Effect of neutral silica particles on the macroscopic swelling and elastic properties of polydimethyl siloxane networks

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An investigation is reported of the elastic and osmotic properties of end-linked polydimethyl siloxane networks swollen in toluene. These were prepared both in the presence and in the absence of silica filler particles. A comparison is made between the values of the elastic moduli of the unfilled gels, obtained by uniaxial compression experiments and from the concentration dependence of the swelling pressure respectively. For all the gels studied, the elastic modulus was found to vary with polymer volume fraction φ as $\varphi^{1/3}$. The osmotic behaviour can be described by a power law relation in agreement with scaling theory, but cannot be interpreted in a consistent manner by using the osmotic pressure data relevant to the uncrosslinked polymer. For the filled gels, the neutral filler particles produce a reinforcement of the elastic modulus. The concentration dependence of the swelling pressure is affected mainly through the volume occupied by the filler in the network.

(Keywords: end linked networks; polydimethyl siloxane; swelling pressure; elastic modulus; silica filler)

INTRODUCTION

Polydimethyl siloxane (PDMS) has been used extensively as a model system to investigate the swelling properties of polymer networks[1–7]. The high flexibility and low glass transition temperature of this polymer gives it properties that are desirable for a wide range of technical applications. In many of these applications, improvement of the mechanical strength is achieved by introducing a solid filler, usually finely divided silica particles, which substantially modifies the properties of the unfilled elastomer. The silica particles interact with the polymer matrix either through physical adsorption of the polymer chains at the free interface, or through chemical adsorption if the polymer reacts to form a permanent link. As the latter can lead to an unacceptable increase in viscosity of the mixture prior to crosslinking, it is avoided in certain applications by deactivating the reactive sites at the interface using a suitable treatment, e.g. by irreversibly depositing a hydrophobic organic reactant.

The principal objective of this investigation is to study the elastic and osmotic properties of pure PDMS networks and compare them with those containing silica particles. The silica content of the networks investigated here is 10% weight fraction. It is also intended to examine how the macroscopic properties of the resultant gels can be interpreted in the framework of current theories of polymers.

THEORETICAL BACKGROUND

Current understanding of gel swelling is that the free energy of the swollen network is a sum of two independent terms: an elastic and a mixing term. Although the possibility of coupling between these has been suggested[7–9], incontrovertible proof of the existence of cross-terms has not yet appeared. On the contrary, for simple systems observations of swelling can be more readily explained without coupling[10,11]. For fully swollen gels at equilibrium with the pure diluent, the two terms compensate each other in such a way that the osmotic swelling pressure ω becomes zero. At other concentrations

$$\omega = \Pi_m - G_v \tag{1}$$

where Π_m is the osmotic contribution arising from the crosslinked polymer and G_v is the osmotic volume elastic modulus of the gel. Π_m (where the subscript denotes mixing) has frequently been identified with the osmotic pressure of the equivalent solution of the linear polymer of infinite molecular mass.

In classical rubber elasticity theory[12,13] no distinction is made between the shear modulus G_s and the volume elastic modulus G_v. According to this theory, G_s varies

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with polymer volume fraction φ as

$$G_s = G_{so}\varphi^{1/3} \qquad (2)$$

It follows that the expected variation with swelling for the volume elastic modulus is

$$G_v = G_{vo}\varphi^{m} \qquad (3)$$

where G_{so} and G_{vo} are constants that depend on the network investigated, and $m = 1/3$.

In the polymer solution theory of Flory and Huggins[14], the mixing contribution Π_m is represented by the expression

$$\Pi_m = (RT/v_1)[\ln(1-\varphi) + \varphi + \chi\varphi^2] \qquad (4)$$

More recent scaling theories of polymer solutions[15,16] predict a power law behaviour for the concentration dependence of the osmotic pressure of polymer solutions in the semi-dilute regime:

$$\Pi_m = A\varphi^{n} \qquad (5)$$

where $n = 9/4$ in a good solvent and $n = 3$ in theta conditions. The numerical constant A depends on the particular polymer solvent pair. For gel homologues swollen in a diluent to their equilibrium volume fraction φ_e, equations (1) and (5) give the concentration dependence of the volume elastic modulus

$$G_v(\varphi_e) = A'\varphi_e^{n} \qquad (6)$$

where A' is a new constant, related to A.

EXPERIMENTAL

Sample preparation

The samples were generously provided by the Département Silicones of Rhône Poulenc, in a pre-mixed form containing hydroxyl terminated PDMS chains of molecular weight (M_η) approximately 40 000 Daltons, together with the crosslinking agent, ethyl triacetoxy silane (ETAS). For the filled samples, 10% by weight of fumed silica beads (approximate radius 4.5 nm) was also included by mechanical mixing. Light scattering measurements showed that the silica particles are present in the form of aggregates. Crosslinking occurs when the mixture is exposed to atmospheric water, which allows the acetyl groups to react with the hydroxyls, and releases acetic acid.

The gels were prepared in Teflon or polystyrene moulds of the desired shape. The time allowed for the reaction was at least one week for thin (1 mm) samples and several months for samples of dimensions c. 1 cm. At the end of this period, the samples were removed from the moulds and swollen to equilibrium in octane to extract the sol fraction. The measured sol fraction of the samples was less than 5% by weight. Two silica-free samples were prepared by dilution of the pre-mixed batch with chlorobenzene, at 40% and 60% by volume of polymer (samples u40 and u60, where 'u' denotes unfilled). The others were made directly from the undiluted parent mixtures: one sample without filler (u100) and two containing filler particles of different nominal surface area, namely 60 and 300 m^2 g^{-1} (samples f100a and f100b respectively).

After washing, the diluent was changed to toluene, which is also a good solvent for PDMS at 25°C. The swelling equilibrium concentration of the samples in excess toluene was measured. Subsequently the gels were enclosed in dialysis bags and allowed to come to equilibrium with a solution of poly(vinyl acetate) in toluene of known osmotic pressure[17–19]. After reaching equilibrium (1–4 weeks, depending on the sample size), the concentration of both the solution and the gel was measured. The swelling pressure of the PDMS gels as a function of the concentration of the network polymer was obtained from the osmotic pressure of the equilibrium polymer solution. The polymer volume fractions were calculated from the known densities of PDMS[4] ($\rho_{PDMS} = 0.97$ g cm^{-3}) and toluene, using the assumption of volume additivity.

The measurements of the shear modulus were made at different swelling degrees in an apparatus described elsewhere[20]. This measurement was performed by applying a uniaxial compression to the cylindrical samples (diameter = height = 1 cm), in a time short ($\leqslant 5$ min) compared with the deswelling time of the gel due to the hydrostatic component of the applied stress. No barreling or volume change could be detected. All measurements were carried out at 25°C.

RESULTS AND DISCUSSION

Figure 1 shows the variation of the swelling pressure *versus* the dry weight fraction w for the unfilled samples and for two representative filled gels. For simplicity in this comparison, w includes the filler in the latter case. The curves for the filled gels display a stronger concentration dependence than the unfilled samples.

Figure 2 shows in a double logarithmic representation the volume elastic moduli of the unfilled PDMS samples, $G_v(\varphi_e)$ calculated at swelling equilibrium with the pure diluent, as a function of polymer volume fraction φ_e. This latter quantity was obtained from the dry weight fraction w, assuming volume additivity of the respective components and from the known proportion of polymer in the dry networks (c. 0.9 w/w). $G_v(\varphi_e)$ was calculated by fitting equation (1), together with equations (3) and (5), to the swelling pressure measurements. In this fitting procedure the exponents n and m are allowed to vary, as described below. Also plotted in the same figure are the volume elastic moduli data for freely swollen PDMS/toluene networks, prepared by Langley and Ferry[2] using high

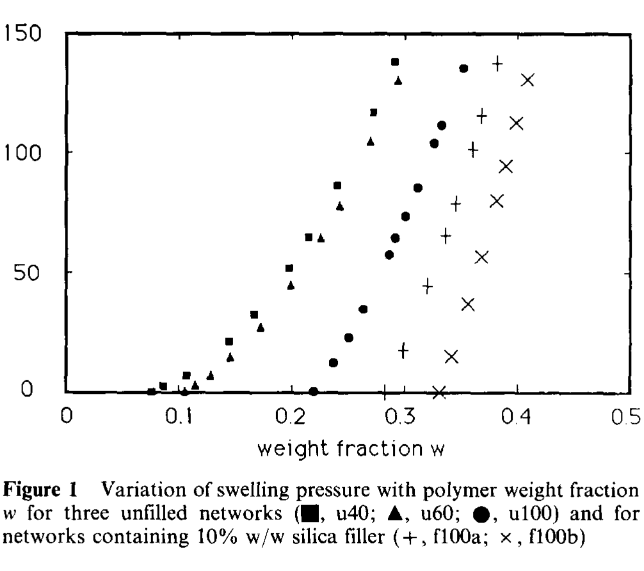

Figure 1 Variation of swelling pressure with polymer weight fraction w for three unfilled networks (■, u40; ▲, u60; ●, u100) and for networks containing 10% w/w silica filler (+, f100a; ×, f100b)

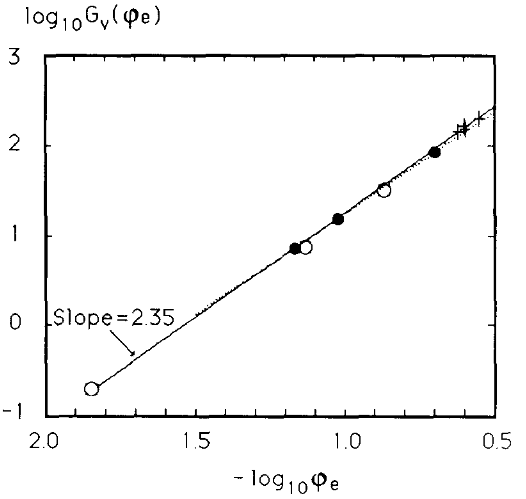

Figure 2 Double logarithmic plot of the elastic modulus G_v at swelling equilibrium in toluene as a function of polymer volume fraction φ (●). ○, Volume elastic modulus calculated from ref. 2 for high energy electron radiation crosslinked PDMS gels. +, Samples containing 10% w/w silica filler particles. Dotted line represents simple scaling slope of 9/4. Continuous straight line is the least squares fit through all the data points

energy electron radiation. These moduli are obtained from equations (1) and (4) together with the values of χ and φ_e supplied in ref. 2.

All the data appear to scatter about the same straight line. The curve corresponding to the slope $n = 9/4$ is represented by the dotted line on *Figure 2*. The results from the samples of Langley and Ferry (open circles), in spite of their rather different conditions of preparation, match satisfactorily with those of the present networks (solid circles). Crosses designate the PDMS networks containing silica filler. These points are displaced towards higher volume fractions along the continuous straight line of *Figure 2*. This result means that the presence of silica particles increases the modulus in a similar way to an increase of the crosslinking density, and clearly demonstrates their reinforcing effect. Although the enhancement of elastic modulus is more pronounced when the specific surface area of the filler is greater, the differences detected between the filled samples are minor.

From equation (1) and a knowledge of Π_m, an independent estimate can be obtained for the elastic contribution G_v. In *Figure 3* the quantity $\Pi_m - \omega$ is shown as a function of the volume fraction, where Π_m is calculated using equation (4) together with the value of χ reported by St Pierre *et al.*[1]. In this figure it can be seen that as the concentration increases, the calculated values of $\Pi_m - \omega$ progressively deviate from the measured values of the shear modulus. This discrepancy has already been remarked for various systems[1-11], and its cause attributed to the failure of either or both of the two underlying assumptions: that G_v is numerically equal to G_s; or that Π_m of the gel is the same as that of the solution of the corresponding linear polymer of infinite molecular weight. Observations of the swelling equilibrium concentration of networks[2,10] have led to the conclusion that the second assumption is at fault.

In the present case, similar information is provided by analysis of the swelling pressure data in terms of equations (1), (3) and (5), which yield

$$\omega = A\varphi^n - G_{vo}\varphi^m \qquad (7)$$

where n and m are varied alternately in a non-linear least squares fitting procedure to obtain the point of minimum variance[11]. The value for G_v at equilibrium swelling calculated in this way as well as the measured G_s for two of the unfilled samples are listed in *Table 1*. The relatively good agreement between these values obtained by completely independent means leads us to the same conclusion as refs 2 and 10, namely that Π_m for the crosslinked polymer is distinct from that of the non-crosslinked solution of infinite molecular weight.

Further information can be obtained by returning temporarily to the Flory–Huggins expression, equation (4) for Π_m. The apparent interaction parameter χ, calculated on the basis of the above conclusion that $G_s = G_v$, is given by

$$\chi = -[v_1(G_s + \omega)/RT + \ln(1-\varphi) + \varphi]/\varphi^2 \qquad (8)$$

The values of χ calculated in this way for the two gels of *Figure 3* at various degrees of deswelling are plotted as a function of φ in *Figure 4*. It is clear from this figure that χ cannot be treated as a constant depending only upon crosslink density. Pronounced inherent concentration dependence is revealed that it is closely similar for the two gels investigated. This result suggests that the

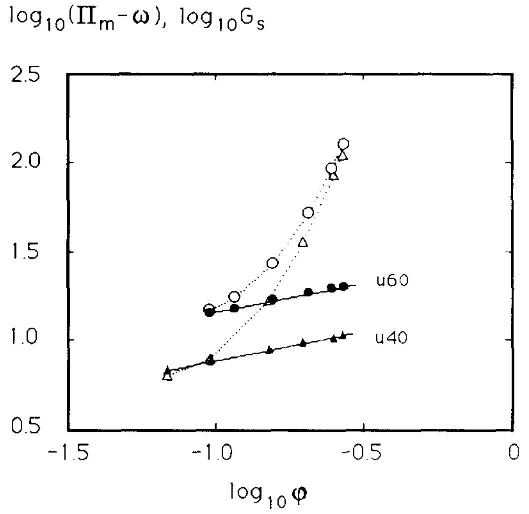

Figure 3 Plot of $\Pi_m - \omega$ (open symbols) as a function of polymer volume fraction φ for two of the unfilled PDMS networks (u40 and u60) swollen in toluene. Π_m is calculated using equation (4) with $\chi = 0.465$ (ref. 1). The dotted lines are guides for the eye. Filled symbols: shear modulus G_s obtained by uniaxial compression of the samples under conditions of constant swelling degree. The slopes of least square fits to G_s in this representation are: sample u40, 0.338 ± 0.008; sample u60, 0.332 ± 0.007

Table 1 Parameters of least squares fits to equation (7) and shear elastic moduli of unfilled PDMS networks swollen in toluene at 25°C. $G_v(\varphi_e) = G_{vo}\varphi_e^n$, where φ_e is the polymer volume fraction at swelling equilibrium with toluene. $G_s(\varphi_e)$ is the shear modulus of the gels obtained by uniaxial compression measurements at constant volume at swelling equilibrium with toluene. Sample designation: u40 indicates an unfilled network prepared at 40% polymer volume fraction in chlorobenzene

Sample	u40	u60	u100
A/kPa	2780	2720	2520
n	2.22	2.21	2.12
m	0.347	0.343	0.336
$G_v(\varphi_e)$/kPa	7.1	15.0	84.8
$G_s(\phi_e)$/kPa	6.7	14.2	–

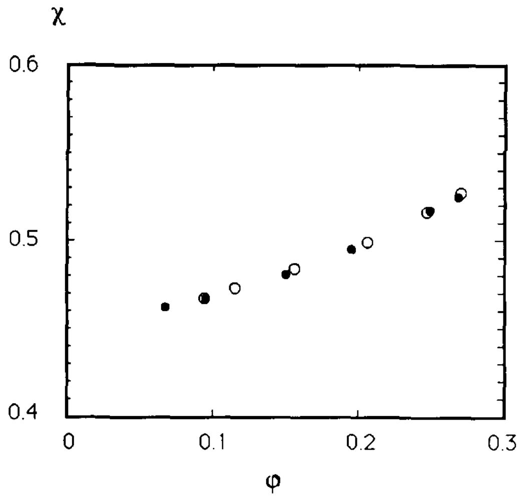

Figure 4 Values of the apparent interaction parameter χ, calculated using relation (8), as a function of polymer volume fraction, for samples u40 (open circles) and u60 (filled circles). In this calculation the measured values of G_s at each volume fraction were used

apparent crosslink density dependence[2,10] of χ observed in gels at their swelling equilibrium concentration φ_e is the consequence of the φ-dependence of χ and the fact that φ_e varies with crosslink density. It remains, however, that χ for the networks is quantitatively different from the solutions at the same concentration. A similar effect has already been noted for poly(vinyl acetate) gels[11].

The above observations are of relevance to recent theoretical work that predicts a linear relationship between χ and crosslinking density[21]. The invariance of χ with crosslink density, observed in ref. 11 and implied here, is not accounted for in current theories.

We return to the scaling analysis. In *Table 1* are summarized the parameters obtained from the fits of the swelling pressure data to equation (7). It can be seen that the exponents n and m lie close to the theoretically expected values of c. 9/4 and 1/3, respectively. These results indicate that the swelling pressure of the unfilled PDMS networks swollen by toluene are satisfactorily described by the two terms of equation (7), and that the volume elastic modulus is entirely consistent with the shear modulus. The agreement with the scaling form also implies that the concentration dependence of χ referred to in the preceding paragraph is an artefact of the Flory–Huggins representation that disappears when polymer–polymer correlations are taken into account[16].

The simple behaviour found for the unfilled gels makes it natural to apply a similar procedure to the filled networks. There is, however, no generally accepted theory describing the effect of a dispersion of neutral solid particles on the osmotic properties of a network. As a first approximation, nevertheless, it seems reasonable to analyse the curves displayed in *Figure 1* by an equation analogous to equation (7) in which the volume fraction is replaced by the directly measured weight fraction w:

$$\omega = aw^n - g_{vo}w^m \qquad (9)$$

The parameters from these fits are listed in *Table 2*. The resulting exponent n for the gels containing silica particles considerably exceeds 9/4, but m remains throughout very close to its theoretically expected value.

Because of their small number, relative immobility and absence of mutual repulsion, neutral filler particles cannot be expected to make a significant direct contribution to the osmotic properties of the swollen network. We assume therefore that the solid particles intervene merely by occupying a fixed volume in the system, so that the effective osmotic pressure is governed by the volume fraction of the network polymer alone. Least squares fits to equation (7) using φ for the filled gels give the results shown in *Table 3*. The principal effect of this transformation is to reduce the exponent n to a value consistent with that obtained for the unfilled gels. It is also noticeable that the filler enhances the value of the coefficient A by about 50% over that for the unfilled networks. The exponent m remains close to 1/3 throughout.

CONCLUSIONS

The effect of neutral silica particles on the elastic and osmotic properties of chemically crosslinked polydimethyl siloxane networks swollen in toluene is investigated and compared with the corresponding unfilled gels. The elastic modulus of the filled samples considerably exceeds that of the unfilled gels, highlighting the reinforcing effect of the silica particles, which behave like additional crosslinks. For the unfilled gels, the concentration dependence of the elastic modulus agrees well with that reported by Langley and Ferry[2] for PDMS networks crosslinked by electron radiation.

The osmotic swelling pressure of the unfilled gels can be described satisfactorily by a two term equation of the form

$$\omega = A\varphi^n - G_{vo}\varphi^m$$

where the exponents n and m adopt values close to 9/4 and 1/3, respectively. Comparison with osmotic pressure data taken from the literature[1] reveals that the osmotic term $A\varphi^n$ for the network polymer is significantly smaller than that of the non-crosslinked polymer of infinite molecular weight. For the networks containing neutral filler particles, the osmotic behaviour seems to be governed mainly by the polymer. The filler particles make their presence felt principally through the volume they occupy. Furthermore, for the filled gels, the value of the coefficient A is enhanced over that of the unfilled gels.

Table 2 Parameters of least squares fits to equation (9) for filled gels (Sample f100a contains silica filler with 60 m^2/g; f100b 300 m^2/g). $g_v(w_e) = aw_e^n$, where w_e is the weight fraction at swelling equilibrium with toluene

Sample	f100a	f100b
a (kPa)	3483	3743
n	2.61	2.69
m	0.324	0.343
$g_v(w_e)$ (kPa)	129.4	189.2

Table 3 Parameters from least squares fits to equation (7) for filled gels

Sample	f100a	f100b
A (kPa)	3720	4208
n	2.29	2.41
m	0.327	0.340
$G_v(\varphi_e)$ (kPa)	142.9	199.7

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REFERENCES

1 St Pierre, L. E., Dewhurst, H. A. and Bueche, A. M. *J. Polym. Sci.* 1959, **36**, 105
2 Langley, N. R. and Ferry, J. D. *Macromolecules* 1968, **1**, 353
3 Shih, H. and Flory, P. J. *Macromolecules* 1972, **5**, 758
4 Shih, H. and Flory, P. J. *Macromolecules* 1972, **5**, 761
5 Brotzman, R. W. and Eichinger, B. E. *Macromolecules* 1982, **15**, 531
6 Brotzman, R. W. and Eichinger, B. E. *Macromolecules* 1983, **16**, 1131
7 Neuburger, N. A. and Eichinger, B. E. *Macromolecules* 1988, **21**, 3060
8 Gottlieb, M. and Gaylord, R. J. *Macromolecules* 1984, **17**, 2024
9 Gee, G., Herbert, J. B. M. and Roberts, R. C. *Polymer* 1965, **6**, 541
10 McKenna, G. B., Flynn, K. M. and Chen, Y.-H. *Polymer Communications* 1988, **29**, 272
11 Horkay, F., Hecht, A. M. and Geissler, E. *J. Chem. Phys.* 1989, **91**, 2706
12 James, H. M. and Guth, E. J. *J. Chem. Phys.* 1943, **11**, 455
13 Treloar, L. R. G. 'The Physics of Rubber Elasticity', Oxford University Press, Oxford, 1975
14 Flory, P. J. 'Principles of Polymer Chemistry', Cornell University Press, Ithaca, NY, 1953
15 de Gennes, P. G. 'Scaling Concepts in Polymer Physics', Cornell University Press, Ithaca, NY, 1979
16 Muthukumar, M. *J. Chem. Phys.* 1986, **85**, 4722
17 Vink, H. *Europ. Polym. J.* 1974, **10**, 149
18 Nagy, M. and Horkay, F. *Magy. Kem. Folyoirat* 1979, **85**, 513 (in Hungarian)
19 Nagy, M. and Horkay, F. *Acta Chim. Acad. Sci. Hung.* 1980, **104**, 49
20 Horkay, F., Nagy, M. and Zrinyi, M. *Acta Chim. Acad. Sci. Hung.* 1980, **103**, 387
21 Freed, K. F. and Pesci, A. I. *Macromolecules* 1989, **22**, 4048