Changes in Morphology with Milling of the Commercial Microcrystalline Cellulose

It is generally known that crystallinity of crystalline polymers decreases with milling, and a few authors have shown this to be true for cellulosic materials.[1-3] But the detail mechanism has not been clear.

In the present note, the relation between changes in crystallinity and morphology with milling of commercial microcrystalline cellulose is reported.

Well-dried commercial microcrystalline cellulose (Avicel, Asahi Chemical Industry) was treated with a micromill for 1, 2, 3, 5, 10, 15, 20, or 25 hr. Crystallinity of each sample was determined with x-ray method according to Hermans.[4] The level-off DP values of the samples were determined from Cadoxen viscosity measurements. The

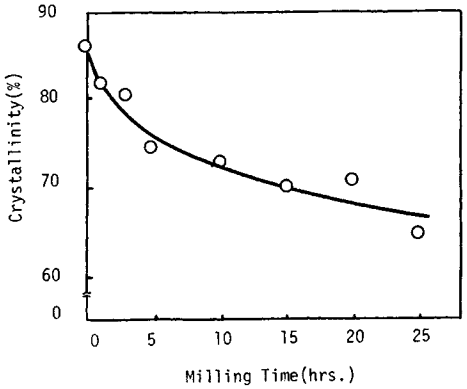

Fig. 1. Relation between crystallinity of microcrystalline cellulose and milling time.

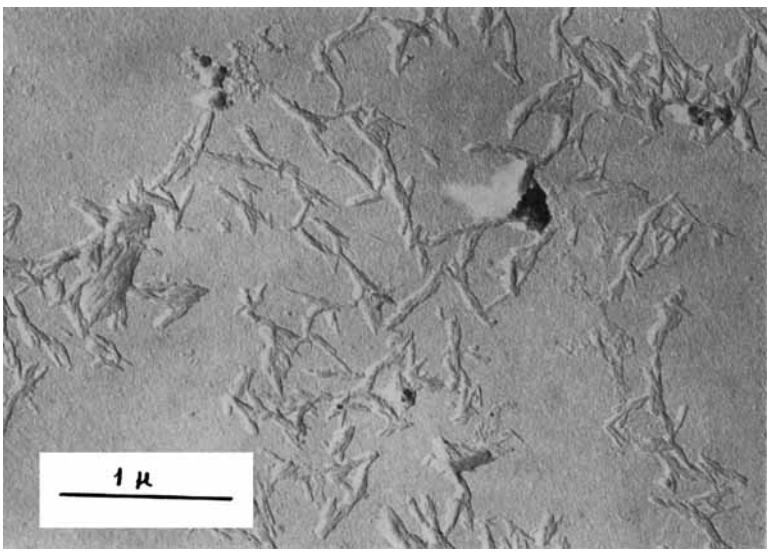

Fig. 2. Electron micrograph of untreated microcrystalline cellulose. Crystallinity 86% (2.25 × 10,000).

morphology was observed with an electron microscope (Hitachi HU-11B-type, Cr shadowing) method.

Crystallinity of each sample is plotted against milling time in Figure 1. It is confirmed that crystallinity decreases with milling, but is still relatively high after milling for 25 hr. The data of Nelson[2] showed that for cotton cellulose the original crystallinity of 87% decreased to 0% with milling for 1 hr and for Fortisan hydrocellulose the original

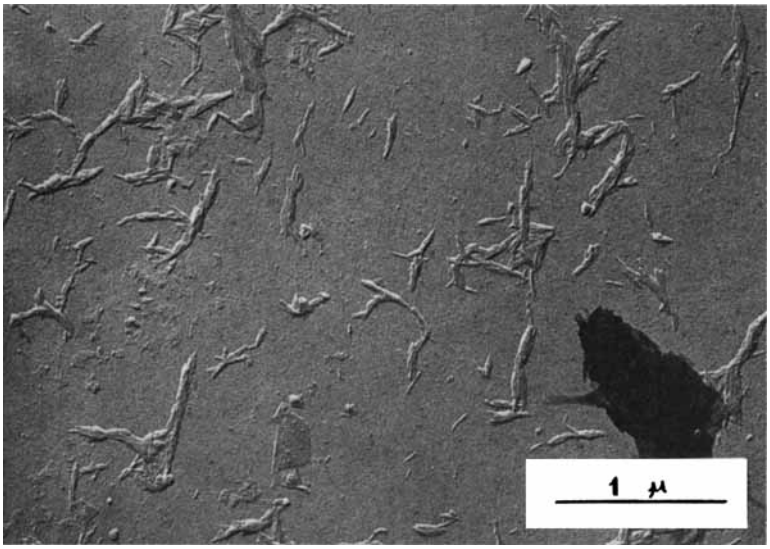

Fig. 3. Electron micrograph of microcrystalline cellulose treated with micromill for 1 hr. Crystallinity 82% (2.25 × 10,000).

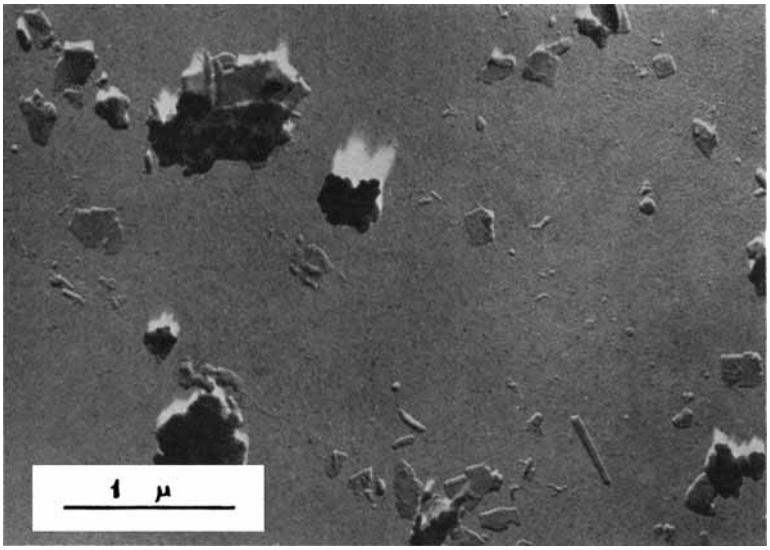

Fig. 4. Electron micrograph of microcrystalline cellulose treated with micromill for 10 hr. Crystallinity 73.3% (2.25 × 10,000).

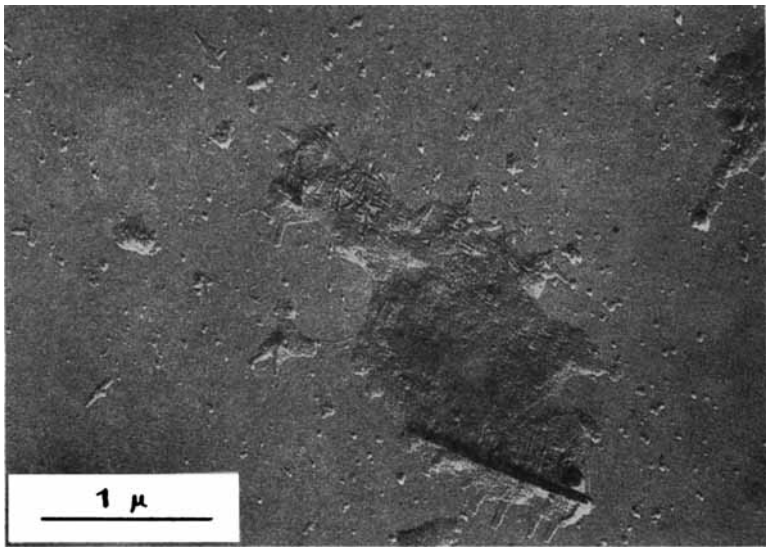

Fig. 5. Electron micrograph of microcrystalline cellulose treated with micromill for 25 hr. Crystallinity 65% (2.25 × 10,000).

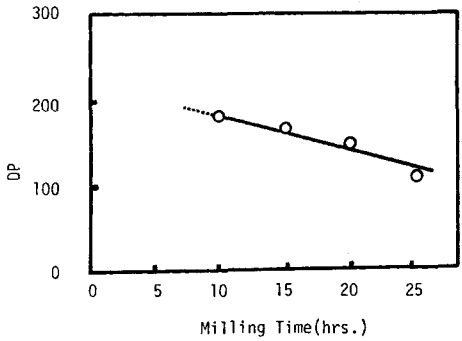

Fig. 6. Relation between DP of microcrystalline cellulose and milling time.

crystallinity of 85% decreased to 20% after 2 hr of milling. One reason for this difference may be that our milling apparatus is smaller and weaker than that of Nelson.

The morphology of each sample is shown in Figures 2–5, respectively. From only these photographs, details of the mechanism cannot be discussed. But some relations between changes in crystallinity and morphology with milling can be observed. The untreated microcrystalline cellulose (crystallinity 86%) has a characteristic fringe shape. The shape of the cellulose milled for 1 hr (crystallinity 82%) is almost the same except for the thin plate-like shape observed in Figure 4 (10 hr milling, crystallinity 73%). From level-off DP measurements (Fig. 6), it appears that the microcrystals probably become smaller and smaller. Thus, the sample with milling for 25 hr (crystallinity 65%) shows a large shape because the smaller particles aggregate with each other (Fig. 5).

The authors would like to express their gratitude to Mr. Abe and Mr. Kurokawa for measurements of the electron micrograph and to Mr. Miyamura of Asahi Chemical Industry for kind discussions.

References

1. O. A. Battista and P. A. Smith, *Ind. Eng. Chem.*, **54**(9), 20 (1962).
2. M. L. Nelson and R. T. O'Conner, *J. Appl. Polym. Sci.*, **8**, 1325 (1964).
3. J. A. Howsman and R. H. Marchessault, *J. Appl. Polym. Sci.*, **1**, 313 (1959).
4. P. H. Hermans and A. Weidingen, *J. Appl. Phys.*, **19**, 491 (1949).

Katsuyuki Ogura
Hiroshi Sobue

Department of Industrial Chemistry
College of Technology, Seikei University
Musashino-shi, Tokyo, Japan

Received February 11, 1970