

The Ball-Milling of Cellulose Fibers and Recrystallization Effects

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I. INTRODUCTION

Cellulose as a polymeric chemical entity is a substance of precise and regular structure, irrespective of source. With respect to morphology and crystallinity, however, there can be wide variations, and in relation to these variables, several workers¹⁻⁵ have studied the properties of ball-milled or ground cellulose. The present study was begun ten years ago with the determination of the kinetics of decrystallization of various types of cellulose fibers. More recently, when samples of widely varying crystallinity were required for fine structure analysis, the same ball-milled samples were used for density, x-ray, and mercerization studies. The samples had undergone little or no change on standing. The following is an accumulation of the pertinent data which are novel in some respects and shed further light on the polymorphous structure of cellulose.

II. EXPERIMENTAL

A. Materials

All fibrous material used in the investigation was treated first of all in a Wiley mill to pass a twenty mesh screen. Aside from this, samples were used "as received" except for some special drying procedures described below. The materials examined were: an acetate-grade wood pulp (P-A, B, C, D), the same pulp after mercerization (P-E) and three experimental rayons (R-A, B, C). The important spinning conditions and some properties of these yarns are listed in Table I.

B. Milling Treatment

An ordinary rotary mill with steel balls was used in all milling experiments, which were carried out at 18°C. The charge always consisted of 1200 grams of steel balls and 40 grams of cellulose. The mill was rotated at a constant speed of 47 r.p.m. in a room where the temperature was maintained at 18°C. The use of steel balls

made it possible to keep the ash content of the samples, which increases due to abrasion of the balls, to less than 0.2% after 150 hours of milling. Depolymerization of the cellulose due to the process was quite severe, and was followed by measuring the cuene viscosity at a single concentration. The degree of polymerization was calculated with the use of a relation between DP and specific viscosity which is based on Kramer's constant.⁶

C. Fine Structure Study

A previously described procedure was used to measure moisture regain at 58% R.H.,⁷ while a density gradient column served to measure densities.^{8,9} Actually, a lapse of ten years occurred between the former and latter determinations, during which time the samples were stored in tightly stoppered bottles in the dark. Because all the samples were essentially powders, the measured density was of necessity an average value arrived at by observing the point of maximum concentration of the powder in the column. The fine particles for a given sample were usually spread over a range 0.003 to 0.007 density unit.

III. RESULTS

In this section, data from eight separate millings will be cited; these differed from one another either in the material investigated or the method of drying. Time of treatment in the ball-mill, degree of polymerization, moisture regain, density, and some copper numbers of the various series are collected in Table II and Figures 1 and 2.

Very cursory examination of the dry, ball-milled material in the light microscope showed that the fibrous structure is lost after about 20 hours of milling, although traces of undamaged fiber can still be found after 100 hours. The powdered samples, which become finer and slightly greyish with extended milling, are made up of irregularly shaped particles, often aggregated as if fusion had occurred.

TABLE I
Properties of Rayon Samples Used in Ball-Milling Experiments

Sample	Salt test	Godet stretch, %	Bath composition			Tensile, g./d. (58% R.H.)	Elongation, % (58% R.H.)	Regain, % (58% R.H.)
			Acid	Zn	Na ₂ SO ₄			
R-A	7.4	50	7	5	20	2.71	22.3	13.72
R-B	2.0	50	2	0	20	2.03	7.5	11.93
R-C	—	80	11	5	20	—	—	12.51

TABLE II
Milling and Fine Structure Data on Ball-Milled Cellulose Samples

Series	Treatment	Sample	Time, hr.	D.P.	Regain at 58% R.H., %	Density, g./cc.	Cu. No.
P-A	Dried 3 hrs. at 105°C., conditioned at 58% R.H. for seven days	P-A-0	0	1205	7.84	1.541	0.22
		P-A-1	16.0	1160	9.22	1.533	
		P-A-2	34.8	1107	10.35		
		P-A-3	50.8	1030	11.01	1.530	
		P-A-4	62.9	990	11.79	1.524	
		P-A-5	80.5	855	12.39		
		P-A-6	96.5	815	12.90	1.518	
		P-A-7	116.5	770	13.24	1.511	
		P-A-8	132.6	740	13.67		
		P-A-9	151.1	710	13.73	1.514	
		P-A-10	173.3	655	14.12		
P-A-11	192.3	642	14.51	1.511	2.07		
P-B	Conditioned at 58% R.H. for seven days, dried in vacuo over P ₂ O ₅ for 4 hr.; drying repeated each time mill was opened						0.22
							3.22
P-C	Same conditions as P-B, except CO ₂ atmosphere used						0.22
							1.15
P-D	Dried 5 hr. at 105°C.; procedure repeated each time mill opened	P-D-0	0	1200	7.97		0.22
		P-D-1	141.5	562	12.18		
P-E	Dried in vacuo at room temperature for 1.5 hr.	P-D-2	402.4	289	14.72		5.90
		P-E-0	0	1183	10.54		
		P-E-1	40.0	1082	12.27	1.517	0.05
		P-E-2	80.0	742	13.67	1.519	
		P-E-3	107.0	697	14.10	1.514	
		P-E-4	149.7	528	15.16	1.511	
		P-E-5	174.8	471	15.19	1.513	
		P-E-6	215.9	422	15.57	1.498	3.37
R-A	Dried in vacuo over P ₂ O ₅ 2 hr. first time and 1 hr. each time mill was opened	R-A-0	0	460	13.72		
		R-A-1	40.0	468	14.38		
		R-A-2	70.0	433	14.70	1.505	
		R-A-3	110.0	429	14.58	1.506	
		R-A-4	159.7	412	15.13	1.502	
R-B	Same conditions as R-A						
R-C		R-C-0	0	445	12.51		
		R-C-1	141.5	355	13.73		
		R-C-2	402.4	281	15.09		

A. Rate of Decrystallization and Depolymerization

Since ball-milling consists essentially in the conversion of crystalline to noncrystalline cellulose, the process can be followed kinetically by the change in moisture regain. (What is being measured is essentially the average lateral order.¹⁵) When this variable is plotted against time of milling, as

in Figure 1, it is obvious that the variations in the degree of dryness of the sample and in the initial degree of crystallinity exert a real influence on the rate of decrystallization. Thus, over the first fifty hours, the rate of decrystallization of the conditioned pulp sample was considerably greater than that of either of the dried samples. This

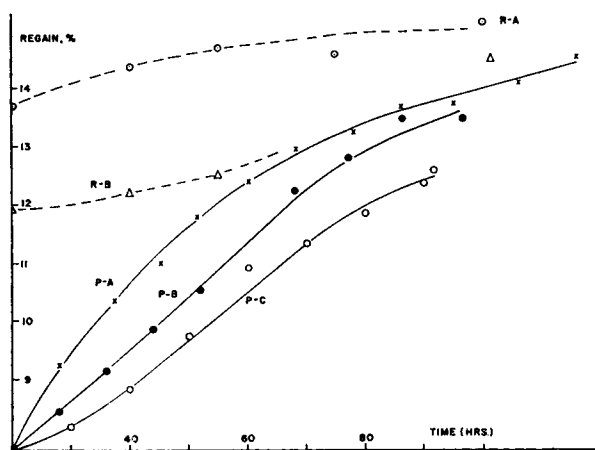


Fig. 1. Moisture regain vs. time of ball-milling for the various samples listed in Table I.

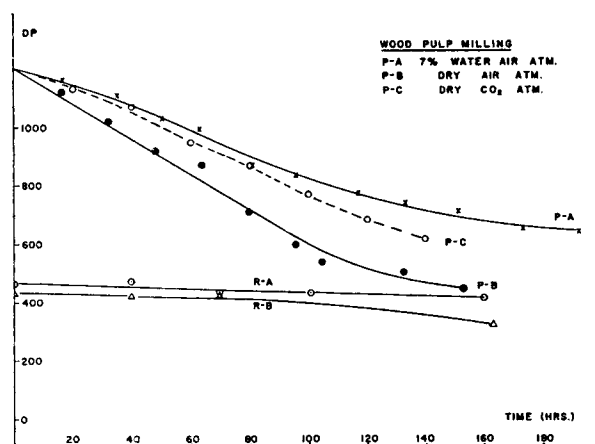


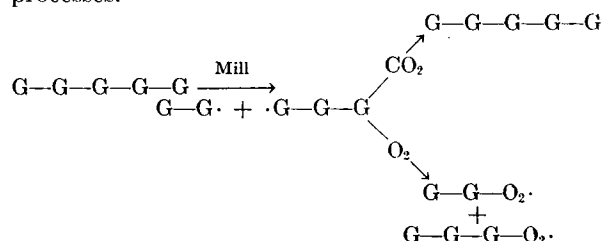
Fig. 2. Degree of polymerization vs. time of ball-milling for the various samples listed in Table I.

result is not unexpected, since it is well known that the grinding of minerals is facilitated by the presence of water.¹⁰ The explanation is based on the simple fact that grinding involves the creation of new surface and the water vapor-solid interface is of lower energy than the solid-air interface. In the case of cellulose, the added feature of water-induced recrystallization, which is discussed below, makes it probable that a maximum rate of decrystallization will be found at some intermediate relative humidity.

The effect of fine structure on the rate of decrystallization is illustrated by samples R-A and R-B which, to judge from their regains at zero time, differ in lateral order. Both samples were given the same drying treatment, yet the more accessible or lower-ordered sample (R-A) showed a more rapid rise to the leveling-off moisture content

of about 15%. If any possible differences in moisture content are discounted, the more rapid response of R-A to milling is probably related to the uniformity of structure of the zinc-spun rayon which allows more uniform absorption of the impact energy.

On the question of depolymerization (cf. Fig. 2), we have the very plausible result that for any given time of milling, series P-B has lower DP than P-A, since with the dry pulp the absorbed energy will be more localized. On the other hand, the difference between P-C and P-B suggests that the atmosphere is also a factor in the chain cleavage process. The presence of oxygen increases the amount of chain cleavage, probably by acting as a radical acceptor for the free radical chains produced by the mechanical cleavage. The peroxy radical probably goes on to initiate other oxidative processes as evidenced by the considerably higher copper number of sample P-B over that of P-C. In the absence of oxygen, the probability of chain recombination is much greater; hence the degradation is less. The following reactions are intended to illustrate these processes.



B. Density-Regain Relation

It has been suggested previously that the density and degree of crystallinity of cellulose fibers should bear a linear relation to one another.¹¹ Preston and Mhatre¹² have tested this hypothesis quantitatively, using the Hailwood Horrobin adsorption theory to convert the regain data to degree of crystallinity. By extrapolation they concluded that the density of completely amorphous cellulose was 1.47 g/cc. Since the data in Table II cover an unusually wide range of densities and regains with the unique feature that the same starting sample covers almost the entire range of densities, it seemed worthwhile to check the hypothesis further.

The data of Table II are plotted in Fig. 3 along with the density and regain data of Howsmon⁷ which included data for four typical rayons. Also added to the comparison were the values for bleached ramie: mercerized (1.530, 10.38%) and

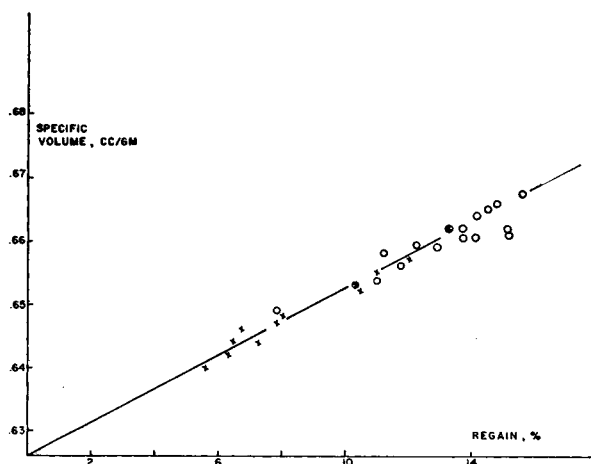


Fig. 3. Specific volume vs. regain: (O) data of Table I; (X) supplementary data (cf. text).

unmercerized (1.557, 7.30%), purified cotton linters (1.550, 6.40%) and the same material after hydrolysis in 2.5 *N* HCl at 105°C. for 15 minutes (1.559, 5.59%). All of our density values are in reasonable agreement with those recorded by other workers for similar samples. At the same time as the densities were measured, the regain of several ball-milled samples was remeasured to ensure that no change had occurred during storage. Small decreases of the order of a few percent of the measured regains were recorded and these values were used in making up Figure 3. The best straight line was drawn through the twenty-seven points, the average of the values for the specific volume of the cellulose I and II unit cells (0.628 and 0.624, respectively) being taken as origin. It is readily seen that, if there is any difference in the relation for these two crystal forms, it is masked by the scatter of the experimental points.

To deduce the specific volume of amorphous cellulose, use was made of the relation given by Valentine:¹³

$$SR = 2.6F_{am} \quad (1)$$

relating sorption ratio, SR, and the amorphous fraction F_{am} , the latter quantity being based on the deuterium exchange reaction. Assigning a value of 6.70% for the regain of cotton cellulose at 58% R.H., we obtain a value for completely amorphous cellulose of 17.4%, which corresponds to a specific volume of 0.673 in Figure 3. From the slope of Figure 3 and eq. (1), the following expression was derived relating specific volume and F_{am} :

$$v = 0.048F_{am} + 0.626 \quad (2)$$

Likewise, the conventional equation relating specific volume and crystalline fraction becomes

$$F_{cr} = \frac{v_{am}}{v_{am} - v_{cr}} - \frac{v}{v_{am} - v_{cr}} = 14.32 - \frac{v}{0.047} \quad (3)$$

The value of 0.673 for the specific volume of amorphous cellulose is lower than the 0.68 which was proposed by other workers.^{12,16} This is simply due to the difference in method used to convert moisture regain to a crystallinity value.

It is noteworthy that moisture regains of the ball-milled samples level off at less than 16%. This leveling-off appears to represent an upper limit of disorder which can be reached by the method. Even after 400 hours of milling, very little deviation from the value reached at 150 hours was observed. Since both native cellulose and rayons approach the same limit, it is entirely possible that it does not concern the actual process used but rather represents the highest possible degree of disorder consistent with the mechanics of the process. For example, the observed leveling-off may be the result of an equilibrium between mechanically induced decrystallization and recrystallization processes.

The suggestion that density measurements can provide a rapid and accurate measure of crystallinity,¹² especially if the convenient density gradient technique is employed, is very worthwhile. Unfortunately, not all samples of regenerated cellulose lend themselves to this technique. Some of the newer high tenacity rayons give such low densities in relation to their regain value that one cannot help but suspect the presence of micro voids which are not penetrated by the buoyancy medium. Such voids can indeed be observed in electron micrographs of thin cross sections¹⁷ of these materials and probably contribute to their low-angle x-ray scattering curve.¹⁴ For such fibers, densities can be derived from refractive index measurement by use of the Gladstone-Dale relation.²⁶

C. Mercerization of Ball-Milled Cellulose

Variations in the inflection point of the regain-% NaOH curves of native celluloses is a well known phenomenon which has been interpreted in terms of lateral order differences.¹⁵ On the basis of this interpretation, it was reasoned that even a slightly ball-milled sample should mercerize at lower alkali strength than its control. A test of this hypothesis was made by treating samples of PA-3 with alkali of different strengths at room tempera-

ture and following the transition by means of x-ray diffraction. The results indicated clearly that the milled sample begins to show transition to cellulose II at about 1% lower alkali strength than the original. Thus, 10% alkali was sufficient to bring about complete transition in the milled cellulose at 25°C., while nearly 12% was required for the control sample. This is in agreement with the finding of Hermans and Weidinger¹ that milling tends to increase the ease of swelling and solution in sodium hydroxide. In the present study, actual solubility as observed in the polarizing microscope did not appear to be extensive in 10% NaOH even for sample PD-2. This points to a fundamental difference between the effect of a rotating vs. a vibrating ball-mill which was used by these workers. The action of the latter is due mainly to impact of the balls whereas in the former the main effect is due to friction and accordingly the degradation and decrystallization are proportionately less.

D. The Recrystallization of Ball-Milled Cellulose

The concept of recrystallization which is frequently evoked to explain the small weight loss and pronounced sharpening of the x-ray diffraction pattern of cellulose after hydrolysis^{18,19} (in such a case, it is called crystallization) was first proposed to explain the change in properties which are observed when ball-milled cellulose is wetted.² These changes can be followed qualitatively by changes in the x-ray diagram and quantitatively by any of the usual fine structure parameters such as density moisture regain or integral heat of wetting.

A number of recrystallizations were brought about with the use of samples from the various series in Table II. The experiments consisted in putting the air dry powders into a large excess of appropriate liquid, e.g., water or 5 N HCl at various temperatures. After treatment, the samples were air-dried, and crystallinity evaluations were made on these materials according to standard pro-

cedures. A typical set of data are shown in Table III, from which it appears that acid treatment is slightly more effective in bringing about recrystallization, although the slightly greater density of the latter set is probably due to the usual hydrolysis effect of removing noncrystalline material and promoting crystallization. The slight difference in regain is also in line with this interpretation.

The effect of time on the recrystallization process is illustrated by the data of Figure 4, from which it may be judged that the primary process, whether in acid or water, is complete in less than 15 minutes. The subsequent slow drop in regain of the acid-treated sample is quite comparable to that which a rayon-type structure undergoes under these conditions and suggests that the degree of crystalline perfection of the two samples is quite similar. This is further supported by the fact that the leveling-off degree of polymerization¹⁸ after hydrolysis (2.5 N HCl at the boil for 15 minutes) and the per cent hydrocellulose residue for sample P-C-8 were 75 and 83.1%, respectively. These values are typical of those for ordinary viscose rayon.

Recrystallization can be very conveniently fol-

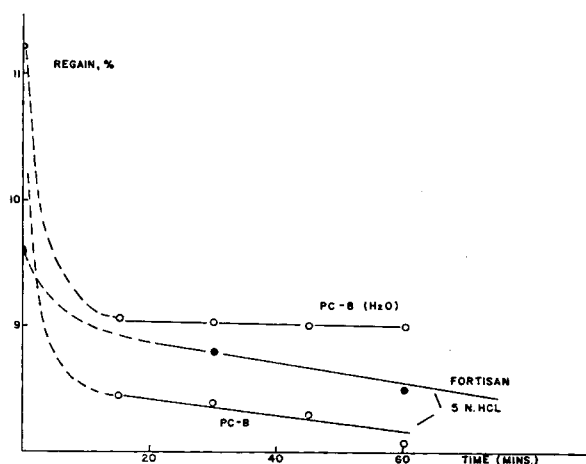


Fig. 4. Regain vs. time of recrystallization for sample PC-8 in water and in HCl. The curve for Fortisan rayon is included for comparison.

TABLE III
Properties of Ball-Milled Cellulose after Recrystallization

Sample	Density, g./cc.	Crystallinity, % ^a	Regain, % (58% R.H.)	X-ray data	Recrystallization treatment
P-A-0	1.541	52	7.85	cellulose I	H ₂ O, 80–85°C., 5 hr.
P-A-11	1.511	22	14.51	amorphous	None
P-A-11'	1.525	35	10.64	cellulose I	H ₂ O, 80–85°C., 5 hr.
P-A-11''	1.530	40	9.97	cellulose I	5N HCl, 50°C., 1 hr.

^a Calculated from eq. (3).

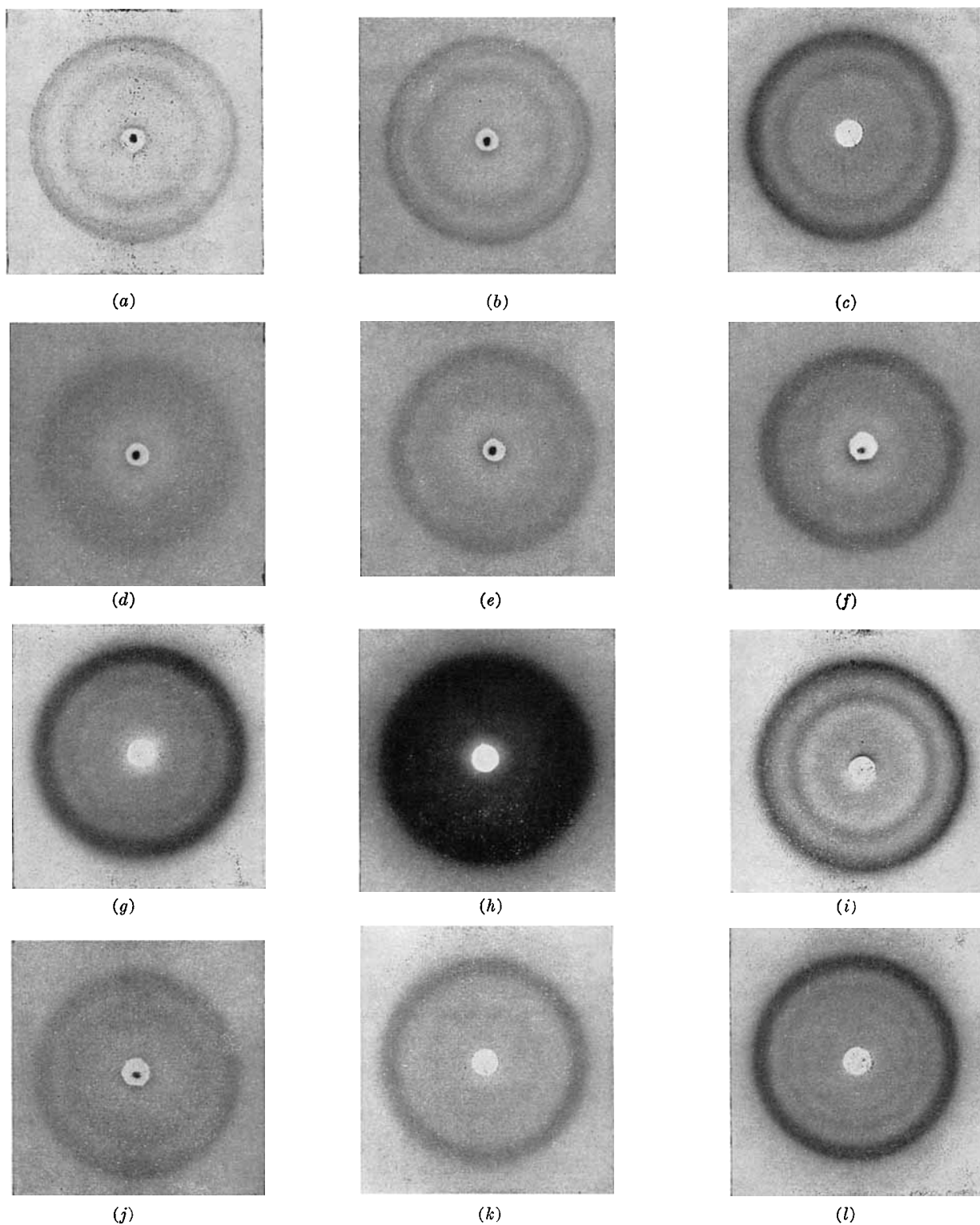


Fig. 5. Recrystallization of ball-milled cellulose: (a) Wood pulp (PA-0), water-treated, 25°C.; (b) Wood pulp (PA-11), ball-milled; (c) PA-11, water treated, 25°C.; (d) same as (c) at 83°C.; (e) PA-0 treated with 5 *N* HCl, 50°C., 1 hr.; (f) PA-11 treated as in (e); (g) PA-11 treated with glycerine at 200°C.; (h) Wood pulp (PD-2), ball-milled; (i) PD-2 treated one week at 95% R.H., 25°C.; (j) PD-2 treated with water, 25°C.; (k) PD-2 water-treated, 83°C.; (l) rayon (RC-2) water treated, 100°C.

lowed by x-ray diffraction measurements, and the various diagrams are shown in Figure 5. Although the amorphous patterns are similar to those reported by Hermans,¹ i.e., they show a broad ring whose maximum occurs within the position of the $10\bar{1}$ interference of cellulose II, generally only cellulose I was obtained on wetting at room temperature and temperatures intermediate up to at least 50°C. At 83°, samples which have been milled for a sufficient length of time begin to show a mixed pattern which is probably a mixture of patterns for cellulose II and IV. It was not until milling times of 400 hours were used (sample PD-2) that ball-milled native cellulose was found to recrystallize, on wetting at room temperature, in the cellulose II lattice. At 83°C. the mixed structure was again in evidence, and it seems only reasonable to assume that this structure is a mixture of celluloses II and IV, since the ball-milled rayon sample R-C-2 could be made to give a similar pattern and here there can be no question of this pattern being that of cellulose I.

As suggested by Hess,² the appearance of cellulose I on wetting is probably due to incomplete disruption of this lattice form so that a sort of "memory" effect establishes a preference for growth of the cellulose I lattice. In support of this thesis, it could be shown that when sample PD-2 which had been milled 400 hours was recrystallized over a period of one week in an atmosphere of 95% relative humidity only the pattern of cellulose I appeared. The pattern, which is shown in Figure 5*i*, is uncontaminated by that of cellulose II, and, although the density was found to be still relatively low (1.513), it appears that well-defined crystallites have been produced. This effect of slow growth no

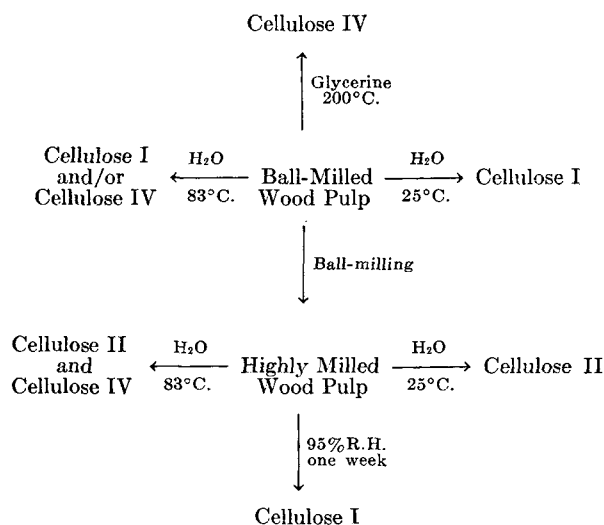
doubt explains the lower permeability of cellophane and gelatin films which are dried slowly at high relative humidity and low temperature compared to high temperature, low relative humidity conditions.^{20,21} Our results on the recrystallization of native cellulose are summarized in the diagram in the preceding column.

E. Hydrolytically Induced Crystallization of Rayons

Although the crystallization of rayons on hydrolysis is well-established,^{7,18,19} little attention has been given to the relation between hydrolysis conditions and the crystal form of the new diffracting material. The following experiments were directed to this end and it will be shown that hydrolytic crystallization has many features common to water-induced recrystallization of ball-milled cellulose.

The phenomenon is readily demonstrated by considering the equatorial traces of Figure 6, which were obtained with a Guinier powder camera, the sample being an experimental tire yarn of high strength. The rather low initial crystallinity of the yarn before hydrolysis is clearly indicated by the complete lack of peak resolution which is characteristic of super tire yarns. Hydrolysis in 2.5 N HCl at the boil results in a distinct sharpening of the x-ray diagrams, which can be interpreted only as the result of a process of crystal growth. The total loss in material in the present case was 21.2%, but the contribution of this effect to the phenomenon must be considered negligible, since the same result is obtained with only 1 minute of hydrolysis when the weight loss is less than 5%. Hence, as suggested by Hermans and Weidinger,¹⁹ it is likely that recrystallization is concurrent with chain cleavage.

An unusual feature of these rayons is that their polyphase structure includes two lattice forms: cellulose II and cellulose IV. The main reflection corresponding to the cellulose IV occurs at $\sin \theta = 0.1346$; it is visible only as a broad shoulder to the 101_{II} and $10\bar{1}_{II}$ reflections in Figure 6*a*. As seen in Figure 6*b*, however, it is made distinct by the hydrolysis which causes crystals of both lattice forms to grow. This fact is significant, for it shows that the recrystallizing material is not entirely free to adopt the thermodynamically stable lattice at the temperature of hydrolysis. Most probably, local strains develop in the vicinity of the crystallite ends during regeneration, and these can only be removed by further growth of the crystallites in the same lattice. If the strain energy is sufficiently large, this condition would favor the



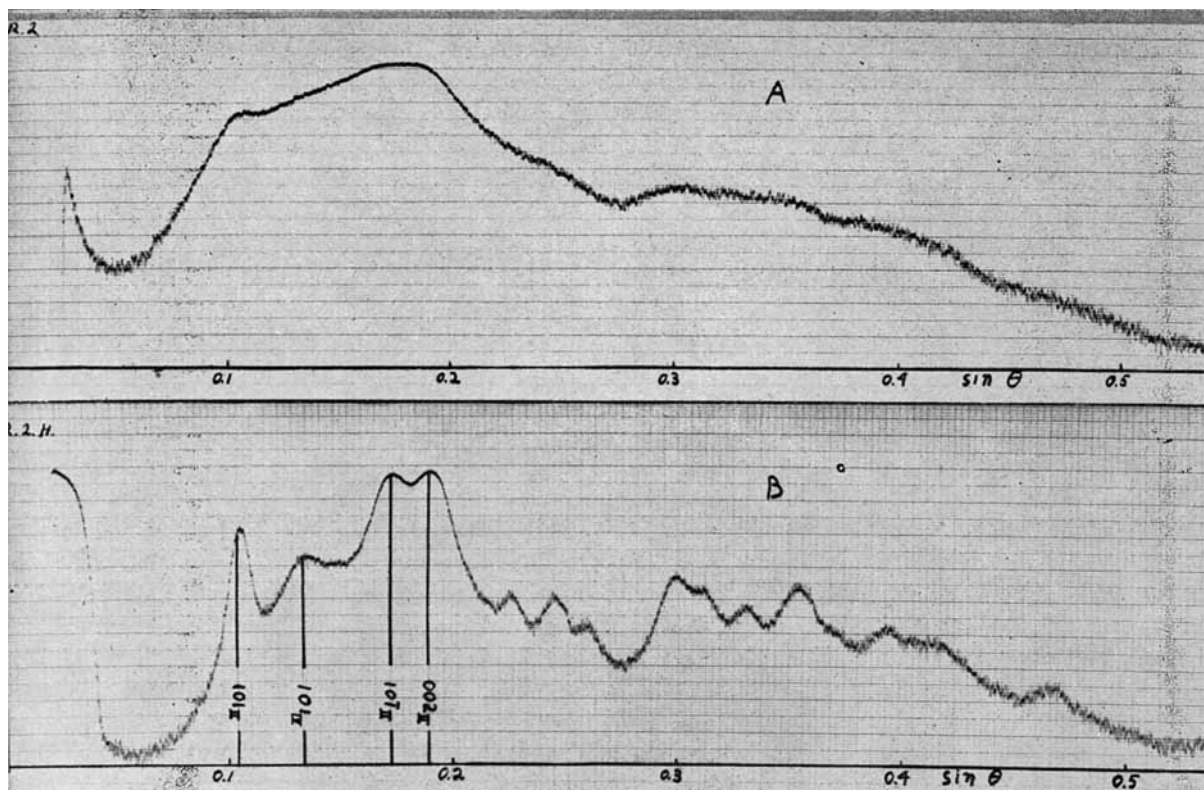


Fig. 6. Recrystallization of hydrolyzed tire cord rayon. Equatorial traces of powder diagrams before (A) and after (B) hydrolysis in 2.5 *N* HCl for 15 minutes at 105°C.

formation of cellulose II in certain parts of the fiber, even at temperatures above the normal transition value. The mechanism is probably a fairly general one and can be used equally well to explain the fact that mixtures of cellulose II and IV were frequently obtained from the hydrolysis, in boiling HCl, of samples which contained initially only cellulose II or only x-ray amorphous material. When a rayon containing only cellulose IV was used as starting material, only cellulose IV could be detected in the hydrocellulose, even when the hydrolysis was carried out at as low a temperature as 50°C. This again emphasizes the importance of the form which is present initially.

Admittedly, the "strain" concept is rather nebulous, but it is easy to conceive that a highly anisotropic molecule such as cellulose would experience some difficulty in adjusting to a new conformation when part of it is fixed. Apparently, it can do so only when at least one end is freed, which is what happens during hydrolysis. Thus, a very low crystallinity rayon (regain at 58% R.H. = 14.5%) could not be made to recrystallize to any appreciable degree by boiling in water. However, even mild hydrolytic treatment was highly effective.

IV. DISCUSSION

It is interesting to speculate on the state of matter of the ball-milled material. Three possibilities seem to suggest themselves: (1) it is in a glassy state, (2) it is a finely divided crystalline solid, or (3) It is some combination of (1) and (2). The rubbery state is ruled out, for in this case there should be spontaneous recrystallization, and this does not occur. If it is assumed that crystallites of native cellulose have cross-sectional dimensions of 150×50 Å.²² and a regain at 58% R.H. of 6% or less, then it is clear that the same crystallites will be reduced to a thickness of about 3 glucose units when the regain has reached 15%. At this level of regain, then, the ball-milled material is best thought of as possessing only short-range order, and, because of this, its state of matter is likely to be closer to that of a glass than anything else. It appears reasonable to compare the material to a crystallizing thermoplastic which has been rapidly quenched so as to bring it to a glassy state with only a minimum amount of crystallinity. In the latter case, as for ball-milled cellulose, the glassy state is metastable, and the absorption of heat in one case and water in the other is sufficient

to raise the polymer above its glass transition temperature, where crystallization readily occurs. Water added to a glass would serve to introduce new lattice sites, hence increasing the configurational entropy and lowering the glass temperature.²³

Perhaps the most significant observation of this report is the fact that, under conditions of slow recrystallization or after short times of milling, amorphous cellulose could be made to return to the cellulose I configuration. This was a very unexpected finding, since cellulose II is the lower enthalpy state.²⁴ However, it is in agreement with the observation of Hess² that ball-milling for short periods produces a decrystallized cellulose but subsequent wetting allows return to the cellulose I lattice. Hermans and Weidinger¹ suggested that the observation of Hess was due to residues of unmilled native fibers, but this explanation appears unacceptable in view of the above finding that the same sample could be made to crystallize as cellulose I, II, or IV, depending on the conditions of crystallization. Apparently, energy and/or entropy considerations are such that, in the amorphous state, the chains return to the cellulose I configuration under conditions of moderate swelling, which allow only slow recrystallization initiating from points of residual order which favor the cellulose I lattice. This aspect appears to be important, for slow recrystallization of ball-milled rayon samples RC-1 and RC-2 produced only the cellulose II form. These observations may have some significance in explaining why undried cotton fibers, direct from the developing boll and giving an amorphous x-ray pattern, crystallize as cellulose I.²⁵ Perhaps the essential factor governing lattice form is simply a particular chain conformation which is produced by the enzyme system.

From the foregoing data the following mechanism for the growth of cellulose crystals from highly concentrated solutions or in partially crystalline cellulosic media is proposed. The initial degree of lateral order at the time the process begins is the most important single factor in determining the crystal form which appears. When crystallization occurs from solution, a temperature in the vicinity of 80°C. appears to be the transition point above which cellulose IV is the stable form and below which cellulose II is obtained. Any kind of molecular interaction or strain raises the transition temperature so that, for wet amorphous cellulose, 100°C. appears to be in the critical temperature region at which both cellulose II and IV are ob-

tained. Above 100°C. increasing percentages of cellulose IV are obtained.

In the case of incompletely decrystallized native cellulose, the II lattice is not readily formed on wetting at any temperature. Apparently, there exists a strong constraint to return to the native lattice even though the samples are x-ray amorphous. This constraint is probably connected with the length of the chains and the cohesive energy of the polymer superstructure. This constraint is removed only when comminution produces relatively amorphous fiber fragments of sufficiently low degree of polymerization that a cooperative phenomenon of this nature can proceed.

In the case of hydrolysis, if conditions are such that the crystalline regions are unaffected, then the crystalline, noncrystalline continuity is the constraining influence. Only chain cleavage in the latter regions can bring about recrystallization, and the lattice form which develops is a function of the hydrolysis temperature and the original lattice. If the original lattice happens to be the same as the thermodynamically favored one, then a pure crystalline phase results. If it is not, polymorphism is encountered.

The units involved in hydrolytic crystallization may equally well be very thin lamellar crystallites collapsing on top of one another like the pages of a book, in which case the chains are even less free to adopt any other lattice form than that of the growing crystallite. Native celluloses consisting predominantly of ribbon-like microfibrils probably recrystallize by a lateral aggregation of this sort, as opposed to growth by addition of individual chain units. This is suggested by the fact that treatment with acid is accompanied by pronounced lateral shrinkage, relatively small loss in weight, and only slight sharpening of the x-ray diagram. It is noteworthy also that formation of cellulose IV never results from the hydrolysis of a native sample in 2.5 *N* HCl at 105°C., whereas some of this lattice form does develop in the fiber diagram of a textile rayon under these conditions.

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References

1. P. H. Hermans and A. Weidinger, *J. Am. Chem. Soc.* **68**, 2547 (1946).
2. K. Hess, H. Kiessig, and J. Gunderman, *Z. physik. Chem. (Leipzig)*, (B)**49**, 64 (1941).

3. E. Steurer, and F. Katheder, *Kolloid-Z.*, **114**, 78 (1949).
4. E. Huseman, *Makromol. Chem.*, **1**, 158 (1944).
5. C. F. Wijnman, *TAPPI* **37**, 96 (1954).
6. O. A. Battista, *Ind. Eng. Chem., Anal. Ed.*, **16**, 351 (1944).
7. J. A. Howsmon, *Textile Research J.*, **19**, 152 (1949).
8. R. S. Orr, L. C. Weiss, H. B. Moore, and J. N. Grant, *Textile Research J.*, **25**, 592 (1955).
9. L. H. Tung and W. C. Taylor, *J. Polymer Sci.*, **21**, 144 (1956).
10. J. J. Bikerman, *Surface Chemistry for Industrial Research*, Academic Press, New York, 1948, p. 355.
11. P. H. Hermans, *J. Textile Inst.*, **38**, 63 (1947).
12. S. H. Mhatre and J. M. Preston, paper presented at International Congress of Pure and Applied Chemistry, London (1947).
13. L. Valentine, *Chem. Ind. (London)*, **1956**, 1279.
14. W. O. Statton, *J. Polymer Sci.*, **22**, 385 (1956).
15. R. H. Marchessault and J. A. Howsmon, *Textile Research J.*, **27**, 30 (1957).
16. W. Kast, *Z. Electrochem.*, **57**, 525 (1953).
17. F. F. Morehead, American Viscose Corporation, Marcus Hook, Pa., unpublished data.
18. O. A. Battista, *Ind. Eng. Chem.*, **42**, 502 (1950).
19. P. H. Hermans and A. Weidinger, *J. Polymer Sci.*, **4**, 317 (1949).
20. J. M. Kuzmak, Ph.D. thesis, McGill Univ., Montreal, Canada, 1952.
21. D. W. Jopling, *Research (London)*, **6**, 275 (1953).
22. S. M. Mukherjee and H. J. Wood, *Biochim. et Biophys. Acta*, **10**, 499 (1953).
23. J. H. Gibbs and E. A. DiMarzio, *J. Chem. Phys.*, **28**, 373 (1958).
24. B. G. Ranby, *Acta Chem. Scand.*, **6**, 101 (1952).
25. E. E. Berkley and T. Kerr, *Ind. Eng. Chem.*, **38**, 304 (1946).
26. D. N. Tyler and N. S. Wooding, *J. Soc. Dyers Colourists*, **74**, 283 (1958).

Synopsis

A study has been made of the effect of fine structure on the decrystallization process which results from the ball-milling of cellulose. The rate of decrystallization is sensitive to the type of fine structure and is accelerated by the presence of moisture. The extent of chain degradation was greater in air atmosphere than in carbon dioxide, suggesting that mechanically induced free radical degradation occurs along with other chain-breaking processes. A study of the density and moisture regain of the samples after various times of milling showed that a linear relation between regain and density held over the entire range studied. The relation was the same for native and regenerated cellulose. The process of recrystallization of the ball-milled samples was studied under various conditions and compared to the hydrolytically induced recrystallization of rayons. The type of lattice which develops on recrystallization was

found to depend on the original lattice, the extent of ball-milling and the conditions of recrystallization. A highly ball-milled sample could be made to recrystallize as cellulose I, II, or IV depending on the conditions.

Résumé

On a effectué une étude de l'effet de la structure fine sur le processus de décrystallisation de la cellulose en cours de broyage. La vitesse de décrystallisation dépend du type de structure fine et est accélérée par la présence d'humidité. La dégradation des chaînes est plus importante à l'air atmosphérique que dans l'anhydride carbonique, ce qui suggère un mécanisme par radicaux libres, induit par l'action mécanique, à côté d'autres processus de rupture de chaîne. Une étude de la densité et de l'absorption d'humidité des échantillons après des temps de broyage variable indique une relation linéaire entre cette absorption et la densité dans tout le domaine étudié. Cette relation est la même pour la cellulose native que pour la cellulose régénérée. Le processus de recristallisation des échantillons broyés a été étudié dans diverses conditions et comparé à la recristallisation des rayons induites par l'hydrolyse. Le type de réseau qui apparaît en cours de recristallisation dépend du matériau initial et de son réseau, du degré de broyage et des conditions de recristallisation. Suivant les conditions un échantillon fortement broyé peut être amené à recristalliser soit sous la forme I ou II ou IV de la cellulose.

Zusammenfassung

Eine Untersuchung des Einflusses der Feinstruktur auf die Dekristallisation, die durch Kugelmahlung von Cellulose hervorgerufen wird, wurde durchgeführt. Die Dekristallisationsgeschwindigkeit ist vom Feinstrukturtyp abhängig und wird durch die Gegenwart von Feuchtigkeit erhöht. Das Ausmass des Kettenabbaus war unter Luft grösser als unter Kohlendioxyd, was dafür spricht, dass ein mechanisch induzierter Abbau über freie Radikale neben andern Ketenspaltungsprozessen stattfindet. Eine Untersuchung der Dichte und der Feuchtigkeitsaufnahme der Proben nach verschiedenen Mahlungsdauern zeigte, dass zwischen der Aufnahme und der Dichte über den ganzen untersuchten Bereich eine lineare Beziehung besteht. Diese Beziehung war die gleiche für native und für regenerierte Cellulose. Der Rekrystallisationsprozess wurde bei den in der Kugelmühle gemahlten Proben unter verschiedenen Bedingungen untersucht und ein Vergleich mit der hydrolytisch induzierten Kristallisation von Kunstseide angestellt. Es wurde gefunden, dass der bei der Rekrystallisation entstehende Gittertyp vom ursprünglichen Gitter, vom Ausmass der Kugelmahlung und von den Rekrystallisationsbedingungen abhängt. Je nach den gewählten Bedingungen konnte eine intensiv in der Kugelmühle gemahlene Probe zur Rekrystallisation als Cellulose I, II oder IV gebracht werden.

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