Short Communications

Sorption studies of modified cotton

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The sorption behaviour of esterified, formalized and grafted cotton fabrics has been studied. The pick-up of saline solutions by the unmodified and modified cottons has also been evaluated. It is observed that by esterification, formalization and grafting the hydrophilicity of cellulose decreases by crosslinking hydrophilic centres, making them less accessible for sorption of water and salt solution.

Keywords: Cotton fabrics, Esterification, Formalization, Grafting, Sorption behaviour

The presence of hydrophilic hydroxyl groups imparts water sorptivity and swellability to cellulosic materials. Esterification or acetylation of hydroxyl group reduces the capacity of modified cottons to sorb water and, therefore, affects its water swelling characteristics. The swellability and solubility of partially substituted esters crosslinked with formaldehyde were studied by Petropavlovskii et al. Rowland used several combinations of vinyl monomers for grafting onto fibres for modifying their hydrophilicity. Pavlyuchenko et al. observed that sorption of methanol by cellulose styrene graft copolymers or blends decreases with increasing styrene content, presumably owing to the building up of hydrophobic groups. The sorption of NaCl from aqueous and aqueous ethanol solutions increases with increasing ethanol concentration and is related to the donor-acceptor interaction between ions and OH group of alcohol. The correlation between sweat and clothing has been considered by Gwosdow et al. The present paper deals with the water sorption characteristics of some modified cotton fabrics.

Cotton fabrics used for studies were warp—40s Gaddag DCH-32 type, and weft—36s H-4 type. The fabrics were destarched by treating alternately with boiling water and cold water several times and dried.

In the case of formalization, the fabric was treated with polyvinyl alcohol, semidried and placed in a solution of paraformaldehyde and Na2CO3. The mass was heated under reflux and neutralized with hydrochloric acid. The fabric was then dried, placed in acetic anhydride and heated under reflux for 1 h after which it was washed and finally dried.

In the case of esterification, powdered acid anhydride or acid chloride was dissolved in dimethylformamide and the weighed fabric was soaked in it at a fixed temperature. Pyridine was added in the case of acid chloride treatment. The fabric was then washed and dried.

In the case of grafting, cotton fabrics were treated with acrylonitrile or acrylamide. The reduct initiators used were potassium persulphate and sodium bisulphite under acidic condition and iron (II) ammonium sulphate and hydrogen peroxide. The homopolymer was removed from the product.

The unmodified and modified cotton fabrics were conditioned at 25 ± 2°C and 50 ± 5% RH for 24 h in a standard atmosphere before testing. The fabrics were then cut into pieces weighing 1-2 g and the samples weighed accurately.

For determining the moisture content, the fabric sample was placed in an oven for 24 h at 90°C and weighed again. The moisture content (%) was calculated as follows:

\[ \text{Moisture content, } \% = \frac{W - W_i}{W} \times 100 \]

where \( W \) and \( W_i \) are the weights of the sample before and after oven drying respectively.

For determining the water sorption, the fabric sample was soaked in 100 ml distilled water for 24 h and then surface dried. The wet sample was first weighed (WAS) and then placed in an oven at 90°C for 24 h and again weighed (WDS). The experiment was repeated 2-3 times and the average value was determined. Water sorption was calculated as weight gain per g of dried fabric.

\[ \text{Water sorption} = \frac{\text{WAS} - \text{WDS}}{\text{WDS}} \]
For determining the sorption from salt solution, the fabric sample was placed in an oven at 95°C for 24 h and weighed. The dried fabric was soaked in 1% or 10% aqueous solution of sodium chloride for 24 h, surface dried under vacuum at room temperature and weighed (WAS). The swollen fabric was dried in an oven at 90-95°C for 24 h and weighed (WDS). It was then washed with water, dried and again weighed (WWD).

The moisture content and weights WAS, WDS and WWD are given in Table 1.

The cellulosic materials contain hydrophilic (OH, CH₂OH) groups. Hence, these materials sorb water and may swell. Decrease in hydrophilicity of cotton may decrease its degree of water sorption. Hydrophilicity of cellulose has been expressed as the equilibrium sorbed water content (a) at a given temperature (T) and relative humidity (ψ). Young and Nelson’s equations have been applied to the sorption of water vapour by cellulosic materials. Heat of wetting (ΔHf) of cellulosic materials is directly proportional to their surface area calculated from water vapour sorption isotherm. NMR studies showed that the molecular mobility of water sorbed by hemicellulose increased with increasing moisture content. Recently, the determination of water value by textiles and the relation of sweat to skin wettedness have been reported by McDowell et al. and Gwosdow et al. respectively. Sweat is a saline solution with about 5% salt concentration under normal conditions. Hence, it was imperative to investigate water and salt sorption by unmodified and modified cotton fabrics from water and 1% and 10% solutions. The values of salt up-take and water sorption per g of dried fabrics were obtained by using the following relationships:

$$\text{Salt up-take} = \frac{\text{WDS} - \text{WWD}}{\text{WWD}}$$

$$\text{Water sorption} = \frac{\text{WAS} - \text{WDS}}{\text{WDS}}$$

Table 1 shows that in the case of untreated cotton fabrics, the moisture content is about 6.8% and water sorption increases with increase in salt conc. in the solution. In the case of CVPn fabrics, the moisture content increases to 7.6% and water sorption and salt up-take increase with increase in salt conc. in the solution.

Fig. 1 shows the plots of salt up-take vs. NaCl conc. in solution for the untreated and CVPn fabrics. It is observed from Fig. 1 and Table 1 that

<table>
<thead>
<tr>
<th>Product</th>
<th>Moisture content %</th>
<th>NaCl in solution %</th>
<th>Weight, g</th>
<th>Salt up-take g per g of dried fabric</th>
<th>Water sorption g per g of dried fabric</th>
</tr>
</thead>
<tbody>
<tr>
<td>Untreated fabric</td>
<td>6.6</td>
<td>0</td>
<td>2.610</td>
<td>-</td>
<td>1.462</td>
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<tr>
<td></td>
<td>7.0</td>
<td>1</td>
<td>2.633</td>
<td>0.945</td>
<td>0.070</td>
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<tr>
<td></td>
<td>6.7</td>
<td>10</td>
<td>2.925</td>
<td>0.965</td>
<td>0.221</td>
</tr>
<tr>
<td>CVPn</td>
<td>7.7</td>
<td>0</td>
<td>1.053</td>
<td>-</td>
<td>1.410</td>
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<tr>
<td></td>
<td>7.4</td>
<td>1</td>
<td>3.630</td>
<td>1.337</td>
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<tr>
<td></td>
<td>7.6</td>
<td>10</td>
<td>2.928</td>
<td>0.978</td>
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<td>Csab2</td>
<td>4.4</td>
<td>10</td>
<td>1.870</td>
<td>0.765</td>
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<td>Csbc</td>
<td>5.0</td>
<td>10</td>
<td>1.909</td>
<td>0.719</td>
<td>0.210</td>
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<tr>
<td>K-An-g-C-1</td>
<td>7.9</td>
<td>10</td>
<td>2.758</td>
<td>0.937</td>
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<tr>
<td>F-An-g-C-1</td>
<td>7.3</td>
<td>10</td>
<td>2.601</td>
<td>0.992</td>
<td>0.171</td>
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<tr>
<td>K-Aa-g-C-2</td>
<td>9.1</td>
<td>10</td>
<td>2.665</td>
<td>0.977</td>
<td>0.170</td>
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<tr>
<td>F-Aa-g-C-2</td>
<td>10.5</td>
<td>10</td>
<td>2.788</td>
<td>0.989</td>
<td>0.190</td>
</tr>
</tbody>
</table>

*Salt up-take, ± 0.02 g

K – Potassium persulphate initiator
An – Acrylonitrile
g – Grafting
C – Cotton fabric
F – Ferrous ammonium sulphate + H₂O₂ initiator
Aa – Acrylamide

V – Polyvinyl alcohol
P – Paraformaldehyde
n – Acetic anhydride
sb – Sebacic anhydride
sbc – Sebacoyl chloride
Salt up-take and water sorption of CVnP fabrics are lower than those of untreated fabrics for the same salt concentration. These results indicate that formalization lowers the hydrophilicity by crosslinking hydrophilic centres, making them less accessible for sorption.

In the case of esterified fabrics Csb-2 and Csbc, the moisture content decreases to 4-5% and 5% respectively (Table 1). Water sorption and salt up-take of Csb-2 and Csbc fabrics are also lower than those of untreated fabrics for 10% NaCl. These results indicate that the hydrophilicity of cellulose decreases by esterification.

In the case of grafted fabrics (K-An-g-C-1, F-An-g-C-1, K-Aa-g-C-2 and F-Aa-g-C-2), the moisture content increases up to 7.3-10.5% (Table 1). Water sorption and salt up-take of the grafted fabrics are also lower than those of the untreated fabrics for 10% NaCl. These results indicate that the hydrophobicity of the cotton fabrics increases due to grafting.

If the salt up-take and water sorption by the modified fabrics from 10% NaCl solution are compared, it is observed that the values of salt up-take increase in the order K-Aa-g-C-2 < F-An-g-C-1 < K-An-g-C-1 < Csb-2 < F-Aa-g-C-2 < CVnP < Csbc < untreated, and the values of water sorption increase in the order Csb-2 < Csbc < F-An-g-C-1 < K-Aa-g-C-2 < F-Aa-g-C-2 < K-An-g-C-1 < CVnP < untreated. The results can be generalized in terms of modification of fabrics as:

(i) Salt up-take: Grafting < formalization < esterification < untreated

(ii) Water sorption: Esterification < grafting < formalization < untreated.

The water sorption in cellulose block graft polymers has been related to the crystallinity of blocks, block size, etc. Water sorption is generally considered a property of the less ordered region of cotton fibres, as crystallite regions are relatively less accessible. Esterification, formalization and grafting, in general, are expected to lower hydrophilicity by crosslinking hydrophilic centres, making them less accessible for sorption. Hence, generally for both water sorption and salt up-take (for low concentration in solutions) one may expect modified cotton to sorb less than natural cotton.

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References