Journal of Thermal Analysis and Calorimetry, Vol. 64 (2001) 617–627

THERMOMECHANICAL ANALYSIS OF POLYSACCHARIDE HYDROGELS IN WATER

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Abstract

Application of thermomechanometry to the measurement of hydrogels containing a large amount of water was carried out by static and dynamic methods. A thermomechanical analyzer (TMA) equipped with a quartz compression probe immersed in water was used. Polysaccharide hydrogels containing ca 98% water were measured. Creep of hydrogels in water was analyzed in a stress range from $1.04\cdot10^3$ to $5.2\cdot10^3$ Pa and loading rate from $0.3\cdot10^3$ to $3.0\cdot10^3$ Pa min^{-1}. Stress relaxation was measured in compressed ratio range from 0.02 to 0.45 m m^{-1} and in compressing rate was 0.09 to 0.15 m m^{-1} min^{-1}. Dynamic viscoelasticity was measured by TMA when dynamic Young's modulus which was larger than $1\cdot10^4$ Pa in frequencies ranging from 0.02~0.2 Hz.

Keywords: creep, hydrogels, stress relaxation, TMA, viscoelasticity, water

Introduction

Hydrogels usually contain 95 to 99.5% water. Mechanical properties of hydrogels have mainly been investigated by viscoelastic measurement using a cone-plate or plate-plate type rheometer. The dynamic storage modulus and dynamic loss modulus are obtained as functions of temperature and frequency [1–3]. Static mechanical properties of hydrogels have been measured using a stress strain testing machine. Even when the gel is rigid, mechanical testing of hydrogels using a custom made machine has limiting, since the gel frame is frequently destroyed by cramping. In our previous study, we introduced a special sample cell attached to a thermomechanical analyzer (TMA) in order to measure the swelling behaviour of gel films [4]. Using this sample cell, the thickness of the gel could be recorded as a function of time at a constant load, immediately after water was introduced in the sample cell. The master curve of equilibrium swelling was obtained by dynamic swelling and accorded well with the results obtained under static measurements. The above results suggest that

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1418–2874/2001/ $ 5.00

Akadémiai Kiadó, Budapest
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TMA have a potential to analyze the samples containing a large amount of water, such as polysaccharide hydrogels.

A large variety of polysaccharides are known to form physical gels. There are either thermoreversible, such as gellan gum [5–7], agarose [8, 9], carraggeenan [10] or thermoirreversible, such as alginic acid [11–13], pectin [11, 12, 14] and carboxymethylcellulose [15]. In this study, static and dynamic mechanical properties of hydrogels in water are studied by TMA. In order to obtain reliable results, experimental conditions are precisely examined.

Experimental

Sample preparation

Pectin, as a representative ionic crosslinking gel [11, 12, 14], and gellan gum, as a representative physical crosslinking gel [5–7], were used in this study. The chemical structure of both polysaccharides is shown in Fig. 1.

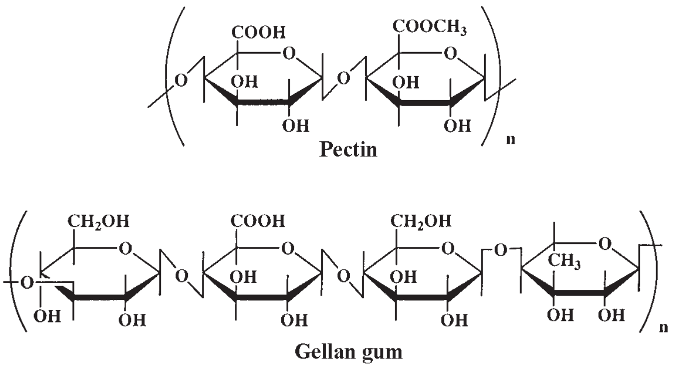

Fig. 1 Chemical structures of pectin and gellan gum

Pectin with the degree of methylesterification (DE)=25.6% was obtained from Taiyo Kagaku Co. Japan. Molecular mass calculated from viscosity measurement was $8.5\cdot10^4$ [16, 17]. Gellan gum was obtained from Sanei Chemical Co. Osaka, Japan. Characterization were reported elsewhere [18].

Pectin gel was prepared as follows. Powder samples were solved in deionized water at 25°C. The solutions were stirred at 80°C for 3 h. An aqueous solution of calcium chloride ($CaCl_2$) (2.3 mass%) was poured to an aqueous solution of pectin in a 20 ml glass container and mixed at 25°C. Transparent, flexible gels were formed immediately. Pectin concentration of samples at this stage was 1.7%. After stirring the glass container, samples were maintained at room temperature for 24 h in order to complete the substitution. The $CaCl_2$/pectin ratio was calculated according to the following equation.

$$CaCl_2/\mathrm{Pectin}=(\mathrm{mass\ of\ }CaCl_2)/(\mathrm{mass\ of\ pectin})\ (\mathrm{g\ g}^{-1}) \qquad (1)$$

The gels were desalted by dialysis in flowing water for 24 h. The mass of gel was calculated before and after dialysis. Gel samples were used for TMA measurements after equilibrated sufficiently in water. Water contents (W_c) of the samples were calculated according to the following equation [19].

$$W_c=(\text{mass of water})/(\text{mass of dry gel})\ (\text{g g}^{-1}) \qquad (2)$$

The mass of the dry sample was obtained by annealing the samples at 120°C for 3 h. A Sartorius micro-balance (MC210S, $\pm 0.1\cdot 10^{-4}$ g) was used for sample mass measurements.

Gellation of gellan gum was carried out as follows; gellan gum powder was dissolved in water at 25°C, annealed at 105°C for 10 min and was maintained at 25°C for one day. Transparent and flexible gels were obtained.

Measurements

A Seiko thermomechanical analyzer TMA 150 was used. Quartz rod with uniform cross-sectional area ($9.616\cdot 10^{-6}$ m^2) was used as a probe. The gel sample was placed in an aluminium sample pan with diameter 7 mm and height 3 mm (open type sample pan for a differential scanning calorimeter procured by Perkin Elmer) and immersed in water. The gel was immersed in water to prevent evaporation from the gel during the measurement. Sample setting in the probe is illustrated in Fig. 2.

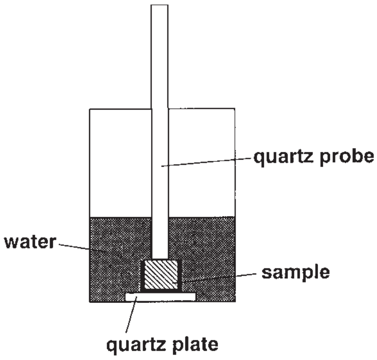

Fig. 2 Schematic conformation of TMA sample probe

Creep

Creep measurements were carried out as follows. (1) The sample was compressed in water (temperature was 25°C) at various compressed stress (σ) and loading rates. (2) The applied maximum load varied from 10 to 50 mN and loading rate varied from $0.3\cdot 10^3$ to $3.0\cdot 10^3$ Pa min^{-1}. (3) The initial sample length decreased until applied load reached predetermined stress and then the load was maintained constant. (4) Compressed height at a constant load was measured as a function of time, (5) measurement was completed at 60 min. The compression was expressed by negative.

Stress relaxation

Stress relaxation measurements were carried out as follows. (1) The sample was compressed in water (temperature was 25°C) at various compressing ratio (0.02 to 0.45 m m^{-1}) and compressing rates (0.09 to 0.15 m m^{-1} min^{-1}). The length was normalized by initial length (2). After length reached predetermined value, the length of the sample was maintained constant (3). Variation of applied stress at a constant sample length was measured as a function of time, (4) The time of measurement was 60 min.

Dynamic measurements

Dynamic measurements were carried out in water at 25°C by using a quartz rod probe. The probe was the same as used in creep and relaxation measurements. Operating frequency was varied 0.01~0.2 Hz. Stress at the initial length (ca $2.0\cdot10^{-3}$ m) was $1.04\cdot10^{3}$ Pa. Measurements were carried out for 5 min. The above conditions were employed for all measurements to facilitate comparison of the variation in E' as a function of frequency.

Results and discussion

Figure 3 shows the schematic TMA curves of creep of hydrogel in water at 25°C, where t – time (min), t_c – time reached predetermined stress (min), t_e – time when sample length reached a constant value (min), l_0 – initial length (m) , l – length as a function of time (m), l_c – length at t_c (m), l_e – length at t_e (m) and σ; applied stress (Pa) as a function of time, respectively. Accordingly, loading rate is σ_i/t_c (Pa min^{-1}). When the sample is not well equilibrated in water, water was adsorbed during measurements and l increases gradually for a characteristic time. As stated in the experimental

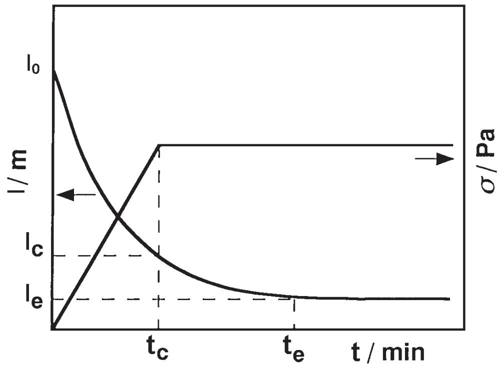

Fig. 3 Schematic TMA curves of creep of hydrogel in water at 25°C. t – time (min), t_c – time reached predetermined stress (min), t_e – time when length reached constant (min), l_0 – initial length (m), l – length as a function of time (m), l_c – length at t_c, l_e – length at t_e (m), σ – applied stress as a function of time (Pa),

section, gel samples were immersed in water for a sufficiently long time for equilibration and then measured.

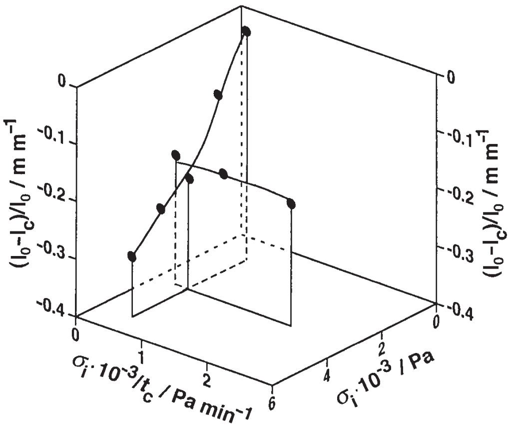

Fig. 4 Relationships between elongated lengh $(l_0–l_c)/l_0$, m m^{-1}, applied stress σ_i (Pa) and loading rate σ_i/t_c (Pa min^{-1}) of pectin hydrogels in water at 25°C

Figure 4 shows the relationship between compressed length by loading $(l_0–l_c)/l_0$ (m m^{-1}), loaded stress, σ_i (Pa), and loading rate, σ_i/t_c (Pa min^{-1}) of pectin hydrogel in water at 25°C. The length of samples was normalized by initial length. The loading rate was varied from $3.12\cdot10^2$ to $2.08\cdot10^3$ (Pa min^{-1}). Applied stress was varied from $1.04\cdot10^3$ to $5.2\cdot10^3$ Pa. As shown in Fig. 4, loading rate (σ_i/t_c) scarcely affects $(l_0–l_c)/l_0$ values. However, $(l_0–l_c)/l_0$ increases (compression is expressed in negative number) linearly with increasing applied stress.

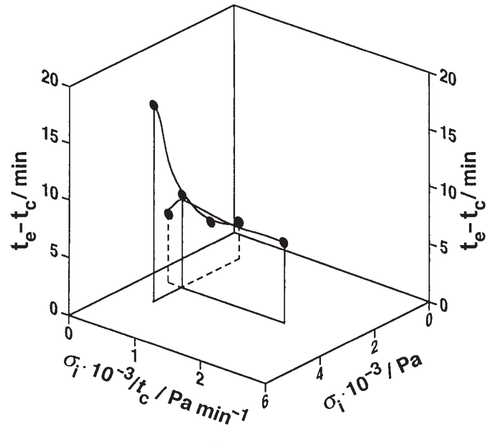

Fig. 5 Relationships between $t_e–t_c$ (min^{-1}), applied stress σ_i (Pa) and loading rate σ_i/t_c (Pa min^{-1}) of pectin hydrogels in water at 25°C

Figure 5 shows three dimensional diagram of time required to attain the equilibrium condition, $t_e–t_c$ (min), as functions of loading rate σ_i/t_c (Pa min^{-1}) and loaded stress σ_i (Pa). $t_e–t_c$ depends on applied stress not loading rate.

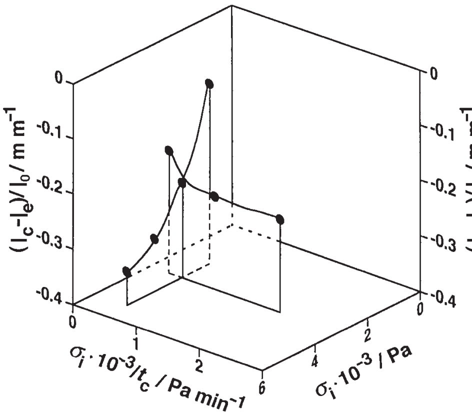

Fig. 6 Relationships between elongated length $(l_c–l_e)/l_0$ (m m^{-1}), applied stress σ_i (Pa) and loading rate σ_i/t_c (Pa min^{-1}) of pectin hydrogels in water at 25°C

Figure 6 shows the relationship between elongated length $(l_c–l_e)/l_0$ (m m^{-1}) loading rate σ_i/t_c (Pa min^{-1}) and loaded stress σ_i (Pa) of pectin hydrogels in water at 25°C. The value of $(l_c–l_e)/l_0$ depends on applied stress not loading rate.

The above results of creep measurements indicate that hydrogels linearly deform as a function of applied stress. The effect of the loading rate is negligible. However, retardation of creep almost linearly depends on applied stress. The similar experiments were tried to carry out for gellan gum hydrogels. However, dimension of gellan gum hydrogels in water was not stable, on this account reliable data could not be obtained.

Figure 7 shows a schematic stress relaxation curve of a hydrogel in water measured by TMA. In this case, applied compression length $(l_c–l_i)/l_0$ was predetermined from 0.02 to 0.45 m m^{-1}, and stress (σ) under the constant compressed length was recorded as a function of time. The stress immediately after $(l_c–l_i)/l_0$ reached the predetermined value defined as σ_c. The required time to attain σ_c is defined as t_c. The value of σ_e is the stress at t_e where σ was supposed to reach equilibrium. The dotted line shown in Fig. 7 indicates that stress relaxation is terminated at t_e. However, when the compressed ratio is small, σ gradually increases in this experiment as shown in the real line, i.e. the stress increases after reaching the minimum relaxation point at time t_e, and continuously increases until a characteristic time. Concerning this, it will be discussed in the latter section.

Figure 8 shows the three-dimensional diagram between σ_i, compressing rate $(l_c–l_i)/l_0t_c$ (m m^{-1} min^{-1}) and compressed ratio $(l_{c0}–l_i)/l_0$. Compressing rate dependency on σ_c is negligible. However, σ_c increases with increasing compressing length. It was

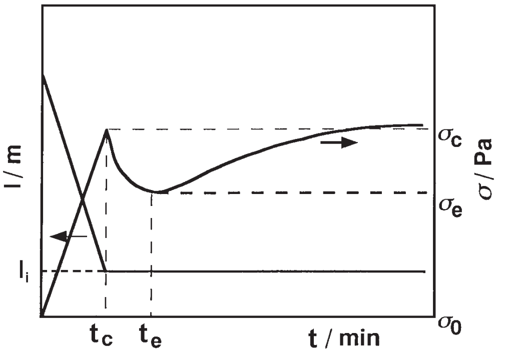

Fig. 7 Schematic TMA curves of stress relaxation of hydrogel in water at 25°C
t – time (min), t_c – time reached predetermined length (min), t_e – time when applied stress reached constant (min), l – length as a function of time (m), l_i – predetermined length (m), σ_c – stress at t_c (Pa), σ_e – stress at t_e (Pa)

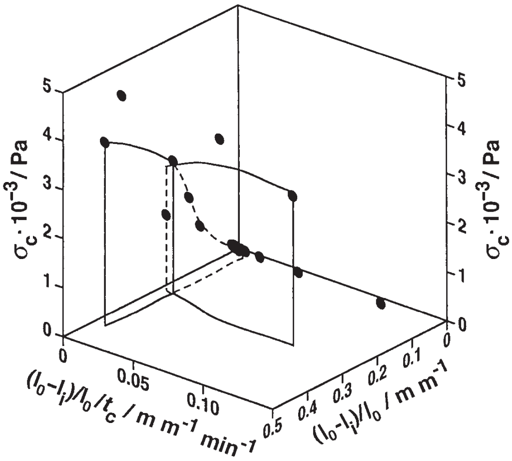

Fig. 8 Relationships between stress at t_c (min) σ_c (Pa), $(l_0-l_i)/l_0/t_c$ (m m^{-1} min^{-1}) and $(l_0-l_i)/l_0$ (m m^{-1}) of pectin hydrogels in water at 25°C

found that the sample length completely recovers if the compressing length is less than 0.5 (50% of initial length) for the samples employed in this study.

Figure 9 shows a relationship between time required to the minimum stress. The value of (t_e-t_c) (Fig. 7), and compressing rate $(l_c-l_i)/l_0t_c$ (m m^{-1} min^{-1}). It is clear that values of (t_e-t_c) increases with increasing compressing rate in a broad range.

Figure 10 shows relationship between relaxed stress, $\sigma_c-\sigma_e$ (Fig. 7) compressed ratio $(l_c-l_i)/l_0$ (m m^{-1} min^{-1}). It is clear that relaxed stress, $\sigma_c-\sigma_e$, increases with increasing compressed ratio in a broad range. Effect of compressing rate on $\sigma_c-\sigma_e$ was examined at 0.03 and 0.2 m m^{-1} min^{-1}, however, rate dependency was negligible, although obtained data was slightly scattered.

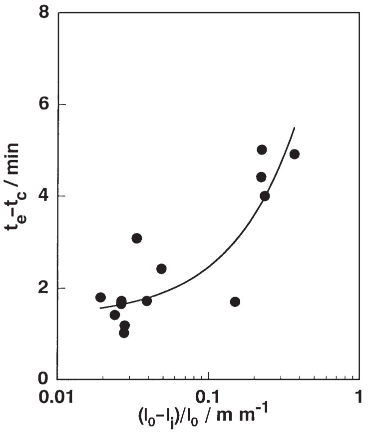

Fig. 9 Relationship between, t_e–t_c (min) and compressed ratio, $(l_0–l_i)/l_0$ (m m^{-1}) of pectin hydrogels in water at 25°C

Figure 11 shows schematic oscillation curves of applied force and deformation. Lissajous diagram, which is shown in the upper left corner, can be obtained from oscillation curves. Dynamic Young's modulus (E'), dynamic loss modulus (E'') and tanδ are calculated from Lissajous diagram using the following equations.

$$|E^*|=(1/A)(F_1/L_1) \tag{3}$$

$$E''=(1/A)(F_2/L_1) \tag{4}$$

$$\sin\delta=F_2/F_1 \tag{5}$$

$$E'=|E^*|\cos\delta \tag{6}$$

$$\tan\delta=E''/E' \tag{7}$$

where $|E^*|$ is complex modulus, E' dynamic modulus, E'' is dynamic loss modulus and A is cross sectional area of the sample ($9.616\cdot10^{-6}$ m^2). Other symbols are shown in Fig. 11. In this experiment, frequency was varied from 0.02 to 2.0 Hz. However, reliable data could be obtained at a frequency less than 0.2 Hz. Measurements were carried out for 5 min under applied stress at $1.04\cdot10^3$ Pa and compressed length of 0.05 m m^{-1} in water at 25°C. Under the above conditions, oscillation of pectin hydrogels taken at the frequency of 0.05 Hz showed good repeatability, i.e. the same oscillation cycles could be maintained for a longer time than the other frequencies.

Figure 12 shows frequency dependency of E' of pectin hydrogels at 25°C. E' values are maintained at a constant value although data scatter slightly. E' is $1.5\cdot10^4$ Pa. Values of tanδ were ca 0.4, although data was not shown in Fig. 12. Dynamic rigidity measured by cone-plate type rheometer is reported $1\cdot10^2$ to 10^3 Pa. It is known that E' of the gel is constant regardless of frequency [20]. The result obtained in this figure proves that the sample is in a gel state. When the sample is homogeneous, $G'=3E'$ can be adopted. The reported G' values reported in many hydrogels are lower than

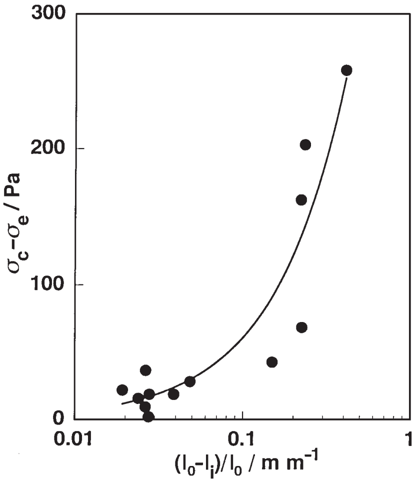

Fig. 10 Relationship between, $\sigma_c-\sigma_e$ (Pa) and compressed ratio, $(l_0-l_i)/l_0$ (m m^{-1}) of pectin hydrogels in water at 25°C

that obtained in this experiment. This suggests that TMA is advantageous to measure dynamic viscoelastic data of rigid gels, although frequency range is very narrow compared with that of cone-plate type rheometer.

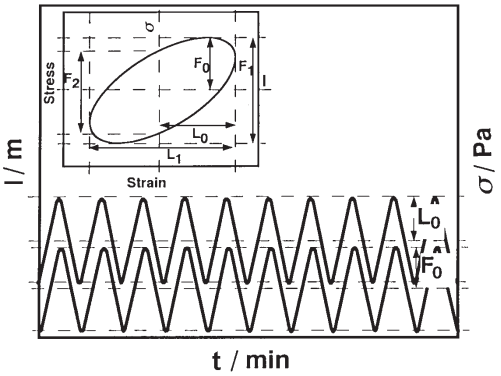

Fig. 11 Schematic TMA curves of hydrogel applied sinusoidal oscillation in water at 25°C. Load and compressed length=constant. Upper left shows Lissajous diagram

In this study it is attempted to investigate the potential of TMA to measure the hydrogels containing a large amount of water by static and dynamic methods. By static measurements, creep and stress relaxation phenomena of hydrogels in water are successfully analyzed, if measurement conditions are carefully chosen. Dynamic viscoelasticity is able to be measured by TMA when dynamic Young's modulus is larger then $1\cdot10^4$ Pa. Applied stress and strain were completely recovered for pectin hydrogels which are corsslinked via Ca ions. In contrast, difficulties caused by the

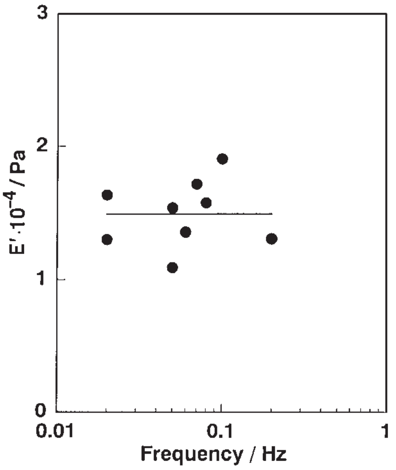

Fig. 12 Relationships between dynamic modulus, *E′* (Pa) and applied frequency (Hz)

nature of gelling materials occured for TMA measurement. Physical gels, the junction of which is formed by coaggregation of molecular chains, such as gellan, is not a suitable sample for TMA in water, since the size and the number of the junction zone vary during the measurement. Among physical gels, stable gels crosslinked by ionic linkage was applicable to TMA, even though the gel is flexible. For these weak hydrogels, by the extreme experiment conditions, such as high stress applied or strain bring about the structural change. Experimental conditions covering Hookian condition is broad for rigid hydrogels.

At the same time, it is thought that swelling of water under the stress is not the same as free swelling. Among unique phenomenon obtained in the stress relaxation study is that stress increases after reaching the minimum stress. Concerning this phenomenon, it is difficult to explain based on the previous concepts on physical properties of hydrogels. On this account, further investigation is necessary in order to reach fully understanding.

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