

Some Experiments on Viscose Rayon "Stabilized" by Heat Treatment

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INTRODUCTION

In a previous paper¹ it has been shown experimentally that when viscose rayon, after being pre-swollen in sulfuric acid baths of the range of pH optimal for maximum hydration, is heat-treated at the temperature near, or just above, the glass transition temperature of regenerated cellulose, i.e., at 60–70°C., the effects of the heat treatment stabilizing viscose rayon, as exhibited by various physical and mechanical properties, are most marked.

The present paper is concerned with the result of an experimental study, in which acetic acid is used as the swelling agent instead of sulfuric acid because it is expected that acetic acid, being volatile, is held less strongly, if at all, in the structure during the heat treatment and accordingly is more desirable than less volatile inorganic acids which may cause more severe degradation of the fibrous structure.

Also in the present work, as attention has been concentrated on the change in internal structure of fibers caused by heat treatment, some qualitative as well as quantitative studies of the heat effects were made by infrared spectroscopy and x-ray methods.

EXPERIMENTAL

1. Original Sample of Viscose Rayon

The original sample of viscose rayon supplied by the Teikoku Rayon Co. was in the form of 50-den. multifilament (20 single filaments). It was extracted in a Soxhlet extractor by refluxing with a 1:1 benzene-ethyl alcohol mixture for 8 hr., care being taken to prevent overheating of the sample during the extraction and to keep the temperature below 30°C. at all times.

The sample was then air-dried and stored in a

desiccator over CaCl_2 for about one week prior to the following treatments.

2. Pretreatment of Fibers

a. Pretreatment in Acetic Acid Solutions

A series of aqueous acetic acid solutions were so prepared that the pH of the solutions, after the swelling equilibrium had been attained, was in the range (2.5–5.8) corresponding to that at which there is maximum swelling of cellulose at room temperature. In each case a 3-g. sample, reeled loosely on a glass frame, was soaked in the solution (500 cc.) for 5 hr. at 25°C., after which the pH was determined. The swollen fiber samples were then squeezed, vacuum-dried at room temperature, and stored overnight in a desiccator over P_2O_5 before the heat treatment described below.

b. Heat Treatment

A temperature range of 50–150°C. was used for the heat treatment, and a paraffin bath was chosen as an inert heating medium, as described in the previous paper. The procedure of the heat treatment and of handling the heat-treated fibers was nearly the same as in the experiments given in the previous paper;¹ after being removed from the paraffin bath, each sample was extracted successively with petroleum ether and the benzene-alcohol mixture, and this was followed by drying in vacuum at 25°C. for 2 hr. and storing in a desiccator over CaCl_2 for one week prior to the following tests.

3. Examination of the Effects Caused by the Stabilizing Treatments

a. Breaking Properties and Transient Modulus

Bundles containing 60 filaments were stored in a desiccator over a sulfuric acid solution of 55%

R.H. for five days before being used in the stress-strain measurements.

Measurements were made at 25°C. at 60% R.H., specimen length being 20 mm. and rate of elongation being 1 mm./23 sec. A constant speed fiber tester designed in our laboratory³ was used for stress-strain measurements. From the stress-strain diagram obtained at different rates of elongation, beside breaking strength and elongation, transient moduli were evaluated according to the method suggested by Eyring and Halsey.² Details are given in the original paper² or our previous report.³

b. Dynamic Elastic Modulus

For measuring complex Young's modulus and internal friction of the samples, the added mass method⁴ was used. The measurements were performed at a frequency of 200 cycles/sec. and at 60% R.H. and 25°C.

4. Changes of Structure Caused by the Heat Treatments

a. Study by Infrared Spectroscopy

A qualitative study was made by means of infrared spectroscopy of the change caused by the heat treatments according to the deuteration method of Marrinan and Mann.⁵ This method, when the deuteration is carried out in D₂O vapor, permits the study of the OH groups in amorphous regions separately from those in crystalline regions.⁶

For convenience in the spectroscopic investigation, a viscose film, rather than rayon fibers, was used as the sample of regenerated cellulose because of the possible reduction of intensity of the infrared spectra as a result of diffused scattering when fibers are taken as the specimen.

According to Mann and Marrinan,⁶ a deuterated viscose film which has been dried at about 60°C. before being rehydrogenated in H₂O continues to show

after rehydrogenation, bands in the infrared spectrum ascribed to OD groups in crystalline regions which have not been rehydrogenated. However, the conditions for the formation of these resistant peaks, which are due to OD groups (which have not been replaced by OH because of crystallization of the amorphous regions made of deuterated molecules), have not been studied in detail, for instance, as to the temperature and the time of drying the deuterated sample.

Because of this fact, a qualitative study was made of the effect due to heat treatments by means of infrared spectroscopy, taking the following materials as the samples.

Untreated Sample (Specimen 1). A viscose film, 20 μ thick, extracted with an ethyl alcohol-benzene mixture and air-dried after being washed with distilled water was used.

Treated Samples. Samples of Specimen 1 were subjected successively to swelling, deuteration heat treatment, and rehydrogenation, as shown in Table I. Deuteration in the vapor phase was carried out in a cell similar to that used by Mann and Marrinan as given in Figure 1.

Spectroscopic measurements were carried out on a Perkin-Elmer 112 spectrometer with a LiF prism.

Sulfuric acid was used as the swelling agent for the pretreatment of fibers instead of acetic acid, in this study, as well as in the following x-ray investigation, simply because mechanical and physical properties of the fibers preswollen in sulfuric acid baths have been more fully investigated, as reported in the previous paper.¹

b. X-Ray Study

Quantitative determinations of the crystallinity of viscose rayon fibers by the x-ray diffraction method have been made by Hermans and Weidinger.⁷ In this method, the photometer trace of the diffraction pattern from a fiber pellet without

TABLE I
Treatment of Specimens for Infrared Spectroscopy

Specimen	Swelling	Deuteration	Heat treatment	Rehydrogenation
Specimen 1	None	None	None	None
Specimen 2	Specimen 1, swollen 1 hr. in H ₂ SO ₄ , pH 3.0	Vapor phase	54°C., 1 hr.	Placed in distilled H ₂ O 1 hr.
Specimen 3	"	"	70°C., 1 hr.	"
Specimen 4	"	"	90°C., 1 hr.	"
Specimen 5	"	"	150°C., 1 hr.	"
Specimen 6	"	"	None	"
Specimen 7	"	Steeped in liquid D ₂ O for 4 hr.; air-dried	None	"

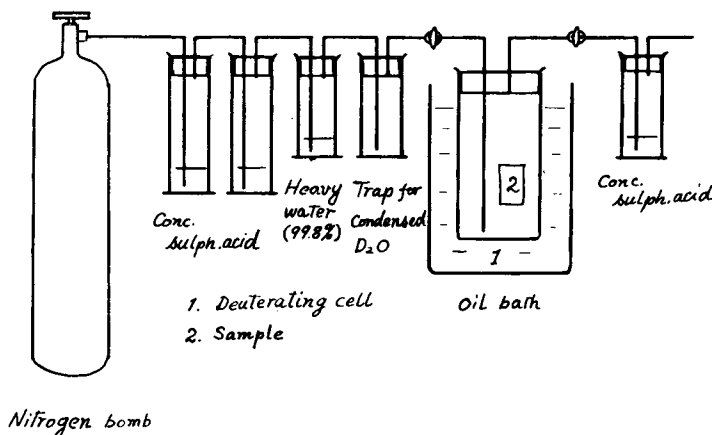


Fig. 1. Laboratory assembly for deuterating viscose film.

preferred orientation, after correction for incoherent and air scattering, was resolved into peaks representing amorphous material and the reflections from (110), (101), and (002) planes (A_0 , A_3 , and A_4) in the crystalline portions.

The method used in the present studies is similar to that of Hermans and Weidinger but instead of a photometer trace of the diffraction pattern, an x-ray diffractometer (scanning goniometer and associated Geiger-counter circuits for measuring intensities of the diffracted x-rays) manufactured by North American Philips Co., Ltd., was used. Also, in view of the anticipation that there may be no perceptible change of crystallite orientation during the pretreatments and heat treatment of fibers, and because it is our aim to obtain a relative measure for the effect on crystallization produced by heat treatment of fibers, preparation of the samples, such as the fiber pellet used by Hermans and Weidinger,⁷ to eliminate orientation effects was not considered in the present study.

The Geiger-counter registration curve of the reflections along the equator for the diffraction pattern of the fiber bundle with $\text{CuK}\alpha$ radiation (with the fiber axis perpendicular to the x-ray) was made. The trace of the diffracted intensities for the diffraction angles of 7–30° was resolved into amorphous and crystalline peaks, correction being applied for radiation scattered by air and for incoherent scattering (background components due to Compton scattering and thermal agitation according to the method given by Hermans and Weidinger).⁷

In Figure 2 are shown the Geiger counter registration curves of the A_0 , A_3 , and A_4 reflections of some typical rayon samples.

It was assumed according to Hermans and

Weidinger⁷) that the background line (broken curves *a* in Fig. 2A) representing the separation between the background and crystalline interferences superimposed thereon in the form of peaks, just touches the minimum between the A_0 and A_3A_4 peaks. From the background line, thus obtained by extrapolating the final downward boundary of the A_3A_4 peak, the intensity of the radiation scattered by the air in the camera (curves *b* in Fig. 2A) was subtracted so that a background curve with a flat maximum located somewhere between the two main crystalline peaks was obtained (curves *c*, Fig. 2B). This background radiation was then corrected for the thermal and Compton components (shown as the shaded areas in Fig. 2A). In order to find this correction, exposures were made of several crystal plates of cane sugar; the background line thus obtained after correction for radiation scattered by air was assumed to be equal to the scattering due to the Compton and thermal components of the background for cellulose. When this correction was made, a symmetrical background with a flat maximum located at a diffraction angle of 17° (curves *d* in Fig. 2B), was obtained. This curve was quite symmetrical, however, if the maximum was taken as the center. The area under the background radiation curve thus obtained was assumed to represent a relative measure of the quantity of the amorphous regions of the sample.

As a relative measure of the crystalline fraction (integrated intensity of the coherent radiation selectively diffracted by the crystalline portion), the area under the surface of the two main peaks A_0 and A_3A_4 beyond the background curve (curve *e* in Fig. 2A) was taken. Also given in Figure 2B are net intensity curves for the crystalline portion

thus obtained by graphic subtraction of the background (curves *f*), together with those for the amorphous portions obtained as above (curves *d*). Also very symmetrical "crystalline" peaks were thus obtained, although the peaks A_3 and A_4 were

so near to each other that they appeared as single peaks on photographs.

When the x-ray runs are carried out under carefully standardized conditions (constant intensity of the x-ray beam and constant mass in the beam),

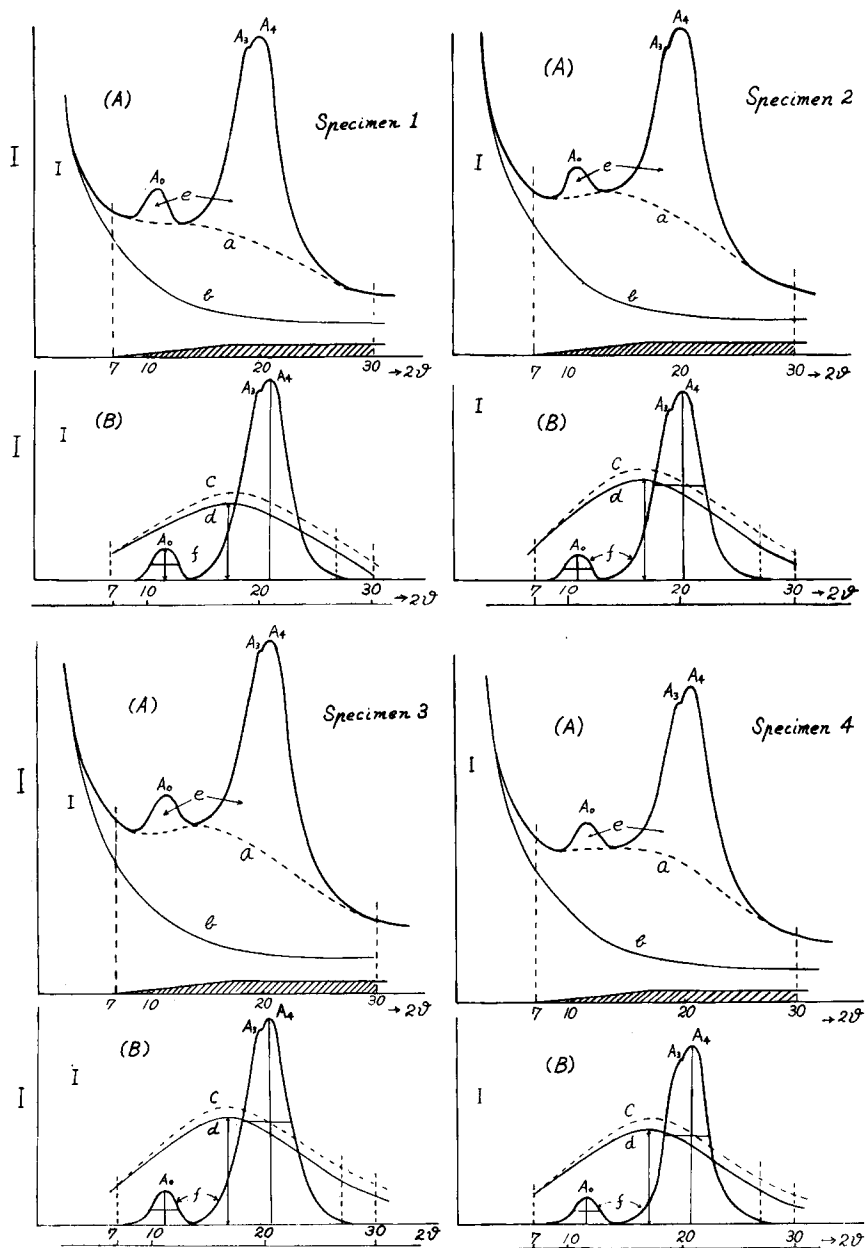


Fig. 2. Geiger counter registration curves resolved into amorphous and crystalline peaks: (a) background curve; (b) air scattering; (c) background curve, air scattering; (d) net intensity curve for amorphous portion; (f) net intensity curve for amorphous portions; shaded area: correction for incoherent scattering. The details of preparation of specimens are shown in Table III.

the ratio of the total integrated intensity (planimetered area) of the peaks I_{cr} to that of the amorphous background I_a is expected to be related to the ratio of crystalline and amorphous portions in the sample M_{cr}/M_a by

$$M_{cr}/M_a = \alpha/(1 - \alpha) = (A/B)(I_{cr}/I_a) \quad (1)$$

The degree of crystallinity α is given by

$$\alpha = I_{cr}/[I_{cr} + (B/A)I_a] \quad (2)^8$$

However, from the following approximate estimation we have found it plausible to assume that the ratio B/A , a constant involving the relative scattering efficiency of unit weight of amorphous and crystalline portions of regenerated cellulose, is nearly equal to 1.0 under the conditions at which the spectroscopic trace was obtained; in this estimation the constancy of the amount of specimen taken and the primary x-ray radiation intensity used were especially carefully taken into account.

In view of the well-known fact⁹ that the degree of crystallinity of most regenerated celluloses, irrespective of the method of regeneration used or mild physical pretreatment, is strikingly equal and approximately 39%, we can safely assume that the three typical samples, the details of which are shown in Table III, the original untreated sample (4), that heat-treated at 70°C. without pretreatment, (2), and that obtained after heat-treatment of rayon pretreated in sulfuric acid bath (pH = 3.0) (3), have a crystallinity of approximately 39%. On the basis of this assumption, the values of B/A calculated according to eq. (2) from the experimentally observed value of the ratio of the planimetered area of the two fractions I_{cr}/I_a , for the three samples are, respectively:

$$39/61 = (A/B)(I_{cr}/I_a) = (A/B)(450/734);$$

$$A/B = 1.04$$

$$39/61 = (A/B)(I_{cr}/I_a) = (A/B)(481/708);$$

$$A/B = 0.94$$

$$39/61 = (A/B)(I_{cr}/I_a) = (A/B)(435/735);$$

$$A/B = 1.08$$

$$\text{av. } A/B = 1.02$$

Thus, to obtain the degree of crystallinity of fiber samples by the x-ray method, we simply regard the ratio of $I_{cr}/(I_{cr} + I_a)$ as obtained under carefully controlled diffractometric tracing conditions to be a relative measure of the crystallinity.

However, preferred orientation of any crystal plane may give rise to unpredictable change in relative intensity of the corresponding interferences. Also, to obtain a true measure of crystallinity which is not influenced by orientation effects, diffractometric tracings must consist of as many interferences as possible and should be measured in more than one direction. The degree of crystallinity as expressed as above by the relative integrated intensity $I_{cr}/(I_{cr} + I_a)$, however, was obtained from the measurement of the distribution of intensity only along the equator and, for a limited range of diffraction angles around only three typical reflexes, therefore it is, at best, a relative measure and never represents the true crystallinity of the whole fiber structure.

Of the equatorial "crystalline" peaks A_0 and A_3A_4 , measurements were made also of the half-width as the half-maximum angle in order to determine whether there is widening or sharpening of the peaks. The half-maximum angle was obtained as usual by placing a line parallel to the zero-intensity line at half of the maximum height.

RESULTS AND DISCUSSION

Elastic Modulus and Breaking Properties

The data obtained are given in Table II and shown graphically in Figures 3-6. The general trend of the curves indicating the effects of pH and the temperature of the heat treatment are similar in the following respects to those reported in the previous paper¹ in which acetic acid, rather than sulfuric acid, was used as the swelling medium.

In the temperature range from room temperature up to 150°C. the dynamic modulus E' and the breaking strength f_{max} attain their maximum values in the range of pH 3.0-3.5. This is in the neighborhood of the pH range at which regenerated cellulose shows maximum swelling.

Also, in the pH range 2.7-5.8 f_{max} attains maxima at temperatures around 70°C.; however, the values of E' do not tend to decrease at higher temperatures (90-150°C.) as is the case when sulfuric acid is used as the swelling agent.¹ In general, the dynamic modulus tends to increase with increasing temperature of heat treatment over the entire range of pH. This trend is very slight above a temperature of 70°C., however. The modulus E' also increases with increasing crystallinity. This must be expected, when it is considered that the dynamic modulus reflects the behavior of minute regions of polymer structure under a very

TABLE II
The Mechanical Properties in Their Relation to the Conditions of Pretreatment of Viscose Rayon Fibers

Heat treatment	pH of acetic acid bath	Transient modulus G_1 , g./den.	Dynamic modulus $E' \times 10^{-11}$, dynes/cm. ²	Breaking strength f_{max} , g./den.	Breaking elongation, $E'l_{max}$, %
None		0.4	2.1	1.7	16
54°C., 1 hr.	2.7	—	2.0	2.1	17
	2.9	0.5	2.1	2.1	18
	3.5	0.5	2.0	2.3	18
	4.0	—	2.1	2.3	17
	5.8	0.4	2.1	2.2	19
70°C., 1 hr.	2.7	0.5	2.2	2.2	16
	2.9	—	2.3	2.3	18
	3.5	0.6	2.2	2.2	18
	4.0	0.6	2.1	2.5	19
	5.8	0.4	2.1	2.2	19
90°C., 1 hr.	2.7	0.5	2.0	1.8	16
	2.9	0.5	2.3	2.1	16
	3.5	0.6	2.2	2.2	18
	4.0	0.4	2.0	2.2	18
	5.8	0.4	2.1	2.3	16
150°C., 1 hr.	2.7	—	—	—	—
	2.9	—	2.3	1.9	13
	3.5	0.6	2.4	1.9	13
	4.0	0.5	2.1	1.8	14
	5.8	0.5	2.2	2.0	15

small and reversible deformation. This will be considered further, in the discussion of the results obtained by infrared spectroscopy.

In spite of the steady rise of the modulus, the breaking strength decreases as the temperature of the heat treatment increases beyond 70–90°C.

This is not surprising in view of the difference between such a breaking property as the breaking strength and such an equilibrium property as the dynamic modulus. Unlike E' the former is always accompanied by a large deformation involving a region of large dimension. Therefore, such a breaking property is determined largely¹⁰ by a definite flaw or void, i.e., the weakest spot about

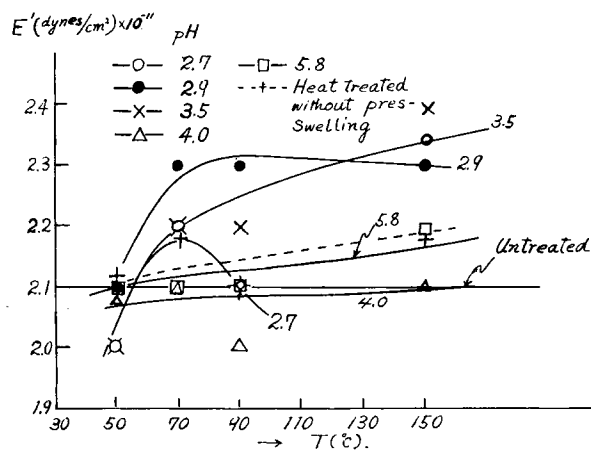


Fig. 3. Plot of temperature of treatment vs. dynamic modulus E' of fibers obtained on heating viscose rayon pretreated in acetic acid baths of various concentrations at various temperatures. (pH = 2.7–4.0, temp. = 50–150°C. as shown in Table II.)

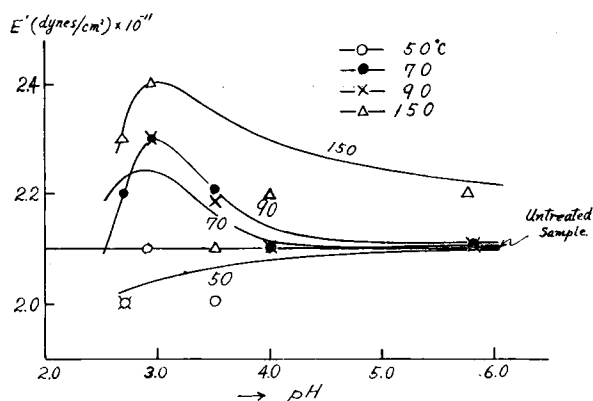


Fig. 4. Plot of pH vs. dynamic modulus E' of fibers obtained on heating viscose rayon pretreated in acetic acid baths of various concentrations at various temperatures. (pH = 2.7–5.8, temp. = 50–150°C. as shown in Table II.)

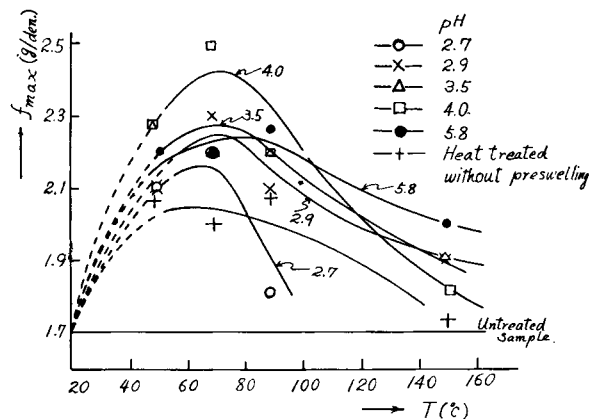


Fig. 5. Plot of temperature of treatment vs. breaking strength, f_{\max} of fibers obtained on heating viscose rayon pretreated in acetic acid baths of various concentrations at various temperatures. (pH = 2.7–5.8, temp. = 50–150°C. as shown in Table II.)

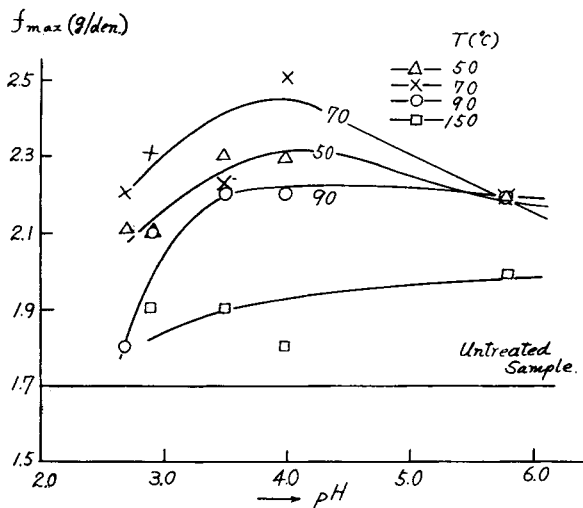


Fig. 6. Plot of pH vs. breaking strength f_{\max} of fibers obtained on heating viscose rayon pretreated in acetic acid baths of various concentrations at various temperatures. (pH = 2.7–5.8, temp. = 50–150°C. as shown in Table II.)

which stress concentrations occur. Such spots are caused by the hydrolytic or oxidative scission of chains at high temperatures.

However, as will be considered later, crystallization which is accompanied by the destruction of fibrous structure at higher temperatures or which is accelerated by breaking of disordered intermicellar chains may be somewhat different in its mechanism from that (mostly nucleus formation) of crystallization which does not involve chain scission at the temperatures of about 70°C.

As the temperature rises above 80–90°C., the elastic moduli and breaking strength of viscose

rayon samples preswollen in sulfuric acid, in contrast with the behavior of samples preswollen in acetic acid, begin to decrease simultaneously; this may indicate that the hydrolytic action of sulfuric acid at comparable concentrations is more drastic and more homogeneous throughout the amorphous region than that of acetic acid.

The results of the present investigation show, however, that no particular effect (on the practical level) was found when acetic acid was used instead of sulfuric acid as the swelling agent in stabilizing viscose rayon.

a. Infrared Spectroscopy

As seen from the spectra shown in Figure 7, samples which have been heat-treated after deuteration generally show, after rehydrogenation, bands characteristic of the so-called "resistant" OD groups, i.e., those of the OD groups in the crystalline regions which have not been rehydrogenated. Moreover, these "crystalline" peaks are more marked as the temperature of heat treatment of the deuterated viscose film rises. Only scarcely perceptible peaks are shown by the sample dried in air at room temperature after being deuterated. Since all the deuterated samples were stored in a desiccator over ClCl_2 for two months, it seems

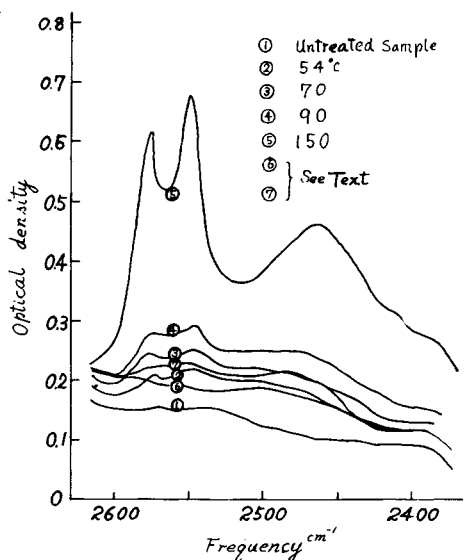


Fig. 7. Infrared spectra in the region of absorption by OD groups at 2700–2400 cm^{-1} of deuterated viscose films after rehydrogenation obtained under various conditions of pretreatment before rehydrogenation: (1) Specimen 1; (2) Specimen 2; (3) Specimen 3; (4) Specimen 4; (5) Specimen 5; (6) Specimen 6; (7) Specimen 7 as shown in Table II.

possible also that some resistant OD groups may be formed during aging.

The fact that deuterated samples generally show distinctively higher absorption than undeuterated samples (Specimen 1) throughout the frequency range (2600–2400 cm^{-1}) characteristic of OD crystalline band may be partly ascribed to the effect of aging.

As the formation of these crystalline peaks (resistant OD groups,) may be ascribed to the effect on crystallinity of the deuterated amorphous regions,⁶ we see from the spectroscopic data that crystallinity in regenerated cellulose which had been swollen in acid ($\text{pH} = 3.0$), and heat-treated becomes clearly apparent at the temperature of heat treatment (just above 55–70°C.). However, the spectroscopic data do not show this at 70°C., the temperature at which, on the basis of data obtained on some physical and mechanical properties,¹ the most typical effect of the heat treatment for stabilizing regenerated cellulose (such as the striking increase of elastic moduli, the sharp drop of accessibility, the remarkable decrease of water absorption, etc.) have made their most prominent appearance.

b. X-Ray Study

The results of X-ray measurements are given in Table III.

The data listed in Table III show that Specimen 3 which, according to its various physical properties, corresponds to the preparation obtained at the best condition for stabilizing viscose rayon (swollen at $\text{pH} = 3.0$ and heat-treated at 70°C.) shows somewhat (about 3%) higher crystallinity than untreated samples (Specimen 4) but not so striking an increase in crystallinity as was expected

from the remarkable change of physical properties caused by heat treatment at these conditions.

From the intensity of the bands characteristic of the resistant OD groups in crystalline regions which have not been rehydrogenated, Mann and Marrinan⁶ have concluded that there was an increase in crystallinity of about $3 \pm 1\%$ when a deuterated sample was dried at 60°C. before its rehydrogenation. This increase roughly corresponds to the increase in crystallinity found by our present x-ray data.

However, it may be possible that this slight increase in crystallinity does not necessarily mean that the effect of the heat treatment is slight in the development of ordered regions which are hydrogen-bonded in a regular manner since (1) there may be ordered regions which are so fine that x-ray interferences barely occur; (2) also, in the case of the deuteration experiment, such minute ordered regions, when they are rehydrogenated, may be largely rehydrogenated so that no resistant OD groups remain. On the other hand, it may be plausible to assume that if a large number of such minute ordered regions develop in fibrous structures on heat treatment, this may have a marked influence upon the physical and mechanical properties of the fibers, as has been verified by our experimental data.

Striking increase in crystallinity is observed in the specimen obtained by heat treatment at 150°C. and $\text{pH} = 3.0$. From a fairly large decrease in the breaking load and elongation, as has been reported in the previous paper, this sample seems to be fairly disintegrated.

It is interesting to note that this increase in crystallinity, amounting to about 10% of the total regenerated cellulose originally present, coincided

TABLE III
Results of X-Ray Measurements

Specimen	Pretreatment	Integrated intensity (planimetered area), arbitrary units			Crystallinity α , % ^a	Half-maximum angle θ , degrees			
		I_{cr}				$I_{A_3A_4}$			
		I_{A_0}	$I_{A_3A_4}$	I_a		I_{A_0}	θ_{A_0}	$\theta_{A_3A_4}$	
4 in (Fig. 2)	Untreated 70°C.,	37	398	735	37.2	(39.0)	10.8	2.6	4.2
2	" no preswelling	33	418	734	38.5	(39.9)	12.0	2.6	4.4
3	" 70°C., pH 3	42	439	708	40.5	(42.3)	10.4	2.6	4.1
1	" 150°C., pH 3	39	458	511	49.3	(51.0)	11.7	2.6	4.3

^a The values in parentheses were calculated according to eq. (2), in which $A/B = 1.08$ (instead of $A/B = 1.00$) is assumed so as to make the value of α of the untreated sample 39%, since this is the value generally accepted for the crystallinity of regenerated cellulose.

almost exactly with the increase in crystallinity of viscose fibers observed by Hermans and Weidinger¹¹ when the fibers were boiled with 2.5*N* sulfuric acid for one-half hour.

In view of the experimental fact discovered by Hermans and Weidinger¹¹ that the per cent crystallinity of rayon fibers hydrolyzed with 2.5*N* sulfuric acid, on the weight of original substance present, approximates to almost a constant value of 49.5% when it is boiled any length of time more than one-half hour and considering the present results, which show that samples obtained by a hydrolytic heat treatment quite different from that used by Hermans and Weidinger, show about the same degree of crystallinity, it seems possible that there may be a certain range of ultimate crystallinity attained in hydrolytic heat treatments.

The remarkable increase in crystallinity of regenerated cellulose on acid hydrolysis may be ascribed to the hydrolytic scission of part of chains interconnecting the crystalline regions, which thus removes in part the entanglements and the insufficient segmental freedom of motion which prevent further crystallization, as has been explained by Hermans and Weidinger.¹¹

Such a mechanism for the increase in crystallinity may be greatly different from that involved in the increase in crystallinity on low temperature heat treatment near or just above the glass transition temperature of regenerated cellulose preswollen in acidic solution.

The heat effect in the latter case seems to be more physical and to consist in intensifying the thermal motion of the segment in the preswollen structure, facilitating segmental motion and lowering the temperature required for thermal rearrangement to an ordered state. That is, the thermal motion is made possible by swelling of the frozen structure rather than by scission of the chains of the entangled structure.

The temperature range for the heat treatment optimal for bringing about the crystallization of the fibrous structure without giving rise to any thermal or hydrolytic scission of chains may be 60–70°C. Below this no perceptible crystallinity may occur, and above this degradation of fibrous structure may become apparent, so that a very stabilized fibrous structure results at this temperature, as shown by physical and mechanical properties of the fibers thus treated.

No definite trend of change in the half-maximum angle, with relation to the integrated intensity of corresponding interferences, as was observed

in hydrolyzed cellulose by Hermans and Weidinger,^{11,12} has been found. While the half-maximum angle of A_0 is nearly constant, irrespective of the sort of specimen, the A_3A_4 peaks of the specimens which have larger intensity $I_{A_3A_4}/I_{A_0}$ ratios, show somewhat wider width, and that of the specimen heat-treated at the condition optimal for stabilizing rayon which has a smaller $I_{A_3A_4}/I_{A_0}$ ratio shows a somewhat sharper width. This result is in contrast with the results of Hermans and Weidinger,¹² who found that, while the half-width and intensity values of the second peak A_3A_4 are unaffected by hydrolysis, the half-width and intensity of the first peak I_{A_0} diminishes (or the ratio $I_{A_3A_4}/I_{A_0}$ increases) as the hydrolysis proceeds.

From such a trend of changes which indicate that order is disturbed in one direction and not affected in the other direction, they have concluded that, in case of hydrolytic crystallization, there is a change from three-dimensional order to two-dimensional order, that is, that two-dimensional recrystallization occurs. Whether the trend shown by the results listed in Table III which is inconsistent with that observed by Hermans and Weidinger may be ascribed to the failure to eliminate orientation effects under the conditions used in the present work or to some special mechanism of crystallization affected by the physical heat-treatment different from that of the hydrolytic crystallization is not clear.

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Synopsis

Making use of very dilute aqueous acetic acid solutions instead of sulfuric acid solutions as the swelling agent, we have confirmed the experimental fact previously observed that, when viscose rayon, after being preswollen in a bath of the pH range optimal for its maximal hydration, is heat-treated at the temperature near or just above the glass transition temperature of regenerated cellulose, i.e., at 60–70°C., the effects of the heat treatment in stabilizing viscose rayon, as exhibited by various mechanical properties, are most marked. By means of infrared spectroscopy by the deuteration method of Mann and Marrinan, a qualitative study was made of the change caused by the heat treatment. That is, infrared spectra in the region of absorption by OD groups at 2700–2400 cm^{-1} were observed on deuterated viscose films obtained by various conditions of pretreatment and subsequent hydrogenation. It was concluded that the crystallization effect shown by regenerated cellulose which was heat-treated after being preswollen in acid bath (pH = 3.0), makes its most marked appearance at heat-treatment temperatures just above 55–70°C. Also x-ray diffraction curves of viscose rayon fiber heat-treated at various conditions were resolved according to the method of Hermans and Weidinger into amorphous, background, and crystalline peaks. It was found that the preparation obtained at the best condition for stabilizing viscose rayon (preswollen at pH = 3.0 and heat-treated at 70°C.) shows about 3% higher crystallinity than the untreated sample or as the sample which was heat-treated without preswelling.

Résumé

Il a été démontré expérimentalement au préalable que l'action stabilisatrice due au traitement thermique de la rayonne viscosée à une température voisine ou légèrement supérieure à la température de transition vitreuse de la cellulose régénérée—c'est à dire 60–70°C—après lui avoir fait subir un prégonflement dans un bain de pH optimum pour l'hydratation maximum, est la plus marquée ainsi qu'il ressort de l'examen de diverses propriétés mécaniques. Ceci a été confirmé par l'emploi de solutions aqueuses très diluées d'acide acétique au lieu de solutions d'acide sulfurique comme agent de gonflement. Grâce à la spectroscopie infrarouge et à la méthode de deutération de Mann et Marrinan on a effectué une étude qualitative des changements provoqués par le traitement thermique. Des spectres infrarouges dans la région d'absorption des groupes OD à

2700–2400 cm^{-1} ont été observés sur des films de viscosée deutérés obtenus dans des conditions de traitement préalable variées et d'hydrogénation subséquente. On en a conclu que l'effet de cristallisation observé pour la cellulose régénérée ayant subi un traitement thermique après avoir été soumise à un prégonflement dans un bain acide (pH = 3,0) est le plus apparent pour des températures de traitement légèrement supérieures à 55–70°C. De même les courbes de diffraction de rayons X de fibres de rayonne viscosée ayant subi un traitement thermique dans des conditions variées ont été résolues suivant la méthode de Hermans et Weidinger en pics amorphes cristallins et de fond continu. Il a été démontré que la préparation obtenue dans les meilleurs conditions de stabilisation de la rayonne viscosée (prégonflement à pH = 3,0 et traitement thermique à 70°C) montre une cristallinité plus élevée de 3% par rapport à celle qui a été observée pour l'échantillon non traité ou pour l'échantillon traité thermiquement sans prégonflement.

Zusammenfassung

Wir haben schon früher beobachtet, dass bei Viskoseseidefasern, die in einem Säure-Bad, dessen pH dem Quellungsmaximum der Fasern entspricht, gequollen wurden und anschliessend bei der dem Einfrierbereich der Regeneratcellulose entsprechenden Temperatur, 60–70°C, wärmebehandelt werden, die festigkeitserhöhende oder die stabilisierende Wirkung der Wärmebehandlung auf die Fasern, gemessen an verschiedenen mechanischen Eigenschaften der Fasern, am stärksten auftritt. Diese Beobachtung wurde nun bei Verwendung sehr verdünnter wässriger Lösungen von Essigsäure anstatt derjenigen von Schwefelsäure als Quellungsmittel bestätigt. Unter Verwendung der Deuterierungsmethode von Mann und Marrinan, wurde eine qualitative Ultrarotuntersuchung der durch die Wärmebehandlung bewirkten Veränderung der Fasern durchgeführt. Ebenso wurden IR-Absorptionsspektren im Absorptionsbereich der OD-Gruppen bei 2700–2400 cm^{-1} deuterierter Viskosefilme unter verschiedenen Bedingungen der Vor- und Wärmebehandlungen der Fasern sowie nach ihrer Wiederhydrierung aufgenommen. Es wurde der Schluss gezogen, dass der Kristallisationseffekt bei Hydratcellulose bei Wärmebehandlung nach einer Quellung im Säurebad vom pH 3,0 erst deutlich bei einer Temperatur der Wärmebehandlung über 55–70°C auftritt. Überdies wurden die Röntgenbeugungsdiagramme einiger Viskoseseidenfasern, die unter verschiedenen Bedingungen wärmebehandelt wurden, nach der Methode von Hermans und Weidinger in den Anteil der interferierenden Streuung des kristallinen und den der diffusen Streuung des nichtkristallinen Bereiches zerlegt. Aus diesen Ergebnissen wurde gefolgert, dass das Präparat, welches bei der für die Stabilisierung (gemessen an den mechanischen Eigenschaften der Fasern) der Fasern geeignetsten Bedingung (pH = 3,0, 70°C) erhalten wurde, eine um ungefähr 3% höhere Kristallinität als die unbehandelte sowie die ohne Vorquellung wärmebehandelte Probe zeigt.

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