tencel® and viscose, conditioned at 97%RH, are a little lower. This may have been explained by loss of moisture as the samples were transferred from the conditioning chamber to the sampling vial, however this does not explain why the KFT measured MC for cotton is higher than that given by DVS.
The experiments in Chapters 4 and 5 were all aimed at determining a viable and reproducible set of conditions under which the glass transition temperature of each cellulose sample may be measured. As a means of confirming a glass transition, the questions: “Does the measured $T_g$ change with moisture content?” and “Can physical ageing be achieved by holding the sample just below the measured $T_g$ for a given sample?” will also be addressed.

This chapter will cover the experimentation and results collected using the most common techniques for measuring $T_g$: DSC and DMA.

### 4.1 DIFFERENTIAL SCANNING CALORIMETRY (DSC)

The aim of using DSC is to determine the $T_g$ of various cellulose products by monitoring changes in endothermic and exothermic heat flow as heat is applied to or removed from the samples. An endothermic step change in heating or an exothermic step change on cooling is indicative of $T_g$. Physical ageing will also be examined.

### Materials and Methods

All DSC experiments were carried out on a TA Instruments Discovery series differential scanning calorimeter with attached RSC90 refrigerated cooling system, which has a working temperature range of -90°C to 550°C. Nitrogen purge gas was used for all tests, at a flow rate of 50 mL min$^{-1}$. Where possible all tests were carried out over a range of the “expected $T_g$” ± 30°C in order to produce curves with sufficient baseline stability to allow accurate measurement of the transition. The midpoint of the temperature range was chosen to represent the $T_g$ of the tested samples. DSC heat flow curves were plotted endothermic transitions upwards.

Standard DSC runs were carried out as a heat/cool/heat cycle, the first cycle used to remove any previous thermal history (such as physical ageing) that might interfere with visualisation of the glass transition. The heating rate was varied between experiments. These details are noted in the results section.
Modulated DSC runs were set to heat (or cool) only, with a heating rate (ramp) of 5°Cmin⁻¹ and a modulation period of 30sec, aiming to produce 4-6 modulations per transition of interest.

In order to induce ageing, samples were held at a temperature around 30°C below the suggested T_g for a set period of time as listed, after an initial de-ageing step. After ageing, the temperature was reduced and the standard DSC procedure, as described above, was performed. Samples used to measure dry T_g were weighed into aluminium Tzero pans of known mass (weighed). Lids were punctured to avoid pressure build-up at high temperature. The samples were then dried in situ at 120°C for 30 mins at the start of each run (unless otherwise stated).

Whole (uncut) fibre samples used for all DSC tests are as described in Chapter 3; CF – cotton fibre (supplied by P Henry, CSIRO), TF – Tencel® fibre (Lenzing), VF – viscose fibre (supplied by M Pate, CSIRO), MCC - microcrystalline cellulose powder (Sigma Aldrich ~20 µm). MCC, was also used to replicate experiments reported by other authors.

Samples were used as supplied and also conditioned at 33%, 76%, 85% and 97% relative humidity (RH) in chambers containing saturated salt solutions; magnesium chloride, sodium chloride, potassium chloride and potassium sulphate (consecutive order). After a period of conditioning (1 week +), these samples were placed into aluminium Tzero pans of known mass, then returned to the chambers overnight to ensure correct conditioning. Pans were then hermetically sealed and weighed to determine sample mass. All hermetic pans were reweighed at intervals between tests to ensure no loss of moisture.

**RESULTS AND DISCUSSION**

Preliminary testing was based on the methods used by Szczesniak (2008). Samples of MCC, CF and regenerated cellulosics (VF and TF) were run at varying ramp rates of 5-20°Cmin⁻¹ and varying moisture content from dry to saturated. These tests typically showed no obvious change in heat flow, with the exception of intermittent exotherm
around -35-40°C on cooling (Figure 4.1) at high moisture contents on all samples. Results similar to these have been interpreted as $T_g$ by Szcześniak et al. (2008), who give a measured $T_g$ in the region of -55°C for cellulose samples containing 20% moisture content, however the results of this project are more likely to have occurred as a result of freezing water within the system. Like others, (Salmen and Back, 1977; Batzer and Kreibich, 1981 and Picker and Hoag, 2002) Szcześniak et al. (2008) also found that the $T_g$ of dry cellulose was unable to be measured using this method.

**Figure 4.1: Initial DSC results**

This DSC trace shows an exothermic step change at approximately -35°C (on cooling) for MCC conditioned at 97% RH and run using a standard heat/cool/heat cycle at 5°Cmin$^{-1}$. With no clear evidence of $T_g$ seen when run at 20°Cmin$^{-1}$, focus moved to using a high temperature ramp of 60°Cmin$^{-1}$ (as shown by Picker and Hoag, 2002), to increase the sensitivity of the instrument (refer to Table II, page 44). Dry MCC was analysed, this time from 20-270°C to determine the viability of this method. Having found a weak endotherm at around 150°C, which concurred somewhat with Picker’s findings, further tests were carried out and showed repeatability of the endotherm in CF, TF and VF (VF results shown in Figure 4.2). Again there was no evidence of a $T_g$ at 220°C as suggested by the literature. The larger endothermic peaks seen in Figure 4.2a
represent degradation of the VF sample. All samples showed peak degradation at approximately 270°C. Degraded samples were visibly changed (Figure 4.2b) and demonstrated a loss of mass. Repetition of the cycle from ambient conditions to 270°C revealed that the endotherm at 150°C remained, but reduced with subsequent cycles as did the degradation peak.

![Graph (a) demonstrated the first three runs produced for VF at high heating rate. Viscose starts to degrade at temperatures just above 200°C, and will undergo further degradation on subsequent runs.](image)

![Image (b) shows discolouration of all samples after three heating cycles to 270°C with nitrogen purge.](image)

**Figure 4.2: First 60°Cmin⁻¹ heating run for VF**

Graph (a) demonstrated the first three runs produced for VF at high heating rate. Viscose starts to degrade at temperatures just above 200°C, and will undergo further degradation on subsequent runs. The inset in graph (a) corresponds to the results shown in graph (c), which shows that while degradation is apparent, there is still repeatability of the endotherm at 150°C. Image (b) shows discolouration of all samples after three heating cycles to 270°C with nitrogen purge.
New pans using fresh material of the above sample types were made up and the tests repeated again. These runs showed greater repeatability due to the drop in upper temperature, to a maximum of 220°C, reducing the sample degradation. The overall results from these runs are shown in Table VI.

**Table VI: Overall results of “dry” T_g for all samples**
Tabulated results for the second round of “dry” DSC runs at a reduced maximum temperature. Lack of high temperature degradation improved repeatability and demonstrated T_g in a similar temperature region for all samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Initial</th>
<th>Repeat 1</th>
<th>Repeat 2</th>
<th>Repeat 3</th>
<th>Average</th>
<th>Std Dev</th>
</tr>
</thead>
<tbody>
<tr>
<td>MCC</td>
<td>151.7</td>
<td>150.9</td>
<td>153.5</td>
<td>153.6</td>
<td>152.4</td>
<td>1.3</td>
</tr>
<tr>
<td>CF</td>
<td>146.7</td>
<td>151.2</td>
<td>152.8</td>
<td>153.1</td>
<td>151.0</td>
<td>2.9</td>
</tr>
<tr>
<td>VF</td>
<td>144.4</td>
<td>144.9</td>
<td>145.3</td>
<td>146.0</td>
<td>145.2</td>
<td>0.7</td>
</tr>
<tr>
<td>TF</td>
<td>142.2</td>
<td>143.6</td>
<td>147.4</td>
<td>145.6</td>
<td>144.7</td>
<td>2.2</td>
</tr>
</tbody>
</table>

Although early tests, run at low heating rate, proved inconclusive, increasing the ramp rate to 60°Cmin⁻¹, shows weak but repeatable endotherms at similar temperature regions across a range of cellulose products. This is suggestive of a glass transition temperature of cellulose samples in the dry state.

Assuming that these oven-dried samples in this experiment are thoroughly dry, the value of T_g in the region of 150°C for cellulose concurs reasonably well with those measured by Picker and Hoag (2002) for dry MCC, at 174°C. This result is however at odds with the dry T_g of cellulose reported by Kargin, Kozlov et al. (1960) after extrapolation of the results obtained on a series of plasticized samples. If it is assumed that the observations and subsequent calculations by Kargin et al. (1960) of cellulose having a dry T_g of 220°C are correct, it indicates that although the samples were heated for a thirty minute period at 120°C directly prior to testing, they still contain a quantity of water which is likely to be strongly bound and very difficult to remove.

Given the observation of water content after oven drying, in all samples, using Karl Fischer titration (Section 3.3) of 1.5 – 3% MC, it is most likely that the samples in this experiment and potentially those carried out by Picker et al. (2002) did contain residual moisture. Szcześniak et al. (2008) also noted difficulty in obtaining moisture
free samples. That being the case, the experimental value of $T_g$ in the region of 150°C for cellulose concurs better with the extrapolated data provided by Kargin et al. (1960) (220°C – dry) and the results observed by Faroongsarng and Peck (1994) (143°C – 2.5% MC) or Bryant and Walter (1959) (>240°C – dry).

In an effort to confirm the endotherm seen at 150°C as $T_g$, an attempt was made to induce physical ageing peaks. Physical ageing, as discussed in Section 1.2.3, occurs in all polymers below their glass transition. The rate at which this occurs is determined by how close to the $T_g$ the sample is kept. Close proximity to the transition allows faster relaxing of the polymer into an aged form, however with a weak, broad transition, such as that seen in cellulose, being too close to the transition may not allow for this molecular relaxation. Holding the samples for 30 mins at 110°C or 130°C followed by heating from ambient to 220°C at 60°Cmin$^{-1}$ as used previously, an optimum ageing temperature could be determined. Samples dried and aged at 130°C were found (in general) to show less of a peak than samples dried at 120°C, suggesting that 130°C was too close to $T_g$ for adequate ageing to occur. The lower drying temperature (110°C) generally showed a greater peak than when dried at 120°C. For this reason, 110°C was chosen as the temperature at which to age the samples.

Samples of CF, TF, and VF all showed an increase in size of the endothermic peak with an increase in isothermal hold of 10, 15 and 20 hours at 110°C (VF shown in Figure 4.3). It was also noted that an increase in the hold time, saw a shift in the ageing peaks to the right. This may be a result of drying over time, but may also be a time dependant rather than temperature dependant shift, based on an increase in sample relaxation (Struik 1978). The ability to grow an ageing peak by holding a given sample at a temperature just below its suspected $T_g$ further validates the hypothesis that cellulose does show a transition at 150°C, although some have suggested that ageing is not a reliable method of ascribing $T_g$ (Paes, Sun et al. 2010).

Following on from the apparently successful use of the high ramping rate to produce a visible endotherm on dry samples, the fast heating rate (60°Cmin$^{-1}$) was used to
determine whether transitions could be seen at lower temperatures in moisture conditioned samples. A window of 50°C on either side of the reported data (Szczęśniak et al. 2008) was used to investigate samples conditioned at 76%, 85% and 97% relative humidity. The 97% RH samples showed weak but repeatable transition, particularly on the cooling cycles, however these appear as exothermic peaks which are indicative of freezing water (as demonstrated for slower rates in Figure 4.1). The first two repeat samples conditioned at 85% RH found a possible transition between 5-15°C, however these were very difficult to see and therefore were regarded as inconclusive.

Further repeats were run using weighted reference pans (extra aluminium lid attached) to reduce noise and improve sensitivity (refer to Table II). This proved successful in reducing background noise, revealing a very small repeatable step in the 5-15°C region across all samples. Similarly pans containing samples conditioned at 76% RH, when referenced against weighted pans, appeared to show small but repeatable changes in the region of 35-50°C. The step changes for these samples were more evident in the cooling cycle of the DSC curve, however despite the fact that these results appear to support the work of Szczesniak (2008), there is currently
no explanation of the exothermic step changes seen in their results at -34°C (at 15% moisture content) and 48°C (at 5.3% moisture content).

Modulated DSC (MDSC) was used to duplicate all standard DSC runs, as a means of verifying the reported data. All samples were subjected to a modulated run, set to the upper heating rate of the MDSC mode (see page 75 for method). Initial investigation showed that there may be multiple (up to 4) transitions in dry cellulose, consistent across all samples, similar to the findings presented by Picker et al. (2002). However, despite the positive result shown using standard DSC methods and a slight reduction in background noise with modulation, $T_g$ could not be any more easily resolved using MDSC. This may be due to the fact that this method is limited to a low overall heating rate of 5°C min$^{-1}$. Sample masses used (limited by pan size) may also not have been large enough to elicit the required response in the modulated test. Consequently the multiple $T_g$'s reported by Picker et al. (2002) using MDSC have not been substantiated.

Moist and dry runs were also compared to one another over a range of -90 to 90°C for the conditioned samples and extending up to 220°C for the dry samples, using both standard and modulated DSC. MDSC results for cotton are shown in Figure 4.4. Unfortunately, the comparison of the data over this range effectively nullified the results of all moist samples. Thermal changes previously thought to indicate $T_g$, within the expected window for each conditioned moisture, (e.g. 5-15°C for samples conditioned at 85% RH) appear to be reasonably consistent across all moist and dry samples.

This then substantiates the peaks seen in both cooling and heating of samples conditioned at 97% RH as being related to freezing of water. Although it is unexpected to see freezing water in conditioned samples, when considered in reference to the moisture sorption isotherms (Figure 1.7, page 15) for these cellulosic samples it is not unreasonable. The isotherms for all samples suggest that they are indeed likely to be saturated when conditioned at 97% RH.
Freezing of water in the cellulose-water system will only occur when the mixture reaches a critical moisture content. Pierlot (1999) described this effect in wool. Below 31.7% regain (24% MC) in wool, molecular motion is limited and water within the sample is unable to freeze; while above this point any water in excess of the stated 31.7% regain will freeze. The freezing point (and consequently melting point) of water is depressed due to the colligative nature of the system. Colligative solutions are affected by the ratio of solute particles, in this case cellulosic fibres, to the number of solvent particles. Solute particles within solution act to reduce the partial free energy of the solvent, which depresses the freezing point (and increases the boiling point) of the solution.

This critical moisture content (or regain) occurs as a result of the polymer going through its $T_g$, restricting further crystallisation from occurring. Thus determining this critical point gives another point on the $T_g$ versus moisture content graph. When plotted as a state diagram (Figure 4.5) this point is described by the intersection between the curve of the $T_g$ versus moisture content and the freezing temperature of water.
Polymer-water mixtures exist in two states at sub-ambient temperatures: free water (freezing) and bound water (non-freezing) (Sakabe, Ito et al. 1987). Assuming that the peaks seen in the 97% RH conditioned samples are a result of saturation, the coincidence of sub-ambient glass transition with the supercooling of water means that the enthalpy of the water melting peak (calculated using the area under the peak) and the temperature at peak maximum, can be used to determine the “freezing” $T_g$ using DSC (Pierlot 1999).

To determine the freezing $T_g$, samples of known moisture content (as measured using Karl Fischer titration) were prepared as described for conditioned samples, with a known volume of water to saturate the sample. Samples were initially equilibrated at -90°C to ensure complete freezing of water and then run at 0.1°Cmin$^{-1}$ from -25°C to 3°C to study the melt profile. Three pans of each sample were run in triplicate giving a total of 9 results. Figure 4.6 shows melt endotherms typical of each sample, including the temperature at the endotherm peak and the enthalpy of the change. The mass of freezing water in the samples is calculated using the equation:

\[
\text{Mass of sample and water added} \times \text{measured freezing enthalpy} \\
\text{Freezing enthalpy of water}
\]
The amount of non-freezing water is then calculated using the known sample water content and the freezing water content. Results for cotton, Tencel® and viscose are shown in Table VII.

**Table VII: Calculated non-freezing moisture content and ice melt temperature using DSC**

Each pan listed (3 per sample) was run in triplicate and the average results for each is shown here. MC and temperature results for each sample were then averaged. See Appendix 3 for full results.
When compared to the freezing $T_g$ for cotton, reported by Sakabe (1987), of 19.8% regain (16.5% MC) and -10°C the present results show a slightly higher freezing point temperature at a very similar non-freezing moisture content. Similar experiments run by Ur'yash, Larina et al. (2010), finding evidence of a $T_g$ of 0°C at a water content of 15.1%, also support this data.

Plotting the averaged results (Figure 4.7) along with the predicted $T_g$ using the Fox equation (as shown in Section 1.3.2, page 17), suggests that cotton is more crystalline than the regenerated cellulose samples which is consistent with the crystallinity results obtained using x-ray diffraction (page 63), although Tencel® does not follow this pattern. Tencel®’s increased moisture content does however fit with the isotherm result measured using DSC.

![Figure 4.7: Fox equation – graph, including DSC data](image)

Freezing point transition results for cotton, Tencel® and viscose overlaid on the plot of predicted $T_g$ constructed using the Fox equation. Error bars are based on the standard deviation between measured water contents.

**4.2 DYNAMIC MECHANICAL ANALYSIS (DMA)**

The aim of using the DMA is to determine the glass transition of cotton and other cellulose products through the application of stress and the examination of change in modulus, when heat and moisture are applied.
Materials and Methods

All DMA experiments were carried out on a TA Instruments Q800 dynamic mechanical analyser, fitted with the TA DMA humidity accessory when applicable. The film/fibre tension clamp was used for all experiments. A frequency of 0.8 Hz was used for all tests, unless stated otherwise.

Stress-strain curves used to determine the elastic region (Figure 4.8) of the samples were conducted at 35°C, from 0 to 18 N (no oscillation) at a rate of 0.01 Nmin⁻¹. Runs were ended upon sample rupture. Force and strain settings were then optimised for each sample to maintain the best possible signal without breaking the sample. For each single fibre it was found that the fibres should be tested at less than 1% strain with a preload force of 0 – 0.03 N, in order to remain within the elastic range. It needs to be noted that though the stress-strain curve can act as a guide to choosing instrument parameters, it is not definitive, due to the fact that it is developed using a static force, which is not equal to the dynamic force applied in these experiments.

Samples run under dry conditions were equilibrated at 200°C and held for 5 mins to dry the sample and remove and previous thermal history, at the beginning of the cycle. Samples were then cooled to 50°C, held for 5 mins and heated to 300°C at a rate of 2°Cmin⁻¹. The onset point of a drop in storage modulus was used to determine Tg.

Figure 4.8: Force-strain curves of cotton, Tencel® and viscose
Force-strain curve of cotton shown on the left Y-axis and Tencel® and viscose shown on the right Y-axis.
Samples run under humid conditions were initially equilibrated to 90°C and 10% RH. The humidity was then increased at a rate of 1% every 8 mins to 90% RH (or the maximum attainable humidity – whichever was lower). This cycle was initially run at 90°C, to remove any previous thermal history. A second experimental cycle at 90°C was then run. Once complete, the experimental cycle was then repeated at 80°C. This cycle was repeated at (negative) 10°C increments down to 10°C.

Samples tested using DMA are as described in Chapter 3; CF – cotton fibre (supplied by P Henry, CSIRO – MSE), VF – viscose fibre (supplied by M Pate, CSIRO – MSE), TF – Tencel® fibre (Lenzing). Samples were tested as single fibres and fibre arrays (Figure 4.9). A nominal diameter of 0.01 mm was used for all fibre samples. fibre arrays were measured as 'film' samples, with a measured width and standard depth (0.01 mm) as used for single fibre samples.

Figure 4.9: Photo of fibre array and single fibre mounted in DMA film tension set-up
The left image shows an array of fibres mounted in the DMA file tension clamp. Note the variation in thickness along the width and gaps between fibres. The right image shows a close up view of a single fibre mounted in the same clamps.

All fibre array runs were repeated at least once. Single fibre runs were rarely repeated, this was due to both the length of each run (4+ days) and the very high incidence of fibre breakage at the beginning of, and often during the test. This high rate of fibre breakage was a result of running at the very limits of the instrument’s capabilities.
RESULTS AND DISCUSSION

Fibres were first run as arrays under both dry and humid conditions. Arrays of cotton, Tencel® and viscose were initially run from 50 – 350°C without annealing prior to the test. Data for these samples is shown in Figure 4.10.

![Figure 4.10: Dry tensile testing of fibre bundles](image)

Dry fibre bundle testing shows softening and degradation of all three fibre types between 230°C and 300 °C.

All three fibre types show softening at approximately 230°C, seen as a small but distinguishable change in the modulus of cotton and Tencel® and a large drop in the modulus of viscose. This softening may be related to the glass transition of the cellulose within the fibres, slightly higher than the dry $T_g$ as suggested by Kargin et al. (1960). However, given the degradation results seen using DSC at just under 250°C,
this drop may also occur as a result of the start of degradation, or crystal slippage prior to degradation.

Samples were then run through multiple changes in temperature, with varying humidity conditions, as described on page 87. Fibre arrays run under these conditions show a late drop in storage modulus at about 62% RH and 80°C, suggesting that there is a transition occurring at the upper limits of the instrument’s capabilities, as seen in Figure 4.11.

![Figure 4.11: Fibre bundle tensile testing under varying humidity](image)

Fibre bundle tested under varying humidity shows softening of viscose at high relative humidity.

Although this was a promising result, the lack of levelling off after the drop in storage modulus, however, rendered these tests inconclusive. It is also worth noting that the change in modulus at this point is reasonably small in comparison to those seen in synthetic polymers (normally a drop of around three orders of magnitude), however this may be accounted for by the diluting effects of a highly crystalline polymer. The comparatively small drop in storage modulus also means that the ratio of change between storage and loss modulus is insufficient to create a peak in Tan delta (see Section 2.1.2). For this reason, Tan delta cannot be used to determine T_g in cellulose.

Using fibre arrays has the disadvantage of making it difficult to accurately determine the width of the array because of the potential for fibres to not line up perfectly (overlaying or gaps), in turn diminishing the accuracy of the measured moduli. It is also suspected that use of fibre arrays reduces the sensitivity of the instrument due to slight variations in tension, angle, temperature and moisture equilibration.
between fibres, or any combination of these factors. Therefore, in an effort to improve the sensitivity, these tests were repeated using single fibres.

Moving to the use of single fibres, it was necessary to determine the optimal force and strain working range. This was done using the force-strain curve as described on page 86. With the limitations of force and strain identified from the stress-strain curves, single fibre samples were run dry to high temperature as well as under humid conditions.

The data for a single Tencel® fibre shows a small change in slope just prior to 200°C (Fig 4.12). While the overall trend of the storage modulus data is downward, there appears to be a slightly steeper slope between 200°C and 230°C, which indicates a softening of the sample.

![Graph showing relative storage modulus vs. temperature for a single Tencel® fibre](image)

**Figure 4.12: Dry DMA of single fibres**
Single fibre testing of Tencel® shows softening at just under 200°C.

This result is similar to those seen in the fibre arrays, albeit with the softening temperature slightly lower than the 237°C quoted earlier. This shift may be due to thermal gradients across a large number of fibres and reduced sensitivity of the bundle as discussed previously, however it is more likely an artefact of a change in sample size as reported by Liu (2009). Unfortunately, it has not been possible to produce similar graphs for cotton and viscose without considerable background noise.
Singles fibres were then run under humid conditions, as described for the fibre arrays. The results obtained from these runs are shown in Figure 4.13.

![Graph showing single fibre tensile testing under varying humidity](image)

**Figure 4.13: Single fibre tensile testing under varying humidity**

Single fibres tested under varying humidity show clear softening of all three fibre types at 70°C and 80°C relative humidity, and also at 60°C in cotton and viscose. Results for cotton (dotted line), Tencel® (dashed line), Viscose (solid line) are shown for the 70°C cycle, giving critical RH (W_H) values of 73%, 75.5% and 76% RH respectively.

It can clearly be seen for all samples that there is a softening in the fibres as they approach high humidity and this is particularly evident at high temperature. This trend showing a drop in the humidity as temperature increases and the shape
displayed by the storage modulus are both strongly indicative of a glass to rubber transition.

The critical relative humidity ($W_g$) is used to describe the humidity at which the transition occurs for a given temperature, $T_g$. At 70°C and 80°C, this can be read fairly easily from these graphs using tangential lines, as shown in Figure 4.13. At lower temperatures however this is not possible to do with any accuracy. To get around this hurdle, the graphs can be superimposed using a shift factor of $a_T$ such as used in time temperature superposition (Dealy and Plazek 2009). Figure 4.14 shows this for viscose, with all cycles shifted to 10 °C.

Whilst the superposition is not perfect it does enable values of $W_g$ to be obtained at the lower temperatures. All the results are listed in Table VII and plotted in the graph of temperature against relative humidity (Figure 4.15).

![Figure 4.14: Superposition of viscose experimental data](image)

Viscose data collected using DMA superimposed using the shift factor $a_T$ to the 10°C position, indicates that a relative humidity of 89% is necessary to allow cellulose to pass through its glass transition.
Looking at the graph of $T_g$ against relative humidity, it shows the data collected using the superposition method concurs reasonably well with the data read directly from the measured fibres. The curves also follow the trends expected according to the Fox equation. However, in order to properly compare this data with the Fox equation model and other experimental data, it is necessary to determine the moisture content of the samples using moisture sorption isotherms.

![Figure 4.15: Glass transition temperature against relative humidity of DMA data](image)

Data collected using the superposition method (●) concurs reasonably well with the data read directly from the measured fibres (×), for cotton (blue), Tencel® (purple) and viscose (green).

Using these isotherms, the accuracy of the translation from relative humidity to moisture content is dependent on the temperature at which the isotherm is produced. Isotherms produced at 35.5°C, 70°C and 100°C (Wiegerink 1940) have been used to determine the moisture content of DMA experimental data collected at 40°C, 70°C and 90°C. While these temperatures are not perfectly matched, they will significantly improve the accuracy of the sample water content.

By plotting this data on a graph of moisture content versus relative humidity, trend lines could be fitted to the data. A second order polynomial equation for each was then determined using the trend lines (Figure 4.16). Due to the fact that no high temperature moisture sorption isotherms were found for Tencel®, it was assumed that the moisture content read from the isotherm (on page 15) was correct at 23°C...
and 30°C, and all samples were assumed as having 0% MC at 0% RH forming a third point in the Tencel® series.

Figure 4.16: Polynomial regression of moisture content with respect to relative humidity
Regression lines are fitted to known (assumed for Tencel®) temperature corrected moisture contents for each sample. Calculated equations can be identified according to the colour of the sample line.

These equations then made it possible to calculate the expected moisture content of the samples at each humidity with reference to the measured temperature. Results are shown in Table VIII.

Table VIII: Single fibres under changing humidity by DMA
This table lists the results of single fibre humidity ramp study as read directly from the graph using tangential lines (WgD) and via superposition of the data (WgS) using a, along with the associated moisture content (MC) determined using equations shown in Figure 4.16. Averages of WgD and WgS are plotted in Figure 4.17.

<table>
<thead>
<tr>
<th>Temp</th>
<th>Cotton WgD [MC] (%)</th>
<th>Tencel WgD [MC] (%)</th>
<th>Viscose WgD [MC] (%)</th>
<th>Cotton WgS [MC] (%)</th>
<th>Tencel WgS [MC] (%)</th>
<th>Viscose WgS [MC] (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>---</td>
<td>85 [10.5]</td>
<td>---</td>
<td>84 [17.7]</td>
<td>---</td>
<td>87 [18.2]</td>
</tr>
</tbody>
</table>

The averaged results obtained from the plot of moisture content versus relative humidity, plotted along with the DSC data and the predicted Tg using the Fox equation are shown in Figure 4.17.
Softening temperatures for cotton, Tencel® and viscose have been corrected using the polynomial equations determined in Figure 4.16, and overlaid on the plot of predicted $T_g$ constructed using the Fox equation. Error bars on DMA data are based on the standard deviation between $W_gD$ and $W_gS$.

When taken at face value, the raw DMA data collected on single fibres appears to show strikingly little change in measured critical humidity ($W_g$), despite a temperature range of 10-90°C. However, when converted to moisture content, it is clear that the difference in critical moisture content between temperatures is considerably higher.

These results conform well to the $T_g$ predictions of the Fox equation suggesting that the results are both indicative of the glass transition and that the Fox equation is a suitable model for describing this transition in cellulose. These results, specifically Tencel® and viscose, also concur somewhat with those reported by Paes (2010) of 12.3% MC at 71°C and 14.5% MC and 65°C DMA in ball milled wood cellulose (further results can be seen in Figure 2.14).

### 4.3 SUMMARY OF RESULTS

Overall the results obtained within this chapter strongly support the presence of the glass transition in cellulose. Negative results using both modulated and standard DSC techniques, together over 700 cycles, meant that DSC data alone was unable to provide sufficient evidence of a $T_g$. The overall failure of DSC for measuring $T_g$ in cellulose, appears to be due to both the limited sample mass that can be put in the
pans and the weak signal given by the samples. This may be further exacerbated by the slow overall heating rate used in MDSC. DSC showed potential for indicating $T_g$ through ageing endotherms, but the large discrepancy between the temperature at which these appeared (160-170°C) and the dry $T_g$ quoted by Kargin (1960) of 220°C, suggests this is unlikely. More positive results were obtained when moist samples were used to determine the “0°C” $T_g$ of cellulose. At moisture contents of 15.8% in cotton, 23.7% in Tencel® and 22.2% in viscose, the samples showed a freezing-point glass transition at approximately -1°C, concurring well with the data from Sakabe et al. (1987) and Uryash, Larina et al. (2010) paper.

Despite the difficulty in obtaining dry results in either of the methods in this chapter, Tencel® showed softening at approximately 200°C when run dry on the DMA. DMA results for samples run under moist conditions were considerably stronger. Cotton and viscose showed a clear drop and levelling off in modulus at 60°C (7.0 / 12.7% MC), 70°C (6.7 / 12.0% MC) and 80°C (5.7 / 9.9% MC), while Tencel® showed changes at 70°C (12.6% MC) and 80°C (11.5% MC).

While the “0°C” $T_g$ determined using DSC, alone, is unable to provide sufficient evidence of a $T_g$, when considered in conjunction with the results obtained on single fibres under humid conditions using DMA, they provide strong evidence of a $T_g$ in cellulose. Not only do the results follow a similar curve, they also correspond well with the data modelled using the Fox equation. Unfortunately however, neither technique was sufficiently robust to provide clear evidence of a dry $T_g$ to confirm Kargin’s (1960) extrapolated result.
This chapter will cover the experimentation and results obtained using less common methods measuring $T_g$: inverse gas chromatography, dynamic vapour sorption, atomic force microscopy, and pycnometry.

### 5.1 INVERSE GAS CHROMATOGRAPHY (iGC)

The aim of using iGC is to determine the glass transition of cotton and other cellulose products through the study of changes in the moisture sorption properties as temperature is increased. An increase in moisture sorption, occurring as a result of increased polymer mobility at $T_g$, is measured by a marked increase in probe retention time in iGC.

#### Materials and Methods

Inverse gas chromatography measurements were carried out on a Surface Measurement Systems – Surface Energy Analyser, using hydrogen as the carrier gas and methane as the column reference. Nonane was used as the probe gas for all tests. Water, loaded alongside the probe solvents, allowed the running humidity of the instrument to be chosen, Figure 2.11 shows the range of temperature and humidity over which the instrument can operate. Unfortunately the upper temperature limit of the instrument was well below the dry $T_g$ suggested by Kargin, Kozlov et al. (1960) and others (Alfthan, de Ruvo et al. 1973, Back and Didriksson 1969, Baldwin and Goring 1968, Paes, Sun et al. 2010, Salmén and Back 1977, Salmén and Back 1978, Takamura 1968, Yano, Hatakeyama et al. 1976), so a measurement of this was not attempted.

Sample was weighed into the glass columns and the ends ‘plugged’ using glass fibre, to ensure material did not escape and damage the instrument. Surface coverage was determined using Brunauer–Emmett–Teller (BET) analysis, which measures the surface adsorption of probe molecules on a sample. At infinite dilution this gave a result of 0.0008%. All subsequent tests were run at this surface coverage. The flame ionisation detector (FID) was set to amplify the signal x500 to ensure high sensitivity.
and tests were run slightly beyond the expected elution time of the probe to guarantee complete elution.

Sample tested using iGC is as described in Chapter 3; CF – cotton fibre (supplied by P Henry, CSIRO – MSE).

**RESULTS AND DISCUSSION**

Preliminary tests were run at 5, 20, 30, 50, 60, 70 and 80% RH at 5 to 10°C intervals within the instrument range for each humidity (see Figure 2.11). The cotton was heated to 120°C for 60 mins between cycles to ensure the same thermal history for each test. These initial tests gave an indication of an increase in the molecular mobility of the sample, when graphed as retention time – t_R (net) against temperature (Figure 5.1). The midpoint of the curve of the t_R versus T graph was chosen, using tangential lines, to determine the point of increasing sample mobility. The graph of lnV_N versus 1/T, discussed in Chapter 2 (page 36), did not display a clear deviation from linearity as would be expected for a sample passing through its glass transition region and could therefore not be used.

![Figure 5.1: Nonane retention time on cotton](image)

Results plotted for each equilibrated relative humidity as the temperature is increased. The data shows that the retention time decreases as temperature and humidity increase.

Using this data, the same sample was re-run at each humidity with a 20°C window on either side of the expected transition where possible. The temperatures were...
sampled at 2-5°C intervals at the outer limits of this range and 1°C intervals in the temperature range of interest. When the data was plotted as per the previous run the graphs shown in Figure 5.2 were generated.

![Graph showing nonane retention time on cotton](image)

**Figure 5.2: Nonane retention time on cotton**
Results plotted for each equilibrated relative humidity as the temperature is increased. Again the data shows that the retention time decreases as temperature and humidity increase. The decreased interval between test temperatures substantially increasing resolution of the change.

It was assumed that the midpoint of each curve represented the point of increasing mobility, which signifies the glass transition of the sample, giving the following results (Figure 5.3).

![Glass transition and humidity results using iGC](image)

**Figure 5.3: \( T_g \) and humidity results using iGC**
Results plotted of glass transition at each measured humidity. Moisture content results were established using the moisture sorption isotherm for cotton on page 69.

While this data follows the general trend expected for \( T_g \), in terms of showing a decrease in the transition temperature as the relative humidity increases, it does not
concur with the result obtained using DMA nor does it fit with the theoretical model of the Fox equation. Figure 5.4 compares this iGC data with the storage modulus onset temperature as determined using DMA.

![Graph showing glass transition temperature vs. moisture content](image)

**Figure 5.4: Fox equation – graph, including iGC and DMA**

Results plotted of glass transition in cotton, at each measured humidity for iGC compared with DMA data.

Interestingly the two methods do have points which intersect at around 30°C and 80% relative humidity (~9.3% MC), which is also in agreement with observations made on the AFM by Maxwell and Huson (2002). However, overall, the two datasets show very little similarities, outside the similarly curved shape.

The initial reason thought to be responsible for the different results obtained by iGC and the theoretical model, was incomplete drying of the sample used in the iGC. The high degree of packing in the column along with the (relatively) short duration allowed for drying, meant that it is likely that the sample was unable to dry sufficiently before the test was run. To assess this, the cotton was left to dry in a vacuum overnight at 40°C and the experiment repeated. Despite the repetition of these tests in an attempt to determine whether the sample was sufficiently dry, the results remained inconclusive. Inability to produce a Z-shape in the graph of lnV_N versus 1/T as used by Nastasović and Onjia (2008) to determine T_g (see Figure 2.8), reduced confidence in this method. Later consideration of the DMA results (which
were run in parallel with iGC) which exhibited transitions at much higher RH than anticipated, revealed that in comparison with the relative humidity specifications of the iGC instrument, the glass transition of cellulose was well outside the capabilities of the instrument (Figure 5.5). For example, at 80% RH the iGC can just reach the required 30°C to monitor the $T_g$ whereas at 70% RH the iGC can only reach 40°C, well short of the 80°C needed to go through the $T_g$. Owing to the fact that the two methods were run in parallel, the DMA data was not initially compared with the known instrument matrix prior to testing on cotton. Further testing using this method was therefore not continued.

![Figure 5.5: Instrumental working range under humid conditions – Overlaid with DMA data](image)

The area coloured on the graph for each instrument indicates the working humidity of each instrument with respect to temperature. Yellow points indicate the results of data collected under moist conditions using DMA. Overlaid, this data clearly shows that the $T_g$ as measured using DMA is well outside the working range of the iGC.

### 5.2 Dynamic Vapour Sorption

Like DMA and iGC, the aim of using DVS is to determine the glass transition temperature of cotton and other cellulose products by ascertaining the critical relative humidity ($W_g$). Determination of the critical relative humidity is possible due to the change from surface adsorption of water to bulk absorption of water at $T_g$, at which moisture sorption rate increases. $W_g$ is established as the humidity at which the graph of relative change in mass of the sample against time shows a distinct increase in slope. Unlike the stepwise mode used for establishing the moisture sorption isotherms of samples, this method requires a steady increase in relative humidity.
**MATERIALS AND METHOD**

Samples used for DVS tests are as described in Chapter 3; CF – cotton fibre (supplied by P Henry, CSIRO), TF – Tencel® fibre (Lenzing), VF – viscose fibre (supplied by M Pate, CSIRO) were sent to Imperial College, London and were tested by J. Yamazaki under the supervision of Dr D. Williams. Samples were tested using a Surface Measurement Systems - Dynamic Vapour Sorption Advantage instrument, using nitrogen carrier gas. Tests were carried out at 25°C, on a sample size of approximately 20mg (measured to ±0.001), dried in-situ prior to sorption studies, using a flow of dry air. Humidity was then increased at a rate of 5% per hour up to 90% RH and then returned back to dry conditions at the same rate. This was repeated at a rate of 15% per hour.

**RESULTS AND DISCUSSION**

Each fibre type was, in turn, loaded into the DVS instrument and dried under dry air at 25°C for 250mins. Humidity was increased at a rate of 5%min⁻¹ (Figure 5.6) up to 90% relative humidity. Fibres were then re-dried and the cycle repeated at a rate of 15%min⁻¹ (Figure 5.7).

*Figure 5.6: W₆ as measured using DVS – 5% RH.min⁻¹*

Cellulosic fibre mass change with an increase in humidity at a rate of 5% RH.min⁻¹. Test run at 25°C. Coloured curves give the mass against time for each sample on Y1, while the black line represents RH against time on Y2.
The graphs of sample mass against time for each sample (coloured lines) show a rapid drop in mass as samples are dried. Once the samples have reached equilibrium (±0.2%), the humidity is then steadily increased (black line) to 95% RH and the mass of the samples increased. Mass loss was then measured after 2 hrs equilibration at 95% RH. Table IX shows the minimum and maximum mass of each sample for both cycles. This change in mass can be directly attributed to an increase in water content in the sample and therefore the change in moisture content within that sample.

Table IX: Change in mass of Cotton, Tencel® and Viscose with changing humidity at 25°C

<table>
<thead>
<tr>
<th>RH ramp rate (RH.min⁻¹):</th>
<th>5%min⁻¹</th>
<th>15%min⁻¹</th>
<th>5%min⁻¹</th>
<th>15%min⁻¹</th>
<th>5%min⁻¹</th>
<th>15%min⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>Minimum mass (mg)</td>
<td>19.7</td>
<td>19.7</td>
<td>19.6</td>
<td>19.6</td>
<td>21.3</td>
<td>21.4</td>
</tr>
<tr>
<td>Maximum mass (mg)</td>
<td>22.1</td>
<td>22.1</td>
<td>24.0</td>
<td>23.9</td>
<td>25.6</td>
<td>25.5</td>
</tr>
<tr>
<td>Moisture content (%)</td>
<td>10.8</td>
<td>10.7</td>
<td>18.2</td>
<td>17.9</td>
<td>16.6</td>
<td>16.3</td>
</tr>
</tbody>
</table>

Figure 5.7: \( W_0 \) as measured using DVS – 15% RH.min⁻¹
Cellulosic fibre mass change with an increase in humidity at a rate of 15% min⁻¹. Test run at 25°C. Coloured curves give the mass against time for each sample on Y1, while the black line represents RH against time on Y2.

These results concur reasonably well with the results seen in all three samples when tested using Karl Fischer titration (Section 3.4.1) showing Tencel® to have the highest uptake of moisture and cotton to have the lowest, however the figures measured using DVS do appear slightly lower. This is likely to be due to incomplete drying of
the sample under air flow at ambient temperature. Any residual moisture within the samples used in DVS would be included in the minimum mass measurement and would therefore not be included as part of the calculated moisture change at 90% RH.

The increase seen in the rate of moisture uptake, at approximately 1200 mins indicates the point at which the samples go from surface adsorption to bulk absorption. This point is regarded as the sample’s critical humidity at 25°C (\(W_g\)), as described for DMA (page 93). Tangential lines were used to determine the centre point of the change. The moisture content of each sample was determined from the humidity at which the change occurred (dotted lines) using sample moisture sorption isotherms (page 70), and from the change in mass of the samples (solid lines). The critical humidity and moisture contents for cotton, Tencel® and viscose are shown in Table X.

| Table X: Measured critical humidity for Cotton, Tencel® and Viscose at 25°C |
|---------------|---------------|---------------|---------------|---------------|---------------|
|               | 5% RH.min\(^{-1}\) |               | 15% RH.min\(^{-1}\) |               | Average       |               |
|               | \(W_g\) [MC] (%) | \(\Delta m\) (%) | \(W_g\) [MC] (%) | \(\Delta m\) (%) | \(W_g\) [MC] (%) | \(\Delta m\) (%) |
| Cotton        | 75.9 [8.5]     | 6.6            | 76.6 [8.6]     | 6.8            | 76.2 [8.6]     | 6.7            |
| Viscose       | 73.0 [12.4]    | 9.5            | 73.0 [12.4]    | 9.6            | 73.0 [12.4]    | 9.5            |

Comparing the two cycles, there is a clear reduction in the sharpness in the peak formed by the graph of mass against time when the humidity is increased at a fast rate, however this appears to have had little effect on the measured relative humidity at which the fibres go from surface to bulk absorption. Though it is not expected for the \(W_g\) of a given sample to change, it is not unreasonable to expect that an increase in the rate of moisture addition may result in a delay in moisture uptake and therefore an artificially high critical moisture content result. This however appears not to have occurred. It is interesting to note that there is a difference between the moisture content calculated using the \(W_g\) compared to the change in mass (as a direct result of moisture uptake), of 2-3%. This will relate directly to the amount of moisture left within the sample after drying, as discussed in Section 3.4.1.
Plotting the averaged results (Figure 5.8) along with the DMA results and the predicted \( T_g \) using the Fox equation (as shown in Section 1.3.2, page 18), suggests that while the results are consistent with the order of measured maximum moisture content, they do differ considerably from the results gathered using DMA.

This discrepancy between the experimental DVS and DMA data is likely to be due to the rate dependent nature of the transition, giving a higher \( T_g \) result for DMA due to the frequency applied, compared to the passive DVS moisture sorption test. However, it may also be related to other factors such as a difference in sample equilibration time under humid conditions (though similar processes were used in both methods), or drying of the sample in DMA caused by the nitrogen purge gas. This discrepancy serves to demonstrate how it is that there have been so many different reported values of \( T_g \) for cellulose described in the literature.

Figure 5.8: Fox equation – graph, including DMA and DVS
Results plotted of glass transition at each measured humidity for DVS compared with DMA data.

5.3 ATOMIC FORCE MICROSCOPY

The aim of using AFM is to determine the glass transition of cotton and other cellulose products through the study of changes in the penetration depth under varying relative humidity and temperature conditions. It is hypothesised that introduction of
moisture and increased temperature will soften the sample as cellulose moves from
the glassy to rubbery state, increasing probe penetration into the sample.

**Materials and Methods**

All AFM measurements were carried out on a Digital Instruments Dimension 3000
Scanning Probe Microscope fitted with an optional hot stage for high temperature
experiments. The instrument was operated in tapping mode using silicon
“Pointprobes” for all tests. Cantilevers typically measured 125 x 30 x 4 μm and had a
nominal spring constant and resonance frequency of 42 N/m and 320 kHz
respectively. At the end of each cantilever were square pyramidal tips of
approximately 10–15 μm height, 5–10 nm tip radius and 20° half cone angle.

The position sensitive detector was calibrated prior to each round of force-distance
testing, against the hard surface of the sample holder (steel or glass). The deflection
trigger was set to 50 nm for all samples. Force-volume mode was used to map the
force required to penetrate the sample in a 16 x 16 point matrix, within an area of 3
x 3 μm. Penetration was determined from each Force-volume plot using Matlab
generated software written in house.

For fibres examined at (ambient) room temperature (22°C ±1°C) under varying
relative humidity, 3-5 single fibres were mounted on a glass slide using double sided
tape and measured at 3 different positions per humidity. The slide was then enclosed
within a Perspex chamber into which moist nitrogen was allowed to flow (Figure
5.9a). The relative humidity was controlled by alteration of the flow rate (Figure
5.9b), as described by Maxwell et al. (2002). The relative humidity was monitored
using a calibrated humidity sensor (Honeywell) inserted into the sample chamber.

Samples examined under high temperature conditions were secured to the surface
of a mild steel plate using double-sided, high temperature resistant Kapton® tape (-
269 to 260°C) and then attached to the Vecco Instruments Thermal Application
Controller (TAC) magnetic hot stage of the instrument. The set point temperature of
the instrument was calibrated (Figure 5.10) using standard room temperature and
the melting point temperatures of PEG 20,000 (64.5°C) and indium (156.6°C), to account for potential thermal lag. During calibration and measurement, the tip was heated to reflect the temperature of the hot stage, as such it was necessary to retune the cantilever at each new temperature and recalibrate the position sensitive detector. Samples run at high temperature were conditioned at ambient room humidity, approximately 65%, but were considered to be dry (±2%) at high temperature.

Figure 5.9: AFM humidity control set-up
A Perspex chamber (a) is used to enclose samples along with the AFM probe and humidity sensor. A series of bottles (b) containing water and glass beads are used to moisten the nitrogen to provide a humidified atmosphere and ensure that water droplets are not carried into the sample chamber (Adapted from Maxwell et al. 2002).

Figure 5.10: AFM hot stage calibration
AFM set-point temperature compared to the measured temperature, using the melting temperature of PEG 20,000 and indium as well as ambient temperature conditions.

Samples used for DSC tests are as described in Chapter 3; CF – cotton fibre (supplied by P Henry, CSIRO), TF – Tencel® fibre (Lenzing), VF – viscose fibre (supplied by M Pate, CSIRO).
RESULTS AND DISCUSSION

Raster scans collected over a 3x3 μm area produced 256 penetration points per test and these were collected over a range of humidities from 35 – 95%. Figure 5.11 shows the raw data collected for cotton. Each point represents the average penetration of a 256 penetration point test.

Figure 5.11: Raw penetration data results for cotton at varying humidity using AFM. AFM penetration data, points represent the average penetration of a 256 penetration raster, at 22°C.

Considering the data in this format, a slight overall softening of the fibres (increase in penetration) is evident as humidity is increased. As a means of discerning whether there was any underlying pattern, the results were grouped in (approximately) 5% RH batches and averaged to produce single data points (Figure 5.12).

Figure 5.12: AFM penetration data for cotton under varying relative humidity – averaged. Averages taken from the raw data in 5% RH bundles. The increase in penetration depth against relative humidity allows the $T_g$ of cotton to be estimated.
While the scatter seen in the raw data still puts some question over the validity of these results, refinement of the data into batched lots shows a clearer increase in the penetration depth at higher humidities. Using linear trend lines to fit the data either side of the change, the softening point with respect to RH ($W_g$) of cotton cellulose was measured at 61% RH (6.5% MC) at 22°C. This is somewhat lower than both the result indicated by Maxwell et al. (2002) of approximately 80% and the experimental results found using DMA (85%).

Measurements were also carried out on fibres of Tencel® and viscose (Figure 5.13), however the scatter for these fibre types was equally as unclear as that seen in cotton. The results for penetration in Tencel® showed a positive linear relationship with relative humidity, with no deviation to indicate a glass transition within the fibre. Viscose showed a minor change at around 71% RH (11.8% MC) but, like the results shown in cotton, the weakness of the change in penetration casts doubt on the results.

![Figure 5.13: AFM penetration data for Tencel® and viscose with varying relative humidity.](image)

Figure 5.13: AFM penetration data for Tencel® and viscose with varying relative humidity.

Using the same technique as demonstrated for cotton, Tencel® shows no clear change in the rate of penetration depth increase, while viscose shows a weak change at approximately 71% RH.

Samples were also examined in the dry state from 25 – 242°C, however, despite exceeding the temperature suggested in the literature as the dry $T_g$ of cellulose (220°C) by over 20°C, no clear increase in the penetration-temperature curve was
seen as temperature increased. Figure 5.14 demonstrates the results as seen for Tencel®.

![Figure 5.14: AFM penetration data for Tencel® at varying temperature.](image)

The increase in temperature of dry Tencel® showed no obvious change in the rate of penetration depth increase.

While these results show no clear increase in slope in the expected $T_g$ range, there is an increase in variance of the penetrations measured above 100°C, which most likely reflects the difficulty in operating at high temperature. The fact that this technique is able to pick up generalised softening as temperature or humidity is increased and the positive results reported in the literature (Buenviaje, Dinelli et al. 2001, Ge, Pu et al. 2000, Gracias, Zhang et al. 1999, Maxwell et al. 2002, Pu, Ge et al. 2001, Schmidt, Haugstad et al. 1999) suggests further investigation of this method is warranted. Despite the perceived sensitivity of this method, the weakness of the results seen in these tests may be a result of the small sample size combined with the weakness of the transition. It is also possible that use of sharp (new) cantilever tips could be influencing the measurement of $T_g$, as described by (Gracias et al. 1999) who found variations in $T_g$ of up to 20°C when using sharp tips.

5.4 Pycnometry

As an extension of the density studies discussed in Chapter 3, pycnometry will be used to investigate the change in the volume of conditioned samples over time, as they are exposed to dry air flow.
**MATERIALS AND METHODS**

All density studies were carried out with a Micromeritics AccuPyc II 1340 pycnometer, as described in Section 3.3.1. The instrument was set to repeat the volume/density test 999 times to maximise the likelihood of samples reaching equilibrium. Samples were required to have completed at least 50 tests with an average relative change <0.2% to be considered to have reached equilibrium. If this was not achieved the cycle of 999 tests was repeated without removing the sample from the pycnometer chamber.

Sample tested in this pycnometry study is as described in Chapter 3; CF – cotton fibre (supplied by P Henry, CSIRO – MSE).

Cotton was conditioned at 33%, 59% 76%, 85% and 97% relative humidity (RH) in chambers containing saturated salt solutions; magnesium chloride, sodium chloride, potassium chloride and potassium sulphate (consecutive order). Conditioning occurred for a minimum of 70 hours. Samples were dried as discussed on Page 60.

**RESULTS AND DISCUSSION**

During examination of the sample’s density using pycnometry, cotton was conditioned at varying humidities and run through 999 helium purge cycles within the pycnometer to look at the trends displayed by cellulose as dried in the instrument. Results are shown graphically in Figure 5.15, with pre and post-test figures listed in Table XI.

The most prominent feature in Figure 5.15 is the loss of volume seen for the sample conditioned at 97% RH. This loss relates to water loss as the sample is dried by flow of dry helium gas. Volume loss is also perceptible when the sample has been conditioned at 85% RH and 76% RH, and even to a small extent at 59% RH and 33% RH (not shown).
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Figure 5.1: Conditioned CF – Relative volume versus cycle number

This graph shows the change in volume over time for cotton conditioned at various relative humidities, assuming a common endpoint, of 100%.

Table XI: Mass, volume and density of conditioned FP

The change in mass, volume and density of cotton conditioned at varying humidity, as seen over 999 pycnometer cycles. *Measured MC show oven dried cotton to contain 2.5%MC.

<table>
<thead>
<tr>
<th>Conditioning</th>
<th>Sample Mass (g)</th>
<th>Sample Volume (cm$^3$)</th>
<th>Sample Density (gcm$^{-3}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Humidity [MC] (%)</td>
<td>Start</td>
<td>End</td>
<td>% Δ m</td>
</tr>
<tr>
<td>97 [15.0]</td>
<td>0.206</td>
<td>0.185</td>
<td>-11.3</td>
</tr>
<tr>
<td>85 [10.4]</td>
<td>0.217</td>
<td>0.202</td>
<td>-7.4</td>
</tr>
<tr>
<td>76 [8.5]</td>
<td>0.194</td>
<td>0.185</td>
<td>-4.8</td>
</tr>
<tr>
<td>59 [6.3]</td>
<td>0.248</td>
<td>0.241</td>
<td>-2.9</td>
</tr>
<tr>
<td>33 [3.9]</td>
<td>0.245</td>
<td>0.239</td>
<td>-2.3</td>
</tr>
<tr>
<td>Dry [0.0]*</td>
<td>0.230</td>
<td>0.229</td>
<td>-0.5</td>
</tr>
</tbody>
</table>

When conditioned at 97% RH, the sample shows a rapid drop in volume reaching a minimum at around 500 cycles. From this point it shows a steady increase in volume over approximately 500 cycles and begins to plateau toward the end of the run. Conditioning at 85% and 76% RH follows a similar pattern in volume change, differing by a less dramatic drop at the beginning of the run and plateauing earlier – appearing to have reached equilibrium by the end of the run. When conditioned at 59% RH or less the sample deviates slightly from this pattern, showing a small drop over the first 20 cycles, then increases steadily until around cycle 700 at which point it appears to reach equilibrium. The only sample to show no volume loss, but rather a small and rapid increase (over approximately 50 cycles) in volume was that ‘dried’ in the oven. This apparent increase in dry sample volume was later shown to be principally related
to an artefact of the instrument, which measures reasonably constant volume increases when run both empty and with the tungsten carbide calibration ball in situ.

If it is assumed the loss of moisture between removal from the humidity chambers and loading into the pycnometer is negligible, moisture loss during the 999 cycle experiment can be calculated. Using the equation \( V = \frac{m}{\rho} \) and the density of water \( (\rho = 1\text{gcm}^{-3}) \), the volume \( (V) \) of water lost \( (\text{cm}^{-3}) \) from the sample is numerically equivalent to the loss of sample mass \( (\text{in g}) \). Figure 5.16 shows the change in mass, volume and density over 999 cycles relative to the initial mass, volume and density.

Mass lost during the 999 cycles increased steadily with the increase in moisture content of the sample, up to around 11% MC (approximately 80% RH), after which the rate of mass loss increased. Change in the measured sample volume on the other hand increased steadily with increasing MC to around 11% MC, where it peaked and the change began to reduce.

**Figure 5.16: Relative change of mass, volume and density**

The total relative change in mass, volume and density of the sample (as a percentage of the dry mass/volume) over the course of 999 pycnometer cycles at 25°C.

Despite the obvious loss of moisture in the conditioned cotton tests, the loss in volume cannot be directly related to the loss of moisture content. This is because there is a discrepancy between the volume loss and the mass loss. Mass loss can however be used to calculate moisture loss, as it is very unlikely that there was a loss in sample during measurement.
A proposed explanation of the phenomena at play during the drying of cotton from a conditioned state is shown in Figure 5.17. Cellulose is a porous material, however while it is possible for moisture to gather in these pores, most water taken up by the material will be absorbed into its bulk, in the amorphous regions. This means that as the sample dries over time, it is unlikely to register a change in the sample volume, only mass, unless the sample is over saturated and there is free water sitting in the porous network. Free water evaporating from cellulose pores should translate into a loss of volume.

Figure 5.17: Proposed water loss and pore closure
The red arrows in this diagram show the suggested mechanism of pore closure and apparent volume increase in pycnometry. The blue arrows describe the likely paths of water loss.

The reason for the increase in volume (particularly obvious in dry samples) seen once the majority of moisture is lost, is unclear. It may be occurring as a result of a small amount of residual moisture in the purge gas, though it is unlikely that it would reach a low point and then increase again over time. An alternative and perhaps more likely reason for the increase in volume is that there is a restriction of cellulose pores. Remembering that the pycnometer runs at a pressure of 135 kpa (19.5psi), it may be that as the sample is put under pressure, pores are forced shut or covered by adjacent sample ‘particles’. Should this be the case, there would be a reduction in the purge gas’s ability to access these areas, resulting in a measured increase in volume. These hypotheses assume that helium is less able to associate with the cellulose structure than water, which may be explained by the difference in polarity rather than size.
It may also be possible to determine $T_g$ from the graph of change in mass/volume and relative humidity. The sudden drop in both mass and volume as seen at 80% RH implies that the sample is contracting under pressure when it contains enough moisture. Softening of cellulose at ambient temperatures and a relative humidity of 80% concurs somewhat with the results measured using DMA (85% at 20°C). $T_g$ can also be used to explain the trough exhibited by the samples conditioned at high relative humidity (76%, 85% and likely 97% with further cycles) as seen in Figure 5.15. The trough suggests that the cellulose becomes less pliable once most of the moisture content is lost, at which point volume then begins to increase in the same manner as seen in the dry samples.

If this is an indirect measure of sample $T_g$ then repeating the method at higher temperatures of 35°C and 45°C should result in a shift of $T_g$ to lower MC. Figure 5.18 shows very little change in the mass loss at higher temperatures.

![Figure 5.18: Relative change of mass, volume and density at 25°C, 35°C and 45°C](image)

This graph illustrates the total relative change in mass, volume and density of the sample (as a percentage of the dry mass/volume) over the course of 999 pycnometer cycles at 25°C, 35°C and 45°C.

This is not surprising since the amount of water taken up by the samples during equilibration (all at room temperature) is finite and will not be affected by the testing...
temperature. Both volume and density however show more obvious changes when the testing temperature is increased. Both move to slightly lower moisture contents as the testing temperature increases, indicated by the arrows in Figure 5.18, with a much greater volume change (and consequently density change) demonstrated between temperature changes.

While the results are not yet well understood, they are quite compelling, showing reasonable agreement with the results previously established using DMA, as shown in Figure 5.19. This suggests that extended pycnometry may in the future be a credible method of measuring $T_g$ in moisture sensitive samples, however further work is necessary to fully understand the changes taking place in the samples.

![Figure 5.19: Fox equation – graph, including pycnometer, DMA and DSC data](image)
Results plotted of glass transition for each sample using pycnometry compared with DMA data.

### 5.5 SUMMARY OF RESULTS
Measurement of the $T_g$ using these alternative methods has had mixed success. Inverse gas chromatography showed the right trends as far as moving to lower temperature as the moisture content was increased, however the results obtained proved to be considerably different to those obtained by all other methods. In practice this technique has proven effective for other authors (Ambarkhane, Pincott et al. 2005, Buckton, Ambarkhane et al. 2004, Minagawa, Kanoh et al. 2002), but despite repeating the test multiple times and drying the sample under different conditions.
conditions the results remained inconclusive. The most likely explanation is that the temperature/humidity window is not quite large enough to encompass the glass transition of cellulose.

Use of AFM to measure the glass transition under both moist and dry conditions also produced inconclusive results. Though it was expected that this technique would produce good results due to its high sensitivity toward changes in modulus, only weak changes were seen in cotton and viscose under moist conditions and no change was seen in any sample with the addition of heat (to dry sample).

The foremost motive of the pycnometry experiments was to determine the density and consequently crystallinity of the chosen cellulose samples, and this objective has been achieved as shown in Chapter 3. It was the aim of this pycnometry work to attempt to relate the mass and volume changes occurring in moist samples to precise measurement of initial and final moisture contents, in order to understand the nature of the volume increase in the samples over time. Additionally, it was hoped that the changes seen in the sample over the course of 999 cycles would be useful in predicting the moisture content at which softening (collapse) occurs. The results demonstrated in this chapter concur well with the results obtained using DMA on cellulose and show that, in principle, this has potential as being a predictor of \( T_g \). However further work is necessary to confirm this hypothesis.
6 PROPERTY CHANGES DURING DEVELOPMENT AND BETWEEN VARIETIES

6.1 VARIETY AND MATURITY SAMPLES

Sicot 74BRF is a variety of *Gossypium hirsutum* species, and is the current industry standard for cotton in Australia. It contains both herbicide and insect resistance genes, has good resistance to diseases (Bacterial Blight, Verticillium Wilt and Fusarium Wilt) and yields 5% more fibre than its predecessor, Sicot 71BRF (Cotton Seed Distributors 2010). As the industry standard it is a logical choice for a varietal comparison. The other variety chosen for this comparison is *Gossypium hirsutum* Coker 315. Originating in America, this variety was once used as a commercial variety in Australia, but has since been surpassed and cannot compete with the current industry standard, Sicot 74BRF. It is however readily available, as it is grown year round in glass houses for use in the transformation of foreign genetic material (such as bacterial genes) into cotton to produce transgenic plants (Kumria, Leelavathi et al. 2003).

Fibres of both varieties were sourced at a different maturity, so as to determine changes as the fibre grows. Immature samples of Coker were collected at early developmental maturity, specifically 5 – 25 days post anthesis (DPA). These samples contain fibres which are visible microscopically, but are little more than powder to the naked eye. Sicot samples of varying maturity were picked from the first node at varying heights on mature plants: top, middle and bottom. Cotton plants begin

Figure 6.1: Cotton flowering interval
Starting at the first node on the first branch (day 0), expected flowering time increases by 3 days for each step in branch height and 6 days per node along each branch (adapted from Oosterhuis 1990).
flowering on the lowest, most mature part of the plant and continue to flower as the plant grows. Picking the bolls from varying heights on the plant therefore results in a variation in maturity due to a difference in flowering time of 3 days per node (Oosterhuis 1990) (Figure 6.1). It is estimated that the Sicot samples used in this project have approximately 30 days’ difference in maturation time between the bolls picked from the bottom (more mature) and top (less mature) of the plant.

### 6.2 PHYSICAL CHARACTERISTICS

#### 6.2.1 SCANNING ELECTRON MICROSCOPY (SEM)

Images taken using scanning electron microscopy will be used to examine surface changes from immature to mature fibres and compare the surface morphology between varieties.

### MATERIALS AND METHOD

Longitudinal images were taken of fibres mounted onto SEM sample holders using conductive carbon tape. Mounted samples were then coated with approximately 2 nm of Pt/Pd using a Cressington 208HRD coater. Images were produced using a FEI Phenom desktop SEM.

Images were taken of cotton variety, Coker 315, of varying development maturity (20, 25 DPA and mature) supplied by F. Pettolino (CSIRO – Plant Industries), and Sicot 74BRF of various nodal heights (low, mid, top), collected from Warren, NSW in the 2014/15 season by S. Gordon (CSIRO – Manufacturing).

### RESULTS

Images of developmental maturity samples – mature, 25 and 20 DPA, are shown in Figure 6.2. The mature Coker appears rounded and full in appearance. Reversals can be seen along the length of the fibre and microfibrils are clearly distinguishable. In contrast the 25 DPA fibre appears withered, and the 20 DPA fibre flat and “empty” in comparison to the mature fibre. Microfibrils are visible in both immature fibres when zoomed in (not visible in Figure 6.2), but reversals are only apparent in the 25 DPA fibre. The differences between the fibres at these maturities are primarily due to the amount of cellulose deposition in the secondary wall of the cell. In comparison to
the mature fibre, the 25 DPA fibre has begun to lay down cellulose in the secondary wall but has not established enough to prevent it from collapsing in on itself and appearing withered. The 20 DPA fibre appears flat as it is at the beginning of secondary wall deposition and only has a primary wall, the same appearance is also apparent in the low maturity samples (not shown). The lack of reversals in this fibre is also due to the lack of secondary wall deposition.

Figure 6.2: SEM images of Coker of varying maturity
Single fibres of mature (a) Coker 315 and at 25 (b) and 20 (c) days post anthesis. Microfibrils and reversals (arrow) are visible in mature fibre.

Unlike the Coker samples, microfibrils and reversals are clearly visible in all imaged Sicot fibres, from low (mature) to high on the plant (Figure 6.3a only). Though these do appear to become more dominant with maturity.

Figure 6.3: SEM images of Sicot of varying maturity
Single fibres of Sicot 74BRF selected from the low (a), middle (b) and top (c) of an individual plant. Microfibrils visible in all fibres.

6.2.2 COTTONSCOPE
These tests will be used to compare the linear density, maturity ratio (birefringence), micronaire and width of cotton of various maturities and those of different variety, to the results measured in cotton, Tencel® and viscose given in Chapter 3 (page 55).

MATERIALS AND METHODS
All linear density studies were carried out on a BSC Electronics Cottonscope as described in Chapter 3 (page 54). Two samples from each specimen were tested in triplicate, with the exception of 5 DPA – this had only one sample tested in triplicate.
Samples tested using Cottonscope include; CF – cotton fibre (supplied by P Henry, CSIRO – MSE), as described in Chapter 3. Samples of cotton variety Coker 315, of varying development maturity (5, 10, 15, 20, 25 DPA and mature) supplied by F. Pettolino (CSIRO – Plant Industries) and Sicot 74BRF of various nodal heights (low, mid, top) collected from Warren, NSW in the 2014/15 season by S. Gordon (CSIRO – Manufacturing).

Immature Coker samples were prepared by hand using a scalpel and were cut to roughly 1 mm lengths before weighing 20 mg into capped bottles to which 3 mL of 0.4% Teric solution was added. Samples were then agitated overnight at 60°C. On testing, 3 mL of fresh Teric solution was removed from the Cottonscope bowl prior to the addition of the wet sample, so as not to upset the calibrated volume.

RESULTS AND DISCUSSION

Fully developed Sicot and Coker cottons were examined using Cottonscope to compare differences between varieties and examine changes with maturity. Overall the two chosen varieties gave similar results to one another and to the cotton standard (CF) used for all previous tests. The lower linear density of CF, seen in Figure 6.4, is likely to be due to this sample having previously been ginned and combed. These processes remove immature and short fibres which would also account for the greater variation between the Sicot and Coker samples.

![Figure 6.4: Cottonscope results – Varietal comparison](image)

Linear density, maturity ratio (birefringence – MRBF) and width results for various CF, mature Sicot and mature Coker, using Cottonscope. Annotations 1 and 2 refer to the average triplicate tests performed on two samples of each specimen. Error bar reflects the average standard deviation between tests.
Comparing the results for samples of Sicot taken from varying heights on the same plant (Figure 6.5), it is clear that fibres from low on the plant (more mature) have a higher maturity ratio and greater linear density than those high on the plant (less mature). This is predominantly due to higher cellulose deposition in the more mature fibres. There is less difference seen between the linear density and maturity ratio results in samples from low on the plant compared to the middle of the plant. This suggests that the two samples may either be of similar age, or the boll from low on the plant may have been mature for some time prior to picking. The results do however show a decrease in the fibre width as bolls mature, which is due the circularity of the mature fibre compared with the flatter yet broader ribbon of the immature fibre (Gordon 1995).

Figure 6.5: Cottonscope results – Sicot of varying nodal height
Linear density, maturity ratio (birefringence – MRBF) and width results for Sicot 74BRF of differing nodal height, using Cottonscope. Annotations 1 and 2 refer to the average triplicate tests performed on two samples of each specimen. Error bar reflect the average standard deviation between tests.

Similarly, the results seen for immature Coker (Figure 6.6) show greater width at lower maturity. The maturity ratio measure by the Cottonscope for these highly immature fibres, shows an incremental decrease as the fibre develops, up to 25 DPA followed by a substantial increase at maturity. This may be an artefact brought about by small sample and fibre size, but may also be a result of differing polymer or crystallite orientation between primary and secondary walls. Linear density results for immature Coker below 25 DPA are unlikely to be meaningful due to the limited ability of the instrument to deal with clumps of fibres and small sample size.
While this method is certainly not ideal for examining highly immature fibres, it gives some insight into the size of the fibres during development and the crystallite structure within the fibre samples.

![Graph](image)

**Figure 6.6: Cottonscope results – Immature Coker**
Linear density, maturity ratio (birefringence – MRBF) and width results for mature Coker 315 and at 5 to 25 DPA, using Cottonscope. Error bar reflects the average standard deviation between tests.

### 6.3 CRISTALLINITY / DENSITY

#### 6.3.1 PYCNOMETRY

The aim of these experiments is to determine the changes in density and crystallinity of cotton fibre as it matures and determine where there is a difference in density and crystallinity between two selected varieties.

**MATERIALS AND METHOD**

All density studies were carried out with a Micromeritics AccuPyc II 1340 pycnometer, as described in Section 3.3.1. The instrument was set to repeat the volume/density test 100 times to maximise the likelihood stable sample measurement after instrument equilibrium.

Samples tested in this pycnometry study are; CF – cotton fibre (supplied by P Henry, CSIRO – MSE), as described in Chapter 3. Samples of cotton variety Coker 315, of varying development maturity (5, 10, 15, 20, 25 DPA and mature), supplied by F. Pettolino (CSIRO – Plant Industries). Samples of Sicot 74BRF of various nodal heights
(low, mid, top) were collected from Warren, NSW in the 2014/15 season by S.Gordon (CSIRO – Manufacturing).

Cotton was conditioned at 33%, 76%, 85% and 97% relative humidity (RH) in chambers containing saturated salt solutions; magnesium chloride, sodium chloride, potassium chloride and potassium sulphate (consecutive order). Conditioning occurred for a minimum of 70 hours. Sicot and mature Coker samples were dried as discussed in Section 3.3.1 while immature (DPA) samples were received freeze-dried and subjected to a further 24 hours drying using a dry nitrogen flow. Immature samples could not be dried as described in Section 3.3.1 due to sample degradation.

RESULTS AND DISCUSSION
Oven dried samples of Sicot and Coker were tested in the pycnometer over the course of 100 cycles and the sample density was determined. Due to instrument equilibration over the first (approximately) 50 cycles, the average sample density as collected over the last 40 cycles of the run (Figure 6.7) was used to calculate the fibre’s cellulosic crystallinity (equation on page 59). The calculated cellulosic crystallinity of each sample is listed in Table XII, along with the previously measured density and crystallinity for the cotton fibre standard, CF.

![Figure 6.7: Density of dry cotton samples – Varietal comparison](image)

Density of CF, Sicot and Coker as measured using pycnometry.
Table XII: Density and calculated crystallinity of dry cotton samples – Varieties
Calculated crystallinity of cellulose based on measured sample density.

<table>
<thead>
<tr>
<th>Fibre</th>
<th>Measured Density (g cm⁻³)</th>
<th>Crystallinity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CF</td>
<td>1.538</td>
<td>80</td>
</tr>
<tr>
<td>Sicot</td>
<td>1.529</td>
<td>77</td>
</tr>
<tr>
<td>Coker</td>
<td>1.527</td>
<td>76</td>
</tr>
</tbody>
</table>

The crystallinity results obtained using this method for Sicot and Coker are very similar. They are however slightly different from the results measured for the standard cotton sample (CF). This may be a developmental property of the fibre caused by environmental pressures during growth, such as heat or water stress; on the other hand, the higher density (and therefore calculated crystallinity) may have occurred as a result of carding the standard cotton sample, a process which the Sicot and Coker samples were not subjected to. In carding the sample, fine immature fibres and neps are removed, potentially increasing the population of more mature (denser) fibres.

Density testing was then repeated on samples of Sicot bolls taken from the bottom (low), middle and top plant nodes and Coker samples collected at 5, 10, 15, 20 and 25 days’ post anthesis. Results are shown in Tables XIII and XIV.

Table XIII: Density and calculated crystallinity of dry Sicot of varying nodal height - Maturity
Calculated crystallinity of cellulose based on measured sample density.

<table>
<thead>
<tr>
<th>Fibre</th>
<th>Measured Density (g cm⁻³)</th>
<th>Crystallinity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sicot – Low</td>
<td>1.529</td>
<td>77</td>
</tr>
<tr>
<td>Sicot – Mid</td>
<td>1.527</td>
<td>76</td>
</tr>
<tr>
<td>Sicot – Top</td>
<td>1.530</td>
<td>77</td>
</tr>
</tbody>
</table>

Table XIV: Density and calculated crystallinity of dry immature Coker
Calculated crystallinity of cellulose based on measured sample density, crystallinity measured quantitatively by Pettolino (2013)* acid digestion of amorphous material and Lee et al. (2015)** using XRD.

<table>
<thead>
<tr>
<th>DPA</th>
<th>Measured Density (g cm⁻³)</th>
<th>Crystallinity (%)</th>
<th>*Crystallinity (%)</th>
<th>**Crystallinity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>1.33</td>
<td>--</td>
<td>2</td>
<td>--</td>
</tr>
<tr>
<td>10</td>
<td>1.43</td>
<td>33</td>
<td>3 (11 DPA)</td>
<td>--</td>
</tr>
<tr>
<td>15</td>
<td>1.43</td>
<td>33</td>
<td>13</td>
<td>27 (17 DPA)</td>
</tr>
<tr>
<td>20</td>
<td>1.44</td>
<td>37</td>
<td>50</td>
<td>--</td>
</tr>
<tr>
<td>25</td>
<td>1.42</td>
<td>30</td>
<td>62</td>
<td>53 (23 DPA)</td>
</tr>
</tbody>
</table>

Despite the potential age difference of approximately 30 days between these samples, there was very little difference in their crystallinity. This data is consistent
with the findings of (Lee, Kafle et al. 2015), which show cotton reaching crystallite maturation at approximately 45 DPA.

The calculated crystallinity values of samples in the low DPA range differ somewhat from those reported by Pettolino (2013) and Lee et al. (2015). At 5 to 15 DPA, the calculated crystallinities are higher than those previously reported, which is likely to be linked to the polysaccharide composition of the samples. Compared with more mature cotton, these immature samples contain relatively high quantities of hemicellulose, callose and pectins which have similar or higher density to crystalline cellulose, at approximately ~1.58 (Beldman, Schols et al. 1997, Thompson and Fry 2001, Youssefian and Rahbar 2015), 1.62 (Zimmermann and Milburn 2012) and 1.5-1.6 (Salbu, Bauer-Brandl et al. 2010) respectively.

Calculated crystallinities for the 20 and 25 DPA samples also differ from those previously measured, but unlike the 5 to 15 DPA, these are lower than reported. While these samples still have slightly higher hemicellulose and callose levels than mature cotton, the low measurement is probably due to residual water (1gcm⁻³) in the samples. Residual water may also exist within the 5-15 DPA samples. Overall the use of pycnometry to estimate crystallinity of very immature cotton samples is not reliable. Improvements might be possible by fractionation of the sample to isolate cellulose, but this may itself change the crystalline fraction of the samples.

### 6.3.2 X-RAY DIFFRACTION (XRD)

This set of experiments was run with the aim of verifying the crystallinity calculated from the measurement of density and to measure the crystallinity of the samples that could not be calculated using density.

### MATERIALS AND METHOD

All x-ray diffraction studies were carried out on a Panalytical X’Pert³ MRD (XL). The Cu x-ray source was operated at 40 kV and 30 mA. Fibre samples were mounted onto zero background plates using double sided tape and secured within the instrument. Scans were obtained for 2θ from 10 to 40 degrees, in 0.02 degree steps, at 5sec intervals.
Samples of cotton variety ‘Coker’, of varying development maturity (5, 10, 15, 20, 25 DPA and 4x mature) were supplied by F. Pettolino CSIRO – Plant Industries. Mature Sicot 74BRF (low) was collected from Warren, NSW in the 2014/15 season by S. Gordon (CSIRO – Manufacturing).

RESULTS AND DISCUSSION

Mature fibres of Sicot and Coker were bombarded with x-rays and the resultant x-ray diffraction patterns were analysed and used to calculate the crystallinity of the samples. The diffraction patterns for Sicot and Coker are compared in Figure 6.8.

The peaks were analysed using the same Gaussian peak deconvolution method (Park, Baker et al. 2010, Teeäär, Serimaa et al. 1987) described in Chapter 3, and the ratio of the area of crystalline peaks compared to the total area was used to determine the percentage crystallinity of each sample. Coker and Sicot were measured as having 70% and 77% crystallinity respectively, which makes a close comparison with CF XRD data from Chapter 3, at 70% crystallinity (also shown in Figure 6.8). Samples of Coker of varying developmental maturity were also analysed (Figure 6.9).

The intensity of x-ray diffraction patterns from 5 to 20 DPA shows a very similar shape, which when deconvoluted is indicative of a fairly amorphous sample. This shape begins to change in the 25 DPA sample. It shows greater height in the peak at
22.7° and greater resolution of a peak at approximately 16°, as it begins to take the shape formed by mature cotton (shown in orange).

\[ \text{Figure 6.9: X-ray diffraction data for Coker of varying maturity (background corrected)} \]

X-ray diffraction pattern intensity graph for 5 – 25 DPA and mature Coker.

The resulting crystallinities calculated for these samples, again using the Gaussian deconvolution method, are 19%, 23%, 24%, 42% and 70% at 5 DPA, 15 DPA, 20 DPA, 25 DPA and mature, respectively. These results concur well with the results of Pettolino (2013) and Lee et al. (2015) (Figure 6.10) showing marginally higher measured crystallinity in the immature samples, and slightly lower measured crystallinity in the mature sample.

\[ \text{Figure 6.10: Crystallinity of Coker of varying maturity, compared with literature data} \]

Crystallinity results for 5 – 25 DPA and mature Coker (blue), compared with the results of Pettolino (2013) (yellow) and Lee et al. (2015) (red).
6.4 WATER CONTENT

6.4.1 KARL FISCHER TITRATION (KFT)

These tests were used to compare the water content of wet and dry cottons of various maturities and those of different variety. The experiment was run primarily to compare the dry state water content of these samples to those measured in cotton, Tencel® and viscose, in Chapter 3 (page 68).

MATERIALS AND METHOD

All water content measurements were carried out using a Metrohm 852 coulometer with an 874 oven sample processor. Standard ‘Hydranal Coulomat CG’ and oven specific reagent ‘Hydranal Coulomat AG Oven’ were used for all tests. Samples were weighed and sealed in 6 ml vials with silicone/aluminum septum caps prior to testing. Control vials were taken on each separate day that vials were sealed, to account for the ambient humidity within the laboratory. The instrument was set to heat samples to 150°C and dry nitrogen was used as a carrier gas to deliver the liberated water to the reaction vessel. The reaction endpoint was set as 50mV. Varietal comparison samples were run in triplicate and the results reported as percentage moisture content. Air-dry versus freeze-dry, and washing experiments were run as singlets only as they were preparatory trials.

Samples tested using KFT include; CF – cotton fibre (supplied by P Henry, CSIRO – MSE), as described in Chapter 3. Samples of cotton variety Coker 315, of varying development maturity (5, 10, 15, 20, 25 DPA and mature) and Sicot 71BRF (NO – unopen boll ~20DPA, JO – just open boll and mature), supplied by F. Pettolino (CSIRO – Plant Industries) and Sicot 74BRF of various nodal heights (low, mid, top) were collected from Warren, NSW in the 2014/15 season by S. Gordon (CSIRO – Manufacturing).

RESULTS AND DISCUSSION

Mature fibres of Sicot and Coker were oven dried and then tested for residual water content using KFT. The results for these samples are compared with the water
content of oven dried CF in Table XV. All samples showed considerable variation with repeat measurement, but on average they all had about 2.5% moisture content.

**Table XV: Water content measured using Karl Fischer titration – Varietal comparison**

Water content as measured using KFT, in CF, Sicot and Coker.

<table>
<thead>
<tr>
<th>Fibre</th>
<th>Measured Water Content (%)</th>
<th>Avg. Water Content (%) [Std.dev.]</th>
</tr>
</thead>
<tbody>
<tr>
<td>CF</td>
<td>3.64</td>
<td>2.27</td>
</tr>
<tr>
<td>Sicot</td>
<td>2.44</td>
<td>2.61</td>
</tr>
<tr>
<td>Coker</td>
<td>1.27</td>
<td>3.96</td>
</tr>
</tbody>
</table>

Due to the need to freeze-dry immature samples, so as to avoid microbial contamination and damage, a preliminary study was used to compare the moisture content between air-dried and freeze-dried samples. Microbial attack occurs prominently in damp conditions, resulting in digestions of the cellular sugars (including cellulose), deposition of contaminants and overall degradation of the fibres (Gordon 2007).

To do this, duplicate samples of Sicot 71BRF (for preliminary investigation only) were taken at the CSIRO agricultural laboratory in Canberra, one of which was air-dried at room temperature, while the other was freeze-dried (after snap freezing). Both samples were then packaged with desiccant and sent to Geelong under ambient temperature conditions. Curiously, when these samples were tested the freeze-dried samples were measured as having a higher water content than the air-dried samples (Figure 6.11). This was most prominent in the fibre from the unopened (NO) boll, which showed 6% higher water content than the air-dried sample.

![Figure 6.11: Comparison of air-dried and freeze-dried water content in cotton of varying maturity](image)

Samples of mature Sicot 71BRF cotton fibre and also from open and un-open bolls.
Comparing the unopened boll to the mature boll (mat), there was 8% higher water content in the unopened than the mature, freeze-dried fibre, and only a 2% difference seen when air-dried. Despite this, the immature freeze-dried samples remained undamaged and uncontaminated for significantly longer than the immature air-dried samples (all kept with desiccant).

Though this is surprising, it is most likely that even though the freeze-dried samples are wetter, there was less microbial activity (Figure 6.12) within the samples after freezing for several days at -80°C, followed by exposure to the low pressures produced during freeze-drying.

It is more difficult to account for the comparatively low moisture contents measured in the unopen air-dried samples. Given that the difference in moisture content between drying methods is largest in the most immature sample, it may be due to the hygroscopic effect of higher ‘sugar’ content within the sample. If it is assumed that there is more microbial activity in the air-dried samples and these microbes live off the sugars contained in the (immature) sample, it follows that this hygroscopic effect and thus sample moisture content would be reduced. It is also possible that microbes living on the samples may themselves be utilising the water within the air-dried samples and reducing the measured moisture content.
To test this hypothesis, samples of freeze-dried unopen and mature fibres were taken and weighed into eight individual vials (4 for each sample). Half of each were washed (2 mat and 2 NO samples), through three changes of RO water with agitation, and all (eight samples) were dried overnight at ~105°C. All samples were weighed post-drying. Half of these samples (1 mat and 1 NO washed, 1 mat and 1 NO unwashed) were then sealed immediately after drying, and the other half were then conditioned at 97% RH for several days. These were then weighed again and sealed. The results can be seen in Figure 6.13 as mass relative to initial mass (ambient conditions) and percentage water content.

Figure 6.13: Water content changes in mature and immature cotton when washed
Fibre samples from mature and un-opened bolls of Sicot 71BRF were washed and compared to unwashed fibres of the same samples. Samples were run in pairs. The relative mass of all samples was calculated after oven-drying or conditioned at 97%RH (blue). All samples (wash-dry, wash-conditioned, unwashed-dry and unwashed-conditioned of both samples) then underwent KFT (green) to determine absolute water content.

This data shows that washed NOFD cotton has a lower dry mass than unwashed and is unable to hold the same quantity of water when it is conditioned. Unlike the mature FD cotton which appears to have around the same dry mass and affinity for water regardless of washing. This suggests that something which is able to hold water, likely cellular sugars, is being washed from the NOFD cotton.

During the preparation of the more comprehensive Coker developmental set, samples were taken prior to and post freeze-drying and compared to oven dried
samples of the same specimens. All immature fibre samples were removed from the seed (de-linted) in liquid nitrogen (N2), sampled prior to freeze drying and sampled again after freeze-drying. Mature specimens were sampled in duplicate (as more sample was available), de-linted under both ambient (mat 1 & 2) and N2 conditions (mat 3 & 4) and treated the same as the immature fibres. Figure 6.14 compares the samples at each stage.

![Graph showing water content in immature and mature Coker samples](image)

**Figure 6.14: Water content in mature and immature Coker – Pre and post freeze-drying**

Mat 1 & 2 de-linted at room temp. All others done under N2. Note: singlet tests only.

Immediately obvious is the very high water content present in the immature samples prior to freeze-drying, noting that there is a massive difference in fibre development between the 25 DPA and the mature samples. While these figures most likely represent the real water content, the presence of water droplets in the vial after defrosting (sealed vials were kept frozen until testing to reduce likelihood of microbial degradation) suggests that there may be excess moisture in the vial as a result of the de-linting and freeze-drying process. However, the comparatively low water content seen in mature samples 3 and 4, suggests that this is unlikely to be the case. Figure 6.14 also shows a gradual decrease in the water content of the freeze-dried samples as the maturity of the samples increases and a roughly even amount of water held in each of the samples after being dried in the oven.
6.5 CHANGES IN MEASURABLE GLASS TRANSITION

From the earlier studies on cotton, Tencel® and viscose, it was found that DMA, DVS instruments and the study of freezing bound water using DSC could be used to detect the glass transition in cellulose samples. Furthermore, the result gained from the three different instruments concurred well with one another. DMA was chosen from these methods to determine whether any changes could be detected in the measured transition with changes in the maturity of cotton or the variety tested.

Using the same method as described in Chapter 4 (page 86), single fibres of mature Coker 315 and Sicot 74BRF were examined in individual runs to determine any difference between the samples. Figure 6.15 gives the resultant storage modulus for both samples as humidity increases at 70°C, relative to the maximum modulus measured.

![Figure 6.15: Measurement of $T_g$ by critical humidity using DMA – Sicot versus Coker](image)

DMA results for single fibres of mature Sicot and Coker run at 70°C. Critical relative humidity results for Sicot and Coker were measured at 77% and 78% respectively.

The results of this comparison show that both cotton varieties gave results of approximately 77%RH (±1%), although it was difficult to determine the beginning of the transition with certainty due to the gradual change in slope. As expected however, these results were very similar to those seen in cotton, Tencel® and viscose
in Chapter 4, of 76-78%RH. It is also worth noting the difference in relative modulus between the two samples. The Sicot appears to have a modulus greater than Coker despite having a smaller average width and being of only marginally higher crystallinity.

Some effort was also made to look at the change in glass transition at varying levels of maturity too. Unfortunately it was not only impossible to mount the highly immature Coker fibres in the DMA, we were also unable to run the less mature Sicot sample from the top node due to continual fibre breakage. Figure 6.16 gives the relative storage modulus of Sicot samples taken from the lower and middle bolls of a single plant.

![Graph showing relative storage modulus vs. relative humidity for Sicot samples](image)

**Figure 6.16: Measurement of $T_g$ by critical humidity using DMA – maturity changes in Sicot**

DMA results for single fibres of Sicot low and mid, at 70°C. Critical relative humidity results for both measured approximately 76%.

Similar to the result shown in the variety trial, the Sicot of varying maturity gives a resultant critical relative humidity of 76%. Again, this is not unexpected, due to the fact that it is the same polymer being tested in both samples. The fibre taken from the middle of the plant does seem to have a slightly lower modulus than the more mature fibre. However this may just be a result of fibre-to-fibre variation rather than a true measure of the relative stiffness based on maturity. Maxwell, Gordon et al.
(2003) showed data using AFM which supported this, however further work is needed to establish whether this trend is consistent for DMA. Although the results are not shown here, both the maturity and variety measurements were run at multiple temperatures (as shown for cotton, Tencel® and viscose in Chapter 4) and showed a clear shift to lower critical humidity as temperature was increased, confirming the glass transition.

Ideally, these samples would have been run using multiple techniques which have been shown to work in early tests, particularly DVS. This would have allowed of the $T_g$ measurement of immature samples which could not be mounted or were too fragile to be run in the DMA. However, due to the unforeseen length of time taken to acquire the results for cotton, Tencel® and viscose, it was simply not possible to repeat the test on these samples.

6.6 SUMMARY OF RESULTS

Samples of Sicot 74BRF and Coker 315 cottons, of varying maturity were characterised using a number of techniques with the aim of using these samples to study changes in the measureable $T_g$ of cotton with variety and maturity. The core results of this characterisation are shown in Table XVI.

The widths of Sicot 74BRF samples are very similar, with the most mature of the three (low) having the smallest width and the lower maturities having incrementally greater diameters. Given that these samples were either mature (low) or only days from maturation (mid and top) this is a reasonable result. The difference in width is due to an increase in circularity as cellulose is laid down within the fibre. The widths of the Coker 315 are slightly more varied in their results. While the mature Coker sample has very similar width results to all other cotton samples tested, the highly immature “DPA” samples actually show a gradual increase in width with maturity and give results greater than that of all other cottons tested. This most likely occurs via the same mechanism described for Sicot, however, it may also be enhanced by the very early stage of fibre development and fibres having both a greater affinity for water, as shown in the washing studies on page 132, and a greater ability to swell.
**Table XVI: Summary of characterisation results of Sicot 74BRF and Coker 315 at varying maturity**

Sicot samples are shown in order of maturity (Top – least mature to Low – most mature), and mature Coker and Sicot samples are highlighted. BF= Birefringent maturity, DPA= Days post anthesis.

<table>
<thead>
<tr>
<th>Instrument</th>
<th>Property</th>
<th>Sicot 74BRF</th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Width (μm)</td>
<td>Top</td>
<td>Middle</td>
<td>Low</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cottonscope</td>
<td></td>
<td>17</td>
<td>16</td>
<td>15</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>BF maturity</td>
<td>0.68</td>
<td>0.93</td>
<td>0.81</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pycnometer</td>
<td>Density (g/cm³)</td>
<td>1.53</td>
<td>1.53</td>
<td>1.53</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Calc. crystallinity</td>
<td>77%</td>
<td>76%</td>
<td>77%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>XRD</td>
<td>Crystallinity</td>
<td>--</td>
<td>--</td>
<td></td>
<td>77%</td>
<td></td>
</tr>
<tr>
<td>KFT</td>
<td>Oven &quot;Dry&quot; MC</td>
<td>--</td>
<td>--</td>
<td></td>
<td>2.6%</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Instrument</th>
<th>Property</th>
<th>Coker 315</th>
<th>5DPA</th>
<th>10DPA</th>
<th>15DPA</th>
<th>20DPA</th>
<th>25DPA</th>
<th>Mature</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Width (μm)</td>
<td>17</td>
<td>18</td>
<td>20</td>
<td>19</td>
<td>20</td>
<td>16</td>
<td></td>
</tr>
<tr>
<td>Cottonscope</td>
<td>BF maturity</td>
<td>0.63</td>
<td>0.65</td>
<td>0.65</td>
<td>0.55</td>
<td>0.49</td>
<td>0.87</td>
<td></td>
</tr>
<tr>
<td>Pycnometer</td>
<td>Density (g/cm³)</td>
<td>1.33</td>
<td>1.43</td>
<td>1.43</td>
<td>1.44</td>
<td>1.42</td>
<td>1.53</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Calc. crystallinity</td>
<td>--</td>
<td>33%</td>
<td>32%</td>
<td>37%</td>
<td>30%</td>
<td>76%</td>
<td></td>
</tr>
<tr>
<td>XRD</td>
<td>Crystallinity</td>
<td>19%</td>
<td>--</td>
<td>23%</td>
<td>24%</td>
<td>42%</td>
<td>70%</td>
<td></td>
</tr>
<tr>
<td>KFT</td>
<td>Pre freeze dry MC</td>
<td>73.2%</td>
<td>69.1%</td>
<td>73.7%</td>
<td>76.5%</td>
<td>78.3%</td>
<td>5.5%</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Post freeze dry MC</td>
<td>15.4%</td>
<td>14.8%</td>
<td>12.6%</td>
<td>11.5%</td>
<td>8.5%</td>
<td>4.5%</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Oven &quot;Dry&quot; MC</td>
<td>3.0%</td>
<td>4.3%</td>
<td>2.2%</td>
<td>2.8%</td>
<td>2.1%</td>
<td>2.4%</td>
<td></td>
</tr>
</tbody>
</table>

The birefringent maturity of the Sicot samples showed reasonably expected results, with the measured maturity ratio increasing with the maturity of the cotton. The Coker results on the other hand were less straightforward. The result for mature Coker was within a similar range to the other mature cotton samples, as expected, however the DPA samples (while being low overall) showed a slight increase in maturity from 5 to 15 DPA and then a drop at 20 and 25 DPA. This may simply be an artefact brought about by highly immature fibres and limited sample availability, but it may also be indicative of the change in crystallite structure between the primary and secondary walls.

Density measurements for the Sicot samples and the mature Coker, using pycnometry, found that the density of these samples concurred reasonably well with those stated in the literature of 1.55 (Gordon and Hsieh 2007) for dry cotton. Lower density values were calculated for the DPA (Coker) samples, which appear reasonable due to the lower crystallinity of the cellulose at these maturities and the reduced cellulosic fraction in comparison with other cellular components. This lower
cellulosic fraction in the DPA samples also meant that calculation of the cellulose crystallinity for these samples was unreliable. Calculated crystallinity for all other cotton sample however gave similar results to those seen using XRD.

Similar to the results found in Chapter 3, the measurement of water content in all oven dried samples showed a residual moisture content of 2-4%. Again reinforcing the fact that oven drying (at 105°C overnight) does not appear to sufficiently dry cotton fibres.

Apart from the characterisation of the Sicot and Coker samples, these samples – where possible – were also tested in order to define their glass transition. Measurement of the Sicot samples from the low and mid nodes using DMA allowed for some comparison of the $T_g$ between maturity levels, while the same techniques used on the mature samples of Sicot and Coker meant that a varietal comparison could be made. The results of both the varietal and maturity tests showed critical relative humidity measurements for each were within the same range, 76-77%. These also concur with the results shown for cellulose, in Chapter 4. The variation in modulus between the low Sicot sample and the mid sample, would be expected to increase with the linear density of the samples, however the standard deviation between samples measured using Cottonscope (page 129) does not show sufficient separation for conclusive results. Further work is necessary to determine whether there are significant changes in strength between the Sicot and Coker samples.
CONCLUSIONS

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.

The initial aim of this work was to determine whether the glass transition of cellulose could indeed be measured, in both the wet and dry state, using a variety of techniques. To do this, three samples, cotton, Tencel® and viscose, were chosen as standards to be used for all techniques. They were chosen with the aim of covering a range of characteristics including length, strength, crystallinity and sorption properties. The benefit of having a set of standard samples used for each technique meant that the techniques could not only be compared to one another, but the results could also be more easily compared to the results for various samples used in the literature.

Once chosen, these samples were characterised for size and ‘maturity’ (using SEM and Cottonscope), density (pycnometry), crystallinity (XRD) and water content and sorption properties (KFT and DVS). The results of these studies showed cotton, Tencel® and viscose fibres used in this study have average diameters of 17 μm, 21 μm and 16 μm and dry density measurements of 1.54 gcm⁻³, 1.52 gcm⁻³, 1.50 gcm⁻³ respectively. Birefringent (BF) maturity measurements and polarising microscopy of the cotton fibres had a high degree of maturity. Maturity measurements were not
 applicable to the solid Tencel® or viscose fibres, however, photographs of fibres under cross-polars of a polarising microscope, are indicative of greater crystallite/polymer orientation within Tencel® fibres, than seen in cotton or viscose. X-ray diffraction was used to determine the crystallinity of each fibre type, giving results of 70%, 60% and 57% for cotton, Tencel® and viscose. These results concurred with the order of crystallinity calculated using the density results for each fibre, though they were slightly lower than 80%, 71% and 65% calculated using pycnometry. Karl-Fischer titration and DVS studies of these fibres showed a residual moisture content of around 2.5% for cotton and viscose, to just over 3% moisture content in Tencel®, after oven drying overnight at 105°C. Moisture sorption isotherms were shown to be similar to those reported in the literature (Hill 2009, Okubayashi, Griesser et al. 2005).

**EXPERIMENTAL SUMMARY**

Glass transition experimentation started with the most common technique used for measuring the glass transition temperature of polymers, differential scanning calorimetry (DSC). Samples were run through many 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, with the exception of a repeatable ageing endotherm seen in each, seemingly dry sample, at around 160-170°C. While these results may appear to call into question the results of Batzer and Kreibich (1981) and Szczęśniak, Rachocki et al. (2008), the inability to produce results in these experiments may simply be related to a higher level of crystallinity in samples of the current work, or the limitations of sample size, diminishing the signal picked up by the DSC.

Having failed to successfully measure a glass transition in either a wet or dry state using the methods of Batzer et al. (1981), Picker and Hoag (2002) and Szczęśniak et al. (2008); Pierlot’s (1999) freezing point method for measuring the glass transition (in wool) was used to compare these samples to the results of Sakabe, Ito et al. (1987) and Ur’yash, Larina et al. (2010). 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
Moving forward, dynamic mechanical analysis (DMA) became the focus for experimentation. DMA offered a method of detecting more subtle changes within the samples, as well as the ability to detect changes occurring as a result of varying humidity within the cell, rather than temperature applied. Initially fibres were tested as bundles. In doing this 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. Yet the modulus failed to level off within the humidity constraints of the instrument. So despite the fact that the samples appeared to have no obvious colouration and the fibres remained intact, it was not possible to be completely confident that there was no degradation of the samples occurring. It was suspected however, that the use of fibre bundles may be reducing the sensitivity of the measurement, mostly due to minor variations in fibre tension and alignment, but also potentially due to longer temperature and humidity equilibration times.

It was, therefore, decided that both the dry tests and those run under moist conditions would be repeated on single fibres. This presented significant technical problems as far as selecting method parameters (such as pre-load force and maximum strain) was concerned. This was primarily due to the slight differences seen between fibres, most notably the variation in width, but also minor differences in crystallinity, alignment and, in cotton, the degree of convolution within the fibre. Given the fibre size (width) of 15-20 μm, it would take only minor differences to dramatically affect the stresses within the fibre. However, accounting for these differences in every fibre run was difficult and impractical. This meant applying a set strain to each fibre with a minimum possible force, so as to reduce the likelihood of breakage, and testing each fibre under ambient conditions prior to the beginning of the cycle. Despite this, many fibres were broken prior to completing each multi-day cycle. Nevertheless, once this was achieved, the results from all three samples proved to have significantly greater sensitivity to the glass transition (via critical
relative humidity) than the fibre bundles tested, showing a clear drop and levelling off of modulus in cotton and viscose at 60°C (6.9%MC / 12.4%MC), 70°C (6.4%MC / 12.0%MC) and 80°C (5.2%MC / 10.7%MC), and 70°C (13.1%MC) and 80°C (12.2%MC) in Tencel®. The onset of critical humidity was then extrapolated for the lower temperature cycles using superposition of all cycles. These result compared well with the freezing point transitions shown using DSC (Figure 7.1, page 144).

In parallel with running these standard methods for determining \( T_g \), alternative methods were run to determine their validity for determining the glass transition in cellulose.

Inverse gas chromatography was the first alternative method chosen to test cellulose. This method held promise as being a good method for measuring the glass transition in cellulose, due to its ability to detect subtle changes in probe sorption, at the glass transition. The high sensitivity of iGC, aided by large sample size and coupled with the ability to run under conditions of varying temperature and humidity, appeared to be a winning combination. However, despite several attempts at running the instrument and ensuring that the sample was thoroughly dry, there was very little in the way of positive results. Comparison of the results obtained compared with predicted values provided by the Fox equation showed a considerable difference and suggested that the results were unlikely to be valid. Later superimposition of the measured DMA results onto the instrumental working range of the iGC concurred with this, as the measured critical humidities (in DMA) sat well outside the humidity capabilities of the iGC. Even taking into account the fact that the humidities measured using DMA appear to be a little high, compared with the results determined using DVS and DSC (freezing-point transition), the iGC was at best running at the very limit of its capability. Measurement of a dry \( T_g \) was also beyond the capability of this instrument, consequently use of iGC for measuring \( T_g \) was discontinued.

Dynamic vapour sorption was another technique utilised as a method for determining the \( T_g \) of cellulose. Again, this method relied on the application of moisture, rather
than heat to measure the transition, by increasing the moisture content over time and monitoring the mass of the samples. Run by colleagues at Imperial College in the UK, it was found that samples had an increased uptake of moisture at 76.8%, 72.6% and 71.2% relative humidity, therefore giving a critical moisture content at 8.6%, 13.7% and 12.4% for cotton, Tencel® and viscose (consecutively) at 25°C. While these results were graphically quite subtle, the results were positive and concur well with the data collected using DMA and freezing-point transitions on DSC (Figure 7.1).

Atomic force microscopy (AFM) was chosen as a method for studying the $T_g$ of cellulose because of its high accuracy and ability to respond to small changes in modulus that may be brought about by the addition of heat or moisture. It was also of particular interest because, if it worked, it would enable the study of immature fibres that cannot be mounted in the DMA. Unfortunately, the results obtained from using AFM on both moist and dry samples, were inconclusive. Weak transition results were obtained for cotton and viscose fibres at 61%RH (6.5%MC) and 71% RH (11.8%MC) respectively, at 22°C. However, these results relied heavily on averaging of the raw data and estimation of the trend lines, making them unconvincing, and no transitions were found when heating the dry fibre samples to high temperature.

Pycnometry was the final method considered as a potential candidate for measuring the glass transition. Though it was not initially considered as a possible method, the measurement of density of cotton samples of varying moisture content led to the observation that there appears to be a minimum volume reached by all moist samples dried in the pycnometer, prior to volume equilibration. It was also observed that this volume loss did not equate precisely to the volume of water lost over the same period. As a means of examining the change in the sample during the pynometry run, the changes in mass, density and water content (measured using KFT) for each conditioned sample were calculated and compiled graphically. Although the studies carried out using pycnometry are by no means conclusive, the net change in density, mass and volume when graphed all indicate a change in the material at around 85%RH (10.4%MC) at room temperature (25°C). The fact that this change is seen at lower conditioned humidities as temperature is increased also adds weight
to the argument that this change is indeed the glass transition, warranting further investigation of this technique. These results also make a reasonably close comparison with those measured using DMA (Figure 7.1).

Figure 7.1 shows the positive results as reports for DSC – freezing point transition, DMA, DVS and pycnometry.

![Figure 7.1: Fox equation graph with experimental glass transitions for cotton, Tencel® and viscose](image)

The predicted $T_g$ for cellulose as calculated using the Fox equation, as discussed in Section 1.3.2, overlaid with $T_g$ results from DSC, DMA, DVS and pycnometry as reported in this thesis.

Once a satisfactory method (DMA) was found for determining the glass transition in cellulose, the characterisation techniques used on the standard samples were then applied to chosen maturity and varietal samples: Coker – mature and 5 to 25 DPA developmental maturity samples; and Sicot – Low (mature), middle and top node variation samples. In these studies, Sicot showed a slight increase in width, from 15 to 17 μm and BF maturity, from 0.68 to 0.81 between the least to most mature of these samples, but no obvious variation in the density with maturity, with all measuring 1.53 gcm$^{-3}$. Mature Coker was very similar to the mature Sicot with a width of 16μm, BF maturity of 0.87 and density of 1.53 gcm$^{-3}$. While the width measurements of the low developmental maturity samples increased from 17 to 20μm between 5 and 15 DPA and then remained reasonably steady to 25 DPA. BF maturity also varied around the time of change from primary to secondary wall synthesis (15 DPA), showing a slight increase from 0.63 to 0.65 from 5 to 15 DPA and
then a decrease to 0.55 and 0.49 at 20 and 25 DPA. Density results showed a similar trend increasing from 1.33 to 1.44 gcm$^{-3}$ from 5 to 20 DPA and then dropping slightly to 1.42 gcm$^{-3}$ at 25 DPA. All cotton samples tested also showed a residual moisture content of 2.1 to 4.3%, with the highest being measured in 10 DPA cotton fibre.

Repetition of the DMA protocol on Sicot samples of varying fibre maturity (based on nodal height) and between mature Sicot and Coker found the $T_g$ to be 70°C at 76%RH. This confirmed the hypothesis that the glass transition would not change as a result of varying maturity or cotton variety. However, these tests did not allow for the comparison of the samples due to the low separation of the standard deviation shown in the measurement of linear density.

**Overall outcomes**

As mentioned in the introductory chapter, 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. This is particularly evident in the results of Pillay (1971) on spinning (at 21°C), where it was shown that strength was at a maximum when the humidity was high (75%) and elongation was at a maximum when humidity was low (34%). As far as changes in cotton variety and maturity are concerned, it is not the $T_g$ which effects the fibre’s ability to resist breakage. The difference in modulus and resilience between these fibres is related predominantly to the different diameter of the fibres, as shown in Chapter 6.
Overall acquisition of glass transition data for cellulose has been time consuming and somewhat more difficult than anticipated. 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. 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 $T_g$ 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
- 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 $T_g$
- Post-harvest processing studies (in-mill/gin) to trial application of moisture and temperature conditions known to bring cotton above its $T_g$, with comparison of results with empirical studies

The primary objective of this thesis was to determine whether or not cotton cellulose has a glass transition and if it could be reliably measured. Successful measurement of a reduction in modulus in DMA; calculation of a freezing point $T_g$, using DSC to measure the colligative effect of cotton in water; and measurement of mass change with the addition of water using DVS, have all indicated that cellulose does in fact go through a glass transition and it is measureable. Furthermore, it has been established that there is no significant variation in the $T_g$ of cotton of different maturity or between varieties, although a wider varietal survey is needed to confirm this.


THE GLASS TRANSITION TEMPERATURE OF COTTON


**APPENDIX 1**

KFT results for samples conditioned under various humidities.

<table>
<thead>
<tr>
<th>Fibre</th>
<th>Conditioning RH (%)</th>
<th>Measured MC (%)</th>
<th>Average MC (%)</th>
<th>St. Dev</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cotton</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>33</td>
<td>5</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td></td>
<td>59</td>
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<td>7</td>
<td>5</td>
</tr>
<tr>
<td></td>
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<tr>
<td></td>
<td>97</td>
<td>23</td>
<td>11</td>
<td>12</td>
</tr>
<tr>
<td>Tencel®</td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
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<td>9</td>
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<td>76</td>
<td>11</td>
<td>10</td>
<td>14</td>
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<tr>
<td></td>
<td>97</td>
<td>16</td>
<td>17</td>
<td>19</td>
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<tr>
<td>Viscose</td>
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<td>5</td>
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<tr>
<td></td>
<td>85</td>
<td>11</td>
<td>11</td>
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<tr>
<td></td>
<td>97</td>
<td>14</td>
<td>16</td>
<td>17</td>
</tr>
</tbody>
</table>
Stepwise versus Continuous DVS. Figures in red are extrapolated from trend lines.

<table>
<thead>
<tr>
<th>RH (%)</th>
<th>Cotton MC (%)</th>
<th>Tencel MC (%)</th>
<th>Viscose MC (%)</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>Stepwise</td>
<td>Continuous</td>
<td>Calculated</td>
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<td>Error (%)</td>
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<td>0.0 0.0</td>
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<td>0.5 1.6</td>
<td>50.6 -5.6</td>
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<tr>
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<td>1.5 2.3</td>
<td>17.5 1.0</td>
</tr>
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<td>11.0 0.5</td>
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<td>14.3 14.3</td>
<td>13.5 13.5</td>
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</tbody>
</table>

The graph shows the comparison between stepwise and continuous measurement methods over time and relative humidity (%).
Calculated non-freezing MC and ice melt temperature determined using DSC.

<table>
<thead>
<tr>
<th></th>
<th>Cotton</th>
<th>Tencel®</th>
<th>Viscose</th>
</tr>
</thead>
<tbody>
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<td>MC (%)</td>
<td>Temp</td>
<td>MC (%)</td>
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<tr>
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<td>-1.7</td>
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<tr>
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<td>15.1</td>
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<tr>
<td>Ave</td>
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<tr>
<td>R1</td>
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<tr>
<td>Std Dev</td>
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<td>0.09</td>
<td>0.92</td>
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</tbody>
</table>
Defining the Glass Transition Temperature of Cotton

C.M. Denham\textsuperscript{1, 2}, M.G. Huson \textsuperscript{1}, S.G. Gordon \textsuperscript{1} and X. Wang \textsuperscript{2}

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\textsuperscript{2} Deakin University, Institute for Frontier Materials

Abstract. Single fibre samples of cotton, Tencel\textsuperscript{®} and viscose were studied using dynamic mechanical analysis (DMA) under changing humidity conditions. This enabled the softening of these cellulosic fibres to be observed through measurement of the storage modulus with the addition of water, at various temperatures. At high temperature and humidity, a significant drop in measured storage modulus of all three samples, allowed the glass transition to be determined.

Keywords: Cotton, cellulose, glass transition, relative humidity, DMA

1. Introduction

Cotton lint fibre is produced by the epidermal cells of the cotton seed and is made up primarily of cellulose, found in the secondary cell wall. Cellulose, a polymer made up of glucose residues in a straight chain (non-branching) configuration, accounts for over 90\% of the entire cell mass\textsuperscript{1}. As the world’s most abundant biopolymer, much is known about cellulose, yet it still remains controversial as to whether cellulose and therefore cotton, goes through a glass transition.

The glass transition ($T_g$) of a polymer occurs as the molecules of the polymer reach a temperature sufficient to allow free rotation around the polymer backbone. At low temperatures molecules only have enough energy for small vibrational movements making the material stiff and glass-like. As the temperature increases there is sufficient energy to allow greater molecular movement and the material softens, becoming more rubbery. Many polymer properties change during this transition, such as heat capacity, elasticity, refractive


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index, conductivity and permability\textsuperscript{2}, and these may be used as a means of measuring the transition.

This transition from a glassy to rubbery state can also occur as the moisture content of a sample is increased\textsuperscript{3}. Water within the polymer structure lubricates molecular motion, plasticising the polymer and reducing the temperature at which the glassy transition is measured. This means that by holding the sample at a constant temperature, the glassy transition may be observed with the addition of moisture (W\textsubscript{g}).

There have been several studies published, which have been aimed at determining the T\textsubscript{g} of cellulose. Of these most have focused on microcrystalline cellulose (MCC)\textsuperscript{4,5,6,7} as used in the pharmaceutical industry and to a lesser extent as wood pulp for paper production\textsuperscript{8,9,10,11}.

Kargin in 1960\textsuperscript{12} first reported a dry T\textsubscript{g} of cellulose of 220°C. This was done using a thermomechanical method to investigate solvent doped regenerated cellulose. Since then, the Tg of cellulose has been studied using predominantly differential scanning calorimetry (DSC)\textsuperscript{6,7,10,11} and mechanical methods\textsuperscript{8,9,11} with mixed success. There have been many reported T\textsubscript{g}'s for cellulose under moist conditions, but these have been shown to vary by up to 100°C between authors\textsuperscript{4,11}. Some of this variation may be accounted for by differences in cellulose origin and measurement technique, nevertheless it is clear that though several authors have measure transitions, there is a great deal of variation in the measured temperature both between samples of different cellulose sources and those of similar origins.

Further work is therefore needed to find a reliable and reproducible method of measuring the T\textsubscript{g} of cellulose. This investigation aims to do this by utilizing the plasticisation effect of the addition of water to cellulose, primarily cotton, to study the glass to rubber transition.

2. Experimental

Dynamic mechanical analysis was used to determine the W\textsubscript{g} of three cellulose samples. Single cotton, Tencel\textsuperscript{®} and viscose fibres were mounted in the film/fibre tension clamp of a TA Instruments Q800 dynamic mechanical analyser, fitted with the TA DMA humidity
accessory. Preliminary stress-strain curves were conducted at 35°C at a rate of 0.1N/min\(^{-1}\) (data not shown).

The instrument strain and static force were programmed based on the stress-strain curves of each sample; programmed strain and force for each shown in Table 1. A minimum dynamic force of 0.001N was applied to each sample. Samples were equilibrated at each set temperature, (from 10 to 90°C) for 20mins. At each temperature, the relative humidity was taken to 50% and equilibrated for a further hour before increasing the humidity in 1% steps every 8mins, up to a maximum of 90% relative humidity. The onset of \(W_g\) is defined here as the initial downward inflexion in storage modulus, measured using tangential lines before and after the inflection. The storage modulus is relative only, due to the difficulty of accurately defining the fibre cross-sectional area.

<table>
<thead>
<tr>
<th>Table 1: DMA strain and force parameters set for each sample.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oscillating Strain (%)</td>
</tr>
<tr>
<td>Cotton</td>
</tr>
<tr>
<td>0.0375</td>
</tr>
<tr>
<td>Static Force (N)</td>
</tr>
<tr>
<td>Cotton</td>
</tr>
</tbody>
</table>

3. Results and Discussion

The results obtained for each temperature were overlaid and the change in storage modulus compared, as relative humidity (RH) was increased. Figure 1 shows the results for cotton; this result is typical for each fibre type. Singles fibres under humid conditions showed a clear lowering of modulus over the course of each humidity cycle. Of chief interest is the rapid decrease in modulus at high humidity most prominent in the 70°C and 80°C cycles. This drop and leveling off of the modulus is consistent with the behaviour of a polymer which is plasticised by moisture, going through its glass transition. Furthermore this transition is shown to shift to lower humidity as temperature increases. This pattern is consistent across all three samples. It is also worth noting that the change in modulus is reasonably small in comparison to those seen in synthetic polymers, most likely due to the diluting effects of a highly crystalline polymer.
Figure 1: Typical example of the change in storage modulus in a single fibre as humidity is increased under different temperature conditions, as determined by DMA. Cotton shown here.

The glass transition results for all fibres measured as a function of humidity, $W_g$, are summarised in Table 2. Moisture sorption isotherms for each fibre type\textsuperscript{14,15} allow for the determination of their moisture content (MC) at each humidity. Ideally, the moisture sorption isotherms used to translate RH in MC would be collected at the same temperature as the experimental data, because sorption decreases at elevated temperature. However the literature contains very few isotherms collected at elevated temperatures for cotton and viscose, and none for Tencel\textsuperset{®}. For this reason all results were initially converted using isotherms collected at 25°C, and then the 40°C, 70°C and 90°C cycles of cotton and viscose were also converted using isotherms produced at 35.5°C, 70°C and 100°C\textsuperscript{13} to estimate the error.

Table 2: Glass transition expressed as the RH and MC at which softening occurs for a given temperature.

<table>
<thead>
<tr>
<th>Cycle</th>
<th>Cotton $W_g$</th>
<th></th>
<th>Tencel\textsuperset{®} $W_g$</th>
<th></th>
<th>Viscose $W_g$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Temp (°C)</td>
<td>RH (%)</td>
<td>MC (%)</td>
<td>$MC_{cor}$ (%)</td>
<td>RH (%)</td>
</tr>
<tr>
<td>40</td>
<td>79.2</td>
<td>10.3</td>
<td>8.9</td>
<td></td>
<td>77.4</td>
</tr>
<tr>
<td>50</td>
<td>77.6</td>
<td>9.7</td>
<td>---</td>
<td></td>
<td>76</td>
</tr>
<tr>
<td>60</td>
<td>76</td>
<td>9.2</td>
<td>---</td>
<td></td>
<td>74.6</td>
</tr>
<tr>
<td>70</td>
<td>75.1</td>
<td>9.1</td>
<td>7.1</td>
<td></td>
<td>73</td>
</tr>
<tr>
<td>80</td>
<td>72</td>
<td>8.3</td>
<td>---</td>
<td></td>
<td>70.5</td>
</tr>
<tr>
<td>90</td>
<td>71.1</td>
<td>8.1</td>
<td>5.3</td>
<td></td>
<td>---</td>
</tr>
</tbody>
</table>
These experimental results are shown in figure 2, along with the results expected when calculated using the Fox equation:

\[
\frac{1}{T_g} = \frac{w_1}{T_{g1}} + \frac{w_2}{T_{g2}}
\]

The Fox equation calculates the \( T_g \) of a ‘mixture’ by accounting for the \( T_g \) of the individual components, \( T_{g1} \) (cellulose \( T_g = 220^\circ C \)) and \( T_{g2} \) (water \( T_g = -137^\circ C \)), with reference to the weight fraction of each (\( w_1 \) and \( w_2 \)). It is necessary to take polymer crystallinity into account using this equation, as water can only enter the amorphous fraction of the polymer. Without doing so, a crystalline polymer such as cellulose would have a significantly higher weight fraction of water within the amorphous regions than the calculated weight fraction of water for the whole sample. Figure 2 shows the Fox equation graphically at varying crystallinity.

![Figure 2: Experimental glass transition results for cellulose both raw (•) and corrected for temperature (×)[13], overlaid on the predicted results calculated using the Fox equation (—).](image)

While the raw data does not conform well to the \( T_g \) predicted using the Fox equation, correcting for temperature when converting to moisture content improves the correlation. There is a significant difference in the moisture content at \( T_g \) between cotton and the regenerated cellulose fibres. This is likely due to the difference in the crystallinity of the samples, but may also relate to the change in molecular configuration of the cellulose due to processing, from cellulose I to cellulose II.

The results found in this study show similar trends in cotton as those shown by Ogiwara[9], and between regenerated cellulose and ball milled wood cellulose as studied by Paes[11]. That
said, there are differences in temperature for given humidities of up to 25°C in cotton, which may be accounted for by difference in method. Method of examination is important to consider, for example comparing the \( T_g \) as measured by softening in DMA to temperature dependence of water binding using NMR\(^5\) may show different results due to varying sensitivity to the transition or shifting of the measured temperature due the rate dependant nature of the transition.

What is surprising about this data is that even at the higher temperatures, a reasonably high humidity is necessary to produce a change in the sample. This is because even at high relative humidity, the moisture content within the fibre sample remains fairly low. These findings are inconsistent with results reported by Batzer\(^10\) and Hancock\(^4\) who claim sub-ambient temperatures for \( T_g \) of cellulose conditioned at high relative humidity. Similarly low \( T_g \) measurements were also reported by Szczesniak\(^7\) using DSC. It is worth noting that the moisture contents reported by Batzer\(^10\) and Hancock\(^4\) at high humidity are somewhat greater than the generally accepted literature values of 15-30% for untreated cellulose.

4. Conclusion

The glass transition of cotton, viscose and Tencel\(^\circledR\) were studied with respect to moisture content using dynamic mechanical analysis. A clear transition is seen in cotton at 70°C and a relative humidity of 75%. This transition seen during the addition of water then lowers to 72%RH at 80°C, consistent with the behavior of a polymer going through its glass transition. Regenerate celluloses also showed clear transitions at similar humidities for each temperature. Further work is underway to confirm these result using alternative techniques.

5. References


THE GLASS TRANSITION OF COTTON

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CSIRO Manufacturing, Waurn Ponds, Geelong, Australia.

ABSTRACT

The glass transition temperature is a fundamental property of all amorphous and semi-crystalline polymers, including cotton and other celluloses. At this temperature many properties, such as modulus, heat capacity, density, refractive index, dielectric constant, thermal expansion and rate of diffusion show a distinct change. It is thus important to be able to measure the glass transition temperature, however this has proved challenging for cotton due mainly to its high level of crystallinity. This chapter outlines the relationship between the chemical structure and the glass transition temperature of polymers in general as well as the effect of physical ageing and plasticization. Models to predict the effect of plasticization are also discussed. The moisture uptake of cotton and the attempts to measure the glass transition temperature of cotton and other celluloses, in both the dry state and as a function of moisture content, are detailed. Dry cotton is estimated to have a glass transition temperature of 220°C, with the value dropping to below zero when saturated with water.

Cotton is the purest natural form of the biopolymer cellulose. It is important to understand the glass transition behaviour of cellulose and utilise this knowledge to optimise temperature and moisture levels during processing. Doing so will reduce the vulnerability of fibres to damage and improve overall fibre, yarn and fabric quality.

Keywords: cotton, cellulose, glass transition temperature, sorption isotherm, plasticization, physical ageing, Fox equation

INTRODUCTION (WHAT IS A GLASS TRANSITION?)

Non-crystalline (amorphous) polymers, when heated, undergo a transition from a rigid and glass-like state to a more malleable rubbery state; the so-called glass transition. The glass transition temperature (T_g) is a fundamental property of all polymers, being the temperature at which many properties change. Besides the fore-mentioned change in rigidity or modulus, other properties including heat capacity, density, refractive index, dielectric constant, thermal expansion and rate of diffusion all show a distinct change at the T_g.

At a molecular level, T_g is the temperature at which the molecule has sufficient energy to allow free rotation about the bonds in the main chain or “backbone” of the polymer. For this rotation to occur neighbouring molecules, or segments of molecules, generally need to move
out of the way. In other words, cooperative segmental motion is a necessary requirement for a polymer to transition from a glassy state to a rubbery state. It follows that molecules incorporated in crystalline regions are not free to rotate and hence $T_g$ is a property of amorphous polymers or the amorphous regions of semi-crystalline polymers. Furthermore, the $T_g$ is strongly dependent on the structure of the polymer, in particular the flexibility of the polymer backbone and the size of the pendant groups (Table 1).

**Table 1:** Effect of structural variation in the main repeat unit and side groups, on the glass transition temperature of a range of polymer (data from [1] and [2]).

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Main chain (backbone) influence</th>
<th>Unit structure</th>
<th>$T_g$ (ºC)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Poly(dimethyl siloxane) PDMS</td>
<td></td>
<td><img src="image" alt="Structure" /></td>
<td>-123</td>
</tr>
<tr>
<td>Polyethylene PE [-CH2CH2-]n</td>
<td></td>
<td></td>
<td>-93</td>
</tr>
<tr>
<td>Poly(ethylene oxide) PEO [-CH2CH2O-]n</td>
<td></td>
<td></td>
<td>-67</td>
</tr>
<tr>
<td>Poly(ethylene terephthalate) PET</td>
<td></td>
<td><img src="image" alt="Structure" /></td>
<td>69</td>
</tr>
<tr>
<td>Poly(phenyl ether) PPE</td>
<td></td>
<td><img src="image" alt="Structure" /></td>
<td>83</td>
</tr>
<tr>
<td>Bisphenol A polycarbonate PC</td>
<td></td>
<td><img src="image" alt="Structure" /></td>
<td>149</td>
</tr>
<tr>
<td>Poly(p-phenylene oxide) PPO</td>
<td></td>
<td><img src="image" alt="Structure" /></td>
<td>208</td>
</tr>
<tr>
<td>Poly(p-xylylene) PPX</td>
<td></td>
<td><img src="image" alt="Structure" /></td>
<td>280</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Side chain influence</th>
<th>Side group</th>
<th>$T_g$ (ºC)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyethylene PE</td>
<td></td>
<td>-H</td>
<td>-93</td>
</tr>
<tr>
<td>Polypropylene PP</td>
<td></td>
<td>-CH3</td>
<td>-20</td>
</tr>
<tr>
<td>Poly(1-butene) PB-1</td>
<td></td>
<td>-C2H5</td>
<td>-24</td>
</tr>
<tr>
<td>Poly(1-pentene)</td>
<td></td>
<td>-C3H7</td>
<td>-40</td>
</tr>
<tr>
<td>Poly(1-hexene)</td>
<td></td>
<td>-C4H9</td>
<td>-50</td>
</tr>
<tr>
<td>Poly(vinyl chloride) PVC</td>
<td></td>
<td>-Cl</td>
<td>81</td>
</tr>
<tr>
<td>Polyacrylonitrile PAN</td>
<td></td>
<td>-CN</td>
<td>105</td>
</tr>
<tr>
<td>Polystyrene PS</td>
<td></td>
<td></td>
<td>100</td>
</tr>
</tbody>
</table>
The flexibility of the polymer backbone is enhanced by groups such as −CH2−CH2−, −CH2O−CH2− and −Si−O−Si− thus polymers such as polyethylene (−93°C), poly(ethylene oxide) (−67°C) and poly(dimethyl siloxane) (−123°C) all have exceptionally low values of \( T_g \). Inserting groups that stiffen the main chain by impeding rotation has the opposite effect, raising the \( T_g \). This is particularly evident in polycarbonate, poly(\( p \)-phenylene oxide) and poly(\( p \)-xylylene) which all show the effect of having a phenyl ring in the main chain.

The effect of pendant group size is well illustrated by the group of alkyl polymers listed in Table 1. They are all asymmetric with the repeat unit (backbone) structure of the general type −CH3:CHX−. It is clear that as the side group (X) increases in size the \( T_g \) rises; from −93°C for polyethylene with only hydrogen as a pendant “group” to −20°C for polypropylene with a methyl pendant group and finally polystyrene, with a bulky benzene ring as a side group which has a \( T_g \) of 100°C.

Other factors such as symmetry of the repeat unit, polarity and flexibility of the side chain also play a role. Thus the symmetrical poly(\( \text{vinylidene chloride} \)), with two pendant chlorine groups, has a \( T_g \) of −17°C [3] whereas PVC has a \( T_g \) of 81°C. PP, PVC and PAN all have similar sized side groups and yet the \( T_g \) increases from −20°C to 81°C to 105°C as the polarity increases. For long flexible side groups, \( T_g \) decreases with chain length, as shown by the sequence poly(1-butene), poly(1-pentene) and poly(1-hexene).

Cellulose is a polymer made up of many glucose subunits (residues), in a straight (non-branching) chain of (1,4)-\( \beta \)-D-glucan, shown in Figure 1. Given the presence of the rigid cyclic structure of the glucose residues in the main chain, we would expect cellulose to have a high \( T_g \). Furthermore, cellulose is highly crystalline thus the glass transition is expected to be weak and difficult to measure. The exact degree of order is not clear. Many sources report that cotton is about two-thirds crystalline, however others believe that the fibres are virtually 100% crystalline, and that the measured disorder is due to the imperfect packing of the very small crystallites, with very little material that is not part of a crystal lattice [4, 5].

Cellulose

![Molecular structure of β-D-glucose](image1)

**Figure 1:** Molecular structure of β-D-glucose (left), the building block of cellulose (right). Adapted from Klemm et al. [6].

It is worth noting that whilst Table 1, and the literature in general, lists a single value for \( T_g \) this is a somewhat simplistic representation [7]. The transition occurs over a wide temperature range, thus in practice it is necessary to carefully define how \( T_g \) is measured. Often the onset temperature is chosen. The transition is also sensitive to the rate of testing, thus different measurement techniques invariably yield different numbers.

**ABSORPTION OF WATER**

Mature cotton takes up approximately 15-20% moisture at saturation [8-10], where moisture content is defined as the mass of water expressed as a percentage of the moist sample mass. The sorption isotherm for mature cotton (Figure 2 left) is sigmoidal in shape (IUPAC type II) and exhibits a degree of hysteresis, with equilibrium moisture content (EMC) values a few percentage points lower when the samples are conditioned from the dry side (solid circles), i.e. the sorption arm of the isotherm.
The general understanding of water sorption in cellulose is that it occurs predominantly within the amorphous regions of the material. Consistent with this view Mihranyan et al. [11] showed, for five different cellulose powders, that the moisture content (MC) decreased with an increase in crystallinity. Furthermore using days of growth after flowering, or anthesis, as a measure of fibre development, it was shown that moisture content decreased [8, 12] and crystallinity increased [12] with fibre development. Figure 2 (right) shows a rapid decrease in the equilibrium moisture content at 95 % RH (EMC95) up until about 25 days post anthesis (DPA), followed by a more gradual decrease as the fibre approaches maturity at approximately 60-80 DPA. This change corresponds to the transition from the elongation phase of growth into the development of the secondary cell wall. The implication of water only occupying the amorphous regions, is that a semicrystalline sample with a sample moisture content of 15%, could have 3-4 times that level of moisture in the amorphous region.

![Figure 2: Moisture content as a function of the relative humidity for mature (80 DPA) cotton fibres (left) showing absorption (●) and desorption (○). Equilibrium moisture content at 95% RH (EMC95) for developing cotton fibres (15–80 DPA) (right). Reproduced with permission from [8].](image)

The shape of the isotherm is common to many amorphous materials including milk powder [13], wool [14, 15], silk, nylon, collagen, egg albumin [14], and poly(vinylpyrrolidone), PVP [16-18]. Similarly shaped curves are obtained for the adsorption isotherms of gas and these are most often modelled by the Brunauer, Emmett and Teller (BET) equation [16]. In this case the first inflection is interpreted as corresponding to the formation of a complete monolayer of gas on the surface [19]. This similarity of shape has often led to these models, most often the BET equation, being applied to water vapour sorption isotherms. Whilst these curves fit the data extremely well and identify the initial inflection point, they do not advance our understanding of the molecular processes occurring as water is absorbed into amorphous solids [16]. Several authors [8, 20, 21] have used the Hailwood Horrobin (HH) model [22], which assumes that the water exists in two states; water in simple solution, and water combined to form a mono-hydrate with a defined unit of the polymer molecule. Analogous to gas adsorption models these two states are sometimes, incorrectly, referred to as polylayer and monolayer water respectively [23]. Figure 3 shows the contributions from water in simple solution (dissolved water) and water of hydration for a jute water system. Willems [24] reviewed the HH model critically and concluded that surface multilayer-sorption models, such as the HH model, do not apply to wood. He claimed that a sorption site occupancy model provided a more comprehensive, thermodynamically consistent and quantitative basis for the analysis of sorption isotherms of wood.
A more general model which applies to all penetrant/polymer systems was developed by Vrentas and Vrentas [25, 26]. By allowing for structural changes in the glassy polymer with increasing penetrant concentration, the model was developed to give a good prediction of the isotherm, provided the polymer is in the glassy state. They [25-27] demonstrated the applicability of their model on a number of systems including penetrants such as water, carbon dioxide, benzene, and methyl ethyl ketone and polymers such as polycarbonate, polystyrene and poly(methyl methacrylate). The second inflection in the absorption isotherm is explained as being associated with a glass to rubber transition. At higher penetrant levels, the isotherm is well modelled by the Flory-Huggins model developed for freely mobile polymers, in other words rubbery polymers above their $T_g$. The combined Vrentas/Flory-Huggins approach has also been used by other workers to describe the sorption of water in wool [15] (Figure 4) and PVP [16], as well as hexane in polystyrene [28].

The exact reason for the hysteresis between the sorption and desorption cycles is unclear [8, 21]. Vrentas and Vrentas [30] developed mathematical expressions for both the absorption and desorption of a penetrant into or from a glassy polymer matrix. The difference is ascribed to different structural arrangements of the glassy polymer in the two cases. It is likely that this
difference includes increased free volume in the polymer from which the penetrant is being desorbed [31]. Other proposed explanations include failure to establish a true equilibrium condition, and the ability of the matrix to deform in response to the adsorption or desorption of penetrant molecules into or out of the glassy materials [8]. The hysteresis loop has been shown to be sensitive to the size of the sorption step in wool-water systems [32, 33], the maturity (DPA) of cotton samples [8], the temperature at which the isotherms of flax and Sitka spruce were measured [20, 21] and the type of cellulose under investigation [20]. Hysteresis in cellulose has also been linked with lignin and amorphous cellulose content. Studies of cotton, flax and hemp, which have lower lignin content and higher crystallinity than jute, coir and Sitka spruce, show much lower levels of hysteresis [20].

**EFFECT OF PLASTICIZATION**

A plasticiser is, in essence, a substance which increases the free volume in a polymer system, facilitating the free movement of the polymer backbone and its side chains. This increase in molecular mobility manifests itself as a decrease in the glass transition temperature. For synthetic polymers, low molecular mass organic compounds are often added as plasticizers to modify the properties of the polymer and/or improve the processibility of the material. For example PVC, with a \( T_g \) of 81°C, is a hard rigid material at room temperature and is routinely used to make pipes, window frames etc. When plasticized, generally with phthalate esters [34], PVC becomes soft and flexible at room temperature and finds application in artificial leather, swimming pool linings, etc.

Most natural polymers, such as cellulose, as well as a few synthetic polymers like nylon, have an affinity for water and readily absorb moisture from the air. The absorbed moisture acts as a plasticiser for these materials lowering their \( T_g \). For example, bone dry wool or hair has a \( T_g \) of 170°C, whereas fully saturated wool contains 26% moisture and has a \( T_g \) of -10°C [35]. The \( T_g \) of Nylon 6 has been shown to decrease from 42°C to -13°C upon the uptake of water [36] whereas for cellulose the decrease is almost 300°C [37].

There are numerous mathematical models which have been developed to aid in determining the amount of plasticiser required to bring about a desired glass transition [38-44]. One of the most widely used models was derived independently by both Gordon and Taylor [39] as well as Kelley and Bueche [41]. The model relates the glass transition temperature of the mixture \( (T_g) \) to the glass transition temperature of each separate component and their mass fractions \( (m) \):

\[
T_g = \frac{m_1 \cdot T_{g1} + K \cdot m_2 \cdot T_{g2}}{m_1 + K \cdot m_2}
\]

Where:

\[
K = \frac{\rho_1 \cdot \Delta \alpha_2}{\rho_2 \cdot \Delta \alpha_1}
\]

Subscripts 1 and 2 refer to the polymer and plasticizer respectively, \( \Delta \alpha \) is the difference in the coefficient of thermal expansion of the component in the liquid and glassy state, and \( \rho \) is the true density of the material. \( K \) is considered to be the ratio of the free volumes of the two components under any given conditions [45]. Using a classical thermodynamic approach Couchman and Karasz [38] derived an identical equation with the exception that:
\[ K = \frac{\Delta C_p^2}{\Delta C_p^1} \]  

\[ \Delta C_p \text{ being the change in specific heat capacity at the } T_g. \]

Kaelble [40] recommended an equation similar to that of equation (1) based on a variation of the work of Gordon and Taylor [39] proposed by Wood [46]. He used mole fraction rather than mass fraction which has the advantage that the constant (Wood’s constant) can be given a molecular interpretation:

\[ \text{Wood’s constant} = \frac{M_1 \cdot h_2}{M_2 \cdot h_1} \]  

where \( M \) is the molecular mass and \( h \) is the degrees of freedom for the monomer and plasticizer. Salmen and Back [47] later rearranged Kaelble’s equation, showing it was identical to equation (1) except that the mass fraction (\( m \)) was replaced by molar fraction and \( K = h_2/h_1 \).

Thus four different approaches result in equation (1); three are identical and differ from one another only in the definition of the constant \( K \) whilst the Kaelble equation has an identical form but uses mole fractions rather than mass fractions. By applying the Simha-Boyer rule [48] (\( T_g = \text{constant} \)) and also assuming that the densities of the two components are equal, then equation (1) simplifies to:

\[ \frac{1}{T_g} = \frac{m_1}{T_g1} + \frac{m_2}{T_g2} \]  

which is commonly referred to as the Fox equation [44].

As stated earlier, water sorption in cellulose occurs predominantly within the amorphous regions of the material, thus the weight fractions in the above equations need to be based on the amorphous content of the material. Taking this into account, the water mass fraction (\( m_2 \)) needs to be written as:

\[ m_2 = \frac{r}{r + (1 - X_c)} \]  

where \( X_c \) is the fraction of crystalline material in the polymer and \( r \) is the regain or water present expressed as a fraction of the dry polymer weight.

Hancock and Zografi [45] discuss the different models and list \( K \) values for a range of polymers, with the value for cellulose given as 0.173. Kaelble [40] lists values of \( h \) for several polymer structural units, allowing Wood’s constant to be calculated. Hancock and Zografi [45] showed an excellent fit of the Gordon-Taylor/Kelley-Bueche model to experimental \( T_g \) versus water content data for a range of synthetic polymers. The model also held for the cellulose-water data provided an adjustment was made for the crystallinity of the sample. Salmen and Back’s earlier paper [47] as well as Szcześniak et al. [49] also accounted for the degree of crystallinity, finding that the “Kaelble approach” to plasticisation worked well to explain the effect of water on the \( T_g \) of cellulose. Szcześniak et al. [49] further suggested that the measured \( T_g \) and moisture content data may be useful in determining the crystallinity of cellulose and other materials.
EFFECT OF PHYSICAL AGEING

Physical ageing is a spontaneous process which occurs in all glassy polymers. It involves a reduction in free volume, and hence chain segment mobility, resulting in slow changes in physical properties over long periods of time [50]. Rough estimates suggest that for most polymers ageing persists for the entire service life of a product (10-50 years), except when held at temperatures close to Tg [50]. Properties affected include density, modulus, creep compliance, stress-relaxation, dielectric constant, gas diffusivity and rates of swelling and dissolution.

When an amorphous polymer is cooled from a temperature above Tg, it’s volume decreases linearly before departing from the equilibrium line at Tg, a temperature which depends upon the rate of cooling of the sample [51, 52] (Figure 5). Holding the polymer at the ageing (or annealing) temperature (Ta), below Tg, results in a slow decrease in volume with time as the free volume reduces. Ageing is a self-retarding process, with the rate of volume decrease slowing as the equilibrium volume is approached. The rate of ageing is also dependent on how far below Tg the polymer is held, i.e. it is dependent on Tg – Ta [50].

**Figure 5:** Schematic diagram of volume change with temperature on cooling for an unaged polymer (AB) and a polymer aged at a temperature T<sub>a</sub> (ABC) (adapted with permission from Yoshimisiu [53]).

Volume in Figure 5 can be replaced with a range of properties including entropy and enthalpy. Enthalpy changes on ageing are readily apparent during calorimetric studies, thus knowledge of the effects of ageing are important when Tg measurements are made by differential scanning calorimetry (DSC), a commonly used technique (see later). Figure 6 shows the effect of ageing on heat flow in a DSC experiment as a poly(vinyl acetate) (PVAc) sample goes through the typical step-change at Tg. The enthalpy lost during ageing generally manifests itself as an endothermic peak as the sample is heated through the Tg range [50-52, 54] and as such can interfere with the accurate measurement of Tg. For this reason the ASTM standard method (ASTM D3418, Test Method for Transition Temperatures of Polymers by Thermal Analysis) requires the measurement to be made on a de-aged sample. In samples where the transition is weak, the ageing endotherm can sometimes be used as an indicator of the presence of a Tg.
This needs to be used with caution however, as several authors have shown that Tg may shift as a function of ageing time, as seen in Figure 6 [52, 55-59]. Furthermore whilst the ageing endotherm normally occurs in the region of the Tg this is not always the case. Endotherms have been reported well below the Tg [35, 57] and in some cases multiple endotherms are possible [35, 54, 55, 58, 59], particularly for materials which have a broad spectrum of relaxation times, e.g. proteins [35, 55] and polymer blends [54]. Montserrat and Cortes [58] report a double endotherm upon ageing of semicrystalline poly(ethylene terephthalate) (PET), which they ascribe to different rates of enthalpy relaxation for inter and intra spherulitic amorphous regions.

**Figure 6:** Effect of ageing time on the DSC heating curves of PVAc after quenching and after ageing at 27°C for 1, 10 and 100 hours (reproduced with permission from Bair [54]).

### MEASUREMENT OF Tg

Since many properties change as a polymer goes through the glass transition, one can in principal measure any of these properties as a function of temperature in order to measure the Tg. Historically the most common method was volume dilatometry, where a solid sample is sealed in a pyrex tube to which is attached a graduated precision capillary (Figure 7). The dilatometer is filled with mercury and immersed in a heating bath. Volume changes are recorded as the temperature is changed.

**Figure 7:** Schematic diagram showing the experimental setup for the accurate measurement of volume change with temperature.
Currently there are two prominent methods which are used to measure $T_g$. Differential scanning calorimetry (DSC) exploits changes in calorimetric properties as a sample is heated through the glass transition temperature range, whilst dynamic mechanical analysis (DMA) utilizes changes in the modulus and damping properties. DSC has the advantage that, if sealed pans are used, constant moisture content can be maintained during heating. On the other hand DMA is more sensitive than DSC, the modulus changing by approximately three orders of magnitude at $T_g$ [60]. It is however much harder to maintain a constant environment in DMA experiments than in DSC experiments. Other less common methods include nuclear magnetic resonance [61], gas chromatography [62], inverse gas chromatography [63], refractometry [64, 65], scanning probe microscopy [66], dielectric spectroscopy [67], Raman and Brillouin scattering measurements [68] and dynamic vapour sorption (DVS) [69-72].

In a DSC measurement, a small sample (typically 10 mg) is placed in a pan and heated at a constant rate, typically 5°C/min. The heat flow (mW = mJ/sec) into the sample (S) is compared to the heat flow into an inert reference (R, often an empty pan) heated at the same rate (Figure 8a). The power required to maintain zero temperature differential between the sample and the reference is measured and recorded as a function of temperature. A phase change in the sample, such as melting, requires additional heat and thus results in an endothermic peak in the DSC trace. Crystallization is an exothermic process, as are many chemical reactions such as curing of resins and degradation, and they all give rise to exothermic peaks. Second order transitions, such as a glass to rubber transition, result in a step change in the heat flow signal. Typical changes are shown schematically in Figure 8b whilst Figure 8c shows the actual glass transitions for bovine serum albumin (BSA) and poly(ethylene terephthalate) (PET), highlighting the broad nature of the transition, particularly for the protein BSA.

![Figure 8: Schematic diagram (a) showing the experimental setup as well as (b) the possible transitions typically measured by DSC. Actual glass transitions (c) for BSA and PET highlighting the broad nature of the transition, particularly for the protein BSA. Different definitions of $T_g$ are shown as (i, ii and iii).](image-url)
DMA measurements most often involve a stress being applied in an oscillating fashion, with the amplitude and phase of the responding sample deformation being measured. This allows the measurement of the viscoelastic properties of the sample, such as modulus and damping. Most commercial instruments are capable of applying bending, compression, shear or tensile stress to a sample as a function of temperature, frequency and in some cases humidity. For moisture sensitive materials such as cotton, the glass to rubber transition can thus be measured isothermally by increasing the moisture content; at constant humidity by increasing the temperature; or by reducing the frequency of deformation at constant temperature and humidity. A typical DMA trace for a moisture insensitive sample, measured at constant frequency in the region of the glass transition, is presented in Figure 9. The decrease in modulus and the peak in damping (tan δ and loss modulus) is clearly evident.

Figure 9: Storage modulus, loss modulus and Tan δ curves for PET film showing a number of different definitions of Tg (iv – vii).

As can be seen from Figures 8 and 9 the transition from a glassy to a rubbery state occurs over a range of temperatures. It is common however to report a single value and this needs to be carefully defined. DSC utilises the onset (i), midpoint (ii) and offset (iii) temperatures (Figure 8) with the onset being the most common. According to ASTM E 1640-04 [73], the Tg as measured by DMA can be the onset of the storage modulus drop (iv), the peak of the loss modulus (v) or the peak of the tan δ curve (vi) (Figure 9). Occasionally the inflection in the modulus curve (vii) is also used.

THE Tg OF CELLULOSE

While there is a great deal of published work on the determination of the glass transition temperature of synthetic polymers, there are relatively few studies available which investigate cellulose. Of these, a range of cellulose types have been investigated using many different techniques with varied results (Table 2). Many studies focused on microcrystalline cellulose
and methylated derivatives of cellulose ethers [45, 77] as used in the pharmaceutical industry. Other authors investigated cellulose from paper pulping [61, 74, 78-82], cotton [37, 61, 66, 69, 83, 84] and regenerated or derivatised cellulose [74, 85-88].

**Table 2:** Literature values for the T<sub>g</sub> of dry cellulose.

<table>
<thead>
<tr>
<th>Date</th>
<th>Sample</th>
<th>Method</th>
<th>T&lt;sub&gt;g&lt;/sub&gt; (°C)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1960</td>
<td>Plasticized regenerated cellulose</td>
<td>Mechanical deformation - collapse of powder. Extrapolation to zero plasticizer</td>
<td>220</td>
<td>[86]</td>
</tr>
<tr>
<td>1963</td>
<td>MCC, wood pulp and regenerated cellulose powders</td>
<td>Mechanical deformation - collapse of powder</td>
<td>231-253</td>
<td>[74]</td>
</tr>
<tr>
<td>1968</td>
<td>Wood pulp</td>
<td>Mechanical deformation - collapse of powder</td>
<td>240</td>
<td>[82]</td>
</tr>
<tr>
<td>1968</td>
<td>Wood pulp</td>
<td>Mechanical deformation - collapse of powder</td>
<td>234</td>
<td>[81]</td>
</tr>
<tr>
<td>1969</td>
<td>Paper</td>
<td>Sonic pulse technique</td>
<td>230</td>
<td>[78]</td>
</tr>
<tr>
<td>1973</td>
<td>Cellodextrin</td>
<td>Torsional braid analysis. Peak logarithmic decrement. Extrapolated to infinite mass</td>
<td>217</td>
<td>[89]</td>
</tr>
<tr>
<td>1976</td>
<td>Saponified cellulose triacetate</td>
<td>DMA - tan δ peak</td>
<td>200</td>
<td>[88]</td>
</tr>
<tr>
<td>1977</td>
<td>Paper</td>
<td>Tensile test - modulus change</td>
<td>220</td>
<td>[90]</td>
</tr>
<tr>
<td>1978</td>
<td>Paper</td>
<td>Tensile test - modulus change</td>
<td>220</td>
<td>[91]</td>
</tr>
<tr>
<td>1979</td>
<td>Paper</td>
<td>Tensile test - modulus change</td>
<td>230</td>
<td>[92]</td>
</tr>
<tr>
<td>1985</td>
<td>Cellulose acetate</td>
<td>DSC - heat flow onset. Extrapolated to zero substitution</td>
<td>250</td>
<td>[85]</td>
</tr>
<tr>
<td>1986</td>
<td>Regenerated cellulose</td>
<td>DMA - tan δ peak</td>
<td>240</td>
<td>[87]</td>
</tr>
<tr>
<td>2003</td>
<td>Cellulose model</td>
<td>Molecular modeling - volume change</td>
<td>377</td>
<td>[93]</td>
</tr>
<tr>
<td>2004</td>
<td>Cellulose model</td>
<td>Molecular modeling - volume change</td>
<td>227</td>
<td>[94]</td>
</tr>
<tr>
<td>2010</td>
<td>Moist ball milled wood pulp</td>
<td>DMA - tan δ peak. Extrapolated to dry</td>
<td>205</td>
<td>[80]</td>
</tr>
</tbody>
</table>
Cotton was first investigated by Bryant and Walter [83] who used a tensile tester and measured stiffness of cotton yarn as a function of temperature in air and water. Their results were not definitive, however they concluded that the dry Tg was above 200°C and the wet Tg below 0°C. Kargin et al. [86] established that the glass transition of regenerated cellulose doped with triethylphenylammonium hydroxide could be measured using a mechanical deformation method. They carried out measurements at a range of plasticizer concentrations and obtained an unplasticised Tg of 220°C by extrapolation. Goring [74] used a similar method and obtained values of Tg from 231°C to 253°C for a range of dry cellulose powders but found that the softening point was not meaningfully affected by absorbed water. Takamura [82] too found no dependence of the Tg of cellulose on moisture, reporting a value of 240°C. Baldwin and Goring [81] used the collapse of Poplar and Birch wood pulp powder to show a Tg of at 234°C. Back & Didriksson [78] reported a glass transition temperature of 230°C for dry paper made from cotton linters as well as bleached kraft pulp. Salmen and Back [90, 91] carried out tensile tests up to 250°C on a range of dry papers and concluded, like Kargin [86], that the Tg of cellulose was 220°C. In a later paper Salmen [92] revised this estimate, suggesting that cellulose, hemicellulose and lignin act as separate components in the composite material of paper with glass transition temperatures of 230°C for cellulose, 205°C for lignin and 165°C to 175°C for the hemicelluloses. Salmen defined the glass transition as the inflection point of the decreasing S-shaped curve of modulus versus temperature. Yano et al. [88] saponified cellulose triacetate to produce amorphous cellulose film and used DMA to show the Tg was at about 200°C. An interesting approach was taken by Alfthan and Ruvo [89] who used torsional braid analysis to determine the Tg of cellodextrins with a range of molecular masses (M). When plotted according to the theory proposed by Ueberreiter and Kanig [95], the Tg of cellulose (cellodextrin of infinite molecular mass) was determined as 217°C (Figure 10). If the more commonly used Flory-Fox equation, where Tg decreases linearly with 1/Mn [1-3, 96], is used, a value of 207°C is obtained. Kamide and Saito [85] used a similar approach, measuring the Tg of a range of cellulose acetate samples by DSC. Extrapolating the data to zero substitution gave a value of 250°C for the Tg of cellulose. Paes et al. [80] used DMA on ball milled cellulose, equilibrated at a range of moisture contents. Fitting their data with the Couchman–Karasz model yielded a dry Tg of 205°C. Taking all the experimental evidence into account, both direct and indirect, on a range of cellulosic materials, a value of 220°C to 230°C for the dry Tg of cellulose seems to be acceptable. This is supported by molecular modelling studies by Chen et al. [94] which predicted a value of 227°C although it is at odds with the modelling prediction by Mazeau and Heux [93], who estimated the Tg of dry cellulose to be around 377°C.

![Figure 10: The glass transition temperatures (Tg) of cellodextrins of varying molecular mass (M). Reproduced from [89].](image-url)
It is also worth noting that, with respect to cellulose, calorimetric methods have proven less successful than mechanical measurements. Paes et al. [80], along with several other authors ([69, 97], were unable to confidently detect a glass transition using DSC. The work of Szczesniak et al. [49] is the exception, their studies yielding Tg versus moisture content data that fits well with that from other methods. Modulated DSC (MDSC) is able to separate out reversing heat flow events such as the glass transition from non-reversing heat flow events such as enthalpic relaxations and is thus ideally suited for measuring Tg. In spite of this, studies on cellulose have not yielded definitive results. Picker and Hoag [75] investigated dry microcrystalline cellulose (MCC) using MDSC and reported three transitions at 132, 159 and 184°C, although they did not heat the sample beyond 200°C. Using standard DSC they measured a Tg at 174°C but had to heat the sample at 60°C/min to increase the sensitivity to the point that a transition was detectable. Denham [69] also used MDSC, on samples of cotton, lyocell and viscose. Multiple transitions were noted, however these did not shift with changes in moisture content.

Several studies have measured Tg of cellulose as a function of moisture content, all showing the expected decrease in Tg with increasing moisture content. Ogiwara et al. [61] used an NMR technique on cotton fabric whereas Batzer and Kreibich [37] and Szczesniak et al. [49] both used DSC; Batzer working on cotton fabric and Szczesniak on MCC. Salmen and Back [98] measured the modulus of paper from kraft sack, neutral sulphite semi-chemical (NSSC) fluting medium and cotton linters as a function of temperature and moisture content. They used the inflection point in the declining modulus as a measure of Tg. Maxwell and Huson [66, 99] used an AFM indentation technique and Denham [69] used dynamic vapour sorption to determine the critical moisture content at which the Tg of cotton fibres was at room temperature. Other authors [15, 69] have pointed out that DSC freezing curves of cellulose/water, and the fact that water crystallization is hindered below the Tg of the cellulose, can be used to estimate values for the temperature/moisture content associated with the glass transition. Denham [69] has employed this method using data from studies on cotton yarn [84], cotton fibre [69] and MCC [76]. In spite of using different techniques and different cellulose samples these results all follow the same trend; the data being reasonably modelled by the Fox equation for a sample containing 75% crystalline material, and using a value of 220°C for the Tg of dry cellulose and a value of -137°C for the Tg of pure water [100] (Figure 10). Note that Batzer and Kreibich [37] do not fully define what is meant by water content and report values for water content greater than the generally accepted maximum value of 15-20% for cellulose, thus these data points need to be treated with caution. The DMA results of Paes et al. [80] as well as the torsional pendulum data of Tokita [101] and the DMA data of Denham [69] are shifted to higher temperature. For the results of Paes et al. [80] this is most likely due to the fact that they worked on ball milled Eucalyptus cellulose with a measured crystallinity of <6%, and in fact their data is well modelled by the Fox equation assuming 10% crystallinity. Denham’s data is on regenerated cellulose which is likely to have a lower level of crystallinity than cotton or MCC. Tokita [101] also worked on regenerated cellulose, however using acid hydrolysis he measured the crystallinity at 72%, thus his results are less easily explained. The DMA results obtained by Denham [69] on cotton are also shifted slightly to higher temperature, particularly under more moist conditions. Results on Lyocell, a regenerated cellulose expected to have lower crystallinity, coincide well with the data from Paes et al. [80].
The glass transition temperature of cotton

Figure 11: Literature data for Tg as a function of moisture content for a range of cellulose samples measured by a variety of techniques. Symbol colours represent different authors/cellulose type as depicted in the legend. Symbol shapes represent different techniques; DSC (×), DMA (◇, ◆), NMR (▲), SPM indentation (●), DVS (□, ■) and freezing point (+). Roman numerals in the legend indicate the definition used for Tg measurement as shown in Figures 8 & 9. Lines show the predicted value calculated by the Fox equation for 75% (green) and 25% (blue) crystallinity using a value of 220°C for dry cellulose [86] and a value of -137°C for pure water [100]. *Hydrolysed **Ball milled.

The results detailed above are a clear indication that cotton has a glass transition temperature, albeit one that is extremely difficult to measure. The difficulties of measurement arise mainly because of the high levels of crystallinity, further exacerbated by the fibrous (bulky) nature of the material which makes thermal conduction difficult. There is clear evidence that, as expected, the Tg of unmodified cotton decreases with increasing moisture content; the data being reasonably modelled by the Fox equation for a sample containing 75% crystalline material and using a value of 220°C for the Tg of dry cellulose. For modified cotton and other cellulose materials, for a given sample moisture content, the Tg is shifted to higher temperatures as a result of the decreased crystalline content. The processing of cotton involves several steps that involve physical manipulation of the fibres, resulting in the application of stress and the possibility of fibre breakage. It is common knowledge that, in order to maximise the fibre quality, there are optimum moisture levels for these processes [9]. This dependence on moisture is most likely due to the fact that mechanical properties are being manipulated by adjusting Tg. Research into the optimum moisture levels has been carried out for picking [102, 103], ginning [104-106], carding [107] and spinning [108], however no attempt has been made as yet to try to link this work to the glass transition temperature.
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