A new static method to determine the ratio of the shear modulus over the longitudinal osmotic modulus for swollen gels

M. Zrinyi[1] and F. Horkay[2]

[1]Department of Physical Chemistry, Technical University of Budapest, Egry J. u. 20–22, H-1111 Budapest, Hungary
[2]Department of Colloid Science, L. Eötvös University, Pázmány sétány 2, H-1117 Budapest, Hungary

Summary

Swelling equilibrium of cylindrical gels under uniaxial compression has been studied. Based on the equivalence of the response of a network to osmotic deswelling and to deswelling induced by unidirectional compression a new method has been developed in order to determine the ratio of the shear modulus over the longitudinal osmotic modulus. For the experiments chemically cross-linked poly(vinyl acetate) gels swollen in toluene and iso-propyl alcohol have been used.

Introduction

In swollen chemically cross-linked networks, the swelling properties are usually described by considering two opposing effects: the osmotic pressure and the restraining force. The characteristic quantity of these effects are the swelling pressure which involves the osmotic pressure causing the expansion of the network and the restraining preessure exerted by the elastic (shear) modulus. This latter quantity plays an important role in keeping the gel in shape by minimizing the nonisotropic deformation.

The osmotic (bulk) modulus, K_{os}, is defined as

$$K_{os} = \Phi \left(\frac{\partial \omega}{\partial \Phi} \right)_T \qquad (1)$$

where Φ means the volume fraction of the polymer in the gel, ω stands for the swelling pressure and T represents the temperature.

The longitudinal osmotic modulus, M_{os}, is a combination of shear and osmotic bulk moduli [1-5]:

$$M_{os} = K_{os} + 4/3\, G \qquad (2)$$

where G is the shear modulus.

The longitudinal osmotic modulus can be determined by quasi-elastic light scattering, the osmotic bulk modulus by swelling pressure measurements and the shear modulus by mechanical deformation.

An important quantity is the ratio of the shear modulus over the the longitudinal osmotic modulus:

$$R = G/M_{os} = G/(K_{os} + 4/3\, G) \qquad (3)$$

According to theories R is independent of molecular details, it provides information on the osmotic Poisson ratio, σ_{os}, of the polymer coils composing the network [5-7]:

$$R = \frac{(1 - 2\sigma_{os})}{2(1 - \sigma_{os})} \qquad (4)$$

Table I. contains the predicted value for σ_{os}, as well as for R.

Measurements of osmotic bulk-, and shear moduli, or longitudinal osmotic modulus together with shear modulus can provide the value of R [3,5]. The kinetics of swelling and shrinking also allows us to determine the parameter R [8-10].

Table I   Predicted values for σ_{os} and for R. These data are taken from ref. [6,7].

quality of the solvent	σ_{os}	R
good	1/4	1/3
theta	1/3	1/4
poor	1/2	0

It seems that R is a very important quantity which controlls many static and dynamic phenomena. In this paper a new method is reported in order to determine the value of R by means of uniaxial compression.

Theoretical part

Our proposed method is based on the equivalence of the response of a network to deswelling induced by lowering the diluent activity and to deswelling induced by unidirectional compression. Beside the theoretical results, this equivalence has been proved by experiments in our previous papers[11-13,20,21].

If the swollen gel equilibrated with a diluent is deformed, the chemical potential of the diluent inside the gel is altered through the influence of the isotropic component of the stress arising from the deformation of the network. Thus the swelling degree changes: in case of a simple elongation it increases, while in the case of unidirectional compression the swelling degree decreases. The effect of deformation on the swelling equilibrium has long been recognized and was discussed intensively by many researchers [14-17 and 11-13]. Deswelling can also be achieved by lowering the chemical potential of the diluent around the freely swollen network by dissolving a polymer in the equilibrium liquid phases, or through the vapor phase [17]. The correspondence between anisotropic deswelling induced by unidirectional deformation and isotropic deswelling due to lowering the chemical potential of the diluent can be formulated as follows [12,17]:

$$\Delta\mu_1 = G(\Phi)\left[1 - \Lambda^{-1}\right] V_1 \qquad (5)$$

where $\Delta\mu_1$ is the change in the chemical potential of swelling agent, V_1 means the partial molar volume of the solvent and Λ stands for the deformation ratio relative to the undeformed length of the same volume as for the deformed gel. It is convinient to introduce another deformation ratio, Λ_e, relative to the undeformed length of the freely swollen gel. The relationship between Λ and Λ_e can be given by

$$\Lambda = \Lambda_e \left(\frac{\Phi}{\Phi_e}\right)^{1/3} \qquad (6)$$

Let us introduce the swelling pressure of the gel, ω:

$$\Delta \mu_1 = - \omega V_1 \tag{7}$$

Combyning Eqs. 5-7 we get

$$\omega(\Phi) = G(\Phi) \left[\Lambda_e^{-1} \left(\frac{\Phi}{\Phi_e} \right)^{-1/3} - 1 \right] \tag{8}$$

By using the definition for the osmotic bulk modulus (Eq.1) one obtains:

$$K_{os}(\Phi) = \Phi \frac{\partial G}{\partial \Phi} \left[\Lambda_e^{-1} \left(\frac{\Phi}{\Phi_e} \right)^{-1/3} - 1 \right] - G(\Phi) \left[\Phi \Lambda_e^{-2} \left(\frac{\Phi}{\Phi_e} \right)^{-1/3} \frac{d \Lambda_e}{d \Phi} + \frac{1}{3} \Lambda_e^{-1} \left(\frac{\Phi}{\Phi_e} \right)^{-1/3} \right] \tag{9}$$

This equation also provides the osmotic bulk modulus for a freely swollen gel in equilibrium with a pure solvent: $\Lambda_e = 1$ and $\Phi = \Phi_e$.

$$K_{os}(\Phi_e) = - G(\Phi_e) \left[\Phi_e \left(\frac{d \Lambda_e}{d \Phi} \right) \Big|_{\Phi = \Phi_e} + \frac{1}{3} \right] \tag{10}$$

Thus one can derive R by combyning Eqs. 3 and 10 and our main result can be written in a simple form:

$$R = \frac{1}{1 - \Phi_e \left(\frac{d \Lambda_e}{d \Phi} \right) \Big|_{\Phi = \Phi_e}} \tag{11}$$

Eq. 11 means once the $\Lambda_e - \Phi$ dependence is established, then it is possible to obtain the ratio of shear modulus over the longitudinal osmotic modulus.

Experimental part

Experiments were performed on chemically cross-linked poly(vinyl acetate) (PVAc) networks swollen to equilibrium by toluene (T) and by iso-propyl alcohol (iPrOH). Toluene can be considered as a good solvent for PVAc, while the iPrOH has a theta temperature at $T = 52\ C^o$.

The gels were prepared by acetylation of poly(vinyl alcohol) gel samples cross-linked by glutaric aldehyde according to a previously described method [12,18].

Cylindrical-form gel speciments of equal height and diameter (approx. 1 cm) were made. Both the degree of cross-linking, DC, and initial PVA concentration,C, at which the cross-links were introduced were varied. DC means the moles of monomer units relative to the moles of cross-linking agent. The gel samples are identified by the C/DC figures, e.g. "6/100 " means C =6wt% and DC=100 .

Deswelling induced by unidirectional compression was performed in a home made apparatus. Cylindrical gels were deformed between two paralell flat plates, whose distance of separation could be adjusted in order to to impose the desired deformation on the sample. During the experiments the whole apparatus was immersed in pure diluent. The time required to reach equilibrium was found to be between 3 and 5 days. The measurements were performed at successively increasing compression ratios. The swelling degree was calculated from the height and diameter data of swollen and dry cylinders on the other hand, and from the masses of swollen and dry networks on the other. More details can be found in our other papers [11,12,20,21].

Results and discussion

Fig. 1 shows the effect of deformation on the equilibrium volume fraction of polymer in the swollen gel.

The effect of unidirectional compression is apparent: the gels deswell under the applied pressure. The same holds true for the PVAc/iPrOH gels as well. The analysis of data was performed by fitting the $\Lambda_e - \Phi$ data for each gel by an expression:

$$\Lambda_e(\Phi) = B \left(\frac{\Phi}{\Phi_e}\right)^P \qquad (12)$$

where B and p are constants.

It must be mentioned that there is strong theoretical reason to choose the above formular [11,12,20,21] . According to cited papers, B=1 and the

value of p depends on the quality of the solvent only. At theta condition one expects that p=-3 and for good solvent condition p=-9/4 is predicted. A combination of Eqs. 11 and 12 results in:

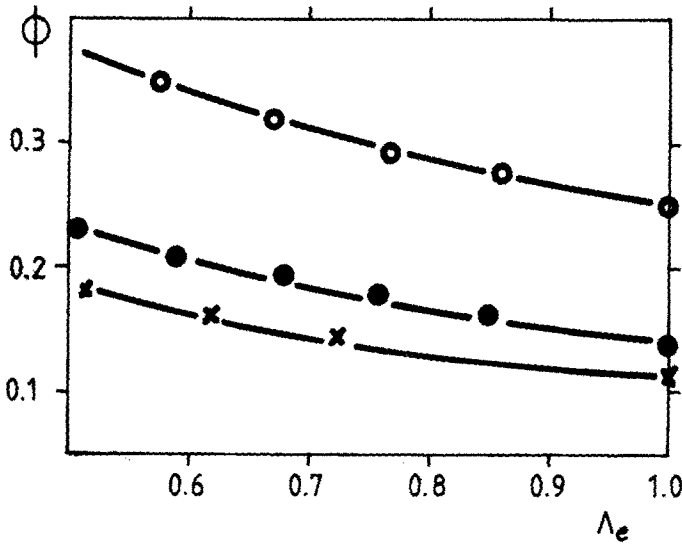$$R = \frac{1}{1 - B p} \tag{13}$$

Fig. 1 Volume concentration of polymer in the PVAc/T gels as a function of deformation ratio. Symbols: o; 12/100 , ●; 12/200, x; 6/100
Solid lines are guide for eyes.

In Table II. are listed the values of the B and p parameters of the least-squares fits to the data for each gel as well as the quantity obtained by Eq. 13. The R values shown here are consistent with the predictions for good and theta solvent conditions (see Table I.). An average R=0.32 has been found for PVAc/T gels which is in acceptable agreement with that deduced by completely different methods. From measuring the osmotic bulk modulus and shear modulus independently, we found that R= 0.36 [3].From swelling kinetics R=0.34 was obtained [19]. It is worth to mention that for polyacrylamide-water gels R=0.32 was obtained from the swelling pressure and the shear modulus measurement [5]. On the basis

of kinetics of swelling R=0.35 has been also found for polyacrilamyde gels [10]. For PVAc/iPrOH gels at theta condition the observed agreement is excellent.

Table II. Deswelling data of PVAc/T and PVAc/iPrOH gel cylinders under unidirectional compression. The data are taken from refs. 12. and 20.

gel	symbol	Φ_e	B	-p	R
PVAc/T	6/100	0.107	0.981	2.34	0.30
PVAc/T	12/200	0.121	0.995	2.17	0.32
PVAc/T	12/100	0.175	0.999	2.20	0.31
PVAc/iPrOH	6/50	0.253	0.994	2.98	0.25
PVAc/iPrOH	6/200	0.149	1.008	3.04	0.25
PVAc/iPrOH	9/100	0.237	1.005	3.03	0.25
PVAc/iPrOH	12/200	0.219	0.998	2.98	0.25

Conclusion

Based on the equivalence of the response of a network to osmotic deswelling and to deswelling realized by unidirectional compression a simple and accurate method has been developed for the determination of the ratio of the shear modulus over the longitudinal osmotic modulus. The experimental results presented here are in agreement with the results of other methods as well as with the theoretical predictions.

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