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Influence of surface charge on viscosity behavior of cellulose microcrystal suspension*

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Abstract Microcrystalline cellulose with minimal surface charge was prepared from softwood kraft pulp via hydrolysis by 4N hydrochloric acid instead of sulfuric acid. To this material, sulfate ester groups as surface charge were introduced by treating with 55% (w/w) sulfuric acid. A treatment at 60°C for 2h gave nearly the same level of surface charge as that of the H₂SO₄-hydrolyzed microcrystal. The number of sulfate groups were controlled by changing the H₂SO₄ treatment conditions. Although the microscopic size and shape of the microcrystalline particles were the same irrespective of the preparation method, the introduction of surface charge drastically reduced the viscosity and removed its time dependence. These changes in viscosity behavior are considered to result from charge-induced dispersion of loose aggregates existing in the initial charge-free microcrystals prepared by HCl hydrolysis.

Key words Cellulose microcrystal · Sulfate ester · Surface charge · Viscosity behavior

Introduction

In a previous study we reported that hydrolysis of native cellulose by 4N HCl hydrolysis gave a stable suspension of cellulose microcrystals.¹ The viscosity of the HCl-hydrolyzed suspension was severalfold higher than that of the suspension prepared by 65% (w/w) sulfuric acid from the same material. Unlike the H₂SO₄-hydrolyzed suspension, the HCl-hydrolyzed suspension showed complex vis-

cosity behavior dependent on both shear application time and microcrystal concentration, i.e., thixotropy at a concentration higher than 0.5% (w/v) and antithixotropy lower than 0.3% (w/v). The conductometric titration revealed that the negative surface charge of the particles was significantly less than that of H₂SO₄-hydrolyzed microcrystals because sulfate groups were not introduced by the HCl treatment. The difference in viscosity behavior between the two types of suspension therefore can be ascribed to the difference in the amount of surface charge, which governs the interparticle forces.¹ To confirm the influence of surface charge and provide a means of controlling it, we studied conditions to introduce surface charge to the HCl-hydrolyzed cellulose microcrystals by secondary treatment with H₂SO₄.

Materials and methods

Bleached softwood kraft pulp (10g) was hydrolyzed in 300ml 4N HCl at 80°C for 225 min with continuous stirring. The acid-free microcrystalline cellulose suspension was obtained by repeated centrifugation at 1600 G for 5 min. When the sample reached about pH 4 the microcrystals became nonsedimenting, and the supernatant became turbid. After collecting the supernatant, the sediment was redispersed in deionized water and centrifuged again, yielding another turbid supernatant; this procedure was repeated until no visible material remained in the supernatant. The fractions of turbid supernatant were combined and dialyzed against deionized water to neutrality. The suspension was concentrated to about 1%–5% solid content by strong centrifugation (18800 G, for 60–90 min at 4°C), sonicated with a rod-type sonicator (Nissei Ultrasonic homogenizer) for 1 min, and stored in a refrigerator.

Esterification was carried out as follows: The suspension was first concentrated by centrifugation at 2000 G (this step was facilitated by the addition of H₂SO₄ to give 0.1N acid). After removing the supernatant, 65% (w/w) H₂SO₄ was added to the precipitate to make a final H₂SO₄ concentration of 55% (w/w). The mixture was shaken in a waterbath

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and allowed to react for 2 h. The reaction temperature was 40°C or 60°C. After the reaction the sample was diluted immediately with a large amount of cold water and washed by repeated centrifugation-decantation cycles until the microcrystals became non-sedimenting. Dialysis, strong centrifugation, and sonication were performed following a protocol similar to the one described above. The result was a sulfated microcrystal suspension. For comparison, a H₂SO₄-hydrolyzed suspension was prepared by direct treatment of the same kraft pulp with 65% (w/w) H₂SO₄.¹⁻⁸

Transmission electron microscopy, X-ray diffraction, conductometric titration,^{4,9} and viscosity measurements by a Brookfield-type viscometer were performed as in our previous study.¹ Aliquots of 150 ± 5 mg of freeze-dried microcrystals were pressed into a tablet, 20 mm wide and 1 mm thick, in which the sulfur content of the microcrystals was measured with an X-ray fluorescence analyzer (HORIBA MESA-500) at the automatic measurement mode.

Results and discussion

Figure 1 shows the micrographs of the microcrystal specimens with different degrees of esterification; no significant changes in the size and shape of the particles were observed. The average size of the single microcrystal was 3.5 ± 0.5 nm × 180 ± 80 nm.¹ The X-ray diffraction pattern was the same for all samples, being that of typical cellulose I (data not shown). These results indicate that the sulfate groups were introduced to the surface of microcrystals without causing further fibrillation or disruption of the rod-like particles.

Table 1 shows the sulfur content and the amount of acidic groups in the microcrystals. The strong and weak acid groups in Table 1 correspond to sulfate and carboxyl groups, respectively.^{1,4,9} The amount of strong acid groups and the sulfur content were negligible for the HCl-treated starting material; these values increased after H₂SO₄ treatment, indicating the introduction of sulfate groups. The values gained from titration, however, are about one-third to one-half those derived from fluorescent X-ray analysis. A discrepancy has been also reported by another group for H₂SO₄-hydrolyzed microcrystals.¹⁰ The cause of this discrepancy is not clear at present, but it may result from the introduction of nonacidic sulfur groups or the existence of sulfate groups inaccessible to the titrant. The weak acid

(carboxyl) content of the HCl-treated sample was 16 mmol/kg, and it increased to 28–29 mmol/kg after the H₂SO₄ treatment, nearly equal to that of the H₂SO₄-hydrolyzed sample.

Though the size and shape of these samples were almost the same as in Fig. 1, the viscosity behaviors of the four suspensions were remarkably different. Figure 2 shows the time dependence of the viscosity of the four microcrystalline suspension samples. The significant time dependence observed for the HCl-treated microcrystal suspension¹ (Fig. 2a) disappeared after the H₂SO₄ treatment at 40°C for 2 h (Fig. 2b); only slight increases in viscosity with time (antithixotropy) were seen at high solid contents (14.9 and 19.9 g/l). The suspension esterified at 60°C for 2 h showed no

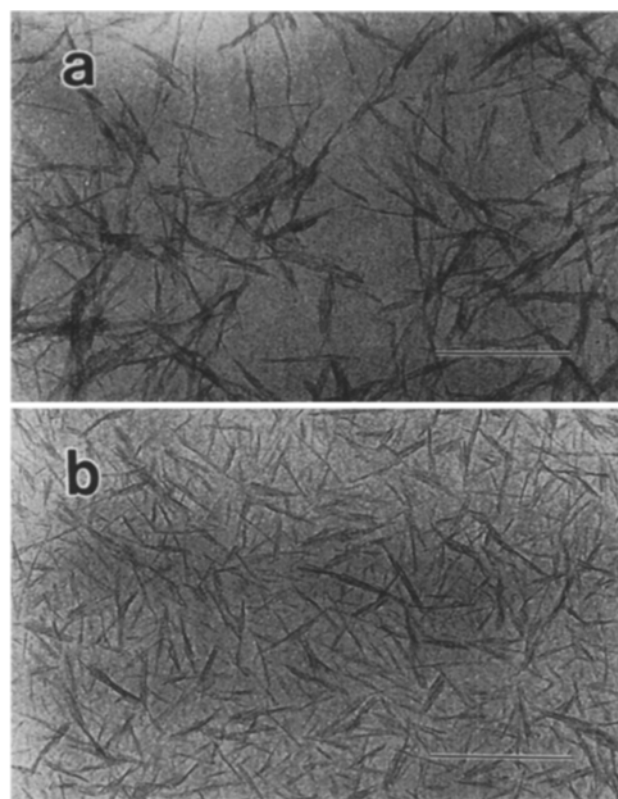


Fig. 1. Micrographs of the microcrystals sulfated at 40°C for 2 h (a) and at 60°C for 2 h (b). Bar 500 nm

Table 1. Sulfur content and the amount of acidic groups in cellulose microcrystals

Conditions	Sulfur content ^a (mmol/kg)	Amounts of acidic groups ^b (mmol/kg)	
		Strong acid groups	Weak acid groups
Hydrolyzed by H ₂ SO ₄	240	84	26
Hydrolyzed by HCl	2	0	16
Esterified at 40°C	101	53	29
Esterified at 60°C	158	60	28

The results of conductometry for the H₂SO₄-hydrolyzed suspension are from our previous study

^aDetermined by X-ray fluorescence analysis

^bDetermined by conductometric titration

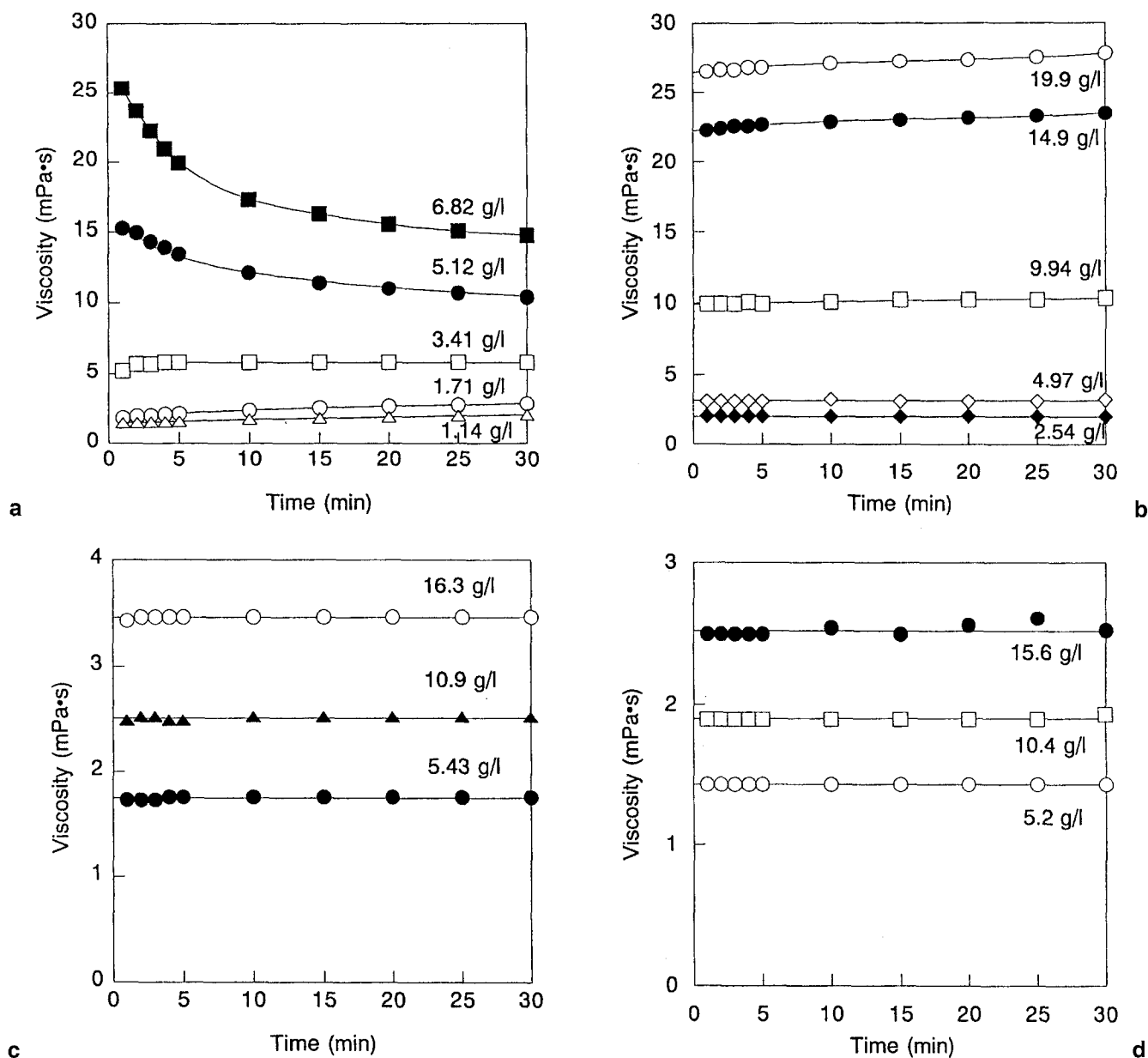


Fig. 2. Time dependence of the viscosity of cellulose microcrystal suspensions. **a** HCl-hydrolyzed suspension. **b** Suspension sulfated at 40°C for 2h. **c** Suspension sulfated at 60°C for 2h. **d** H₂SO₄-hydrolyzed suspension. (a, d, from Araki et al.¹)

time dependence up to solid content of 16.3 g/l and showed nearly the same levels of viscosity as those of the H₂SO₄-hydrolyzed suspension.

Thus the introduction of surface charge by secondary H₂SO₄ treatment drastically alters the viscosity behavior of the suspensions. Thixotropy and antithixotropy in general are considered to result from the disruption and formation, respectively, of aggregates by application of shear.^{11,12} In a previous report we concluded that the time-dependent viscosity of the HCl-hydrolyzed suspension results from the lack of surface charge.¹ The present results show that the secondary introduction of sulfate groups to the microcrystals significantly stabilizes the dispersion of individual microcrystals and removes shear-induced formation or disruption of the aggregates.

Figure 3 shows the volume fraction dependence of the relative viscosity of microcrystalline cellulose suspensions with varied surface charge. The plotted value was the viscosity at 30 min after the start of the measurement. Figure 3, as well as Fig. 2, shows that the viscosity behavior approaches that of the H₂SO₄-hydrolyzed suspension with the increase in surface sulfate content. The inclination of the curve in this graph at $\phi = 0$ is related to the aspect ratio of rod-like particles according to the Einstein-Simha equation.¹³ Because the appearance of particles observed by electron microscopy was the same for the samples examined here, the change in Fig. 3 is believed to result from the difference in the amount of surface charge. Although the two suspensions prepared by esterification at 40°C and 60°C show only a small difference in the amount of surface

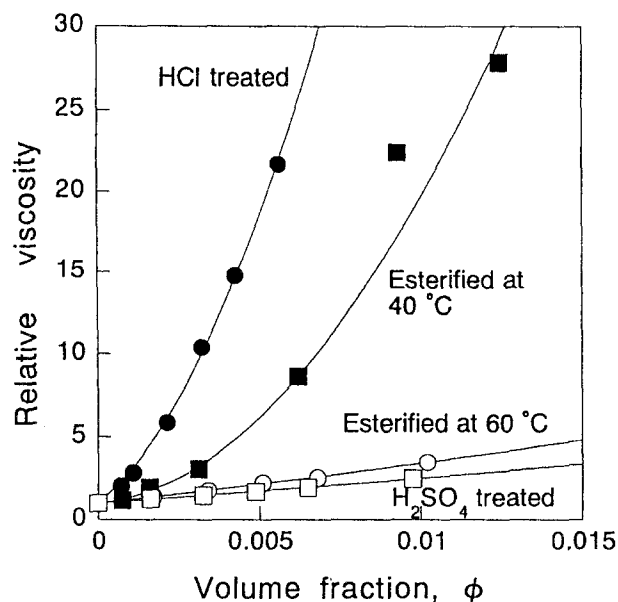


Fig. 3. Relative viscosity of the cellulose suspensions plotted versus volume fraction of cellulose, ϕ

charge (Table 1), their viscosity behavior is drastically different from that of the solid content, which suggests that the viscosity behavior is strongly affected by the surface charge in a range around 50–60 mmol/kg.

Conclusions

The present results, as a whole, show that HCl treatment is effective in preparing microcrystalline cellulose particles, to which the secondary sulfuric acid treatment can introduce sulfate groups as surface charge. To our knowledge no other rod-like particle systems are known whose surface charge can be controlled by preparation conditions, except for chitin crystallites.¹⁴ Our system is the first instance of a rod-like colloidal system having controlled the surface charge from zero to various levels. Because the level of surface

charge drastically alters the viscosity behavior of the system, as described above, this two-step procedure of preparing charged microcrystalline cellulose will be useful in further attempts to elucidate and utilize the colloidal cellulose systems.

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