Effect of solvent treatment on mechanical, structural and dyeing properties of regenerated cellulosic yarns

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The mechanical, structural and dyeing properties of conventional viscose and solvent-spun lyocell yarns have been studied in untreated condition as well as after treatment with trichloroacetic acid-methylene chloride (TCAMC) reagent. It is observed that the lyocell yarn has higher tensile strength and abrasion resistance than the conventional viscose yarn. The tensile strength of viscose and lyocell yarns increases on treatment with 5% (w/v) TCAMC for 2 min. The TCAMC treatment has no effect on the elongation of viscose yarn but the elongation of lyocell yarn shows a drop. There is no change in the abrasion resistance of both the yarns due to the treatment. TCAMC modifies the structure of both the regenerated cellulosic yarns. Decrystallisation and disorientation take place on treatment. The crystallite size of lyocell is smaller than that of viscose. The treatment decreases the crystallite size. The dyeability study shows that the dye uptake of lyocell yarn is higher than that of viscose yarn. The TCAMC treatment improves the dye uptake of viscose yarn. Wash and light fastness of both the yarns are not altered due to the treatment.

Keywords: Dye uptake, Lyocell yarn, Trichloroacetic acid-methylene chloride, Viscose yarn, X-ray diffraction

1 Introduction

With increased emphasis on ecological criteria, efforts are required to avoid the use of carbon disulphide in the production of viscose fibres. A great deal of R&D efforts is, therefore, being undertaken at the international level to develop an alternative process to produce regenerated cellulosic fibres with improved mechanical and dyeing properties. These efforts have resulted in the production of solvent-spun regenerated cellulosic yarns under different brand names, such as Tencel (Courtaulds), Lenzing Lyocell (Lenzing), Newcell (Akzo Faser) and Alceru* (Titk Rudolstadt/Schwarza). The advantages of the new cellulosic fibres over the conventional viscose fibres include high tenacity, high wet modulus, and rapid and deep dyeing2.

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The solvents3,4 used for direct dissolution of cellulose are lithium chloride/dimethyl acetamide, ammonia/ammonium thiocyanate dinitrogen tetraoxide/dimethylformamide, dimethyl sulphoxide/para formaldehyde and N-methyl-morpholine-N-oxide (NMMO) of which only NMMO offers a viable alternative to the existing method of commercial production of solvent-spun cellulosic fibres. The ability of amine oxide to directly dissolve the cellulose has been known since last 60 years but the systematic development of a fibre spinning technology has only come around 1970 (ref. 5).

Lyocell is produced through a process of direct dissolution of wood pulp in NMMO solvent. The solution is then filtered and extruded to form fine filaments which are washed, dried and cut into known length to form staple fibres. It is reported6 that the NMMO solvent is non-toxic and the process does not pollute the environment. The
solvent is almost completely recovered (97-99%). The purification of NMNO is done by adding an oxidant in solution.

The structure of lyocell is different from other cellulose fibres, both natural and man-made. The degree of crystallinity of lyocell is greater than that of staple viscose. The tensile strength of Lenzing lyocell fibre is about 27% higher than that of viscose fibre. The elongation is lower by 24%. Similarly, the wet tenacity of lyocell fibre is more than 100% and wet elongation is 19% lower than that of the viscose. Another significant feature of lyocell is the very high initial wet modulus (133%) compared to that of viscose. The main disadvantage associated with solvent-spun fibres is that they tend to fibrillate under mechanical stress in the wet state which is undesired especially in the processing from fibre to fabric. However, crosslinking treatment with chemical compounds reduces the fibrillation to some extent. As lyocell is also a cellulose fibre, it can be dyed with dyes similar to those used for cotton and viscose.

This paper deals with the comparative study of structural, mechanical and dyeing properties of conventional viscose yarn and the solvent-spun lyocell yarn. The above properties of both the yarns have also been compared after trichloroacetic acid-methylene chloride (TCAMC) treatment.

2 Materials and Methods

2.1 Materials

Viscose (Ne, 30/1; TPI, 17; and staple length, 38 mm) and lyocell (Ne, 30/1; TPI, 19; and staple length, 40 mm) yarns supplied by SIV Industries, Coimbatore, India, and Lenzing Lyocell GmbH & Co. KG, Lenzing, Austria, respectively were used for the study. The laboratory grade trichloroacetic acid, methylene chloride and acetone were used for the treatment of yarn samples. The C.I. Direct Black 19 was used for dyeing the yarn samples.

2.2 Methods

2.2.1 TCAMC Treatment

The yarns were treated with TCAMC in relaxed state at an ambient temperature (~30°C).

2.2.2 Tensile Strength and Extension at Break

The tenacity of the yarn samples (length, 100mm) was measured on Instron tensile tester (Model No.6021). The rate of extension was kept at 50 mm/min. More than 30 specimens were tested in each case. From the load-extension curves, the average breaking strength and per cent extension at break were determined. The stress-strain curves were drawn by superimposing 5-10 selected load-extension curves, where the breaking load was close to the average value, normalising the characteristic curves and reconstructing the same in terms of stress (g/tex) and strain (%). The area under the stress-strain curve was measured and the work of rupture was thus calculated.

2.2.3 Abrasion Resistance

A Zweigle G-550 yarn abrasion tester was used to measure the abrasion resistance of yarns. An emery paper as abrader and a pretension weight of 30 g were employed. The results were recorded as the number of strokes required to break the specimen. For each sample, 19 tests were conducted and the average values noted.

2.2.4 X-Ray Diffraction Analysis

A Philips X-ray generator (Model No. PW 1710) fitted with a texture goniometer attachment and a microprocessor recorder was used. The nickel filtered CuKα radiation was used (λ=1.5418Å). The yarn sample was scanned by reflection mode. The yarn was cut and made into fine powder, passed through a 300 mesh and made into circular pellet weighing 100 mg making use of a special die. The powdered sample was scanned between 2θ angle 8° and 30°. The crystallinity was calculated using Segal's formula. The total order in the fibres was estimated by measuring the half width of the combined (002+101) peak. The orientation angle was calculated from azimuthal distribution of 002 peak by rotating the sample through 360° at 2θ=20.4°.

2.2.5 Dyeing and Colour Evaluation

Both TCAMC-treated and untreated samples were dyed simultaneously at 80°C with direct dye in Ahiba Polymat dyeing machine following the commercial dyeing practice as mentioned in the manufacturer's shade card. After soap boil, the samples were dried under atmospheric conditions. The colour measurement was done under D65 illuminant at 10° observer using a Milton Roy spectrophotometer. Wash and light fastness were assessed as per the BIS procedures.

3 Results and Discussion

3.1 Mechanical Properties

Table 1 shows that the tensile strength of untreated viscose and solvent-spun lyocell yarns is not noticeably different from those of the respective TCAMC treated samples, except for the viscose yarn treated with 5% TCAMC for 2 min where the increase in strength is about 9%. There is no appreciable change in elongation of viscose yarn due to the treatment. However, a decrease in elongation is observed in the case of treated lyocell yarn. It may be observed from Table 1 that the increase in treatment time and TCAMC concentration do not influence the change in tensile properties noticeably after 5% TCAMC treatment for 2 min. It is also observed that the lyocell yarn has improved tensile strength than the regular viscose yarn; the tensile strength of lyocell yarn is higher by 85%. However, the elongation of lyocell yarn is lower by 11% of that for viscose yarn. It may be mentioned here that the published literature on tensile and other properties of Lenzing lyocell yarn is scanty. However, the studies on various properties of Courtaulds solvent-spun tencel yarn show that the tenacity of tencel fibre is higher than that of other cellulosic fibres. This increase in fibre strength is considerably higher in yarn. It appeared that the individual microfibres (fibrils) are firmly connected to the main fibre and thus contribute to strength.

The stress-strain curves of TCAMC-treated viscose and lyocell yarns are shown in Figs 1 and 2 respectively. The treatment with 5% TCAMC for 2 min modifies the structure and improves the mechanical properties of both viscose and lyocell in terms of higher strength, higher yield point, higher modulus, comparatively higher yield strain and lower elongation. The curves show a distinct deviation in the stress-strain behaviour after the

![Stress-strain curve of viscose yarn](image)

**Table 1—Effect of TCAMC treatment on mechanical properties of regenerated cellulosic yarns**

<table>
<thead>
<tr>
<th>Property</th>
<th>Viscose yarn</th>
<th>Lyocell yarn</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Untreated</td>
<td>5% TCAMC</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2 min</td>
</tr>
<tr>
<td>Breaking strength g/tex</td>
<td>12.66</td>
<td>13.81</td>
</tr>
<tr>
<td>Breaking elongation, %</td>
<td>14.3</td>
<td>13.9</td>
</tr>
<tr>
<td>Yield stress, g/tex</td>
<td>4.46</td>
<td>5.67</td>
</tr>
<tr>
<td>Yield strain, %</td>
<td>2.4</td>
<td>2.9</td>
</tr>
<tr>
<td>Initial modulus g/tex</td>
<td>203.9</td>
<td>221.3</td>
</tr>
<tr>
<td>Work of rupture gm wt cm</td>
<td>211</td>
<td>240</td>
</tr>
<tr>
<td>Average number of strokes to cause a break</td>
<td>72</td>
<td>68</td>
</tr>
</tbody>
</table>
and/or treatment time decreases the extent of improvement observed in 5% TCAMC treatment for 2 min. The TCAMC treatment induces a plasticisation effect. It reduces crystallinity index, produces wider distribution of crystal size and induces more plasticity in the yarn. Owing to this, the modulus and the strength of the yarn are decreased.

Table 1 also shows that the work of rupture of all the treated yarns, except that of the viscose yarn treated with 5% TCAMC for 2 min, is lower than that of the corresponding untreated control ones. It is also observed that there is no appreciable change in resistance against abrasion after TCAMC treatment. However, the abrasion resistance of lyocell yarn is about one and half times higher than that of the viscose yarn, perhaps due to the high crystalline structure.

![Stress-strain curve of lyocell yarn](image.png)

**Fig. 2**—Stress-strain curve of lyocell yarn

yield point, which is the transition point from elastic to plastic behaviour. The process of transition involves breaking and reconstitution of atomic bonds. On the other hand, the elastic modulus is a property of crystal lattice and resists deformation. Owing to this, it can be stated that treatment with 5% TCAMC for 2 min improves the resistance power to deform the material with higher interchain bonding. Further, there is a marked increase in flow stress values in the plastic range of deformation. It may be noted that the breaking strength of this sample is also high.

The lower strength or failure of the material is due to the structural defects responsible for microcrack nucleation and growths leading to sample failure. High strength indicates lesser defects for the nucleation and growth. In addition, the presence of smaller crystals may improve the fibre properties as these crystals can act like a crosslink. This helps to transmit the stress uniformly through the structure and delays stress concentration and brittle fracture. Concisely, it can be visualised that the treatment with 5% TCAMC for 2 min improves structural order of the yarn, generates more number of smaller crystals, and improves yield, modulus and breaking tenacity (Table 1). However, the increase in TCAMC concentration and/or treatment time decreases the extent of improvement observed in 5% TCAMC treatment for 2 min. The TCAMC treatment induces a plasticisation effect. It reduces crystallinity index, produces wider distribution of crystal size and induces more plasticity in the yarn. Owing to this, the modulus and the strength of the yarn are decreased.

Table 1 also shows that the work of rupture of all the treated yarns, except that of the viscose yarn treated with 5% TCAMC for 2 min, is lower than that of the corresponding untreated control ones. It is also observed that there is no appreciable change in resistance against abrasion after TCAMC treatment. However, the abrasion resistance of lyocell yarn is about one and half times higher than that of the viscose yarn, perhaps due to the high crystalline structure.

3.2 Structural Modification

An interaction of TCAMC reagent with the normal and solvent-spun cellulosic yarns is evidenced by the X-ray diffraction analysis. The diffractometer tracings of viscose and lyocell yarns are shown in Figs 3 and 4 respectively. The crystallinity of treated viscose and lyocell samples is lower than that of the corresponding control ones (Table 2). As the duration of the treatment increases, the crystallinity decreases. Moreover, the broadening of half width peak takes place due to the treatment. This shows that decrystallization occurs on TCAMC treatment. It can also be seen that the orientation angle increases, indicating the disorientation of molecules due to the treatment. Another feature observed is the high crystallinity of solvent-spun lyocell compared to that of the normal viscose yarn. Coulsey and Smith observed that the degree of crystallinity in tencel is greater than that in the staple viscose. They have concluded that the high level of orientation is associated with high tensile strength. Researches on the structure of lyocell show that the solvent spinning process causes the formation of a large fraction of highly oriented crystalline regions. Besides, the relationship between the degree of crystallinity and the fibrillation of lyocell is stressed by Lenz et al. Fibres with a lower degree of fibrillar structure, for instance viscose, and the fibres with a helical arrangement of the fibrils, like
cotton, show a less pronounced tendency to
fibrillation than the fibres with a marked fibrillar
structure and fibrils arranged longitudinally along
the fibre axis (lyocell).

From the above discussion, it may be concluded
that the treatment with 5% TCAMC for 2 min
modifies the structure and resultant properties.
Besides, the orientation decreases and the half
peak width increases (Table 2), indicating a wider
distribution of crystal size. This shows that the
treatment with 5% TCAMC for 2 min modifies the
crystal size distribution and induces more smaller
and larger crystals. This can be visualised as the
decrystallisation and recrystallisation effects of
TCAMC. The treatment partially solubilises the
existing crystals and amorphous region, disorients
the chain molecules, particularly the chain
molecules of the amorphous region, and
recrystallises the crystals. Table 2 also shows the
results of change in crystallite size as measured
from 002+101 plane due to the treatment. The
crystallite size (I) was calculated according to the
following Scherrer's equation:

\[ I = \frac{K\lambda}{\beta \cos \theta} \]

where K is the Scherrer's constant (0.94); \( \beta \), the
half width of peak of (002) plane; \( \theta \), the Bragg
angle of (002) plane; and \( \lambda \), the wavelength of
CuK\(_{\alpha} \) (1.542 Å).

It may be noted that since 002 and 101 peaks are
not resolved, the half width of combined peaks
(002+101) were taken for calculation. Table 2
shows that the crystallite size of both viscose and
lyocell yarns decreased due to the treatment and
that the crystallite size of lyocell is smaller than
that of viscose. It may be mentioned that the
structure and the physico-chemical properties of

<table>
<thead>
<tr>
<th>Property</th>
<th>Viscose yarn</th>
<th>Lyocell yarn</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crystallinity index, %</td>
<td>Untreated</td>
<td>5% TCAMC (2 min)</td>
</tr>
<tr>
<td></td>
<td>64.1</td>
<td>62.9</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Crystallite size, Å</td>
<td>40.9</td>
<td>34.5</td>
</tr>
</tbody>
</table>
the cellulosic materials depend on the size distribution spectrum of crystallites\textsuperscript{21}.

3.3 Dyeability Characteristics

The dyeability behaviour of TCAMC-treated viscose and lyocell yarns dyed with Direct Black 19 dye is shown in Table 3. It is observed that the colour depth of lyocell is deeper than that of viscose, irrespective of % shade. The increase in dye uptake of lyocell is justified by the decrease in lightness \( L \). An interesting observation is that the treated yarn samples dyed darker than the corresponding control ones.

Dyeability of the sample is related to the amorphous region or the space available for the penetration of dye molecules. In general, viscose and lyocell fibres are thermosetting in character. This means that the material follows porous matrix model for dyeability. According to this model, the fibre structure consists of rigid matrix with interconnected pores. The dye molecule migrates into the water filled micro channels or pores. It may be possible that the decrystallisation and recrystallisation process, observed after the TCAMC treatment (Section 3.2), creates more cavity or micropores. These pores allow more dye

### Table 3—Dye uptake and colour parameters of viscose and lyocell yarns

[Dye. C.I. Direct Black 19]

<table>
<thead>
<tr>
<th>Conc. of TCAMC (w/v) * and duration of treatment</th>
<th>K/S value *</th>
<th>Colour coordinates</th>
<th>Colour coordinates</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Viscose</td>
<td>Lyocell</td>
<td>Viscose</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>( L )</td>
</tr>
<tr>
<td>Untreated</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>0.98</td>
<td>2.04</td>
<td>66.0</td>
</tr>
<tr>
<td>2</td>
<td>1.36</td>
<td>3.69</td>
<td>60.4</td>
</tr>
<tr>
<td>3</td>
<td>2.42</td>
<td>5.92</td>
<td>53.0</td>
</tr>
<tr>
<td>5%; 2 min</td>
<td>1</td>
<td>1.18</td>
<td>2.09</td>
</tr>
<tr>
<td>2</td>
<td>1.49</td>
<td>3.92</td>
<td>59.5</td>
</tr>
<tr>
<td>3</td>
<td>2.57</td>
<td>6.17</td>
<td>52.2</td>
</tr>
<tr>
<td>5%; 20 min</td>
<td>1</td>
<td>1.24</td>
<td>2.30</td>
</tr>
<tr>
<td>2</td>
<td>1.61</td>
<td>4.21</td>
<td>59.5</td>
</tr>
<tr>
<td>3</td>
<td>2.45</td>
<td>6.29</td>
<td>52.8</td>
</tr>
<tr>
<td>10%; 90 min</td>
<td>1</td>
<td>1.26</td>
<td>2.22</td>
</tr>
<tr>
<td>2</td>
<td>1.70</td>
<td>4.24</td>
<td>58.4</td>
</tr>
<tr>
<td>3</td>
<td>2.41</td>
<td>6.44</td>
<td>52.9</td>
</tr>
</tbody>
</table>

### Table 4—Fastness properties of viscose and lyocell yarns

<table>
<thead>
<tr>
<th>Conc. of TCAMC (w/v) * and duration of treatment</th>
<th>Wash fastness</th>
<th>Light fastness</th>
<th>Wash fastness</th>
<th>Light fastness</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Change in colour</td>
<td>Staining</td>
<td></td>
<td>Change in colour</td>
</tr>
<tr>
<td>Untreated</td>
<td>1</td>
<td>3-4</td>
<td>3-4</td>
<td>3-4</td>
</tr>
<tr>
<td>2</td>
<td>3</td>
<td>3-4</td>
<td>4</td>
<td>3-4</td>
</tr>
<tr>
<td>3</td>
<td>3</td>
<td>3-4</td>
<td>3-4</td>
<td>3-4</td>
</tr>
<tr>
<td>5%; 2 min</td>
<td>1</td>
<td>3-4</td>
<td>3-4</td>
<td>4</td>
</tr>
<tr>
<td>2</td>
<td>3-4</td>
<td>3-4</td>
<td>4</td>
<td>3-4</td>
</tr>
<tr>
<td>3</td>
<td>3-4</td>
<td>3-4</td>
<td>3-4</td>
<td>3-4</td>
</tr>
<tr>
<td>5%; 20 min</td>
<td>1</td>
<td>3-4</td>
<td>3-4</td>
<td>3-4</td>
</tr>
<tr>
<td>2</td>
<td>3-4</td>
<td>3-4</td>
<td>3-4</td>
<td>3-4</td>
</tr>
<tr>
<td>3</td>
<td>3-4</td>
<td>3-4</td>
<td>3-4</td>
<td>3-4</td>
</tr>
<tr>
<td>10%; 90 min</td>
<td>1</td>
<td>3-4</td>
<td>3-4</td>
<td>3-4</td>
</tr>
<tr>
<td>2</td>
<td>3-4</td>
<td>3-4</td>
<td>3-4</td>
<td>3-4</td>
</tr>
<tr>
<td>3</td>
<td>3-4</td>
<td>3-4</td>
<td>3-4</td>
<td>3-4</td>
</tr>
</tbody>
</table>
molecules to penetrate inside the structure. Higher concentration of TCAMC or higher treatment time produces more amorphous or disordered regions. Therefore, it is expected that more pores and/or higher dimension pores may be created. This can lead to higher dye uptake. It is also seen from Table 3 that the lyocell yarn takes more dye than the viscose yarn. This may perhaps be due to the difference in structure, induced by differences in processing conditions. Treatment with TCAMC does not alter the wash and light fastness properties of viscose and lyocell yarns (Table 4). The fastness properties are comparable with those of the control yarn.

4 Conclusions
The tensile strength of regenerated viscose yarn is not significantly varied except in case of 5% TCAMC treatment for 2 min when a moderate increase in strength is observed. There is no appreciable change in the tenacity of treated lyocell. However, the strength of lyocell is higher than that of normal viscose. While there is no appreciable change in elongation of viscose yarn due to the treatment, a drop in elongation is observed in the case of treated lyocell yarn. The increase in treatment time and concentration does not influence the change in tensile properties significantly after 5% TCAMC treatment for 2 min. TCAMC treatment produces decrystallisation and disorientation of regenerated and solvent-spun cellulosic yarns. There is no appreciable change in abrasion resistance of both the yarns due to the treatment. However, the abrasion resistance of lyocell yarn is significantly higher than that of viscose. Dye uptake of lyocell yarn is higher than that of viscose yarn. The relative dye uptake of viscose at 1% and 2% shades is higher for treated yarns. Not much increase is observed at higher depth of 3% shade. Increase in treatment time influences the higher dye uptake of both the cellulosic yarns. The lightness of the treated viscose and lyocell is lower than that of respective untreated yarn, irrespective of the depth of shade. The fastness properties are not altered due to the treatment.

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