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Compression measurements on dry and swollen networks

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Summary

The elastic behavior (uniaxial compression measurements) of PDMS-networks swollen in pure solvents of different thermodynamic quality is described. The results are discussed in the framework of the model for phantom networks. It is shown that the calculated M_C is a function of the swelling degree and that the corresponding curve consists of two different parts. The shape of the first part can be explained by a change of the microstructure factor A and the second by a change of the memory term η.

Introduction

Different methods were developed to obtain exact network parameters and to get a better understanding of the correlation between structure and properties. The measurement of swelling degree and elastic behavior is among the most powerful and efficient method for determining cross-linking densities or molecular masses of network chains.

The fundamental hypothesis concerning the swelling of networks and changes of rubber elasticity associated with swelling was introduced by Flory and Rehner: the elastic strain energy density function is invariant to swelling. Early measurements on dry and swollen networks indicated a change of rubber elasticity with swelling (1, 2). What is found experimentally and also predicted by various theories is that under uniaxial deformation the modulus decreases as deformation increases. None of the theories can predict correctly the forms of stress-strain behavior for different types of mechanical deformations and different levels of strains. Similar conclusions have been drawn regarding swelling behavior. It depends on the chemical nature of networks and solvents (3). In (4) it was found that the dry-state properties (compression measurements) can be used to predict the swollen-state properties by assuming that the elastic behavior of swollen networks is unaltered by the presence of the solvent. The effect of swelling on the elasticity seems to depend on the cross-linking density and can be understood by the "localization model" (5).

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The aim of this work is the characterization of networks swollen in different solvents by compression and swelling measurements. The results are discussed in the framework of the phantom network model.

The relation between stress and uniaxial deformation with respect to measurements of swollen samples (6) is represented by eq (I). All quantities (area, cross-linking density) are referred to the dry state.

$$\sigma = \frac{f}{A_0} = A\eta\,\nu_P RTQ^{1/3}\,|\lambda - \lambda^{-2}| \qquad V = const. \qquad \text{(I)}$$

$$G^{*} = \frac{f/A_0}{Q^{1/3}|\lambda - \lambda^{-2}|} = A\eta\varrho_P RT/M_C \qquad \text{(II)}$$

σ	stress	f	force
A_0	area	A	mikrostructure factor
η	memory term	ν_P	cross-linking density (ϱ_P/M_C)
ϱ_P	density	M_C	molecular weight between
R	gas constant		cross-links
T	absolute temperature	Q	equilibrium swelling degree
λ	deformation	G*	modulus per unit area of unstrained dry gel

Two limit cases exist in the picture of the phantom network: the affine (e.g. Hermans-Flory-Wall, A=1) and the free-fluctuating (e.g. James-Guth, A depends on the functionality f of the network, A=1-2/f). Prins and Dušek (7) defined the memory term η (often designed as $h^{2/3}$) as the ratio of the mean square end-to-end distance of an elastic chain in the dry network to the mean square end-to-end distance of a free chain at the concentration at which the network was formed. So it depends on the solution properties of the chains during cross-linking. If no solvent is present η=1.

$$\eta = \langle r_d^2 \rangle / \langle r_0^2 \rangle \qquad \text{(III)}$$

Experimental

Networks formed by polycondensation of end-linked polydimethylsiloxane were investigated. α,ω-dihydroxypolydimethylsiloxane was cross-linked with tetrafunctional tetraethoxysilane (TEOS) and trifunctional methyltrimethoxysilane (MTMOS) in the presence of the catalyst dibutyltin didodecanoate (8, 9). It is assumed that the networks formed in the process were not ideal model networks. (Model networks would have no free chain ends and rings and M_C would be equal to M_N of α,ω-dihydroxyPDMS.)

The samples were sliced into cylinders (about 5 mm in diameter by about 2 mm in height). Before measuring the samples were extracted for 3 days in toluene to remove the non-cross-linked fractions.

The swelling degree was determined gravimetrically and also optically with a cathetometer. Compression measurements were carried out on both dry and swollen samples (at 20±1°C).

The tests carried out in the swollen state were performed by first swelling the networks to equilibrium and then testing them in an excess of solvent (10, 11). The applied forces were in the range from 20 to 300 N ($1<\lambda^{-2}<1.2$). In all cases a linear relation between σ and $|\lambda-\lambda^{-2}|$ was found, the requirement for the evaluation of the data with eq (I). (The C_2-parameter of the Mooney-Rivlin-equation is equal to zero for compression measurements (12)).

For a further discussion apparent molecular weights of network chains M_C' were calculated:

$$M_C' = \varrho_P RT/G^* = M_C/A\eta \qquad \text{(IV)}$$

($\eta=1$, $A=1$: $M_C'=M_C$)

Results and Discussion

The choice of the swelling agents, which should cover a wide range of swelling degrees, based on the results in (13, 14). A graph of the swelling degrees of the networks versus the solubility parameters of the solvents has normally a maximum at the point at which the solubility parameter of the polymer is equal to the one of the solvent. In our case we obtained separate curves for the aliphatics and aromatics (Fig. 1). This is an indication of different kinds of interactions between solvents and networks.

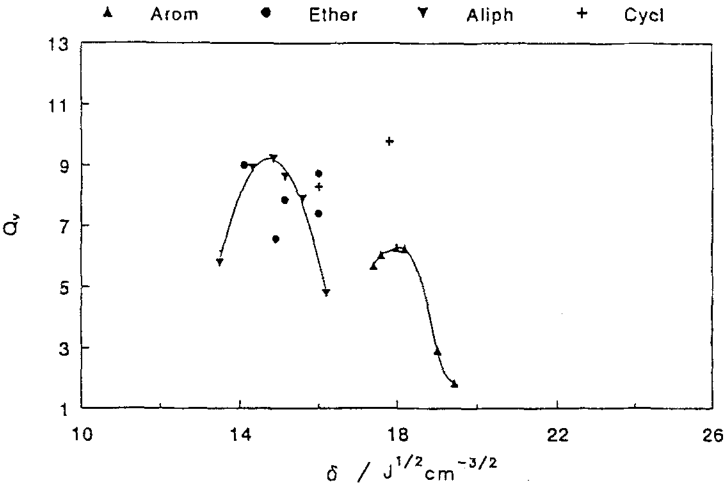

Fig. 1 Swelling degrees of PDMS-networks swollen in different pure solvents versus solubility parameters of solvents (aromatics, ethers, aliphatics, cyclics)

The tetrafunctional sample TEOS 350T having the largest expected M_C was investigated first. Results calculated by use of eq (I), (IV) from compression measurements of polymer networks swollen in different pure solvents, were not in agreement with the expectation that M_C is independent of the swelling degree (Fig. 2). The observed change of the calculated M_C'-

data with Q implicates that the equation, used for the evaluation, and thereby also the model of the phantom network are inappropriate. It is possible to explain an increase in M_C' to a constant number, the f/(f-2)fold, by transition from the affine to the free fluctuating model (change of microstructure factor). This is reasonable because the mutual hindrance of the chain-movements decreases with increasing swelling degree. That means at the same time a growing mobility. However, the calculated points do not seem to approach a constant number.

The graph in Fig. 2 consists of two different parts. Extrapolation of the two linear parts yields a point of intersection (so-called bend point).

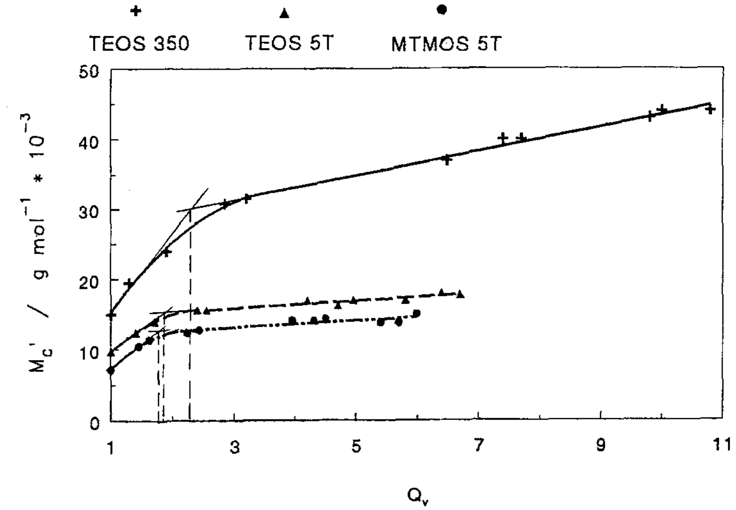

Fig. 2 Apparent M_C' for PDMS-networks swollen in different pure solvents (acetone, 1,2,3,4-tetrahydronaphthalene, MEK, styrene, benzene, toluene, n-decane, n-octane, cyclohexane, n-hexane)

The M_C'-value at the bend point is $3*10^4$ g/mole. That is approximately twice the value of the same sample in the dry state. Here it is necessary to remember that the results for the affine and the free fluctuating network would also differ by a factor of two. Hence it is supposed that this first part of the curve is determined by a transition from the affine to a free fluctuating network. To check this hypothesis further two samples were investigated. The second one (TEOS 5T) is also a tetrafunctional network but its initial polymer has a shorter chain length than TEOS 350T. The third network (MTMOS 5T) consisted of the same initial polymer as the second one but with a trifunctional cross-linker. The results are also shown in Fig. 2 and in the following Table. The ratio of M_C at the bend point to M_C of the dry network is in both cases smaller than expected (2 for f=4, 3 for f=3). This might be explained by an incomplete realization of the free fluctuating state because of the rather short network chains. However, the ratio for the trifunctional sample, though having the shorter chains in the dry state, is significantly higher. So we are not able to prove our hypothesis clearly. But it can be assumed that the behavior of the network in the range of small swelling degrees is determined by a change of the parameter A (transition from affine to free fluctuating).

network	M_C'(dry) [g/mole]	$\frac{M_C\text{'(bend p.)}}{M_C\text{'(dry)}}$	$\frac{M_C\text{'(Q=6)}}{M_C\text{'(dry)}}$	Q(bend p.)	M_N(SEC)[1] [g/mole]
TEOS 350T	15 000	2,0	2,4	2,3	24 800
TEOS 5T	9 800	1,6	1,76	1,8	15 300
MTMOS 5T	7 200	1,8	2,0	1,7	15 300

An other phenomenon can be observed in the shape of curves. A nearly linear relation can be recognized between the calculated molecular weight and the swelling degree in the second part, i.e. at higher swelling degrees. We try to explain this by an influence of the memory term η on G* discussed in (15, 16). Starting from the definition of η (eq III), $<r_0^2>$ was replaced by an expression derived from the well-known Kuhn-Mark-Houwink-equation. Though dilution in swollen networks is not infinite and $<r_0^2>$ is referred to the measurement conditions (according to definition $<r_0^2>$ has to be referred to the cross-linking conditions) Belkebir-Mrani et al. got a very good agreement with the experimental data.

$$G^* = K_{SOL} M_c^{-\alpha} \qquad \alpha = 1 + \frac{2}{3} a \qquad \text{(V)}$$

a subscript of Kuhn-Mark-Houwink-equation K_{SOL} constant

From this relationship it is qualitatively concluded that with increasing swelling degree (better solvation, higher a) the modulus decreases (M_C=const.). Further it can be concluded that for a sample with a smaller molecular weight G* is higher and less dependent on the swelling degree (smaller basis M). (This is only valid if the influence of the parameter K_{SOL}, which also depends on the solvent, is negligible compared to the exponential influence of α.) The modulus is reciprocal to the calculated M_C' used in the present paper (eq II). So the behavior described above is the same as we found.

To get a quantitative result we also replaced G* by the calculated M_C' and used the intrinsic viscosity $[\eta]$ instead of KM^a.

$$M_C' \sim [\eta]^{2/3} \quad ; \quad M_C'[\eta]^{-2/3} = const. \qquad \text{(VI)}$$

In the discussed region we found approximately constant values of $M_C'[\eta]^{-2/3}$ (independent of Q, Fig. 3).

An other interesting aspect is the existence of the bend point. It is worth mentioning that the

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[1] Dr. Rautschek, Chemiewerk Nünchritz, private communication

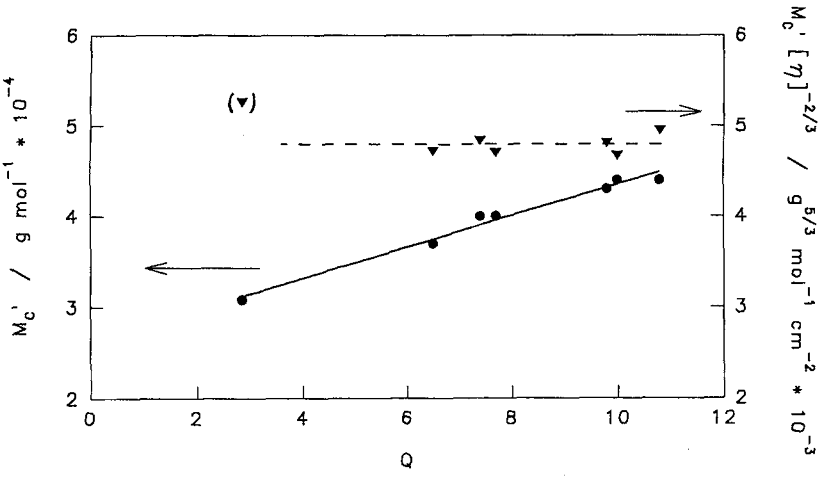

Fig. 3 Apparent M_C' of TEOS 350T and intrinsic viscosity of PDMS 5T ($M_C \approx M_N$) in good solvents (benzene, toluene, n-decane, n-octane, cyclohexane, n-hexane; (▾) theta-solvent MEK)

bend points of all curves are close to the experimental point obtained with the solvent methylethylketone, which was designated as a Θ-solvent in reference (17). With decreasing M_C all corresponding experimental points and thus the bend points are shifted towards smaller swelling degrees. Hence it seems possible that the bend points mark the limit between good and bad solvents, the Θ-condition.

Conclusion

In this work results of compression measurements of networks swollen in solvents of different thermodynamic quality are described. It is shown that the elastic behavior is a function of the swelling degree, i.e. it depends on the swelling agent. The elastic behavior is expressed by the calculated molecular weight between the cross-links as a function of the swelling degree. This function has two regimes. In the range of small swelling degrees (bad solvents) a strong increase in M_C' is observed. This is explained by a transition from an affine to a free fluctuating network. The slow rise in the range of good solvents seems to result from a change in the memory term. These explanations have to be proved by further experiments. This would also mean a new understanding of the memory term which does not only depend on the solution state during the cross-linking but also depends on the solution state during the measurement.

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