Decrystallization and Acetylation and Benzoylation of Cotton Fibers

V. SUBRAMANIAM and N. VASUGI, *Department of Textile Technology, Alagappa College of Technology, Anna University, Madras-25, India*

Synopsis

The general effects of chemical modification such as acetylation and benzoylation on cotton yarns and fabrics are described and it is demonstrated that the physical properties of yarns and fabrics in terms of their elongation, moisture regain, friction, abrasion resistance, and recovery are enhanced significantly. Thermal analysis data show that benzoylated sample is the most stable product.

INTRODUCTION

A considerable amount of work was carried out on the chemical modification of cotton fibers to enhance their utilization some 40 years ago. Chemical modification of cotton fibers means any change involving covalent bonds of the cellulose molecule which makes it a useful product.

An interesting development that took place some 10 years ago is the chemical modification of cotton fibers by alkali swelling and substituting the cellulose molecule by acetyl group partially. Even in dyeing of cotton, it has been reported that the cotton in the swollen state takes up more dye. Kulshreshtha and Dweltz[1,2] have carried out work in this direction with particular reference to acetylation and reported the results in 1977. In 1986, Tsuji et al.[3] have extended their investigation to benzoylation, cyanoethylation, acetylation, and oleoylation and presented some interesting results. The main advantages that accrue by this process are that the cellulose becomes highly accessible and decrystallization takes place. The moisture regain of cotton fibers treated is higher than the untreated ones and there is no deterioration in tensile strength; crease recovery of the treated products is higher than that of the untreated materials, and it has been reported that dyeability for direct dye has increased substantially. The resistance to heat or acid and soil removal shows a significant improvement.

Tsuji et al.[3] claim that they are the first to carry out work on modification by this route and Kulshreshtha and Dweltz[1,2] have reported their results later. Kulshreshtha and Dweltz[1,2] and Tsuji et al.[3] have conducted only limited studies on the fibers and fabric characteristics. The breaking load of the yarn and fabrics has not been normalized to compare the fabrics subjected to various chemical modifications.

It is pertinent to note that Tsuji et al.[3] have unravelled the yarns from the treated fabrics in warp direction and have tested them for strength. However, there is a lack of information on the other properties of cotton yarns modified

Journal of Applied Polymer Science, Vol. 38, 207–218 (1989)
 CCC 0021-8995/89/020207-12$04.00

by these processes. It is necessary to normalize the strength of the fabrics and use is made of specific stress as suggested by Hearle[4] for comparing the fabric characteristics. Certain other properties such as yarn friction, yarn abrasion, and wicking have been measured to obtain a better understanding of the processes. We have measured the bending parameters of the treated fabrics using the cyclic bending tester which constitute the objective measurements of fabric mechanical properties and have reported the results for the first time.

The work reported in this paper is concerned with the physical properties of cotton yarns and fabrics swollen by alkali treatment and then substitution reaction such as acetylation and benzoylation. A systematic work on chemical modification of cotton yarns and fabrics has been undertaken with a view to studying the yarn and fabric properties.

EXPERIMENTAL

Materials

Ring spun grey yarns of 34s count (17 tex) were used for various treatments on cotton in yarn form. Cotton fabric of 94 × 84 was woven with this yarn and used in the study.

Pretreatment

The yarn and fabric samples were scoured by following a standard procedure. They were boiled in a solution containing 2.0% hydroxide, 1.0% sodium carbonate, and 0.5% wetting agent in a stainless steel vessel for 4 h and rinsed thoroughly with hot and cold water, scoured with a solution of 1% hydrochloric acid, further washed thoroughly until free from acid, squeezed, and dried in air.

Chemicals

All chemicals used for acetylation were of C.P. grade (BDH). All chemicals used for analytical purposes were ANALAR grade (BDH).

Mercerization

Cotton yarns and fabrics were treated in slack state with 22% aqueous solution of NaOH at 25°C for 30 min. After being squeezed to about 100% pickup, they were rinsed in water for 30 min and then scoured with 0.5% acetic acid and for 30 min rinsed again with water and air dried.

Acetylation

Acetylation represents an esterification reaction between acetic anhydride and one or more of the three of the cellulose chain. Cotton yarns and fabrics were immersed in 22% aqueous solution of NaOH at 25°C for 30 min, squeezed and reacted in the mixture of acetic anhydride, acetic acid, and benzene at 30–40°C for 30 min, and thoroughly washed in water and dried.

Benzoylation

Benzoylation of cotton cellulose also represents an esterification reaction between benzoyl chloride and one or more of the three hydroxyl of the anhydrous glucose units of the cellulose chain. Cotton yarns and fabric in slack form were treated with a solution of 10% benzoyl chloride and 90% sodium hydroxide of 22% concentration for 30 min at room temperature. Benzoyl chloride is not soluble in sodium hydroxide. The floating benzoyl chloride randomly penetrates inside the cellulose so that the treated fabric is only partially esterified.

Benzoylated and acetylated products were dyed with Navilene Navy Blue RE 2%, and Navilene Yellow 5 RX 3%. Foron Brown and Vat dye were also used as a combination.

Analytical and Physical Test Methods

Degree of Acetylation

Acetyl values were measured according to the standard chemical method using duplicate samples. Basically the method consists of saponification in a standard aqueous solution of sodium hydroxide, 0.5N. After saponification the excess alkali is titrated with 0.5N standard aqueous hydrochloric acid. A similar treatment was given to the blank (unacetylated) material and from the titration readings the percentage of acetyl content was calculated.

Degree of Benzoylation

Degree of benzoylation was calculated from the dry weights of the fabrics before and after treatments from the following formula:

$$\text{degree of substitution (DS)} = \frac{w_1 - w_0}{w_0} \times \frac{162.08}{M_s - 1}$$

where w_0 and w_1 are dry weights of the fabrics before and after treatments (g) and M_s is the molecular weight of the substituting group,

$$\text{Degree of benzoylation (mol \%)} = \text{DS}/3 \times 100$$

Benzoyl content was estimated by the method based on the alcoholic alkali process for the determination of acyl value, as given by Genung and Mallatt.[5] Degree of substitution (DS) of benzoyl cellulose was calculated by the formula suggested by Gloor and Klug.[6]

Moisture Regain

Fabric samples were conditioned at 25°C, 65% RH for 24 h and weighed. They were then dried at 105°C for 1 h and weighed. Values of moisture regain were calculated from the following formula:

$$\text{moisture regain (\%)} = \frac{W_0 - W}{W} \times 100$$

where W_0 and W are weights of the fabrics before and after drying (g).

Density

Fabric samples cut into 5 × 5 mm were dried for 1 week in a desiccator containing P_2O_5 under vacuum. Density was measured by the flotation method using a mixture of carbon tetra chloride and xylene. Readings were taken after 24 h and the mean of 20 readings was taken.

Breaking strength, tenacity, and elongation under standard conditions were determined according to ASTM[13] specifications using an Instron tensile tester. Coefficient of friction of the yarns was measured by Howell's[7] method. Yarn and fabric wicking tests were performed by the method developed by the longitudinal wicking method.[8]

Crease recovery was measured by a Monsanto type tester using 1 × 4 cm test fabric of warp and weft direction. A load of 500 g (5000 mN) was applied for 5 min and the crease angle was determined after 5 min after unloading.

Stiffness was measured by using a centilever bending tester in accordance with B s 3356:1961. The bending parameters of the treated fabrics were determined using a bending hysteresis tester developed on the principle of Owen.[9] The parameters, namely, coercive couple, initial elastic flexural rigidity, final flexural rigidity, and bending recovery were extracted from the hysteresis curves. Five tests were made for warp and weft and the mean of the two was taken for each parameter. The bending recovery represents the degree of flat set as suggested by Nielson and Elder.[10]

Tear strength of fabrics was measured using the Elmendorf tear tester. Yarn abrasion resistance was measured by the abrasion tester working on the principle of Faasen and Van Harten's[11] and Veers'[12] method.

Air permeability was measured by using the Metafem air permeability tester. Abrasion resistance was measured by using the Martindale wear tester.

Thermal Analysis

Thermogravimetric analysis of the sample were carried out by using a Perkin-Elmer thermobalance with professional computer, TGA standard software, and a printer plotter. A few milligrams of the different samples were automatically weighed with the thermobalance. All these samples were heated up with 40 K/min in oxygen (gas flow of 40 mL/min) from ambient temperature up to 500°C. All the curves were obtained in the derivative form.

RESULTS AND DISCUSSION

Density and Moisture Regain

Table I shows the density, moisture regain, and the degree of acetylation and benzoylation of yarn samples. The drop in density and increase in moisture regain can be taken as an indication of decrystallization.

TABLE I
Density, Moisture Regain, and Degree of Acetylation and Benzoylation

Sample	Density	Moisture regain (%)	Degree of acetylation/ benzoylation (%)
Untreated	1.54	6.0	—
Mercerized	1.49	7.9	—
Acetylated	1.47	8.0	25
Benzoylated	1.37	4.5	14

TABLE II
Yarn Characteristics after Chemical Modification

Sample no.	Description	Tenacity (g/tex)	Elongation (%)	Linear density (tex)
1	Untreated	15.67	4.2	17.0
2	Mercerized	16.13	5.4	19.2
3	Acetylated	12.95	7.4	22.4
4	Benzoylated	10.97	11.7	21.0

The drop in densities with respect to benzoylated and acetylated samples is due to the replacement of hydroxyl groups by these bulkier groups. It can be noticed that the moisture regain of the acetylated sample shows an increase compared to the untreated control and the benzoylated sample shows a significant drop.

Yarn Characteristics

In Table II are listed the physical properties of the yarns. It can be seen that the acetylated sample shows a drop in strength of 16% and the benzoylated sample shows about a 30% drop. This is due to the change in the structure of the yarn and also due to the loss in crystallinity of the fiber following chemical modification. That considerable swelling takes place in the yarn is seen from the increases in linear density of the yarns. Elongation of the yarn shows a significant increase in acetylated and benzoylated samples.

Yarn Friction and Abrasion Resistance

Table III shows the results of the friction and abrasion resistance of the yarn samples. The coefficient of friction shows an increase in all the treated samples and this is explained by the increase in the area of contact following swelling. The abrasion resistance is maximum in acetylated sample and minimum in benzoylated sample. The increase in abrasion resistance is due to the consolidation of structure and also to the change in structure following substitution by acetyl groups.

TABLE III
Effect of Various Treatments on Yarn Friction and Abrasion Resistance

Sample no.	Treatment	Yarn to yarn friction	Abrasion cycles
1	Untreated	0.314	94
2	Mercerized	0.451	37
3	Acetylated	0.333	123
4	Benzoylated	0.376	40

TABLE IV
Wicking Time (s) for Various Heights of Chemically Modified Cotton Yarns

Sample no.	Description	10 mm	20 mm	30 mm	40 mm
1	Untreated	—	—	—	—
2	Scoured	5	12	35	75
3	Mercerized	10	43	104	—
4	Acetylated	19	66	269	—
5	Benzoylated	6	14	50	127

Yarn Wicking Tests

Wicking tests on yarn samples were done with a view to finding out the changes that occur in the yarn structure following chemical modification and the results are given in Table IV. It is noticed that the rate at which water is absorbed by the scoured sample is higher than that of the other samples. The acetylated sample has taken more time to wick and the mercerized and benzoylated samples lie intermediate between the scoured and acetylated samples.

Fabric Properties

Some details of the fabric samples are given in Table V. The parameter density index, which is the ratio of fabric density to fiber density, is a measure

TABLE V
Some Details of Fabric Samples

Description	Threads per cm		Yarn count (tex)		Cover factor		Fabric wt (g/m^2)	Thickness (mm)	Density (g cm^{-3})	Density index
	W^a	F^b	W	F	W	F				
Untreated	37	34	17	17	16.5	15.1	156	0.24	0.652	0.42
Mercerized	48	42	20	18	21.5	17.8	171	0.31	0.549	0.36
Acetylated	49	39	25	20	24.5	17.4	187	0.28	0.668	0.45
Benzoylated	46	36	22	20	21.6	16.1	186	0.27	0.690	0.51

[a] W = warp.
[b] F = weft.

TABLE VI
Properties of Chemically Modified Cotton Fabrics

	Untreated	Mercerized	Acetylated	Benzoylated
Specific stress (N/tex)	0.071	0.073	0.061	0.058
Tear strength (kg)				
Warp	1.42	1.82	1.32	1.28
Weft	1.26	1.65	1.26	1.02
Shrinkage in warp (%)	—	21	24	23
Extension (%)	18.5	27.8	32.6	30.6
Flexural rigidity mgf. (cm)				
Warp	371	211	232	174
Weft	257	219	233	142
Crease recovery $(W + F)^0$	144	178	154	153
Wicking height in mm for 900 s				
Warp	—	45	42	63
Weft	—	41	39	59
Abrasion resistance (% wt loss)	12.3	0.31	0.94	0.31
Air permeability (C $c/m^2/s/cm^2$)	0.064	0.034	0.026	0.031

of fiber volume fraction in the fabric and it will be noticed that acetylated and benzoylated fabric samples show an increase in this value. Values of cover factor of the treated fabrics are generally higher than that of the untreated sample. Fabric densities are high for the treated samples except for the mercerized sample.

The geometrical properties reflect the consolidation brought about by the treatments. It can be seen that values of the cover factor of the treated samples are higher than those of the untreated control fabric properties. The physical properties of the fabrics are given in Table VI.

It can be seen that the specific stress of the acetylated and benzoylated sample is lower than that of the untreated sample. Kulshreshtha and Dweltz[1] have reported that the tensile strength of the acetylated sample is higher than that of the untreated control and extension is also high. It is relevant to note that these authors have not normalized tensile strength and thus comparison becomes difficult as fabric weight and thickness change following chemical modification. The results show that while breaking extension values of acety-

TABLE VII
Bending Parameters of Treated Fabrics

Sample no.	Description	C_0 (mN mm)	G_0 (mN mm^2/mm)	G_ϕ (mN mm^2/mm)	Bending δ recovery
1	Untreated control	0.36	4.7	3.5	77.0
2	Scoured	0.19	2.67	2.1	74.5
3	Mercerized	0.31	4.77	4.0	77.5
4	Acetylated	0.27	4.10	2.72	79.3
5	Benzoylated	0.11	2.37	1.76	82.1

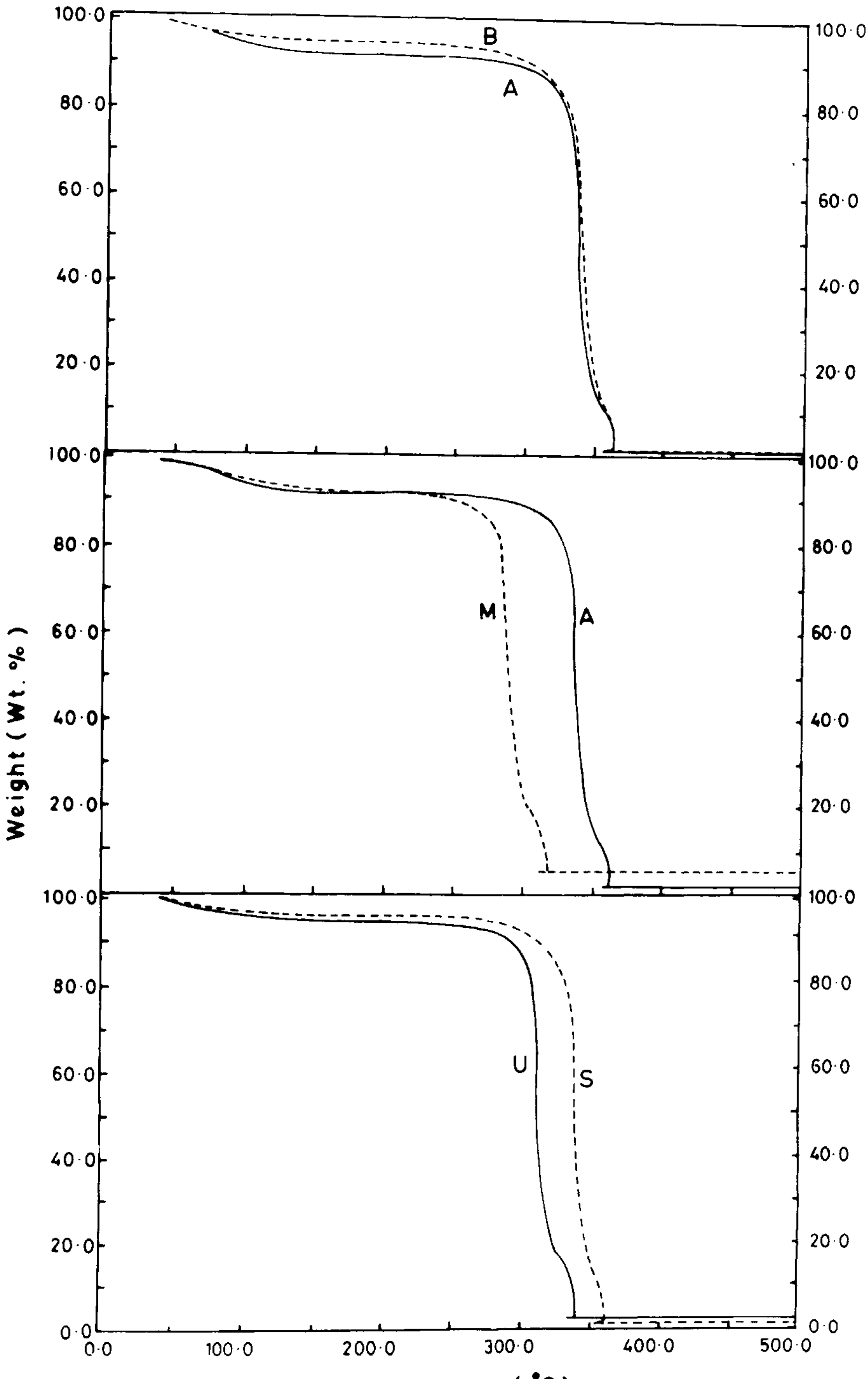

Fig. 1. TGA curves for the untreated and treated cotton fabrics: (A) acetylated; (B) benzoylated; (U) untreated; (S) scoured; (M) mercerized.

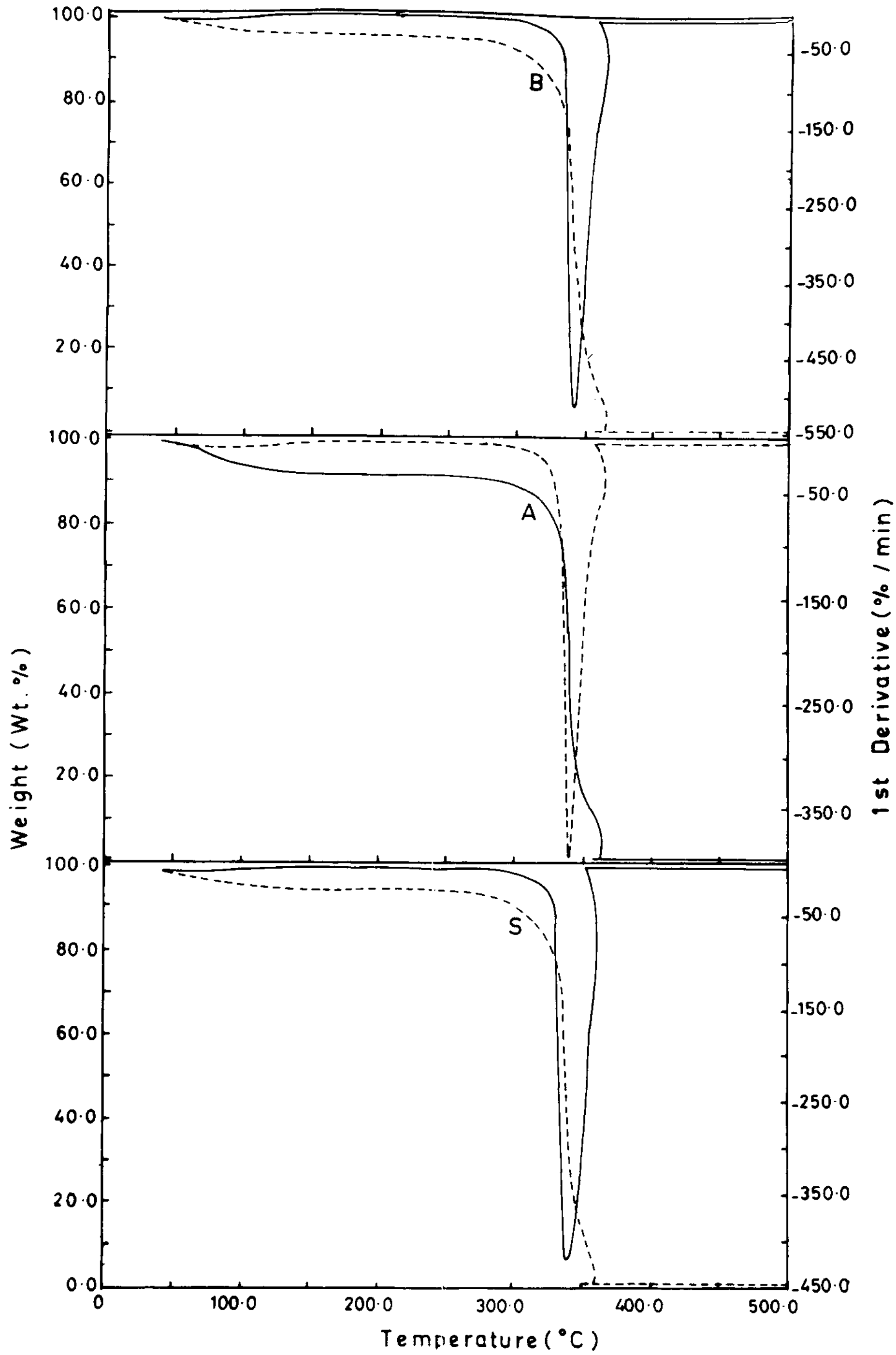

Fig. 2. TGA curves for the untreated and treated cotton fabrics: (A) acetylated; (B) benzoylated; (S) scoured.

lated and benzoylated samples are significantly high, the specific stress is low. Tear strength values of the acetylated sample compare favorably with untreated sample while those for benzoylated sample are lower. Shrinkage values of the treated samples are comparable. All the treated samples show a marked decrease in flexural regidity, which is a clear indication that the handle becomes lively. Crease recovery values are better for all the treated samples. Wicking behavior is better in the benzoylated sample and the values are equivalent for mercerized and acetylated samples. It is interesting to note that all the treated samples have good resistance to abrasion, presumably due to the increase in consolidation. Further, support for consolidation comes from air permeability values, which are low for the treated samples.

The bending parameters measured by the bending hysteresis tester are given in Table VII. It can be seen that the acetylated and benzoylated fabric samples exhibit a significant improvement in bending recovery. It has already been mentioned that the crease recovery of these two samples is greater than that of the untreated. It is also observed that the G_0 values, which represent

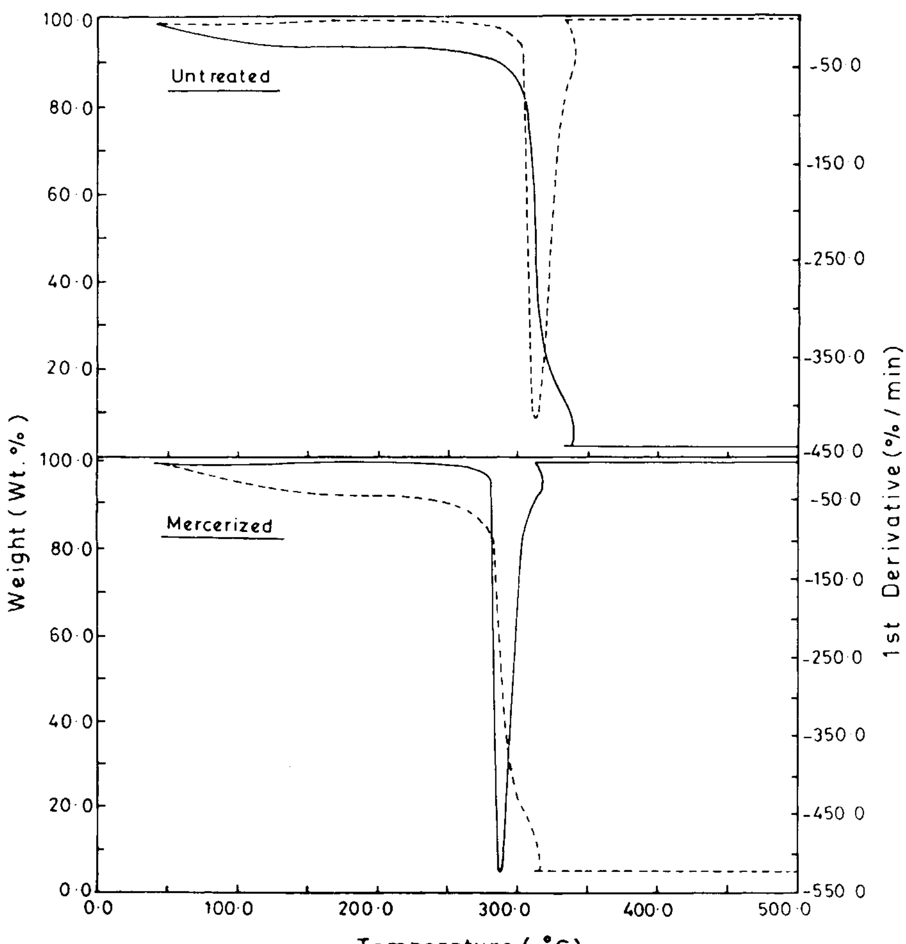

Fig. 3. TGA curves for the untreated and treated cotton fabrics.

TABLE VIII
TGA Data for the Samples

Sample no.	Description	Step 1 (%)	Step 2 (%)	Residue (%)	Thermal stability in O_2
1	Untreated	5.0	91.8	1.8	4
2	Scoured	4.5	94.4	0.9	3
3	Mercerized	7.8	87.3	4.7	5
4	Acetylated	8.0	91.1	0.8	2
5	Benzoylated	4.9	93.8	1.1	1

initial elastic flexural rigidity, are lower for the acetylated and benzoylated samples.

The acetylated and benzoylated samples take considerably higher direct dye uptake than the untreated and slack mercerized samples. This demonstrates the increase in accessibility as a result of treatment. Acetylated and benzoylated samples can be dyed with mixtures of vat and disperse dyes.

Figures 1, 2, and 3 contain TGA curves for untreated, scoured, mercerized, acetylated, and benzoylated samples. The rate at which weight was lost, as indicated by the first derivative curves, was slower for mercerized cotton. This may be attributed to the fact that some of the weight of the untreated cotton was in the form of inorganic salts, which may have retarded decomposition of cellulose via levoglucosan formation and favored the dehydration process. The most noticeable difference in the TGA results between the various samples is the percentage of residue remaining at the conclusion of the tests. The mercerized sample has shown the highest residue and scoured and acetylated samples show almost the same value. In Table VIII, TGA data for the samples are given. Results of TGA show that the benzoylated sample is the most stable and the mercerized is the least stable. Acetylated and scoured samples are found to be practically equal in oxidative stability.

CONCLUSIONS

Chemical modification of cotton cellulose by alkali swelling and substitution is in general beneficial to cotton by enhancing many of its properties. Properties of acetylated cotton that may prove of economic importance include increase in yarn and fabric densities, increase in friction and abrasion resistance, increase in moisture absorption improvement in extension of crease recovery and dye uptake. Bending recovery values of the acetylated and benzoylated samples are significantly high. The benzoylated sample shows a lower moisture regain, increase in yarn and fabric densities, crease recovery, and flexural rigidity. Abrasion resistance is good and wicking ability is better. The samples can be cross-dyed with vat and disperse combination to obtain certain fancy effects. The main disadvantage is a drop in tensile strength in the case of acetylated and benzoylated samples.

References

1. A. K. Kulshreshtha and N. E. Dweltz, *J. Appl. Polym. Sci.*, **21**, 2085 (1977).
2. A. K. Kulshreshtha and N. E. Dweltz, *J. Appl. Polym. Sci.*, **24**, 1139 (1979).

3. W. Tsuji, T. Nakao, K. Ohigashi, K. Maegama, R. N. Kobayashi, S. Shukri, S. Kasai, and K. Miyanaga, *J. Appl. Polym. Sci.*, **32**, 5175 (1986).
4. J. W. S. Hearle, in *Mechanics of Flexible Fiber Assembly*, Sijthoff and Noordhoff, The Netherlands, 1980, p. 7.
5. L. B. Genung and R. C. Mallatt, *Anal. Chem.*, **22**, 401 (1950).
6. W. E. Gloor and E. D. Klug, in *Cellulose and Cellulose Derivatives*, 2nd ed., Appendix B, Interscience Publishers Inc., New York, 1954, p. 1422.
7. H. G. Howell, *J. Text. Inst.*, **42**, T521 (1951).
8. P. R. Harnett and P. N. Mehta, *Text. J.*, **54**, 471 (1984).
9. J. D. Owen, *J. Text. Inst.*, **58**, 589 (1967).
10. E. Nielsen and H. M. Elder, *J. Text. Inst.*, **65**, 488 (1974).
11. N. J. Faasen and K. Van Haten, *J. Text. Inst.*, **57**, T269 (1966).
12. L. S. Veer, *J. Text. Inst.*, **68**, 424 (1977).
13. *Annual Book of ASTM Standards*, American Society for Testing Materials, Philadelphia, 1971.

Received April 25, 1988
Accepted May 24, 1988