

Infrared-Deuteration Study of Regenerated Cellulose Fibers

R. J. E. CUMBERBIRCH and R. JEFFRIES, *The Cotton Silk and Man-made Fibres Research Association, Shirley Institute, Manchester, England*

Synopsis

This paper describes a study by infrared, deuteration, and other techniques of the fine structure of three regenerated cellulose fibers (Fortisan, a super tire yarn, and a fiber of high wet modulus). The infrared and deuteration measurements provide information on the amount and perfection of the hydrogen-bond ordered material in these celluloses. The three fibers are markedly different in structure: the Fortisan contains about 40% ordered cellulose of a high average degree of perfection, whereas the super tire yarn contains a smaller amount (about 20%) of ordered cellulose of a lower average degree of perfection: the yarn of high wet modulus contains about as much ordered material as the Fortisan, but of an average degree of perfection more similar to that of the super tire yarn. Infrared-dichroism measurements on the fibers are described. The infrared and dichroism studies are discussed in relation to the results of x-ray, moisture regain, acid hydrolysis, and birefringence measurements on the fibers. The infrared-deuteration behavior of acid hydrolysis residues prepared from the three fibers is described; these residues are more highly ordered than the parent fibers, but yield no information of any value in characterizing the structures of the parent fibers.

INTRODUCTION

The purpose of the present work was, first, to determine whether the fine structures of different types of regenerated cellulose filaments can be differentiated and characterized by means of infrared-deuteration techniques, and second, to compare the characterization data derived from these techniques with those obtained by other methods of examination. Three widely different types of regenerated cellulose fiber were chosen for study. The first fiber studied was Fortisan, a continuous-filament yarn made by the stretching and saponification of secondary cellulose acetate yarn. The second fiber was a viscose super-tire yarn; this material has an "all-skin" structure, whereas the Fortisan has what might be referred to as an "all-core" structure. The third fiber chosen for study was a recently developed type of regenerated cellulose fiber; made from viscose, this fiber is very highly stretched during production, thereby producing a very strong but inextensible fiber. It will not be easy to assign a position for this fiber on any scale of structural character known at present.

It is first necessary to discuss briefly the nature and significance of the infrared-deuteration technique¹⁻⁴ in relation to cellulose structure. Basically, the method provides information on the relative amounts of order and disorder in the hydrogen bonding of the cellulose and also on the character of these ordered and disordered components. The structure of cellulose, both native and regenerated, can be divided into two distinct parts as regards the order in the hydrogen-bonding system. One fraction of the hydroxyl groups is hydrogen-bonded in a regular, "ordered" manner and gives rise to a hydroxyl-stretching band containing well defined and characteristic peaks and shoulders. The second fraction of the hydroxyl groups is hydrogen-bonded in an irregular, "disordered" manner and gives rise to a broad, featureless, hydroxyl-stretching band. Deuterium oxide readily penetrates these hydrogen-bond disordered parts of the structure, and hydroxyl groups in these regions rapidly exchange to OD groups. The broad, featureless hydroxyl-stretching band resulting from these "disordered" OH groups is thus removed and replaced by a similar band in the OD-stretching region of the spectrum. The hydrogen-bond ordered (crystalline) parts of the structure are largely inaccessible to deuterium oxide, and the exchange reaction in these regions is thus slow and incomplete. Thus the infrared spectrum at the end of the rapid exchange reaction enables (with suitable calibration) the relative proportion of the two components to be calculated.*

One part of the present study was to make these infrared-deuteration measurements on the three types of fiber. A second part of the study was to investigate the range of degrees of perfection present in the ordered regions of the three fibers. This was attempted by the study of the shape and resolution of the OH band of the ordered component (i.e., after the rapid exchange of the disordered component) and the rate of deuteration of this component; the more perfectly ordered regions would be expected to be associated with a better resolved OH band than the less perfectly ordered regions³ and would, perhaps, also be expected to give rise to different relative intensities of the various peaks in this band. The rate of deuteration of the ordered regions is probably related to the range of degrees of perfection present in the ordered regions, i.e., the faster the rate of deuteration, the less perfect the ordered regions involved in this deuteration.

Measurements of the infrared dichroism of the OH band of the ordered regions were also made to provide additional information on the perfection and orientation of the ordered regions.

The infrared-deuteration behavior of the residues remaining after acid hydrolysis of the three fibers was also investigated. Though the effect of acid hydrolysis on the structure of cellulose, particularly regenerated cellulose, is thought to be complex, it was hoped that the residues would have structural properties of value in the characterization of the differences in structure that were found between the parent fibers.

* It is emphasized for clarity that in the discussion "order" and "disorder" are used only as described and defined in this paragraph, unless otherwise stated.

EXPERIMENTAL

Materials

All three types of continuous filament yarn used in these experiments were supplied by Courtaulds, Ltd. They are identified as: Fortisan (45 den., 168 filaments), Super Tyre Yarn (1106 den., 1500 filaments), and an experimental high wet modulus fiber (86 den., 148 filaments), designated below as HWM.

Preparation of Oriented Layers of the Fiber Samples

To enable the infrared absorption spectra of the three materials to be studied, filaments from each of the yarn samples were formed into thin cohesive layers, and these layers were used in a similar manner to films in the infrared-deuteration studies. To form a layer, a tow of parallel filaments, about 2.5 cm. in length, was formed and placed on the polished surface of a stainless steel plate.⁵ The tow was stroked with polished, mounted needles into a single layer of close-packed, parallel, filaments with the end of the tow held onto the plate with a finger. A suitable layer having been obtained (care is needed to avoid the presence of "splits" in the layer), the layer was then pressed and mounted for infrared examination as previously described.⁵ The thickness of the final layer, which depended on the diameter of the filaments and the state of packing, was between 6 and 12 μ .

Preparation of Films of Acid-Hydrolyzed Cellulose Samples

Samples of the yarns were hydrolyzed in boiling 1*N* hydrochloric acid for 1 hr. The sample residues were washed in water and were then partially disintegrated by high-speed stirring in a blender for 10 min.; a fraction of the residues became finely divided and suspended in the water. After standing, the supernatant liquor over the undisintegrated residues was poured into a beaker containing microscope coverslips and the water evaporated in an open oven at about 100°C. The residues, initially suspended in the liquor, then formed a reasonably uniform and transparent film on the coverslips. The cover slips, carrying the films, were found suitable for use in the infrared-deuteration measurements.

Infrared and Deuteration Measurements

Infrared measurements were made on a Grubb-Parsons DB1 double-beam spectrometer with a lithium fluoride prism. In the infrared-deuteration studies, three separately prepared layers of each fiber were investigated. The layers were mounted in brass vacuum cells with calcium fluoride windows and evacuated to dryness; the spectra were then measured.

The effects of instrument polarization on the spectra of the oriented fibers were investigated by running spectra with the fiber direction both parallel and perpendicular to the entrance slits of the spectrometer. The spectra

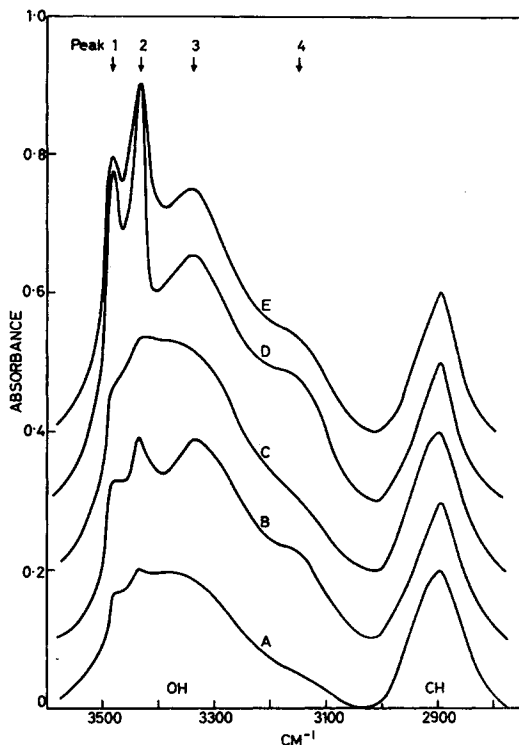


Fig. 1. Hydroxyl-stretching band of hydrogen-bond ordered (deuteration-resistant) regions: (A) super tire fiber; (B) Fortisan fiber; (C) HWM fiber; (D) acid hydrolysis residue from Fortisan fiber; (E) acid hydrolysis residue from super tire fiber. In calculations of the fraction of hydrogen-bond ordered cellulose from spectra of this type, the baselines to the OH and CH bands are drawn from about 3650 cm^{-1} to the trough near 3000 cm^{-1} , and from this trough to about 2760 cm^{-1} , respectively. For clarity, the spectra in this figure are spaced by separating each of the baselines by an absorbance of 0.1.

given in Figure 1 are the spectra estimated to correspond to zero instrument polarization.

The first deuteration treatment, to deuterate the hydrogen-bond disordered regions and thus obtain a measure of the fraction of the latter, was done in deuterium oxide vapor of 75% R.H. for 5 hr. at 20°C. This differs from the usual technique for deuterating the disordered regions,^{3,4} which employs saturated deuterium oxide vapor, because of a tendency for the layers of fibers to deteriorate on wetting in the saturated vapor and drying; splits in the layers sometimes occur, presumably because of the dimensional changes during the wetting and drying. The partially deuterated fibers were evacuated to dryness prior to infrared measurement. After this initial deuteration, the fibers were rehydrogenated in water vapor at 57% R.H. for 16 hr. at 20°C. to enable the small amount of ordered material that had deuterated during the 5 hr. deuteration to be measured.

In general, deuterated ordered regions tend to resist rehydrogenation, because of increase in the perfection of these regions during the deuteration and the drying;¹⁻³ the low humidity used in the rehydrogenation process was chosen to make the rehydrogenation of the ordered regions even slower. After this rehydrogenation, the fibers were redeuterated in saturated vapor for 1 day and then for 18 days at 20°C. the fibers being evacuated to dryness after each deuteration prior to infrared study. These more severe deuteration treatments were made to provide information on the degree of perfection (perhaps the range of degrees of perfection) of the ordered regions, as explained above. Saturated vapor had to be used for these experiments because of the slow rate of deuteration of the ordered regions at 75% R.H.;³ the deterioration of the fiber layers in saturated vapor (referred to above) is not in general enough to make this impracticable.

With the films of hydrolysis residues, the deuteration of the disordered regions was done in saturated vapor for 12 min. at 20°C.

The infrared-dichroism measurements on the fibers were made with polarizers of the silver chloride type. The polarization produced by these polarizers is by no means complete, and the dichroic ratios discussed below are suitable only for semiquantitative comparison of the three fibers.

General Characterization of the Fiber Samples

Skin-Staining. The method of Cumberbirch and co-workers was adopted.⁶

Moisture Regain. The samples were placed in weighing bottles, dried *in vacuo* at 20°C. over P₂O₅ and weighed. They were then conditioned at equilibrium in evacuated desiccators over saturated salt solutions. Two series of measurements were made: at 70°C. and 75% R.H. (sodium chloride solution) and at 20°C. and 58% R.H. (sodium bromide solution).

Water Retention. Samples of yarn were immersed in water for 1 hr. and centrifuged at 925 RCF for 7 min. in stoppered sintered-glass crucibles. The centrifuged samples were weighed, dried at 110°C. for 3 hr., and reweighed.

Measurement of Degree of Polymerization. Intrinsic viscosities were measured in cuprammonium hydroxide solution by the method described by Calvert and Clibbens,⁷ and the value of the intrinsic viscosity found by the use of the nomogram given in Table VIII of that publication. Values of degree of polymerization were obtained from the relation $i = KP^\alpha$, where i is the intrinsic viscosity, P is the degree of polymerization, $K = 0.0319$ and $\alpha = 0.657$.⁸

Acid Hydrolysis Measurements (Loss in Weight). Samples (2 g.) were refluxed in 1N HCl for 1 hr. The residues were filtered off rapidly, washed in cold 1N HCl, water, and acetone, dried in air, and finally dried *in vacuo* over P₂O₅ at 20°C. The loss in weight was determined.

Acid Hydrolysis Measurements (Limit D.P.) The intrinsic viscosities of the hydrolysis residues were determined as described above.⁷ The

limit D.P. values were calculated from the relation $P = 175i$ (this relation is used for D.P. values of less than 100).

RESULTS AND DISCUSSION

Fibers

Figure 1 shows typical infrared spectra in the 3000 cm.^{-1} region of the three types of fiber after deuteration of the hydrogen-bond disordered fraction. The hydroxyl-stretching band of the (undeuterated) ordered regions is cellulose II in character in each case, as expected. From each of these spectra, the fraction of ordered cellulose was calculated from the ratio of the intensity of the hydroxyl peak near 3350 cm.^{-1} to that of the CH band near 2900 cm.^{-1} (the CH band is not affected by the deuteration and constitutes an internal thickness standard); previous work on regenerated cellulose films^{1-4,9} has provided the necessary calibration data (see note b on Table I). In these simple calculations it is assumed that the relation between the intensity ratio and the fraction of ordered cellulose for each of the fibers is similar to the relation previously obtained with the cellulose films; this assumption is likely to be valid, at least as an approximation. Table I lists the fractions of ordered cellulose calculated in this way. Despite considerable scatter between the triplicate results for each fiber it may be concluded that the ordered fraction in the experimental high wet-modulus yarn (HWM) is slightly greater than that in Fortisan and much greater than that in the super tire yarn. The value for Fortisan is in good agreement with the value obtained for this cellulose with a gravimetric deuteration technique.⁴

The differences in the resolution of the hydroxyl-stretching band of the three fibers (Fig. 1) suggest that differences exist in the perfection of the ordered regions in the fibers. The band given by Fortisan is much better

TABLE I

Fiber	Intensity ratio ^a		Ordered cellulose, % ^b
	Results	Average	
Fortisan	1.43	1.46	38
	1.45		
	1.51		
Super tire	0.89	0.93	24
	0.99		
	0.91		
HWM	1.75	1.63	42
	1.60		
	1.55		

^a Ratio of absorbance at OH peak near 3350 cm.^{-1} (peak 3 on Fig. 1) to absorbance at CH peak near 2900 cm.^{-1} after deuteration of the hydrogen-bond disordered material.

^b Hydrogen-bond ordered cellulose, calculated by multiplying the intensity ratio by 26 (this factor obtained from previous work).

resolved than those of the other two fibers, which suggests that Fortisan has distinctly the more perfect ordered regions. The band given by the super tire yarn is somewhat better resolved than that of the HWM indicating a smaller difference in the perfection of the ordered regions between these two fibers. Figure 1 also shows that the two low-frequency peaks on the OH bands (which probably involve intermolecularly bonded OH groups¹⁰) are somewhat more intense relative to the two high-frequency peaks (intramolecularly bonded OH groups) with the Fortisan than with the other two fibers. Since any slight disorder in a crystal lattice might tend to disorganize the intermolecular hydrogen bonding before the intramolecular bonding, this difference in relative intensity might be a further indication of more perfect ordered regions in the Fortisan. The differences, it should be pointed out, cannot be attributed merely to differences in orientation between the various fibers; both x-rays and birefringence measurements (see below) indicate that the Fortisan is more oriented than the super tire yarn, and this would be expected, if anything, to produce differences in relative peak intensities of the type opposite to those actually observed. It should be emphasized, however, that this interpretation of relative peak intensities in terms of lateral order is very speculative. Results presented below on the hydrolysis residues do not, in fact, seem to support this interpretation in terms of perfection of order. A further point against this interpretation is the fact that treatment of regenerated cellulose films (prepared from viscose dope) with aqueous solutions of sodium hydroxide tends to produce a marked improvement in the resolution of the OH stretching band of the ordered regions (presumably resulting from an increase in the perfection of these ordered regions) without causing any great change in the relative intensities of the four OH peaks.⁹

This difference in the perfection of the ordered regions of the three fibers was substantiated by the results from the measurement of the rates of deuteration of these regions. The percentages exchanged after 5 hr. in 75% R.H. D₂O vapor, and after 1 day and 18 days in saturated D₂O vapor are listed in Table II. The rate of deuteration of the ordered regions clearly increases in the order: Fortisan < super tire yarn < HWM. Assuming that the resistance of ordered regions to deuteration is related to their perfection, it may be concluded that a range of degree of perfection exists in the ordered regions of each of the fibers, and that, again, the Fortisan has the more perfectly ordered structure in the ordered regions than the other fibers. On this criterion of order, the super tire yarn has a more perfectly ordered structure in the ordered regions than the HWM, again in agreement with the conclusion drawn above from the resolution of the ordered OH bands. The existence of a range of degrees of perfection in the ordered region is confirmed by the fact that the resolution of the OH bands increases as the deuteration of the ordered material progresses; the less perfect regions, which give rise to less well resolved OH bands, exchange first, and thus the resolution of the OH band of the remaining ordered material increases.³

TABLE II

Fiber	Ordered regions deuterated, %		
	After 5 hr. in 75% R.H.	After 1 day in 100% R.H.	After 18 days in 100% R.H.
Fortisan	7.5	20	41.5
Super tire	15	29	49
HWM	17	40	61

The results of the infrared-dichroism measurements on the hydroxyl bands of the ordered regions are listed in Table III. All four of the peaks on the hydroxyl band are more dichroic in the case of Fortisan than with the HWM and super tire yarn. This may be partly a reflection of the greater perfection of the ordered regions of the Fortisan and partly the result of a greater degree of orientation of these regions, compared with the HWM and super tire yarn. As the deuteration of the ordered regions progresses, the dichroism of the remaining OH band increases (Table III).

TABLE III

Fiber	Deuteration	Infrared dichroic ratio (I_{\parallel}/I_{\perp})			
		OH peak 2 on Fig. 1	OH peak 3 on Fig. 1	OH peak 4 on Fig. 1	
Fortisan	5 hr., 57% R.H.	3.37	0.67	0.22	
	18 days, 100% R.H.	4.95	0.58	0.18	
	Super tire	5 hr., 57% R.H.	1.88	1.09	0.55
Super tire	18 days, 100% R.H.	2.45	0.98	0.37	
	HWM	5 hr., 57% R.H.	1.84	0.89	0.34
	18 days, 100% R.H.	3.72	0.65	0.20	

The OD band of the disordered regions also show dichroic behavior. The part of the OD band corresponding in frequency to the two high-frequency peaks on the ordered OH band shows distinct parallel dichroism (similar to the two ordered peaks); the parts of the OD band corresponding to the two low-frequency peaks on the ordered OH band do not reveal any pronounced dichroic behavior (though precise measurements are difficult because the instrument cuts off the low-frequency tail of the OD band, thus making the position of the baseline doubtful). This dichroic behavior shows that part at least of the disordered material contains elements of order in the hydrogen-bonding arrangement; these parts may, in fact, merely be a very blurred version of the ordered regions.

The x-ray diffraction diagrams showed the Foristan and HWM to have typical, well-oriented diagrams of the cellulose II type; the super tire yarn gave an additional reflection from the small fraction of cellulose IV present

in this fiber. These x-ray diagrams showed that the orientation in the Fortisan is markedly greater than that in the other two fibers. Fortisan gives the best defined diagram; only with this fiber are the $10\bar{1}$ and 002 peaks resolved. The presence of the cellulose IV component in the super tire yarn makes comparison of this fiber and the HWM difficult, but it seems that as a first approximation the resolution of the diagrams of these two fibers is similar. Since the resolution of an x-ray diagram is related to the lateral order of the structure (increasing the size and/or perfection of the crystalline regions increases the sharpness of the x-ray reflections), it may be concluded that the lateral order of the Fortisan is better than that of the HWM and super tire yarn; these two fibers cannot be readily graded for lateral order by this technique, as a result of the interference from the cellulose IV in the super tire yarn.

Acid Hydrolysis Residues

The infrared-deuteration results for these materials are given in Figure 1 and Table IV. Figure 1 shows typical spectra of hydrolysis residues after deuteration of the hydrogen-bond disordered regions. Values for the fraction of hydrogen-bonded ordered region (calculated from the OH/CH ratio used with the fibers) are given in Table IV. Two main conclusions can be drawn from the figure and table. First, the hydrolysis residues in general contain a larger fraction of ordered material than the unhydrolyzed fibers. Second, the scatter of the results is high; it is sufficient, in fact, to prevent any conclusions on the relative amounts of ordered material in the three types of residues. The reason for this irreproducibility of the residue films is perhaps not difficult to find. Any hydrogen-bond disorder in the residue particles in the aqueous suspension is probably mainly associated with the surface of the particles. On drying down the residues, these particles bond together to some extent, and a certain amount of ordering of the hydrogen bonding of the surfaces might be expected as these disordered surfaces form an interface; it seems reasonable to think that the perfection and extent of this ordering would depend critically upon the precise conditions during the final stages of the drying, and these conditions may well not be very reproducible.

TABLE IV

Acid hydrolysis residue	OH/CH intensity ratio ^{a,b}	Ordered cellulose, % ^c
Fortisan	1.45-1.92	38-50
Super tire	1.58-2.10	41-55
HWM	1.63-1.88	42-49

^a Ratio of absorbance at OH peak near 3350 cm.^{-1} (peak 3 on Fig. 1) to absorbance at CH peak near 2900 cm.^{-1} .

^b Range of values covered by the various samples studied.

^c Hydrogen-bond ordered cellulose, calculated by multiplying the intensity ratio by 26.

The resolution of the OH band of the ordered regions (Fig. 1) shows clearly that the perfection of these ordered regions is greater in the residue films than in the parent fibers, this difference being particularly obvious with the super tire yarn and HWM. Once again, however, the sample variation was sufficient to mask any difference between the three residues; the difference between the two residue films shown in Figure 1 is illustrative of the variability observed in these films in general, and is not meant to be indicative of any genuine, reproducible difference between the types of residue films. It is clear from the spectra in Figure 1 that the two low-frequency peaks are less intense relative to the two high-frequency peaks than is the case with the parent fibers. The fact that this lower relative intensity is associated with an apparently higher degree of perfection of the order seems to be against the suggestion made earlier that the relatively greater intensity of the two low-frequency peaks with the Fortisan fiber (compared with the other two fibers) is an indication of a greater degree of lateral order in the Fortisan. However, it is probably of doubtful validity to compare the band shapes of disoriented residue films with those of highly oriented fibers.

The rate of isotopic exchange of the ordered regions of the hydrolysis residues is distinctly lower than that of the parent fibers; the ordered regions of residues of Fortisan and HWM exchanged to the extent of about 10% and 20% after 1 day and 18 days deuteration (compare with the values in Table II). This supports the validity of interpreting differences in rate of exchange in terms of differences in perfection of order.

It may be concluded that though the residue films may be of interest in infrared-deuteration studies as a highly ordered form of cellulose II, the high sample variability prevents any useful comparison of the three residues in relation to the structures of the parent fibers.

GENERAL DISCUSSION

The infrared-deuteration work has shown that Fortisan contains about 40% of ordered material of a high degree of perfection; HWM contains about 40% of ordered material of a lower average degree of perfection, and the super tire yarn contains about 20% of ordered material, also of a lower average degree of perfection. It is interesting to compare these deuteration results with values for other physical and chemical properties as listed in Table V.

The regain measurements at 20°C. place Fortisan and HWM, taken as a pair, much lower than the super tire yarn. This is as would be expected from the lower amount of disordered cellulose in the Fortisan and HWM: there is a roughly linear relation between the fraction of disordered material and the moisture regain,^{4,11-14} and it is thought, in fact, that practically the whole of the absorbed water is held in these disordered regions. However, on this basis, the regains appear to be the wrong way round in a comparison of the Fortisan and the HWM; this apparent anomaly may be re-

TABLE V

Property	Fortisan	Super tire	HWM
	Patchy but deep stain left	Deep, uniform staining	Patchy, pale, central spot of stain left
Behavior on skin-staining			
Moisture regain, g./100 g. dry cellulose			
70°C., 75% R.H.	10.4	13.8	10.3
20°C., 58% R.H.	10.6	14.0	11.6
Water retention, g./100 g. dry cellulose	61	72	58
Degree of polymerization	190	795	920
Acid hydrolysis			
Loss in weight, %	5	19	7
Limit DP	45	32	49
Refractive index			
n_{\parallel}	1.5622	1.5495	1.5635
n_{\perp}	1.5150	1.5142	1.5136
Birefringence			
Δn	0.047	0.035	0.050
n_{iso}	1.5307	1.5260	1.5302
Tenacity, g./den.			
65% R.H.	4.0	3.6	8.1
Wet	2.7	3.1	7.9
Extension at break, %			
65% R.H.	5.6	11	6.2
Wet	5.2	22	8.2
Initial modulus, g./den.	173	87	245
Wet	37	3	67

lated to the lower perfection of the ordered regions of the HWM, i.e., the more poorly ordered parts of these regions may absorb a significant amount of water. The fact that the regain at 75% R.H. and 70°C., is if anything, lower for the HWM than for the Fortisan lends support to this view; there is evidence from infrared-deuteration studies that the treatment of fibers in water vapor at high temperatures increases the amount and perfection of the ordered regions, and this increase in perfection would be expected to decrease markedly any moisture sorption by the ordered regions.

The acid hydrolysis results in Table V are also in reasonable qualitative agreement with the infrared-deuteration results, i.e., the Fortisan and HWM have a considerably lower loss of weight and higher L.O.D.P. than the super tire yarn. It may perhaps be emphasized here that the crystallinity values given by the deuteration technique are lower than by any other method;¹⁵ for example, with the present samples the lowest crystallinity deduced from the weight loss on hydrolysis would be 81%. These values are low because the infrared-deuteration technique measures order at a high level of perfection, i.e., a level sufficiently high to permit the formation of a regular hydrogen-bond system. It would be expected, therefore, that

the disordered fraction as measured by this technique (i.e., the fraction of the structure in which the hydrogen bonding is disordered, and which is thus readily accessible to water) would be greater than the disorder measured by, say, the hydrolysis technique, since the latter measures not the fraction accessible to the acid (which is probably similar to that accessible to water) but merely the fraction of the cellulose able, after chain scission, to be dissolved out of the cellulose structure. Many parts of cellulose chains must be accessible to acid and yet be locked or trapped in the cellulose structure.

The birefringence results in Table V show the Fortisan and the HWM to be similar in orientation, and appreciably better oriented than the super tire yarn. There is thus some apparent disagreement between the birefringence results and the infrared dichroism values, which place the HWM nearer to the super tire yarn in orientation. This difference must be related, partly at least, to the fact that birefringence measures the overall molecular orientation, whereas the infrared-dichroism values in Table III relate only to the ordered regions. Also, the dichroism values are probably affected by the perfection of the hydrogen-bonding arrangement in the ordered regions, as well as the orientation of the cellulose chains in these regions; this might explain why the Fortisan shows more infrared dichroism than the HWM, though it is similar in birefringence. The dichroism of the residual OH band increases as the deuteration of the ordered regions progresses (Table III); this is to be expected, since the deuteration exchanges the least perfectly hydrogen bonded, and probably the least perfectly oriented, parts of the ordered regions.

The orientation values obtained from the x-ray measurements are in qualitative agreement with the infrared-dichroism values; thus, Fortisan has a considerably higher orientation value than the HWM, and super tire yarn. Comparison of the crystallinity results given by the two methods is more difficult. The infrared-deuteration technique allows the amount and the perfection of the ordered regions to be measured more or less separately, whereas the x-ray data permit at most a semiquantitative assessment of the general level of lateral order. The x-ray grading for order (the Fortisan more ordered than the other two fibers) agrees, so far as it goes, with the infrared-deuteration results, but a more detailed and quantitative comparison is not at present possible.

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Résumé

Ce manuscrit décrit une étude par la technique infrarouge, par deutération et par d'autres méthodes de la structure fine de trois fibres de cellulose régénérée (Fortisan, un fil de pneu super et une fibre à module humide élevé). Les mesures par infrarouge et par deutération fournissent une information concernant la quantité et la perfection du matériau ordonné à liaison hydrogène dans ces celluloses. Les trois fibres sont remarquablement différentes de structure: le Fortisan contient environ 40% de cellulose ordonnée avec un degré moyen élevé de perfection tandis que le fil de pneu super contient une plus petite quantité (environ 20%) de cellulose ordonnée de degré moyen de perfection plus bas: la filament à module humide élevé contient environ autant de matériau ordonné que le Fortisan mais à un degré moyen de perfection plus similaire à celui du fil de pneu super. Les mesures de dichroïsme infrarouge sur la fibre sont décrites. Les études infrarouges et de dichroïsme sont discutées en comparaison avec les résultats aux rayons-X, le regain d'humidité, l'hydrolyse acide et les mesures de biréfringence sur ces fibres. Le comportement infrarouge et à la deutération, de résidus d'hydrolyse acide préparés au départ de ces trois fibres est décrit; ces résidus sont beaucoup plus ordonnés que les fibres parentes mais ne fournissent pas d'informations de quelque valeur pour la caractérisation des structures des fibres parentes.

Zusammenfassung

Eine Untersuchung der Feinstruktur von drei Fasern aus regenerierter Cellulose (Fortisan, ein Super-Reifengarn und eine Faser mit hohem Nassmodul) mit Infrarot-, Deuterierungs- und anderen Methoden wird beschrieben. Die Infrarot- und Deuterierungsmessungen liefern Aufschluss über die Menge und die Güte der Ausbildung des durch Wasserstoffbindungen geordneten Materials in diesen Cellulosen. Die drei Fasern besitzen ausgeprägte Strukturunterschiede: Fortisan enthält etwa 40% geordnete Cellulose mit hoher mittlerer Ordnungsbildung, während das Super-Reifengarn eine kleinere Menge (etwa 20%) geordneter Cellulose mit einem niedrigeren mittleren Ausbildungsgrad enthält; das Garn mit hohem Nassmodul enthält etwa ebensoviel geordnetes Material wie Fortisan, jedoch mit einem, demjenigen des Super-Reifengarns ähnlicheren mittleren Ausbildungsgrad. Die Messung des Infrarotdichroismus der Fasern wird beschrieben. Die Ergebnisse der Infrarot- und Dichroismusuntersuchungen werden in ihrer Beziehung zu denjenigen von Röntgen-, Feuchtigkeitsaufnahme-, Säurehydrolyse- und Doppelbrechungsmessungen an den Fasern diskutiert. Das Verhalten der aus den drei Fasern hergestellten Rückstände der sauren Hydrolyse im Infrarot bei der Deuterierung wird beschrieben. Die Rückstände sind besser geordnet als die ursprünglichen Fasern, liefern aber keine brauchbaren Aufschlüsse zur Charakterisierung der Struktur der ursprünglichen Fasern.

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