Macromolecules 1993, 26, 3092-3096

Poisson's Ratio of Poly(vinyl alcohol) Gels

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Received October 14, 1992; Revised Manuscript Received February 25, 1993

ABSTRACT: We have investigated Poisson's ratio (μ) of three types of poly(vinyl alcohol) (PVA) gels. The μ values of PVA hydrogel swollen by water and PVA gels swollen by a mixed solvent of dimethyl sulfoxide and water are a little less than 0.5. On the other hand, μ of PVA gels swollen by ethanol, which is a poor solvent for PVA, was 0.33, which is much lower than those for hydrogels and gels swollen by the mixed solvent. The μ value of each gel was found to be independent of the polymer concentration in the gel. μ is also independent of the initial strain rate, so far as the measurement is completed within a relatively short time period such that the effect of solvent flow can be eliminated. Experimental conditions for measuring Poisson's ratio of gel swollen by a solvent were discussed in relation to the diffusion of solvent flow under deformation. Using the values of μ obtained, we calculated the true stress to obtain an exact stress-strain curve for each gel.

Introduction

Studies on the stress-strain behavior and elasticity of gels have been performed extensively,[1-5] but there are only a few[6-9] on the Poisson's ratio (μ) of gels in spite of its importance. It is well-known that the rubberlike materials show μ close to 0.5,[10-12] but μ of glassy polymers is much lower than that of rubbers; for example, μ of glassy polystyrenes is reported to be 0.33.[13] The experimental conditions to determine the value of μ for swollen gels are much more complicated than those for solid polymers, because gels contain solvents. When no flow of solvent occurs during extensional experiments, μ of acrylamide gels with flexible polymer chains is supposed to be near 0.5.[14] However, if the solvents move without friction through the gel network, μ is expected to become smaller than 0.5.[6,7] Namely, μ of gels must depend on the diffusion of the solvent. In other words, μ is a time-dependent quantity. Alexander et al. suggested[15] that gel with flexible chains swells in the long time scale because of the increased osmotic pressure due to the stretching. Poisson's ratio was determined by using the equilibrium dimensions of a swollen gel in the stretched state.[9] In this case, however, the composition (concentration) of the gel changes because of a further swelling during elongation. The value obtained under this condition is the osmotic Poisson ratio ($\tilde{\mu}$), which should be distinguished from μ as a material constant of original, strain-free gels. Therefore, μ must be determined under the condition that no flow of solvent occurs. In most cases, the experimental time scale in a mechanical test is much shorter than that of the flow of solvent. Even in this condition, μ might depend on the experimental time scale because μ depends on the strain rate in general. In conclusion, it is necessary to measure μ in the same time scale as that of the experiments to estimate true stress-strain relations of gels.

Poly(vinyl alcohol) (PVA) dissolved in a mixed solvent of dimethyl sulfoxide (DMSO) and water forms a physical gel when the solution is quenched to low temperatures.[3] PVA gels containing ethanol (EtOH) are obtained by exchanging the mixed solvent for EtOH. This gel shows a stress-strain curve quite different from that of PVA gels swollen by the mixed solvent,[16] due to the heterogeneous structure caused by aggregation of the polymer chain. It has been reported[17] that PVA hydrogels, which were prepared from the PVA gels in EtOH through several preparation steps, are good materials for medical uses, because of the transparency and the high tensile strength. It is important to know exactly the mechanical properties of PVA gels for the applications as well as for scientific interests. The measurement of μ is necessary for these purposes. In this study, we have measured μ of three types of gels: PVA gels swollen in a mixed solvent and in ethanol and PVA hydrogels swollen in water. The polymer content and initial strain rate dependences of μ have been investigated for PVA gels swollen in a mixed solvent. The annealing temperature dependence of μ has also been discussed for PVA hydrogels. Finally, we have obtained a true stress-strain behavior of the gels using the estimated value of μ.

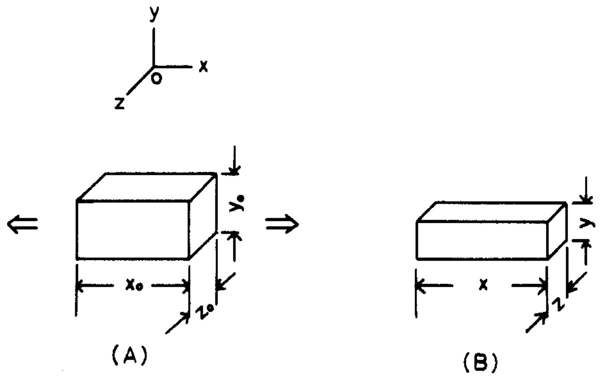

Figure 1. Schematic representation of the sample before and after deformation: (A) before; (B) after.

Theoretical Background

In order to describe the deformation of gel samples, we set 3-dimensional Cartesian coordinates as shown in Figure 1. When a sample is extended in the x-direction, the sample dimension in the x-direction is increased, and the dimensions in the y- and z-directions are reduced in most cases. In this case, the deformation gradient tensor has only the diagonal components. Each component (λ_1, λ_2, λ_3) of the diagonal part can be written as follows.

$$\lambda_1 = \frac{x}{x_0},\quad \lambda_2 = \frac{y}{y_0},\quad \lambda_3 = \frac{z}{z_0} \tag{1}$$

Here, x_0, y_0, and z_0 are the initial dimensions, and x, y, and z are those after extension in each direction. y and z can be time (t)-dependent quantities. Here we deal with the limit values of y and z at $t \to 0$. The Finger-type deformation gradient tensor ($\mathbf{F}^{-1}$) can be written as

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follows.[18] For isotropic materials, $\lambda_2 = \lambda_3$.

$$F^{-1} = \begin{bmatrix} \lambda_1 & 0 & 0 \\ 0 & \lambda_2 & 0 \\ 0 & 0 & \lambda_2 \end{bmatrix} \quad (2)$$

A generalized definition for Poisson's ratio μ is given by[19]

$$\lambda_2 = \lambda_1^{-\mu} \quad (3)$$

When the deformation is applied to the sample, the increase of volume is given by

$$\det(\mathbf{F}^{-1}) = \lambda_1^{-2\mu+1} \quad (4)$$

It can be easily shown from eq 4 that μ is equal to 0.5, when the material is incompressible ($\det(\mathbf{F}^{-1}) = 1$). The cross-sectional area (S) perpendicular to the direction of extension is given by

$$S = S_0\lambda_1^{-2\mu} \quad (5)$$

Here, S_0 is the initial value which is y_0z_0. Under a uniaxial elongation, all the components except the xx one of stress tensor σ are equal to zero. The true stress (σ) is given by

$$\sigma \equiv \sigma_{xx} = (\sigma_{xx})_E\lambda_1^{2\mu} \quad (6)$$

Here, $(\sigma_{xx})_E$ is the xx component of the engineering stress tensor (σ_E). When the specimen is extended in the x-direction with a constant speed of v, Hencky strain (ϵ) in the x-direction is given by[20]

$$\epsilon = \ln \lambda_1 \quad (7)$$

The initial rate of strain ($\dot{\epsilon}_0$) can be given by

$$\dot{\epsilon}_0 = v/x_0 \quad (8)$$

Experimental Section

Gel Samples. The 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 %. The solvent used was a mixture (D/W) of DMSO and water (4:1 by weight). PVA was dissolved into the solvent at 105 °C. The hot solution was casted into a 6- × 6- × 20-mm metal mold. Three types of gels were prepared. (1) The gel sample-coded as PVA gel (D/W) was prepared by cooling the solution to −20 °C and then maintaining in a freezer for 24 h. (2) The gel sample-coded as PVA gel (EtOH) was obtained from PVA gel (D/W) by exchanging the mixed solvent for ethanol. (3) In order to obtain PVA hydrogel samples, which were coded as PVA hydrogel, PVA gel (EtOH) were dried in a vacuum oven at 30 °C and then annealed in an oil bath for 1 h. The annealing temperatures, designated by T_a, were 100, 105, 110, and 115 °C, as shown in Table I, in which all the experimental data obtained in this study are tabulated. PVA hydrogel was finally obtained by immersing the annealed gel in water until the equilibrium swelling was achieved. It is well-known that PVA gels display aging effects. To avoid the effects, all the experiments in this study were completed within 2 h. This will be discussed later.

Measurements. Uniaxial elongation of PVA gels was performed in solvent by using an Orientec RTM-250 tensile tester with a specially designed solvent bath. The extension processes of the samples were recorded with video camera. The nominal extension rate (λ_a) was determined by the distance between the sample clamps. λ_1 was determined by measuring the distance between two marked points with relatively short distance (~3 mm) in the central region of sample. The distance was measured on the monitor screen. By comparing λ_1 with λ_a, we confirmed that (λ_1-1) is proportional to (λ_a-1), as shown by the following equation with usig a constant $k \simeq 1$:

$$\lambda_1 - 1 = k(\lambda_a - 1) \quad (9)$$

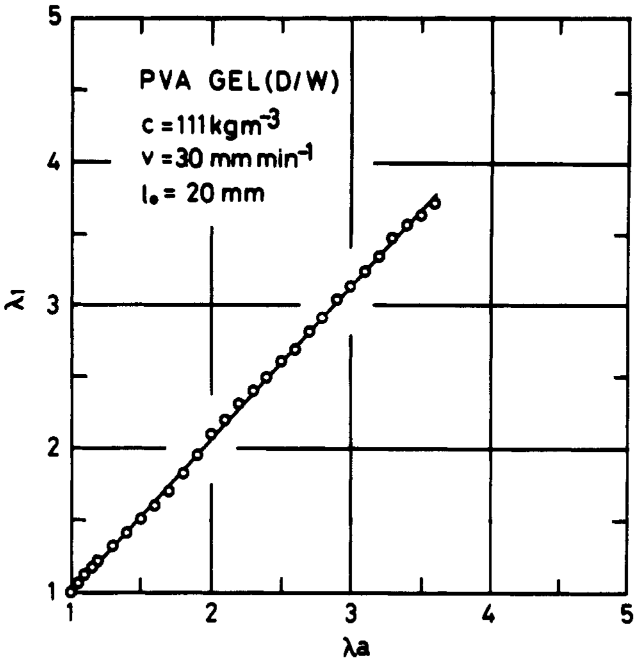

Figure 2. Plots of actual extension rate (λ_1) *versus* nominal extension rate (λ_a) for PVA gel (D/W) at c=111 kg/m³, v=30 mm/min.

Table I. Polymer Concentration (c), Crosshead Speed (v), the Constant of Eq 13 (k), Poisson's Ratio (μ), and the Initial Young's Modulus (E_0) for PVA Gel (D/W), PVA Gel (EtOH), and PVA Hydrogel

	c (kg/m³)	v (mm/min)	k	μ	E_0 (Pa)
		PVA Gel (D/W)			
	77.3	30	0.99	0.474 ± 0.006	5.8×10^4
	111	0.5	1.18	0.455 ± 0.003	1.3×10^5
	111	3	1.05	0.453 ± 0.002	1.6×10^5
	111	30	1.07	0.472 ± 0.004	1.2×10^5
	111	100	1.04	0.463 ± 0.004	1.4×10^5
	111	300	1.10	0.456 ± 0.005	1.1×10^5
	145	30	1.06	0.470 ± 0.003	3.1×10^5
in air	111	30	0.99	0.485 ± 0.005	1.1×10^5
		PVA Gel (EtOH)			
	413	30	1.10	0.338 ± 0.003	4.0×10^7
		PVA Hydrogel			
T_a = 100 °C	542	30	1.18	0.429 ± 0.002	4.5×10^6
T_a = 105 °C	617	30	1.02	0.430 ± 0.002	6.1×10^6
T_a = 110 °C	723	30	1.04	0.447 ± 0.003	1.0×10^7
T_a = 115 °C	798	30	1.05	0.426 ± 0.003	2.1×10^7

Figure 2 shows the plots of λ_1 *vs* λ_a for PVA gel (D/W) with c=111 kg/m³ and v=30 mm/min. As can be seen from this figure, all data points fall on a straight line. The slope of the straight line corresponds to the value of k in eq 9. The value of k determined by the least-squares method was 1.07. For the other samples, λ_1 and λ_a show the linear relation similar to those for PVA gel (D/W) with c=111 kg/m³ and v=30 mm/min. The values of k for the other samples are listed in Table I. As is seen from Table I, the experimental values of k are a little scattered, but they are slightly larger than unity, except for PVA gel (D/W) with c=77.3 kg/m³ and that with c=111 kg/m³ measured in air. The value of k larger than unity suggests that the central region of the specimen is elongated to a larger extent than the edges. This nonuniform elongation is due to the effect of clamps; the edge part of the sample is collapsed at the clamps. When deformation is applied to the system, the extent of elongation at the collapsed edges would be smaller than that at the central region. The value k=0.99 for the two samples is close to unity and indicates that the effect of the clamps is small.

λ_2 was determined by measuring the width at a guide line position on the monitor screen. The true stress (σ)–strain (ϵ) curves of the various PVA gels using the obtained value of μ at 25 °C in solvents were estimated.

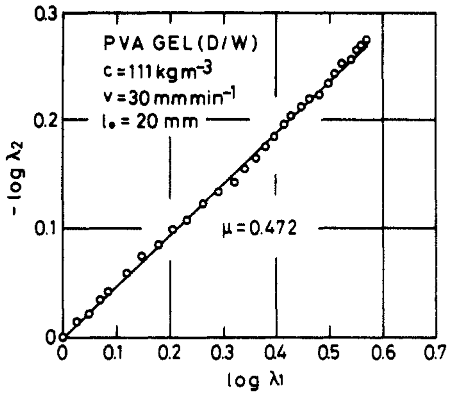

Figure 3. Double logarithmic plots of λ_2 *versus* λ_1 for PVA gel (D/W) at c=111 kg/m^3, v=30 mm/min.

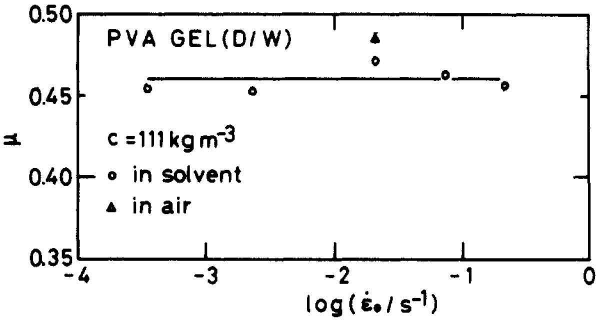

Figure 4. Poisson's ratio (μ) plotted against the logarithm of the initial rate of strain ($\dot{\epsilon}_0$) for PVA gel (D/W) at c=111 kg/m^3. Symbols: (○) extension in solvent; (△) extension in air.

Results and Discussion

Figure 3 shows the plots of −log λ_2 *vs* log λ_1 for PVA gel (D/W) with c=111 kg/m^3 and v=30 mm/min. The relation between −log λ_2 and log λ_1 is expressed by a straight line. The slope determined by the least-squares method was 0.472 ± 0.004. The standard deviation, 0.004 in this case, stands for the scattering of data points in the figure. As is evident from eq 3, the slope of the line corresponds to μ of the sample. The values of μ for the samples studied are listed in Table I. There was a linear relation between −log λ_2 and log λ_1 in all specimens examined in this study, suggesting that μ of each sample is independent of ϵ. Namely, μ is constant over a wide range of strain examined here.

It is interesting to consider the case of the compression mode. The initial Young moduli (E_0) for all the samples used in this study were estimated experimentally in the elongation and compression modes. The moduli obtained agreed with each other, indicating that the value of μ might be also identical in the elongation and compression modes.

μ values measured at various v for PVA gel (D/W) at c=111 kg/m^3 in solvent and in air are tabulated in Table I. We plotted μ against $\dot{\epsilon}_0$ calculated using v. The plots are shown in Figure 4. μ for samples stretched in solvent shows almost the same value in the $\dot{\epsilon}_0$ range of 4.17 × 10^{-4} to 2.50 × 10^{-1} s^{-1}. This means that μ is almost constant in the time scales used for the experiments. The experimental time scale estimated by $1/\dot{\epsilon}_0$, ranges from 4.0 to 2.4 × 10^3 s. As is seen from Figure 4, the value of μ estimated by extension in air is a little larger than, but almost the same as, that in solvent. This suggests that little solvent flow between inside and outside of a gel occurs in the time scale of experiment.

It was suggested[15] that a gel swells because of the increased osmotic pressure due to the stretching in the long time scale. This condition is obtained only when $1/\dot{\epsilon}_0$ is much larger than the characteristic relaxation time for diffusion (τ_D), which is on the order of $y^2/(4D)$ with the diffusion coefficient (D). D for PVA gel (D/W) is unknown at present, but D for the polyacrylamide–water system was reported to be on the order of 10^{-7} cm^2/s.[14,21] Using this value for PVA gel (D/W), τ_D is roughly estimated as 10^6 s. For the experiment under osmotic equilibrium conditions, the sample should be elongated at $\dot{\epsilon}_0$ less than the order of 10^{-6} s^{-1}, where the osmotic Poisson ratio $\tilde{\mu}$ is obtained. However, such a slow extensional experiment is difficult to perform for PVA gel (D/W) because of sample aging. For example, we have observed a stress increase after about 3 h in the stress relaxation experiment at the fixed strain of 0.05. The increase in stress is due to the aging effects and/or the crystallization caused by orientation. This fact implies that a very slow elongational experiment inevitably involves a structural change in PVA gel (D/W). On the other hand, a stress relaxation experiment on the polyacrylamide–water system, in which no structural change in the gel occurs, shows[22] that the width of sample increases at the long times. In this case, the gel composition in the elongated state is different from that in the initial state. As mentioned before, Poisson's ratio obtained under this condition is $\tilde{\mu}$, which differs from μ.

The values of $\tilde{\mu}$ for polyacrylamide gels swollen in water have been extensively investigated by Geissler et al.[6–8] They have reported[8] $\tilde{\mu}$ of polyacrylamide gels to be 0.278. They obtained the osmotic bulk modulus by osmotic swelling measurements and the shear modulus by mechanical measurements. The value of $\tilde{\mu}$ was calculated by using the relation which holds between the various elastic moduli.[23] As Geissler et al. mentioned,[6,7] the "Poisson's ratio" obtained is that under the condition that the solvent can freely leave the gel. We should emphasize again that the value obtained under such a condition is $\tilde{\mu}$, and the values obtained in this study are μ. These two kinds of Poisson's ratio are essentially different.

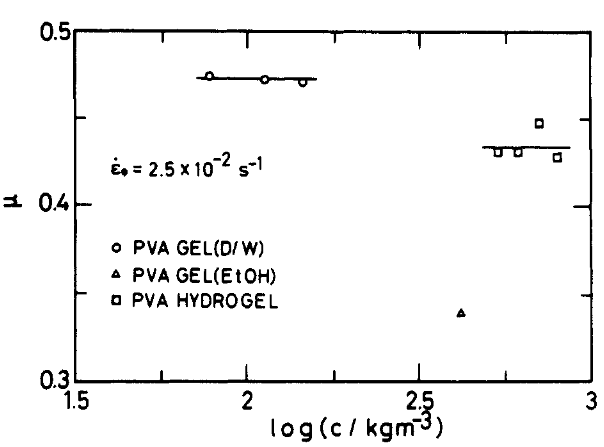

Figure 5. Poisson's ratio (μ) plotted against the logarithm of the polymer concentration (c) at $\dot{\epsilon}_0$=2.50 × 10^{-1} s^{-1}. Symbols: (○) PVA gel (D/W); (□) PVA hydrogel; (△) PVA gel (EtOH).

The μ values measured at v=30 mm/min ($\dot{\epsilon}_0$=2.50 × 10^{-1} s^{-1}) were plotted against the polymer concentration c in Figure 5. μ of PVA gel (D/W) is independent of c in the range from 75 to 145 kg/m^3. The log σ–log ϵ curves for PVA gel (D/W) in the c range examined here do not show the shoulder, and the mechanical behavior resembles that of cross-linked rubbers, as also reported by us before.[16] The cross-link density increases with increasing c. The result shown in Figure 5 indicates that the cross-link density has little effect on μ of PVA gel (D/W).

We have already reported[24] that swelling and mechanical properties of PVA hydrogels are controlled mainly by T_a

in the course of the hydrogel preparation process. PVA hydrogel shows a shoulder on the log σ–log ϵ curve, and the shoulder is closely related to a breakdown process of the microcrystalline domains which behave as cross-link points. The shoulder becomes pronounced as T_a increases, which originated from the increase in degree of crystallinity. In this study, the same behavior was also observed. Namely, the stress–strain relation is linear at small strains and becomes nonlinear in the large strain range. All the points in the plot of $-\log \lambda_2$ *vs* $\log \lambda_1$ for all specimens of PVA hydrogel fall on a straight line over the entire ϵ range studied here. This clearly suggests that the μ value for PVA hydrogel is kept constant through the whole extension process, regardless of the breakdown of the microcrystalline domains. This experimental fact is a little surprising, because it implies that the structural change in the gel has no effect on μ. The stress–strain behavior for PVA hydrogel is reversible within the linear range where no structural change occurs.[24] When the strain exceeds an elastic limit, the stress–strain relation for PVA hydrogel becomes irreversible to show a hysteresis.[24] It is expected that the measurements for μ are reversible at least within the elastic limit.

As can be seen from Table I and Figure 5, the values of μ for PVA hydrogel at different T_a are almost identical, suggesting that the crystallinity has little influence upon μ for PVA hydrogel. The μ values for PVA hydrogel were slightly lower than those for PVA gel (D/W). The difference might be due to the difference in the structure of the gel network. Naito has reported[25] that water as well as the mixed solvent is a good solvent for PVA. This means that the chains between the cross-linking domains in PVA hydrogel and PVA gel (D/W) are also flexible. The domains in PVA gel (D/W), which has never been annealed, are relatively small, and the chains between cross-linking domains are more flexible.[16] On the other hand, the network of PVA hydrogel consists of the microcrystalline domains with finite sizes formed by annealing.[24] The flexibility of amorphous chains for PVA hydrogel should be restricted to some extent near the cross-linking domains. The lower flexibility of polymer chains leads to the creation of a void in the network structure during elongational deformation. The difference in the degree of flexibility of the PVA chains might explain why μ of PVA hydrogel is slightly lower than that of PVA gel (D/W).

The μ value of PVA gel (EtOH) is much lower than those of PVA gel (D/W) and PVA hydrogel, as shown in Figure 5. Ethanol is a poor solvent for PVA, and PVA gel (EtOH) has a phase-separated structure, which consists of the PVA-rich phase and a solvent-rich phase.[16] Most PVA chains exist in the PVA-rich phase. The glass transition temperature (T_g) of PVA has been reported[26] to be 85 °C. The PVA chains in PVA gel (EtOH) can be assumed to be in the glassy state at the measuring temperature (25 °C). The low value μ=0.338 obtained for PVA gel (EtOH) must correspond to the value μ=0.33 of a glassy polystyrene.[13]

Figure 6 shows log σ–log ϵ curves for PVA gel (D/W) with c=111 kg/m^3 at various v. The curves are shifted vertically by a, indicated in the figure, in order to prevent overlaps. The values of E_0 for PVA gel (D/W) at different v are summarized in Table I. The shapes of all the curves are identical, and no shoulder is observed. E_0 is independent of v, as shown in Table I. This suggests that all curves can be superposed by vertical shifts. The stress relaxation during extension was not observed for PVA gel (D/W) in the $\dot{\epsilon}_0$ range from 4.17 × 10^{-4} to 2.50 × 10^{-1} s^{-1}.

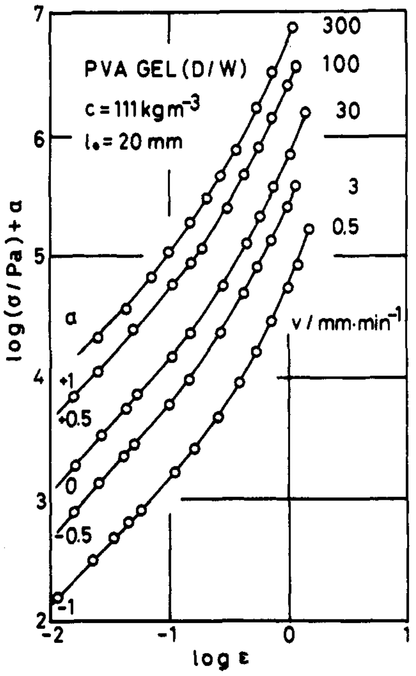

Figure 6. Double logarithmic plots of stress (σ) *versus* strain (ϵ) for PVA gel (D/W) at c=111 kg/m^3. Numerals in the figure indicate the crosshead speed (v).

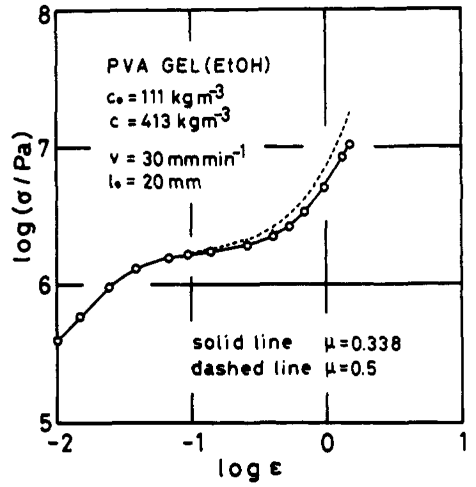

Figure 7. Double logarithmic plots of stress (σ) *versus* strain (ϵ) for PVA gel (EtOH) at c = 413 kg/m^3, v=30 mm/min. The solid line is for μ=0.338; dashed line for μ=0.5.

On the other hand, the shape of the log σ–log ϵ curve for PVA hydrogel was changed depending on $\dot{\epsilon}_0$ ranging from 1.67 × 10^{-3} to 5.00 × 10^{-1} s^{-1}.[24] This change is closely related to the stress relaxation in the course of extension.[24] The difference in behavior of the PVA gels can be attributed to the crystalline domain size and the stress concentration on the cross-link domains.

In Figure 7, plots of log σ *vs* log ϵ for PVA gel (EtOH) at c=413 kg/m^3 and v=30 mm/min are shown. c was determined by measuring the weight of an equilibrium deswollen gel in ethanol. c_0 is the polymer concentration at which PVA was initially dissolved in the mixed solvent. σ is calculated by using μ=0.338, which is obtained in this study. For a comparison, the curve obtained by assuming μ=0.5 is also shown by a dashed line. The value of E_0 of PVA gel (EtOH) is listed in Table I. The true σ value calculated by μ=0.338 is lower than that by μ=0.5 especially in the higher ϵ region. At the breaking point (ϵ=1.59), the ratio of σ for μ=0.338 to that for μ=0.5 is 1.67. The curve of μ=0.338 shows a steeper upturn in the high ϵ region, compared with that of μ=0.5. It might be easily imagined that the true log σ–log ϵ relations are not much different from those obtained by assuming μ=0.5, for the cases of PVA gel (D/W) and PVA hydrogel for which μ are close to 0.5.

Conclusions

The values of Poisson's ratio μ for three types of PVA gels were obtained by uniaxial elongation experiments. The values for PVA gels swollen by water and by a mixed solvent of DMSO and water, which are good solvents for PVA, were close to 0.5, independent of polymer concentration. On the other hand, μ of PVA gels swollen by ethanol, which is a poor solvent, was much lower than those of PVA gels swollen by good solvents. There was a linear relation between $-\log \lambda_1$ and $\log \lambda_2$ over a wide range of ϵ for each sample, indicating that μ is kept constant throughout the whole extension process. The difference in μ values between those gel samples could be explained by the degree of flexibility of the PVA chains. It was found that μ is time-independent in the relatively short time region, in which no flow of solvent occurs. Also it was emphasized that the μ value estimated in this study by elongational experiments should be clearly distinguished from the osmotic Poisson ratio $\tilde{\mu}$ obtained in the equilibrium state under deformation. The true stress–strain curve for each gel was obtained by using the μ value measured in this study.

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