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The effects of solution concentration on network properties of thin films of polyorganosiloxanes crosslinked in the solid state

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The stress–strain properties of polyorganosiloxane networks crosslinked in the solid state but cast from trichloroethylene solutions with polymer volume fractions in the range 0.018 to 0.158 were investigated. The polyorganosiloxane studied was polydimethylsiloxane (PDMS) containing crosslinkable Si–CH = CH_2 and Si–H functional groups. The moduli were found to increase with increasing concentration of the solution from which the network was cast, the same trend that has been previously observed for networks actually crosslinked in solution. These results were explained in terms of the theories of rubber elasticity. The PDMS networks formed from concentrated solution had a relatively higher effective interconnectivity of the network chains and a higher degree of constraints of fluctuations of the network junctions than did the networks formed from more dilute solutions. Since the chemical crosslink density was the same for all the networks, those formed from the more concentrated solutions had a higher number of physical entanglements. These results suggest that the time scale for conformational rearrangement of the rubber is longer than that for solvent evaporation, so that the solution conformation is maintained in the solid state. © 1997 Elsevier Science Ltd.

(Keywords: PDMS networks; modulus; elasticity)

Introduction

The mechanical properties of crosslinked polymeric materials are most frequently investigated in the bulk state. As more interest is focused on applications involving thin films, surface effects, as well as possible effects of the process used to solvent cast the films, need to be considered. While most theories and experimental work on rubber elasticity have concentrated on systems crosslinked in the solid state, there have been more limited investigations on polymers crosslinked in solution. The dependence of the structure and properties of crosslinked polymers on the concentration at which the network was formed in solution has been reported[1–4]. The effect of crosslinking in solution is to decrease the modulus and increase the elongation to break relative to samples crosslinked in the solid state. Both effects have been attributed to decreased chain entanglements for the networks crosslinked in solution compared with the bulk.

The purpose of this article is to study the effect that the polymer concentration has on the stress–strain properties of cast films that are dried and crosslinked in the solid state and to explain the molecular origin of the effect in terms of rubber elasticity theories. The polyorganosiloxane investigated is polydimethylsiloxane (PDMS) with Si–CH = CH_2 and Si–H crosslinkable functional groups.

Experimental

Materials and sample preparation. The PDMS used in this study was obtained from GE and had a Mooney viscosity of 13. The i.r. spectrum, shown in *Figure 1*, shows the presence of the Si–CH = CH_2 and Si–H bonds. The peaks at 1598–1600 and 2161 cm^{-1}, representing the C = C bonds and the Si–H stretching vibrations, respectively, were used to calculate the relative amounts of Si–CH = CH_2 and Si–H in the PDMS. The spectral data were normalized using the 2905 cm^{-1}, symmetric -CH_3 stretching vibration. The relative amounts of Si–CH = CH_2 and Si–H bonds in the PDMS were 37 and 12%, respectively.

The procedure for preparing thin, crosslinked films consisted of: (i) dissolution of the PDMS at volume fractions ranging from 0.018 to 0.158 in trichloroethylene (TCE) for 24 h without stirring, followed by stirring for 48 h at 45 r.p.m. and 20 min at 1500 r.p.m.; (ii) addition of 2% (by weight of PDMS) platinum-divinyltetramethyldisiloxane catalyst, followed by stirring for 10 min both at 125 and 1500 rpm and then slowly for 2–5 h until the removal of air was complete; (iii) casting of the films in PTFE moulds; (iv) removal of solvent by drying overnight at room temperature; and (v) final crosslinking of the films in the solid state by heating in an oven at 80°C for 2 h and at 182°C for 3 h to form the network structure via the addition reaction,

$$-\mathrm{SiCH}=\mathrm{CH_2}+\mathrm{HSi}- \rightarrow -\mathrm{SiCH_2CH_2Si}-$$

Care was taken to carry out the dissolution in the dark in order to avoid premature crosslinking of PMDS in solution. Since it was previously determined that the modulus depended on the film thickness[5], films with thicknesses of 0.090 ± 0.005 mm were used.

Measurement of tensile modulus. The tensile modulus measurements were performed on an Instron Universal Testing Instrument Model 1122 at 25°C with a crosshead speed of 50 mm min^{-1}. The width of the samples was 5 mm and the grip distance was 25 mm. The film

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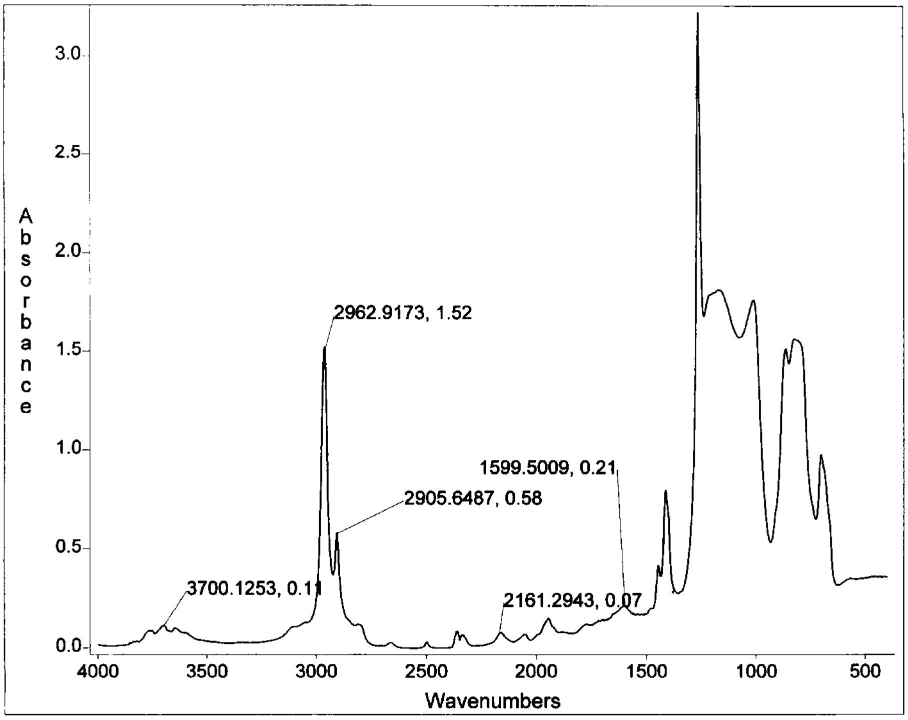

Figure 1 I.r. spectrum of PDMS

thickness was measured using a micrometer (Mitutoyo), with 0.001 mm accuracy.

Rubber elasticity theories. The Mooney–Rivlin equation[6–9], which can be derived strictly from phenomenological approaches, is often used to analyse the uniaxial stress–strain relationship of elastomers at moderate elongations:

$$[f^*] = 2c_1 + 2c_2\alpha^{-1} \tag{1}$$

where $2c_1$ and $2c_2$ are constants independent of elongation. Many studies have been carried out to interpret the constants $2c_1$ and $2c_2$, but the results are inconclusive[10,11].

Several theories of rubberlike elasticity have contributed to the interpretation of the stress–strain relationship of network elasticity. The modulus used frequently in elasticity studies for uniaxial extension is defined in terms of the reduced stress, $[f^*]$:

$$[f^*] = f/(\alpha - \alpha^{-2}) \tag{2}$$

where the nominal stress, f, is the force per unit original area, and α represents the elongation ratio, $\alpha = L/L_i$, where L and L_i are the dimensions of the sample in the strained and initial states, respectively. Equation (2) is used only for the unswollen state.

In the affine model network[12,13], the strain-induced displacement of connective points are considered to be linear in the macroscopic strain. Fluctuations of crosslinks are completely suppressed by local intermolecular entanglements. The reduced stress, $[f^*]$, is independent of elongation, and in the unswollen state

$$[f^*]_{\text{aff}} = vkT/V \tag{3}$$

where v/V is the density of network chains, k is Boltzmann's constant and T is the absolute temperature.

In the phantom model network[12–14], the modulus is independent of elongation, but the configuration available to each network chain is also independent of the configuration of neighbouring chains with which they share the same region of space. The chains are viewed as being able to move freely through one another. Thus, this reduction in strain sensed by the network chains makes the modulus predicted by the affine model [equation (3)] decrease. For the unswollen state:

$$[f^*]_{\text{ph}} = \xi kT/V \tag{4}$$

where the factor ξ is the connectivity of the network:

$$\xi = (1 - 2/\phi) \tag{5}$$

and ϕ is the crosslink functionality.

The constrained-junction model[15–19] provides an explanation for the decrease in modulus with increasing elongation at low and moderate elongations. The theory suggests that the modulus of a real network usually falls between the affine and phantom limits. At small strains, local intermolecular entanglements among chains and steric constraints on the fluctuations of junctions make the deformation relatively close to the affine limit. As the elongation increases the chains are gradually disentangled, and the modulus is diminished. Some networks show an abrupt increase in modulus at high elongations, that, for noncrystalline PDMS model networks, has been attributed to limited chain extensibility[12,20].

According to Flory and Erman[19],

$$f = f_{\text{ph}} + f_{\text{c}} \tag{6}$$

where f_{ph} is the force that would be exerted by the equivalent phantom network, f_{c} is the contribution to the force, f, from local intermolecular entanglements among chains and steric constraints on the fluctuations of junctions at the same elongation. The reduced force can thus be written as

$$[f^*] = [f^*_{\text{ph}}](1 + f^*_{\text{c}}/f^*_{\text{ph}}) = [f^*_{\text{ph}}](1 + f_{\text{c}}/f_{\text{ph}}) \tag{7}$$

Table 1 Mechanical properties of PDMS networks cast from different concentrations of PDMS, crosslinked in the solid state

Volume fraction	Stress at break ($N\ mm^{-2}$)	Strain at break (%)	Modulus at break ($N\ mm^{-2}$)	Modulus at 5% strain ($N\ mm^{-2}$)
0.018	5.20	576	0.90	2.50
0.062	5.89	631	0.93	2.64
0.115	7.38	777	0.95	2.86
0.158	6.01	600	1.00	3.07

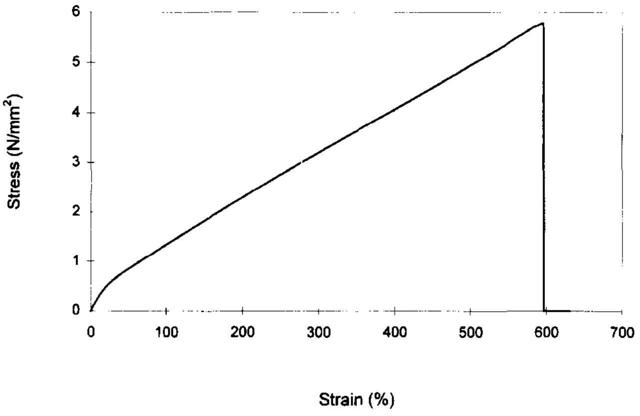

Figure 2 Stress–strain curve of PDMS film

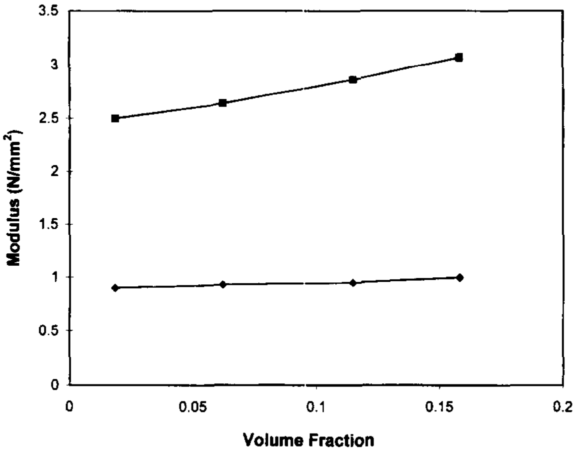

Figure 3 The relationship between modulus and concentration of PDMS solutions, modulus at 5% strain (■) and at break (◆)

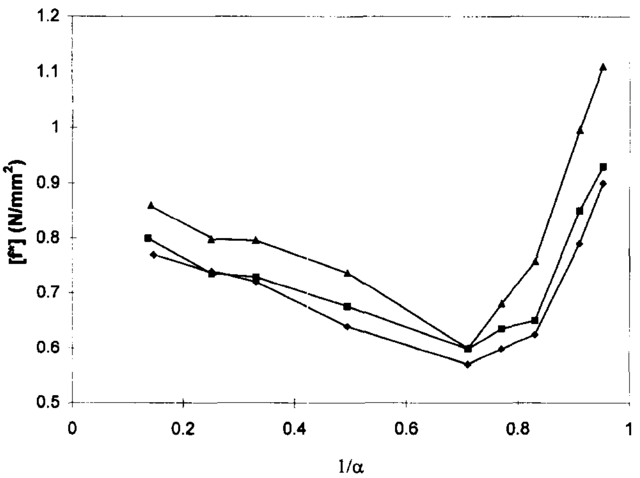

Figure 4 $[f^*]$ vs the reciprocal elongation at volume fractions 0.018 (◆), 0.062 (■) and 0.158 (▲)

Where $[f^*_{ph}]$ is the reduced force for the equivalent phantom network and is proportional to the effective interconnectivity of the network, i.e. to the number of chemical crosslinks. There may be a few local intermolecular entanglements among the chains of the network at break (strain of 500–600%), but the value of f_c/f_{ph} at break can be assumed to be approximately similar to that at infinite elongation, where f_c (the contribution to the force from local intermolecular entanglements) is zero. This approximation makes it possible to compare qualitatively the effect of concentration on modulus. The approximate value of $[f^*_{ph}]$ can thus be obtained from the measured value of $[f^*]$.

Since equation (7) applies for all elongation ratios, it can be rearranged so that values of f_c/f_{ph} for any elongation ratio can be calculated:

$$f_c/f_{ph} = \{[f^*] - [f^*_{ph}]\}/[f^*_{ph}] = [f^*]/[f^*_{ph}] - 1 \qquad (8)$$

The value of f_c can also be obtained at any elongation ratio using the relationship

$$f_c/f_{ph} = f_c/[f^*_{ph}](\alpha - \alpha^{-2}) \qquad (9)$$

since in the phantom network model, $[f^*_{ph}]$ is independent of the strain.

Results and discussion

Figure 2 is a typical stress–strain curve of a PDMS network, where a pronounced decrease in slope at about 25% strain can be observed. *Table 1* and *Figure 3* give the measured moduli at 5% strain and at break for networks formed from solution concentrations of between 0.018 and 0.158 volume fraction of PDMS. The modulus increases with increased concentration of the casting solution, but the effect is more pronounced for the modulus obtained at 5% strain. *Figure 4* is a plot of reduced stress $[f^*]$, calculated from equation (1), as a function of reciprocal elongation for these same samples. The increase in modulus at high elongation (small $1/\alpha$) has been previously observed[21,22] and discussed[13,20].

The magnitudes of $[f^*]$ at break and at 5% strain, using the data from *Table 1*, are presented in *Table 2*. The value of $[f^*]$ at break is equal to $[f^*_{ph}]$, as f_c/f_{ph} vanishes [equation (7)]. Since in the phantom network model, $[f^*_{ph}]$ is independent of the strain, this same value for $[f^*_{ph}]$ can be used at 5% strain. The values of $[f^*_{ph}]$ at break, f_c/f_{ph}, f_c, and f_{ph} calculated according to equations (8) and (9) are given in *Table 3* and plotted in *Figure 5*.

These data indicate that with increasing volume fraction of PDMS in the casting solution, the networks formed after drying in the solid state have higher values of f_c at low (5%) strain. A ten fold increase in volume fraction of PDMS results in a 100% increase in f_c, indicating that there are increased interchain entanglements with increasing volume fraction of PDMS in the casting solution.

Table 2 Magnitude of $[f^*]$ at break and 5% strain

	$[f^*]$ (N mm^{-2})			
	Volume fraction			
$1/\alpha$	0.018	0.062	0.115	0.158
at 5% strain 0.952	0.87	0.92	1.00	1.07
at break 0.147	0.77			
0.142				0.86
0.137		0.80		
0.114			0.84	

Table 3 $[f^*_{ph}]$ at break and (f_c/f_{ph}), f_c and f_{ph} at 5% strain for networks cast from PDMS/TCE solutions with different volume fractions of PDMS, crosslinked in the solid state

Volume fraction	$[f^*_{ph}]$ (N mm^{-2}) at break	f_c/f_{ph}	f_c (N mm^{-2}) at 5% strain	f_{ph} (N mm^{-2})
0.018	0.772	0.133	0.015	0.110
0.062	0.808	0.143	0.017	0.115
0.115	0.843	0.187	0.020	0.120
0.158	0.861	0.247	0.030	0.123

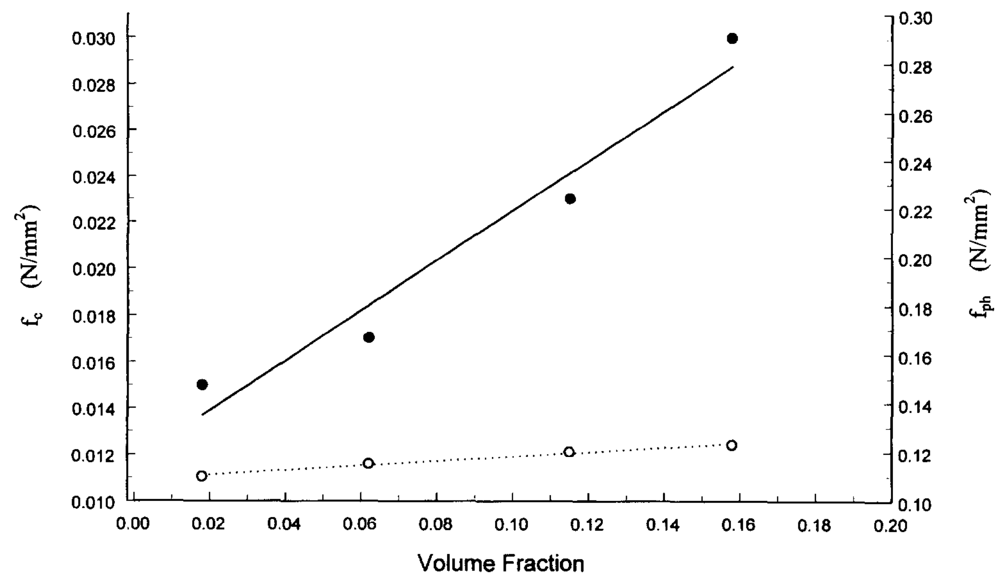

Figure 5 f_c (●) and f_{ph} (○) vs volume fraction at 5% strain

The value of f_{ph} at 5% strain also increases, but only by 10%, over this same concentration range. Similarly, $[f^*_{ph}]$, obtained at break, increases by 10% over the concentration range investigated. $[f^*_{ph}]$ is related to the effective interconnectivity of the network chains and contains contributions from the chemical crosslinks and trapped physical permanent entanglements of the chains. Since the number of chemical crosslinks is the same for all the samples, the higher values of $[f^*_{ph}]$ and f_{ph} at 5% strain also indicate that there is a higher effective interconnectivity in the networks formed from the more concentrated solutions. The higher values of f_c/f_{ph} with increasing concentration similarly reflect the increased constraints on the fluctuations of the network chains.

The fact that networks formed from different solution concentrations but containing the same chemical crosslink density exhibit different mechanical properties and different magnitudes for $[f^*_{ph}]$, f_{ph} at 5% strain, and f_c/f_{ph}, suggests that the solution conformations of the chains are different. In particular, with increasing volume fraction of polymer, the chains become increasingly entangled. Furthermore, although this is expected, and has been observed for networks crosslinked in solution, the fact that these properties are observed for samples cast from solution and crosslinked in the solid state suggests that the solution conformation is preserved in the bulk phase. This would be possible if the time for the molecular rearrangement of the chains was long compared with the time for solvent evaporation from the films.

Conclusions

Thin films of PDMS with crosslinkable $Si–CH = CH_2$ and Si–H functional groups were solvent cast from TCE solutions with different volume fractions of polymer. The films were dried and then crosslinked in the solid state. The moduli of the films increased as the volume fraction of polymer in the casting solvent increased from 0.018 to 0.158. The modulus at 5% strain increased by 20% while the modulus at break increased by 10%. The model of Flory and Erman was used to separate the contributions of chain entanglements from hat due to chemical crosslinks and permanently trapped physical entanglements. With increasing concentration of polymer in the casting solvent, both the constraints on the fluctuations of network junctions and the effective interconnectivity of the network chains increased. These results indicated that the greater chain entanglement that occurred in solution with increasing PMDS concentration persisted in the solid state.

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