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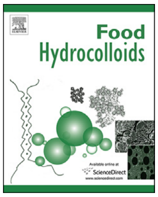

Water/glycerol mixed solvent transportation behavior of mechanically constrained agarose gels

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A B S T R A C T

The effect of glycerol on the solvent transportation behavior of mechanically constrained agarose gels was studied. The sample hydrogels were prepared using a water/glycerol mixed solvent containing various concentrations of glycerol. The compression load relaxed under the compression, and the volume of the agarose gels decreased synchronously with mechanical relaxation. This implied that the solvent is squeezed out due to mechanical constraints; the time constants for both the mechanical relaxation and the volume change are directly related to the friction between the solvent and the gel network structure. Both time constants increased with an increase in glycerol concentration. These results indicate that glycerol changes the gel network structure, and this is confirmed by other experimental evidence. The compression fracture stress and strain improved with an increase in glycerol content. Moreover, scanning electron microscope images showed that the mesh size of the gel network decreased with an increase in glycerol content.

1. Introduction

How is the solvent squeezed out from foods when they are compressed in mouth? It is quite interesting research topics. Generally, the taste or flavor of food is due to the solvent (usually water), and therefore, we cannot enjoy the food unless the solvent is squeezed out. Solvent transportation from hydrogels has attracted attention in the field of food science and technology because this process is strongly related to flavor release and water-holding ability. Although solvent transportation from edible gels has been extensively studied (Stieger & van de Velde, 2013), the main focus has been on the passive diffusion of flavor from edible gels (Wang, Yang, Brenner, Kikuzaki, & Nishinari, 2014). Solid like foods obviously must be bit or chewed during mastication. Therefore we should consider not only passive diffusion of solvent, which contains flavor, but also squeeze behavior of the solvent under the compression pressure. The solvent transportation behavior can be explained in terms of the friction between the gel networks and the solvents (Tanaka & Fillmore, 1979). A few studies have focused on clarifying the friction within the gel network for chemically cross-linked gels (Fatin-Rouge, Milon, Buffle, Goulet & Tessier, 2003; Suzuki & Hara, 2001; Tokita & Tanaka, 1991). The solvent transportation behavior of chemically cross-linked hydrogels under mechanical constraints has also been studied (Kneabel & Lequeux, 1998). The solvent is squeezed out from chemically cross-linked polyelectrolyte gels under compression. However, no such clarification has been provided for polysaccharide gels, which are physically cross-linked gels.

In this study, we focused on agarose gels as a simple food model. The idealized structure of agarose constitutes a disaccharide repeating unit comprising (1 → 3) linked β-D-galactose and (1 → 4) linked 3,6-anhydro-α-galactose (Morris, 1998). Agarose solutions of sufficiently high concentrations give rise to thermally reversible gels that are slightly turbid and brittle below the gelling temperature. Although the polysaccharides dissolve in water as coils at higher temperatures, they adopt a helical conformation at lower temperatures (Arnott et al., 1974). The mechanism of formation of the network structure of an agarose gel is proposed to be as follows: if the concentration of the polysaccharide is sufficiently high, the helices form bundles, which then associate to generate a network structure. Small angle neutron scattering study of the "swollen gels" has revealed the cross-sectional radius of the agarose cylindrical fibers to be a few nanometers (Boral & Bohidar, 2009). The reported mesh sizes of agarose gel network are various values ranging from the order of a few 10 nm to a few 100 nm depending on the experimental method. For example, the size estimated by

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using the wave length exponent is on the order of a few 10 nm (Normand et al., 2003). The value estimated from the diffusion coefficient of a probe with NMR is also on the order of a few 10 nm (Dai and Matsukawa, 2013). On the other hand, the size estimated by using electrophoresis of a probe is on the order of a few 100 nm (Xiong et al., 2005). These sizes are obviously quite larger than the size of water molecular. Although we observe syneresis that is spontaneous solvent excluding phenomenon, it is clear that the solvent never easily flow out from the hydrogels. Therefore, it is one of the most interesting research topics to investigate the solvent transportation from such hydrogels in a various conditions. Recently, we studied solvent transportation from constrained agarose gels. We observed that the compression load and the volume of the agarose gels decreased with time during compressive restraint, as the time constants for the relaxation of the compression load and the volume change of the constrained agarose gel were changed. It means that the decrease in volume was induced by squeezing of the solvent from the gel under compressive constraint (Kaneda & Iwasaki, 2015).

In this study, we focused on glycerol as a possible additive for gel-type foods containing agarose. The effect of glycerol on the physical properties of agarose gels has already been reported (Nishinari & Watase, 1987). However, to the best of our knowledge, the solvent transportation behavior of mechanically constrained agarose gels has not been reported. Therefore, we studied the effect of glycerol on the solvent transportation from constrained agarose gel using the method developed in the previous study. We observed the time development of the mechanical load and the volume change under compressive strain for agarose gels containing glycerol as a solvent. The relationship between the mechanical response and the volume change, i.e., the mode of solvent transportation from the gel, was also analyzed.

2. Materials and methods

2.1. Materials

Agarose type IV (Sigma–Aldrich) was purchased and used without further purification. The sample contained less than 0.25% sulfate. Aqueous solutions of glycerol were used as the solvent. The concentrations of glycerol ranged from 0 to 80 wt % in distilled water. Sample gels were prepared as follows: agarose powder was dispersed in the solvent and stirred at room temperature for 18 h to allow sufficient swelling. The swollen dispersion was heated at 95 °C for 1 h to ensure complete dissolution. The hot solution was poured into a polycarbonate tube ($\varphi = 20$ mm), and both ends of the tube were sealed with polyvinylidene chloride film. Then, the tube was immediately placed in a water bath for temperature control. After 24 h of quenching in the water bath at 10 °C, the sample gels were squeezed out of the tube and cut to a length of about 20 mm using a razor blade. The cylindrical gels were immersed in the solvent and incubated at 5 °C for at least 5 days so that they reached the equilibrated state before the experiments. The dimensions of the gels (diameter and length) were measured with a caliper immediately prior to the experiments. The sample codes used herein are “G-XX”, where “XX” indicates the molar ratio of glycerol in the solvent.

2.2. Monitoring of compression load and volume change

For experiments evaluating the mechanical properties and volume change of the sample, the polymer concentration was fixed at 1.5 wt%. The temporal evolution of the compression load and changes in the shape of the agarose gel were simultaneously monitored. The details of the measurement system are described in elsewhere (Kaneda & Iwasaki, 2015). Compression and monitoring of the compression load were performed with an INSTRON MINI 55 (Instron, USA) instrument. The sample gel was compressed at a rate of 1 mm/s, and when the compression strain reached 0.05, the compression was held constant. The time development of the compression load was monitored for 18 h. The side view of the sample was monitored with a CCD camera, and still images were acquired at regular time intervals. The diagram of the measurement setup is shown in Fig. 1. In this study, the top and bottom surfaces of the cylindrical gel were sealed with cyanoacrylate to prevent slipping. The digital images of the samples and the sample width were analyzed using image analysis software (Image-J). Since the gel deformed to a barrel-like shape, the width was measured at five different points and the average width (w_m) was obtained. The height of the gel could be determined during the INSTRON MINI 55 measurements; therefore, the volume (v) of the gel was calculated using Eq. (1), and each measurement was performed at least three times.

$$v = \pi\left(\frac{w_m}{2}\right)^2 \cdot h \tag{1}$$

2.3. Fracture behavior

To study the general mechanical properties of the agarose gels containing glycerol, compression fracture tests were performed. The cylindrical gels were compressed by the INSTRON MINI 55 system. The crosshead speed was 1 mm/s. The values of fracture stress and strain were estimated from the peak position in the stress–strain curves. In this estimation, we assumed that the compression area was constant during compression fracture.

2.4. Viscosity measurement

The apparent viscosities of water/glycerol mixed solvents were measured ARES (TA instruments) equipped a bob (16 mm diameter) and cup (16.5 mm diameter) fixture. The steady state viscosity at 50 s^{-1} was measured at 30 °C.

2.5. Scanning electron microscopy (SEM) observation

The microstructure of the agarose gels was observed with a scanning electron microscope (HITACHI S-2460N). The sample gels were immersed in D.W. for at least 10 days to remove the glycerol present in them. The washed gels were rapidly cooled under liquid nitrogen before being placed in a freeze dryer. The completely

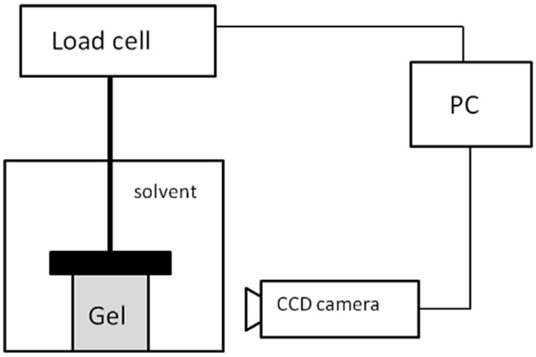

Fig. 1. Block diagram of the experimental apparatus for mechanical property and volume change analysis.