Water Soluble Cellulose Acetate and Its Application

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Qualitative filter grade cellulose was acetylated using acetic anhydride and sulphuric acid, and the product was hydrolysed with dilute acetic acid using sulphuric acid or sodium acetate as the catalyst for hydrolysis. The acetyl content decreased continuously on increasing the duration of hydrolysis with sulphuric acid as the catalyst. The product was initially soluble in acetone, the solubility decreasing with decrease in acetyl content, and the product finally becoming insoluble. However, with acetyl content in the range 18-20%, the product became water soluble. On increasing the temperature of hydrolysis, the rate of hydrolysis increased. The system with sodium acetate as the catalyst for hydrolysis showed the same trend. However, the water soluble product could not be obtained with sodium acetate as the catalyst. The water soluble product was evaluated for application as a size for cotton yarns and the results were compared with those for starch and polyvinyl alcohol. In general, water-soluble cellulose acetate had tensile and flex abrasion properties intermediate between those of starch and polyvinyl alcohol. However, its ease of removal by water treatment is highest of the three sizes.

The reaction of acetic anhydride with cellulosic hydroxyl groups in the presence of acetic acid, using sulphuric acid as the catalyst, gives rise to cellulose triacetate. In the initial stages, the product is nearly completely substituted cellulose acetate. Through judicious use of water (in the form of dilute acetic acid), the degree of substitution (DS) can be lowered. The hydrolysis, depending upon DS, gives a wide range of substituted products. The hydrolysis is influenced by the duration and temperature of reaction, rate of addition of water$^1$ and the presence and quantity of the hydrolytic catalyst (sulphuric acid)$^2$. The aim of the present study was to study the effect of sulphuric acid and sodium acetate as hydrolytic catalysts on the production of cellulose acetate. The solubility of different products has also been evaluated. A water-soluble product synthesized can be used as a cheap sizing material.

Materials and Methods

Filter paper having DP of about 600 (determined by cuprammonium viscosity method) was used. Acetic anhydride, acetic acid, sulphuric acid, acetone and 2-methoxyethanol (AR grade) were used as such. Starch and PVA were purified before use.

Preparation of cellulose acetate—To 50 g filter paper taken in a 500 ml beaker, 300 ml acetylating mixture (acetic anhydride-acetic acid-sulphuric acid) was added at 30°C under vigorous stirring. Within 2 hr, a homogeneous product was obtained. A small amount of the product was taken out from time to time to test its solubility in chloroform. Within 4 hr, a chloroform-soluble product was obtained$^3$.

Acetic acid (60%, soln vol/vol.; 100 ml) was then added to the flask and the hydrolysis was allowed to take place at the same temperature. When an acetone-soluble product had been formed, the heating was stopped. The acetone soluble secondary cellulose was then precipitated through the addition of a large amount of water under continuous stirring. The reaction was over within 8 hr. The product was dried under vacuum.

Hydrolysis—Cellulose acetate formed as above was used for hydrolysis$^4$. The sample (50 g) was dissolved in 200 ml acetic acid (85%) containing sulphuric acid or sodium acetate by continuous stirring for 4 hr at room temperature. This dissolved material was transferred to a three-necked flask equipped with a stirrer, and the temperature was raised to 60°C. The material was taken out from time to time and tested for its solubility; its acetyl content was also determined. The reaction was stopped as soon as a water-soluble and acetone-insoluble product was obtained.

To isolate the above product, excess of acetone was added to precipitate the water-soluble cellulose acetate; it was washed to remove traces of acetic acid. The acetyl content of the products at various stages of the reaction was determined by the method reported earlier$^5$.

Preparation of sizing solutions—Three sizing materials—starch, polyvinyl alcohol and water-soluble cellulose acetate—were used for preparing sizing solutions. Starch and polyvinyl alcohol solutions of 2 and 4% concentrations were prepared. A 4% solution of cellulose acetate in water was also prepared.

Hank preparation—A hank of 120 rounds was prepared for carrying out various tests. The hank was kept in all the five solutions for 5 min. It was kept
rotating using rods as is done in laboratory hank dyeing. Finally, it was passed through rollers of the padding mangle at a constant pressure. The squeeze was found to be 50%. The products were then dried.

Tests—The characteristics of cotton yarn sized with different sizing materials (cellulose acetate, PVA and starch) were evaluated.

Mechanical properties were determined using an Instron-ModeIII12, with the following setting: Gauge length, 5 cm; jaw speed, 5 cm/min; and chart speed, 5 cm/min.

Flex abrasion tester was used to determine flex abrasion. The head load was kept at 15 lb and a tension load of 4 lb was applied. The yarn samples were prepared using 15 threads for each test. The 15 threads were laid straight and parallel to one another, giving an appearance of a narrow strip of fabric.

Ubbelhode viscometer was used to determine the viscosities of various sizing materials. The flow time for the solution and the appropriate solvent was determined.

The properly sized and weighed samples were compared for the ease of removal of the sizing material. Each of the five samples was washed in 200-ml distilled water in a 500-ml beaker heated to 60°C. Washing was done for 10 min. The washed samples were dried and reweighed to find out the loss in weight. The percentage removal of the size was calculated.

Results and Discussion

Cellulose acetate prepared by the method described showed an acetyl content of 41.4% (equivalent to DS = 2.8). This cellulose acetate was used for further studies.

Effect of duration and temperature of reaction on the hydrolysis of cellulose acetate with sulphuric acid as catalyst—Cellulose acetate of 41.4% acetyl content was hydrolyzed in a mixture containing glacial acetic acid and water (15% of the volume of the hydrolysing mixture), in the presence of 3% sulphuric acid, with material-liquor ratio 1:4 at three different temperatures for different durations. The results are presented in Table 1. It is seen that on increasing the duration of hydrolysis, the acetyl content decreases continuously. Increase in the rate of hydrolysis with increase in temperature has been reported by earlier workers also. However, the cellulose acetate becomes more susceptible to degradation with decrease in acetyl content. For this reason, a lower temperature and a longer duration will ensure chances of less degradation and will also give rise to a more uniform product. Keeping this in view, a temperature of 30°C is preferable to a higher temperature.

There is a continuous decrease in solubility with decrease in acetyl content. This can be ascribed to the more irregular structure of the cellulose derivative to that of pure cellulose or cellulose triacetate. It is obvious from Table 1 that the product remains soluble in acetone up to about 40% acetyl content and beyond this it becomes insoluble in acetone. However, with increase in temperature, insolubility appears at a slightly lower acetyl content. The acetone-insoluble product becomes soluble in 2-methoxyethanol up to an acetyl content of 30% with hydrolysis temperature 50°C and up to 27% with hydrolysis temperature 60°C. The acetone-insoluble product obtained at 30°C is, however, not soluble in 2-methoxyethanol. On further hydrolysis, the product remains insoluble until it attains an acetyl content of 18-19% (irrespective of the temperature of hydrolysis), when the product becomes water soluble. A patent mentions a similar product without giving details.

The water-soluble product must be quickly precipitated out with acetone to stop the hydrolysis at this stage; otherwise, further hydrolysis will render the product again insoluble in hydrophilic solvents like water.

Effect of duration and temperature of reaction on hydrolysis of cellulose acetate with sodium acetate as catalyst—Sulphuric acid acts not only as a catalyst for the hydrolysis reaction of cellulose acetate, but also as a degrading agent. If the reaction is carried out in the absence of a catalyst, completion of hydrolysis takes a long time. As mentioned earlier, a temperature of 30°C is more suitable than higher temperatures. A long duration is also favourable. Therefore, a mild catalyst,
sodium acetate (AcONa), has been used at three different concentrations for the hydrolysis reaction. The results are presented in Table 2.

On increasing sodium acetate concentration, the rate of hydrolysis increases, but the rate is always lower than that in the case of sulphuric acid-catalyzed reaction.

Though sodium acetate is capable of giving rise to decreased acetyl content, resulting in lower solubility in acetone followed by solubility in 2-methoxyethanol and ultimately an insoluble product (Table 3), it is incapable of giving rise to a water-soluble product. Sodium acetate, being a mild catalyst, lowers the rate of hydrolysis, and probably is not efficient enough to reduce the acetyl content to the level necessary for a water-soluble product (18-19%) under the experimental conditions.

Comparison of viscosity values and % add-on of different sizes—To evaluate the properties of watersoluble cellulose acetate (18-19% acetyl content), it was dissolved in water and used for sizing cotton hank. Similar experiments were conducted with starch and polyvinyl alcohol solutions. The results are presented in Table 3. It is seen that 2% starch and PVA solutions have higher viscosities than 4% cellulose acetate solution. However, these three solutions are capable of giving rise to more or less the same % add-on on the yarns. The evaluation (reported later) of the sized yarn can be compared only with that of yarn having similar % add-on. It is evident that cellulose acetate gives a much less viscous solution than other materials. It is important that the higher the viscosity, the lower is the rate of penetration into the yarn.

Table 2—Variation of Acetyl Content of Cellulose Acetate with the Duration of Hydrolysis at Different Concentrations of Sodium Acetate
(Material, Secondary cellulose acetate of 41.4% acetyl content; temperature, 30°C; water in hydrolysing mixture, 15%; material-liquor ratio, 1:4)

<table>
<thead>
<tr>
<th>NaOAc conc. g/litre</th>
<th>Duration hr</th>
<th>Acetyl content %</th>
<th>Solubility</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>60</td>
<td>40.2</td>
<td>Acetone soluble</td>
</tr>
<tr>
<td>&quot;</td>
<td>80</td>
<td>38.1</td>
<td>Acetone soluble</td>
</tr>
<tr>
<td>&quot;</td>
<td>100</td>
<td>34.4</td>
<td>Acetone soluble</td>
</tr>
<tr>
<td></td>
<td>130</td>
<td>26.6</td>
<td>2-Methoxyethanol soluble</td>
</tr>
<tr>
<td>15</td>
<td>60</td>
<td>40.2</td>
<td>Acetone soluble</td>
</tr>
<tr>
<td>&quot;</td>
<td>80</td>
<td>39.3</td>
<td>Acetone soluble</td>
</tr>
<tr>
<td>&quot;</td>
<td>100</td>
<td>35.9</td>
<td>Insoluble</td>
</tr>
<tr>
<td></td>
<td>130</td>
<td>29.3</td>
<td>2-Methoxyethanol soluble</td>
</tr>
<tr>
<td></td>
<td>150</td>
<td>26.4</td>
<td>Insoluble</td>
</tr>
<tr>
<td>50</td>
<td>60</td>
<td>40.2</td>
<td>Acetone soluble</td>
</tr>
<tr>
<td>&quot;</td>
<td>80</td>
<td>39.6</td>
<td>Acetone soluble</td>
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<tr>
<td>&quot;</td>
<td>100</td>
<td>38.9</td>
<td>Acetone soluble</td>
</tr>
<tr>
<td></td>
<td>130</td>
<td>37.3</td>
<td>Acetone soluble</td>
</tr>
<tr>
<td></td>
<td>150</td>
<td>35.0</td>
<td>Insoluble</td>
</tr>
</tbody>
</table>

Table 3—Comparison of Viscosity and % Add-on of Different Sizes
(Material, Cotton hank; count of yarn, 18; and duration of steeping, 5 min)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Specific viscosity ((\eta_\text{sp}/C)) of soln dl/g</th>
<th>Add-on %</th>
<th>Flex abrasion cycle to break</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unsized</td>
<td>2.80</td>
<td>6.3</td>
<td>13.25</td>
</tr>
<tr>
<td>2% Starch</td>
<td>1.69</td>
<td>6.1</td>
<td>19.50</td>
</tr>
<tr>
<td>4% Cell. Ac.</td>
<td>1.93</td>
<td>12.8</td>
<td>23.75</td>
</tr>
<tr>
<td>2% PVA</td>
<td>1.93</td>
<td>12.8</td>
<td>25.00</td>
</tr>
<tr>
<td>4% PVA</td>
<td>1.93</td>
<td>12.8</td>
<td>25.75</td>
</tr>
<tr>
<td>4% Cellulose acetate</td>
<td>1.93</td>
<td>12.8</td>
<td>20.75</td>
</tr>
</tbody>
</table>

*Non-measurable in an Ubbelhode viscometer.

Table 4—Mechanical Properties of Sized Cotton Yarns
(Count of yarn, 18)

<table>
<thead>
<tr>
<th>Size</th>
<th>Breaking load g</th>
<th>Elongation at break %</th>
<th>Initial modulus (g/m^2 \times 10^6)</th>
<th>Flex abrasion cycle to break</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unsized</td>
<td>463.70</td>
<td>9.50</td>
<td>29.6</td>
<td>13.25</td>
</tr>
<tr>
<td>2% Starch</td>
<td>648.90</td>
<td>9.16</td>
<td>37.0</td>
<td>19.50</td>
</tr>
<tr>
<td>4% Cell. Ac.</td>
<td>592.80</td>
<td>9.40</td>
<td>24.4</td>
<td>23.75</td>
</tr>
<tr>
<td>2% PVA</td>
<td>590.50</td>
<td>9.20</td>
<td>37.0</td>
<td>25.00</td>
</tr>
<tr>
<td>4% PVA</td>
<td>Only 2% solutions of starch and PVA gave approximately the same % add-on as in the case of 4% cellulose acetate solution. Therefore, the mechanical properties of only these three sized yarns (having similar % add-on) have been determined for comparative study.</td>
<td>25.75</td>
<td>20.75</td>
<td></td>
</tr>
</tbody>
</table>
Table 5 — Ease of Removal of Various Sizes
(Washing liquor used, water; temp. of washing liquor, 60 C; and duration of washing, 10 min)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Add-on removed (on the parent yarn)</th>
<th>Size removed %</th>
</tr>
</thead>
<tbody>
<tr>
<td>2% Starch</td>
<td>6.34</td>
<td>55.769</td>
</tr>
<tr>
<td>4% Starch</td>
<td>12.767</td>
<td>40.78</td>
</tr>
<tr>
<td>4% Water soluble Cell. Ac.</td>
<td>6.94</td>
<td>84.327</td>
</tr>
<tr>
<td>2% PVA</td>
<td>6.077</td>
<td>40.5</td>
</tr>
<tr>
<td>4% PVA</td>
<td>12.26</td>
<td>36.74</td>
</tr>
</tbody>
</table>

removed easily as compared to the other sizes. In fact, about twice the amount of size is removed in the case of cellulose acetate-sized yarns compared to the other sized material treated under similar conditions. Hence, this material has an advantage over other size materials.

References
5 Interlaboratory study on determination of acetyl in cellulose acetate, Analit Chem, 24 (1952) 400.
7 Fordyce C R, Chem Abstr, 32 (1938) 8777.