

Properties and Structure of Never-Dried Cotton Fibers.

III. Cotton Fibers from Bolls in Early Stages of Growth

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SYNOPSIS

Like other kinds of cotton fibers already studied, American cotton fibers taken from cotton bolls immediately before and after opening show high angles of torsional rotation during ambient humidity changes. Cotton fibers taken from cotton bolls at 19 and 24 days postanthesis show remarkably higher angles of rotation and much lower dry and wet tensile strengths than the fibers taken from cotton bolls immediately before and after opening. The wet tensile strength of cotton fibers at 24 days postanthesis is higher than the dry strength like the fibers taken from bolls immediately before and after opening, but fibers at 19 days postanthesis show almost the same tensile strength in the never-dried, dried, and rewetted states. CP/MAS ¹³C NMR spectroscopy reveals that the never-dried cotton fibers at 19 days or longer postanthesis have high crystallinities. It seems that the degree of crystallinity is somewhat decreased in the dry state and restored by rewetting. The crystallinity increases with the age of growth.

INTRODUCTION

In previous papers^{1,2} Tsuji et al. have reported that field-opened cotton fibers show remarkable torsional rotation during the ambient humidity change between relative humidities (RH) of about 30 and 100%. This is a specific property of cotton fibers that cannot be found in other kinds of fibers. It has also been recognized that never-dried cotton fibers which were subsequently dried by freeze-drying showed a small number of convolutions and low angles of torsional rotation during the humidity change. These facts interested us in a detailed study on the properties and structure of never-dried cotton fibers.

Meanwhile, it is well known that the wet tensile strength of cotton fibers is higher than the dry strength. This is a specific property of natural cellulose fibers such as cotton and flax. How this phenomenon is related to the tensile properties of never-dried cotton fibers is an interesting problem.

We have carried out research on the properties

and structure of never-dried cotton fibers which have been taken from unopened cotton bolls immediately before opening. It was found in Asian³ and American⁴ cotton that the wet tensile strengths of the never-dried fibers were low but irreversibly increased after the first drying. This was attributed to irreversible formation of hydrogen bonds between cellulose molecules during drying.

In the present research the properties and structure of never-dried cotton fibers taken from cotton bolls in earlier stages of growth are investigated.

Hitherto, it was presumed from X-ray studies that cotton fibers in the never-dried state were amorphous⁵ or at least have only a very low crystallinity.⁶ In contrast, Morosoff⁷ and Ingram et al.⁸ found by X-ray diffraction that never-dried cotton fibers had in the wet state nearly the same crystallinity as the samples obtained after drying and rewetting. Ohno⁹ reported similar results from hydrolysis studies.

Recently, an analysis of the solid state structure has become possible by cross-polarization/magic angle sample spinning (CP/MAS) ¹³C NMR spectroscopy. Horii et al.^{10,11} developed a MAS rotor with an O-ring seal which prevents the loss of water during MAS. By using this rotor a CP/MAS ¹³C NMR

spectrum of never-dried fibers collected from Asian cotton bolls immediately before opening was taken and compared with spectra of field-opened fibers in the dry and wet states.³ It was found that these samples have almost the same high crystallinity. Then similar research was carried out using American cotton bolls in earlier stages of growth.¹² The never-dried fibers taken from cotton bolls picked at 25 days postanthesis showed in the wet state a highly crystalline spectrum similar to that of the field-opened fibers. Even cotton fibers taken from the boll at 15-day postanthesis showed a low but distinct crystallinity. In the present research more extended NMR study has been carried out for never-dried cotton fibers taken from American cotton bolls in the early stages of growth.

It has generally been presumed that the growth of cotton fibers falls in two phases, viz. (1) a period of elongation with formation of only a thin primary wall and (2) a period of secondary cell wall thickening.⁹ It was found that the length of cotton fibers (lint) showed a rapid increase from about 3 days postanthesis until about 24 days postanthesis, while the wall thickness increased linearly from about 20 days postanthesis until about 40 days postanthesis.⁹ Recently some authors^{13,14} have presented new concepts of fiber growth suggesting that the cell elongation and wall thickening take place concurrently at an earlier stage (10 days postanthesis or earlier). In any event, it is presumed that cotton fibers taken from cotton bolls picked at 15 to 20 days postanthesis are chiefly composed of a thin primary wall with a little or no secondary wall thickening, and that about 20 days postanthesis the spiral layers of the secondary wall begin to appear as shown by electron microscopy by Boylston et al.¹⁵ With these points in mind, it is interesting to examine the properties and structure of the cotton fibers during these early stages of growth.

EXPERIMENTAL

Cotton Samples

The same seeds of American cotton as used in our previous studies,^{4,12} which were presented by Japan Cotton Promotion Institute (Nihon Mengyo Shinkokai), were cultivated in pots in 1987, 1988, and 1989 at Kyoto City, Japan. Cotton bolls were picked at 15, 19, and 24 to 25 days postanthesis, immediately before opening (66 days postanthesis), and after field-opening, though the cultivation years were different, as shown in Tables I, II, and III. The never-

dried cotton fibers collected from these unopened bolls were kept in water, which was renewed every day. In some cases a small amount of formalin was added to the water to prevent bacterial growth.

Torsional Rotation of Cotton Fibers Due to Ambient Humidity Change

Using the same method as described in the previous reports,^{1,2} the angle of torsional rotation of a cotton fiber suspended in a closed box under a slight weight (about 4 mg) was measured during humidity change. The relative humidity (RH) in the box was increased from about RH 30% up to nearly 100%, then decreased; each process was performed within about 30 min. The never-dried cotton fibers were air-dried and used for the test. For each kind of boll, 30 fiber samples were tested.

Tensile Properties

Dry and wet tensile strengths and elongations were measured for cotton fibers using a pendulum type single fiber tensile tester (K.S. Senimeter). The clamp distance was about 10 mm. The number of test pieces was 20 to 25. As previously reported,^{3,4} on the test of wet tensile strength of never-dried wet fibers, the wet sample fibers were immersed in a 50% aqueous solution of glycerin. One fiber was taken out from the glycerin solution and attached to the clamp of the tester. Glycerin attached to the sample fiber prevents the rapid evaporation of water from the sample fiber, and dissolved out from the fiber into water during keeping it in water for some minutes before start of tensile test; there is no effect of glycerin on the breaking load as previously proved.⁴

Some of the never-dried cotton fibers were taken from the glycerin solution, and the dry tensile strength was measured after water-rinsing and air-drying. Some of these air-dried fibers were immersed again into the glycerin solution and the tensile strength was measured under water (Rewet, in Table II). Dry and wet tensile tests of the naturally dried fibers were carried out without using the glycerin treatment.

The never-dried cotton fibers obtained at 15 days postanthesis had so short a length that the torsional rotation and tensile tests could not be carried out.

¹³C NMR Measurements

The never-dried cotton fibers were packed into the MAS rotor with an O-ring seal which prevents the loss of water. CP/MAS ¹³C NMR measurements

Table I Distribution of the Maximum Angle of Rotation during Humidity Increase of American Cotton Fibers Taken from Cotton Bolls in Different Stages of Growth

Cotton Bolls			Maximum Angle of Rotation (degree) ^a			
Boll No.	Cultivation Year	Time of Picking	<540	540-900	901-1260	>1261
HA-3	1986	Field-opened	18	4	1	7
HA-2		Immediately before opening ^b	14	7	5	4
KA87	1987	Field-opened	10	9	4	7
KA88A-1	1988	24 days postanthesis ^b	2	3	4	21
KA89B-1	1989	19 days postanthesis ^b	2	5	1	22

^a Total number of test samples: 30.

^b Test was carried out using cotton fibers air-dried after picking of boll.

were carried out on a JEOL JNM-FX 200 spectrometer equipped with a CP/MAS unit operating under a static magnetic field of 4.7 T. ¹H and ¹³C Rf field strengths, $\gamma B_1/2\pi$, were 69.4 kHz for the CP process, while the ¹H dipolar decoupling (DD) field was reduced to 54 kHz. The contact time was 1 ms and the recycle time after acquisition of the FID was 10 s. ¹³C chemical shifts relative to tetramethylsilane were determined by using the peak at 32.89 ppm of

a small chip of crystalline linear polyethylene inserted as an internal standard.

RESULTS AND DISCUSSION

Torsional Rotation Due to Humidity Change

The distribution of the maximum angle of torsional rotation during humidity increase (RH from 30 to

Table II Tensile Properties of American Cotton Fibers Taken from Cotton Bolls in Different Stages of Growth

Cotton Bolls				Tensile Breaking		
Cultivation Year	Time of Picking	Boll No.	Drying		Load (g)	Elongation (%)
1986	Immediately before boll opening	HA-2-1	Never-dried	Wet ^a	3.0 (0.85) ^d	13
				Dry ^b	4.2 (1.04)	14
				Rewet ^c	5.4 (1.72)	21
	Field-opened	HA-2-4	Air-dried	Dry	3.7 (1.19)	15
				Wet	5.7 (1.43)	17
				Dry	4.2 (1.41)	12
1987	Field-opened	KA87	Air-dried	Wet	5.1 (2.12)	15
				Dry	2.6 (0.95)	14
				Wet	3.3 (1.43)	22
1988	24 days postanthesis	KA88A-1	Air-dried	Dry	0.9 (0.43)	7
				Wet	1.3 (0.39)	15
1989	19 days postanthesis	KA89B-1	Never-dried	Wet ^a	0.51 (0.13)	9
				Dry	0.46 (0.12)	11
				Rewet	0.52 (0.19)	15

^a To prevent drying of the fiber during attachment of the sample fiber to tensile tester, never-dried fibers kept in water were immersed in a 50% aqueous solution of glycerin and fixed between the clamps of the tester without washing of glycerin, then tested in a glass vessel containing water.

^b Sample fiber taken from the aqueous solution of glycerin above described, was rinsed with water and tested at RH 65% after air drying.

^c Sample fibers described in (b) were immersed again in an aqueous solution of glycerin and tested as described in (a). In other cases tests were carried out without using glycerin treatment.

^d Standard deviation.

100%) of American cotton fibers at 19 and 24 days postanthesis, and of the field-opened boll are shown in Table I. Data on American cotton fibers cultivated in 1986 at Higashi Osake City (HA)⁴ are also shown for comparison in the table. Like other kinds of cotton fibers already reported,^{1,2} the American cotton fibers taken from cotton bolls immediately before and after opening show fairly high angles of rotation that could not be seen in other kinds of fibers (above several hundred degrees). It is notable that the cotton fibers obtained at 19 and 24 days postanthesis show remarkably high angles of rotation reaching to more than 30 turns (10,000 degrees). These cotton fibers are supposed to be chiefly composed of the primary cell wall and to have a flat ribbon-like cross-section as shown in the microscopic photographs (Fig. 1). It is not known at present whether these extraordinarily high torsional rotations have some connection with the fibers' flat cross-section.

The direction of rotation was indefinite in all cases as in other cases previously reported.⁴

Tensile Properties

Dry and wet tensile strengths and elongations of American cotton fibers taken from cotton bolls harvested at 19 and 24 days postanthesis, and after field-opening are shown in Table II. Some data already reported⁴ on American cotton cultivated in 1986 at Higashi Osaka City are also included in the table for comparison. The cotton fibers taken immediately before opening have almost the same dry and wet tensile strengths as the field-opened fibers, while the fibers at 19 and 24 days postanthesis show much lower tensile strengths. The wet tensile strength of the never-dried cotton fibers harvested immediately before opening is low, and increases irreversibly after the first drying. When the fiber is rewetted,

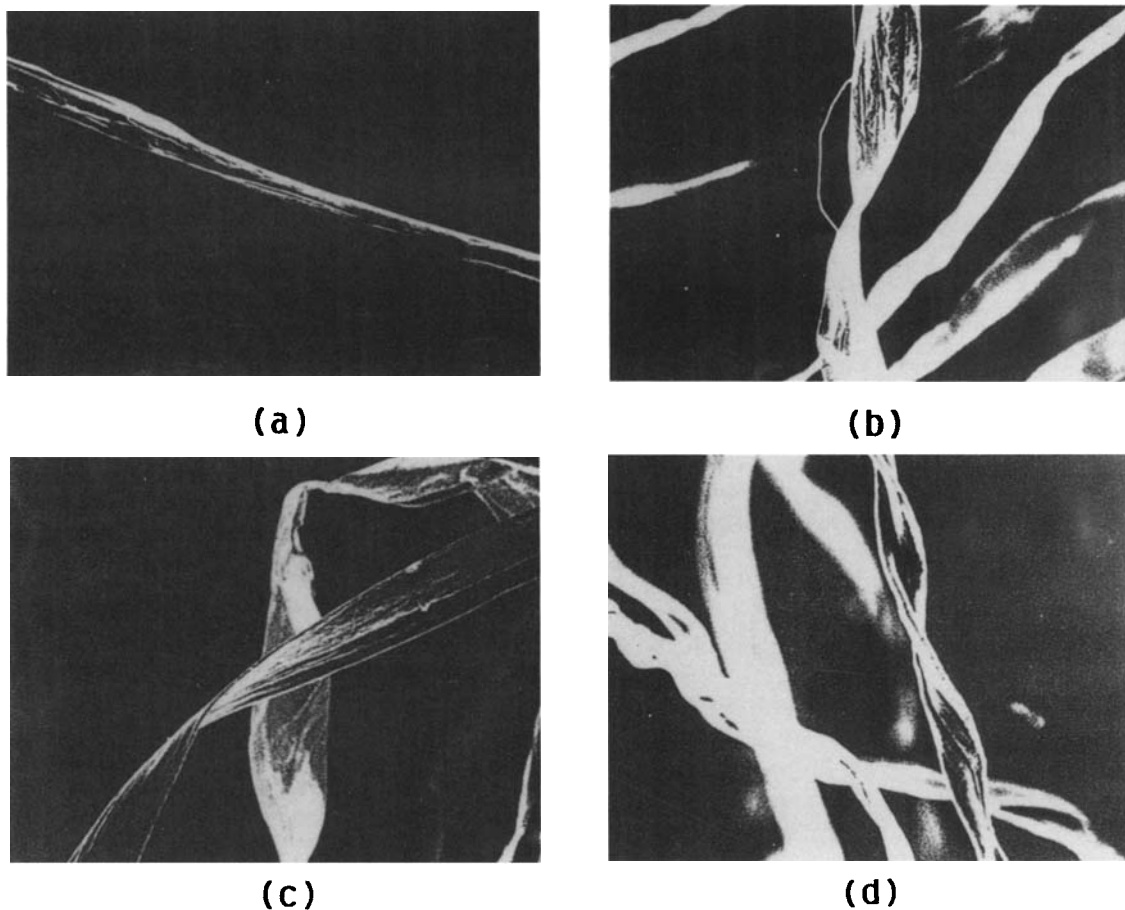


Figure 1 Electron microscope photographs of American cotton fibers at various times of growth ($\times 600$): (a) 15 days postanthesis, (b) 19 days postanthesis, (c) 24 days postanthesis, (d) field-opened.

the wet strength does not decrease, but further increases as in the case of the field-opened cotton fibers. This specific property of cotton fibers, higher wet tensile strength than the dry strength, is seen for the cotton fibers at 24 days postanthesis but not for the fibers at 19 days postanthesis. The tensile strength of the sample is nearly equal in the wet, dry, and rewet states.

The degree of polymerization is an important factor affecting mechanical properties of fibers. It was previously reported by Negishi¹⁶ and Tsuji¹⁷ that the wet tensile strength of cotton fibers became lower than the dry strength when the degree of polymerization was chemically reduced to 1000 or lower by oxidation or hydrolysis. Ohno⁹ reported that the degree of polymerization of cotton fibers at 17 days postanthesis was as low as one-third of that of the fibers obtained immediately before opening. Under

these circumstances the low degree of polymerization of the cotton fibers at 19 days postanthesis may be presumed to play an important role in the disappearance of this specific property i.e. that the wet tensile strength is higher than the dry strength.

Structural Analysis by NMR Spectroscopy

CP/MAS ¹³C NMR spectra in the wet state of the field-opened American cotton and never-dried American cotton taken from cotton bolls at various postanthesis periods are shown in Figure 2. The assignments of the resonance lines in the CP/MAS spectrum are also shown in Figure 2. The sharp downfield and broad upfield components of the C-4 and C-6 carbons of cellulose molecules are the crystalline and noncrystalline components, respec-

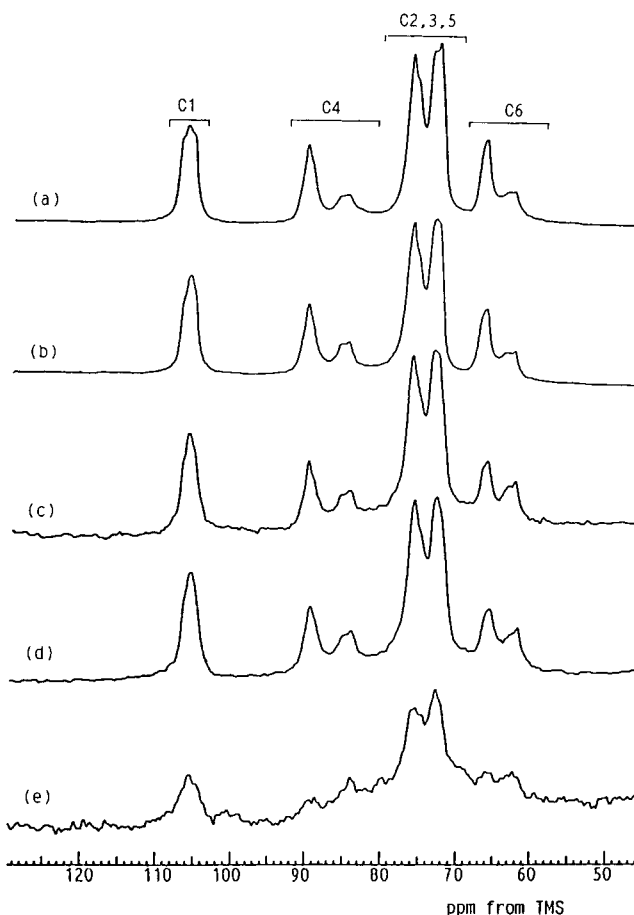


Figure 2 CP/MAS ¹³C NMR spectra in wet state of field-opened and never-dried American cotton fibers at various stages of growth: (a) field-opened (KA87), (b) immediately before opening (KA89A-3), (c) 25 days postanthesis (KA88D-1), (d) 19 days postanthesis (KA89A-1), (e) 15 days postanthesis (KA88C-2, B-1).

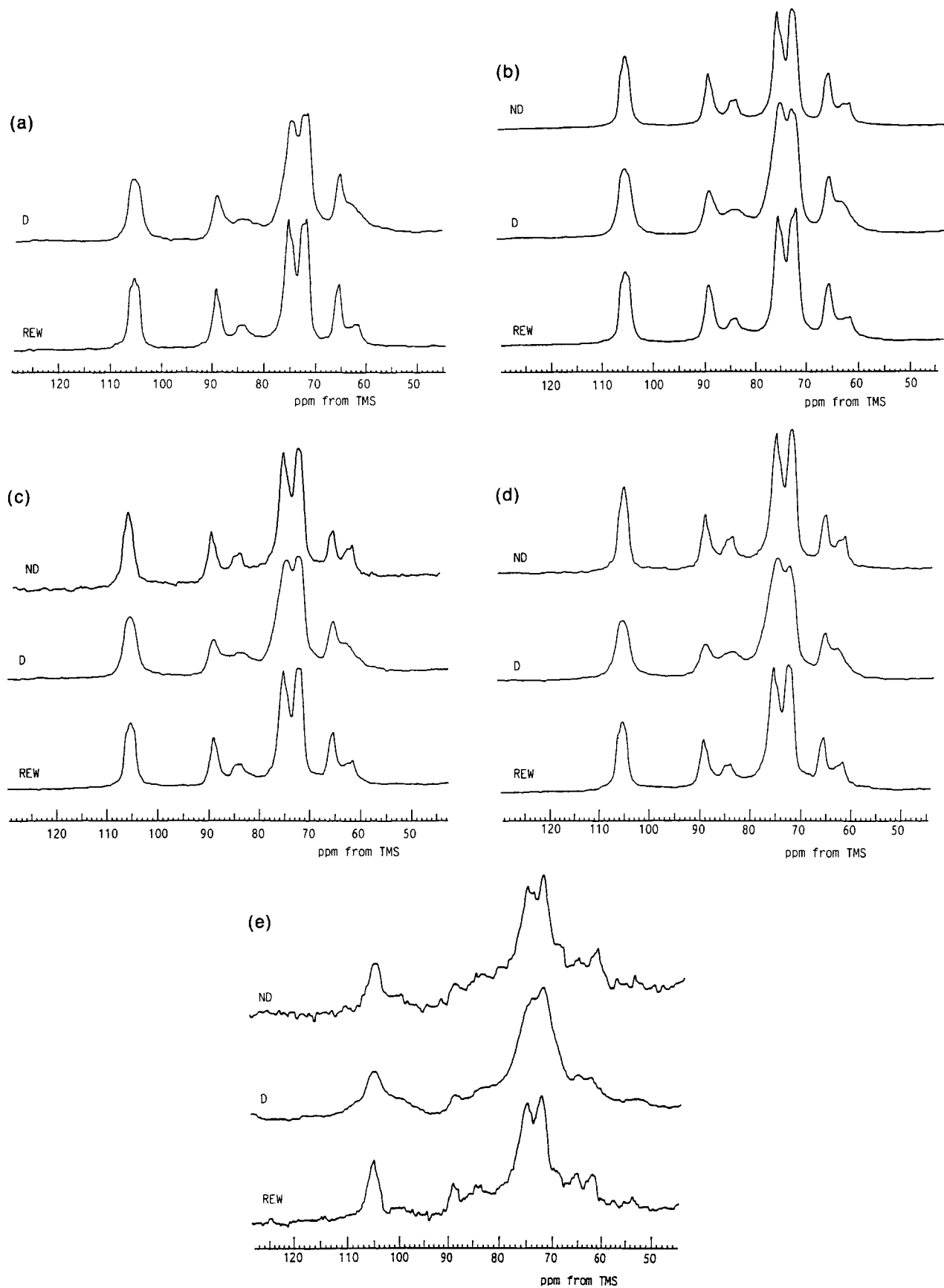


Figure 3 CP/MAS ^{13}C NMR spectra of American cotton at various growing stages in never-dried (ND), dried (D), and rewetted (REW) states: (a) field-opened (KA87), (b) immediately before opening (KA89A-3), (c) 24 days postanthesis (KA88A-1), (d) 19 days postanthesis (KA89C-1), (e) 15 days postanthesis (KA89B-3, C-2).

tively.^{10,12,18,19} Though the never-dried cotton fibers at 15 days postanthesis have a very low crystallinity, never-dried cotton fibers at and after 19 days postanthesis are highly crystalline. It is found that the degree of crystallinity increases with the growth of cotton fibers, as will later be discussed quantitatively.

NMR spectra of the cotton fibers collected at various growing ages in never-dried, dried, and rewetted states are shown in Figure 3 (a-e). As shown in these figures, each resonance line of the never-dried cotton is narrower than that of the dried cotton although there is no change in chemical shifts. A similar difference in line width is also observed between the dried cotton and the rewetted cotton. These results show that some distortion of the molecular chain is produced by drying and that this is relaxed by the sorption of water as previously reported.^{10,12}

The degree of crystallinity of the cellulose sample in the dried state can be estimated by an analysis of the integrated intensities of the crystalline and noncrystalline components of the C-4 resonance line.^{10,12,19} The reason is that the relative carbon intensities of the respective resonances are proportional to the number of carbons, even if the cross-polarization technique is employed.²⁰ It is rather difficult to examine whether it is true for the never-dried or wetted cotton. In the case of cotton samples, however, the noncrystalline component is not associated with rubberlike molecular motion even upon the addition of water.²¹ Therefore, we assume

that the CP efficiency does not greatly differ in the crystalline and noncrystalline regions and that the degree of crystallinity of never-dried and rewetted samples may be simply estimated by the line-shape analysis for the CP/MAS spectra as described below.

Figure 4 shows a typical example of computer line-shape analysis of the C-4 resonance region for fibers KA88A-1 in the rewetted states, where each line is assumed to be a Lorentzian. The crystalline component of the C-4 line is composed of a triplet for native cellulose.²² As for the noncrystalline component we assume two Lorentzians in order to reproduce the rather broad noncrystalline line. The resonance lines for carbons C-2, C-3, and C-5 from 70 to 80 ppm are simply assumed to be composed of four Lorentzians to estimate the influence of the C-2, C-3, and C-5 regions on the noncrystalline region of the C-4 resonance. The composite curve is in good accord with the observed curve, particularly in the C-4 resonance region. According to this analysis, the degree of crystallinity was estimated to be the integrated fraction of the downfield crystalline components of the C-4 resonance.

Table III shows the degrees of crystallinity estimated from line-shape analysis for various cotton fibers shown in Figure 3. Generally, the degree of crystallinity increases with the fiber growth. Though the numerical values of the crystallinity for wet and dry fibers cannot be strictly compared owing to the effect of water as described above, it seems that the degree of crystallinity of the dried cotton fibers is

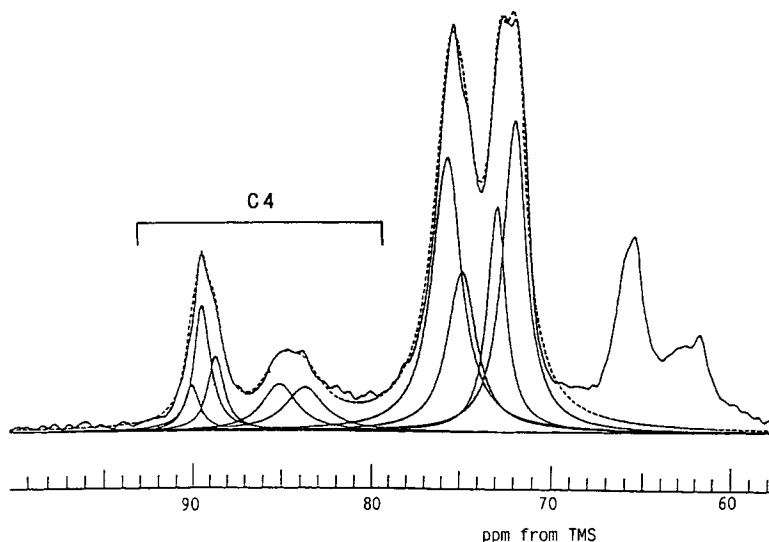


Figure 4 Estimation of the degree of crystallinity by analysis of the crystalline and noncrystalline components of the C-4 resonance region for fibers KA88A-1 in the rewetted states. The broken line indicates the composite curve of nine Lorentzians.

Table III Degree of Crystallinity Estimated from CP/MAS ^{13}C NMR Spectra for American Cotton Fibers Taken from Cotton Bolls in Different Stages of Growth

Cotton Bolls			Degree of Crystallinity (%)		
Boll No.	Cultivation Year	Time of Picking	Never-Dried	Dried	Rewetted
KA87	1987	Field-opened	—	54	63
KA89A-3	1989	Immediately before boll opening	57	49	63
KA88A-1	1988	24 days postanthesis	—	45	59
KA88D-1	1988	25 days postanthesis	49	—	—
KA89A-1	1989	19 days postanthesis	47	46	58
KA89C-1	1989	19 days postanthesis	50	43	56
KA89B-3, C-2	1989	15 days postanthesis	low	low	low

somewhat lower than that of never-dried fibers and that it increases on rewetting.

Thus it has been confirmed by NMR spectroscopy that never-dried cotton was crystalline in the early stage of growth at or after 19 days postanthesis. Further, in order to confirm this finding X-ray diffraction photographs were taken. The diffraction patterns of the American cotton fibers at 19 days postanthesis in the never-dried and dried states are shown in Figure 5. The never-dried fibers were gently removed from the seed in water and sealed into a capillary. Wide angle X-ray diffraction patterns were obtained using $\text{Cu-K}\alpha$ radiation monochromatized by graphite crystals. As an X-ray source, a rotating anode X-ray generator, Rigaku Denki Rotaunit RU-3H was used, operated at 40 kV and 80 mA. Crystalline

talline diffractions are observed in both never-dried and dried states. The lattice distances of (101), (10 $\bar{1}$), and (002) calculated from these patterns are 6.28, 5.33, and 3.92 Å for the never-dried fibers, and 6.01, 5.40, 3.98 Å for dried fibers. These values agree closely with those in literature.²³

As already described, it was assumed from previous X-ray studies that never-dried cotton fibers were amorphous⁵ or of low crystallinity.⁶ In contrast, Morosoff⁷ concluded from X-ray diffraction analysis that never-dried cotton fibers taken from unopened bolls had a high crystallinity, which somewhat decreased on drying due to a build up of stress in fiber and which again increased on rewetting due to stress relaxation with some reorganization of cellulose chains. More recently, Nakamura et al.²⁴ showed by

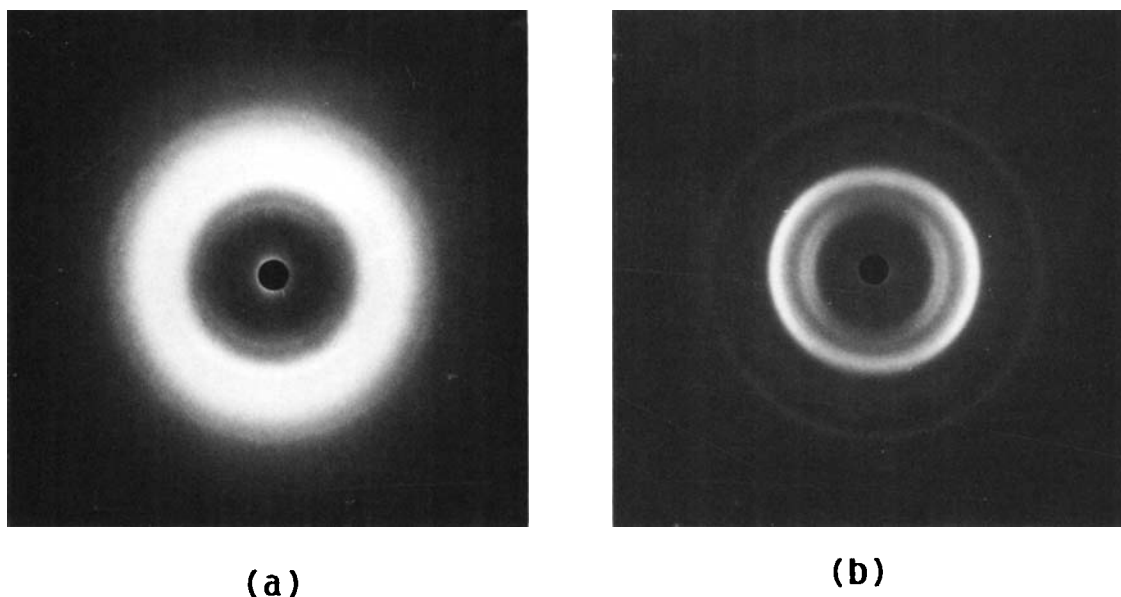


Figure 5 Wide angle X-ray diffraction photographs of American cotton (KA89A-1) at 19 days postanthesis in (a) never-dried and (b) dried states.

X-ray diffractometry that the half-width of the diffraction peak (002) of cotton lint and cloth decreased, and the crystallite size increased, as the amount of sorbed water increased. The results obtained by us in this NMR study are in agreement with those reports of Morosoff⁷ and Nakamura et al.,²⁴ though their experiments differ from ours in that Morosoff used unopened cotton bolls without specifying the time of growth, and Nakamura et al. used field-dried cotton fibers having various water contents.

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