Polymer Bulletin 24, 613–618 (1990)

Polymer Bulletin

Swelling and mechanical properties of polyvinylalcohol hydrogels

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SUMMARY

The swelling and mechanical properties of Poly(vinylalcohol) hydrogels were examined. It was found that the degree of swelling of PVA hydrogels depends on annealing temperature, but is almost independent of the initial polymer concentration. Mechanical properties of the hydrogels were also influenced by the degree of swelling. A shoulder was observed in double-logarithmic plots of stress vs. strain for the hydrogels, and became clearer as annealing temperature increased. This shoulder was closely related to the breakdown of the microcrystalline domains acting as crosslinks. Also, the shape of stress-strain curves plotted double-logarithmically for the hydrogels changed with the extension rate.

INTRODUCTION

Studies on synthesis (1-4) and mechanical properties (1,3,5,6) of gels have been extensively performed by many researchers for both academic and applied purposes. Poly(vinylalcohol) (PVA) hydrogels have been focused on for medical use because of their good transparency and high tensile strength (3). However, the relationship between the structure and mechanical properties of PVA hydrogels remains unclear. The swelling behavior of PVA hydrogels is closely related to structure, and the degree of swelling also affects the mechanical properties of the hydrogels. It is then fundamentally important to examine the relationships between the degree of swelling and mechanical properties of the hydrogels. Here, we investigated the swelling and mechanical properties of PVA hydrogels.

EXPERIMENTAL

1. Materials

PVA used in this study was supplied by Unitika Co., Japan. The degree of polymerization was 1700, and the degree of saponification was 99.5 mol%. We prepared PVA hydrogels by the method reported by Cha et al. (3). First, PVA was dissolved in a mixture of dimethylsulfoxide (DMSO) and water (4:1 by weight) at 105^{o}C, and then cooled to -20^{o}C. The solution was kept for 24h in a freezer. The initial polymer concentration of PVA dissolved in the solvent was designated by c_o. Gels containing the mixed solvent were immersed in ethanol for solvent exchange from the mixed solvent to ethanol. The gels containing ethanol were then dried in a vacuum oven at 30°C, and the dried gels were annealed in a oil bath. The annealing temperature is expressed as T_a. Finally, the hydrogels were prepared by immersing the annealed gels in water till equilibrium swelling was achieved.

2. Measurements

The stress-strain curves of PVA hydrogel samples were measured in water using a Orientec RTM250 with a specially designed water bath. The sample length (L) varies with time (t) as:

$$L = L_0 + vt \tag{1}$$

where L_0 and v are the initial length of specimen and the crosshead speed. The extension rate (λ) is defined as:

$$\lambda = \frac{L}{L_0} \tag{2}$$

The true strain (ε) is given by: (7,8)

$$\varepsilon = \int_0^t \dot{\varepsilon}\, dt = \int_0^t \frac{v}{L_0 + vt}\, dt = \ln \lambda \tag{3}$$

Here $\dot{\varepsilon}$ is the rate of strain defined by:

$$\dot{\varepsilon} = \frac{v}{L} = \frac{v}{L_0 + vt} \tag{4}$$

The true stress (σ) is given by:

$$\sigma = \sigma_E \lambda \tag{5}$$

Here σ_E is the engineering stress.

RESULTS AND DISCUSSION

In obtaining eq(5), it was assumed that the volume of a gel was unchanged before and after deformation. The hydrogels are considered to be composed of hydrated PVA chains, and microcrystalline domains acting as crosslinks. When crystallinity is low, the hydrogels can be regarded as a rubber-like material. In this case, the above assumption is true. Although crystallinity of the hydrogels investigated here was unknown, we feel that the assumption is applicable to the hydrogels as a first-order approximation.

In Figure 1, water contents in wt %, of PVA hydrogels are plotted against c_o. Except the hydrogel at c_o=7 % and T_a=125°C, the water content of the hydrogels at the same T_a appears to be independent of c_o. On the other hand, the water content for the hydrogels at the same c_o decreases with increasing T_a. The swelling behavior of the hydrogels seems to be strongly affected by the structure of the precursor gels formed in the course of the hydrogel preparation. PVA hydrogels experience a drying process in the course of the sample preparation. As

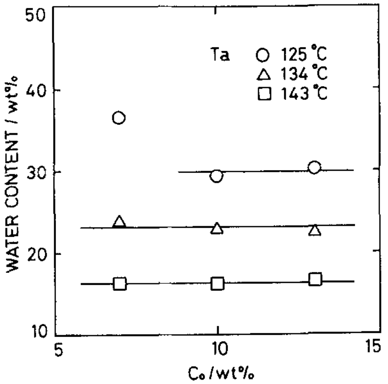

Figure 1. Water content plotted vs. initial polymer concentration (c_o) for PVA hydrogels.

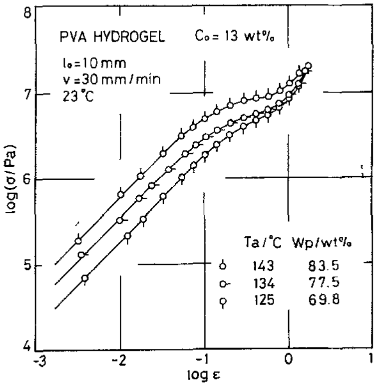

Figure 2. Double-logarithmic plots of stress (σ) vs. strain (ε) for PVA hydrogels at initial polymer concentration, c_o=13 wt%.

shrinkage occurs in the drying process, the structure of the dried gels seems to become nearly similar, regardless of c_o. The structural differences of the hydrogels originating from the difference of c_o disappeared at this stage, as long as T_a was identical. This is the reason why the hydrogels at the same T_a did not show the c_o dependence of the water content. Crystallization occurs at the annealing process, and crystallinity is determined by T_a. As no structural difference existed for the dried gel at various c_o, the difference of the water contents among hydrogels with different T_a is felt to be determined only by the difference of crystallinity. Microcrystalline domains act as crosslinks in the hydrogel. The number of crosslink points in the hydrogel is independent of c_o when T_a is identical for the hydrogels; the number of crosslinks in the hydrogel is determined by T_a, and is identical for hydrogels at the same T_a. However, the number of crosslinks increases with increasing T_a (consequently increasing crystallinity), though the increase of crystallinity also increases the domain size. This is the reason why the water content decreases with increasing crystallinity. It is not clear at present why the gel at c_o=7 %, and T_a=125°C, showed the higher water content than the other gels at the same T_a.

Figure 2 shows plots of log σ vs. log ε for PVA hydrogels at c_o=13 %. Data for each gel in the low ε region can be expressed by a line of slope one. Young's modulus E_o of the initial stage of testing was obtained as a value on the the extrapolated line of slope one at log ε =0. As T_a increases, the value of E_o increases and a shoulder in the middle ε range also becomes more pronounced. The polymer content (W_p) is equal to 100-(water content) in wt%, and increases with increasing T_a. The increase of E_o is due to the decrease of water content, which originates from the increase of crystallinity as T_a increases. The hydrogels contain the microcrystalline domains

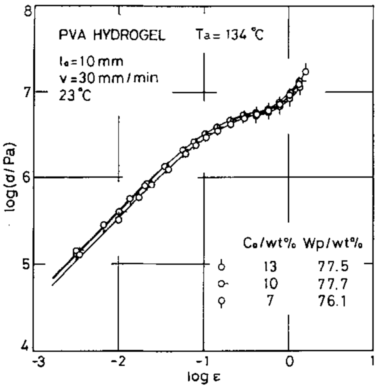

Figure 3. Double-logarithmic plots of stress (σ) vs. strain (ε) for PVA hydrogels annealed at 134^{o}C.

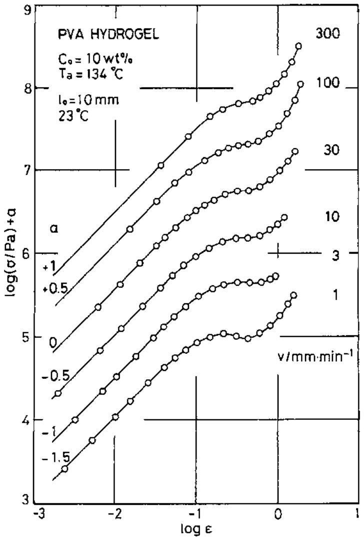

Figure 4. Double-logarithmic plots of stress (σ) vs. strain (ε) of PVA hydrogels. Numerals in the figure indicate extension rate.

formed in the annealing process, and also amorphous chains of high mobility because the chains are hydrated. The shoulder in the figure originates from the breakdown of the microcrystalline domains by the deformation imposed. It can be seen from the figure that the shoulder is enhanced with increasing T_a. This is because the microcrystalline domains increase with increasing T_a.

In Figure 3, similar plots for PVA hydrogel annealed at 134^{o}C are shown. As can be seen from this figure, stress-strain curves for the three specimens agree well. The value of E_o is almost identical for the three samples with different c_o. This is because the number of crosslinks is almost the same for the hydrogels, as discussed previously. The shoulder of the curve in the middle ε region is related to the breakdown of the microcrystalline domains, as mentioned previously. The coincidence of the curves for the three specimens in the middle ε region arises becasuse the extent of microcrystalline domain broken down by the deformation applied is the same for the samples.

The effects of v on the stress-strain behavior was examined for PVA hydrogels. The results are shown in Figure 4. The curves are shifted vertically in order that they do not overlap each other. In the middle ε region, the shape of the curves changes depending on v. The curve at v=1 mm/min clearly exhibits a minimum in the middle ε region. As v increases further, the shape of the curves changes to one with inflection-point characteristics from its original plateau-like shape. The change of shape appears to be closely related to the

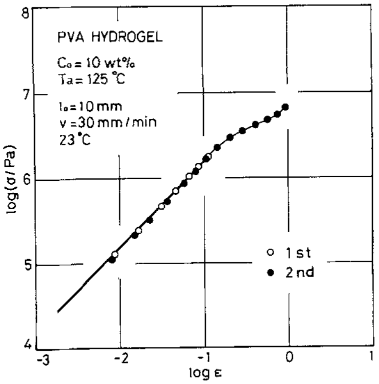

Figure 5. Double-logarithmic plots of stress (σ) vs. strain (ε) for PVA hydrogel of c_0=10 % and T_a=125°C. Open circles indicate the data of the first run, filled circles for the second run. The maximum strain amplitude in the first run experiment is 1.1×10^{-1}.

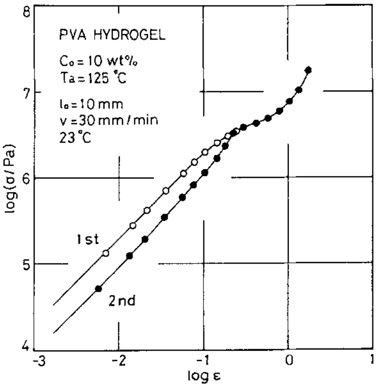

Figure 6. Double-logarithmic plots of stress (σ) vs. strain (ε) for PVA hydrogel of C_0=10 % and T_a=125°C. Symbols are the same as in Figure 6. The maximum strain amplitude in the first run experiment is 2.5×10^{-1}.

stress relaxation in the course of the measurement. At low ε region within the elastic limit, stress relaxation can not occur because the network structure, where microcrystalline domains act as crosslinks, is not broken by the strains. Actually, E_0 of specimens at various v is almost identical, as can be seen from the figure. In the middle ε region, however, the microcrystalline domains are broken down when the deformation is imposed. The breaking down of the domains will originate stress relaxation, and the effect is reflected strongly for the sample at low v, as is observed in the log σ - log ε curve of v=1 mm/min, as a minimum in the middle ε range.

In Figure 5, double-logarithmic plots of σ against ε are shown. The maximum strain amplitude imposed on the sample was 1.1×10^{-1} in the first run, and was within the elastic limit. After the strain was recovered by moving the cross-head of the testing machine in the reverse direction to the zero-force point, the stress-strain curves were again measured (the second run). The data points in the first and second experiments coincide well with each other. This is because the microcrystalline domains are not broken by the deformation imposed in the first run, since the strain amplitude is small enough. Similar plots are shown in Figures 6 and 7. The maximum strain amplitude applied to the sample in the first run is 2.5×10^{-1} in Figure 6 and 4.6×10^{-1} in Figure 7. As can be seen from these figures, E_0 at the second run decreases with increasing maximum strain amplitude, compared with E_0 in the first run. This is because the amount of microcrystalline

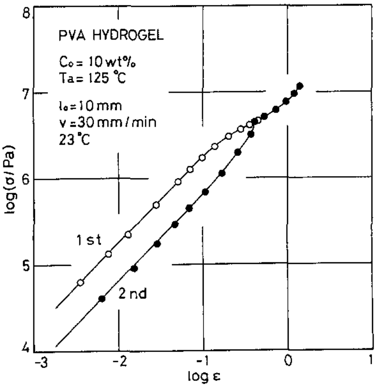

Figure 7. Double-logarithmic plots of stress (σ) vs. strain (ε) for PVA hydrogel of c_0*=10 % and* T_a*=125°C. Symbols are the same as in Figure 6. The maximum strain amplitude in the first run experiment is* $4.6x10^{-1}$.

domains, which are broken in the first run, increases as the maximum strain amplitude in the first run increases. On the other hand, the data points obtained by the first and second runs can be smoothly connected by a single curve for each figure, suggesting that in the second run experiment, the maximum strain amplitude in the first run does not affect the stress-strain behavior in the region of ε larger than the maximum strain amplitude in the first run.

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Accepted August 17, 1990 S