Tensile Properties of Chemically Modified Ring- and Rotor-Spun Cotton Yarns

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SYNOPSIS

The effects of chemical treatments and modifications on the tensile properties of ring- and rotor-spun cotton yarns is discussed. The rotor-spun yarns treated with zinc chloride show a higher tenacity at low stretch levels compared to sodium hydroxide, whereas with sodium hydroxide, the rotor-spun yarns show higher tenacity at higher stretch levels compared with zinc chloride. The aqueous-treated rotor-spun yarns show a higher change in tenacity compared to ring-spun yarns. Sodium hydroxide-treated yarns before resin treatment show a higher retained tenacity compared to zinc chloride-treated yarns. The substitution treatment after swelling and stretching to 100% shows a higher tenacity than that of the slack substituted yarns. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

EXPERIMENTAL

A great deal of work has been carried out on the swelling and stretching of cotton fibers and yarns.¹⁻⁴ The swelling behavior of cotton fibers in sodium hydroxide and zinc chloride has been dealt with extensively in the literature.⁵⁻¹⁶ More recently, Subramaniam et al.¹⁷ discussed the properties of ringand rotor-spun cotton yarns swollen in a slack condition only with zinc chloride and sodium hydroxide. Many authors¹⁸⁻²¹ have dealt with the swelling and subsequent stretching of cotton fibers in water. From the literature, it is noticed that, in most of the cases, the swelling and stretching treatment was given to the yarn only with sodium hydroxide, and virtually no data are available on swelling and stretching treatments with zinc chloride on rotor-spun yarns. In this article, the effects of swelling and stretching treatments, resin finish, and chemical modifications on tensile properties of ring- and rotor-spun cotton yarns are discussed.

Materials

For this study, ring- and rotor-spun yarns spun to a count of 16's Ne (37 tex) from the same fiber mixing were used. All chemicals used for treatments and analytical purposes were of Analar grade. Distilled water was used for making up all solutions. All chemical treatments were given for ring- and rotorspun yarns in the same bath in order to maintain identical treatment conditions.

Chemical Treatments Given to the Yarn Samples

Slack Swelling and Stretching Treatments

The scoured yarns were taken as control samples. The control samples in the form of hanks were subjected to slack swelling for 30 min at $30 \pm 1^{\circ}$ C using two swelling agents, namely, sodium hydroxide (NaOH) (22% w/w) and zinc chloride (ZnCl₂) (64.5% w/w) solutions (specific gravity at $30 \pm 1^{\circ}$ C = 1.8336) separately and stretched to 98, 100, 102, and 104% of their original length in a laboratory stretching machine. The treated yarns were washed¹⁷ and air-dried.

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Aqueous Treatment

The control yarns were swollen for 30 min in hot water (70-80°C) in slack form and stretched to 104% of their original length in the laboratory stretching machine and dried at room temperature while maintaining that length.

Resin Treatment

The resin dimethylol dihydroxy ethylene urea (DMDHEU) used in this study has a built-in catalyst. The cross-linking treatment was given by conventional the pad-dry-cure method to the slack swollen and stretched yarn samples. The samples were impregnated in the respective baths (90 g/literature) for a period of 5 min and the wet pickup of approximately 70% was maintained for all samples. The resin-padded samples were dried at 90°C for 3 min and cured for 5 min at 140°C in a curing chamber.

Chemical Modifications Given to the Yarn Samples

For slack acetylated yarn samples, the control samples were treated with 22% (w/w) NaOH solution at 31°C for 30 min and squeezed to 100% pickup and treated with the reaction mixture (acetic) containing an acetic anhydride (85%) and acetic acid (14%) solution using benzene (1%) as the diluent for about 30 min at 30–40°C. The material-to-liquor ratio of 1 : 30 was taken.

For stretch acetylated yarn samples, the NaOH slack swollen yarns were stretched to 100% of their original length in the laboratory yarn stretching machine and squeezed for 100% pickup at stretch condition; then, the tension was completely released. The yarns was allowed to react with the acetic mixture at $30-40^{\circ}$ C in slack form. The samples were washed^{22,23} and air-dried. The slack-and-stretch cyanoethylation and benzoylation were carried out using acrylonitrile and 10% solution of benzoyl chloride in place of the acetic mixture used in acetylation treatment.

Classification of Treated Samples

The treated yarns were divided into three groups, groups I to III, each group designated to bring out a particular effect. Group I comprises slack swollen and stretched samples in sodium hydroxide, zinc chloride, and water. Group II comprises resin-treated group I samples except water-swollen yarns, and group III comprises samples swollen in sodium hydroxide and subjected to chemical modification.

Chemical Estimations

Acetyl values were measured according to the standard chemical method²⁴ using duplicate samples. From the acetyl content, the degree of acetylation was calculated.²² The nitrogen content (N) is used for the calculation of the degree of cyanoethylation.²² The values of the degree of benzoylation (DS) were calculated²² from the dry weights of the yarns before and after treatment. In the present study, Kjeldahl's method^{25,26} was used to estimate the nitrogen content of the resin-treated and cyanoethylated samples.

Physical Estimation

The treated materials were conditioned before testing for physical and tensile properties at standard atmospheric conditions of $27 \pm 2^{\circ}$ C temperature and relative humidity of $65 \pm 2\%$ for minimum 72 h.

Packing Fraction

The packing fraction of the treated yarns was calculated by the following formula:

$$V = \frac{78,570 \times d^2}{T} \operatorname{cc/g}$$

where V is the specific volume of the yarn; d, the diameter of yarn in cm; and T, the tex:

Packing fraction
$$= \frac{\text{Specific volume of fiber}}{\text{Specific volume of yarn}}$$

The diameter of the yarn was measured using a projection microscope. For each sample, 50 readings were taken and the mean was considered.

Density

Treated yarn samples were cut into small pieces and dried for 1 week in a desiccator containing P_2O_5 under vacuum. The densities were then measured by the floating method using a mixture of carbon tetrachloride and xylene.

Infrared Spectra

Infrared spectra were obtained with a Hitachi IR-270-50 spectrophotometer by use of the potassium bromide pellet technique.²⁷ The infrared index is calculated from the ratio of the a_{1372} cm⁻¹ and a_{2900} cm⁻¹ band intensity.²⁸

Tenacity and Elongation

Tenacity and breaking elongation of the treated yarns were measured on an Instron tensile tester (Model 4301) with a gauge length of 300 mm and a crosshead speed of 300 mm/min. The mean of 50 tests was taken in each case. Yarn linear density was calculated from the weight of the broken pieces.

RESULTS AND DISCUSSION

Tenacity and Elongation

Group I Yarns

The tenacity and elongation of Group I yarns are shown in Table I. It is observed that the scoured ring-spun yarn has a higher tenacity than that of the scoured rotor-spun yarn. After slack swelling in sodium hydroxide, the tenacity drops more (11%)for ring-spun yarns than for rotor-spun yarns (7.6%)(Table I), whereas the slack swollen yarns in zinc chloride show an increase by about 2% in the case of rotor-spun yarns and a decrease by about 4.9% in ring-spun yarns. As the stretch increases, the tenacity increases; the rate of increase in tenacity in the case of the rotor-spun yarns is higher than that of the ring-spun yarns treated with zinc chloride (Table I).

The increase in strength of the cotton yarns following swelling and stretching in zinc chloride and in sodium hydroxide has been attributed to the fibrillar orientation and improvements in the uniformity of strength along the fibers. The relative importance of the orientation and uniformity depends mainly on the tension applied during the mercerizing treatment.^{2,15,29} Also, it has been demonstrated by Lord and Nichols³⁰ that the process of untwisting the yarn and then giving the twist to the original level to the untreated rotor-spun yarn has significantly increased the strength.

In slack swollen 98 and 100% stretched yarns, the percentage increase in tenacity is higher in the case of zinc chloride-treated rotor-spun yarns than in sodium hydroxide-treated rotor-spun yarns (Table I). At low stretch levels, the packing fraction of rotor-spun yarns treated with zinc chloride show a higher value compared to sodium hydroxide treat-

| | Rotor Spun | | | | Ring Spun | | | |
|-----------|------------|------|-------|-------|-----------|-------|-------|-------|
| Treatment | Tena | C.T. | Elong | P.F. | Tena | C.T. | Elong | P.F. |
| Control | | | | | | | | |
| Scoured | 12.24 | 0.0 | 6.84 | 0.370 | 15.68 | 0.0 | 6.32 | 0.447 |
| NaOH | | | | | | | | |
| Slack | 11.31 | -7.6 | 16.81 | 0.291 | 13.92 | -11.2 | 15.08 | 0.344 |
| 98% | 12.76 | 4.2 | 5.59 | 0.404 | 15.05 | -4.0 | 5.54 | 0.480 |
| 100% | 13.88 | 13.4 | 5.47 | 0.422 | 17.24 | 9.9 | 5.25 | 0.488 |
| 102% | 14.47 | 18.2 | 5.01 | 0.438 | 17.60 | 12.2 | 4.58 | 0.498 |
| 104% | 14.89 | 21.7 | 4.92 | 0.483 | 18.75 | 19.6 | 4.54 | 0.552 |
| $ZnCl_2$ | | | | | | | | |
| Slack | 12.51 | 2.2 | 9.56 | 0.277 | 14.91 | -4.9 | 9.64 | 0.339 |
| 98% | 13.30 | 8.7 | 6.36 | 0.407 | 15.99 | 2.0 | 6.72 | 0.453 |
| 100% | 14.01 | 14.5 | 6.06 | 0.427 | 16.72 | 6.6 | 5.47 | 0.484 |
| 102% | 13.82 | 12.9 | 5.27 | 0.431 | 17.01 | 8.5 | 5.17 | 0.505 |
| 104% | 14.15 | 15.6 | 4.95 | 0.453 | 18.15 | 15.8 | 4.59 | 0.536 |
| Aqueous | | | | | | | | |
| Slack | 13.08 | 6.9 | 7.01 | 0.427 | 14.06 | -10.3 | 6.45 | 0.442 |
| 104% | 14.29 | 16.8 | 5.66 | 0.441 | 15.96 | 1.8 | 5.14 | 0.458 |

Table I Tensile Properties of Group I Yarns

Tena = tenacity (g/tex); C.T. = change in tenacity with respect to control yarn (%); Elong = elongation (%); P.F. = packing fraction.

ment. This would help to increase the tenacity of rotor-spun yarns. Even though, in the case of ringspun yarns, the change in tenacity of these samples is not very much, there is some increase in the tenacity of zinc chloride-treated yarns. Between the zinc chloride-treated rotor- and ring-spun yarns, the change in tenacity is significant in the rotor-spun yarns. The rotor-spun yarn initially had the lowest packing fraction value (Table I), which suggests a relatively loose packing for the fiber elements in the yarn. This would lead to a better and more uniform swelling during treatments and to a marked increase in orientation during subsequent stretching. But, in ring-spun yarns, the change in tenacity is small as the orientation increases. The difference in tenacity among varns may be due to the influence of the packing fraction produced by the treatments.

At higher stretch (102 and 104%), the change in tenacity of sodium hydroxide-treated yarns shows an increase in both types of yarns over that of the zinc chloride-treated ones. The swelling accompanied by stretch to the above original length brings the fibers closer to one another in the yarn, thereby making them more compact compared to the zinc chloride treatment. This would serve to increase the tenacity of sodium hydroxide-treated yarns over that of the zinc chloride-treated ones.

From Table I, it is noticed that there is a slight improvement in tenacity of the rotor-spun yarns slack swollen in water; the ring-spun yarns show deterioration. The elongation values are unchanged. One very interesting point is that the tenacity of the rotor-spun varns swollen in aqueous medium and stretched to 104% showed a higher strength compared to the scoured yarns (Table I) and compares more or less favorably with the yarn swollen and stretched to 102% in sodium hydroxide; this clearly demonstrates that simply a water treatment can be given to the rotor-spun yarn to enhance its strength (16.8%). But in the case of ring-spun yarns, the tenacity is not changed (1.8%) by this treatment. These results are contradictory to the result reported recently by Doke and Krishna Iyer.²¹ It may also be noted that the authors tested the strength of the ring-spun carded cotton yarns following stretching to two different levels.

Aqueous treatment alone increased the tenacity of the rotor-spun yarn. The explanation of this phenomenon is that the swelling in water and subsequent stretching to 104% opens up the structure and removes the built-in strains. The fibers that have been stretched in water and then dried in that condition have few or no convolutions, whereas the normal fibers have many. This is also supported by other workers.^{18–21} The packing of the rotor-spun yarn is lower than that of the ring-spun yarn, and this assists in the better absorption of the chemical or water (Table I).

The elongation of scoured rotor-spun yarns is higher than that of the ring-spun yarns (Table I). As the stretch increases, the elongation decreases in both types of yarns, but at all stages, the breaking elongation of rotor-spun yarns is, in general, higher compared to ring-spun yarns. The elongation of zinc chloride slack-treated yarns is less (Table I) compared to sodium hydroxide, because of their low shrinkage value.¹⁷ In all cases, the rate of reduction in the elongation at higher stretch is the same.

In the case of aqueous-treated yarns (Table II), the elongation is more or less equal to that of 98% stretched rotor-spun yarn. In the case of ring-spun yarns, the drop in elongation is significant.

Group II Yarns

The values of tenacity and elongation of ring- and rotor-spun yarns treated with dimethylol dihydroxy ethylene urea (DMDHEU) after the swelling and stretching treatments in sodium hydroxide and zinc chloride (Group II yarns) are shown in Table II. It is observed that there is a drop in tenacity in slackand 98% stretch-treated yarns, but in the other samples, there is an increase in tenacity compared to the scoured yarns (Table II). Slack-treated ringspun yarns show a higher retained tenacity compared to their counterpart. As the stretch increases, the percentage of tenacity retained increases and attains a maximum with the stretch level. In slack and 98% stretch, the tenacity retention is more for zinc chloride-treated and cross-linked rotor-spun yarn than for its sodium hydroxide-treated counterpart. At 100, 102, and 104% stretch levels, the values are lower than those of the sodium hydroxidetreated yarns. The same trend is also observed in ring-spun yarns.

These data provide evidence that yarn strength losses are in no way inherent to the formation of covalent cross-links in cotton cellulose. Strength losses are prevented when the crystallites are aligned and fibrillar spirals as well as fiber convolutions are rather completely removed prior to the cross-linking treatment.² Applying stretch to swollen fibers influences the load distribution on the side of the higher load and renders the distribution asymmetric. Mercerization also reduces low polymeric components by dissolving shorter chains.³¹ Thus, improved te-

| | Rotor Spun | | | | Ring Spun | | | |
|-----------|------------|------|-------|-------|-----------|------|-------|-------|
| Treatment | Tena | R.T. | Elong | P.F. | Tena | R.T. | Elong | P.F. |
| Control | | | | | | | | |
| Scoured | 12.24 | 0.0 | 6.84 | 0.370 | 15.68 | 0.0 | 6.32 | 0.447 |
| NaOH | | | | | | | | |
| Slack | 10.35 | 85 | 15.20 | 0.291 | 12.85 | 82 | 14.39 | 0.353 |
| 98% | 11.69 | 96 | 5.51 | 0.402 | 13.67 | 87 | 4.80 | 0.483 |
| 100% | 12.80 | 105 | 4.83 | 0.430 | 15.91 | 101 | 4.60 | 0.491 |
| 102% | 13.64 | 111 | 4.73 | 0.443 | 16.45 | 105 | 4.42 | 0.496 |
| 104% | 14.05 | 115 | 4.24 | 0.483 | 17.73 | 113 | 4.38 | 0.553 |
| $ZnCl_2$ | | | | | | | | |
| Slack | 10.83 | 88 | 7.95 | 0.272 | 13.88 | 89 | 8.85 | 0.339 |
| 98% | 12.04 | 98 | 5.80 | 0.401 | 14.83 | 95 | 5.60 | 0.449 |
| 100% | 12.69 | 104 | 5.09 | 0.425 | 15.65 | 100 | 5.14 | 0.484 |
| 102% | 13.29 | 109 | 4.89 | 0.424 | 16.10 | 103 | 4.57 | 0.502 |
| 104% | 13.58 | 111 | 4.45 | 0.449 | 17.25 | 110 | 4.47 | 0.536 |

Table II Tensile Properties of Group II Yarns

Tena = tenacity (g/tex); R.T. = retained tenacity with respect to control yarn (%); Elong = elongation (%); P.F. = packing fraction.

nacity may be attributed to the removal of structural imperfections or weak links in cotton during the combined swelling and stretching treatments. Mercerization permits more uniform distribution of cross-links in the network structure of cotton fibers compared to the unmercerized cross-linked yarn and is also responsible for the higher strength and elongation retention of the yarns.⁴

The retention of tenacity in both types of yarns is almost the same and the change in tenacity as stretch increases is followed by the same trend as in the case of swelling and stretching treatments.

It is observed from the nitrogen content that as the stretch percentage increases the nitrogen content decreased. A good correlation between nitrogen content and tenacity with a correlation coefficient r = .98 is obtained (Fig. 1).

The retention of elongation is high at low stretch. As the stretch increases, the percentage retention is low. This is due to the increase in the stiffness of the yarn. The elongation of zinc chloride-treated rotor- and ring-spun yarns is marginally higher than that of sodium hydroxide-treated yarns at all stretch levels (Table II). The same trend as for stretch increases and elongation decreases is observed in the resin-treated yarns also.

Group III Yarns

The tensile properties of chemically modified ringand rotor-spun yarns are given in Table III. The tenacity of acetylated rotor-spun yarns after stretch mercerization in sodium hydroxide shows is higher compared to the slack swollen and acetylated yarns. Among the treatments given to the rotor-spun yarns, the stretched yarns subjected to acetylation show a

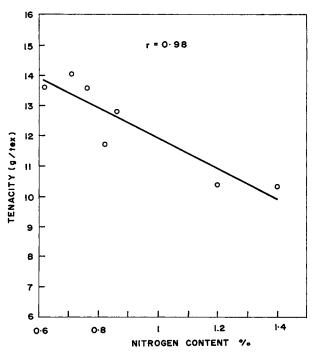


Figure 1 Relationship of nitrogen content to tenacity (Group II yarns).

| | <u> </u> | Rotor Spun | | | | Ring Spun | | | |
|---------------|----------|------------|-------|-------|-------|-----------|-------|-------|--|
| Treatment | Tena | С.Т. | Elong | P.F. | Tena | C.T. | Elong | P.F. | |
| Control | | | | | | | | | |
| Scoured | 12.24 | 0.0 | 6.84 | 0.370 | 15.68 | 0.0 | 6.32 | 0.447 | |
| Acetylation | | | | | | | | | |
| Slack | 11.89 | -2.7 | 16.77 | 0.341 | 11.77 | -24.9 | 15.46 | 0.422 | |
| 100% | 12.70 | 3.8 | 10.15 | 0.384 | 16.55 | 5.6 | 10.46 | 0.452 | |
| Benzoylation | | | | | | | | | |
| Slack | 10.33 | -15.6 | 13.47 | 0.351 | 10.96 | -30.1 | 10.3 | 0.368 | |
| 100% | 12.06 | -1.5 | 11.75 | 0.356 | 15.10 | -3.7 | 8.51 | 0.466 | |
| Cyanoethylati | on | | | | | | | | |
| Slack | 11.32 | -7.5 | 22.77 | 0.367 | 11.11 | -29.2 | 20.73 | 0.466 | |
| 100% | 12.41 | 1.4 | 15.15 | 0.366 | 14.80 | -5.6 | 14.65 | 0.557 | |

Table III Tensile Properties of Group III Yarns

Tena = tenacity (g/tex); Elong = elongation (%); C.T. = change in tenacity with respect to control (%); P.F. = packing fraction.

higher percentage increase, such as 3.8%, with respect to the scoured yarns, whereas slack-treated and acetylated yarns show a drop in tenacity. Whereas the slack cyanoethylated yarn showed a drop in tenacity, the stretched and cyanoethylated one shows an increase of 1.4%. Both the slack and the stretched benzoylated yarns show a drop in tenacity.

In the ring-spun yarns, the stretched and acetylated yarns show higher tenacity compared to the slack-treated and acetylated ones. Cyanoethylated yarns exhibit a drop in tenacity, the slack-treated ones showing a greater drop than do the stretched yarns. The benzoylated yarns also follow the same trend.

Strength losses are found to be greater in ringspun yarns compared to rotor-spun yarns in respect to slack-treated yarns. The substitution treatment after swelling and stretching to 100% shows a higher tenacity than that of the slack-substituted yarns. This is because the stretching treatment improves the yarn orientation, thereby increasing the tenacity.

The decrease or increase in breaking strength on chemical modification (cyanoethylation) of cotton yarns was explained by Grant and co-workers³² in the light of frictional forces brought about by changes in the yarn construction during chemical modification. The loss in tensile strength in the case of benzoylated yarns is due to the changes in the fine structure of the fiber. This is supported by the stretched yarns that show a lower loss than that of the unstretched yarns, probably resulting from better orientation of the fiber structure during stretching in the swollen state.³³ Cyanoethylation treatment applied to the ring- and rotor-spun yarns after slack mercerization has led to higher elongation (Table III). Generally, rotor-spun yarns are characterized by higher elongation.

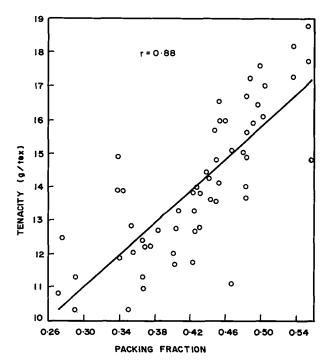


Figure 2 Relationship of packing fraction to tenacity (Groups I, II, and III yarns).

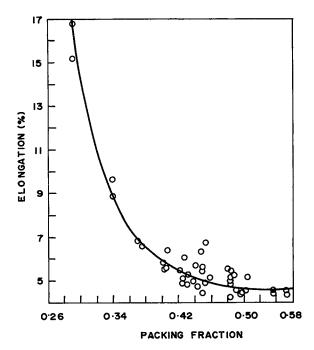


Figure 3 Relationship of packing fraction to elongation (Group I, II, and III yarns).

Packing Fraction

The packing fraction of Groups I, II, and III yarns are given in Tables I–III. The slack-treated yarns show a lower value compared to the equivalent/corresponding scoured yarns. As stretch increases, the packing fraction shows an increase. A good correlation is obtained between tenacity and the packing

Table IVInfrared Index and Density Data onControl, Slack, and 104%Stretch-Treated GroupI And Group II Yarns

| | Infrared a ₁₃₇₂ /a ₂₉₀ I Ya | ₀ Group | Density (g/cc) Rotor | | |
|-----------|---|--------------------|-------------------------|-------------|--|
| Treatment | Rotor | Ring | Group I | Group II | |
| Control | | | | | |
| Scoured | 0.719 | | 1.532 | — | |
| NaOH | | | | | |
| Slack | 0.513 | 0.515 | 1.508 | 1.514 | |
| 104% | 0.521 | 0.522 | | — | |
| $ZnCl_2$ | | | | | |
| Slack | 0.541 | 0.543 | 1.512 | 1.517 | |
| 104% | 0.562 | 0.560 | | | |

Table VDegree of Acetylation, Benzoylation,Cyanoethylation, and Density Values of GroupIII Yarns

| | Degree of | | | |
|-----------------|-----------|------|----------------------------|--|
| Treatment | Rotor | Ring | Density (g/cc) 1.475 | |
| Acetylation | 21.9 | 21.4 | | |
| Benzoylation | 15.3 | 15.2 | 1.369 | |
| Cyanoethylation | 7.8 | 7.7 | 1.468 | |

fraction (Fig. 2) and elongation and packing fraction (Fig. 3). Generally, ring-spun yarns are characterized by higher values of the packing fraction in all cases.

Infrared Index and Density

The values of the infrared ratio and density are given in Table IV. It is observed that sodium hydroxide and zinc chloride treatment have reduced the crystallinity. The same observation was made by Bhama Iyer et al.¹⁵ The values of the degree of acetylation, benzoylation, and cyanoethylation and the density of chemically modified yarns are reported in Table V.

CONCLUSIONS

Changes in tenacity in the case of rotor-spun yarns treated with sodium hydroxide and zinc chloride are found to be higher as the stretch increases from 100 to 104%. The aqueous treatment has led to a significant improvement in the tenacity of rotor-spun yarns without much change in elongation. Swelling with sodium hydroxide has resulted in a significant increase in elongation compared to zinc chloride. Retention of strength by sodium hydroxide-treated yarns subjected to resin finishing is generally found to be greater compared to zinc chloride-treated yarns.

The process of acetylation given to rotor-spun yarns after stretch mercerization in sodium hydroxide is found to result in a higher strength. The packing fraction of the stretched yarns show a progressive increase with increase in stretch, the values being always higher for ring-spun yarns. Generally, all the treatments have led to a sharp increase in packing density. The crystallinity and density of the yarns show a drop following treatments with sodium hydroxide and zinc chloride. The authors wish to thank Council of Scientific and Industrial Research (CSIR), New Delhi, for granting a research fellowship to one of the authors (S.T.).

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