The Swelling Behaviour of Siloxane Elastomers in Relation to Their Microscopic Structure

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SUMMARY: Swelling experiments have been performed in order to characterize elastomer networks. The value of the interaction parameter χ of the Flory-Rehner equation has been evaluated. We were particularly interested in equilibrium swelling and the kinetics of swelling when the solvent was of the same nature as the network polymer; a siloxane fluid in a siloxane elastomer. Now, the swelling capacity of elastomers can easily be predicted and this is of particular importance in relation to their formulation. The swelling experiments also revealed a more complex kinetics than expected. We relate this kinetics to the self-bleeding process and give an interpretation based on the network microstructure. Finally, some data from electron microscopy in relation to light and neutron scattering and also results of a thermoporometry study of the elastomers are discussed.

Introduction

Swelling experiments are often used for the study and characterisation of elastomers because a simple measurement of swelling permit an evaluation of apparent cross-link density using only a few grammes of sample. The well-known Flory-Rehner equation[1)] expresses the value of the junction-point density as a function of swelling ratio.

The calculations, however, require knowledge of the interaction parameter between the polymer of the sample and the swelling solvent. Only a few values of the parameter are tabulated for siloxane elastomers. In this paper, we present a simple way of determination of such a parameter and apply it to siloxane elastomer swollen by methylcyclohexane, a safer solvent than toluene or benzene.

A similar approach is then used to study the swelling of siloxane elastomers by siloxane diluents. The experiments help to make predictions of the ability of an elastomer to accept a diluent to a certain amount or to bleed this diluent out when its critical concentration in the elastomer is exceeded. The kinetics of swelling and that of bleeding have also been studied. Since all these phenomena are governed by the parameters of the network, we present some observations on the structure of our samples of elastomer and discuss them in relation to the swelling behaviour.

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Experimental Part

The Networks

Different polydimethylsiloxane (PDMS) model networks (i.e. simple elastomers) were prepared for this study. The first series consists of the polyaddition (PA) cured elastomers (SiH + SiVi) with the general recipe given in Table 1:

Table 1: Formulation of PA elastomers.

Vinyl terminated PDMS	M_n = 7300 to 250000
Tetrahydrotetramethyltetracyclosiloxane	for SiH / SiVi = 1.05
Karstedt catalyst	10 ppm platinium

The second series was a polycondensation (PC) system containing diluent and prepared according to the formula in Table 2:

Table 2: Formulation of PC elastomers.

Hydroxyterminated PDMS	20	M_n = 40000
Trimethylsiloxy treated silica (300 m^2/ g)	21	
Broken quartz	17	
Tetraethoxysilane	1.4	
Water	0.2	
Stanneous catalyst	700 ppm of Sn	
Methyl terminated PDMS	40	M_n = 5000 - 12500

After degassing, the mixtures were poured into a mould and cured for 1 hour at 150 °C for the polyaddition system or for one day at room temperature for the polycondensation system. In this way 2 mm thick sheets of elastomers were prepared.

Swelling

For the swelling experiments, the samples were washed in advance with an appropriate solvent for siloxanes and dried in order to remove extractible components. A convenient sample area for these experiments was 5 cm^2. The swelling measurements were performed at

predetermined durations in selected solvents. The volume fraction v_r of the polymer in swollen gel was calculated according to:

$$v_r = 1/(1 + 0.97/\rho_s(M_s/M_i - 1)) \quad (1)$$

where M_i and M_s are the initial sample weight and the weight of swollen sample, respectively, 0.97 and ρ_s are the densities of PDMS and the solvent, respectively. The swelling ratio, $1/v_r$, could be measured at room temperature or a chosen temperature. The solvents used in swelling measurements are listed in Table 3.

Table 3: Characteristics of the solvents.

Methylcyclohexane	$\rho = 0.769$	$M = 98.2$
PDMS viscosity 20 m Pa.s (PDMS 20)		$M_n = 1300$
PDMS viscosity 100 m Pa.s (PDMS 100)		$M_n = 5000$
PDMS viscosity 500 m Pa.s (PDMS 500)		$M_n = 12500$

Bleeding

The bleeding experiments were more difficult to perform due to small quantities of diluents that bleed out from elastomers. These quantities were measured as follows. The sample was placed between two absorbent paper sheets, this sandwich was then placed between two metallic plates and put into an oven at the temperature of 80 °C and was gently pressed. The sample was weighed time-to-time in order to establish the bleeding rate. The diffusion coefficient D was calculated according to Fick's law[2]:

$$M_t / M_\infty = 4/h\sqrt{Dt}/\pi \quad (2)$$

where M_t and M_∞ are the weights of the samples at time t and ∞, respectively.

Microscopy

Thin sample slices of elastomers embedded in a methacrylate resin were observed in a transmission electron microscope using the following procedure:

- place a small sample of the siloxane elastomer in methacrylate monomer containing an initiator
- let the sample swell at room temperature
- heat it in an oven at 80°C in order to harden the resin

- cut thin slices (≈100 nm) of the embedded elastomer using a microtome
- observe with the TEM at the appropriate magnification
- record a selected picture and make an image analysis

Neutron Scattering

The neutron scattering from elastomer gels shows an increase of scattering intensity at low values of wave vector, q, compared to the scattering of semi-diluted solutions. This excess (over-scattering) has been attributed by Bastide[3] to frozen heterogeneities, resulting from fluctuations of connectivity, and thus forms a signature of the network superstructure. The characteristic length associated with these frozen heterogeneities is about one order of magnitude larger than that associated with thermal fluctuations[4]. These heterogeneities extend to length scales much larger than the sizes of precursor chains.

Thermoporometry

The thermoporometry is a technique by which one measures the lowering of the melting point of a solvent trapped in the pores of a material. In the case of siloxane elastomers, these measurements have already been made and the presence of pore sizes of the order of some 10 nm was reported[5].

Results

Interaction Parameter of PDMS with Methylcyclohexane

The swelling measurements of a series of polyaddition cured elastomers were made with two solvents; one solvent had a tabulated χ value, the other is the one for which χ will be determined.

When we compare v_r in benzene ($\chi = 0.48 + 0.35\ v_r$)[6] and v_r in methylcyclohexane and apply equation 3 where the subscripts 1 and 2 refer to the respective solvents:

$$F_{\text{FLORY–REHNER}}(\chi_1 v_{r1}) = F_{\text{FLORY–REHNER}}(\chi_2 v_{r2}) \tag{3}$$

we can calculate the value of χ for each experiment in methylcyclohexane. Fig. 1 shows the resulting plot and linear regression gives: $\chi = 0.42 + 0.25\ v_r$.

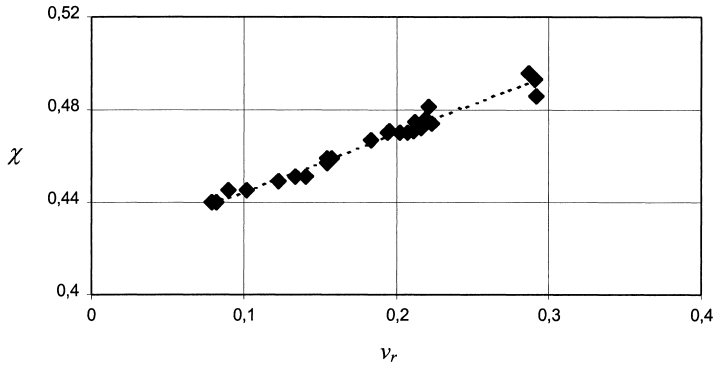

Fig. 1: χ vs. v_r in methylcyclohexane.

Interaction Parameter of PDMS with PDMS

The methodology was the same as in the previous subsection, but in calculations we took the molar volume v_s of the "solvent" to be that of the repeating unit:

$$v_s = M / \rho = 74 / 0.97 \tag{4}$$

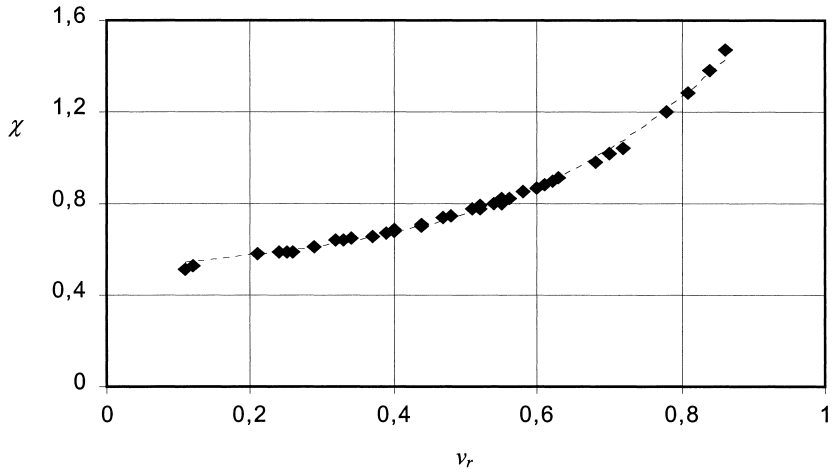

Fig. 2: χ vs. v_r in PDMS.

In accordance with this hypothesis, Fig. 2 looks smooth; all experimental points fit to a single curve described by the equation:

$$\chi = 0.5 + 0.472 v_r - 0.791 v_r^2 + 1.74 v_r^3 \tag{5}$$

The swelling ratios were measured both at room temperature and at 80°C. Similar values were obtained in both cases:

- v_r at room temperature for PDMS 100 = 0.39
- v_r at 80°C for PDMS 100 = 0.38

Swelling Behaviour

The approach to swelling equilibrium, which is not temperature dependent, has been chosen to study the swelling kinetics at 80 °C. The results are shown in Fig. 3.

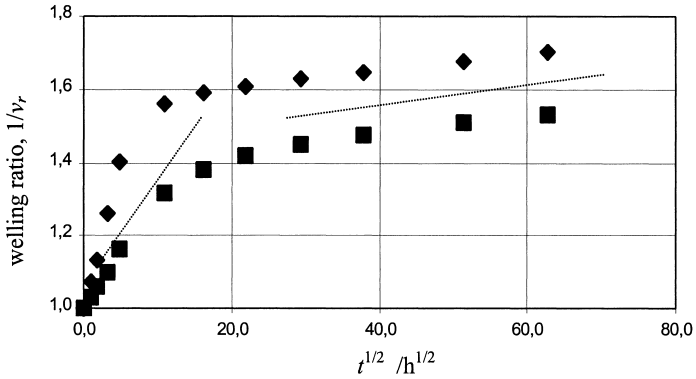

Fig. 3: Swelling ratio vs. square root of time for PC elastomer swollen in PDMS 100 (◆) or in PDMS 500 (■).

In each of the cases presented in Fig. 3, two different diffusion coefficients may be evaluated, a "fast" one for short times and a "slow" one for long times. For PDMS 500 these coefficients are: $D_{swelling}$ "fast" = $4 \cdot 10^{-8}$ $cm^2 s^{-1}$ and $D_{swelling}$ "slow" = $1 \cdot 10^{-11}$ $cm^2 s^{-1}$. For PDMS 100, the diffusion in the fast domain is roughly twice as fast as that for PDMS 500.

Bleeding Behaviour

Fick's law has been applied in a similar way to the results of the bleeding experiments, as presented in Fig. 4. The diffusion coefficient deduced from this figure is : $D_{bleeding}$ = $1\text{-}2 \cdot 10^{-11}$ $cm^2 s^{-1}$.

Microscopy

A micrograph of a slice of one of the unfilled elastomers of this study is presented in Fig. 5. The molecular weight of the precursor polymer was 18000.

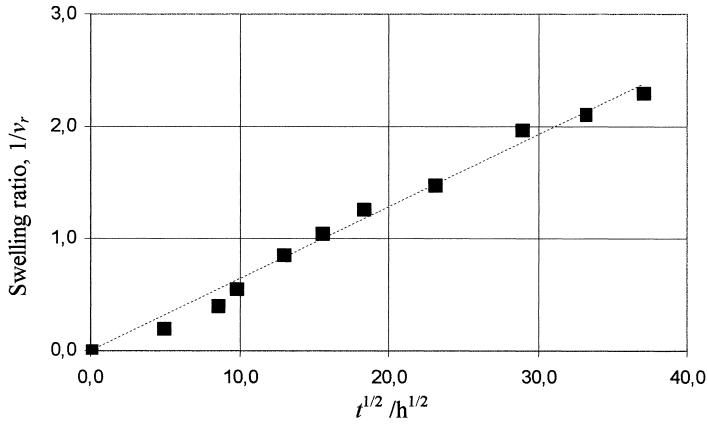

Fig. 4: Bleeding ratio vs. the square root of time for PDMS 500.

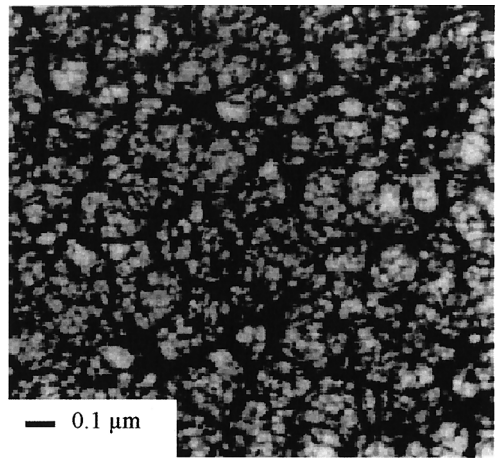

Fig. 5: TEM micrograph of the network.

The PDMS appears dark compared to the embedding polymer. The mesh is clearly revealed. An image analysis performed on this picture shows the mesh size to be 47 nm. The perimeter of this mesh corresponds to end-to-end length of 10 macromolecules and the thickness of the walls is sufficient to contain between one hundred and one thousand chains.

Discussion

A very simple method yields the value of parameter, χ, that quantifies the interaction between elastomer and solvent. In the case of siloxane and methylcyclohexane (a very suitable and safe solvent for swelling experiments) the value has been established to be:

$$\chi = 0.42 + 0.25\ v_r$$

When both the elastomer and the solvent are PDMS we have noticed that the molar volume that can be introduced into the Flory-Rehner equation is that of the repeating unit and the experimental equation that well describes the data is the third-order polynomial:

$$\chi = 0.5 + 0.472v_r - 0.791v_r^2 + 1.74v_r^3.$$

We have found two kinetics operating in the swelling process. The first is the fast kinetics at short times, which is followed by a slow process for the system approaching equilibrium.
The kinetics of bleeding corresponds well to the slow part of the swelling process. A possible explanation is that both phenomena take place when the elastomer is close to saturation by the solvent. Below the saturation limit, the elastomer can still swell, but, over this concentration, a bleeding of the solvent will be observed.

Observations of the elastomer structure with TEM, neutron scattering, and thermoporometry reveal, in each case, a mesh size with dimensions that are much larger than the distance between junctions expected from the molar mass of the precursor polymer. The mesh sizes are of the order of some 10 nm, i.e., larger than the end-to-end distances of the precursor, which are of the order of some nanometers.

Both techniques used these observations were applied to swollen systems. The TEM showed more details of the structure of the network; the mesh is made of fibrils as thick as several tens of nanometers. We can thus imagine that they contain hundreds of chains and network junctions.

We propose that the fast part of the swelling is a conventional one, with standard diffusion coefficient values. We have established that the slow part of the swelling and of the bleeding proceeded with a reorganisation of polymer chains into the fibrils of the net. The process is slow and has a low apparent diffusion coefficient.

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