Carbohydrate Polymers 109 (2014) 166–170

Contents lists available at ScienceDirect

Carbohydrate Polymers

journal homepage: www.elsevier.com/locate/carbpol

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

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ARTICLE INFO

Article history:
Received 28 November 2013
Received in revised form 18 February 2014
Accepted 20 March 2014
Available online 28 March 2014

Keywords:
Agar
Hydrogel
Water transfer
Stress relaxation
Large deformation
Spatial distribution

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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http://dx.doi.org/10.1016/j.carbpol.2014.03.055
0144-8617/

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:

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

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:

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

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

$$V(\alpha) = \sum_{j=1}^{M} (y_j - E(t_j))^2 + K_r \sum_{i=1}^{N-2} f_i - 2f_{i+1} + f_{i+2} \quad (3)$$

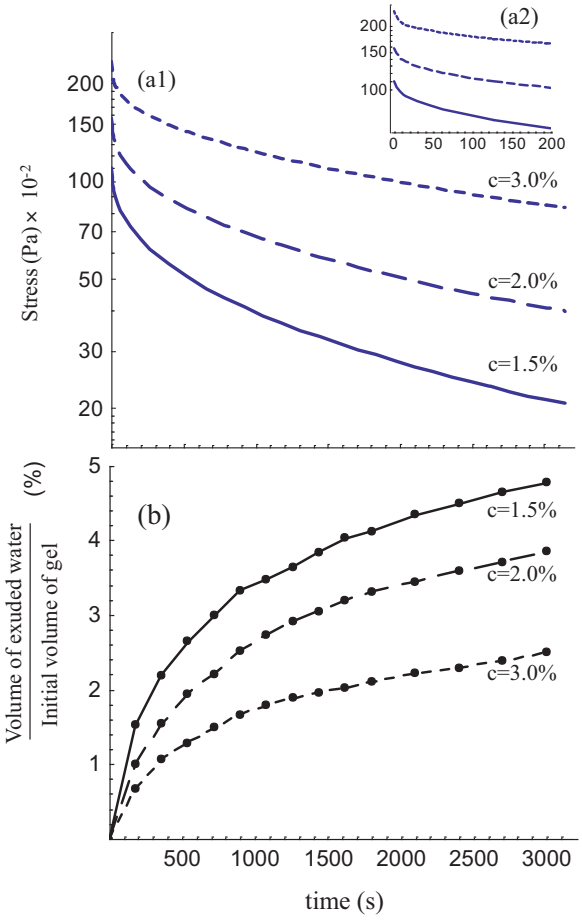

Fig. 1. Stress relaxation (*a*1, *a*2) and time course of exuded water (b) for gels with various agar concentrations. Gels diameter was 20 mm and $\alpha = 0.8$. Stress relaxation from 0 to 200 s is magnified in *a*2.

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

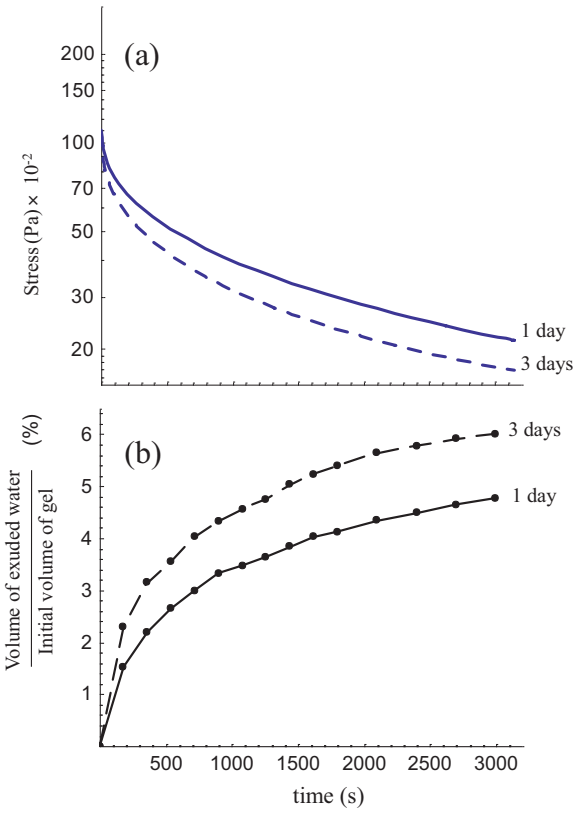

Fig. 2. Stress relaxation (a) and time course of exuded water (b) for the gels with storage times of 1 day and 3 days. Gel concentration was 1.5%, diameter was 20 mm, and $\alpha = 0.8$.

of entanglement to stress generation under large deformation is larger.

On the other hand, the gel with lower concentration had a smaller ratio of rapid stress relaxation, and stress relaxation in the intermediate time (20–500 s) became obvious. The volume of water exuded by the gel with lower concentration was larger than that by the gel with higher concentration, and increased rapidly in the intermediate time (Fig. 1b). Therefore, it is considered that low-concentration gel holds more water and exudes water more easily under large deformation, and that stress relaxation in the intermediate time is affected by water exudation, which causes the shrinkage of gel and consequently decreases the effective strain, as well as by the disentanglement of agar chains and the disaggregation of agar aggregates. As a result, the decrease of agar concentration increased stress relaxation in the intermediate time by increasing the volume of exuded water. The effect of exuded water on the relaxation process was confirmed by measuring the stress relaxation and volume of the exuded water for agar gels with a same agar concentration and different diameters.

3.2. Storage time dependence of stress relaxation

The network structure of hydrocolloids changes with the aggregation of polymer chains, which causes the change of the physical properties of gels. Fig. 2 shows the stress relaxation behavior and the time course of $R_{w,ex}$ of agar gels with storage times of 1 and 3 days. Agar concentration, gel diameter, and α were 1.5% (w/w), 20 mm, and 0.8, respectively. For the gel with the storage time of 3 days, $R_{w,ex}$ was increased and stress relaxation in the intermediate time was large, compared with the gel with the storage time of 1 day. This suggests that the network structure changed during storage.

The molecular chains in agar solution assume a random-coil structure at temperatures above the sol–gel transition temperature (T_{s-g}), and transform into the double-helix structure on cooling to temperatures below T_{s-g} (Arnott, Fulmer, & Scott, 1974; Arnott, Scott, Rees, & McNab, 1974; Kouwijzer & Pérez, 1998). Then, the double helices aggregate to form cross-linking regions that make up the network structure of the gel (Arnott, Fulmer, et al., 1974; Arnott, Scott, et al., 1974). The growth of this aggregation structure is delayed by the generation of three-dimensional network structures and requires a long time to reach thermal equilibrium. Therefore, it is considered that the aggregation structure of agar chains is in the nonequilibrium state during storage within 3 days.

The progress of aggregation decreases the number of solute agar chains with hydrated water and makes the network structure coarse (Dai & Matsukawa, 2012b; Shimizu, Brenner, Liao, & Matsukawa, 2012; Zhao & Matsukawa, 2012). This change decreases frictional force hampering water movement during exudation under compression. As a result, the exudation of water from the gel with long storage time under compression was intense and fast, and this affected stress relaxation in the intermediate time. The same storage time dependence was observed in gels with 2.0% and 3.0% polymer concentrations, and this tendency was remarkable for gels with low polymer concentration.

While there are other proposed models for the gelation process, such as a single-helix model (Foord & Atkins, 1989; Guenet, Brulet, & Rochas, 1993) or phase separation (Emanuele et al., 1991; Pines & Prins, 1973; San Biagio, Bulone, Emanuele, Palma-Vittorelli, & Palma, 1996), we here adopted the double-helix model described above.

3.3. Sample size and compression ratio dependence of stress relaxation

The rate of water exudation from the gel surface would depend on the specific surface area of the sample, which affects stress relaxation in the intermediate time. Fig. 3 shows the stress relaxation behavior and the time course of $R_{w,ex}$ for gel samples with various diameters of 16, 20 and 24 mm, which changed to 17.9, 22.5 and 26.9 mm after the compression with $\alpha = 0.8$, respectively. Gel concentration was 1.5%, storage time was 1 day, and $\alpha = 0.8$. Gels with smaller diameters exuded water faster and showed larger stress relaxation in the intermediate time. These results indicate that water exudation rate depends on sample size, which contributes to the difference of the stress relaxation behavior. The specific surface area, which is the ratio of the total surface that is exposed during compression to the sample volume, is inversely proportional to the diameter. The large specific surface area of small samples would improve water exudation under large deformation. The same sample size dependence was observed in gels with 2.0% and 3.0% polymer concentrations, and this tendency was remarkable for low-concentration gels.

Fig. 4 shows the stress relaxation behavior and the time course of $R_{w,ex}$ for gels under $\alpha = 0.7$ and 0.8. Polymer concentration was 1.5% and storage time was 1 day. The gel with 16 mm diameter showed larger stress under $\alpha = 0.7$ than under $\alpha = 0.8$ (Fig. 4a), as expected from the viscoelastic theory. Close examination revealed that the former had larger stress relaxation in the intermediate time (20–500 s) than the latter, and corresponded to the finding that the former exuded a large volume of water in the intermediate time (Fig. 4b). This indicates that the large deformation induces significant water exudation and accelerates stress relaxation in the intermediate time. The difference in water exudation under $\alpha = 0.7$ between gels with 20 mm and 16 mm diameter (Fig. 4b) was larger than that under $\alpha = 0.8$ (Fig. 3b). This difference is reflected in the difference in stress relaxation in the intermediate time of gels with 20 mm and 16 mm diameter (Fig. 4a). For a clear comparison, the

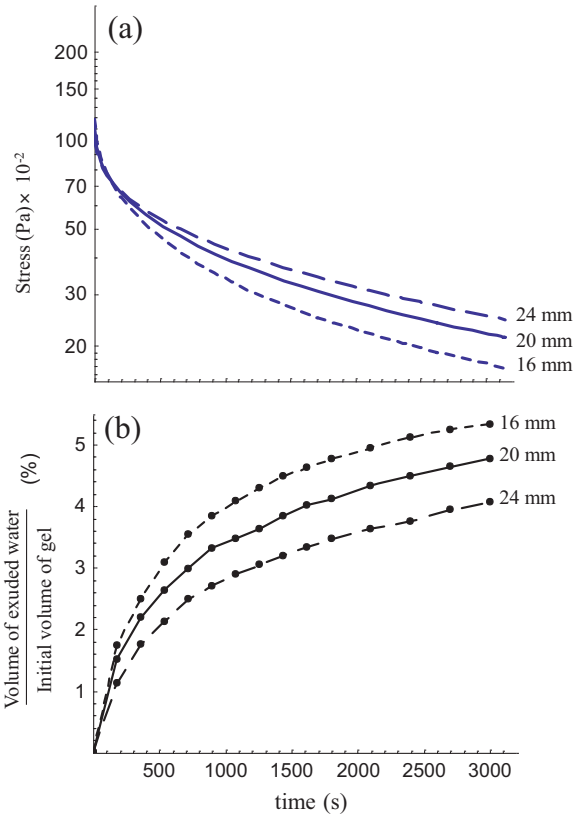

Fig. 3. Stress relaxation (a) and time course of exuded water (b) for gels with various sample sizes. Gel concentration was 1.5%, storage time was 1 day, and $\alpha = 0.8$.

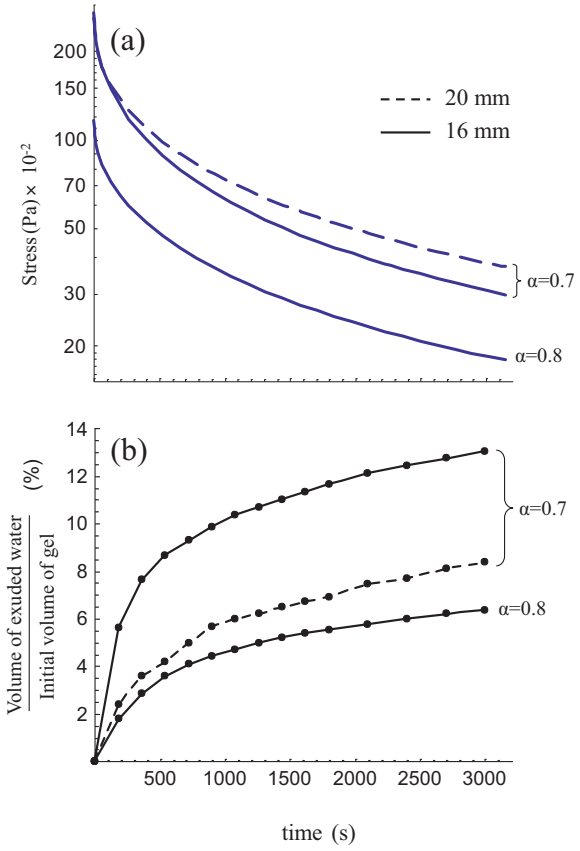

Fig. 4. Stress relaxation (a) and time course of exuded water (b) for gels with various compression ratios. Gels concentration was 1.5% and storage time was 1 day.

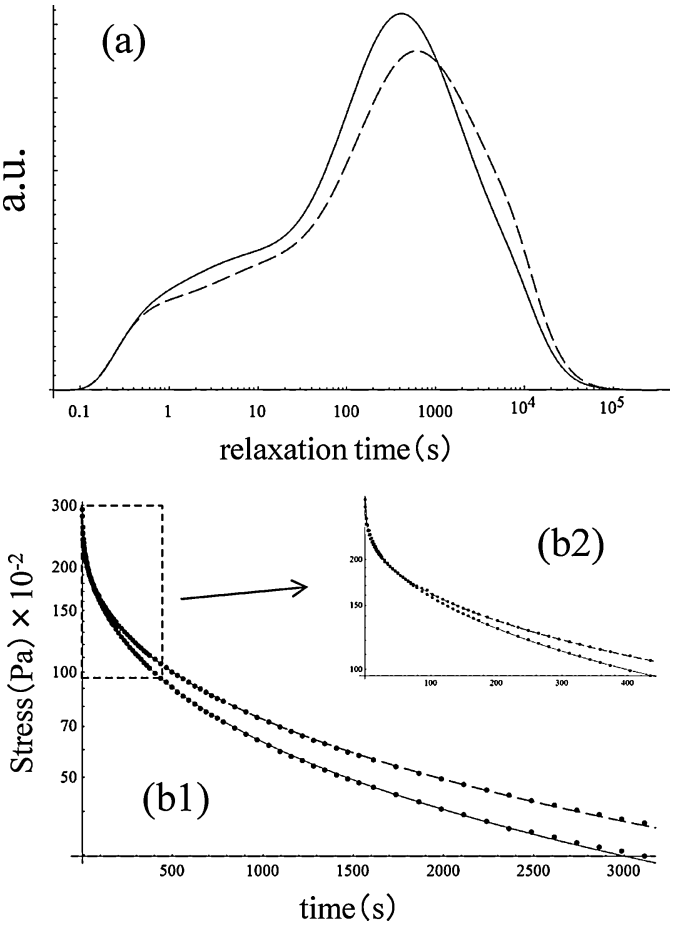

Fig. 5. (a) Distribution of stress relaxation time for samples with diameter of 16 mm (solid line) and 20 mm (dashed line)), and (*b*1,*b*2) corresponding stress relaxation with the fitting lines. Gels concentration was 1.5% and $\alpha = 0.7$.

regularization method was applied on stress relaxation data for 16- and 20-mm-diameter gels under $\alpha = 0.7$, which gave smooth distributions of stress relaxation time (Fig. 5a) and the relaxation curves fit well on the relaxation data (Fig. 5b). Distributions for both gels seem to have two components; one is distributed in relaxation time less than 20 s and another more than 20 s, the former should corresponds to the initial rapid decrease in the stress relaxation caused by the disentanglement of agar chains and the latter the slow and steady decrease in the stress relaxation caused by the disaggregation of agar aggregates constituting cross-linking region. The 16-mm-diameter gel shows larger value from 1 s to 500 s than the 20-mm-diameter gel, which correspond to the larger stress relaxation in the intermediate time. In contrast, the distribution of stress relaxation for the 20-mm-diameter gel shifts to a longer relaxation time. This shift corresponds to the slower water exudation of the 20-mm-diameter gel than that of the 16-mm-diameter gel.

3.4. Spatial distribution of stress

The time course of the spatial distribution of stress in 1.5% agar and 8% gelatin gels under $\alpha = 0.7$ are shown in Fig. 6(a) and (b), respectively. The gelatin gel showed a similar stress to that of the agar gel but exuded no water under this compression. Therefore, the stress relaxation should have no effect of water exudation. Radial profiles of relative stress are also shown in (c) in order to show the difference between the agar gel and gelatin gel.

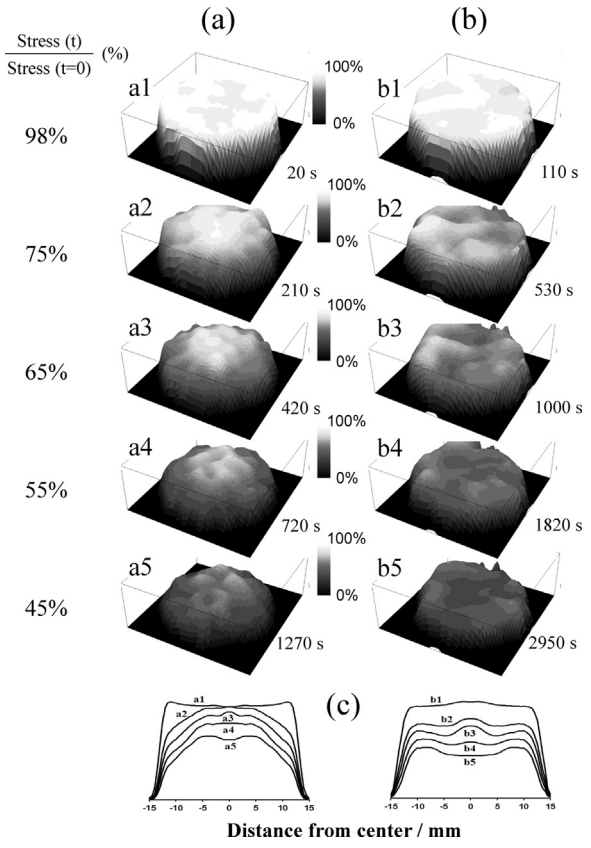

Fig. 6. Spatial distribution of stress in agar gel with polymer concentration of 1.5% (a) and gelatin gel with that of 8% (b) under $a = 0.7$. Diameter of cylindrical sample before compression was 24 mm. Ratios of total stress to initial stress are indicated on the left. Relative stress is indicated as height of protrusion with gray scale. Radial profiles of relative stress are shown in (c). Marks of $a1$–5 and $b1$–5 are corresponding to those in (a) and (b).

The spatial distribution of stress in agar gel and gelatin gel was homogeneous immediately after compression, and the stress was relieved with time. At 210 s, stress at the outer parts of agar gel became lower than that at the inner part, where stress remained high. With the lapse of time, the area of the inner part with high stress decreased with the inward extension of the outer part, and disappeared at about 1270 s. In contrast, stress in gelatin gel decreased without any difference between the inner part and the outer part during the measurement time (Fig. 6b). During the time period where the inner part with high stress existed, agar gel exuded water at a favorable pace while gelatin gel did not exude water under compression. Consequently, the following are considered: (1) at the early stage of the intermediate time, water exudation from gel surface relieves actual compression of the outer part while keeping actual compression of the inner part high, which holds the same volume of water as that before compression, (2) at the late stage of the intermediate time, water exudation from the inner part through the outer part relieves actual compression and the inner part with high stress disappears. This result clearly indicates the effect of water exudation from gel surface on stress relaxation.

4. Conclusions

From the experimental results for stress relaxation and water exudation, it was found that the gel with low polymer concentration, small size, and long storage time exhibited large stress relaxation and exuded much water at an early stage. On the basis of a comparison of the time course of water exudation with the distribution of stress relaxation obtained by a regularization method, it was elucidated that the decrease of gel volume caused by water exudation affected stress relaxation behavior. Furthermore, measurements of the spatial distribution of stress in gels under compression revealed that the water exudation from the gel surface induced the spatial distribution of stress in the gel.

Acknowledgments

The authors are grateful to Ina Food Industry Co., Ltd. for generous donation of agar sample and recommendations for sample preparation. This work partially supported by Grant-in-Aid for Scientific Research (21550203) from Japan Society for the Promotion of Science (JSPS).

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