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Enzymatic Hydrolysis of Cotton, Linen, Ramie, and Viscose Rayon Fabrics

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ABSTRACT

Cotton, linen, ramie, and viscose rayon fabrics along with a cotton/linen blend were hydrolyzed with cellulase from *Trichoderma viride*. Surface fibrils were eliminated by a 6 hour treatment in all cases. The loss of fibrillar matter appeared to be the primary cause of weight loss at this stage. On prolonged treatment, cotton, linen, and viscose rayon lost weight at a faster rate than ramie and the cotton/linen blend. The fall in yarn strength was progressive with increasing weight loss for cotton and viscose, while for linen and ramie it was slight initially and then increased sharply. Retention of strength after 48 hours' incubation time increased in the order viscose rayon < cotton < ramie < linen, whereas weight loss increased in the order ramie < linen < cotton < viscose rayon. X-ray crystallinity and moisture sorption of the samples did not change after the treatment, indicating that the mechanism of endwise attack of the cellulase at accessible cellulose chains on crystallite surfaces appeared to apply to all four fibers. The location of enzymatic attack could be monitored with a light microscope using Congo red staining in the case of cotton and linen, but not ramie or rayon. Changes in surface morphology could be followed for all the enzyme-treated fibers by scanning electron microscopy. Additionally, mechanical tests demonstrated the changes in stretchability and stiffness of the fabrics and the mobility of yarns within the samples.

Recently, enzymatic treatments have been a focus of interest for cotton finishing pertaining to fabric softness, good performance, and fashionable looks as well as the potential to simplify and cheapen manufacturing processes [14, 20, 27]. Complete or partial replacement of pumice stones by cellulase enzymes for the effect of "stone-washing" on denim is well established [20, 27], and the concept of "biopolishing," which originated in Japan, has been extended to knitted structures and blended fabrics [22]. Also, cellulases have been incorporated in detergents [16, 19] to remove fiber fuzz and by this means brighten the colors of the fabrics.

Controlled finishing with cellulase enzymes optimizes the surface properties of the fabric, but a decrease in tensile strength has to be expected. Commercial processes aim for 3–6% weight loss after hydrolysis, and a maximum of 10% loss in strength is considered acceptable [1, 22].

The mechanism of enzymatic hydrolysis of cellulosic materials is complicated and not yet fully understood [10, 12, 29]. Cellulases specifically catalyze the cleavage of the glycosidic bond in the cellulose molecule, provided the formation of the critical cellulase-substrate complex can be accomplished. Direct physical contact

of enzyme and substrate is required to obtain the complex [29]. A substantial prerequisite for the enzyme is its compliance with stereospecific requirements. Synergism of different components in the cellulase complex and inhibition mechanisms further complicate the reaction [12, 31, 32]. Key features for the cellulose substrate are crystallinity, accessible surface area, and pore dimensions [11, 29, 30]. Variation of any of these factors, *e.g.*, structural changes of the cellulose substrate by pretreatments, will influence the course of the entire degradation process [6, 8, 23].

Commercial enzyme treatments have usually targeted cotton. There is no explicit limitation to cotton, however, although little has been reported on other cellulose fibers [1, 22]. Thus, the objective of our work was to determine whether previous findings for cotton were valid for other cellulosic fibers such as linen, ramie, and regenerated cellulose. Although based on identical chemical composition, there are major differences in the fine structure and morphology of these fibers, which will largely determine the course of the enzymatic degradation reaction. Linen and ramie have higher crystallinity [2], and the pitch of the spiral structure is less than in cotton [13]. Furthermore, spiral reversal and convolutions occur in cotton. Significant differences in their pore structure and crystallite sizes have also been found [15]. Bast fibers like linen and

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ramie are multiple cellular systems, in contrast to cotton, which consists only of a single cell. Multicellular fibers contain natural gums and resins that keep the cells together [2]. It is possible that such residual encrusting substances can influence the course of enzymatic hydrolysis. Regenerated celluloses, on the other hand, are much simpler systems than natural cellulose fibers. A textile rayon such as the one we used here has considerably lower degrees of polymerization [18], crystallinity [5], and orientation [13] than cotton. Our additional objective was to quantify the changes in mechanical properties of the fabrics after enzyme treatment using the procedures we have reported previously [21].

In this study, we used a commercial cellulase from *Trichoderma viride*. This enzyme complex has been well characterized by various research groups [3, 9, 10]. Depending on the molecular weight and the method of determination, the average diameter of the molecule has been designated as 35–75 Å, assuming a spherical shape, or between 20 × 110 and 40 × 250 Å, assuming an ellipsoidal shape [3].

Experimental

The specifications of the fabrics are summarized in Table I. All fabrics were obtained from Testfabrics Inc., NJ, except ramie, which was supplied by a fabric manufacturer in China. The cotton/linen blend (52/48) consisted of cotton warp and linen filling yarns. The warp yarns of the ramie fabric were protected by a polyvinyl alcohol finish. Cellulase from *Trichoderma viride* (EC 3.2.1.4) with an activity of 9.0 units/mg solid was obtained from Sigma Chemical Company. All other chemicals were reagent grade.

To prepare an enzyme solution, 1 g of cellulase was dissolved in 40 ml cold 0.05 M sodium acetate buffer (pH 5.0). Fabric strips were immersed in the buffer solution at a liquor ratio of 1:200 and adjusted to 37°C within 15 minutes. For each gram of fabric (conditioned weight), 4 ml of the cellulase solution was added and the fabrics were treated for various periods of time at 37 ± 0.2°C with gentle shaking. To terminate the

reaction, the fabrics were washed with 100% acetone followed by several washings with distilled water before air drying.

Fabric thickness was measured with a C&R tester, model CS-55 (Custom Scientific Instruments Inc.) according to ASTM-D 1777. The diameter of the presser foot was 2.88 cm, and 6.90 kPa pressure was applied for intervals of 5 seconds. The control samples were washed in distilled water and air dried before measurement. The average of five readings is given.

Weight loss was determined using the conditioned weights (65% RH, 21°C) before and after the cellulase treatment. The data given in Table II are the average of 15 samples.

TABLE II. Weight loss as a function of incubation time.

Fabric type	Weight loss, %		
	6 hours	24 hours	48 hours
Cotton	4.20	13.89	23.83
Linen	6.34	13.59	21.13
Ramie	3.80	6.44	10.46
Viscose rayon	2.46	13.63	26.23
Cotton/linen blend	4.58	8.90	15.69

X-ray diffraction spectra were obtained with a Diano-XRD 8000 x-ray machine. The experimental procedure and determination of sample crystallinity are described elsewhere [7, 8]. Infrared spectra were measured with a Perkin Elmer 1600 series FTIR spectrophotometer, using the potassium bromide pellet technique [4].

For absorption moisture regain, triplicate values of control and hydrolyzed samples were determined on 0.5 g fabric, cut into small pieces, conditioned at 65% RH and 21°C. Dry weights were obtained by exposing the samples to P₂O₅ for several days. Water retention values were determined after soaking 0.5 g of the samples, cut into small pieces, in distilled water for 24 hours at 21°C followed by centrifuging for 30 minutes at 900 g [33]. Three determinations for each sample were averaged.

TABLE I. Fabrics specifications.

Fabric type	Fabric count ^a , warp/filling	Weight/area, g/m ²	Fabric thickness, mm
Bleached desized cotton print cloth ^b	30/30	108.15	0.286
Handkerchief linen ^b	23/19	83.86	0.225
Ramie ^b	24/23	135.75	0.358
Bright filament viscose satin	66/24	108.40	0.108
Bleached cotton/linen blend 52/48 ^b	24/18	126.94	0.305

^a Number of yarns per cm. ^b Plain weave.

Yarn breaking strength was determined using an Instron tensile tester at 65% RH and 21°C. The gauge length was 76.2 mm, and tests were performed at a rate of extension of 20 mm/min. Determinations are the average of 15 samples. Scanning electron micrographs were obtained on an ISI-DS-130 microscope as described previously [26]. For the staining with Congo Red, selected samples were dyed in the manner described before [8] and examined under the light microscope at various magnifications. Because of their alkali sensitivity, viscose rayon samples were dyed without preliminary swelling in sodium hydroxide. Mechanical properties such as tensile energy (WT), tensile linearity (LT), tensile resilience (RT), and shear hysteresis (2HG) were measured in the manner described previously [21].

Results and Discussion

WEIGHT LOSS IN RELATION TO INCUBATION TIME

The rate of enzymatic degradation of cellulosic fabrics depends on various factors. The fine structure of the fiber plays an important role, but macroscopic features such as fabric thickness and construction may also have some influence, especially at short treatment times. In cotton, the first step of the hydrolysis process usually involves removing surface fibrils, which causes a small decrease in weight [22, 27]. Prolonged enzymolysis leads to more serious fabric damage accompanied by higher weight loss and a considerable decrease in strength [8].

After 6 hours' incubation time, linen showed the highest weight loss followed by cotton, ramie, and finally viscose rayon (Table II). The reason for the higher weight loss of the linen might be related to the relatively loose plain weave construction, making the fine fibrils on the surfaces of the yarns easily accessible to enzymatic attack. The cotton fabric also had a plain weave structure, but was much denser and therefore possibly retarded access of the enzyme initially. However, it is more likely that the faster weight loss in linen fabric was due to the excessive fibrillar matter on its yarn surfaces, which is easily accessible to the enzyme. Scanning electron micrographs showing this will be reviewed later. After 48 hours' incubation, the cotton fabric had lost slightly more weight than the linen. Thus, the initial higher weight loss of the linen is not because linen fibers are intrinsically more reactive to the enzyme than cotton.

In general, ramie fabric lost weight at a considerably slower rate than the others (Table II). It was constructed from thicker yarns than any of the other sam-

ples (Table I) and had a relatively open structure. The warp yarns were protected with a polyvinyl alcohol size, but the finish did not appear to influence the enzymatic degradation, since another ramie fabric with no size on it was enzymatically treated in the same way and lost virtually the same weight. The probable reason the ramie suffered a lower weight loss than the cotton fabric is its lower porosity and thus its lower accessibility to the enzyme. Ladisch *et al.* [15] have claimed that ramie has 100 to 200% less total pore volume and accessible surface area than cotton, and the pore sizes most contributing to the pore volume in both cases were estimated to be less than 200 Å diameter.

Viscose rayon was the least affected by the 6-hour enzyme treatment (Table II). However, by 48 hours, its weight loss was higher than other fabrics. The lack of fibrils on the rayon filaments (Figure 16) accessible to the enzyme is the probable reason for the initial small weight loss. The high weight loss at 48 hours' reaction time may be due to rayon's low degree of crystallinity and polymerization, which renders it easier to degrade.

After 6 hours' incubation, the cotton/linen blend had lost weight in same range as 100% linen and cotton fabrics, as would be expected (Table II). At higher reaction times, however, weight losses were considerably lower for the blend. We cannot explain this difference in response at this time.

YARN TENSILE STRENGTH OF PRODUCTS

After 6 hours' incubation, the drop in strength of all samples except the viscose rayon was less than 13% (Table III and Figure 1). Ramie lost virtually no strength. After 24 hours incubation time, the natural cellulosic samples maintained more than 50% of their

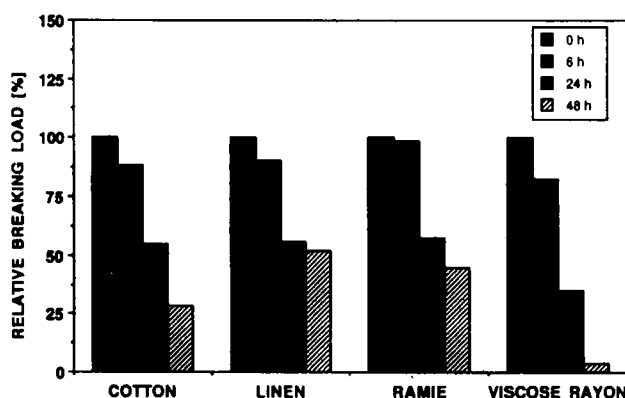


FIGURE 1. Relative breaking loads of cotton, linen, ramie, and viscose rayon after enzymatic hydrolysis for various treatment times.

TABLE III. Warp yarn breaking strength of untreated and enzyme-treated fabrics.

Sample ^a	Breaking strength, N	Relative breaking load, %
Cotton		
Untreated	2.668	100
6 hours	2.345	87.9
24 hours	1.462	54.8
48 hours	0.755	28.3
Linen		
Untreated	5.238	100
6 hours	4.719	90.1
24 hours	2.933	56.0
48 hours	2.727	52.1
Ramie		
Untreated	6.681	100
6 hours	6.602	98.8
24 hours	3.836	57.4
48 hours	3.012	45.1
Viscose rayon		
Untreated	1.776	100
6 hours	1.472	82.9
24 hours	0.618	34.8
48 hours	0.072	4.1

^a Times refer to length of enzyme treatment.

breaking strength, while the viscose rayon sample lost 65%. Further enzymatic degradation clearly reduced the strength of cotton much faster than linen or ramie.

Both cotton and viscose rayon appeared to lose strength progressively with increasing weight loss, while linen and ramie did not seem to lose strength sharply initially and developed a Z-shaped relationship (Figure 2). Both linen and ramie contain cementing materials; the amount of these substances depends on the severity of the processing and is expected to be relatively small [2]. Infrared spectra of the nonhydrolyzed ramie and linen samples did not show any significant evidence of these substances. However, both these fibers, unlike cotton, did not dissolve completely in FeTNa, which is an iron tartrate complex used as solvent for cellulosic fibers [28]. Thus, trace amounts of resins and gums are very likely present in these bast fibers and may be acting as a reinforcing matrix.

After 48 hours' reaction time, both ramie and linen retained a significantly higher percentage of their strength than cotton and viscose rayon, which retained negligible amounts (Table III). Since the linen fabric had twice the weight loss of the ramie sample after 48 hours' reaction, the fact that the strength retention of the linen was slightly higher than that of the ramie is notable. It indicates that the load bearing units in the linen are less affected by the enzyme than those in the ramie. The lower strength retention of the cotton may be due to an overall weakening of the fiber structure. Evidence for a major change in the structure of the

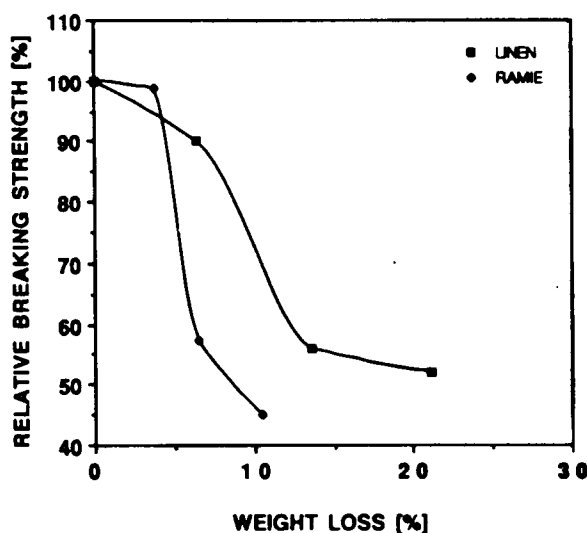
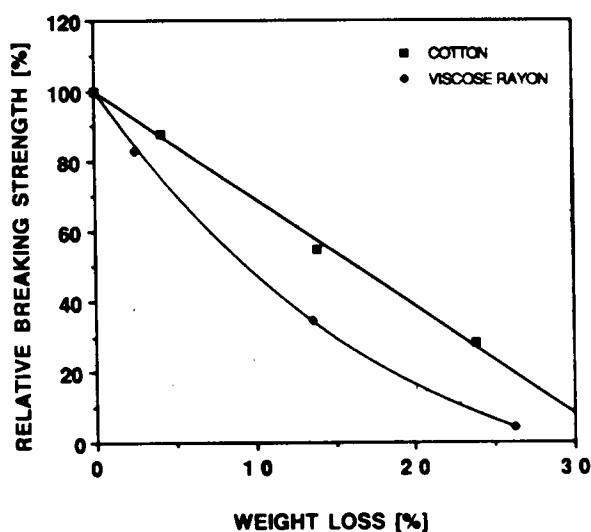


FIGURE 2. Relative breaking strength as a function of weight loss.

enzyme-treated cotton is the occurrence of a significant increase in its water retention value, which is discussed below. The negligible strength of the enzyme-treated rayon is probably related to the starting fiber's having a low degree of crystallinity and polymerization.

CRYSTALLINITY AND ACCESSIBILITY OF SAMPLES

Research has established that crystallinity, pore structure, and accessible internal surface area of the cellulose substrate play important roles in reactions with cellulases [11, 29, 30]. Usually these factors have been found to be mostly unchanged or slightly increased after the enzymatic reaction [29, 31].

There was no indication of any significant alterations in peak height/width or any shift of the maxima upon enzyme treatment for any of our samples. The x-ray

crystallinity indices also remained unchanged for all samples except ramie, where there was a negligible decrease (Table IV). No changes in crystallinity could be seen in the infrared spectra of these samples either.

TABLE IV. Influence of enzymatic hydrolysis on the x-ray crystallinity indices of cellulosic materials.

Fiber type	X-ray crystallinity index	
	Control	48-hour treatment
Cotton	0.87	0.87
Linen	0.87	0.87
Ramie	0.91	0.89
Viscose rayon	0.75	0.76

These findings support the theory of Schurz *et al.* [24] of endwise attack of the cellulase enzyme at an accessible cellulose chain on the crystallite surface. This particular cellulose chain then completely disintegrates before the deterioration continues with the next chain molecule. Amorphous regions are often too narrow for the large enzyme molecules to effectively penetrate, and so there is no change in the ratio of ordered and less-ordered regions. The proposed mechanism proved valid for regenerated cellulosic fibers as well as cotton linters and wood pulp [24, 25], and it is very likely that it could also be applied to other natural cellulosic fibers.

We can estimate the extent of less ordered regions in a fiber by evaluating moisture regain data, while water retention values indicate the water holding capacity of large pores and the lumen. Table V summarizes the moisture regain and water retention data for the untreated samples and the samples hydrolyzed for 48 hours. The moisture sorption properties of all fibers did not change significantly after the enzyme treatment. This result supports the observations from x-ray diffraction experiments that no increase of accessible less-ordered regions had occurred. The water retention values also remained constant within the margin of error, except for cotton and the cotton/linen blend. The water holding capacity of both samples increased by 24–28%. Since the crystallinity of the samples obviously did not change to any significant extent, we can speculate that the reason for the increase is established in the overall degradation pattern of cotton (we must assume that the cotton component in the blend is the contributing factor). As we will demonstrate below, extensive surface peeling and interfibrillar splitting occur in cotton after prolonged enzyme treatment and create very large water accessible surfaces. None of the other fibers we investigated developed similar degradation.

TABLE V. Moisture regain and water retention values of untreated and enzymatic hydrolyzed cellulosic materials.

Fiber type	Moisture regain, %		Water retention, %	
	Control	48-hour treatment	Control	48-hour treatment
Cotton	6.51	6.33	45.75	56.57
Linen	6.99	6.66	53.47	54.27
Ramie	6.37	6.40	46.06	45.97
Viscose rayon	12.73	12.92	81.61	83.97
Cotton/linen blend	6.74	6.66	43.07	55.10

FIBER SURFACE CHANGES

Staining Experiments with Congo Red

It is interesting that all enzyme-treated fibers performed differently upon dyeing with Congo red. As reported previously [8], hydrolyzed cotton stained dark red in areas along the fiber that had been enzymatically attacked. These areas alternated with lightly dyed non-hydrolyzed locations. The distance between intensely stained regions decreased with prolonged treatment, leading to a “string of pearls” appearance and finally to the complete staining of the entire fiber (Figures 3 and 4).



FIGURE 3. Light micrograph of nonhydrolyzed cotton stained with Congo red.

Neither linen nor ramie showed similar dyeing behaviors. The untreated linen samples stained only slightly, while the short surface fibrils dyed somewhat darker (Figure 5). Nodes and cross length-wise markings on enzyme-treated samples where the dye had accumulated could only be distinguished when the treatment exceeded 24 hours. Cracks perpendicular to the fiber axis appeared at some of the cross marks (Figure 6). After 48 hours, the fibers were more or less uniformly dyed in a dark red color, demonstrating evenly distributed surface damage.

ken fiber ends or cracks were visible yet. This fact might account for the relatively high strength retention of the linen yarn (90.1% after 6 hours' treatment). With continuing hydrolysis, cracks in the direction of the fiber axis started to develop and the nodes and cross marks appeared to intensify (Figure 11). After 48 hours' treatment, the fibers disintegrated mostly at the nodes, and occasionally deep cracks led to fiber splitting (Figure 12). The breakdown of the linen fibers at the nodes can be understood when we remember that absorbance of water occurs preferentially in these regions and that dyes and finishing agents often accumulate there [2]. We suggest that the enzyme reacts rapidly at nodes and degradation is concentrated at these areas (compare Congo red test with linen). We found few broken fiber ends during the SEM examination, confirming the results of tensile tests that showed overall weakening of the yarns but obviously still enough mutual support to keep more than 50% strength retention.

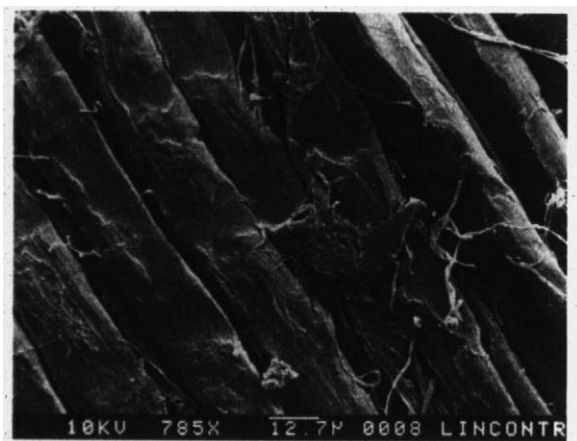


FIGURE 9. SEM micrograph of nonhydrolyzed linen fibers.

Morphological changes in the ramie were much less distinct. The surface of the nonhydrolyzed ramie fiber showed only few fibrils (Figure 13), which were removed after 6 hours' incubation time as observed with cotton and linen. Further degradation was demonstrated by the appearance of cracks at an angle slightly off the axial direction and probably closely related to the spiral pitch (Figure 14). These cracks were unevenly distributed over the entire sample after 24 hours' treatment. Longer treatment deepened the defects rather than spreading the damage to other fibers. The development of cracks was not hindered by the polyvinyl alcohol finish (Figure 15).

Viscose rayon as a regenerated cellulosic fiber already had a very smooth surface. As we see in Figure 16, the

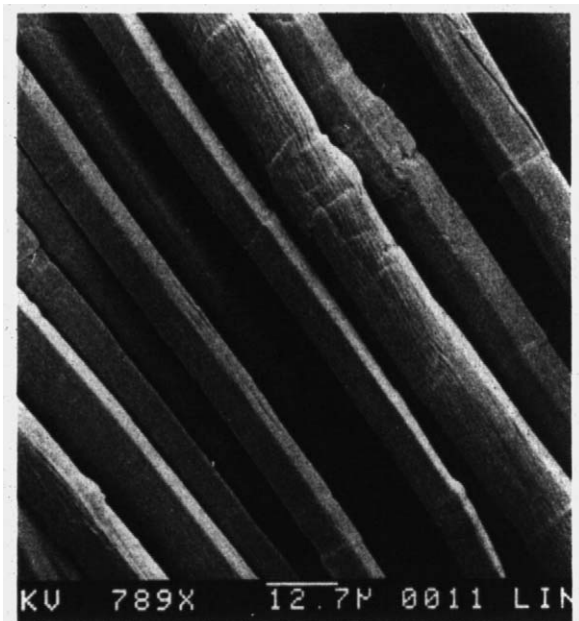


FIGURE 10. SEM micrograph of linen after 6 hours' incubation time.



FIGURE 11. SEM micrograph of linen hydrolyzed for 24 hours.

untreated fiber had the usual striations in the length direction. The enzyme treatment in this case seemed to roughen the surface slightly and to form very small, short cracks in the axial direction (Figure 17). However, up to 24 hours' treatment time produced no significant visible damage. After 48 hours, a few of the filaments appeared to be kinked and bent over as if they had contracted (Figure 18). At these points, the fibers actually broke by splitting along their axes. Overall, damage occurred only occasionally, with the main part of the yarn still appearing visually intact. This is quite surprising considering the high strength loss (95.9%) at this stage of enzymolysis.

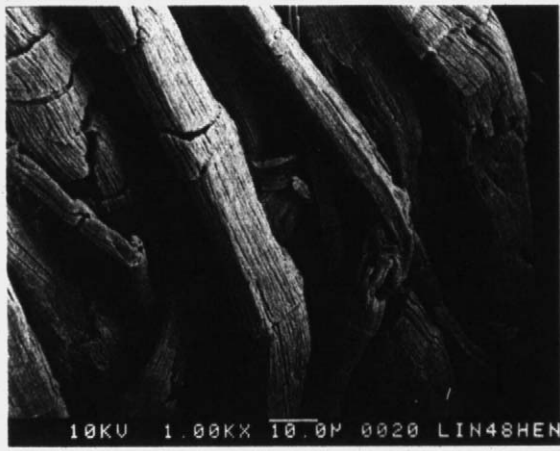


FIGURE 12. SEM micrograph of linen after enzyme treatment for 48 hours.

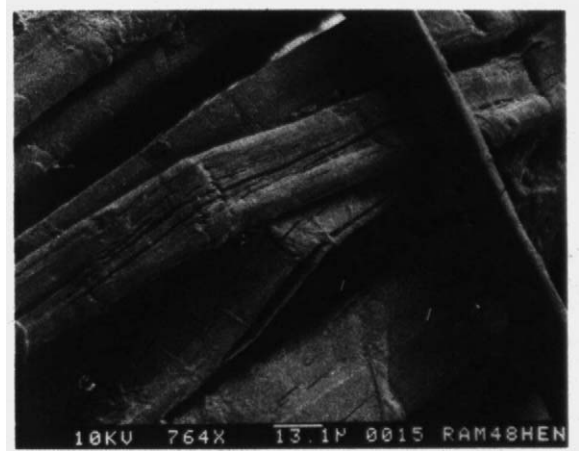


FIGURE 15. SEM micrograph of ramie enzyme-treated for 48 hours (warp direction).



FIGURE 13. SEM micrograph of nonhydrolyzed ramie (filling direction).

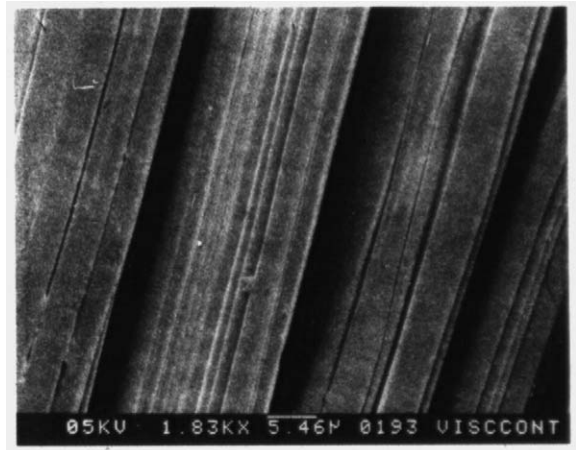


FIGURE 16. SEM micrograph of untreated viscose rayon filaments.

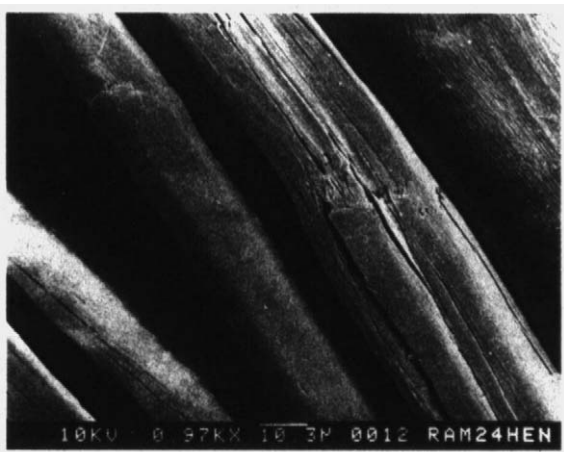


FIGURE 14. SEM micrograph of ramie enzymatically hydrolyzed for 24 hours.

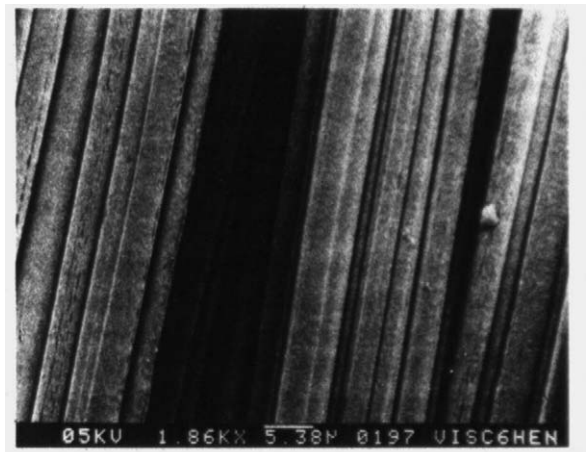


FIGURE 17. SEM micrograph of viscose rayon after 6 hours' enzyme treatment.

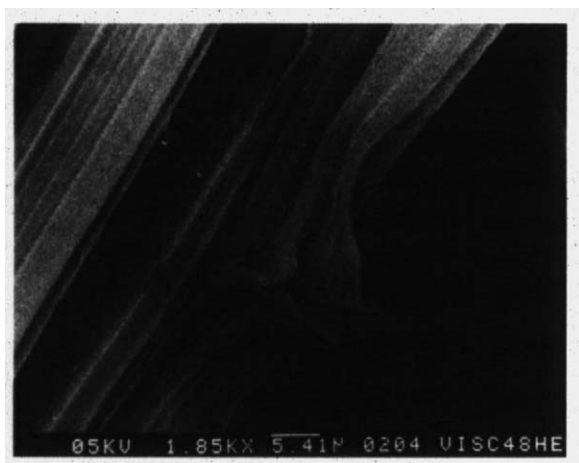


FIGURE 18. SEM micrograph of viscose rayon hydrolyzed for 48 hours.

MECHANICAL PROPERTIES OF FABRICS

The fabric properties we investigated were tensile energy (WT), tensile linearity (LT), tensile resilience (RT), and shear hysteresis (2HG), which are useful as measures of compactness, stretchability, recoverability, and inter-yarn friction, respectively. For all the fabrics, after 6 hours' treatment, there were significant reductions in WT and LT, while RT increased (Table VI), indicating that the fabrics had become less stiff, easier to stretch, and looser in structure. The one exception was the cotton/linen blend in the filling direction, where RT was lower after 6 hours' treatment but increased after the treatment was extended.

After 6 hours' treatment, there was no considerable change in 2HG (Table VI). Thus, even though the fabrics had become looser as evident from WT and LT values, this change did not appear to be significant enough yet to manifest itself in a change of interyarn friction, even though fibrillar matter had been removed from the fiber surfaces. However, after 48 hours' treatment, 2HG values were markedly lower than those of the controls, indicating yarns had become more mobile in the fabrics.

Conclusions

Enzymatic hydrolysis to decrease stiffness, ease stretchability, and generally loosen the structure of fabrics is applicable to all the cellulosic fabrics in this study. After short treatment periods, the cotton, linen, and ramie fabrics manifest the desired effect of removal of surface fibrils without suffering large weight losses or reductions in tensile strength. The strength/weight loss relations of ramie and linen differ from those of cotton and viscose rayon. Light microscopy combined

TABLE VI. Tensile energy (WT), tensile linearity (LT), tensile resilience (RT), and shear hysteresis (2HG) of the fabrics after enzyme treatment.

Fabric	Enzyme treatment for			
	0 hours	6 hours	24 hours	48 hours
Cotton				
WT, cm ²	4.86	3.47	3.11	2.13
LT	0.87	0.77	0.83	0.78
RT, %	41.85	48.61	46.29	49.09
2HG, g/cm	7.04	7.29	5.12	3.36
Linen				
WT, cm ²	5.65	3.00	3.93	4.07
LT	0.72	0.66	0.71	0.69
RT, %	42.14	48.93	42.00	44.05
2HG, g/cm	0.83	1.02	0.56	0.29
Ramie				
WT, cm ²	5.45	2.45	2.40	2.30
LT	0.85	0.63	0.69	0.73
RT, %	52.70	65.69	67.87	68.76
2HG, g/cm	4.59	4.16	3.84	3.36
Cotton/linen (warp)				
WT, cm ²	1.61	1.02	1.25	0.84
LT	0.81	0.69	0.72	0.75
RT, %	44.87	50.27	57.82	46.73
2HG, g/cm	1.08	0.94	1.14	0.97
Cotton/linen (filling)				
WT, cm ²	2.22	1.96	1.84	1.51
LT	0.85	0.84	0.86	0.81
RT, %	56.39	51.24	58.72	57.98
2HG, g/cm	1.08	0.94	1.14	0.97

with Congo red staining can be used to monitor the location of enzymatic attacks for linen and cotton but not viscose rayon and ramie. Scanning electron microscopy can detect changes in fiber morphology for all the fibers as they are progressively degraded. Crystallinity indices of the samples do not change after the enzymatic hydrolysis, nor does accessibility to moisture. This suggests that the ratio of crystalline to less ordered regions does not change upon enzymatic degradation. Thus the proposed mechanism of Schurz *et al.* [24] of endwise attack of the cellulase at accessible cellulose chains on crystallite surfaces appears to be applicable to cellulosic fibers other than cotton and rayon.

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