Structural Change of Alginate Hydrogel Fibres in the Presence of Water

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Abstract: Calcium alginate hydrogel fibres prepared by wet spinning were investigated by polarizing light microscopy and differential scanning calorimetry. Alginate molecules aligned in the direction of the fibre axis in the presence of bulk-like water. However, a disordered structure was formed following the evaporation of water. It was found that the order-disorder transformation was reversible by sorbing and desorbing water in the fibres.

1. Introduction

Alginic acid is a copolysaccharide extracted from brown masse algae, consisting of D-mannuronic acid and L-guluronic acid. The chemical structures of 1, 4-linked β-D-mannuronic acid (M), 1, 4-linked α-L-guluronic acid (G) and a representative copolymer (G-G-M-M) are shown in Fig. 1. M blocks form a flat ribbon-like structure. G blocks form a buckled ribbon-like structure via intra-molecular hydrogen bonds between the carboxyl group and the hydroxyl group attached to C2 of the next G unit. Owing to this structure, G blocks coordinate divalent cations such as Ca\(^{2+}\). It is believed that junction zones in alginate hydrogels form an ‘egg-box structure’, where Ca\(^{2+}\) ions are enclosed by alginate molecules. Support for this model comes from the fact that a tough gel, containing a large proportion of junction zones, is formed in G-component rich alginates.

Ca alginate hydrogel fibres prepared by wet spinning are investigated by polarizing light microscopy and differential scanning calorimetry in an attempt to obtain a more complete understanding of the nature of alginate fibres as well as the effect of varying the concentration of guluronic units on the fibre structure.

2. Experimental

2.1 Sample Preparation

Sodium alginate (NaAlg) in powder form (60 mesh) was obtained from Kibun Chemifar Co. The viscosity, structure [1]. G blocks form a buckled ribbon-like structure via intra-molecular hydrogen bonds between the carboxyl group and the hydroxyl group attached to C2 of the next G unit [2]. Owing to this structure, G blocks coordinate divalent cations such as Ca\(^{2+}\). It is believed that junction zones in alginate hydrogels form an "egg-box structure", where Ca\(^{2+}\) ions are enclosed by alginate molecules [3]. Support for this model comes from the fact that a tough gel, containing a large proportion of junction zones, is formed in G-component rich alginates.

<table>
<thead>
<tr>
<th>Sample</th>
<th>500G</th>
<th>150G</th>
<th>45G</th>
<th>500M</th>
<th>150M</th>
<th>45M</th>
</tr>
</thead>
<tbody>
<tr>
<td>Viscosity</td>
<td>0.53 (^{a} )</td>
<td>0.14 (^{b} )</td>
<td>0.050 (^{b} )</td>
<td>0.550 (^{a} )</td>
<td>0.175 (^{b} )</td>
<td>0.049 (^{b} )</td>
</tr>
<tr>
<td>M/G ratio</td>
<td>0.21</td>
<td>0.20</td>
<td>0.19</td>
<td>0.88</td>
<td>1.13</td>
<td>1.0</td>
</tr>
<tr>
<td>pH</td>
<td>6.6</td>
<td>6.6</td>
<td>6.9</td>
<td>6.7</td>
<td>6.7</td>
<td>6.8</td>
</tr>
</tbody>
</table>

\(^{a} \) Measured at shear rate = 8.55 s\(^{-1}\).
\(^{b} \) Measured at shear rate = 17.10 s\(^{-1}\).
M/G ratio, and pH of each sample are listed in Table 1. The concentration of heavy metals in the samples was less than 20 ppm and that of arsenic was less than 2 ppm. Powder samples were solved in deionized water at 293 K to obtain a 1 wt% solution. The solution was equilibrated at 293 K for 24 h, and then injected into an excess amount of 0.5% CaCl₂ aqueous solution using a 1 mL syringe. Transparent, flexible fibres formed immediately. The samples were wrapped in Whatman No.2 filter paper, inserted into a glass column, 50 cm long, and 0.5% CaCl₂ solution was continuously passed through the column for 48 h. In this way the Na⁺ ions in the fibres were exchanged by Ca²⁺ cations. The fibres were kept in deionized water at 293 K until the measurement. Never-dried samples were used for all measurements. The water contents \( W_c = (\text{grams of water}) / (\text{gram of dry sample}) \) of the samples were determined as previously reported.

2.2 Measurements

A Leitz Orthoplan Pol polarizing light microscope equipped with a camera was used at 293 K. Never-dried single fibres were placed on a glass slide, excess water was added and a cover glass was placed over the fully hydrated fibre.

A Perkin Elmer differential scanning calorimeter DSC equipped with a cooling apparatus was used to measure the phase transitions of the water species in the sample. Temperature and enthalpy calibrations were carried out using chromatographic grade cyclohexane. The scanning rate was 10 K/min, over a temperature range of 290-150 K. The sample weight was 1-2 mg and aluminum hermetically-sealed sample-vessels were used. No weight loss was recorded over the measuring interval. Dried helium was used as a purge gas. A Sartorius ultra micro-balance (± 0.1 μg) was used for sample weight measurements.

3. Results and Discussion

Fig. 2 shows representative polarizing light micrographs of never-dried Ca alginate fibres in an excess amount of water. The samples were observed under the crossed nicol condition with a color sensitive plate ( retardation; \( R=530 \text{ nm} \)). When the sample was observed from the camera position (eye piece position), the analyzer was in \( y \) direction and the polarizer was in \( x \) direction. Retarded polarized light axis (\( Z' \)) is pararell to fibre axis in photographs I -a, II -a, III -a in Fig. 2. Photographs I -b, II -b, and III -b show the samples rotated 90° from the original position. The color change shown in Fig.2 indicates that the structure of alginate fibres is optical positive.

It is clearly seen that alginate molecules align in the direction of the fibre axis. All of the samples listed in Table 1 showed similar behavior, although the color was more intense in G-rich and low molecular weight samples. When the fibres were maintained under ambient conditions the color faded with evaporation of water, completely disappearing 5 min after the surface water was removed. The color reappeared when the fibre was rehydrated. This suggests that alginate molecules align unidirectionally in the presence of a sufficient amount of water, and that the order to disorder transformation is reversible.

In order to determine the amount of water in the sample which shows this transformation, the phase transitions of water in the sample were measured by DSC. Fig. 3 presents DSC curves of water in Ca alginate with \( W_c \) of 24.1 g/g (Curves I-a and I-b) and 18.4 g/g (Curves II-a and II-b).
Fig. 3 DSC curves of water in Ca alginate fibres (45G): Water contents, (I) 24.1 g/g; (II) 18.4 g/g.

(I-a and II-b). Sample I was sealed in a sample vessel immediately after removing the surface water, and sample II after 5 min drying at 293 K. As illustrated in Fig. 3, the crystallization peak of sample II observed at 264 K (Curve II-a) is broader than that of sample I at 264.5 K (Curve I-a). Melting peaks also indicate that water in sample II is more tightly bound. As reported previously, the non-freezing water content of Ca alginate is ±0.4-0.7 g/g, depending on the M/G ratio and the molecular weight (5,6). Therefore almost all of the water in the fibres with water content between 18-24 g/g can be categorized as bulk-like water showing the first-order phase transition. It is clear that a large amount of bulk-like water is retained in these fibres and that molecular alignment is affected by this water.

References