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Measuring the Heat of Wetting of Textile Fibres by Reaction Calorimetry

Abstract
The heat of wetting of regenerated cellulosic fibres (TENCEL®, Viscose and Modal) was investigated by reaction calorimetry in comparison with cotton, polyester and TENCEL® Fabric. Reaction calorimetry is a technique applied for measuring the heat evolved in chemical reactions where very high analytical precision is required. Before the measurements, the fibre samples were dried in an oven at 80 °C for 60 min with a low and constant nitrogen flow to eliminate initial moisture. As final results the amount of heat in Joules per gram fibre is given. The experimental results showed that the highest heat of wetting was measured for man–made cellulosic fibres, middle for cotton, while the lowest heat of wetting was observed for polyester fibres. The heat of wetting depends on the interaction of water with hydroxyl groups in the non–crystalline domains of the fibre. Finally, the results of the heat of wetting obtained by modern reaction calorimetry were compared with results obtained using a self–constructed solution calorimeter, as well as with data reported in earlier studies.

Key words: *man–made cellulosic fibres, sorption properties, heat of wetting, calorimetry.*

◼ Introduction

When a fibre absorbs water, heat is evolved. If liquid water is taken up, this is similar to the heat of solution that occurs, for instance, when sulphuric acid and water are mixed. It results from the interactive forces between the fibre molecules and water molecules. If water vapour is absorbed, there is also heat similar to the latent heat of condensation. The evolved heat may be expressed in various ways. The differential heat of sorption, Q (sometimes called heat of absorption), is the heat evolved when one gram of water is absorbed by the infinite mass of the material at a given moisture regain. It is expressed in joules per gram (of water absorbed). The water may be absorbed from water vapour to give value Q_v, or from liquid water to give value Q_l. The relation between these two quantities is illustrated in Figure 1. It follows from the First Law of Thermodynamics that the total heat evolved must be the same along each path, and therefore [1]:

$$Q_v = Q_l + L \qquad (1)$$

Where L is the latent heat of condensation of water in J/g at the temperature concerned.

Quantity Q_l is sometimes called heat of swelling.

The integral heat of sorption, W (called heat of wetting) is the heat evolved when a specimen of the material at a given regain, whose dry mass is one gram, is completely wetted. It is expressed in joules per gram (of dry material) and is almost always given in terms of absorption from the liquid state. Heat of wetting may be measured calorimetrically. A known mass of the material is placed in a calorimeter, and an excess of water is added. From the rise in temperature and the thermal capacity of the system, the heat evolved can be calculated. Because a large amount of water is needed to secure satisfactory wetting of the fibres, the temperature rise will be small and a careful experimental technique and sensitive temperature measurement are necessary. The differential heats of sorption, which are of more practical and theoretical importance, may be obtained from the experimental values of the heats of wetting or can be calculated from the adsorption isotherms (adsorption from different humidity levels).

As would be expected, heat of wetting is higher for the most absorbing fibres and is very small in non–hygroscopic fibres. The greater the moisture absorption of the fibre, the greater the amount of heat evolved [1].

A study dealing with heat of sorption measurements of man–made cellulosic
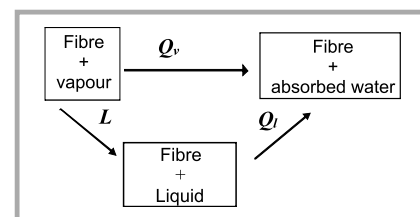
Figure 1. *Relation between heats of sorption from vapour and liquid [1] Qv - Ql, L.*

Table 1. *Used samples.*

Nr.	Sample	Specification	Supplier
1.	TENCEL®	1.3 dtex / 38 mm	Lenzing AG
2.	TENCEL® FILL	6.7 dtex / 60 mm Trilobal cross section	Lenzing AG
3.	Lenzing Viscose®	1.3 dtex / 38 mm	Lenzing AG
4.	Lenzing Modal®	1.3 dtex / 38 mm	Lenzing AG
5.	Cotton	1.69 dtex / bleached	n.d.
6.	Polyester	1.55 dtex / 38 mm (PET, no additives)	Tergal
7.	TENCEL® Fabric	Plain weave, weft and warp Nm 50 (1.3/38)	Lenzing AG

fibres by calorimetry showed that the heat of wetting is lineal depending on the percentage of amorphous regions [2]. Viscose Fibres showed the highest values followed by High Wet Strength Rayon, TENCEL® and Cotton Fibres.

Heat of wetting is an important property of material, not only as physical quantity- but also in textile physiology issues. To-day's speciality textiles, like medical textiles, have to fulfil higher requirements. It is exactly in this field that a high heat of wetting is of crucial importance.

Figure 2. *Reaction Calorimeter CPA202 [10], general view.*

Figure 3. *Scheme of the calorimeter reactor base [10].*

The ability to absorb water into the fibre structure is a common feature of all cellulosic fibres, is a prerequisite for "natural intelligence" and forms the basis of some very important physiological properties in applications of the textile. For cellulosic fibres the following eight physiological properties may be considered as important: absorbency of liquid water and water vapour, high heat capacity and heat buffering, cool feeling to the touch, active temperature reduction, warm and dry as an insulation layer, reduced static electricity, retarded bacterial growth and gentle feeling to the skin [3, 4].

A few well–known methods for the thermal analysis of the materials have been applied in our group to characterise man–made cellulosic fibres. These include conventional differential scanning calorimetry (DSC), temperature modulated DSC (TMDSC) and simultaneous DSC–TGA.

Using conventional DSC, the heat absorption of textile fibres can be measured during the process of heating, and the method is developed for the characterisation of the efficiency of duvet filling materials to buffer heat [5].

TMDSC is applied in material science for measuring heat capacities. As first trials, the specific heat capacity of TENCEL® fibres was measured at different water content levels. It was proven that the heat capacity of wet TENCEL® is higher than the sum of the heat capacity of dry cellulose and the heat capacity of water. These phenomena were first published in Nature [6] and proved by our TMDSC measurements [5].

Simultaneous DSC-TGA enables the measuring of evolved heat in Joules per gram fibres or the mole of adsorbed water when the fibres are exposed to water vapour stream. The results showed that there are three main groups: highly hygroscopic fibres showing the highest

heat of sorption based on fibre weight (TENCEL®, Viscose, Modal and Wool), Middle (Cotton and Polyamide) and Low (Polyester PET generally used for textiles) [7].

The primary objective of this work was to investigate the heat of wetting of man–made cellulosic fibres in comparison to cotton and polyester fibres by very accurate reaction calorimetry techniques and to compare the results obtained from a self–constructed solution calorimeter and literature data.

■ Experimental setup

Materials

Man–made cellulosic fibres (TENCEL®, Viscose and Modal) were supplied by Lenzing AG. All the fibres tested were without spinfinish. Polyester fibres were extracted with ethanol before the measurements to eliminate the influence of finishing agents. All the samples tested and their characteristics are summarized in Table 1.
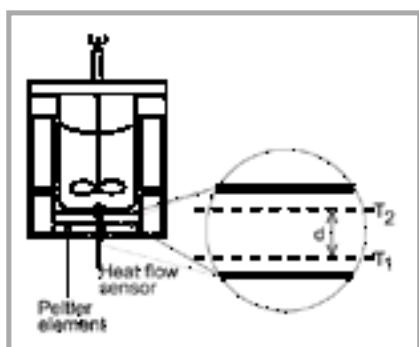
Methods

Reaction calorimetry

The reaction calorimeter (general view - Figure 2, scheme of the calorimeter reactor base - Figure 3) was built by ChemiSens AB in Lund, Sweden. It enables the measurement of the heat evolved dur-

Figure 4. *Batch injector of the calorimeter.*

Figure 5. *Sample holder (with fabric).*

ing chemical reactions , for instance, polymerisation [8, 9]. The instrument was also found to be suitable for measuring the heat evolved during physical reactions like the wetting of textile fibres.

The measuring chamber (Figure 1) of the instrument consists of a very sensitive heat flow sensor and Peltier element. The main heat flow sensor is installed between the reactor base and the Peltier element. The heat flow that is forced through the sensor will create a small temperature gradient difference. The thermal conductivity of the metals in the heat flow sensor is well known, and the heat flow can be calculated according to equation 2 [9]:

$$ \text{Heat Flow} = \lambda \cdot \frac{A}{d} \cdot (T_2 - T_1) \qquad (2) $$

where is: λ - specific heat conductivity in $Wm^{-1}K^{-1}$, A - the heat transfer area in m^2, d - heat flow sensor thickness in m.

The Peltier element used in this reactor is a pile of very efficient semiconductor thermo–couples arranged between two ceramic plates. When a current passes through such an element one side gets warm and one side gets cold. When the reactor needs cooling, the cold side of the Peltier element will absorb heat. If the direction of the current is reversed, the cold and hot side of the element will also be reversed, and the Peltier element will pump heat into the reactor. The Peltier element has nothing to do with the measuring principle, it is just a convenient way of controlling the temperature in a small reaction calorimeter.

To eliminate the initial moisture in the equipment and sample, the reactor cover with attached batch injector (Figure 4) was dried in a heating oven at 50 °C for 30 min. Approximately 1.5 g of the fibre sample was then weighted and placed into the sample holder of the batch injector (Figure 5). The reactor cover and batch injector with the enclosed sample were conditioned at 80 °C for 60 min in a heating oven with a small and constant flow (250 ml/min) of nitrogen gas passing through the fibre sample.

The reactor vessel was charged with 125 ml of water. This amount of water was necessary to completely surround the closed injector holding the sample. The assembled reactor was installed into the thermostating unit and the system

was started up. All experiments were conducted at 25 °C and under isothermal conditions. The same stirring speed of 300 r.p.m. was used for all experiments.

At thermal equilibrium, which was indicated by a stable baseline, the injector chamber was opened and the tempered fibre material enclosed was flushed by the circulating surrounding water. The fibre material was kept in place within the opened injector to prevent direct contact with the rotating stirrer.

The reaction calorimeter was connected to a computer so that the wetting process was monitored by the instrument's software. As a final result, the heat flow (W/g sample) was obtained. By integrating the heat flow over time, the amount of evolved heat in J/g by wetting the fibre sample is calculated.

Solution calorimeter

A solution calorimeter was constructed in the laboratory. It consists of a well insulated Dewar (content 1 l) which is equipped with a stirrer and temperature sensor (Figure 6). A plug in the top insulation can be pulled out to add water through the small hole in the subjacent Plexiglas lid.
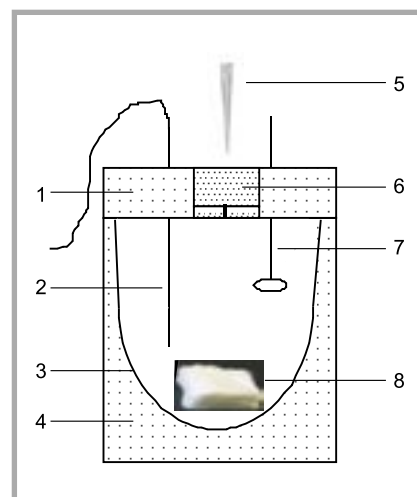
An Eppendorf pipette equipped with another temperature sensor is wholly immersed in a vigorously stirred, thermostat containing water.

Before starting the experiment, samples were placed in the Dewar, which was carefully closed. The stirrer was turned to a low setting and the system was left for 20 min to equilibrate. At the same time the water temperature in the thermostat was precisely adjusted to the temperature inside the Dewar. Then the desired amount of water was fast added . However, care should be taken to wet the sample evenly. All experiments were carried out in a conditioning chamber at 22 °C and RH=55%.

On the basis of the temperature rise in the calorimeter, the heat of wetting was

Figure 6. *Schematic illustration of a/the self–constructed solution calorimeter; 1 - plexiglas disk with small opening, 2 - temperature sensor, 3 - Dewar, 4 - insulation, 5 - eppendorf pipette, 6 - plug (insulating material), 7 - stirrer, 8 - sample (compressed sliver).*

calculated according to the known calorimetric equation [11]:

$$ Q_{fl} = \frac{\Delta T \cdot (m_{H_2O} c_{H_2O} + C_{cal} + m_{fibres} c_{fibres})}{m_{fibres}} \qquad (2) $$

where is: m_{H_2O} - mass of water added in g, c_{H_2O} - specific heat capacity of water in 4.184 $Jg^{-1}K^{-1}$, m_{fibres} - mass of fibres placed in calorimeter in g, c_{fibres} - specific heat capacity of fibres in $Jg^{-1}K^{-1}$, C_{cal} - heat capacity of calorimeter in JK^{-1}, ΔT - temperature rise in calorimeter after adding water to fibres in K.

In Table 2 the methods applied and the pre–conditioning temperature and time are summarised. Additionally, the results from the reaction calorimetry and self–constructed solution calorimetry were compared with the literature data.

■ Results and discussion

The results of the measuring of heat of wetting by reaction calorimetry are illustrated in Figure 7. The heat of wetting for regenerated cellulosic fibres TENCEL®, Viscose and Modal in comparison to cotton and polyester was measured.
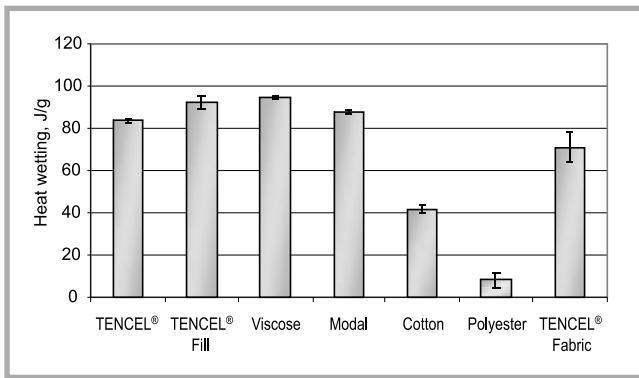
Table 2. *Applied methods for measuring the heat of wetting under sample preparation conditions.*

Method	Sample Preparation
Solution Calorimetry	Equilibration at 55% RH – 2 days
Reaction Calorimetry	Drying 80 °C 105 °C – 60 min
Literature Data (Solution Calorimetry)	Drying 50 °C – 5 days

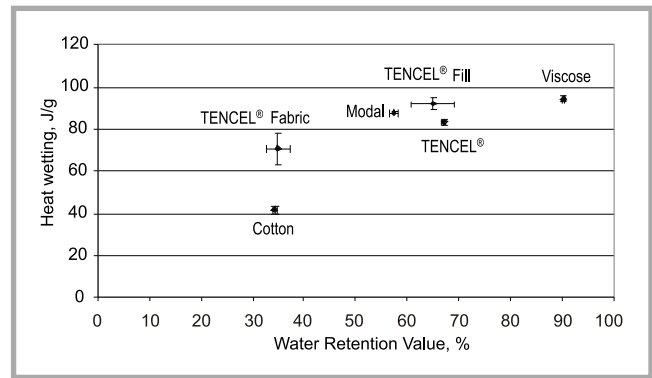**Figure 7.** *Reaction calorimetry measurements of textile fibres.*

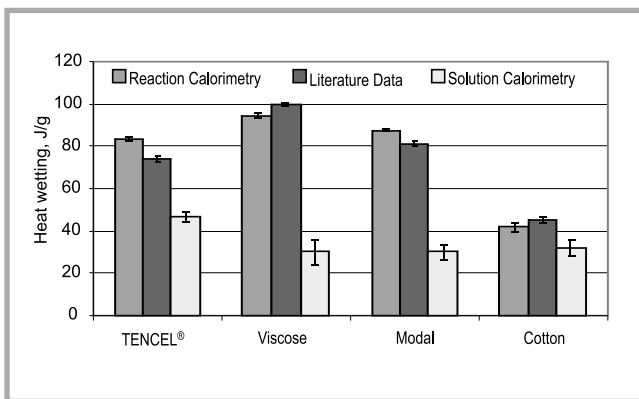**Figure 9.** *Heat of wetting versus water retention values of textiles.*

Figure 8. *Comparison of results from the reaction, solution calorimetry and literature data. Note that for the reaction calorimetry experiments and for literature data, the fibres were dry at the start of the experiment, whereas the solution calorimetry experiment was started from a relative humidity of 55%.*

TENCEL® fabric was also measured to see the influence of textile processing on the evolved heat.

The highest heat of wetting was measured for Viscose fibres. This result was expected since Viscose has the lowest crystallinity among other man–made cellulosic fibres, i.e. more available hydroxyl groups in the amorphous regions capable of binding water. After Viscose, follows TENCEL® Fill, Modal, standard TENCEL® and cotton fibres.

The lowest heat of wetting measured was for polyester fibres. The problem with the wetting of polyester fibres is the hydrophobic character of the fibre. These fibres were immersed twice into water to ensure better wetting of fibres.

Comparing the evolved heat for TENCEL® fibres and fabric, it can be noticed that fabric exhibits much lower evolved

Table 3. *Effect of fibre hornification on the evolved heat of TENCEL®.*

Drying Conditions	Heat of wetting, J/g
80 °C for 60 min	83.30 ± 1,01
105 °C for 60 min	75.30 ± 0,00

heat with high standard deviation between measurements.

In order to enable the processing of fibres into textiles they have to be treated with spinfinish. The most commonly used spinfinish chemicals are various paraffins or silicones. Due to their hydrophobic character, they block the hydroxyl groups of the cellulose molecules, providing lowered heat of wetting. Although the TENCEL® fabric was washed before the measurements, some spinfinish was still immanent on the fibres. Therefore, the TENCEL® fabric exhibits decreased heat of wetting compared to the single TENCEL® fibres. The next step was to compare the results obtained by reaction calorimetry with the self–constructed solution calorimetry results, which are shown in Figure 8.

The literature data are similar to the reaction calorimetric results: for Viscose and cotton fibres literature data for evolved heat are higher and for TENCEL® and Modal Fibres, the literature data are lower compared to our measurements.

The results obtained using solution calorimetry are significantly lower com-

pared to reaction calorimetry results. Since these samples were measured after equilibration at 55% RH for 2 days, the evolved heat values expected were lower.

Sorption heat is highest when the absorbing water bonds directly with the hydroxyl groups. This is so-called primary bound water. Attaching the second layer of water molecules (to the primary bound water), the evolved heat is lower. As absorption continues, the water is more loosely attached, and consequently less heat is evolved. Therefore, the evolved heat measured by solution calorimetry is actually the heat evolved when unbound water (also called free water) attaches to the primary and secondary bond water on the fibre molecules.

The self–constructed solution calorimetry method is also a very imprecise technique because any differences between different man–made cellulosic fibres were not discriminated. The standard deviation between each measurement was also very high, as can be seen in the Figure 7.

As a final investigation, the differences between the heats of wetting for fibres dried at 105 °C and dried at 80 °C were measured.

It is well known that high temperature causes the collapse of pores in cellulose, which cannot be opened even by the re-wetting of the fibres. This effect has been known for a long time as fibre hornification [12]. The TENCEL® fibres were subsequently dried at 105 °C and the evolved heat was measured by a reaction calorimeter. The results are summarized in Table 3. Pore collapse seems to be very

regular due to the absence of standard deviation between the measurements.

In the literature it is reported that the heat of wetting of man–made cellulosic fibres is linearly dependant on the water retention value (also called water regain). Our measurements show that this is not the case (Figure 9).

Heat of wetting is not simply proportional to the water retention value. This shows that the heat of wetting is not only related to the amount of water uptake by swelling, but to other factors, such as the amount of accessible hydroxyl groups of cellulose molecules, pore size distribution, the thermodynamic properties of the accessible inner fibre surface and the effects of textile construction.

Further investigation will be focused on the correlation of the evolved heat with the porosity of the fibres.

■ Conclusions

In this work the heat of wetting of TENCEL® man–made cellulosic fibres, Viscose and Modal cellulose fibres were measured using reaction calorimetry, and compared to that of cotton and polyester. This technique enables the measuring of evolved heat with high analytical precision. It was proven that the heat of wetting is highest for most hygroscopic fibres (Viscose, Modal and TENCEL®), middle for cotton and lowest for polyester. By this method the effect of fibre hornification after drying the samples at 105 °C was determined. Pores of the fibre collapse cannot be reopened by the wetting of the fibres, resulting in decreased evolved heat. The results obtained by solution calorimetry are not precise enough to detect differences between the types of man–made cellulosic fibres. These results differ a lot in comparison to reaction calorimetry results, due to different pre–conditioning of the samples. Finally, the study indicated that the heat of wetting depends not only on water retention values, but also on other properties of the fibre's pore system. This topic will be the subject of further research.

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