Wrinkle Recovery and Tensile Strength of Jute-based Fabrics Modified by Treatment with N-Methylol System: Part II — Effect of Treatment in Presence of Acid Catalysts

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Jute fabrics undergo crosslinking reactions with N-methylol urea systems in the presence of catalysts and the modified fabrics show good wrinkle resistance along with other properties at the expense of tensile strength. The changes in properties of jute fabrics modified by crosslinking with DMEU and DMDHEU in the presence of acid catalysts are discussed.

Keywords: Jute-based fabrics, Dimethyl dihydroxyethylene urea, Dimethylol ethylene urea, N-Methylol urea, Tensile strength, Wrinkle recovery

1 Introduction

The potentialities of crosslinking the jute fabric have been reported by us earlier1. The effects of different types of crosslinking agents with the jute fabric in the presence of different types of metal salt catalysts indicate that the dry crease recovery and tensile strength retention are dependent upon the crosslinking agent and catalyst type and are interrelated. Crosslinking of jute, particularly with dimethylol ethylene urea (DMEU) and dimethylol dihydroxyethylene urea (DMDHEU) in the presence of selected metal salt catalysts, such as magnesium chloride and zinc nitrate, have contributed to satisfactory improvements in the dry wrinkle recovery of the jute fabric.

Inorganic and organic acids were used in the DMEU and DMDHEU pad bath at different pH levels at a given duration and temperature of curing for the crosslinking reaction with the jute fabric. It has been reported2 that cotton cellulose reacted favourably with DMDHEU resin in the presence of a strong inorganic acid catalyst at a temperature range 26-100°C by the pad-cure process. The dry wrinkle recovery angle (DWRA) of cotton fabric is dependent upon moisture and hydrogen ion concentration and is highest when the pad-bath pH is below 2.0 and moisture is between 3 and 10% at any given duration or temperature.

2 Materials and Methods

2.1 Materials

2.1.1 Fabric

Plain weave 100% jute fabric was used throughout the work. It had the following structural characteristics: Warp — 60 ends/dcm (count, 340 tex); Weft — 48 picks/dcm (count, 270 tex); and fabric mass (at 67% RH, 20°C) — 325 g/m².

The fabric was cleaned before use by scouring with 2% sodium carbonate (on the weight of the fabric) at 80°C for 30 min. Bleaching was carried out in a laboratory jigger by means of alkaline hydrogen peroxide. This was followed by washing with water and neutralization with acetic acid to give a fabric pH of 6-6.5.

2.1.2 Chemicals

(1) Ahuramine KETU, an aqueous product containing 40% solid dimethylol ethylene urea (DMEU), and Ahuramine YX, an aqueous product containing 51% solid 1,3-dimethylol-4,5-dihydroxyethylene urea (DMDHEU) were used as crosslinking agents.

(2) Citric acid, oxalic acid, succinic acid, phosphoric acid and hydrochloric acid (analytical grade) were used as catalysts.

2.2 Methods

2.2.1 Measurement of Wrinkle Recovery and Tensile Strength

Dry and wet wrinkle recoveries were measured by a Monsanto crease recovery tester in accordance with ASTM D 1295-67. The tensile strength was measured with the ravelled strip (20 cm x 5 cm) method by using an Instron machine (model TTBM).

The percentage of nitrogen in the untreated and crosslinked jute fabric was determined by the Kjeldahl method.

2.2.2 Application of Crosslinking (Reaction) Agents

The fabric samples of 30 cm x 125 cm were impregnated with aqueous solutions of the crosslinking
agent and catalyst on a 3-bowl laboratory padding mangle using 100% wet pick-up (2 dip, 2 nip). Unless otherwise specified, fabric samples after padding were dried at 80°C for 5 min, cured at 150°C for 5 min in the laboratory curing unit (Ernst Benz-KTF/M model) followed by washing with 5 g/litre soap solution in a laboratory jigger and finally rinsed with water, and dried.

As per add-on requirements, the crosslinking agent was dissolved in 1000 ml of water. To this solution the acid catalyst solution was added slowly, the mixture being stirred constantly. The pH of the solution was measured with a digital pH meter after each addition and the required pH was adjusted accordingly. Six different types of free acid catalyst were used. Experiments were conducted at different pH levels.

The application conditions were identical in all cases: 12% solid resin solution in the pad bath (and making 12% resin add-on on the weight of the fabric), catalyst and 0.1% non-ionic wetting agent (v/v). A few experiments were conducted at different durations and temperatures of curing for selected acid catalysts, at a given pH of the pad bath.

Wet crosslinking of jute fabric was effected by padding the fabric with DMDHEU and the acid catalyst at 100% pick-up; reactions were allowed for 4 to 24 h at 30°C, followed by washing with water and drying at 80°C for 5 min.

3 Results and Discussion
3.1 Dry Wrinkle Recovery

The effect of various acid catalysts at different levels of pH of the pad bath containing DMEU on dry wrinkle recovery angle is shown in Fig. 1. At pH 4.5 and 3.5 in all the acids used, the DWRA is very low but as the pH is lowered below 3.5, DWRA increases slowly and maximum DWRA values are recorded between pH 3 and 2. Below pH 2, DWRA of jute could not be measured owing to the brittleness of the fabric.

Of the organic acids, acetic acid gives the highest DWRA at pH 3, followed by succinic acid, oxalic acid and citric acid. Acetic acid and succinic acid show a rapid rise in DWRA at pH from 3.5 to 3 and a further increase in acid concentration shows a moderate rise in DWRA in the case of acetic acid and little effect in the case of succinic acid. Oxalic acid and citric acid show poor response to DWRA of jute fabric in this range.

Hydrochloric acid and phosphoric acid are less effective in the crosslinking reactions between DMEU and jute than the organic acids, as indicated in DWRA values with hydrochloric acid and phosphoric acid at equivalent pH range. Hydrochloric acid shows a more rapid and sharp rise in DWRA than phosphoric acid and the trend shows a continued rise of DWRA. Organic acids, on the other hand, indicated levelling off of DWRA at pH between 3 and 2.

Under equivalent conditions, all the acid catalysts showed a better effect with DMDHEU than with DMEU, and DMDHEU-treated fabric retained more nitrogen (Table 1).

Fig. 2 shows the effect of pH of the pad bath containing DMDHEU with acid catalysts on DWRA. In the case of DMDHEU also, DWRA increases slowly with increase in acid concentration and levels off at pH between 2 and 3 except in the case of hydrochloric acid where DWRA continues to increase. Irrespective of the acid used, increase of DWRA at pH between 3.5 and 3.0 is sharp and rapid. The maximum DWRA obtained with a given resin/acid catalyst combination is shown in Fig. 3, which shows that DMEU gives a DWRA which is inferior to that given by DMDHEU, irrespective of the catalysts, except phosphoric acid. Acetic acid and succinic acid give the highest DWRA with DMEU, whereas hydrochloric acid gives maximum DWRA with DMDHEU. In general, succinic acid, acetic acid and hydrochloric acid give improved DWRA in both DMEU and DMDHEU finishes.

Acetic acid and hydrochloric acid were considered for further investigation (using DMDHEU) with respect to their effects on duration and temperature of curing as these gave improved retention of physical properties. Figs 4 and 5 show the relationships between DWRA and temperature of curing for hydrochloric acid and acetic acid respectively at bath pH 3. The figures include a series of curves ob-
Table 1 — Add-on, Nitrogen Content and DWRA of Jute Fabrics Treated with DMEU and DMDHEU in Presence of Free Acid Catalysts

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Pad bath pH adjusted by acid</th>
<th>Nitrogen content of W+F (DMEU-treated sample)</th>
<th>W+F (DMDHEU-treated sample)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>—</td>
<td>0.13</td>
<td>0.13</td>
</tr>
<tr>
<td>Citric acid</td>
<td>4.5</td>
<td>1.02</td>
<td>1.26</td>
</tr>
<tr>
<td></td>
<td>3.5</td>
<td>1.20</td>
<td>1.56</td>
</tr>
<tr>
<td></td>
<td>2.0</td>
<td>1.52</td>
<td>1.62</td>
</tr>
<tr>
<td>Oxalic acid</td>
<td>4.5</td>
<td>0.94</td>
<td>1.28</td>
</tr>
<tr>
<td></td>
<td>3.5</td>
<td>1.08</td>
<td>1.57</td>
</tr>
<tr>
<td></td>
<td>2.0</td>
<td>1.25</td>
<td>1.85</td>
</tr>
<tr>
<td>Acetic acid</td>
<td>4.5</td>
<td>1.02</td>
<td>1.24</td>
</tr>
<tr>
<td></td>
<td>3.5</td>
<td>1.31</td>
<td>1.52</td>
</tr>
<tr>
<td></td>
<td>2.0</td>
<td>1.62</td>
<td>1.88</td>
</tr>
<tr>
<td>Hydrochloric acid</td>
<td>4.5</td>
<td>0.92</td>
<td>1.05</td>
</tr>
<tr>
<td></td>
<td>3.5</td>
<td>1.12</td>
<td>1.14</td>
</tr>
<tr>
<td></td>
<td>2.0</td>
<td>1.40</td>
<td>1.92</td>
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<tr>
<td>Succinic acid</td>
<td>4.5</td>
<td>0.96</td>
<td>1.10</td>
</tr>
<tr>
<td></td>
<td>3.5</td>
<td>1.28</td>
<td>1.52</td>
</tr>
<tr>
<td></td>
<td>2.0</td>
<td>1.67</td>
<td>1.94</td>
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<tr>
<td>Phosphoric acid</td>
<td>4.5</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td></td>
<td>3.5</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td></td>
<td>2.0</td>
<td>—</td>
<td>—</td>
</tr>
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</table>

Fig. 2 — Effect of pH (adjusted by different acid catalysts) on wrinkle recovery property of jute fabric treated with DMDHEU (12%)

Fig. 3 — Maximum wrinkle recovery obtained with different resin-catalyst systems

In general, DWRA of jute fabric, when free acid catalysts are used at different pH levels (from 4.5 to 2.0 for citric acid, oxalic acid, and hydrochloric acid) and at different curing durations (from 110°C to 150°C), indicates that the maximum reaction takes place at that temperature range. However, curing for 3 and 5 min durations continues to give improved DWRA at a higher temperature, but levels off at 7 min curing duration.
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Fig. 4 — Effect of duration and temperature of curing on wrinkle recovery of jute fabric in DMDHEU-hydrochloric acid catalyst system

Fig. 5 — Effect of duration and temperature of curing on wrinkle recovery of jute fabric in DMDHEU-acetic acid catalyst system

Fig. 6 — Effect of batching time on wet wrinkle recovery property of jute fabric using DMDHEU-hydrochloric acid/acetic acid catalyst system (temp., 30°C; moisture, 100%)

2), does not go above 250°. Increase in duration and temperature of curing at pH 3 with acetic acid and hydrochloric acid also do not show a promising effect on DWRA as compared to that of metal salt catalysts.

Under a more acidic condition, with hydrochloric acid at pH 1 and with acetic acid at 1.7, DWRA of jute fabric could not be measured owing to the cracking of fabric while measuring DWRA. This indicates a severe degradation of cellulose chain during curing at 110°C, 130°C and 150°C for 5 min. Fabric samples cured at 90°C for 5 min show a DWRA of 220° in both acetic acid and hydrochloric acid.

However, crosslinking in a very strong acidic condition, at pH 0.7 for hydrochloric acid and at pH 1.5 for acetic acid, gives a more improved wet wrinkle recovery than DWRA (Fig. 6).

The wet wrinkle recovery of the jute fabric when DMEU and DMDHEU resins are used in the presence of free acid catalysts were marginally lower than the DWRA and so are not discussed further.

3.2 Tensile Strength

It is established that the crosslinking treatment of cellulotic material causes damage to its several physical properties, the most important one being the tensile strength. The deterioration of tensile strength arises from molecular degradation caused by the catalyst, in addition to embrittlement caused by crosslinking. In the case of a metal salt catalyst, which itself causes a considerable amount of strength loss when treated alone, the loss in tensile strength is halted in the presence of the crosslinking agent. The metal salts act as coordination complexes with cellulose, releasing protons which catalyze hydrolytic degradation of the cellulose chain. In the case of free acid catalyst, when allowed to react with the jute fabric at identical conditions in the absence of the crosslinking agent, the loss in tensile strength is less as compared to that when the metal salt catalyst alone is used. But in the presence of the crosslinking agent, the catalytic reaction with jute cellulose gives a higher strength loss than the acid alone. This is in contrast to the mechanism of strength fall due to metal salt where strength loss is halted in the presence of the crosslinking agent. Fig. 7 shows the tensile strength retention of the jute fabric treated with free acid at different pH values.

Free acid catalysts, such as acetic acid and hydrochloric acid, are volatile, evaporate at the time of intermediate heating, and are not retained in the fabric at the time of curing. Citric acid, succinic acid, etc., though they are degraded to some extent at high temperature, are retained within the fabric and so cause a higher strength loss to jute fabric than acetic acid and hydrochloric acid. The metal salt catalyst, on the other hand, generates a strong acid into the fabric in situ either by thermal decomposition or by its
interaction with jute cellulosic fibres and causes more strength loss as compared to that by the free acid. Fig. 8 shows the tensile strength retention of jute fabric crosslinked with DMEU when different types of free acid are used. This indicates that the tensile strength retention is decreased as the pH of the pad bath is reduced and the fall in tensile strength retention is sharp between pH 3.5 and 3.0, except in the case of phosphoric acid where the tensile strength retention decreases linearly with decrease in pH. The fall in tensile strength retention between pH 3 and 2 continued to decrease but at a slower rate as compared with the value between pH 3.5 and 3.0.

Fig. 9 shows the tensile strength retention values of the jute fabric crosslinked with DMDHEU. Here also, fall in tensile strength retention is sharp between pH 3.5 and 3.0 and the effect is more pronounced than with DMEU. Phosphoric acid and succinic acid give substantially low tensile strength retention values, hydrochloric acid and acetic acid give intermediate values, and citric acid and oxalic acid give the highest values. Figs 10a and 10b show the tensile strength retention of the jute fabric crosslinked with DMDHEU in the presence of hydrochloric acid and acetic acid at pH 3.0 respectively at different durations and temperatures of curing. The
loss in tensile strength at a lower temperature is minimum irrespective of the curing duration in the case of hydrochloric acid catalyst provided the curing duration is 7 min or more. As the temperature of curing is increased, the retention of tensile strength varies widely with progressive increase in curing duration. The retained tensile strength after curing at 150°C for 3 min decreases at a rate of approximately 10% at every increase of 2 min cure time (for both catalysts), from 80% to 50% in the case of hydrochloric acid, and from 95% to 55% in the case of acetic acid. At higher temperatures (170°C), in the case of hydrochloric acid catalyst, increased degradation takes place for 7 min curing duration and onwards, whereas in the case of acetic acid, degradation is activated from 5 min of curing and continues as the curing duration is increased.

3.3 Inter-comparison of Fabric Properties

Figs 11 and 12 show the relationship between DWRA and per cent tensile strength retention of the jute fabric after crosslinking with DMEU and DMDHEU respectively. In general, there is an inverse relationship between these two properties irrespective of the catalyst used. The percentage retention of tensile strength with respect to improvement in DWRA is dependent upon the type of acid catalyst used for the crosslinking reaction. At the equivalent DWRA range (235-240°), phosphoric acid gives the lowest retention of strength (30%) and oxalic acid retains highest (65%) and hydrochloric acid and others are in the intermediate (45-55%) stages.

The rate of loss in tensile strength of jute fabric after crosslinking at lower level of DWRA is slow. There is a sharp increase in the rate of loss in tensile strength above 230° DWRA, indicating the catalytic damage of fibre in DMDHEU finishes. At the initial level of DWRA, i.e. between 190° and 220°, the falls in retained tensile strength are marginal and are in the range 90-70%, and values remain almost at the same level up to the improved DWRA of 240° (except in the cases of phosphoric acid and succinic acid where tensile strength retention goes down to less than 50%), then there is a sharp decline in tensile strength retention value between 65% and 55% with an increase of DWRA from 240° to 250°.

Oxalic acid- and acetic acid-treated samples show a higher strength retention for a given DWRA(240°) value than hydrochloric acid-treated samples. Hydrochloric-acid- and acetic acid-treated samples give a higher (250°) DWRA than other acid catalysts with moderate loss of strength. At a given DWRA, oxalic acid and acetic acid give different strength retentions.

The change in DWRA with tensile strength retention of jute fabric is significant. At the same level of DWRA, the retained tensile strengths of jute fabric treated with DMEU and DMDHEU when different acid catalysts are used are given in Table 2. The table shows that under identical processing conditions

Table 2 — Relationship Between DWRA and Tensile Strength Retention of Jute Fabric Treated with DMEU and DMDHEU in Presence of Different Free Acid Catalysts

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Tensile strength retention (%) of fabric treated with DMEU, at DWRA</th>
<th>Tensile strength retention (%) of fabric treated with DMDHEU, at DWARA</th>
</tr>
</thead>
<tbody>
<tr>
<td>Citric acid</td>
<td>55</td>
<td>60</td>
</tr>
<tr>
<td>Oxalic acid</td>
<td>72</td>
<td>85</td>
</tr>
<tr>
<td>Succinic acid</td>
<td>50/45</td>
<td>78/45</td>
</tr>
<tr>
<td>Acetic acid</td>
<td>78/55</td>
<td>80/80</td>
</tr>
<tr>
<td>Phosphoric acid</td>
<td>45/25</td>
<td>45/30</td>
</tr>
<tr>
<td>Hydrochloric acid</td>
<td>65/60</td>
<td>68/65</td>
</tr>
</tbody>
</table>

Fig. 11 — Relationship between wrinkle recovery angle and tensile strength retention of jute fabric in various DMEU-catalyst systems

Fig. 12 — Relationship between wrinkle recovery angle and tensile strength retention of jute fabric in various DMDHEU-catalyst systems
DMDHEU retains a higher tensile strength than DMEU at a given DWRA in any acid catalyst. The rate of loss in tensile strength of treated jute with respect to improvement in DWRA is dependent upon the type of acid catalyst used. At 250° DWRA the jute fabric shows a considerable loss in tensile strength. Two different strength values at same DWRA indicate a further loss in tensile strength retention without any improvement in DWRA owing to the severity in processing conditions.

4 Summary and Conclusion

The textile properties of jute fabric modified by reaction with DMEU and DMDHEU in the presence of different types of free acid catalyst at different pH levels were evaluated. The reaction mechanism of the crosslinking agent with jute cellulose in the presence of the free acid catalyst at a particular pH postulates the formation of acid-catalysed carbonium ion centres\(^8,9,10\). In the absence of the acid catalyst, no reaction takes place. Therefore, protonation precedes the crosslinking reaction which leads to change in physical properties of jute fabric, such as DWRA and tensile strength. The results obtained with the pad-dry-cure process carried out at 150°C for 5 min show that irrespective of the acid type, a pH between 2 and 3 is necessary to obtain a good degree of DWRA. The crosslinking reaction is dependent essentially on the extent of acidity developed during interaction with jute. The temperature and duration of curing are also significant for obtaining DWRA. DWRA is developed at a curing temperature of 150°C and increases with increasing temperature and curing duration from 5 to 7 min.

Acetic acid and hydrochloric acid give the highest DWRA compared with that obtained with other acid catalysts. When citric, succinic and oxalic acids are used as catalysts, DWRA is not substantial. Values obtained in the presence of acid catalysts are inferior to those obtained by using metal salt catalysts\(^1\). The increase in the DWRA of jute fabric increases with the lowering of tensile strength. The tensile strength retention starts decreasing when DWRA is 230° and there is a sharp decline in tensile strength retention (65-55%) at 250° DWRA. Under identical processing conditions DMDHEU finishes have higher tensile strength retention than DMEU finishes.

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References