

Evaluation of Microcrystalline Cellulose. I. Changes in Ultrastructural Characteristics During Preliminary Acid Hydrolysis

LEI-GUI TANG,¹ DAVID N.-S. HON,^{1,*} SONG-HAN PAN,² YU-QIN ZHU,² ZHEN WANG,²
and ZHEN-ZHI WANG²

¹Wood Chemistry Laboratory, Department of Forest Resources, Clemson University, Clemson, South Carolina 29634-1003; ²Guangzhou Institute of Chemistry, The Chinese Academy of Sciences, Guangzhou, Wushan 510650, People's Republic of China

SYNOPSIS

Several microcrystalline celluloses prepared from viscose staple, bagasse, ramie, and cotton were evaluated by viscosimetry, X-ray diffraction, and scanning and transmission electron microscopies. The changes in crystallinity, size of crystallites, grain-size distribution, morphological features, and degree of polymerization were found to be dependent on and greatly limited by the polymorphic conformations of cellulose. These changes were more conspicuous in cellulose II than in cellulose I. The coexistence of a two-phase system still remains in all the specimens of microcrystalline cellulose powders. Combining the findings with respect to the extent of the changes in the size of crystallites, it appears inevitable that recrystallization in some of the defective crystallites and degradation in the disordered areas of cellulose occurs simultaneously in the preliminary hydrolysis process during the production of microcrystalline cellulose. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Microcrystalline cellulose (MCC) has been the subject of extensive studies since 1950.¹ Because of its unique physical characteristics, it has been used in the cosmetics, plastics, food, and pharmaceutical industries. MCC is a purified, partially depolymerized cellulose prepared by treating high-quality cellulose with hydrochloric acid to the point of leveling off the degree of polymerization (LODP). According to Battista et al.,² the term LODP refers to the weight-average degree of polymerization (DP) of the macromolecules comprising the discrete, colloidal, unhinged microcrystals of polymers. MCC represents a novel physical state of commercial cellulose. It occurs as a fine, white, odorless, crystalline powder. It consists of free-flowing, nonfibrous particles that may be compressed into self-binding tablets that disintegrate rapidly in water. In aqueous sus-

penoids, these much finer particles have a smooth texture resembling uncolored butter and pseudoplastic properties including stable viscosity over a wide temperature range. MCC is insoluble in water, in dilute acids and alkali, and in common organic solvents.

The classical work of Immergut and Ranby³ demonstrated that the heterogeneous hydrolysis of the cellulose fibers in the initial state involves a decomposition of the elementary cellulose fibrils into shorter rodlike fragments giving sharper X-ray reflections than the original fibers. The more resistant cotton cellulose micelles seem to remain unchanged until they disappear by a rapid process, whereas the wood cellulose micelles show a gradual lateral attack during the hydrolysis reaction. Degradation of ramie and cotton fibers by sulfuric acid at 40°C was performed by Mukherjee and Woods.⁴ They found that the hydrolysis leads to a breakdown of fibrils into elongated tabular particles of lateral dimensions about $30 \times 130 \text{ \AA}$ and of widely varying lengths up to 2500 Å. The particles are probably single crystallites of cellulose I and have their 101 crystallo-

* To whom correspondence should be addressed.

graphic orientation persisting over relatively great distances. In recent years, research has been devoted to characterizing the ultra-structures of MCCs from regenerated cellulose,^{5,6} bleached cellulose,⁷ and silk fiber.⁸ Lenz and co-workers⁵ used transmission electron microscopy (TEM), small-angle X-ray scattering (SAXS), and wide-angle X-ray diffraction (WAXD) to determine the crystallite length of weakly hydrolyzed and unhydrolyzed regenerated cellulose fibers. Vasilic-Oprea and co-workers⁹ showed that in the hydrolysis of cellulose by H₂SO₄ at 60°C for 60 min the hydrolytic reactions occur mainly in the amorphous phase of the cellulosic material. The dimensions of the crystalline domains are not modified significantly by the treatment applied. The fractions obtained do not differ as to their crystallinity or dimensions of the crystalline domains. Petropavlovsky and Kotelnikova¹⁰ observed that during acid hydrolysis cellulose fibers were kept in the cellulose I structure while their crystallinity indices and the crystallite dimensionals have higher values as compared with the initial celluloses.

In this study, the effect of dilute acid hydrolysis on the ultrastructural characteristics of viscose staple, bagasse pulp, ramie, and cotton fiber was investigated; the similarities and differences in ultra-structures among the different MCC specimens prepared from these sources were compared.

EXPERIMENTAL

Preparation of Microcrystalline Cellulose (MCC) Specimens

Viscose staple, cotton, ramie fibers, and bagasse pulp were treated with 2.5M HCl at 105°C for 15 min. The MCC powder specimens were obtained by using the washing-and-drying procedures developed by Battista.¹

Table I Changes in Ultrastructural Parameters

Specimens	Crystallinity (%)		DP	
	Starting	MCC	Starting	MCC
Viscose staple	54	64	475	40
Bagasse pulp	65	72	764	117
Cotton fiber	80	84	1010	178
Ramie fiber	83	86	2120	209

Table II Level-off Basic DP of Natural and Regenerated Fibers

Specimen	Starting DP	Level-off DP	
		This Study	Literature
Viscose staple	475	40	40–60
Bagasse pulp	764	117	—
Cotton fiber	1010	178	200–250
Ramie fiber	2120	209	300–350

Methods of Analysis

Determination of Degree of Polymerization (DP)

The DP of the different cellulosic specimens was determined by the intrinsic viscosity [η] of cellulose dissolved in a cupriethylenediamine solution. The DP was calculated based on the following equation¹¹:

$$DP = 190 [\eta]$$

Study of Ultrastructure

The crystallinity, crystallite size, and grain-size distribution for each specimen were measured by means of a Rigaku Rint X-ray diffractometer.

Observations of Morphology of Microcrystal Aggregates

MCC powders were dispersed ultrasonically in water (cellulose:H₂O = 0.5 g:100 mL) for 20 min at room temperature before examination using a JEM-100 CXII transmission electron microscope (TEM). For the scanning electron microscope (SEM) study, the specimens were sputter-coated with gold-palladium and examined by a Hitachi S-430 scanning electron microscope.

RESULTS AND DISCUSSION

Decrease in Degree of Polymerization and Increase in Crystallinity

It is generally accepted that when preparing MCC the disordered regions of cellulose are readily attacked by dilute acid while the crystalline regions are more resistant to attack. Our experimental results, as shown in Tables I and II, illustrate that the production of MCC exerted a fall in the DP and a rise in the crystallinity of celluloses from different sources. This fact clearly suggests that chain scission took place in cellulosic macromolecules due to acid

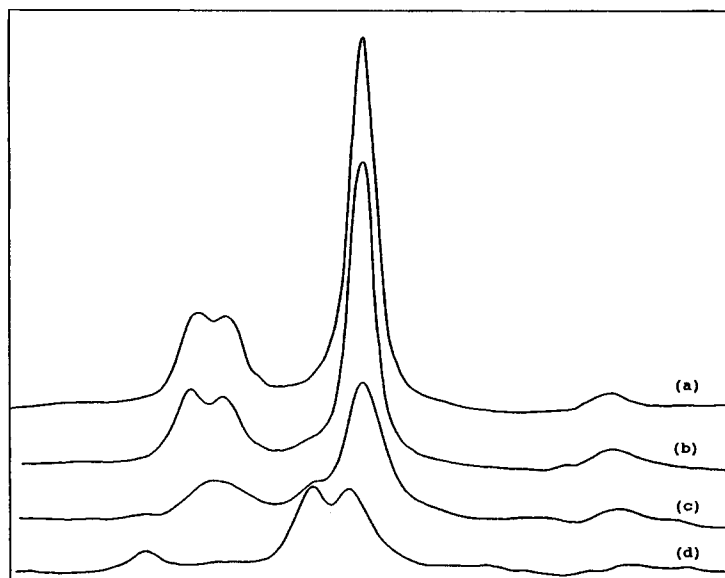


Figure 1 X-ray diffractograms of microcrystalline celluloses: ramie fiber (a), cotton fiber (b), bagasse pulp (c), and viscose staple (d).

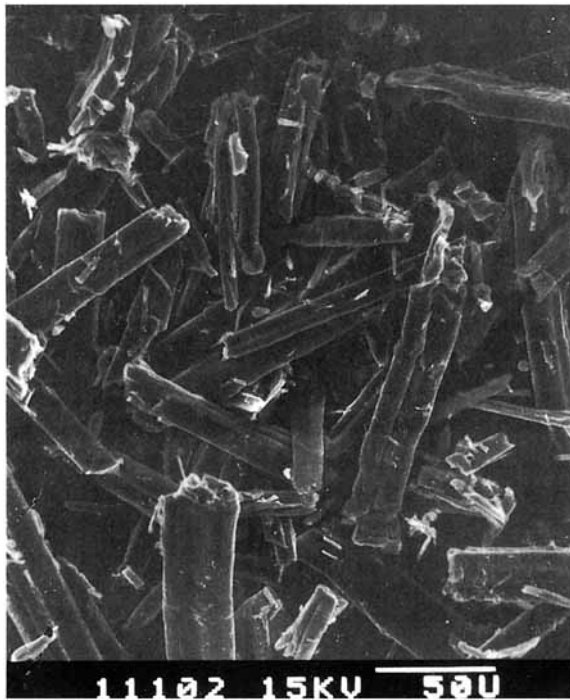
hydrolysis of the amorphous regions of cellulose macromolecules. This result is in agreement with previous studies.^{2,12,13} Moreover, the experimental data showed that the increase in crystallinity and loss in DP in viscose staple, which is in the form of Cellulose II, were more conspicuous than those of bagasse pulp, cotton fiber, and ramie fiber, which are in the form of Cellulose I. For instance, viscose staple MCC increased 18% in crystallinity while cotton and ramie fiber increased only 5 and 4%, respectively. Viscose staple MCC lost 92% of its DP while bagasse MCC and cotton MCC lost 85% and 82%, respectively.

It is clear that hydrochloric acid can penetrate more easily into cellulose with less crystallinity, i.e., cellulose II, than into cellulose with higher crystallinity, i.e., cellulose I. The process of MCC formation occurred under heterogeneous hydrolysis and, hence, is markedly dependent on the diffusion factor of the solvolysis agent, i.e., hydrochloric acid. Accordingly, these results demonstrated that hydrolysis took place preferentially in the amorphous region. Literally, the loss of the amorphous region was occasioned by the apparent increase in crystallinity. The X-ray diffraction patterns revealed that the MCC from different sources retained basically their original polymorphic forms as shown in Figure 1., i.e., viscose staple MCC exhibited the pattern of cellulose II, cotton and ramie MCC exhibited the pattern of cellulose I, and bagasse pulp MCC exhibited essentially cellulose I with a small amount of cel-

lulose II. Apparently, these observations are in agreement with Cabradilla and Zeronian's findings that MCC cellulose I and II retained their original structures in their counterpart LODP form.¹⁴ Hence, these results obviously differ from the previous studies which showed the various types of MCC retained exclusively the cellulose I structure.¹⁰ The X-ray diffraction and crystallinity studies also suggested that MCC obtained by the preliminary acid hydrolysis is not completely a crystal material but showed a considerable degree of disorder. Hence, the classical two-phase model, consisting of crystalline and amorphous domains, remains acceptable for the description of the microstructure of MCC powders.

The Distinct Morphological Features in MCC

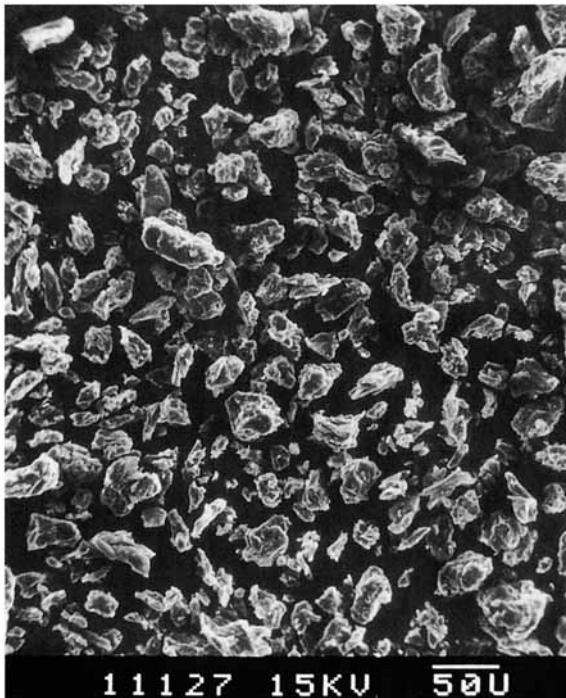
The electron microscope has proven to be a valuable tool for the study of the morphology of MCC specimens. In comparison with the previous method of negative staining with chemicals,^{5,6} a method of using ultrasonic dispersion without staining for MCC powders was employed in this study. By using this method, the dispersed MCC can be examined directly under the electron microscope without additional treatment. The results of the SEM study are shown in Figure 2. It is obvious that most of the morphological units of MCC powders appeared to be in a stage of microcrystal aggregates rather than of individual microcrystals.



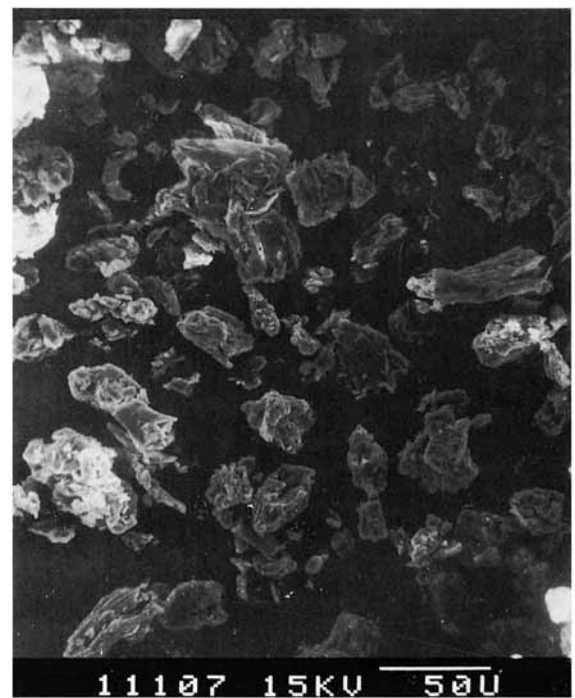
(a)



(b)



(c)



(d)

Figure 2 Scanning electron micrographs of MCC: ramie fiber (a), cotton fiber (b), bagasse pulp (c), and viscose staple (d).

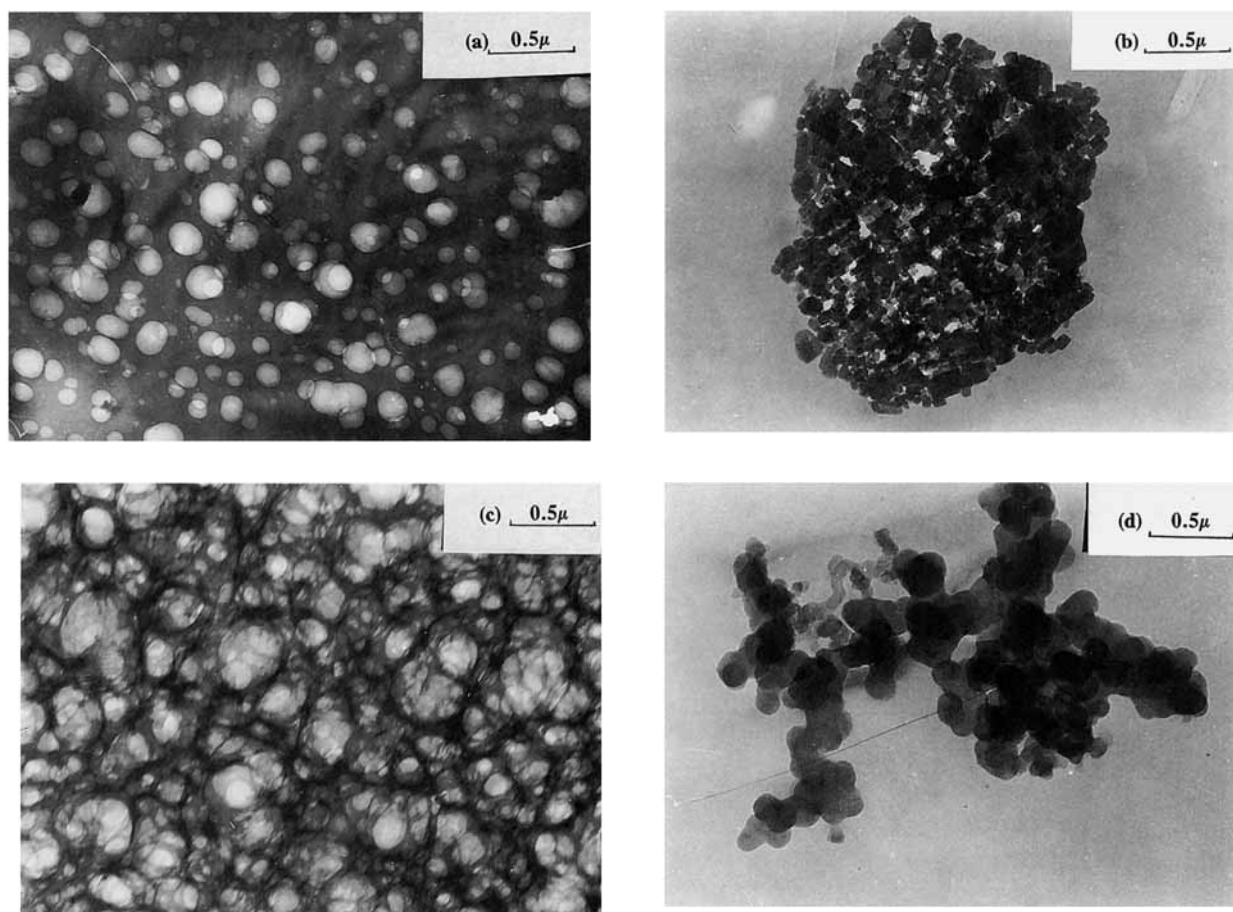


Figure 3 Transmission electron micrographs of MCC: ramie fiber (a), cotton fiber (b), bagasse pulp (c), and viscose staple (d).

It is especially interesting to notice the distinctive surface morphology existing in the various MCC powders (Fig. 2.). The microcrystal aggregates for viscose staple MCC and bagasse pulp MCC displayed a form of clusters in appearance [Fig. 2(a) and (b)]. In contrast, the highly crystalline MCC of ramie and cotton display a rod-shaped morphology in their aggregates [Fig. 2(c) and (d)]. The former MCC resembled glass fibers, and the latter, twisted-rod.

TEM techniques are also very important for the elucidation of details of the MCC microstructure. As shown in Figure 3, although the internal texture of the MCC powders exhibited ultrastructures similar to spherulitic microcrystals [Fig. 3(a), (c), and (d)], some of the morphological units consisting of platelets also appeared in the interior of the cotton MCC [Fig. 3(b)]. This finding implies that the MCC obtained from native cellulose by preliminary acid hydrolysis principally kept the relatively integrative crystal structure in the original material.

Crystallites Size and Grain Size Distribution

The size of the crystallites is characterized by their width and length. Cellulose crystallites are known to be disparate in size; consequently, the value measured could only be as an average. According to the literature,^{6,13,15} the average width and length of crystallites were based on the full width at half maximum of 101, 002, and 040 reflections in the X-ray diffraction, respectively, and it can be calculated by using the Scherrer equation, i.e.,

$$L_{h,k,l} = K\lambda/\beta_0 \cos \Theta$$

where $K = 0.94$. Based on this calculation, the sizes of crystallites of various MCC are summarized in Table II. It is clear that a significant increase in the width of crystallites was observed for viscose staple and bagasse pulp MCC, i.e., the average width of crystallites increased 70 and 20%, respectively. This

Table III Changes in the Size of Crystallites

Reflection	Viscose Staple		Bagasse Pulp		Cotton Fiber		Ramie Fiber	
	Initial	MCC	Initial	MCC	Initial	MCC	Initial	MCC
101	40	68	40	49	57	55	49	48
002	41	66	48	55	72	71	66	65

Unit: $\times 10^{-10}$ m.

result confirms Hattula's idea that acid hydrolysis probably increased the average width of the crystallites.¹⁵ Furthermore, our data reflected the fact that no growth in crystallites for cotton and ramie MCC was observed. This finding enables us to postulate that only the celluloses having the lower crystallinity and loose structure favor the changes in the crystallites size during the dilute acid hydrolysis.

In view of the extent of change in width of crystallites, it is plausible that both the degradation of the smaller crystallites and the growth of the defective crystallites could occur and were responsible for the changes in the size of crystallites during the production of MCC. Unfortunately, no meaningful data has so far been obtained by using the Scherrer equation to estimate the change in length of crystallites reflects on 040.

The use of wide-angle X-ray diffraction to measure the grain size and grain distribution for different types of MCC powders was successfully performed. The results showed that the grain size for all types of MCC used in this study was predominately in the range of $100\text{--}500 \times 10^{-10}$ m, with the exception of a few of $700\text{--}900 \times 10^{-10}$ m. Approximately 82% of all grains have a size of $200\text{--}300 \times 10^{-10}$ m. These experimental results are comparable with those directly observed by TEM (Fig. 3). Accordingly, the different types of MCC powders used in this study could meet the taste standard requirement because the grain size is critical in avoiding perception by the tongue.¹⁶ Thus, MCC powders from various sources can be used for industrial application involving human consumption.

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Support for this research from the National Natural Science Foundation of China is gratefully acknowledged.

Received April 26, 1995

Accepted July 12, 1995