Network Microstructure of PVA Cast Gels Observed by SAXS Measurements

Emiko Otsuka¹, Masaaki Sugiyama² and Atsushi Suzuki¹

¹Graduate School of Environment and Information Sciences, Yokohama National University, 79-7 Tokiwadai, Hodogaya-ku, Yokohama, 240-8501 Japan.
²Research Reactor Institute, Kyoto University, 2 Asashiro-Nishi, Kumatori-cho, Sennan-gun, Osaka 590-0494 Japan.

E-mail: eotsuka@ynu.ac.jp

Abstract. We report the relationship between macroscopic properties (swelling ratio, breaking stress and strain) and the network microstructure of PVA cast gel. Swelling in water solvent and drying in air were alternately repeated, where water was exchanged by new water before each swelling. The effects of the number of water exchange, N on the macro- and microscopic properties were examined in detail. As a result, the swelling ratio of PVA cast gel decreased, and both of breaking stress and strain increased with increasing N. The measurements using X-ray diffraction (XRD) indicated that the average distance between the microcrystallites decreased due to the formation of the additional microcrystallites during the repeated processes of water exchange with drying. On the other hand, the measurements using Fourier Transform Infrared (FT-IR) Spectroscopy suggested that the microcrystallites and hydrogen bonds between polymers increased during the repeated processes.

1. Introduction
Poly(vinyl alcohol) (PVA) gels are useful biomaterials due to its low toxicity and high biocompatibility, and many studies on their practical applications have been reported by researchers in a variety of fields [1,2]. PVA can be physically crosslinked by the freeze-thawing method in water [3-5] or in a dimethyl sulfoxide (DMSO)/water mixed solvent [6-9], which introduces microcrystallites as crosslinks. On the other hand, PVA can be chemically crosslinked by crosslinkers, such as glutaraldehyde (GA) [10,11] or multifunctional reactive compounds [12]. Chemical gels can be also obtained by crosslinking PVA in solid state or in solution by irradiation of γ-ray [13] or electron beam [14,15]. Mechanical properties of physically and chemically crosslinked PVA gel have been extensively studied [16-18].

Recently, a simple method to obtain a physically crosslinked PVA gel (called “PVA cast gel”) was successfully developed [19]. The materials used in this technique were water and PVA powders, and the method just involved drying at room temperature; no special chemicals were used. The formation of hydrogen bonds and microcrystallites was identified during the drying process (gelation process) using X-ray diffraction (XRD) technique, Fourier transform infrared (FT-IR) spectroscopy, and measurements of the swelling ratio under repeated water exchanges [20]. The dried sample could
swell and was insoluble in water even after sufficient water exchange, which indicated that PVA cast gel was a physically crosslinked polymer network, in other words, a swollen hydrogel.

In this paper, we report the swelling and mechanical properties in pure water of a thin plate of physically crosslinked PVA gels prepared by a cast-drying method. The swelling ratio was measured whenever the dried PVA cast gel reached the equilibrium swollen-state in water during the repeated water exchange with drying. For each swollen gel during the repeated processes, the breaking stress, $\sigma_r$, and strain, $\varepsilon_r$, were obtained by a uniaxial loading test. The network structure was analyzed using XRD and FT-IR measurements. The macroscopic properties are discussed in terms of the formation of microcrystallites and hydrogen bonds by the exchange of solvent with drying.

2. Experimental

2.1. Sample preparation
PVA powder was kindly supplied by Kuraray Co., Ltd. (Cat. No. PVA117), and was used without further purification. The average degree of polymerization was 1,700, and the average degree of hydrolysis was between 98 and 99 mol%. An aqueous PVA solution was obtained by dissolving 15.0 wt% of the PVA powder into deionized and distilled water at 90 °C for more than 2 hrs. The PVA solution (15.0 g) was poured into a plastic dish of polyethylene with an inner diameter of 85 mm and left in air at room temperature (ca. 25 °C). The solution became very viscous within several days and solidified (thin disk) within a week or more. The sample was prepared by a single process of drying of the PVA aqueous solution at room temperature. The single gelation method named as “cast-drying method”.

2.2. Measurement of the swelling ratio
Figure 1 shows the schematic diagram of the process of repeated water exchange with drying. The as-prepared sample (PVA cast gel film) was put into 1,000 mL of pure water at room temperature and kept for 24 hrs to reach the equilibrium state. After the weight of the swollen sample, $W_s$, was measured in air, the sample was dried in air at 30 °C for 24 hrs, and hereafter the dehydrated weight, $W_d$, was measured. This process of the swelling in water and the drying at room temperature were alternately repeated, where water was exchanged by new water before each swelling. The swelling ratio, which is defined here as $W_s/W_d$, was calculated. This process of water exchange with drying was repeated 9 times (the number of the repeated processes, $N = 9$).

![Figure 1](image)

Figure 1. Illustration of the treatment for the measurement of swelling ratio of PVA cast gel during repeated water exchange with drying.

2.3. Measurement of the stress-strain curve
For each swollen gel during the repeated processes, $\sigma_r$ and $\varepsilon_r$ were obtained by a uniaxial loading test. In this test, the gel was shaped using a dumbbell cutter in accordance with JIS K-6251-8. The ends of the dumbbell-shaped gel were clamped in rigid, acrylic grips. The gel was stretched in pure water at room temperature with a constant rate of elongational stretch between grips. The forces generated during deformation were measured using a double leaf spring with four strain gauges. Using a food dye two markers were applied to the gel by hand in the gauge section. Images of the gel and markers...
were obtained during the tests using a video camera, which were captured and saved in a computer. The distance between the markers was obtained by analyzing the images after the test. The typical stretch rate in the gauge section was 0.63 mm/sec. From the measured values of force and elongation, the nominal stress, $\sigma$, and strain, $\varepsilon$, were calculated.

2.4. SAXS, SWAXS and ATR FT-IR measurements

To determine the network structures, SAXS measurements were performed at room temperature using a small angle X-ray scattering (SAXS) equipment with the wavelength of 0.1488 nm at BL10C in the Photon Factory, High Energy Accelerator Research Organization (KEK), and using additionally a small and wide angle X-ray scattering (SWAXS) equipment with the wavelength of 0.1542 nm operated at 40 kV and 50 mA (SAXSess, Anton Paar, PANalytical).

To study the change in molecular structures (e.g., the formation of hydrogen bonds) of the PVA cast gel during the water exchange with drying, the measurements of FT-IR with an Attenuated Total Reflection (ATR) method were carried out at room temperature. The ATR FT-IR spectra were recorded on an FT-IR spectrophotometer (Jasco FTIR610) equipped with an ATR attachment with a horizontal ZnSe crystal (Jasco PRO400S). The resolution of the spectra was 4 cm$^{-1}$, and the scans were repeated 100 times. The IR absorbance spectra were normalized based on CH$_2$ bending vibration that appears at ca. 1,500 ~ 1,400 cm$^{-1}$. The components of absorption band were deduced from the second-derivative of spectra and were resolved applying the curve-fitting method. All spectra were found to involve CH$_2$ bending vibration consisting of five peaks, including the peak at 1,427 cm$^{-1}$ [21]. The total absorbance area of five peaks was assumed equivalent under the present experimental conditions, and the spectra were normalized by the total area.

3. Results and Discussion

3.1. Swelling and mechanical properties of PVA cast gels during water exchange with drying

Figure 2 shows $W_t/W_d$ of PVA cast gel as a function of $N$. The $W_t/W_d$ decreased rapidly from $N = 1$ to 3, and hereafter continued to decrease gradually.

![Figure 2](image)

Figure 2. Swelling ratio of PVA cast gels during water exchange with drying. The results of three samples from two different PVA cast gel films, which were prepared by the same method at different times, are presented. Open circles; the gel obtained from one PVA cast gel film used in the uniaxial loading test. Open and closed triangles; the gels obtained from the other PVA cast gel.
Figure 3 (a) shows the nominal stress-strain ($\sigma$-$\varepsilon$) curve of each swollen gel. The slope in the low $\varepsilon$-range, which corresponds to Young's modulus, $E$, increased apparently with increasing $N$ (Fig. 3(b)).

![Figure 3](image)

**Figure 3.** (a) Stress-strain ($\sigma$-$\varepsilon$) curves during the simple elongation test of PVA cast gels during water exchange with drying, where the gels were ruptured at the maximum $\varepsilon$, and (b) Young's modulus of the samples, determined from the $\sigma$-$\varepsilon$ curve in (a).

Figure 4 shows the relationship between $W_t/W_d$ and $\sigma_r$ or $\varepsilon_r$ of swollen gels, which includes the data in Fig. 2. Taking the results of Fig. 2 into account, we found that with increasing $N$, $W_t/W_d$ decreased and both of $\sigma_r$ and $\varepsilon_r$ increased. These results should be attributed to the changes in the network microstructures by the repeated water exchange with drying. It has been well recognized that $W_t/W_d$ decreases and $E$ increases with increasing the crosslinks [22,23]. Therefore, one possible origin of the changes in the network microstructures might be related with the increment of the crosslinks by the repeated treatment.

![Figure 4](image)

**Figure 4.** Relationship between the breaking stress and strain and $W_t/W_d$ of PVA cast gels during water exchange with drying.
3.2. Network structure of PVA cast gel

Figure 5 shows SAXS spectra of three as-prepared PVA cast films with \( W/W_d = \text{ca. 1.05} \) at \( N = 0 \), which were prepared by the same method at different times. Each spectrum was fitted by the Lorenz function, \( I(q) = I_0 + (2A/\pi)[(w/(4(q - q_c)^2 + w^2))] \), where \( I_0 \), \( A \), \( w/2 \), and \( q_c \) are the background, the area, the half-width, and the peak-top position, respectively. Although the fitting parameter, \( A \) was largely different from each other, the parameters, \( w \) and \( q_c \) were almost the same with errors less than 5 and 0.7 %, respectively. A broad peak centered at \( q_c = \text{ca. 0.64 nm}^{-1} \) was characteristic to the PVA cast film, which corresponded to the average distance between the microcrystallites, \( L = \text{ca. 9.8 nm} \).

![Figure 5. SAXS spectra of PVA cast gel film (\( N = 0 \)). Three different samples prepared by the same method at different times were used.](image)

Figure 6(a) shows SWAXS spectra of the PVA cast gel film in a swelling swollen process. Intersection of two extrapolations of lines before and after the broad peak in dried gel with \( W/W_d = 1.05 \) was \( q = 0.65 \text{ nm}^{-1} (L = 9.7 \text{ nm}) \). The peak position agreed well with \( q_c \) obtained by the SAXS measurements (Fig. 5). With an increase in \( W/W_d \) (from 1.05 to 2.6) by slowly adding water, the peak position shifted to a lower wavelength, and finally disappeared above \( W/W_d = 3.3 \) since the scattering from water became dominant in the spectrum. As is shown in Fig. 6(b), \( L \) increased at first, and gradually increased when \( W/W_d \) exceeded 1.8. Therefore, we can approximately consider \( L \) of gel with \( W/W_d = 2 \) to be \( L \) of the swollen gel.
Figure 6. (a) SWAXS spectra of as-prepared PVA cast gels with increasing \( W_t/W_d \). The vertical axis of each spectrum is shifted for clarity. (b) \( L \) of PVA cast gels during increasing \( W_t/W_d \).

Figure 7(a) shows SWAXS spectra of the PVA cast gels in the swollen state with \( W_t/W_d = 2 \). With increasing \( N \), the peak position shifted slightly but evidently to a higher wavelength, indicating that \( L \) decreased by the repeated water exchange with drying (Fig. 7(b)). This observation was consistent with the decrement of the swelling ratio, as is shown in Fig. 2.

Figure 7. (a) SWAXS spectra of PVA cast gels in \( W_t/W_d = 2 \) during water exchange with drying. The vertical axis of each spectrum is shifted for clarity. (b) \( L \) as a function of \( N \). Two sets of data were obtained using different samples prepared by the same method at different times.
Figure 8(a) shows ATR FT-IR spectra of the dried gels with increasing $N$. The large peak at around 3,300 cm$^{-1}$ was due to the O-H stretching of the non-hydrogen bonded and hydrogen bonded O-H groups [24]. Its peak height was almost constant during repeated water exchange with drying. On the other hand, the C-O stretching at 1,143 cm$^{-1}$ due to the formation of microcrystallites [25] slightly changed with increasing $N$. Figure 8(b) shows the peak area at 1,143 cm$^{-1}$, which was obtained by deconvoluting the spectra to remove the effects of the other peaks. The peak area at 1,143 cm$^{-1}$ increased from $N = 0$ to 1 and became almost constant after $N = 1$, resulting from the formation of additional microcrystallites by the repeated water exchanges with drying.

From the present results of SAXS, SWAXS and ATR FT-IR spectra, we found that the repeated processes of the water exchange with drying resulted in the formation of additional crosslinks due to the hydrogen bonds and the microcrystallites. The microstructures of polymer network characterized by the microcrystallites have important roles in determining the macroscopic swelling and mechanical properties.

![Figure 8](image)

**Figure 8.** (a) ATR FT-IR spectra of PVA cast gels in dried state during water exchange with drying. The vertical axis of each spectrum is shifted for clarity. (b) The peak area at 1,143 cm$^{-1}$ of the spectra, where each symbol indicates the same meaning described in Fig. 2.

4. **Conclusion**

We have studied the effects of water exchange with drying on the equilibrium swelling ratio and the mechanical properties of PVA cast gel prepared by a cast-drying method. From the measurements of XRD and FT-IR techniques, the formation of additional microcrystallites due to hydrogen bonds between -OH groups of PVA were detected during the repeated water exchange with drying. These microscopic analyses were consistent with the macroscopic observations that the swelling ratio decreased and the breaking stress and strain increased at first and became constant thereafter. After sufficient water exchanges with drying, the swelling ratio should approach constant, therefore the network structure of PVA cast gel might become stable.
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