Effects of Sodium Hydroxide and Liquid Ammonia Treatments on Shape Changes of Cross-Sectional of Cotton Fibers Due to Swelling

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Abstract

The cotton fabrics treated with formaldehyde vapor show high wash and wear (W&W) properties, but poor tensile strength as compared with the resin treated fabrics. This property is expected to be improved by liquid ammonia pre-treatment before the treatment with formaldehyde vapor. In this study, from a practical viewpoint of formaldehyde vapor treatment of cotton fabrics, the microscopic and macroscopic strain relaxation along the cross sectional direction of cellulose fibers by the pre-treatment with liquid ammonia, sodium hydroxide and sodium hydroxide/liquid ammonia were examined in terms of crystallinity, crystalline transition (microscopic uniformity index), barium activity number (amorphous content index) and aspect ratio of cross section of a fiber (macroscopic index). It was found that all examined pre-treatments bring about considerable changes in fine structural properties, but the liquid ammonia pre-treatment is superior to the other pre-treatments. This is due to the fact that the liquid ammonia pre-treatment brings about a uniform strain relaxation of cellulose fibers.

1. Introduction

Never-dried cotton fibers in the boll have both less convolutions and comparatively circular cross-sections1). Being dried, however, cotton fiber changes gradually giving rise to convolutions (axial strain) and flattened cross-sectional shape (cross-sectional strain) after the boll opens and as a result, cotton fiber has strain. When fiber strain is relaxed and returned as possible as to original state, as well-known, cotton fibers show effectively original mechanical properties2). On the other hand, cotton fabrics finished with formaldehyde vapor phase (VP) show high Wash & Wear property, but have a weak point that tensile strength becomes poor, compared with fibers finished with dimethylol dihydroxy ethylene urea (DMDHEU)3'4). In order to improve such loss of tensile strength in VP finishing, it will be considered that it is important to relax strain of cotton fibers with pre-treatment before VP finishing. In fact, S. H. Zeronian et al. have reported that losses of both tensile strength and elongation of cotton fabrics are improved by pre-treatments with aqueous NaOH solution or liquid ammonia before resin finishing5). K. Bredereck et al. have also shown that the pre-treatment with liquid ammonia before resin finishing is effective to improve abrasion property and hand of cotton fabrics6). Besides these papers, many studies regarding changes of fine structure and fiber properties of cottons due to pre-treatments have been done7–9). However, any report can not be found on the studies made systematically from a view point of the effect of strain--relaxation. This report is focused on the studies of the degree of the cross-sectional strain--relaxation due to pre--treating with aqueous NaOH solution, liquid ammonia and these combinations, from various indexes indicating the degree of strain--relaxation of cotton fibers. Experiments were done on both micro--structural changes in terms of crystalline and amorphous regions and macro--structural changes in terms of cross--sectional shapes.

2. Experimental

2.1 Materials and Pre--Treatment Methods

Preparation of Standard Materials

Supima®(Pima species, extra long staple cotton) as raw cotton and these slivers as untreated cotton (BL–S) were used. Cotton slivers untreated were immersed in 21.5 %w/w aqueous NaOH solution at 25 °C for 16 hr in the slack condition and then sample was rinsed extensively in water, neutralized in 1%w/w aqueous acetic acid solution, again rinsed extensively in water, spin--dried and dried in the air. That sample was used as standard material (SM) pre-treated with aqueous NaOH solution. Cotton sliver dried in a vacuum (20°C, 760mmHg, 5hr) were prepared after immersing in liquid ammonia (about −34°C) for 10min in a Dewar flask (vol.1000ml), followed by...
removal of ammonia in draft chamber and air-dried at room temperature. This sample was used as standard materials (SN) pre-treated with liquid ammonia.

Pre-Treatments with Aqueous NaOH Solution (NaOHaq.)

Broad fabrics (grey fabrics) consisting of warp yarn (6.56tex/two folded yarn, 147yarns/2.54cm) and weft yarn (6.56tex/two folded yarn, 76yarns/2.54cm) were singed, desized, scoured and bleached. These samples were used as untreated cotton fabrics (BL-T) and the pre-treatments with aqueous NaOH solution were done as follows:

M1: mercerization with 18.7% w/w aqueous NaOH solution at 25°C
M2: twice mercerization repeated
M3: mercerization with 25.5% w/w aqueous NaOH solution at 28°C

Immersing time was required for 27sec in order to lead 90% of the degree of swelling in a state of equilibrium in the case of 20% w/w aqueous NaOH solution (at 20°C). As a result, a clip system process was used for mercerization. The necessary time of for immersing in aqueous NaOH solution into rinsing with water-shower was taken about 48sec. The tension was imparted for weft yarn during about 7sec in last stage, and rinsing was extensively with water left unfinished. Cotton fabrics were set for width direction with pintenter after mercerization.

Pre-Treatments with Liquid Ammonia (L.NH₃)

Untreated cotton fabrics were pre-treated with liquid ammonia as follows:

N1: pre-treated with liquid ammonia at about -34°C.
N2: N1 pre-treatment repeated twice.

The immersing time is needed to be 7.5sec in order to lead 90% of the degree of swelling in a state of equilibrium in the case of liquid ammonia (-40°C). As a result, ammonia-dry-process was used for liquid ammonia pre-treatment and the time between immersing in liquid ammonia and entering into cylinder dryer was taken about 5sec. During above process, cotton fabrics have no tension for width direction.

Combination-Treatments with Aqueous NaOH Solution/Liquid Ammonia (NaOHaq./L.NH₃)

Above M1,M2 and M3 were additionally treated with liquid ammonia at about -34°C. Their conjugated pre-treated cotton fabrics are defined simply as M1/N1,M2/N2 and M3/N1.

2.2 Characterization of the Crystal Structures

(1) Wide Angle X-Ray Diffraction

Wide-angle X-ray diffraction patterns were measured using a Rigaku RAD-RA X-ray generator with Ni filtered Cu-Kα at a power of 40KV, an electric current of 100mA and scanning angles(2θ) between 7° and 42°.

(2) CP/MAS ¹³C•NMR

Solid state high resolution ¹³C•NMR spectra were obtained with a Varian XL-300 spectrometer operating at 75MHz using a Doty probe. The ¹³C chemical shifts are quoted with respect to hexamethyl benzene (HMB).

2.3 Crystallinity and Crystalline Transition

Crystallinity was calculated with wide-angle X-ray diffractograms obtained using a tablet consisted of cotton fibers cut finely by a method similar to that described by P.H. Hermans et al. An example of untreated cotton sliver (BL-S) is show in Fig.1. Crystalline (Mcr) and amorphous parts (Ma + air and Compton scatterings) in the X-ray diffractograms were separated by drawing the background lines, and individual areas (Mcr and Ma) were measured. χ% was calculated with the following equation (1).

\[
χ\% = \frac{M_{cr}}{M_{cr} + M_{a}} \times 100 \tag{1}
\]

On the other hand, crystalline transitions were calculated with the following equation (2), after separating crystal structures by a method similar to that described by B.G. Ranby.

\[
a \text{tr.} \% = \frac{\text{Total crystallinity (}% - \text{Cell-I(}%)}{\text{Cell-I(}%)} \times 100 \tag{2}
\]
2.4 Barium Activity Number (Ba No.)

Ba No. has been generally used as industrial index indicating the degree of mercerization. A.E.Zavadskii et al. reported that BaNo. are inverse proportion to crystallinity and in proportion to contents of Cell- II on NaOH aq. pre-treatment (mercerization) of cotton fabrics. It was expected that there is such tendency as same as in the case of NaOH aq. pre-treatment on cotton fabrics pre-treated with liquid ammonia. Therefore, Ba No. was picked up as one of micro-structural index. The warp and the weft yarns separated from cotton fabrics were used as samples for evaluation. Ba No. were measured according to JIS L1096(1990) method.

2.5 Cross-Sectional Aspect Ratio of Cotton Fibers and These Distributions

As the macro-structural evaluation method from a viewpoint of strain-relaxation of cotton fiber, cross-sectional aspect ratio (S/L) of cotton fibers and their distributions were measured. Measurement methods are as follows: warp yarn (bundle state) separated from cotton fabrics were embedded in paraffin wax and sectioned using a microtome. Light photomicrographs of fiber cross-sections were produced at magnification of 800X. Image-analysis of fiber cross-sections was carried out using the PIAS Co., Personal Image Analyzer System LA-500. S/L values were calculated with approximating elliptical short axis/long axis ratio(S/L) of cotton fibers. S/L values were obtained on averages of n ≥ 46.

3. Results

3.1 Characterization of the Crystal Structures

It is well known that the crystal structure of native cellulose transits from Cell- I to Cell- II by the pre-treatment with aqueous NaOH solution and from Cell- I to Cell- III by the pre-treatment with liquid ammonia. In order to calculate the crystalline transition (α tr.%), it was checked that the standard sample SM shows Cell- II and other standard sample SN shows Cell- III. Wide-angle X-ray diffractions and 13C•NMR spectra of above samples were shown as compared with untreated cotton sliver (BL-S) in Fig.1 and Fig.2, respectively. The diffraction peaks in wide angle X-ray diffractograms of BL-S show respectively the existence corresponding to (101),(002),(021) and (040) planes being characteristic of Cell- II around 12.0°, 20.0°, 21.5°, 20.4° and 34.8° ,and the 13C•NMR spectra of SM is similar with that of Cell- II, so the crystal structure considered to be Cell- II. The diffraction peaks in wide-angle X-ray diffractograms of SN corresponding to (101), (002), (021) and (040) planes being characteristic of Cell- III around 11.7°, 20.7°, 20.1°, 34.4° and 17.0° can be found. The 13C•NMR spectra of SN is similar with that of Cell- III, so the crystal structure considered to be Cell- III. From these results, BL-S, SM and SN were assigned as cotton fibers having crystal structure of Cell- I, Cell- II and Cell- III, respectively.

3.2 Results of Measurements on Crystallinity (χ %), Crystalline Transition (α tr.%), and Barium Activity Number (Ba No.) of Cotton Fabrics and Slivers Pre-Treated.

Wide-angle X-ray diffractograms of cotton fabrics pre-treated with aqueous NaOH solution, liquid ammonia and these combination are shown in Fig.3, 4 and 5, respectively. Crystallinity (χ %), crystalline transition (α tr.%), and Barium Activity Number obtained from adsorption values of aqueous barium hydroxide solution are summarized in Table 1.

3.3 Results of Measurements on Cross-Sectional Aspect Ratio (S/L) of Cotton Fibers.

The S/L distribution of BL-T, M1,N1,M2 and N2
obtained using an Image Analyzer System are shown in Fig.6. Numbers (n) of cotton fibers evaluated are 146–272 and these averages are shown in Table 1.

4. Discussion

4.1 Relation between Crystalline Transition (α tr. %) and Cross-Sectional Aspect Ratio (S/L) and These Distributions

From a view point of micro-structural changes, it is considered that the larger α tr. % value, the easier the penetration of liquid ammonia or NaOH molecules to crystalline regions in a single fiber composing yarn as collective body, resulting in the more cross-sectional strain–relaxation progresses. On the other hand, from a view point of macro-structural changes, it was considered that the larger the average of S/L value and the less the region having small S/L values become, the more circular a single fiber composing yarn as collective body become, resulting in the more cross-sectional strain–relaxation progresses. In fact, it is recognized that both relations are shown in Fig.7. And the larger α tr. % values become, the larger S/L values become, leading that both micro-structural and macro-structural changes show fundamentally close relation. Fabric samples N1, N2 and sliver sample SN pre-treated with liquid ammonia are plotted on the same line. The α tr. % value of N2 shows very high value of 88% to be characteristics. On the other hand, the degree of changes of S/L values against α tr. % values of fabric samples M1, M2 and M3 pre-treated with aqueous NaOH solution are large as compared with that of N1, N2. Further, the α tr. % value of M2 is limited 22.4%. The degree of changes of S/L value against α tr. % value of fabric samples M1/N1, M2/N1 and M3/N1 pre-treated with combination of aqueous NaOH solution and liquid
ammonia are large as same as those of M1, M2 and M3. If $a_{\text{tr. %}}$ values are compared with same S/L value, the order of $a_{\text{tr. %}}$ values are as follows:

$$\text{L.NH}_3 > \text{NaOH aq.}, \text{L.NH}_3 > \text{NaOH aq.}$$

From a viewpoint of the percentage of crystalline transition, it is recognized that cotton fabrics pre-treated with liquid ammonia are most effective among them.

4.2 Relation between Crystallinity ($\chi$ %), Crystalline Transition ($a_{\text{tr. %}}$) and Barium Activity Number (BaNo.)

The relationships between BaNo. and $\chi$ % and between BaNo. and $a_{\text{tr. %}}$ are shown in Fig.8 and 9, respectively. Though it is recognized that there are various data by pretreatment methods, Ba No. value as Index indicating volume of amorphous with decreasing of $\chi$ % values increases. The increase of Ba No. is correspond to the increase of amorphous region of cotton fibers due to pretreatments. On the other hand, it is clearly shown that there is close relation between $a_{\text{tr. %}}$ and Ba No. It is shown that $a_{\text{tr. %}}$ is correspond to the degree of changes on amorphous regions of cotton fibers. These results show that ammonia molecule due to various pretreatments penetrates most easily in crystalline regions of single fibers that compose cotton yarns and fabrics. Though it is not clear in detail, these results may suggest the existence of quality and quantity of amorphous regions corresponding to crystal form.

4.3 Relation between Cross-Sectional Aspect Ratio (S/L) and Barium Activity Number (BaNo.)

Relation between cross-sectional aspect ratio (S/L) from a view point of macro-structural changes and Ba No. from that of micro-structural changes are shown in Fig.10. Relation between S/L and Ba No. of cotton fabrics pre-treated with aqueous NaOH solution, liquid ammonia and these combination (Fig.10) are similar to above mentioned relation between S/L and $a_{\text{tr. %}}$ (Fig.7). That is, the relation between S/L and Ba No. of cotton fabrics pre-treated with aqueous NaOH solution (BT-T, M1, M2 and M3), with liquid ammonia (BL-T, N1 and N2) and with these combination (N1, M1/N1, M2/N1 and M3/N1) have individual linear correlations. It is considered to have the tendency that cross-sectional shapes of cotton fibers become more circular increasing with Ba No. values by individual swelling treatments (along cross-section of them). As shown in the case of crystalline transition, if Ba No. values are compared with same S/L values, Ba No. values
of cotton fibers pre-treated with liquid ammonia show larger value than these pre-treated with aqueous NaOH solution.

4.4 The Swelling Mechanism of Cotton Fibers Due to Pre-Treatments

Liquid ammonia (b.p.-33.4°C) shows a weak surface tension and effects as basic, so that it has the characteristics penetrating by interior of cotton fiber in extremely short time. The pre-treatment with liquid ammonia has no rinse process and removes ammonia by heat-treatment different from that of aqueous NaOH solution. Therefore, it is considered that they have the effects on uniform swelling of cotton fibers and easy transition of crystal structures even under tension conditions. As shown in Fig.6, it can be understood from the fact that the small S/L values decrease with increasing the S/L average values of cotton fibers by pre-treatment with liquid ammonia. On the other hand, in the case of pre-treatment of cotton fibers with aqueous NaOH solution, the crystal structure partially is transited Cell- I to Cell- II after forming various complexes among cellulose molecules, Na⁺ and H₂O. In this case, it is considered that NaOH molecules, which differ from liquid ammonia, penetrate first into amorphous regions of intra-microfibrils and swell amorphous region, followed to penetrate to crystalline region connecting with amorphous region. On this swelling process, crystal structure of cotton fibers is transferred from Na- Cell- I to Na-Cell- II. Cell- II was formed by removing NaOH molecules from Na-Cell- II by rinsing with water. In order to make perfectly transition from Cell- I to Cell- II (mercerization), it takes long time, that differ from that by liquid ammonia pre-treatment and its reaction progresses without uniformity. Therefore, the region of small value of S/L in the case of aqueous NaOH solution pre-treatments as compared with the case of liquid ammonia pre-treatment is remained larger (Table1, Fig.6).

5. Conclusion

On vapor phase (VP) finishing with formaldehyde of cotton fabrics, when a pre-treatment relaxing the strain of fiber was given, it was expected to be improved the loss of strength of cotton fabrics after VP finishing. In this report, the pre-treatment with liquid ammonia, aqueous NaOH solution and these combinations were carried out as pre-treatment of cotton fabrics before VP finishing, and the relation between the strain-relaxation of cross-sectional direction of cotton fibers and various pre-treatment methods were studied. Following results were obtained:

Table 1 Morphological changes of cotton fibers treated with LNH₃, NaOHₐq, and NaOHₐq/LNH₃.

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Sample Form</th>
<th>Treatment</th>
<th>Crystallinity and Lattice Type</th>
<th>Ba No.</th>
<th>S/L**</th>
</tr>
</thead>
<tbody>
<tr>
<td>BL-T</td>
<td>Fabric Un-treated</td>
<td>49.0 49.0</td>
<td>N  N</td>
<td>0.0 0.0</td>
<td>0.0 0.0 105.6 105.6 0.97 0.586</td>
</tr>
<tr>
<td>M₁</td>
<td>Fabric 18.7%NaOHₐq</td>
<td>49.1 37.7</td>
<td>N  8.4</td>
<td>0.0 0.0</td>
<td>17.1 126.5 121.0 121.0 0.664</td>
</tr>
<tr>
<td>M₂</td>
<td>Fabric 18.7%NaOHₐq (tissue)</td>
<td>47.3 36.2</td>
<td>N  11.0</td>
<td>0.0 0.0</td>
<td>22.6 140.3 140.3 140.3 0.664</td>
</tr>
<tr>
<td>M₃</td>
<td>Fabric 25.5%NaOHₐq</td>
<td>45.1 30.0</td>
<td>N  15.1</td>
<td>0.0 0.0</td>
<td>30.8 152.3 140.3 140.3 0.668</td>
</tr>
<tr>
<td>SM</td>
<td>Silver 21.5%NaOHₐq (tissue)</td>
<td>44.2 23.9</td>
<td>N  9.9</td>
<td>0.0 0.0</td>
<td>99.4 – – – – 0.777</td>
</tr>
<tr>
<td>N₁</td>
<td>Fabric Liquid Ammonia</td>
<td>44.8 20.3</td>
<td>N  0.0</td>
<td>0.0 0.0</td>
<td>24.5 49.5 161.3 154.8 149 0.689</td>
</tr>
<tr>
<td>N₂</td>
<td>Fabric Liquid Ammonia(tissue)</td>
<td>44.8 11.1</td>
<td>0.0 0.0</td>
<td>42.9 88.2 183.2 171.8 175 0.706</td>
<td></td>
</tr>
<tr>
<td>SN</td>
<td>Silver Liquid Ammonia(tissue)</td>
<td>44.6 20.5</td>
<td>N  0.0</td>
<td>0.0 0.0</td>
<td>44.5 95.9 – – – – 0.724</td>
</tr>
<tr>
<td>M₁/H₁</td>
<td>Fabric M₁ = Liquid Ammonia</td>
<td>45.9 19.2</td>
<td>N  0.0</td>
<td>0.0 0.0</td>
<td>52.8 150.4 150.4 150.4 0.678</td>
</tr>
<tr>
<td>M₂/H₁</td>
<td>Fabric M₂ = Liquid Ammonia</td>
<td>41.8 12.4</td>
<td>N  0.0</td>
<td>0.0 0.0</td>
<td>63.0 175.6 175.6 175.6 0.762</td>
</tr>
<tr>
<td>M₃/H₁</td>
<td>Fabric M₃ = Liquid Ammonia</td>
<td>44.8 8.0</td>
<td>– – – –</td>
<td>74.7 182.8 182.8 172 0.785</td>
<td></td>
</tr>
</tbody>
</table>

*Crystalline Transition G_{N-Cell-I} = \frac{\text{IN-Cell-I after treatment}}{\text{IN-Cell-I before treatment}} = 100

** Cross-Sectional Aspect Ratio of Fibers
1) It was found that crystalline transition \( \alpha \) tr. % shows very close relation with the value of cross-sectional aspect ratio S/L and these are effective as Index indicating the degree of the strain—relaxation of cotton fibers.

2) Among pre—treatments studied, pre—treatment method with liquid ammonia was most effective. Such an effect is brought about by means of having characteristic of liquid ammonia so that the pre—treatments with liquid ammonia have an effect on swelling cotton fibers leading circular cross—section at short times.

3) It was found that \( \alpha \) tr. % shows very close relation with barium activity number (Ba. No.) being useful as index of amorphous regions, but the exact reason is not clear at present time, and solution of these problems will be expected in future.

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