Investigation into the Humidity Dependence Glass Transition of Cellulosic Fibres

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Abstract

The glass transition temperature at different relative humidity for cotton, lyocell and viscose fibres was investigated by Differential Scanning Calorimetric (DSC) technique. The relationship between glass transition temperature and moisture content of the materials was investigated by using the Fox -equation. It was observed and concluded that, the Fox-equation can be used to determine non-water-accessible fraction in materials, which may be equal to crystalline fraction. Taking into account crystallinity effects in cellulosic materials, the Fox- equation can well be used for quantifying the relationship between glass transition temperature and moisture content for all materials. It was found that, the glass transition of each of the investigated material in dry state was above 200°C.

Furthermore, investigations were carried out to compare the performance of large volume stainless steel pans with low volume aluminium pans used for holding the samples. It was observed that, the aluminium pans give a better heat signal, besides lower costs, when compared to large volume stainless steel pans. The challenges related to the use of the two types of pan and ways to overcome the challenges has been recommended.

Key words: cellulose, glass transition, fox theory

1 Introduction

The ability of textile material to deliver comfort is partly contributed by the moisture sorption of the textiles. However as the amount of moisture taken up by the material increases the glass transition of the fibres gets depressed. At the glass transition temperature, the amorphous polymer changes from a hard glassy form into a rubber-like plastic form or to a viscous fluid. This change is due to an onset of certain degree of movement of polymer chains. The movement of polymer chains are explained by the volume not occupied by the molecules (free) volume of the polymer (Salme'n & Back, 1977).

The glass transition temperature is dependent on the time scale of the experiment and the method used to measure the glass transition (Salme'n & Back, 1977). Although the effect of water on glass transition is only realised in the amorphous fraction of the material, the supramolecular properties of the fibres may influence the softening effects of water hence the determination of the glass transition temperature (Salme'n & Back, 1977). The moisture dependence glass transition of wool and human hair has been investigated and was reported to follow the Fox theory (Wortmann, 2006). Previous work on the effects of water on glass transition of cellulosic material have mainly concentrated on wood fibres, cotton and carboxy methyl cellulose. This work investigated into the effect of relative humidity on the glass transition of cotton, lyocell and viscose fibres. The selected fibres are well known to deliver outstanding comfort due to their ability to store substantial amount of water at equilibrium conditions. The understanding of the variation of moisture content of the fibres with the glass transition temperature is important for the prediction of how various finishes applied in the fibres will respond to the variation in relative humidity incidental to the garment usage

Nature and processes that are used to manufacture textiles fibres affect the supermolecular properties of the resultant fibres hence the ability of the fibres to hold water/ moisture under equilibrium conditions (Koh et al., 2005). For instance the properties of cotton fibres are influenced by the environment and conditions during the fibre growth. Unlike viscose and lyocell, cotton fibres have highest degree of crystallinity and modulus but lowest moisture sorption capacity. The viscose fibres are regenerated by chemical derivation of wood pulp by converting the cellulose into cellulose xanthate, solubilisation into sodium hydroxide and finally generate the fibres in the bath of sulphuric acid. The process of making viscose fibres causes the degradation of the cellulose due to drastic chemical conditions used for conversion of the wood pulp into fibres. Lyocell fibres are regenerated by physical dissolution of wood pulp in an environmentally friendly solvent known as N-methyl-n-morpholine oxide, dry spinning of the dope and then reconstitute the fibres in a suitable solvent (Woodings, 1995). Research in the field of cellulose science has revealed other feed stock sources for the lyocell process (Brito, et al., 2012; Haule, Carr, & Rigout, 2015; Xu, Lu, & Tang, 2007) and this demonstrates the importance of the lyocell fibres in the textile and fashion industry. The lyocell fibres are prone to fibrillation due to high degree of oriented with weak inter fibrillar forces (Fink et al., 2001; Klemm et al., 2005).

This work presents the humidity dependency glass transition of the lyocell, viscose and cotton fibres as described by the modified Foxy theory.

The Fox theory, as reviewed by Wortmann (Wortmann, 2006; Hancock & Zografi, 1994) defines the glass transition temperature of polymer-plasticizer system as;

$$\frac{1}{Tg,sys} = \frac{W1}{Tg1} + \frac{W2}{Tg2} \quad \text{---------- 1}$$

Where *Tg* and *W* are the glass transition temperature and the weight fraction, respectively, and subscripts *sys*, *1* and *2* stands for polymer blend, solvent and polymer respectively. The theory assumes intimate mixing between water and polymer and hence no polar effects. This means that, the extent by which the glass transition is depressed depends on the glass transition difference between water and polymer and not on any other specific interaction.

Furthermore the work discusses the suitability of the aluminium capsules against the traditional stainless steel capsules for DSC experiments of fibrous material

2 Material and Methods

2.1 Material

The cellulose fibres (Cotton, Viscose and Lyocell) were supplied by Lenzing AG.

2.2 Conditioning of Samples

To avoid hysteresis effects, it was decided that equilibrium is achieved by initially drying at least 200mg of each material over phosphorous pentoxide in a desiccator for at least 24 hours. Samples at different relative humidity were obtained by conditioning the pre-dried samples over saturated salt solutions for five days as recommended in the literature (Young, 1967). The saturated salt solutions were prepared in accordance to the literature recommendations (Lewis, 1977; O'Brien, 1948). From the pre-dried material, two parallel samples were taken to the conditioning chamber. The first sample was used for the determination of water content, and the second sample for the determination of the glass transition temperature. The samples for the glass transition temperature were weighed prior to conditioning whereas the sample for determination of water content was not weighed. The samples were stored in the conditioning desiccators for five days so that they equilibrate at the intended relative humidity.

2.3 Estimation of Water Content

Water content of the conditioned samples was determined by gravimetric method where by a weighing balance was used. Samples weighing 50mg were contained in an oven-pre dried sample holder and then dried in an oven at 110°C for 2 hours. Upon cooling the

samples were re-weighed and allowed to cool in desiccators containing phosphorus pentoxide. The weighing of the dried sample was done immediately and quickly so as to minimise any chances of moisture sorption by the sample during the weighing process. Finally the water content of the sample was calculated a ratio of sample weight loss to the weight of conditioned sample expressed as a percentage.

2.4 Determination of the Glass Transition Temperature

Differential Scanning Calorimetry (DSC) was conducted to Cotton, Viscose and Lyocell fibres using a calibrated DSC Q100 module DSC Standard Cell FC version 9.9. The machine is a Power compensated DSC cooled by liquid nitrogen flowing at 50mL/min. The machine utilises universal analysis 2000 software. The equipment was calibrated using high purity Indium and Sapphire.

The fibres were cut into snippets of 1-4mm length. The weight of samples used was on a dry basis. From the pre-dried material, a sample of 5-10mg was weighed prior to conditioning at different relative humidity. Two types of pans were used for holding the samples, stainless steel pans and aluminium pans with capacities of 60µL and 40µL respectively.

In order to ensure no moisture variation in the samples during the determination of the glass transition temperature, the sample was covered by 10-15µL silicone oil as recommended in the literature (Wortmann, 2006; Rieger, 1996) and then hermetically sealed.

2.4.1 Scanning Parameters

The samples were scanned by cyclic heating at a rate of 10K/min from 0°C-150°C as recommended in the literature (Rieger, 1996; Wunderlich, 2005). Three cycles were conducted per sample in order to avoid sub-endotherm due to enthalpy relaxation hence only second and third scan were considered for the determination of glass transition temperature.

2.5 Data Analysis

Universal analysis 2000 software was used to determine the glass transition temperature at various relative humidity and water content. The Foxy equation was then fitted into the experimental data, Microsoft excel SOLVER software assisted on getting the corrected theoretical values at the minimum sum of square residues which would provide a theoretical relationship between glass transition and water content of the cotton, lyocell and viscose fibres.

3 Results and discussion

3.1 DSC Performance of Stainless Steel and Aluminium Pans

Both types of pans were used only for 50%, 32.9% and 22.8% relative humidity samples and the results from the two different types of pans are compared. The aluminium pans were not able to seal fibres of more than 8mg. The stainless steel pans were able to accommodate samples of 10mg for all types of materials.

The thermal scanning for all materials was carried cyclically in the temperature range 0°C to 150°C. It was found that both types of pan endured this temperature range. Neither the stainless steel nor the aluminium pan failed at the selected heating temperatures. Large volume stainless steel pans were able to accommodate larger samples than aluminium pans. It was found that, the sealing of stainless steel pans was easier and did not cause any damage of the shape of the capsule. Any damage or deformation of capsule shape may result in rejection of the sample during loading and the DSC test. Due to the size of the pan and shape of the cap, large volume stainless steel pans could accommodate snippets of 3-4mm. This is not recommended because longer snippets cause poor packing density, which can affect the strength of the signal during thermal analysis.

The aluminium pans are more ductile and smaller in volume than stainless steel pans. Sealing of the aluminium pan is done by a flat cap pressed over the pan. The cap and the pan are very ductile and very light. Great care is required to ensure that the flat cap well coincides with the pan; any misalignment may result in a deformed shape of the capsule after sealing. Since the DSC equipment operates with high precision, minor deformation of the sample capsule results in rejection of the sample. From the experiments carried out in aluminium pans, samples were more often rejected by the DSC equipment than the stainless steel pans. Even pans with un-deformed shapes were seen to fail during experiments. For instance, out of sixteen samples composed of 8 samples sealed in stainless steel pans and 8 samples sealed in aluminium pans, no sample was rejected by the DSC equipment from the stainless steel pans, whereas four samples were rejected from the aluminium pans. This is due to the shape of the aluminium pans. The pans have flat sealed tops with a diameter greater than that of its effective depth. This means that, the only part of the pan that can be held during sample picking is the top. With the three jaws of the sample picking arm, it is very difficult to grip the pan firmly and correctly. As a result, either the sample can fall away before taken into the furnace or may get positioned outside the required location in the furnace. Aluminium pans could not accept snippets of greater than 2mm length due to the small size of the pan as well as the type and shape of the sealing cap. Since the cap is flat and if it happens that a fibre is clamped in the cap, sealing will be poor. This may result in heat and mass loss during determination of the glass transition of the material. The ability of aluminium pans to accommodate relatively shorter snippets gives the advantage of high packing density of material in the capsule and hence better signal sensitivity when compared to large volume stainless steel pans.

In terms of signal sensitivity, it may be noted that not only the weight of the sample has an effect on signal sensitivity, but also the ratio of pan to sample weight. Despite the fact that stainless steel pans were able to contain more sample weight that aluminium pans, the signals from stainless steel pans were found to be weaker than the aluminium pans.

The poor signal from the use of large volume stainless steel pan compared to the aluminium pans may be due to the high pan to sample weight ratio. A sample of 10.3mg is contained in a stainless steel pan of 140mg; here the effect of pan tends to obscure the effect of sample itself during thermal analysis. When compared to 5.5mg of sample contained in aluminium pan of 40mg, the effect of pan is not as high as it would be for a stainless steel pan. Indeed the poor signal for large volume stainless steel pans may be resolved by increasing the weight of the sample in the pan. However the weight is restricted to pan volume.

In terms of cost, the large volume, high pressure stainless steel pans are rather expensive when compared to aluminium pans. The cost of one pan of stainless steel is approximated to be as high as 10 times the aluminium pan. Again it is important to think about the cost versus performance requirement associated with the two types of pans before making a decision on the pan to be used for the thermal analysis of the fibres.

3.2 Determination of the Relationship between glass Transition Temperature and Relative Humidity

In order to fit the Fox equation to the experimental data, the glass transition of amorphous solid water was considered to be 140K (an average value of what have been reported in the literature (D. Lourdin, Coignard, Bizot, & Colonna, 1997; Hancock & Zografi, 1994) The data fitting was done by SOLVER software, whereby the minimum sum of squares of residues was calculated and graphs plotted by Microsoft Excel. The model was initially tested for data obtained from each material without considering the crystallinity effect; none of the results obeyed the Fox theory. This means the amount of moisture taken up by the fibre is mainly absorbed in the amorphous regions. The amount of water adsorbed on the surface of crystalline region does not have plasticising effect to the cellulose material. Hence it is important to consider only water associated with amorphous regions, when studying the effect of moisture on glass transition of material.

3.3 Glass Transition Temperature of Cotton Fibres

With the SOLVER software, fitting of Fox equation into the data was possible only with the minimum sum of squares, an amorphous fraction of 0.32 was observed and the model fits well the experiment values, Figure 1, giving the glass transition of dry cotton

fibres as 472.4K. By getting the amorphous fraction of 0.32, implies that the cotton fibres may be considered to have a crystalline fraction of. 0.68 This crystallinity value for cotton agrees with the previously published data which were 0.63-0.79 (Segal et al., 1959) and 0.7-0.91 (Hessler & Power, 1954).

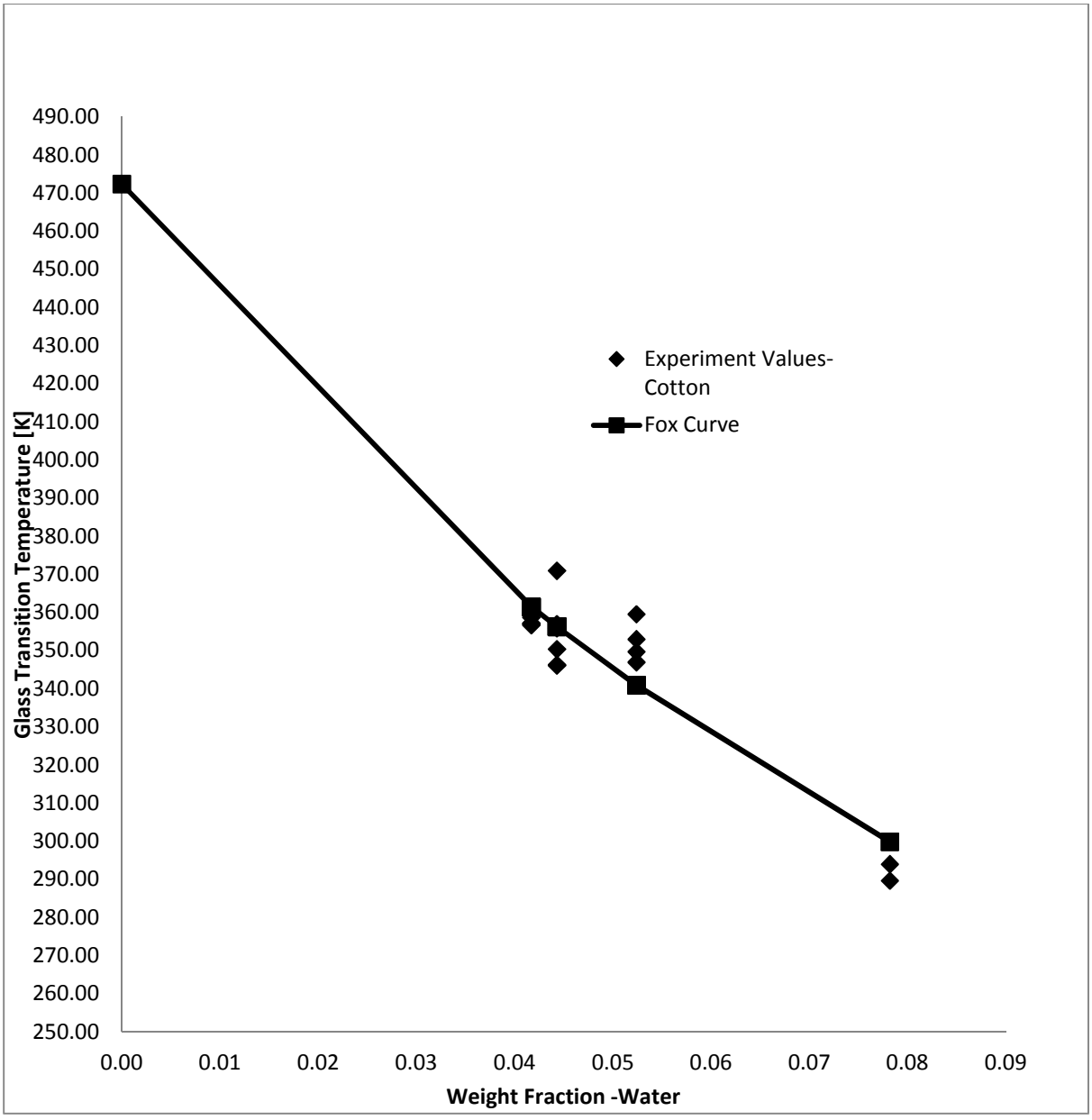


Figure 1: Glass transition of cotton fibres against water content for the cotton-water system

The effect of water on the glass transition of cotton was studied by Salmen et al., (Salme'n & Back, 1977), whereby, they studied the influence of water on the glass transition of cellulose material and modelled their results using Kaelbe's approach. Kaelbe defines the

plasticizer- glass transition relationship based on the lattice theory. By considering the crystallinity effect, Salmen (Salme'n & Back, 1977) analysed the experiment values assuming a crystallinity of 0.8. The glass transition of dry cotton was then determined and reported to be 493K. Other values have been published elsewhere (Batzer & Kreibich, 1981), where the glass transition of dry cotton was found to be 498K. Salmen et al,. (Salme'n & Back, 1980) investigated the effect of moisture and temperature on the mechanical properties of paper, such as the elastic modulus. They quantified the effect of moisture by estimating the glass transition temperature as the turning point with respect to temperature during tensile tests. A large reduction on the elastic mechanical moduli was experienced at the glass transition. The reduction in mechanical properties was found to be more pronounced in less crystalline material with higher water content. The reduction in mechanical properties was due to the plasticizing effect of water. Again the effect of crystallinity on the softening ability of water was clearly explained. They reported the degree of crystallinity of paper as 63% and the glass transition temperature of dry cellulose as between 165°C and 225°C, values which agree with what has been found in this work.

The agreement of the three different studies with the results of this study on the moisture dependent glass transition of cotton can be used as a confident proof of the applicability of the Fox theory on modelling the relationship between moisture content and glass transition of cotton, taking into account the crystallinity effect. Furthermore, the agreement of the crystallinity value of cotton obtained in this research with the literature values is an additional proof that, without taking consideration of crystallinity effect, the Fox equation cannot directly work for cellulose fibres.

3.4 Glass Transition Temperature of Viscose Fibres

From the SOLVER run, it was observed that the viscose fibres has an amorphous fraction of 0.48 (crystallinity 0.52) and the glass transition temperature for dry viscose is 594.5K. Two different researchers (Colom & Carrillo, 2002; Hessler & Power, 1954) investigated the crystallinity of viscose and each of them published the crystallinity to be 0.4-0.46 and 0.41, respectively which satisfactorily agree with the value observed on this research. Figure 2, presents the variation of the glass transition temperature of viscose fibres against water content, whereby the Fox model is tested against the experiment values. The model fits the data well. The shift of the glass transition to lower temperatures as the weight fraction of water increases is due to the plasticising effect of the water.

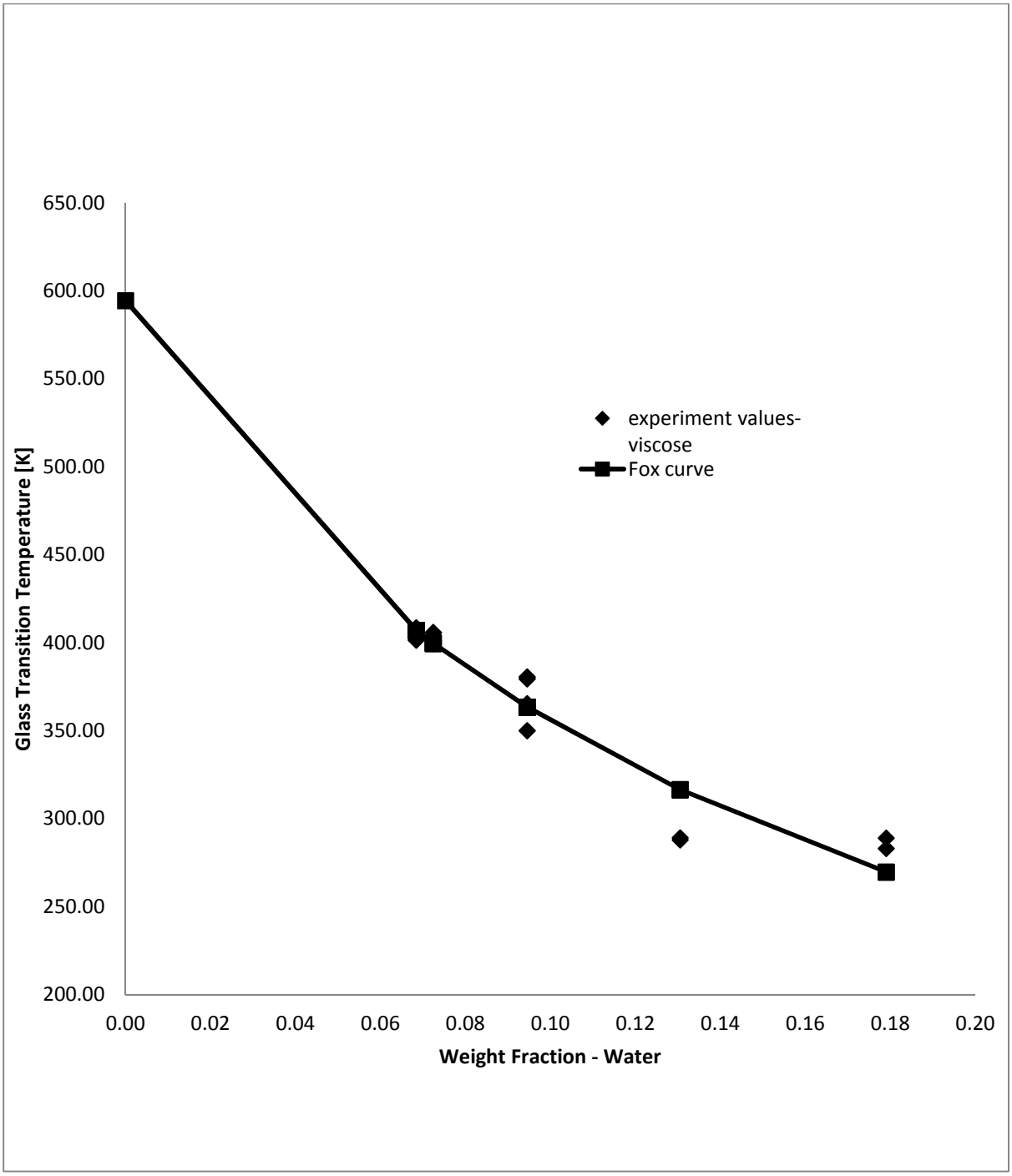


Figure 2. The glass transition temperature against water content for the viscose fibres-water system

Bryant et al., (1959) studied the effect of temperature on mechanical properties of viscose material in the wet and dry state. On measuring stiffness at different temperatures for wet and dry fibres, they observed that the swelling action of water resulted in a lowering of the glass transitions as well as the stiffness of the viscose fibres. They further established that the glass transition temperatures of dry viscose and cotton fibres are above 240°C, and below 0°C in the wet state. The lowering of the glass transition hence the stiffness of the fibres in wet state is explained by the plasticising effect of water. Wallenberger (1978) studied the

effect of absorbed water on the mechanical properties of different fibres. On comparing the strength and elastic modulus of viscose for a wet and a dried sample, it was found that viscose lost 50% of its strength in the wet state. It can be concluded that, the loss in strength in the wet state is due to the tendency of the polar hydroxyl groups in the amorphous regions to bond to water which in turn beak the hydrogen bond system holding the molecular chains of the cellulose together hence increase in molecular mobility. Thus only small amount of energy at relatively low temperature will be required to cause the change of the polymer from the glass to the rubbery state.

The good fit of the Fox model to the experiment data and the agreement with the results from other researchers, as indicated above, is evidence that the Fox theory can be applied for the prediction of the humidity-dependent glass transition of viscose fibres.

3.5 Glass Transition Temperature for Lyocell

The estimation of the humidity –dependent glass transition of Lyocell fibres by the Fox theory without taking into account the crystallinity effect was not successful. Even after considering the crystallinity effect, there was lack of fit of the model to experiment values, figure 3. When SOLVER software was applied, an amorphous fraction of 3 was recorded and is unexplained and this suggests further research on humidity dependence glass transition of lyocell fibres.

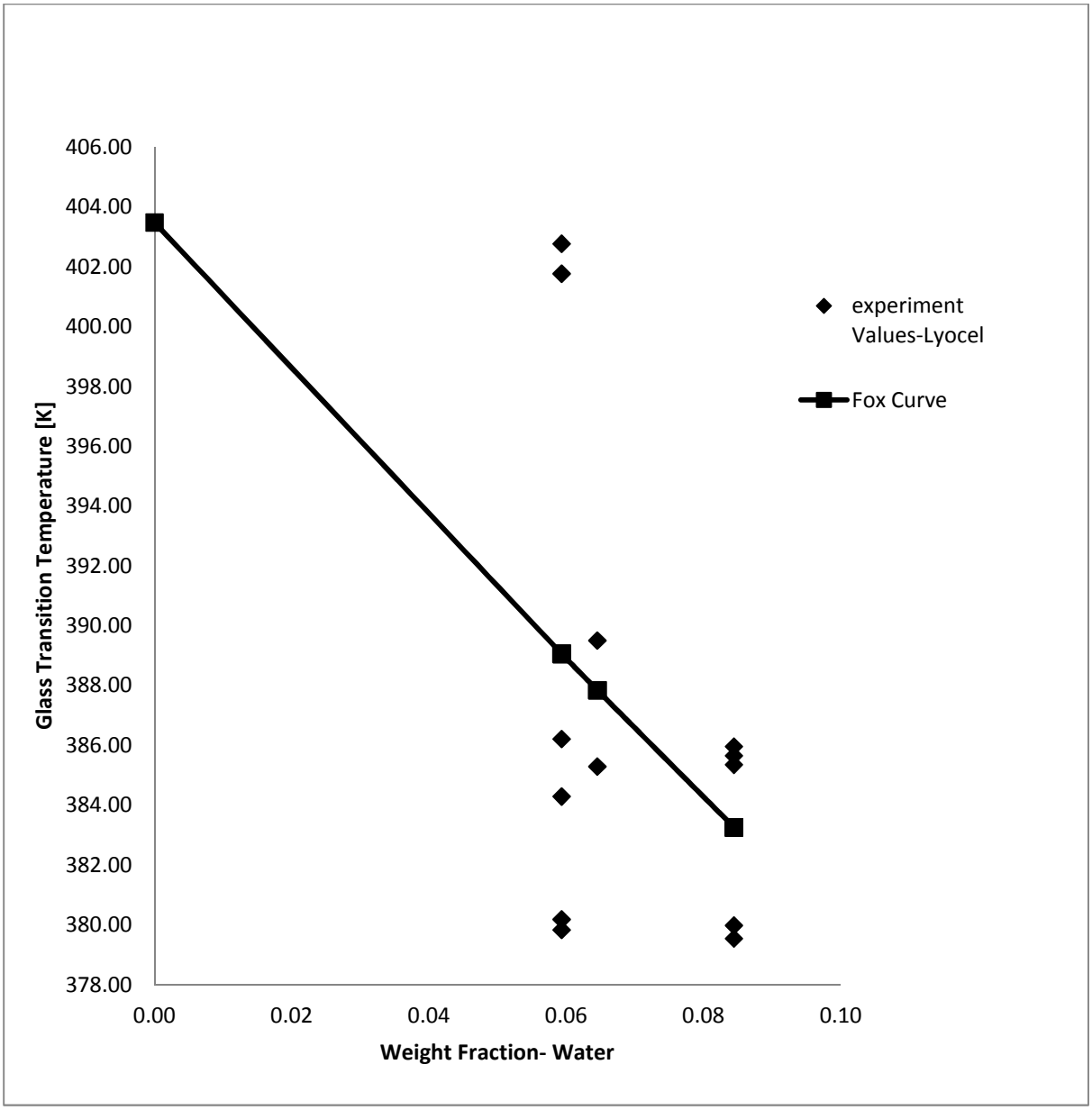


Figure 3. The glass transition temperature against water content for the lyocell fibres-water system

4 Conclusions and Recommendations

From the comparison of the applicability between large volume stainless steel pans and small volume aluminium pans, it can be concluded that, for better heat capacity signal and saving of costs, aluminium pans are better than large volume stainless steel pans for the thermal analysis of cellulose fibres. However, great care is needed during sealing of samples in order to avoid shape deformation of the aluminium capsules. Close monitoring is needed especially during taking the sample in to and out of the heating furnace as the DSC jaws do not support the aluminium capsule properly- there is the possibility of tilting the pan, which results in failure. In order to take advantage of better signal effects and low costs of

aluminium pans relative to large volume stainless steel pans, it is recommended that, the manufacturer improves the shape of the aluminium pans to suit the jaws of the DSC equipment.

For the Foxy equation to be used for prediction of glass transition of cellulosic material, a consideration should be taken into the crystallinity factors. The fit of the theoretical curve to the experimental data obtained from this research leads to the conclusion that, the Fox equation can be used to predict the glass transition and other mechanical properties of cellulose materials at a given moisture content/ relative humidity.

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