

# Mechanochemical Process in Cotton Cellulose Fiber

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## Synopsis

Mechanical processing of cotton cellulose by means of a fiber cutter resulted in the disaggregation and defiberation of fiber bundles, shortening of fiber length, and loss of degree of polymerization. It is evident that the mechanical energy supplied by shear forces is sufficient to cause homolytic scission of cellulose main chains. Mechanoradicals formed in the interim were verified by ESR studies. The crystallinity of cellulose was not influenced by mechanical treatments, but accessibility of the polymer was substantially increased due to the creation of new surfaces. The mechanically treated fiber inclined to proceed oxidative chain reaction during aging. Regardless of their treatment conditions, cellulose fiber reached its limiting lower molecular weight after 100 days of aging.

## INTRODUCTION

Cotton is a major world fiber and cellulose resource, contributing to health, safety, and well-being. It is a renewable organic raw material. Cotton cellulose is the seed fiber of the cotton plant which normally has high purity and a higher molecular weight than cellulose isolated from wood. Although wood cellulose is the major component for paper production, because of its low degree of polymerization, i.e., low molecular weight, and its contamination with other carbohydrates and lignin, cotton fiber is used preferentially in certain industrial applications, such as textile and paper, as well as some of the cellulose derivatives production, where high quality with respect to purity and molecular weight is required.

The manufacture of cotton cellulose products involves complex conversion methods. In order to convert cotton cellulose into useful consumer and industrial products, mechanical processing such as grinding, cutting, stretching, etc., is inevitably carried out at gins, textile and paper mills, and chemical plants, so as to render the cotton fiber processible and commercially useful. The mechanical process has positive and negative influences on the topochemistry and chemical reactivity of cotton cellulose. The rupture of covalent bonds and the rearrangement of molecular ultrastructure of cellulose due to the shear and compression forces can play a significant role in performance and stability.

The mechanical degradation of cellulose and its derivatives has been the object of many studies since the classical observations of Waentig,<sup>1</sup> Staudinger and Heurer,<sup>2</sup> and Hess.<sup>3</sup> The physical damage to the cotton fiber during mechanical processing from seed to yarn was demonstrated by Clegg.<sup>4</sup> However, most of the methods adapted for the study of cellulose stress reactions are either grinding, milling, or crushing, which are the mechanical reactions involving comminution. Despite their industrial importance, no work has been done on cutting and slicing, which are the mechanical reactions involving process machining of polymers.

Surprisingly, even in the field of synthetic polymers, despite the abundance of experimental data generated from mechanochemical studies, relatively little work has been done by cutting or slicing. Several monographs<sup>5-7</sup> have been published in which various aspects of mechanochemical reactions in polymers have been examined. This investigation was undertaken in order to fill this gap by studying the mechanical effect on cellulose fiber properties using a Wiley mill cutter. The changes in degree of polymerization, crystallinity, and accessibility of the cut samples are evaluated.

## EXPERIMENTAL

### Materials

High viscosity, acetate-grade cotton linters (DP = 3211) supplied by Hercules, Inc., in sheet form were used.

### Procedure

Cotton cellulose was cut either in the presence of air or nitrogen in a Wiley laboratory mill (Arthur H. Thomas Co., Model 4). Cotton sheets were fed into the mill from the top through a metal hopper. The bottom of the cutting chamber was fitted with a screen with round perforations with diameters of 0.5, 1, 2, or 6 mm. *The reduction of fiber length* after cutting was determined by a stereological counting method from a projected light microscope.<sup>8</sup> *The change in degree of polymerization* of cellulose before and after cuttings was determined from limiting viscosity numbers obtained by using a capillary viscometer. The measurements were carried out in a thermostat at  $25.00 \pm 0.05^\circ\text{C}$  in cupriethylenediamine solution and converted to degree of polymerization by using<sup>9</sup>

$$\text{DP} = 190 [\eta] \quad (1)$$

*Crystallinity* of cotton cellulose was measured using a density method by means of a density gradient column (Techne Inc., Model DC-2). Xylene and carbon tetrachloride were used to make up the solution. Based on the density data, crystallinity of cellulose can be calculated using<sup>10</sup>

$$\text{crystallinity} = \frac{V_a - V}{V_a - V_c}, \quad \text{density} = \frac{1}{V} \quad (2)$$

where  $V_a$ ,  $V_c$ , and  $V$  are specific volumes of amorphous portion, crystalline portion, and unknown sample, respectively. Due to Kast,<sup>11</sup> the value of  $V_a$  and  $V_c$  are 0.680 and 0.628, respectively.

In any chemical reactions involving cellulose, the accessibility of the cellulose molecules for reaction is a major consideration. While crystallinity is concerned with the solid state, accessibility is concerned with the internal volume accessible to a given reactant. *Accessibility* of cellulose was determined by an iodine absorption method described by Hessler and Power<sup>12</sup> using

$$\frac{\text{mg iodine}}{\text{g sample}} = \frac{(a - b) \times 2.04 \times 2.54}{0.3} \quad (3)$$

where  $a$  is the volume of 0.02N thiosulfate for the blank and  $b$  is the corre-

sponding volume for determination. A ratio of mg iodine absorbed/g cellulose to 412 (mg iodine absorbed/g methocel) gives a value for the amorphous fraction. The percentage of crystallinity is thus equal to 100 minus the percentage of the amorphous fraction.

Mechanoradicals generated in cotton cellulose were measured with an X-band ESR spectrometer (Varian E-12, 100-KHz modulation).

The average number of chain scissions per chain unit ( $\bar{S}$ ) and the degree of degradation ( $\alpha$ ) were calculated based on

$$\bar{S} = \frac{DP \text{ initial}}{DP \text{ cut}} - 1 \quad (4)$$

$$\alpha = \frac{1}{DP \text{ cut}} - \frac{1}{DP \text{ initial}} \quad (5)$$

## RESULTS AND DISCUSSION

### Effect of Mechanical Cutting on Fiber Length

On cutting the cotton sheets through the Wiley mill, they were transformed into fibrillar bundles that were disaggregated by virtue of a mechanical stress reaction. After the cotton sheets were cut through various sieves, the average fiber length of the cut samples was determined by using a stereological counting technique. Results are shown in Table I. It is clear that fiber length was shortened when cotton fibers were cut through any of the sieves used, and the reduction of fiber length accelerated as the perforation sizes of the sieves was decreased. For the fiber cut through the 6-mm sieve, about 40% of the original fiber length was shortened. For the 0.5-mm sieve, about 87% of the original fiber length was shortened; that is, the original length of 2.54 mm was reduced to 0.34 mm after cutting. Hence, it is clear that cotton fiber length was greatly reduced by mechanical cutting. The smaller the sieve used, the shorter the fiber produced. It should be noted here that normally lint cotton fiber has an average fiber length of 7.5 mm,<sup>13</sup> which is much longer than that of the fibers used for this study (i.e., 2.54 mm). This fact also indirectly implies that most of the original fiber length was lost during mechanical processing taking place in the breaker and the picker, carding and ginning operations<sup>14</sup> prior to the formation of the sheet, and most of the fiber length was lost at the picker operation.

TABLE I  
Average Fiber Lengths of Cotton Fiber after Cutting in a Wiley Mill

Sieve size (mm)	Average fiber length (mm)	Retention (%)
Control	2.54	100.0
6.0	1.62	63.8
2.0	1.01	39.8
1.0	0.58	22.8
0.5	0.34	13.4

### Effect of Mechanical Cutting on Degree of Polymerization (DP)

In the mechanical cutting process, cotton fibers are inescapably absorbing mechanical stress, i.e., shear forces. The consequence of this energy uptake normally leads to the slippage of secondary bonds due to the intra- and intermolecular hydrogen bonds, and the rupture of covalent bonds. The latter mechanically activated reaction results in the loss of fiber length and, certainly, in the decrease in DP of the deformed cotton fibers. The decrease in DP observed as a result of cutting fiber through various sieves is shown in Table II. When cotton fiber sheets were cut through a 6-mm sieve in the presence of air or nitrogen, the DP dropped to about 84% and 89% of the original DP value, respectively. This indicated that the kinetic energy supplied by mechanical force (cutting) is sufficient to cause homolytic scission of the cellulose main chains, either in air or in nitrogen. The data also implies that oxygen presence in the cutting system reduced the probability of mechanoradical recombination reactions, since DP reduction is slightly greater when cotton fiber is cut in air. However, the effect of oxygen on the reduction of DP seemed to be insignificant when the fiber was cut through 2 mm or smaller sieves. The drop of DP to 74% and 75% of the original value was observed from the fibers cut through the 0.5-mm sieve in air and in nitrogen, respectively. Practically, the influence of oxygen is negligible. Notwithstanding, it should be borne in mind that when cellulose bonds are ruptured under the mechanical stress in the presence of air/oxygen, autooxidation can occur. The free radicals produced due to cutting, as evident by ESR studies which will be discussed later, are readily interacted with oxygen molecules to form hydroperoxides, which become initiators for autooxidative chain reactions.

The rate of chain scission,  $\bar{S}$ , showed that chain scission increased as the sieve size decreased. It is also clear that the reduction of fiber length and DP due to the cutting shear forces is a statistical degradation process, i.e., a random chain scission reaction.

Moreover, the direct evidence of the rupture of primary bonds was originated from an ESR study. When cotton fiber was cut through an 0.5-mm sieve in nitrogen atmosphere at ambient temperature, a singlet signal with a line width of 18 gauss, due to alkoxy radicals,<sup>15</sup> was observed (Fig. 1). This indicated that mechanoradicals were generated in the cut fiber due to a chain scission reaction. When the cut fiber was stored at ambient temperature for 24 h, the ESR signal intensity decreased, but still could be detected. This implies that a certain amount of free radicals generated are quite stable after 24-h storage at ambient

TABLE II  
Chain Scissions of Cotton Fiber after Cutting in a Wiley Mill with Different Sieve Sizes<sup>a</sup>

Sieve size (mm)	Cut in air		Cut in nitrogen	
	DP	$\bar{S}$	DP	$\bar{S}$
Control	3211	0.0	3211	0.0
6	2698 (84)	0.19	2850 (89)	0.13
2	2565 (80)	0.25	2603 (81)	0.23
1	2565 (80)	0.25	2603 (81)	0.23
0.5	2375 (74)	0.35	2413 (75)	0.33

<sup>a</sup>  $\bar{S}$  = Average number of scissions of main chain links in an original chain. ( ): Percent retention.

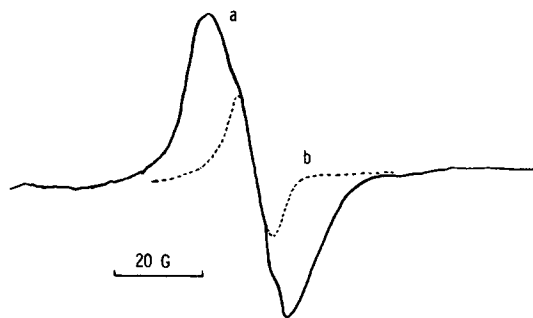


Fig. 1. ESR spectra of cotton fiber cut at ambient temperature in air through 0.5-mm sieve size. (a) Fiber immediately after cutting and stored at liquid nitrogen temperature; (b) fiber stored at ambient temperature after 24 h cutting. ESR spectra were recorded at 77°K (-196°C).

temperature. It should be noted here that since the cutting experiments were conducted at ambient temperature, only those long-lived free radicals are able to be detected by ESR. The short-lived radicals were decayed rapidly at ambient temperature before they could be detected.

In order to determine the effect of cutting time on the change in DP, cotton fiber was cut through the same sieve for several consecutive cycles, and the DP was evaluated. Results are shown in Figure 2. It is clear that the fiber's DP was reduced markedly at the initial cutting, i.e., the first cutting cycle, followed by a slow drop of DP, regardless of the sieve sizes. The DP of fibers was reduced to 84%, 80%, 80%, and 74% of their original value when they were cut through the sieve sizes of 6, 2, 1, and 0.5 mm, respectively. Regardless of sieve size, the DP of cotton fiber remained nearly unchanged after the second cycle of cutting. Figures 3 and 4 show the rate of chain scission and the degree of degradation vs.

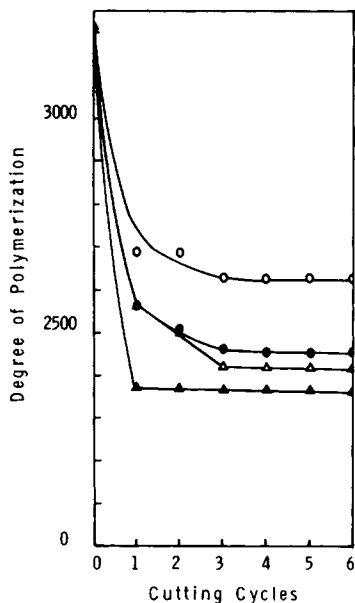


Fig. 2. Decrease in DP of cotton fiber after cutting through sieve sizes of 6 mm (O), 2 mm (●), 1 mm (Δ), and 0.5 mm (▲) for six consecutive cycles.

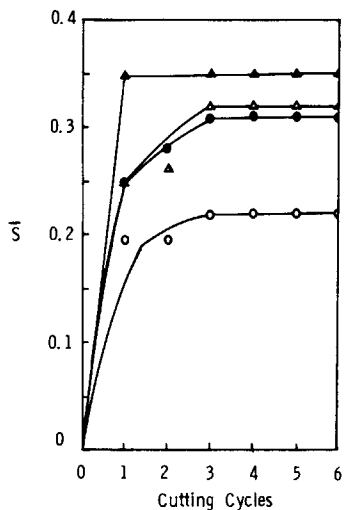


Fig. 3. The rate of chain scission,  $\bar{S}$ , as a function of cutting cycles for cotton fiber cutting through sieve sizes of 6 mm (O), 2 mm (●), 1 mm (Δ), and 0.5 mm (▲) at ambient temperature.

cutting cycles. These curves are characterized by an initially fast rate of chain scission, which decreases rather abruptly after the second cycle of cutting, resulting in straight lines.

### Changes in Accessibility of Cellulose

Much of the chemical behavior of cellulose fiber can be attributed to cellulose structure. Since cellulose is a highly crystalline polymer, it can absorb mechanical energy efficiently for mechanical stress reactions.

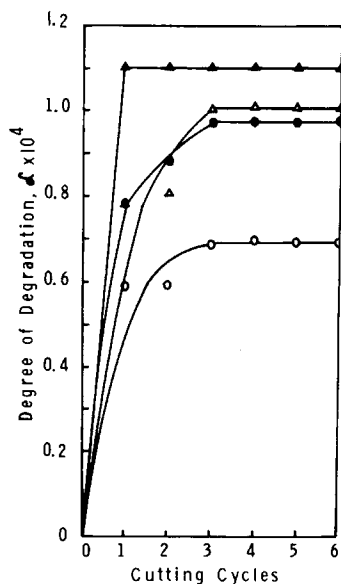


Fig. 4. Degree of degradation,  $\alpha$ , as a function of cutting cycles for cotton fiber cutting through sieve sizes of 6 mm (O), 2 mm (●), 1 mm (Δ), and 0.5 mm (▲) at ambient temperature.

TABLE III  
Changes in Accessibility of Cotton Fiber Cut through a Wiley Mill with Different Sieve Sizes at Different Cycles

Cycle	Assessibility (%)			
	6 mm	2 mm	1 mm	0.5 mm
Control	10.06	10.06	10.06	10.06
1	11.21	15.90	16.28	17.30
2	13.38	16.21	—	17.30
3	13.98	16.55	—	17.62
4	15.55	18.40	—	20.22
5	15.55	18.60	—	20.22
6	18.41	18.60	—	20.75

The mechanically activated thermal energy, in addition to rupturing main chains, may alter morphology or microstructure of cotton fiber. Accordingly, the accessibility of cellulose chains may be influenced. The changes in accessibility were examined by the use of iodine absorption. The values of accessibility of cellulose fibers without mechanical treatment and the cellulose fibers cut through sieves with various sizes up to six cycles of cutting are shown in Table III. The accessibility of uncut cotton fiber was 10.06%, and its accessibility was markedly increased from 10.06% to 11.21%, 15.90%, 16.28%, and 17.30% while cutting through 6-, 2-, 1-, and 0.5-mm sieves, respectively. It is evident that a progressive opening up of unaccessible regions took place due to the absorption of mechanical energy by cellulose molecules. The accessibility also increased with cutting time. When a sample was cut through a 6-mm sieve for six cycles, the accessibility increased from 10.06% to 18.41%. When the screen sizes were reduced, the accessibility increased. At the 0.5-mm cutting, the accessibility doubled. It is apparent that mechanical shear forces generated new surfaces and reactive centers to increase accessibility.

### Effect of Mechanical Cutting on Crystallinity

The density of individual fibers is directly related to the degree of crystallinity.<sup>16</sup> Because the crystalline regions have a higher density than the amorphous regions, the measurements of density allow calculation of the crystallinity of cellulose. Hence, the density and the crystallinity of cellulose fiber were determined using a density gradient column. The values for the cotton fiber cut through various sieve sizes are summarized in Table IV. In a previous section, we have discussed the fact that accessibility of cellulose was increased by mechanical cutting; however, the crystallinity of the uncut samples and the me-

TABLE IV  
Changes in Crystallinity of Cotton Fiber Cut through a Wiley Mill with Different Sieve Sizes

Sieve size (mm)	Crystallinity (%)
Control	64.04
6	64.42
1	63.84
0.5	62.98

chanically cut samples gave nearly the same values of crystallinity. This is in good conformity with the IR studies by other workers<sup>17,18</sup> that cutting in a Wiley mill to pass a 20-mesh (850- $\mu$ m) screen leads to crystallinity retention. It is noted that the crystallinity of cellulose can be entirely destroyed by severe action of mechanical treatment, such as in a vibratory ball mill or a rotary mill.<sup>19,20</sup>

Based on the data of accessibility and crystallinity, we believe that mechanical forces are able to open up the unaccessible regions in cellulose by creating new surfaces without damaging the crystalline structure. It is also likely that the surfaces of crystallites are made more accessible during cutting.

### Effect of Aging on Degree of Polymerization

It has been known that mechanical stress reactions may influence the stability of commercial bulk polymers. The stability of cut fibers was hence examined. Results are shown in Figure 5.

When the cut samples, regardless of their cutting history, were stored in nitrogen in the dark, there was practically no change in DP after 100 days of storage. However, it is surprising to notice that the DP's of all the cut fibers were reduced during 100 days of storage in the presence of air in the dark at ambient atmospheric conditions. As shown in Figure 5, it is obvious that the fiber with higher DP (after cutting through the 6-mm sieve) reduced its DP significantly by 12.4% after 102 days of aging. A slight decrease in DP was observed for the fiber cut through the 0.5-mm sieve (5% reduction at 102 days of aging). Interestingly, all of the cut fibers arrived at similar DP's after 100 days, regardless of their cutting conditions. It is likely that all of the cut samples approached their limiting molecular weight after 100 days of aging. Since a deterioration of cellulose in nitrogen was not observed, it is obvious that oxygen plays a role in the aging of cellulose.

First, since the consequence of cellulose stress reactions is the rupture of the

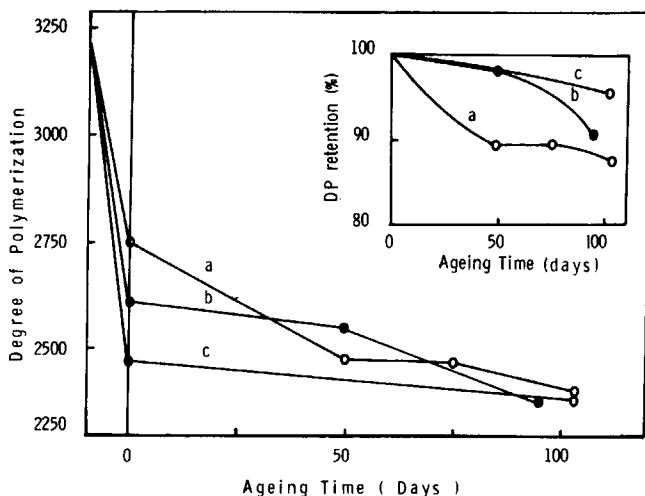


Fig. 5. Change in degree of polymerization of cut cotton fiber during aging at ambient temperature. Keys: (a) fiber cut through 6-mm sieve; (b) fiber cut through 2-mm sieve; (c) fiber cut through 0.5-mm sieve.



main chain with the simultaneous creation of new surfaces and the formation of mechanoradicals, the fate of the mechanoradicals generated may be interaction with oxygen to generate peroxide radical intermediates which are likely to enhance various oxidative reactions that lead to a continuous degradation chain reaction during aging. Second, it is possible that the deformed bonds in cut cellulose are in a higher energy state and are therefore more reactive toward oxygen. Whereas the initiation reaction may be slow, the propagation reaction may be fast. On the whole, it is likely that the post-cutting degradation is due to the chain reactions of mechanoradicals and of peroxide radicals. It is also possible that autooxidation of cut cellulose took place due to the action of oxygen. Details of this study are still under investigation.

## CONCLUSIONS

It is common practice in industry to introduce mechanical stress to polymers in processing and fabrication purposes in order to convert them to commercially useful products. Like many engineering polymers, the manufacture of cotton cellulose products involves complex conversion methods. In this study, the mechanical process in cutting operations was simulated using a Wiley mill. Results reveal that mechanical energy can be absorbed by the cellulose fiber to break down primary and secondary bonds. The consequences of this energy uptake in cellulose were the shortening of fiber length and concurrent formation of fibrillar bundles. The shortening of fiber length accelerated as the sieve size was reduced. Likewise, the degree of polymerization reduced accordingly. The rate of reduction of DP was slightly faster when cellulose fiber was cut through larger sieves in the presence of air rather than nitrogen; however, when cellulose was cut through smaller sieves, the cutting atmosphere appeared to be of no importance. ESR spectra verified the formation of mechanoradicals in cut fibers by virtue of cleavage of  $\beta$ -1,4-glucosidic bonds of cellulose.

The mechanical stress did not have any influence on the percent crystallinity of the cellulose, contrary to other experiments. Nevertheless, due to the disaggregation of fiber bundles, cleavage of glucosidic bonds, and of inter- and intramolecular hydrogen bonds, new surfaces were substantially created. Accordingly, the accessibility of cut cellulose was increased. About a 10% increment of accessibility was observed when cellulose was cut with a 2-mm sieve. The mechanically treated cellulose seemed to undergo oxidative chain reactions in the presence of oxygen during aging at ambient atmospheric conditions. Regardless of cutting history, all cellulose samples reduced in DP to the same level, i.e., reaching a limiting molecular weight after 100 days of aging. No oxidative degradation was observed when cut cellulose was aged in nitrogen for the same period of time.

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