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Swelling behaviour of calcium pectin hydrogels by thermomechanical analysis in water

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Abstract

Aqueous solutions of pectin annealed at various temperatures at sol state were mixed with $CaCl_2$ solution and calcium pectin gels with various cross-linking ratios were prepared. A thermomechanical analyser (TMA) equipped with a sample holder, which was newly designed at our laboratory was used. The sample holder was immersed in water whose temperature was controlled from 30 to 80 °C. Swelling behaviour of hydrogels during equilibration was measured as a function of immersing time. Creep coefficient was calculated as functions of time and temperature using a compression type probe. The creep coefficient of hydrogels increased with increasing swelling temperature and decreased with increasing cross-linking ratio. Dynamic modulus (E') was measured in water in a temperature range from 30 to 60 °C. E' of the gel with cross-linking ratio 0.36 decreased from 5.5×10^4 to 3.5×10^4 Pa with increasing swelling temperature from 30 to 60 °C.

Keywords: Pectin; Thermomechanical analysis; Hydrogels; Swelling behaviour; Dynamic modulus

1. Introduction

A large number of water-soluble polysaccharides are known to form physical gels in aqueous media. The gelation ability of each polysaccharide depends on various factors, such as chemical structure, higher order structure and gelation conditions. We have reported that gellan gum forms rigid gels when it is annealed at a temperature higher than gel–sol transition [1,2]. Although xanthan gum and hyaluronan have been considered as non-gelling polysaccharides, it was found that gels are formed when they are fully annealed in the sol state [3–5].

Pectin is a polysaccharide found in many plant tissues. It consists of galacturonic acid having some carboxyl groups, which are esterified by methyl groups [6–9]. When the degree of methyl esterification (DE) of pectins is low, pectin molecules react with divalent cations and hydrogels are easily formed [10,11]. The gelation mechanism of polyguluronic acid of alginate has mainly been explained by the "egg-box" model. The gelation of low methoxyl pectin is also explained in the same mechanism [12,13]. We have reported that calcium pectin hydrogels, which were prepared after annealing at sol state forms a greater number of soft gels than non-annealed gels [14]. When pectin sol was annealed at a temperature higher than 50 °C, Ca pectin hydrogels formed more soft gels than those annealed at low temperature. The swelling ratio measured by tea-bag method decreased with increasing annealing temperature at sol state. The above fact indicates that the effect of annealing temperature at sol state affects the higher order structure of pectin molecular assembly, which can be fixed by Ca ion.

Mechanical properties of hydrogels have mainly been investigated by viscoelastic measurement using a rheometer

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[15–17]. Even when the gel is rigid, mechanical testing of hydrogels using a custom made machine is limited, since the gel frame is frequently destroyed by cramping. Furthermore, vaporization of water during measurements is neglected in the above method. In our previous study, we introduced a thermomechanical analyser (TMA) to measure dynamic modulus of hydrogels in water [18,19]. By TMA, both static and dynamic mechanical properties of hydrogels in water can be measured [18]. Dynamic viscoelasticity measured by TMA covers dynamic modulus range from 10^4 to 10^5 Pa. Although dynamic viscoelastic properties can be measured using a conventional dynamic mechanical analyser (solid state) and a rheometer (liquid state), it is difficult to measure the values shown in the above dynamic modulus range. In our previous study [18,19], it was suggested that TMA is appropriate in measuring viscoelastic properties of ionically linked hydrogels, such as pectin or alginate. By introduction of a new sample probe, it is possible to measure the hydrogels in water and other solvents.

In this study, TMA equipped with a sample holder, which was newly designed at our laboratory was used. Creep coefficient is calculated as functions of time and temperature using a compression type probe. Dynamic modulus is measured at various temperatures. The Ca pectin gel formation mechanism was investigated.

2. Experimental

2.1. Sample preparation

Pectin with the degree of methylesterification (DE) = 25.6% was obtained from Taiyo Kagaku Co., Japan. Molecular weight calculated from viscosity measurement was 8.5×10^4 [20]. Pectin was solved in deionised water at 25 °C to obtain 2% solutions. The solutions were stirred at 25, 50, 80 and 98 °C for 180 min. An aqueous solution of calcium chloride ($CaCl_2$) 2.28% was poured into an aqueous solution of pectin in a 20 ml glass container and mixed at 25 °C. Transparent and flexible gels were formed immediately. The pectin concentration of samples at this stage was 1.7%. After stirring, samples were maintained at room temperature for 24 h in order to complete the substitution.

Quantitative analysis of Ca in Ca pectin gel was carried out by atomic absorption spectrometer (Shimadzu AA-630-01). The degree of substitution (DS) of the Ca pectin gel was obtained using the measured concentration of Ca ion in the sample and calculated value assuming 100% substitution. In this case, all COOH is assumed to be substituted by Ca ions.

$$\mathrm{DS} = \frac{\text{measured value of Ca}}{\text{calculated value of Ca}} \times (1 - \mathrm{DE}) \qquad (1)$$

Equilibrium DS values decreased with increasing annealing temperature at sol state. DS was 0.423, 0.381, 0.355 and 0.311 at annealing temperature at sol state 25, 50, 80 and 98 °C, respectively [14].

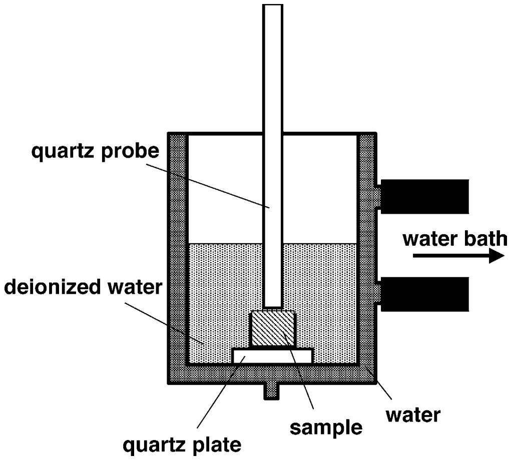

Fig. 1. Schematic conformation of TMA sample probe.

2.2. Measurements

A Seiko thermomechanical analyser (TMA, Seiko Instruments TMA/SS 150) equipped with a newly designed sample holder was used. Quartz rod with uniform cross-sectional area (9.616×10^{-6} m^2) was used as a probe. Sample setting in the probe is illustrated in Fig. 1. The sample holder was immersed in water whose temperature was controlled from 30 to 80 °C by circulation of water from a constant temperature bath (HAAKE F8). In this stage, errors of water temperature were within ±1 °C. The gel sample was placed in a quartz sample pan with diameter 7 mm (inner diameter) and height 5 mm and immersed in 70 ml water. And the sample was compressed by quartz probe. Swelling behaviour by creep measurement and dynamic modulus was calculated.

2.2.1. Swelling behaviour by creep measurement

Creep measurements were carried out as follows:

(1) the sample was compressed in water (at 30–60 °C),
(2) applied maximum stress was varied from 1.04×10^3 to 5.2×10^3 Pa,
(3) initial sample length decreased until applied load reached predetermined stress and then the load was maintained at constant,
(4) compressed height at a constant load was measured as a function of time and
(5) measurement was completed in 60 min.

The compression was expressed by negative value. Creep coefficient was calculated as functions of time and temperature using a compression type probe. Sample compression during equilibration was measured as a function of immersing time. Creep coefficient function of time ($(l_e - l_c)/l_0 t$) calculated.

2.2.2. Dynamic measurement

Dynamic measurements were carried in water at 30–60 °C by using a quartz rod probe. The probe was the same as that