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TMA measurement of swelling behavior of polysaccharide hydrogels

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Abstract

Swelling of polymer hydrogels is measured as a function of time using a newly designed sample cell attached to Thermomechanical analysis (TMA). In order to examine the performance of the TMA sample holder, Ca alginate dry film was used as a sample and measurement conditions of dynamic swelling of water were examined. Swelling ratio under various loading conditions was observed as a function of time. A master curve was obtained using zero loading conditions using extrapolated values of dynamic data obtained under various loadings. Swelling ratio measured by TMA at equilibrium condition accords well with swelling ratio obtained by static measurement.

Keywords: Swelling; Hydrogels; Alginic acid; Thermomechanical analysis

1. Introduction

Thermomechanical analysis (TMA) is used for the measurement of sample deformation, such as expansion and contraction under a temperature controlled condition [1,2]. Ordinarily, linear expansion coefficient (α), glass transition temperature (T_g), softening temperature and stress relaxation data are obtained by TMA. TMA has been extensively applied in the measurement of thermal stability of polymers. TMA results indicate that the values of polyimide films are extremely low compared with those of ordinary polymers [3,4]. Thermal shrinkage of Nylon 6 fiber was measured using TMA equipped with a tensile mode probe. It was found that shrinkage of fiber depends strongly on heat treatment temperature. T_g of polyethylene terephtalate (PET) film was also measured using different types of sample probes, such as expansion, penetration and tension mode probes [5]. It was found that T_g values obtained by the three modes agree well with each other. At the same time, T_g values obtained by TMA accord well with reported values [6].

Swelling behavior of hydrogels has been investigated by the measurements of mass and size changes of the sample at static conditions [7–10]. Dry samples were immersed in a solvent and maintained for a certain time. Removed samples were wiped with filter paper and the weight and size were measured quickly. During the procedure, experimental error occurs due

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to vaporization of the solvent. Moreover, it is not easy to record the swelling process of gels as a function of time. On this account, it is necessary to establish a measuring method to record the swelling behavior of polymeric gels in order to obtain kinetic data.

In this study, dynamic swelling of polymer hydrogels is measured using a newly designed sample cell attached to TMA.

2. Experimental

2.1. Samples

Sodium alginate (NaAlg) substituted with Ca ions (CaAlg) was used as a sample. NaAlg was obtained from Kibun Food Chemifar. Mannuronic and guluronic component of NaAlg were shown in Fig. 1. Mannuronic and guluronic component ratios (M/G ratio) were 0.5 and 1.0. 5 wt.% NaAlg was solved in deionized water at 20°C and was maintained for 24 h. Viscous solution was extended on a glass plate which was horizontally positioned, and water in the solution was gradually evaporated. A partly dried sample on a glass plate was immersed in an excess amount of 3 wt.% of $CaCl_2$ aqueous solution and was maintained for several hours. Following that, the sample was washed under running water for 30 min. Water insoluble CaAlg sheets were carefully removed from the glass plate and dried at 50°C for several days. The sheets (thickness 20–100 μm) were used for TMA measurements.

2.2. Measurements

A Seiko Instruments TMA SS100 equipped with a penetration type probe was used. A sample cell was newly designed and attached to TMA. A schematic diagram of the sample cell is shown in Fig. 2. Deformation of the sample by swelling was detected using a column shaped quartz probe with cross-section 5–50 mm^2 under a predetermined loading condition at a constant temperature. In these experiments, load was varied as follows: 1, 2, 3, 4, 5 and 10 g, and temperature was maintained at 20°C.

Measurement was carried out by the following procedure: (1) Flat sample sheet with ca. 8 mm diameter was placed on a quartz plate with many pinholes and with ca. 10 mm diameter and set in a TMA quartz probe. Expansion coefficient of quartz is 5.5×10^{-7} (°C). On this account, the contribution from quartz was ignored through these experiments. (2) Load was applied on the surface of the sample sheet through the quartz probe with cross-section of 32.869 mm^2. (3) Deionized water was brought into contact with the bottom surface of the sample using a syringe equipped

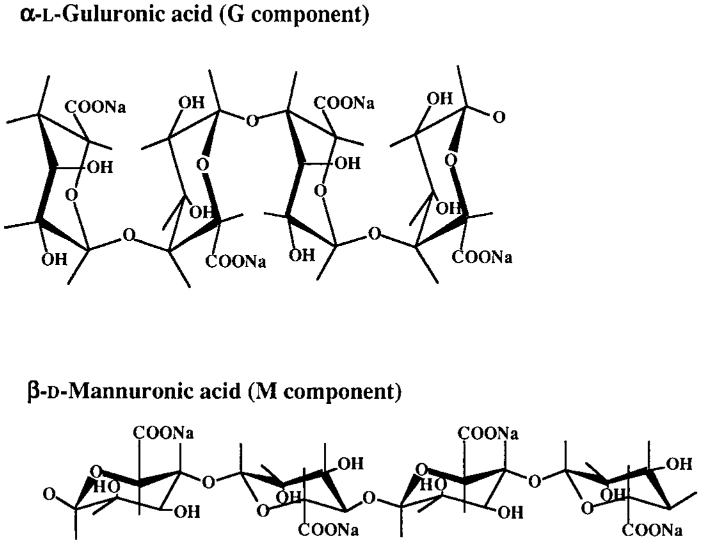

Fig. 1. Chemical structures of guluronic and mannuronic acid components of NaAlg.

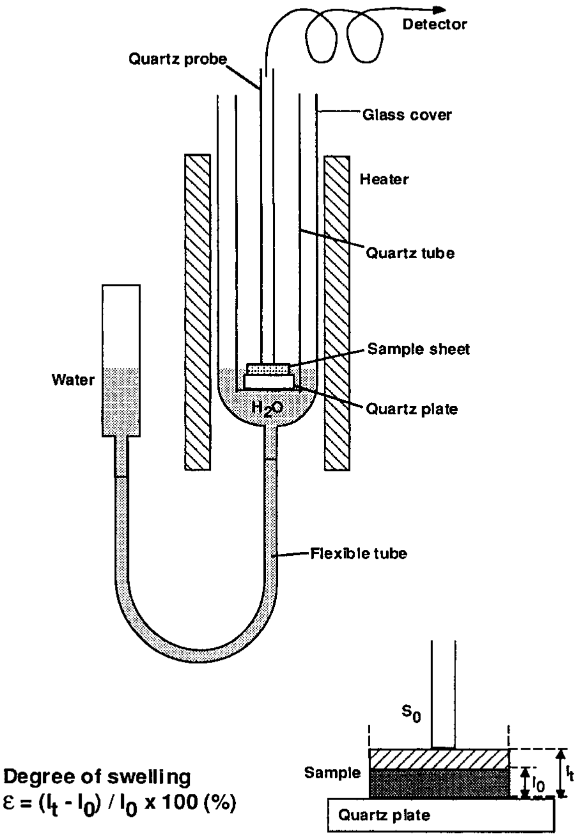

Fig. 2. Schematic diagram of newly designed sample cell of TMA.

with water supplier. The height of water meniscus can be adjusted using a lever. (4) Deformation of sample was detected, as a function of time immediately after that the sample was brought into contact with water. The degree of swelling in this study was defined as

$$\varepsilon = \frac{(l_t - l_0)}{l_0} \times 100\ (\%) \qquad (1)$$

where ε is the degree of swelling, l_t the deformation of the sample at time $= t$, l_0 that of time $= 0$. The rate of swelling $d\varepsilon/dt$ was also calculated.

For comparison, the degree of equilibrium swelling was measured by a microscope equipped with a digital micrometer, i.e. the thickness of dry sample was measured (l_0) and the sample was immersed in deionized water for 2 h. Samples were removed from water, set in the sample holder and measured quickly (l_t). The degree of equilibrium swelling was calculated as Eq. (1). The measurement was repeated three times. The average value was used for the comparison with ε values. The standard deviation was ±2.4%. The thickness of the swelling sample was also measured by a microscope equipped with a micrometer.

3. Results and discussion

Alginic acid (Alg) is a copolysaccharide consisting of D-mannuronic acid (M component) and L-guluronic acid (G component) [11]. Although NaAlg is readily dissolved in water, water insoluble alginates can be prepared when sodium ions of NaAlg are replaced by di- and trivalent cations, such as Cu^{2+}, Fe^{2+}, and Al^{3+}. Ca ions were covered by the guluronic acid unit of Alg and the guluronic unit acts as a junction zone. We have studied thermal properties of water–NaAlg and water–CaAlg systems and found that the functional properties of alginate are affected by the presence of bound water [4–6,12,13]. In this study, replacement of Na–Ca ions was carried out for 30 min at 20°C. CaAlg hydrogels were dried at room temperature and used in order to evaluate a new TMA sample cell.

Fig. 3 shows the schematic TMA swelling curve for about 2 min from the start of measurement. In the initial period of swelling, the sigmoidal curve was obtained as shown in this figure. Therefore, the derivative curve of swelling showed a peak at an inflexion point. However, it is difficult to recognize the sigmoidal shape in the swelling curves for a period more than 60 min.

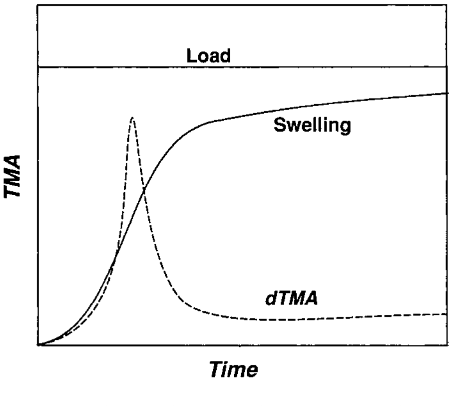

Fig. 3. Schematic swelling curve in initial time of swelling.

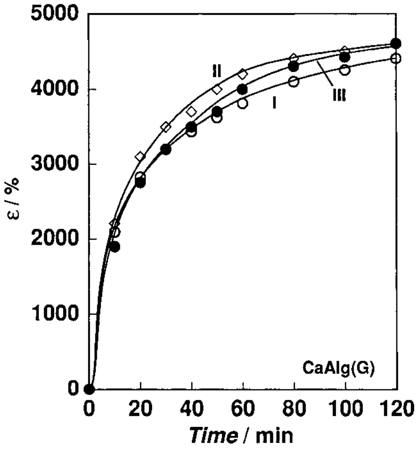

Fig. 4. Representative swelling curves showing repeatability. Temperature (20°C); load (2 g).

Fig. 4 shows the TMA swelling curves of CaAlg sheets as a function of swelling time. Applied probe load was 2 g. As shown in Fig. 4, expansion starts immediately after water comes into contact with the bottom surface of the sample and ε values increase rapidly. In the initial state of swelling, ε values reached 1–3 × 10^3 (%). ε values are gradually saturated at around 60 min. In order to confirm the repeatability of the swelling experiments, swelling was repeated as shown in curves I, II and III. It is clearly seen that curves almost overlap with each other. The degree of swelling in the thickness direction (ca. 4600%) was extremely large compared with that in the diameter direction (ca. 30%). The CaAlg molecules were oriented to the surface direction because the film was prepared by solvent casting on a glass plate. A detailed study of the swelling of the anisotropic CaAlg film will be reported in another paper.

Fig. 5 shows swelling curves of the samples under various loading conditions at 20°C. ε values are extremely large and decreased with increasing probe load. The dotted line shown in the figure represents equilibrium ε values which were measured by static method. As shown in Fig. 5, ε values increased with increasing time and leveled off at about 120 min. It is worthy to note that the CaAlg gel was not crushed when the load was less than ca. 5 g.

The exact equilibrium swelling point under each load can be determined easily using derivative curves

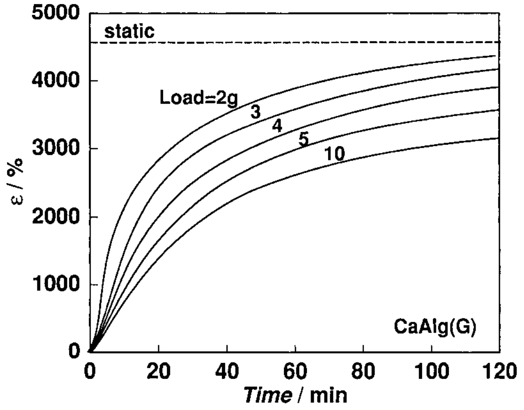

Fig. 5. Swelling curves under various loads. (————); value obtained by static method immersed in water for 120 min.

shown in Fig. 6. The rate of swelling (dε/d*t*) decreased rapidly with increasing time and showed the saturation point at 30 min regardless of loading mass. The rate of swelling decreased with increasing probe load on the sample.

Fig. 7 shows the relationship between ε of CaAlg film and the probe load at 20°C. ε at various times decreased linearly with increasing probe load. The time required to reach the equilibrium swelling increases with increasing applied load. However, a linear decrease can be observed until 5 g, and each line starts to bend gradually. This indicates that the sample does not follow the Fickian law in a load range higher than ca. 5 g. On this account,

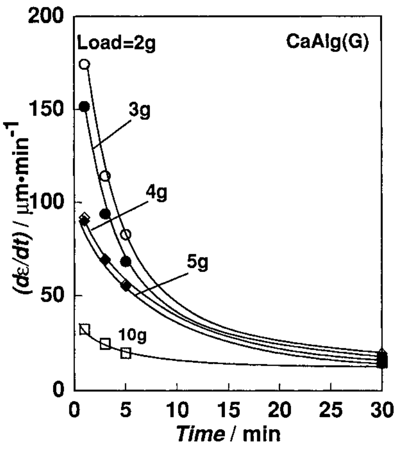

Fig. 6. Derivatograms of swelling curves.

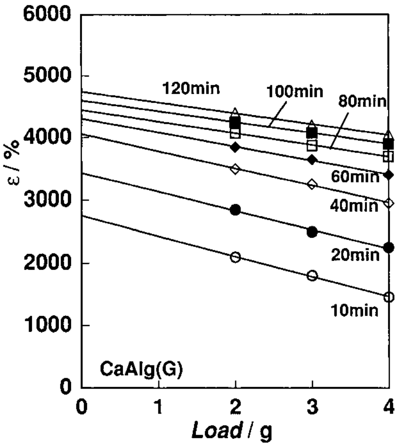

Fig. 7. The relationships between ε of CaAlg and the probe load at 20°C.

extrapolation was carried out using a linear part of each line. It is considered that the extrapolated point to zero load corresponds to the equilibrium swelling of the sample. As clearly seen in Fig. 7, the extrapolated point from the swelling point measured by dynamic method agrees well with the equilibrium value measured by static method. Swelling rates are shown as a function of time in Fig. 8. The swelling rates decreased with increasing load and are maintained at a constant value when swelling time exceeds 30 min.

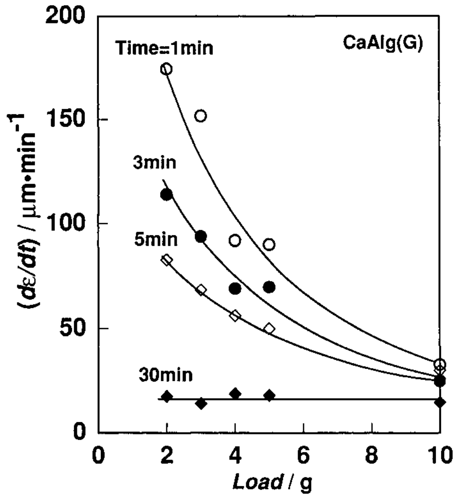

Fig. 8. The relationships between swelling rate and applied probe load.

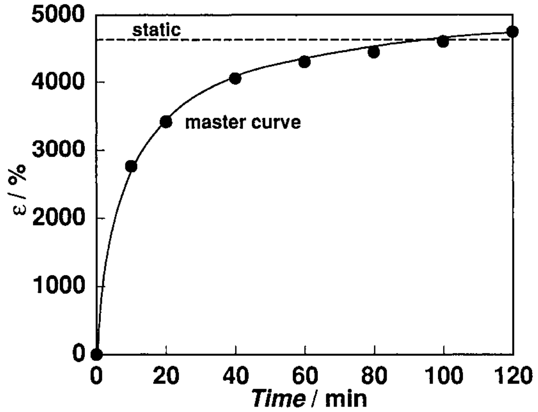

Fig. 9. Swelling curve without load obtained from extrapolated values in Fig. 7. Dotted line shows the static value.

When the extrapolated points from each swelling time under load are connected, the swelling curve under load = 0 can be obtained. Fig. 9 shows the swelling curve thus obtained. The degree of swelling at 120 min which corresponds to the saturation point agrees well with the equilibrium value of swelling measured by the static method.

The above results indicate that dynamic swelling can be investigated using a TMA equipped with a newly designed apparatus. However, further discussions are necessary to analyze the swelling curve theoretically.

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