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Carbohydrate Polymers

Effect of solvent transfer in agar gels on stress relaxation under large deformation

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ABSTRACT

We measured stress relaxation, volume of exuded water, and spatial distribution of stress in agar gels under large deformation. Gels with smaller sample size and lower concentration exuded water faster and had shorter stress relaxation time. Gels with the storage time of 3 days exuded more water and had shorter stress relaxation time than gels with the storage time of 1 day, and this tendency was remarkable for low-concentration gels. Examination of the spatial distribution of stress in a cylindrical gel under large deformation showed that the outer part of the gel had smaller stress than the inner part at an early stage, and the area with small stress gradually extended into the inner part. This result indicates that the inhomogeneity of water content caused by water exudation from the gel surface induces the stress distribution in the gel.

1. Introduction

Polysaccharide gels such as agar gels hold a large volume of water and exude water from the gel surface under compressive deformation. The release of water from the gels leads to stress relaxation (Nakamura, Shinoda, & Tokita, 2001), and is responsible for the distinct texture of Polysaccharide gels. Stress relaxation of Polysaccharide gel has hitherto been analyzed using the viscoelastic theory (de Gennes, 1979; Flory, 1953), where only the disentanglement of polymer chains and not water exudation is considered to affect stress relaxation. The network structure changes with polymer concentration (Dai & Matsukawa, 2012a; Zhao, Brenner, & Matsukawa, 2013) and storage time of Polysaccharide gels (Toncheva, Hadjikinov, & Panchev, 1994), during which the aggregation of polymer chains proceeds. The change of the network structure affects stress strength, stress relaxation behavior, and water transfer in the gel (Yamaue & Doi, 2004). Further, water exudation rate is dependent on the specific surface area of a sample. Therefore, stress relaxation of gels exuding water is affected by sample size. For example, the size of food gels of polysaccharides is altered greatly during mastication; nevertheless, the influence of sample size is not considered in the viscoelastic theory on the stress relaxation behavior of Polysaccharide gels.

In this study, we measured stress relaxation and volume of exuded water in agar gels under large deformation to elucidate the relationship between stress relaxation and water exuded from Polysaccharide gels by compression. We also measured the spatial distribution of stress in agar gels under large deformation to clarify the relationship between spatial distribution of stress and water exudation from gel surface.

2. Materials and methods

2.1. Sample preparation

Agar powder Yamato (Ina Food Industry Co., Ltd., Ina, Nagano, Japan), which has a distinctive physical property of extreme safeness (Uzuhashi & Taki, 2005), was dispersed in distilled water (1.5, 2.0, and 3.0% (w/w)) and stirred at boiling temperature for 30 min to allow for complete dissolution. The solution was poured into plastic cylinders (inner diameter = 16, 20, and 24 mm), degassed by an aspirator, and stored at 25 °C for 1, 3, 5, and 7 days for each measurement. Gelatin powder (Kokusan Chemical Co., Ltd.) was dispersed in distilled water (8.0% (w/w)) and stirred at boiling temperature for 30 min to allow for complete dissolution. The solution was poured into plastic cylinders (inner diameter = 24 mm),

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degassed by an aspirator, and stored at 5 °C for 2 days. The sample gels were cut into cylinders with a height of 20 mm for measurement. The sample gels showed no syneresis during storage time of 3 days.

2.2. Measurement

Stress relaxation was measured with Tensipresser (TTP-50BXII, Taketomo Electric Inc.). Agar gel samples were compressed between parallel plates to a compression ratio α of 0.7, 0.8 or 0.9 ($\alpha = h/h_0$: h_0 and h are heights before and after compression, respectively) at the deformation velocity of 2.0 mm/s and kept under compression for 3200 s at 25 ± 1 °C. The gel samples were covered with a plastic case during measurement to prevent drying.

The volume of water exuded from the gel samples was measured by pipetting with capillary tubes (10 μl and 20 μl) during the stress relaxation measurement. The volume ratio of exuded water (%) was defined as a ratio of the volume of exuded water to the initial volume of gel.

The spatial distribution of stress was measured with a system of stress sensor sheet (I-SCAN™, Nitta Co.) that was laid on the Tensipresser plate. We used a stress sensor sheet of dimensions 44 mm × 44 mm with 44 × 44 sampling points, i.e. a special resolution of 1 mm (Kubo et al., 2009). The gel samples were compressed at the deformation velocity of 2.0 mm/s and kept at $\alpha = 0.7$ for 3200 s at 25 ± 1 °C with the plastic case.

2.3. Analysis of the stress relaxation

The logarithmic plot of stress relaxation shows a curvature over a wide range and indicates that the relaxation process has a distribution that might originate in the heterogeneity of the network structure. For the distribution of the relaxation times $h(\tau)$, a continuous distribution of a linear combination of the gamma distributions with rate parameters equally spaced in logarithmic scale was used:

$$h(\tau) = \sum_{i=1}^{N} f_i \frac{\beta_i^n}{\Gamma(n)} \tau^{-n} \exp\left(\frac{-\beta_i}{\tau}\right) \tag{1}$$

where f_i is the fraction of ith element and β_i is the rate parameter of ith element, which is expressed by the rate parameter of first component β_1 and power increment k as $\beta_i = \beta_1 k^{i-1}$. It should be noted that the component with a τ value much longer than the measurement time practically works as a constant term. The parameters were set as $\beta_1 = 1$, $k = 10^{1/4}$ and $N = 19$. The shape parameter n was set as $n = 3$, then the ith element has the mean value of $\beta_i/2$ and the standard deviation of $\beta_i/2$. On the basis of the assumption that relaxation processes are independent of each other, the total elasticity $E(t)$ was expressed as follows:

$$\begin{aligned} E(t) &= \sum_{i=1}^{N} f_i \int_{\tau=0}^{\tau=\infty} h(\tau) \exp\left(\frac{-t}{\tau}\right) d\ln\tau \\ &= \sum_{i=1}^{N} f_i \int_{\tau=0}^{\tau=\infty} \frac{\beta_i^3}{2} \tau^{-3} \exp\left(\frac{-\beta_i}{\tau}\right) \exp\left(\frac{-t}{\tau}\right) d\ln\tau \\ &= \sum_{i=1}^{N} f_i \frac{\beta_i^3}{(t+\beta_i)^3} \end{aligned} \tag{2}$$

The curve fitting on data of stress relaxation was carried out to minimize the regularized variance $V(k_r)$;

$$V(\alpha) = \sum_{j=1}^{M}(y_j - E(t_j))^2 + K_r \sum_{i=1}^{N-2} f_i - 2f_{i+1} + f_{i+2} \tag{3}$$
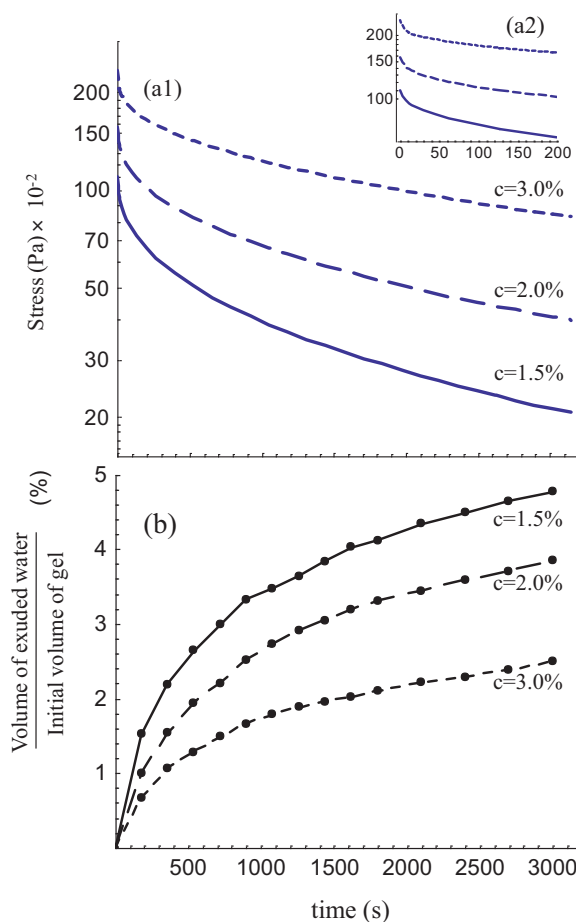
Fig. 1. Stress relaxation (*a1*, *a2*) and time course of exuded water (b) for gels with various agar concentrations. Gels diameter was 20 mm and $\alpha = 0.8$. Stress relaxation from 0 to 200 s is magnified in *a2*.

where y_j is jth experimental data and $E(t_j)$ is the value calculated by Eq. (2). The first term on the right-hand side is the least square fit condition and the second term on the right-hand side is called as the regularizor (Provencher, 1982) or the penalty function (Borgia, Brown, & Fantazzini, 1998), which gives smoothness to $h(\tau)$. The regularization parameter k_r was set as $k_r = 0.1$, where $h(\tau)$ became smooth and $E(t)$ fit well on the data points.

3. Results and discussion

3.1. Agar concentration dependence of stress relaxation

Polymer concentration of gels has large effects on viscoelastic properties and the water holding capacity. The stress relaxation behavior and the time course of the ratio of exuded water volume to initial gel volume ($R_{w,ex}$) of gels under $\alpha = 0.8$ at various agar concentrations are shown in Fig. 1. The storage time and the diameter were 1 day and 20 mm, respectively.

The stress arises from both of the stress of network and the hydrostatic pressure (Yamaue & Doi, 2005). The stress relaxation showed an initial rapid decrease (time less than 20 s, see Figs. 1a and 2) followed by a slow and steady decrease, and was still visible even at the longest measurement times (~3000 s). The former is probably due to disentanglement of network agar chains and also long dangling chains, and the latter, the disaggregation of agar aggregates constituting cross-linking regions. That the gel with higher concentration had a larger ratio of rapid stress relaxation to total stress relaxation is an indication that the contribution