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Rheology of Carboxymethylcellulose Made from Bacterial Cellulose

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SUMMARY: Partly as a result of the high solution viscosity of bacterial cellulose, carboxymethylcellulose (CMC) derived from this material exhibits shear-thinning and thixotropic properties. With suitable sample treatment, the CMC solution shows gel-like rheology suggesting the presence of a three-dimensional network. This behavior is consistent with heterogeneous substitution of the carboxymethyl functionality on the polymer chains. For comparison, bacterial cellulose is also degraded by either acid or ultrasound to reduce its molecular weight and converted to CMC. The flow behavior of the resulting CMC solutions is nearly Newtonian with slight shear thinning but no thixotropy, suggesting that the carboxymethylation reaction is almost random.

Introduction

It has been known for many years$^{1)}$ that cellulose can be produced by bacteria (e.g., *Acetobacter xylinium*). There have been renewed research activities in recent years$^{2\text{-}9)}$ and some companies have shown commercial interest in this material$^{10\text{-}15)}$. Unfortunately, its relatively high price (in excess of $10 per pound) hinders its widespread use. Whereas this material is of interest in its own right, we believe it may be more useful as a model system for fundamental studies.

One reported feature of bacterial cellulose is its high molecular weight$^{5)}$. It would be of interest to derivatize this bacterial cellulose and study the resulting polymers for their properties. We have chosen to study carboxymethylcellulose (CMC) because it is widely used in food applications as a thickener, water binder, extrusion aid, and film former, among others$^{16,17)}$. In an earlier communication, Cheng and Mital$^{18)}$ have reported the preparation of bacterial cellulose and CMC samples. These samples are extensively studied in this paper together with two samples from Hokkaido University. A particular emphasis is the rheological

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properties of the polymers, which are related to molecular weight, molecular weight distribution, and possible association phenomena.

Experimental

Bacterial cellulose was obtained from ATCC (No. 23769) and grown by the static culture method. CMC was produced by the conventional monochloroacetic acid reaction[16)] as adapted by Geyer, et al[19)]. More details on the procedures can be found elsewhere[18)].

Rheology was measured on a Bohlin CVO rheometer. It is well known in the literature that rheological properties of CMC depend strongly on concentration[17,20)]. For consistency, all samples were prepared as 0.5% aqueous solutions. For each sample, viscosity was obtained as a function of shear rate. The temperature in all cases was kept at 25°C. Cone-and-plate configuration was used.

The size exclusion chromatography (SEC) data were obtained on a set of three TSK columns using 0.10M ammonium phosphate buffer at pH 7.6 as the mobile phase (flow rate, 1.0 ml/min) and 40°C column and detector temperature. The molecular weights were calibrated versus poly(ethylene oxide) narrow molecular weight standards.

Results

1. CMC Samples

The samples used are summarized in Table 1. Sample A is a commercial CMC sample made from chemical cotton with a degree of substitution (DS) of 0.89. Samples B is a typical CMC sample made from bacterial cellulose[18)]. Samples B' and B" are CMC's made from bacterial cellulose prepared at Hokkaido. The DS values are 0.75 – 0.90. Samples C, D, E, and X are samples of CMC prepared from degraded bacterial cellulose as indicated in the table.

Table 1. List of CMC Samples and the Sources of Cellulose

Designation	Source of Cellulose
A	Chemical cotton
B	Bac. cellulose, made at Hercules
B'	Bac. cellulose, Preparation 1, made at Hokkaido
B"	Bac. cellulose, Preparation 2, made at Hokkaido
C	Bac. cellulose, degraded with 2N H_2SO_4
D	Bac. cellulose, degraded with 4N H_2SO_4
E	Bac. cellulose, degraded with 6N H_2SO_4
X	Bac. cellulose, degraded with ultrasound

Figure 1. The viscosity of 0.5% CMC solution derived from chemical cotton (Sample A) at room temperature. Viscosity given as squares, and shear stress as diamonds.

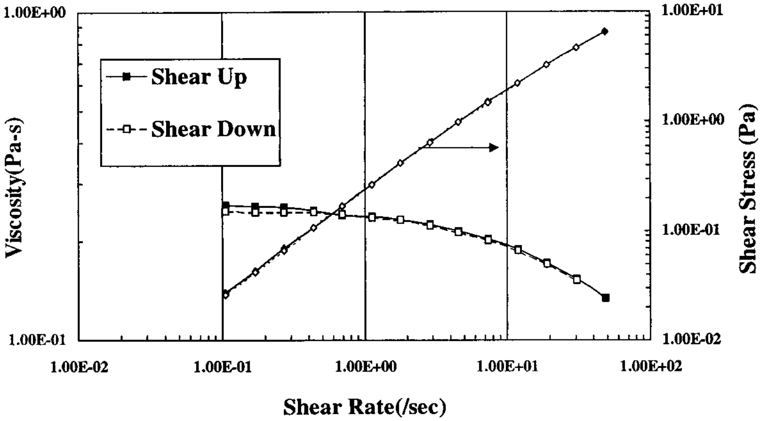


Figure 2. The viscosity function of 0.5% CMC solution made from bacterial cellulose (Sample B) at room temperature.

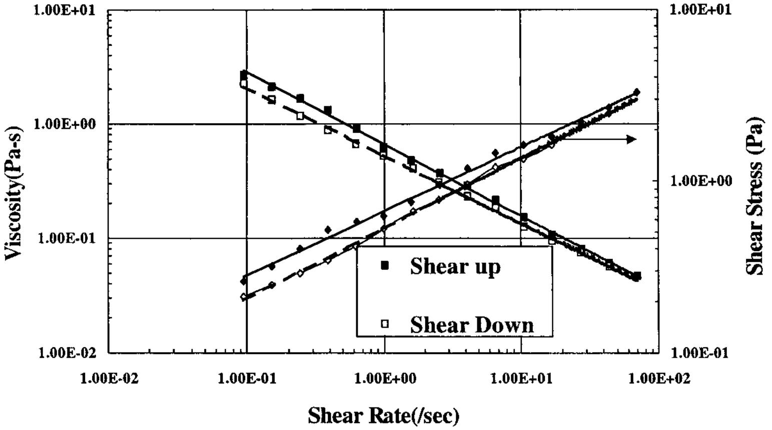


Figure 3. The viscosity function of 0.5% CMC solution made from bacterial cellulose (Sample B') at room temperature.

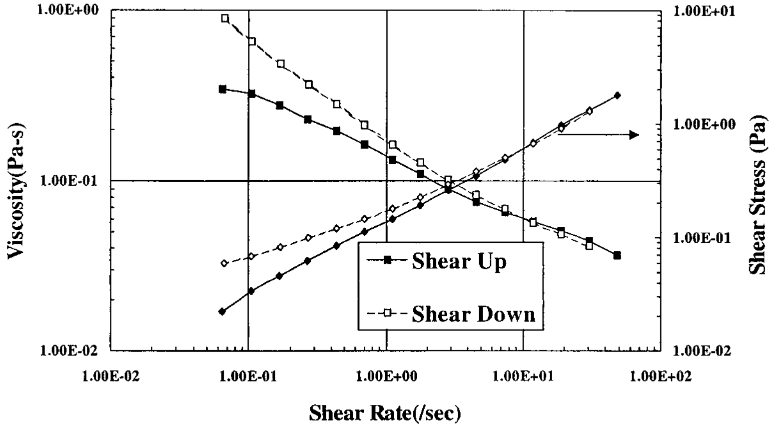


Figure 4. The viscosity function of 0.5% CMC solution made from bacterial cellulose (Sample B") at room temperature.

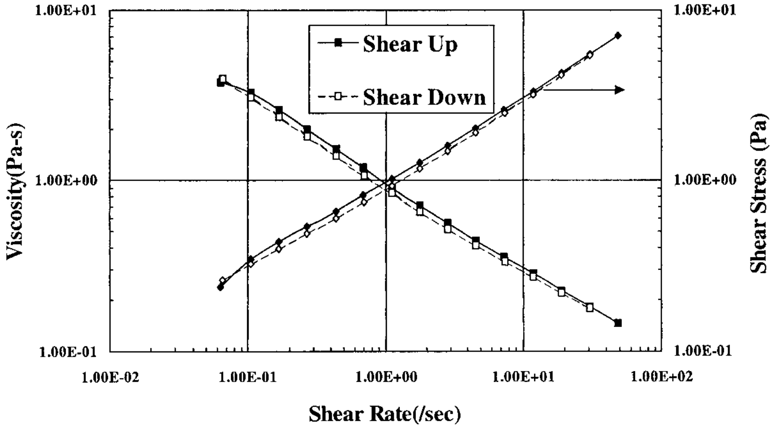


Table 2. Rheology of CMC Solutions (0.5% Concentration)

Sample	Description
A	Some shear thinning is observed. Also, there is a very slight amount of hysteresis indicating the presence of some thixotropy, but the extent is much less than that of the CMC samples made from bacterial cellulose.
B	Much higher viscosity, $\eta_o >> 2000$ mPa.s. Shear thinning observed. Sample also exhibits some thixotropy.
B'	Probably only the water-soluble portion is measured here. $\eta_o \sim 350$ mPa.s at 0.1 s^{-1}. Shear thinning, thixotropy observed.
B"	The rheological behavior of this solution indicates the presence of three-dimensional structure in solution, having gel-like properties. High shear-thinning indicates the breakdown of this structure at high shear rates.
C	Bacterial cellulose degraded in 2N H_2SO_4 and converted to CMC. Probably only the water-soluble portion is measured here. Very low viscosity, $\eta_o \sim 1.2$ mPa.s. Almost Newtonian in flow behavior.
D	Bacterial cellulose degraded in 4N H_2SO_4 and converted to CMC. Probably only the water-soluble portion is measured here. Very low viscosity. $\eta_o \sim 12.5$ mPa.s. Almost Newtonian.
E	Bacterial cellulose degraded in 6N H_2SO_4 and converted to CMC. Fully soluble. Very low viscosity, $\eta_o \sim 1.4$ mPa.s. Almost Newtonian.
X	CMC from ultrasonically degraded bacterial cellulose, $\eta_o \sim 54$ mPa.s. Very slightly shear-thinned. Almost Newtonian in flow behavior.

2. Rheology

Sample A dissolved readily to give a homogeneous solution; its rheology is fairly characteristic of a standard CMC sample (Figure 1). One observation that could be quickly made of the CMC samples derived from bacterial cellulose was the difficulty in dissolution. Samples B and (particularly) B' were only partly dissolved. In fact, when samples B and B' were dried and re-dissolved, part of the samples remained insoluble. For these samples, the rheology data probably only reflect the water-soluble portions of the samples (Figures 2 and 3). Yet it is interesting to note that these samples exhibit strong shear-thinning behavior and thixotropy.

In the case of sample B", the CMC was kept wet after preparation and carefully adjusted to the desired concentration. This sample showed the presence of a networked structure with gel-like properties (Figure 4). The strong shear-thinning behavior was consistent with heterogeneous substitution of the carboxymethyl functionality.

The bacterial cellulose was degraded in either 2N, 4N, or 6N H_2SO_4 and then converted to CMC. The CMC samples derived from 2N and 4N H_2SO_4 degradation also had solubility problems. In Sample C (CMC from 2N acid-degraded cellulose) only 10% re-dissolved in water after drying. In Sample D (CMC from 4N acid-degraded cellulose) only

35% re-dissolved in water after drying. The viscosity of these solutions was very low, reflecting only the water-soluble portions of the samples (Figure 5).

Sample E was made from bacterial cellulose degraded in 6N acid. All of it redissolved after drying, although the solution was somewhat cloudy. Its solution had a low viscosity, $\eta_o \sim 1.4$ mPa.s. The flow behavior was almost Newtonian (Figure 5).

Finally, a sample of bacterial cellulose was degraded via an ultrasonic device (sample X). The degraded cellulose was then converted to CMC. The CMC had a substantial molecular weight, $\eta_o = 54$ mPa.s. It was slightly shear-thinned; however, the flow behavior was almost Newtonian, suggesting that carboxymethylation was almost random (Figure 6). Thus, when the bacterial cellulose has been degraded and derivatized, the CMC insolubility and self-association appear to decrease.

3. Molecular Weight Distribution

For additional information, SEC data were obtained. In many of the CMC samples made from bacterial cellulose, there was a problem with solubility. Sample A (commercial CMC) gave reasonable M_n and M_w for this type of sample. Samples B, B', and B" gave widely different molecular weights. In addition, samples B and B' had very large M_w/M_n; polymer insolubility and/or polymer chain degradation was most likely to be present. Among the degraded samples, C and D were only partly soluble; thus, the SEC results for these two samples were artificial. Samples E and X were soluble, and the SEC results more truly reflected the molecular weight distribution (Table 3).

Table 3. SEC data[a] of CMC Samples

Sample	Comments	M_n	M_w	M_w/M_n
A	commercial CMC, fully soluble	205,000	1,775,000	8.7
B	partly soluble	(31,600)	(456,500)	(14.4)
B'	partly soluble	(94,000)	(1,276,000)	(13.6)
B"	swollen gel	623,000	5,278,000	8.5
C	only 10% soluble	(53,700)	(253,000)	(4.7)
D	only 35% soluble	(78,800)	(892,000)	(11.4)
E	fully soluble	19,000	60,000	3.1
X	fully soluble	24,400	78,560	3.2

[a] Numbers in parentheses reflect only the water-soluble part of the polymers.

Figure 5. The viscosity function of 0.5% solutions, at room temperature, of CMC made from bacterial cellulose that has been degraded by H_2SO_4.

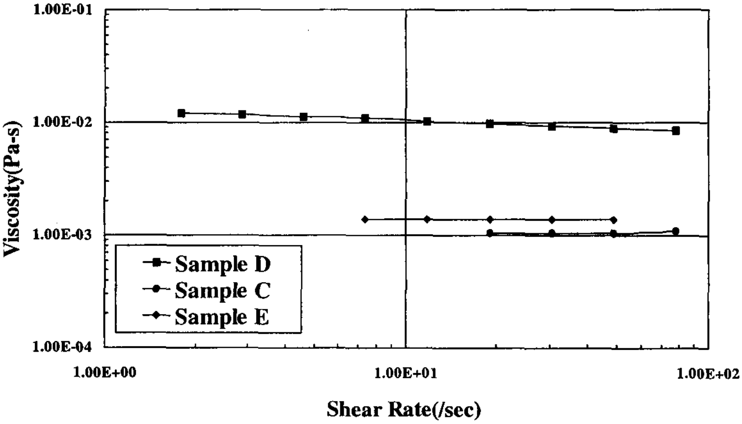
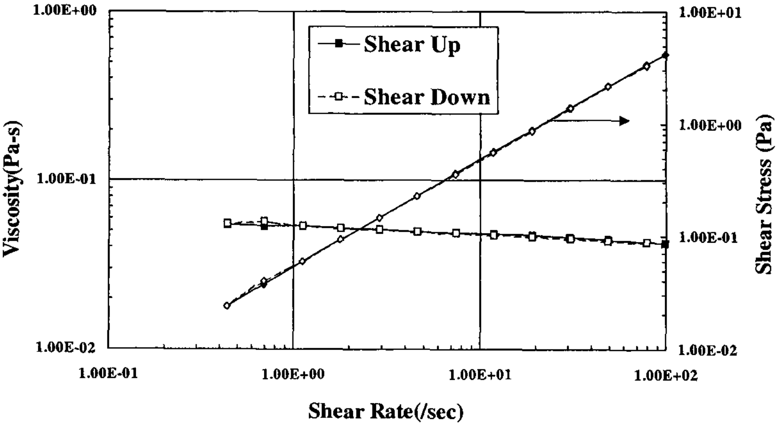


Figure 6. The viscosity function of 0.5% CMC solution, at room temperature, made from bacterial cellulose that has been degraded with ultrasound (Sample X).



Discussion

From the aforementioned data, it is clear that when the molecular weight of bacterial cellulose is very high, the CMC derivatization reaction (alkali cellulose with monochloroacetic acid) becomes highly heterogeneous[21)]. At the DS achieved (0.75 - 0.90) there appear to be long sequences of unsubstituted anhydroglucose units along the polymer chain, leading to strongly shear-thinned and highly thixotropic behavior. In fact, when such a CMC sample is dried, some of the unsubstituted polymer chains aggregate together and render part of the sample insoluble.

An important finding is that when the molecular weight of the bacterial cellulose is lowered, either by acid or by ultrasound, the CMC derivatization reaction becomes homogeneous (leading to soluble polymers and Newtonian rheology).

The rheology results are consistent with the earlier hypothesis[18)]. During the preparation of CMC because of the high solution viscosity of bacterial cellulose the cellulose chain are still in close proximity to each other, separated by Na^+ ions. Thus, the diffusion of monochloroacetate in the immediate neighborhood of the cellulose chains is hindered. However, once carboxymethylation takes place in one location of the chain, subsequent reactions in its immediate neighborhood are facilitated, thereby leading to heterogeneously substituted CMC. When the molecular weight of bacterial cellulose is decreased, the local cellulose chain viscosity also decreases, leading to greater access of monochloroacetate and more uniformly substituted CMC samples.

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[21] The results shown here differed from the previous findings of Geyer, et al.[19] This difference may be due to the higher molecular weight of our bacterial cellulose and also the lower DS value of the CMC (0.75 – 0.90 for our CMC samples versus 1.3 for the CMC prepared by Geyer, et al.). Process variations may also contribute to this difference.