

On the elastic modulus of swollen gels

M. Zrinyi and F. Horkay

Department of Colloid Science, Loránd Eötvös University, H-1088, Budapest, Puskin u. 11-13, Hungary

(Received 17 March 1986; revised 17 November 1986; accepted 26 November 1986)

Elastic moduli of poly(vinyl acetate) networks swollen in toluene and acetone (good solvents) and in isopropyl alcohol (theta solvent) were studied. The influences of crosslinking density and activity of diluent, as well as the interactions between polymer and swelling agent, were investigated. To describe these three different effects, a phenomenological equation was proposed and checked by experiments.

(Keywords: elastic modulus; swollen network; gel homologues; poly(vinyl acetate))

INTRODUCTION

One of the most important quantities that characterizes the static elastic properties of swollen networks is the shear modulus^{1,2}. In most cases it can be measured easily but its interpretation, based on microscopic theories, often meets with difficulties. The main problem arises from the fact that during deformation of gel, induced by either swelling or deswelling, the mechanism for the position change of crosslink points is not exactly known³. Recent small-angle neutron scattering measurements cast some doubt on the assumption of affine deformation in classical rubber elasticity theories. The experimental results of Bastide *et al.*^{3,4} and Beltzung *et al.*⁵ are in contradiction with the fundamental hypotheses of the classical theory of swelling, since the average radius of gyration of the labelled network chains was found to vary with the swelling degree to a much smaller extent than would have been expected on the basis of any affine⁶, phantom⁷ and/or end-to-end pulling⁸ network model.

A new mechanism was put forward to explain the experimental results: that the dimensions of network chains are mainly governed by the nature of their local interactions and the gel can undergo large macroscopic deformation without a significant change of the molecular dimensions⁴. The consequences of this accordion-like mechanism on physical properties of gels have not so far been given by a molecular theory; rather a phenomenological approach has been developed^{3,4,9}.

Based on our earlier work¹⁰⁻¹³ and other results^{1,2} reported in the literature, we propose a phenomenological equation for the elastic modulus G that differs from that given in ref. 3, namely

$$G(\Phi) = G(\Phi_e) (\Phi/\Phi_e)^{1/3} \quad (1)$$

where Φ is the volume fraction of polymer in the gel and Φ_e denotes the equilibrium volume fraction of the gel swollen to equilibrium. The modulus $G(\Phi_e)$ belonging to the equilibrium state with pure diluent can be identified as

$$G(\Phi_e) = RT \left(\delta \frac{\Phi_e(N, T)}{N} + \Psi(N) \right) \quad (2)$$

where δ and Ψ are temperature-independent quantities, N is the polymerization index of the network chains, and

RT has its usual meaning. Equations (1) and (2) are expected to describe the dependence of elastic (shear) moduli on the concentration of gels. The latter quantity as well as the modulus itself can change as a consequence of at least three different effects. These are:

- (i) change in the concentration of network chains,
- (ii) change in the activity of swelling agent, and
- (iii) change in the interactions between polymer and swelling agent either by temperature or by solvent quality.

These three effects are completely independent of one another, as far as the influence of the crosslinking density and the concentration on interaction parameter can be neglected. Any alteration in the above-mentioned quantities shifts the equilibrium concentration and thus the shear modulus of gels.

Case (i), that is the effect of crosslinking density on the modulus for gels in equilibrium with pure diluent, is perhaps the most frequently studied, since analogies between certain problems of polymer physics and critical phenomena were discovered^{3,14}.

For gels differing from each other in their crosslinking density only, the concentration dependence of elastic modulus is given¹⁴ by

$$G(\Phi_e) = A\Phi_e^m \quad (3)$$

where the proportionality factor A depends on the interaction parameter and the exponent m equals 9/4 in a good solvent, and 3 in a theta solvent. Several experimental findings support the validity of equation (3)^{3,10-12}.

Much less investigated and understood are the other two effects.

The first aim of the present work is to study the concentration dependence of the elastic modulus corresponding to cases (ii) and (iii). The elastic behaviour of gels equilibrated with good and theta solvents is discussed. The quantities δ/N and Ψ are determined and an attempt is made to find out the relationship between the parameters governing the static elastic properties of gels.

EXPERIMENTAL

Unidirectional compression measurements and the deswelling measurements were performed at different temperatures on poly(vinyl acetate) (PVAc) gels swollen to equilibrium in toluene, acetone and isopropyl alcohol, respectively.

PVAc gels were obtained by acetylation of PVA gels^{15,16}. PVA networks were prepared by crosslinking of aqueous PVA solutions having concentrations of 3, 6, 9 and 12 wt %, respectively. At each concentration four gel systems differing in degree of crosslinking (50, 100, 200 and 400) were synthesized. (The degree of crosslinking means the ratio of the moles of monomer to the crosslinking agent.) Presence of unreacted (free) PVA chains in the gels could not be detected¹⁵. The details of gel preparation as well as the acetylation procedure have been described earlier¹⁵⁻¹⁷.

The acetylation was performed in a mixture of 40 vol % acetic anhydride, 50 vol % pyridine and 10 vol % acetic acid at a temperature of 90°C for 8 h. After acetylation the gels were washed in acetone. The acetone was renewed several times until the components of the acetylation mixture were completely removed from the gels. The presence of foreign matter in the equilibrated liquid phase was checked by interferometry. Then the gels were dried at 80°C. The dry networks were swollen to equilibrium in acetone (A) and toluene (T) at 25°C and in isopropyl alcohol (I) at 25, 30, 37, 45, 50, 55, 60 and 70°C. The extent of acetylation was found to be about 98–99%. The acetate content of gels was calculated on the basis of stoichiometry and was compared with experimental data obtained by mass measurements as well as by the saponification number. Agreement between measured and calculated values was found within 1–2%^{12,18}.

Unidirectional compression measurements were carried out on both swollen and dry cylindrical network samples (diameter 1 cm, height 1 cm) at each temperature using an apparatus described elsewhere¹⁸. This equipment enables one to determine force and deformation with an accuracy of 0.1 mN and 6 μm, respectively, in the range of 0.1 mN to 2N and 6 μm to 3.333 mm. The compression measurements were evaluated by the following equation^{1,2}:

$$\sigma = C_1(\Lambda - \Lambda^{-2}) + C_2(\Lambda - \Lambda^{-2})\Lambda^{-1} \quad (4)$$

where σ is the nominal stress, C_1 and C_2 are constants and Λ is the deformation ratio. The absence of volume change and barrel distortion was checked. The constant C_2 was found to be equal to zero for all the gels studied; thus C_1 can be identified with the shear modulus, $C_1 = G(\Phi)$.

The reproducibility of the mechanical measurements, including the preparation of the gels, was better than 5%.

In order to change the volume fraction of the network polymer at constant temperature a modified deswelling method was applied¹⁹. This method differs from the methods used earlier, as the gel is not directly in contact with the polymer solution. The gel specimen is surrounded by a semipermeable membrane (Kalle AG, Wiesbaden, FRG) which prevents the penetration of the polymer used for decreasing the activity of the diluent into the gel.

The solvent activity was adjusted by poly(vinyl acetate) (Mowilith M 40, FRG) in PVAc–acetone gels, poly(vinyl pyrrolidone) (PVP K 90, Fluka, Switzerland) in PVAc–isopropyl alcohol gels and polystyrene ($M_w = 37\,000$,

$M_n = 34\,000$) in PVAc–toluene gels. Low-molar-mass polymer, being able to diffuse through the semipermeable membrane, was removed previously by dialysis. The concentration of the polymer solutions was varied in the range 0–25 wt %. The swelling equilibrium was attained between 5 and 15 days depending on the temperature, the size of the swollen gel and the concentration of the polymer solution.

The reproducibility of the deswelling measurements was better than 2%.

RESULTS AND DISCUSSION

In order to check the applicability of equations (1) and (3), different PVAc networks swollen in toluene and isopropyl alcohol were investigated. The activity of the swelling agent within the gel was maintained by the equilibrium deswelling method. As a result of decreased solvent activity ($0.995 < a_1 < 1$) the volume fraction of polymer in the gel increased (osmotic deswelling), and thus we could determine the shear modulus of each gel as a function of concentration.

In *Figure 1* the dependences of shear modulus on polymer volume fraction are presented for PVAc gels swollen in toluene at 25°C (good solvent) and in isopropyl alcohol at 52°C (theta solvent).

The broken lines refer to PVAc gels equilibrated with pure swelling agent (case (i)). The exponent m equals 2.27 for PVAc–toluene and 3.04 for PVAc–isopropyl alcohol gels, respectively, indicating the validity of equation (3).

The full lines show the variation of the shear modulus as a function of the polymer volume fraction for selected gel samples (case (ii)).

The slope of the parallel straight lines for both swelling agents equals 1/3 to within experimental accuracy. It can also be concluded that the exponent 1/3 in equation (1) is independent of the quality of the solvent.

Equation (1) also predicts that the ratio $G(\Phi)/G(\Phi_e)$ should be a function of only Φ/Φ_e . In *Figure 2* the dependence of the reduced shear modulus $G(\Phi)/G(\Phi_e)$ on $(\Phi/\Phi_e)^{1/3}$ is given for PVAc gels swollen in different swelling agents (acetone, toluene, isopropyl alcohol). It is obvious that the experimental points satisfy equation (3) for all the gel systems studied.

Up till now we have discussed the effects of crosslinking density on the modulus at constant temperature (case (i)) and of deswelling induced by changing the activity of the swelling agent (case (ii)). Swelling and deswelling can also be achieved by variation of the temperature.

However, the swelling or deswelling caused by changing either the activity or the temperature (or solvent composition) does not result in the same power law. This is demonstrated in *Figure 3*, where the dependence of $G(\Phi_e)/RT$ can be seen as a function of the equilibrium concentration at different temperatures. We note that in this case the activity of the swelling agent in the gel is the same as in the pure diluent ($a_1 = 1$).

One can see in *Figure 3* that all the straight lines have positive intercepts, and both the slopes and the intercepts seem to depend on crosslinking density. This result supports the validity of equation (2).

In *Table 1* the values of slopes (δ/N), intercepts (Ψ), as well as the correlation coefficients (r) are summarized. On the basis of experimental data given in *Table 1* one can see

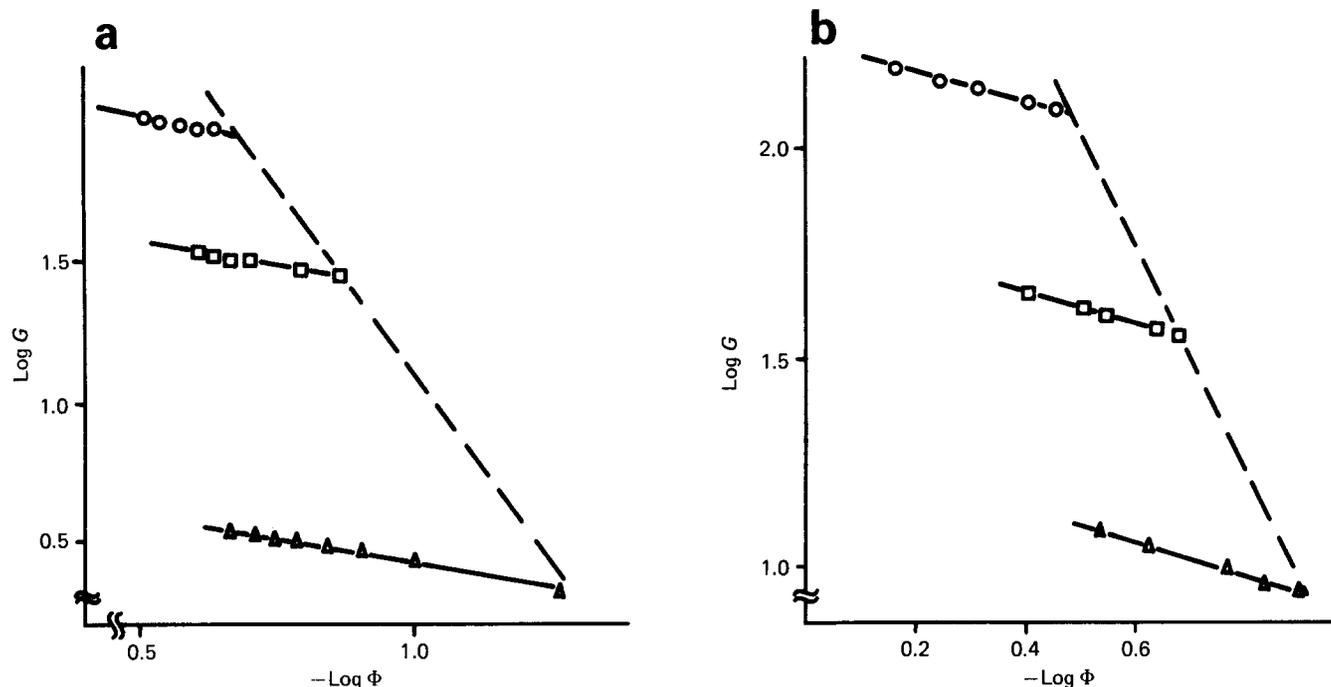


Figure 1 Dependence of the elastic (shear) modulus G on the volume fraction of polymer in the gel for (a) PVAc-toluene and (b) PVAc-isopropyl alcohol gel systems. Full lines refer to selected gel samples at different concentrations achieved by deswelling. Broken lines refer to gels equilibrated with pure diluent. Symbols: \circ , 12/50; \square , 9/100; \triangle , 6/200. (Samples are identified by their polymer concentration at the time of introduction of crosslinks and with their degree of crosslinking; for example, 12/50 means that the concentration of PVA solution at which the crosslinks were introduced was 12 wt% and the degree of crosslinking was 50)

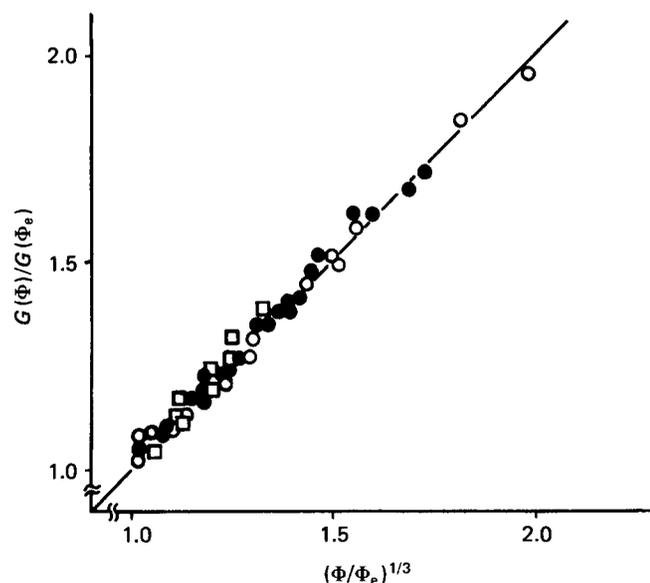


Figure 2 Reduced shear modulus $G(\Phi)/G(\Phi_e)$ against $(\Phi/\Phi_e)^{1/3}$. Symbols: \bullet , PVAc-toluene gels (25°C); \circ , PVAc-acetone gels (25°C); \square , PVAc-isopropyl alcohol gels (55°C). The slope of the straight line is 1

that the values of δ/N and Ψ are commensurable, and thus the quantity Ψ cannot be neglected. If this is so, the question of how equation (3) can be derived from equation (2) needs to be answered.

As is known, equation (3) is the consequence of the assumption that the elastic modulus is proportional to the concentration of network chains ($G \propto \Phi_e/N$) and the c^* theorem. The latter gives the relation between the equilibrium concentration and the polymerization index of network chains through the relations:

$$\Phi_e \propto \Phi^* \propto N^{1-3\nu} \quad (5)$$

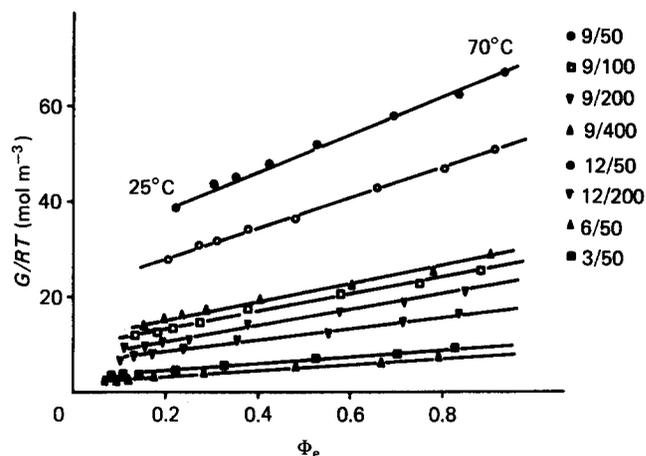


Figure 3 The dependence of G/RT on Φ_e for PVAc-isopropyl alcohol gels. The full lines were calculated by least-squares fitting through the experimental points. Φ_e was altered by changing the temperature from 25°C to 70°C

Table 1 Values of δ/N , Ψ and r for PVAc-I gels

| Sample ^a | δ/N (mol m ⁻³) | Ψ (mol m ⁻³) | r |
|---------------------|-----------------------------------|-------------------------------|-------|
| 3/50 | 7.72 | 3.08 | 0.998 |
| 6/50 | 19.49 | 11.23 | 0.999 |
| 6/200 | 7.37 | 2.09 | 0.999 |
| 9/50 | 31.68 | 22.00 | 0.999 |
| 9/100 | 18.21 | 9.45 | 0.999 |
| 9/200 | 12.97 | 5.54 | 0.998 |
| 9/400 | 6.07 | 2.06 | 0.995 |
| 12/50 | 38.30 | 31.34 | 0.997 |
| 12/200 | 15.90 | 7.29 | 0.996 |

^aSee caption to Figure 1 for details of notation

and

$$G \propto \Phi_e / N \propto \Phi_e^{3\nu/3\nu-1} \propto \Phi_e^m \quad (6)$$

where ν is the excluded volume exponent, which is 3/5 in good and 1/2 in theta solvent condition.

Since both relations (equations (2) and (3)) are strongly supported by experimental evidence, their simultaneous validity requires that the quantity Ψ should depend on N as follows:

$$\Psi(N) \propto N^{-3\nu} \propto (\delta/N)^{3\nu} \quad (7)$$

According to the statements above, the slopes (δ/N) and intercepts (Ψ) of the $G(\Phi_e)/RT$ versus Φ_e (T) straight lines must be interrelated.

In Figure 4 the intercepts against the slopes can be seen. It may be concluded that $\Psi(N)$ is really a power function of δ/N with an exponent 1.54.

We have already seen how the quantities δ/N and Ψ can be determined from experimental data. Another independent way to obtain the sum of them is to study the modulus of the dry networks.

For dry gels equation (2) gives

$$G/RT = (\delta/N) + \Psi \quad (8)$$

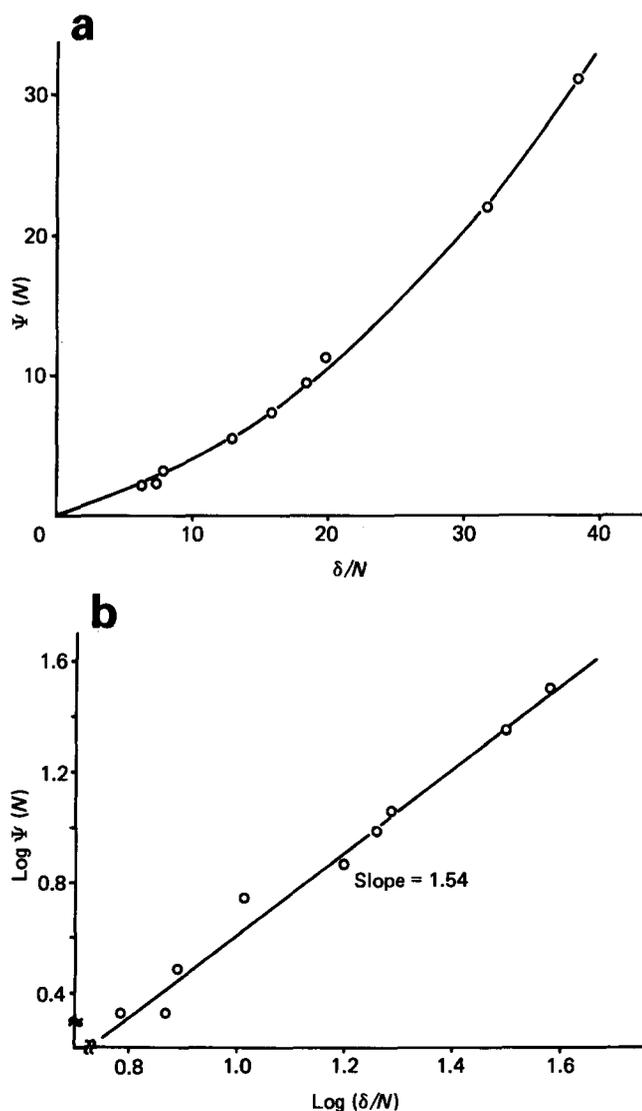


Figure 4 (a) Dependence of the quantity Ψ on δ/N . (b) The log-log representation of Ψ vs. δ/N

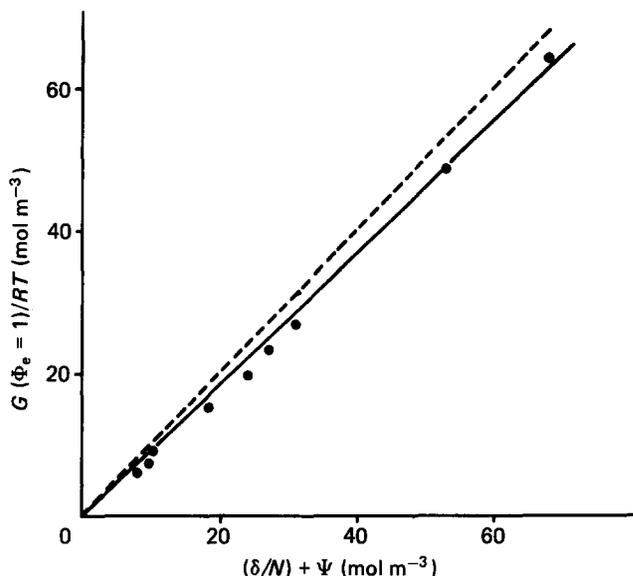


Figure 5 The plot of G/RT vs. $(\delta/N) + \Psi$ for dry PVAc networks. The slope of the broken line is 1. The full line was calculated by least-squares fitting

i.e. from the modulus the sum of δ/N and Ψ can be determined. In Figure 5 the values of G/RT for dried PVAc networks are plotted against $(\delta/N) + \Psi$. The latter data are taken from Table 1.

The experimental points are scattered around a straight line, the slope of which is somewhat smaller than 1. This slight deviation from the theoretically expected behaviour may be attributed to the presence of built-in entanglements. On decreasing the swelling ratio, more and more entanglements may become ineffective and consequently the modulus decreases.

CONCLUSIONS

The concentration dependence of the elastic moduli of poly(vinyl acetate) gel homologues swollen in toluene and acetone (good solvents) and in isopropyl alcohol (theta solvent) has been studied. The influences of crosslinking density, activity of the diluent and interaction between the polymer and the swelling agent have been investigated.

It was established that the shear moduli of PVAc gels obey the power-law dependence predicted by scaling theory. For PVAc-toluene gel homologues the exponent m was found to be 2.27, while for PVAc-isopropyl alcohol gels $m=3.04$ was obtained. The shear moduli of osmotically deswollen gel samples at constant temperature exhibited a one-third power dependence on the polymer concentration in both good and theta solvents.

We found that any change in the elastic modulus can be satisfactorily described by the phenomenological equation

$$G(\Phi) = RT \left(\frac{\delta \Phi_e(N, T)}{N} + \Psi(N) \right) \left(\frac{\Phi}{\Phi_e} \right)^{1/3} \quad (9)$$

where δ and $\Psi(N)$ are temperature-independent quantities. It was proved that the parameters δ/N and $\Psi(N)$ must be interrelated through the relationship $\Psi(N) \propto (\delta/N)^{3\nu}$. The experimentally determined exponent was close to the theoretical value. On the basis of

additional modulus measurements performed on dry PVAc networks the sum of δ/N and $\Psi(N)$ was evaluated. This value proved to be somewhat smaller than that calculated from the temperature dependence of the swelling pressure and modulus.

ACKNOWLEDGEMENT

The support of the Hungarian Academy of Sciences, AKA and OTKA, for this work is gratefully acknowledged.

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