

Rheological Properties of Silicon Polymer Networks: The Influence of the Crosslink Density

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ABSTRACT: This study was focused on the influence of the microstructural properties of a silicon polymer network on its rheological properties. Two commercial silicon oils were mixed in different ratios to form, by hydrosilylation, networks with different crosslink densities. The chemical compositions of the oils were determined by NMR, whereas their molecular weights and viscosities were studied with gel permeation chromatography and viscosimetry, respectively. The different networks were characterized through their crosslink densities. Afterward, the rheological properties were studied. The formulation notably influenced some characteristic values of the rheological behavior: the α -transition temperature and the onset temperature of the caoutchoutic plateau shifted toward higher temperatures as the

crosslink density increased, the storage modulus at the onset temperature of the caoutchoutic plateau increased with the crosslink density, and the amplitude of the peak associated with the α -transition temperature decreased. These behaviors were explained as follows: as the crosslink density increased, a drastic decrease in the amount of free chains in the network occurred, and both phenomena induced a large decrease in the chain mobility, which might explain the aforementioned behavior. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 87: 1152–1160, 2003

Key words: elastomers; networks; rheology; silicones; structure-property relations

INTRODUCTION

Silicon polymers^{1–5} have some typical characteristics: high flexibility of the macromolecular chain, an extremely low glass-transition temperature, good thermal stability, excellent chemical inertia (due to the strength of the —Si—O—Si— chemical bond, 440 kJ/mol), very good resistance to photoaging, and an ability to develop some polar interactions with any polar surface in contact. These characteristics have led to a wide range of technical applications.

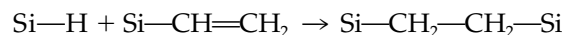
Nevertheless, *silicon polymer* is a generic term that includes a large variety of products and materials. It ranges from oils (reactive or not) to some three-dimensional networks called gels, elastomers, or resins according to their state of reticulation and crosslink density.

The aim of this work was to study, for silicon polymer networks ranging from very low reticulated gel forms to some highly reticulated resin forms, the influence of the state of reticulation and the microstructure on the final macroscopic properties of the materials.

EXPERIMENTAL

Materials

The silicon polymer was provided by Dow Corning (Lyon, France). It was a bicomponent polymer: part A was an oil containing hydrogenosilane (Si—H) and vinylsilane (Si—CH=CH₂) functions, whereas part B contained only vinylsilane functions. These two functions, mixed and heated, reacted together in a reaction called *hydrosilylation*.^{6,7}



Therefore, as they were statistically disposed along the chains of the two initial oils, a network was formed. The crosslink density could be modified and controlled through different ratios of parts A and B.

Characteriation

Characterization of the oils

The chemical structures of the oils were determined by ¹H-NMR. We used a Bruker WP2000 apparatus (Wissembourg, France): the samples were solubilized in deuterated chloroform, and eight scans were made for each sample.

The distribution of the chain length was determined by gel permeation chromatography (GPC). A Spectra-Physics GPC apparatus (Les Ulis, France) was used with three successive columns (two PL gel columns

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and one Waters Styragel HR2 column (St. Quentin en Yvelines, France)), each being 300 mm long and having pore sizes of 200, 100, or 50 Å, respectively. The solvent tetrahydrofuran was employed, and the data were detected with an SP8430 differential refractometer (Spectra-physics, Les Ulis, France). The results were averaged over three measurements.

The viscosities were measured with a Rheometric Scientific advanced rheometric expansion system rheometer (Marne-la-Vallée, France). A parallel-plate (40-mm-diameter) geometry was used in a steady shear test with speeds of 1–1000 s⁻¹. Each time, five samples were tested.

Network characterization

The networks were characterized by their crosslink densities (D_n , which is the number of moles of crosslinks in 1 g of a silicon network) or by the average molecular weight between two crosslinks (M_c , which is the inverse). This characteristic was deduced from swelling measurements. It was based on the capability of a good solvent of a polymer to swell the network until it used all the possible volume. The relations of Flory and Rehner^{8,9} led to

$$\frac{\rho}{M_c} = - \frac{\ln(1 - V_2) + V_2 + (\chi + \beta \times V_2) \times V_2^2}{V_s \times \left(V_2^{2/3} \times V_0 - \frac{2 \times V_2}{f} \right)}$$

where χ and β are the polymer–solvent interaction parameters, V_2 is the volume fraction of the dry polymer in the swollen network, ρ is the density of the dry polymer, V_s is the molar volume of the solvent, V_0 is the volume fraction of linked chains in the dry polymer network (which here is supposed to be equal to 1 because the measurements were made after the removal of the free chains), and f is the functionality of the crosslinks, which here is equal to 4. Furthermore,

$$V_2 = \frac{\frac{p}{\rho}}{\frac{p'}{\rho_s} + \frac{p}{\rho}} = \frac{p \times \rho_s}{(p' - p)\rho + p\rho_s}$$

where ρ_s is the solvent density, p' is the swollen sample weight, and p is the dried sample weight. V_2 was determined by a simple weighing of the samples after swelling and subsequent drying. Toluene was used as the solvent with the following characteristic values:¹⁰ $\chi = 0.44$, $\rho_s = 0.8669$ g/cm³, $\beta = 0.36$, and $V_s = 106$, 3 cm³. The amount of free chains in the sample was evaluated by a comparison of the weight of the initial dry sample with the weight of the sample swollen and then dried.

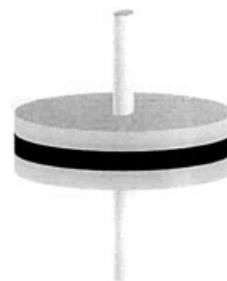


Figure 1 Schematic view of the test geometry.

Viscoelasticity tests

The viscoelastic properties of the silicon networks were also studied with the same rheometer in the dynamic mode. A circular sample was placed between the two plates (Fig. 1), and the imposed deformation (γ) was given by the following relation:

$$\gamma = \frac{r \times \theta}{h}$$

where r is the distance to the rotational axis (m), θ is the angular deformation (rad), and h is the thickness of the sample (m). By the measurement of the torque (T ; N m), the stress (τ) at a point at distance r from the rotational axis could then be calculated:

$$\tau = \frac{2 \times \left(\frac{r}{10} \right) \times T}{\pi \times \left(\frac{R}{10} \right)^4}$$

where R is the radius of the plates (m). Therefore, the maximal stress (τ_{max}) was reached for $r = R$:

$$\tau_{max} = \frac{2 \times T}{\pi \times \left(\frac{R}{10} \right)^3}$$

The measurement of the stress and strain allowed us to calculate the viscoelastic storage modulus (G') and loss modulus (G'').

The rheometer was used in the following ranges: frequencies, 5×10^{-2} to 50 Hz; angles, 5×10^{-6} to 0.5 rad (this range corresponded to strains ranging from 0.001 to 100% for a sample 8 mm in diameter and 2 mm thick); temperatures, -120 C to 175°C; and torque, 2×10^{-4} to 0.2 N m.

Sample preparation

The samples for the rheometric tests were discs 8 or 25 mm in diameter and 2 mm thick. Parts A and B were mixed together and outgassed for 5 min in a vacuum chamber. The mixed liquid was then poured into a

TABLE I
Molecular Concentration of the Different Repeat Units

Structure	Fraction in part A (%)	Fraction in part B (%)
$\begin{array}{c} \text{H} \\ \\ \text{—Si—O—} \\ \\ \text{CH}_3 \\ \text{HC=CH}_2 \\ \\ \text{—Si—O—} \\ \\ \text{CH}_3 \\ \text{CH}_3 \\ \\ \text{—Si—O—} \\ \\ \text{CH}_3 \end{array}$	5.4	0
$\begin{array}{c} \text{—Si—O—} \\ \\ \text{CH}_3 \\ \text{CH}_3 \\ \\ \text{—Si—O—} \\ \\ \text{CH}_3 \end{array}$	2.3	2.6
$\begin{array}{c} \text{—Si—O—} \\ \\ \text{CH}_3 \end{array}$	92.3	97.4

mold (5 cm × 10 cm) to form a 2-mm-thick plate. The whole plate was reticulated at 150°C for 4 h. Finally, after reticulation and cooling, the samples were stamped out. Each measurement was made at least on two similar samples.

RESULTS AND DISCUSSION

Microstructural characteristics of the silicon networks

The concentration of the reactive functions (by NMR),^{11,12} the weight-average molecular weight (M_w), number-average molecular weight (M_n), and polydispersity index ($I = M_w/M_n$; all by GPC), and the viscosity were determined for parts A and B and are presented in Tables I–III.

The different networks were characterized by M_c and by their amount of free chains. Table IV and Figures 2 and 3 give the M_c values and the ratios of free chains for different ratios of parts A and B. In Figure 2, the full curve shows the theoretical data calculated with the NMR results.

In fact, M_c is the inverse of D_n :

$$M_c = \frac{1}{D_n}$$

Consequently, it can be deduced that, for an excess of part A (when the amount of Si—CH=CH₂ functions is the limiting factor for the formation of crosslinks),

TABLE II
Molecular Weight (in Poly Styrene (PS)
Equivalentents—Dalton)

Component	M_w (g/mol)	M_n (g/mol)	I
Part A	17,700	5,280	3.35
Part B	17,700	4,900	3.61

TABLE III
Shear Viscosity of the Oils

Component	Viscosity (Pa s)
Part A	1.86 ± 0.02
Part B	4.76 ± 0.25

$$M_c = \frac{1}{(N_{\text{Si-Vi/gr(A)}} \times (\% \text{ A}) + (N_{\text{Si-Vi/gr(B)}} \times (\% \text{ B}))}$$

where $N_{\text{Si-Vi/gr(A)}}$ is the number of moles of Si—CH=CH₂ functions in 1 g of part A, as measured by NMR; $N_{\text{Si-Vi/gr(B)}}$ is the number of moles of Si—CH=CH₂ functions in 1 g of part B, as measured by NMR; and % A and % B are the weight ratios of parts A and B, respectively. For an excess of part B (when the amount of Si—H functions is the limiting factor for the formation of crosslinks),

$$M_c = \frac{1}{(N_{\text{Si-H/gr(A)}} \times (\% \text{ A}))}$$

where $N_{\text{Si-H/gr(A)}}$ is the number of moles of Si—H functions in 1 g of part A, as measured by NMR. There was a strong similarity between the evolutions of M_c and the amount of free chains. The later represented only 5% of the total weight of the polymer network when this one was strongly reticulated, whereas it could grow up to nearly 50% for the lowest reticulated networks. The measured value of M_c was quite similar to the calculated values from the NMR analysis around the stoichiometric composition, which was reached at about 45% B.

Above this composition, the expected values were considerably lower than the experimental ones. This might have been caused by the viscosity (see Table III): part B had a higher viscosity than part A. Therefore, an increasing amount of part B resulted in a higher viscosity of the mixture (before reticulation).

TABLE IV
 M_c and Amount of Free Chains for Different
Formulations of the Silicon Polymer Network

% B	M_c (g/mol)	Free chains (%)
10	3,700 ± 400	4.5
15	2,700 ± 300	4.5
20	3,200 ± 300	3.8
25	2,400 ± 200	4.4
35	2,300 ± 300	4.3
40	2,300 ± 300	3.7
50	2,900 ± 500	4.0
60	5,000 ± 300	4.7
65	6,500 ± 400	6.0
67	6,600 ± 300	5.8
70	9,000 ± 400	7.1
80	29,500 ± 1,000	18.5
83	33,000 ± 3,000	19.2
91	49,000 ± 5,000	62

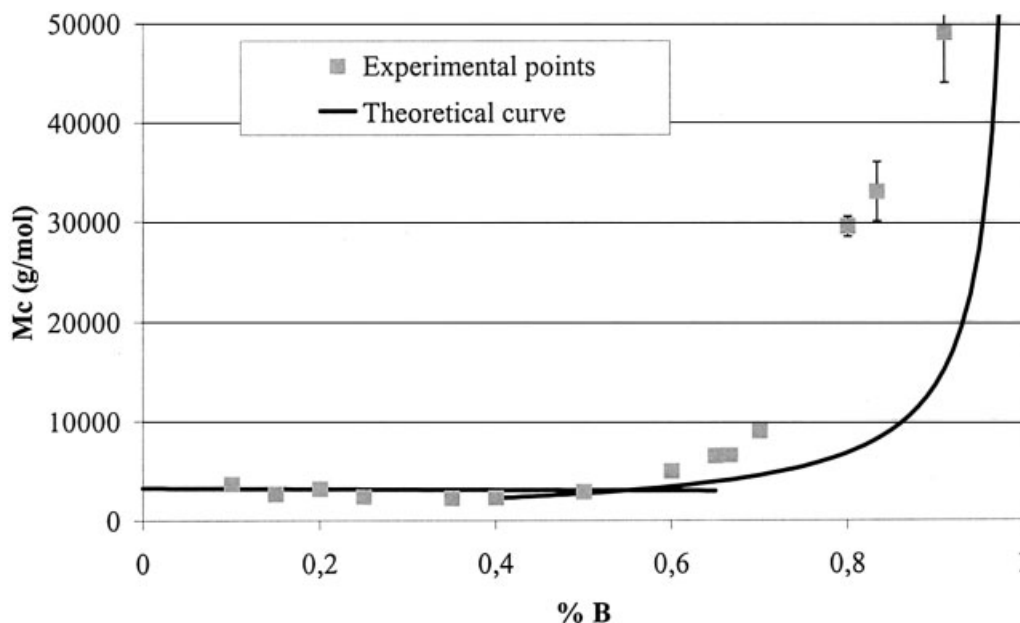


Figure 2 M_c (experimental and theoretical values) as a function of the formulation.

Consequently, the mobility of the polymer chains decreased, and the reticulation could no longer be completed. Moreover, the catalyst was only present in part A, and this resulted in the possibility that below a certain level of part A, the amount of the catalyst could be too small to invoke a complete reticulation.

Below the stoichiometric composition, the experimental and theoretical values remained well correlated, and they seemed to agree with the preceding explanation: below the stoichiometric composition, there was enough catalyst available in the mixture, as it was contained in part A. The viscosity was low

enough to allow the chains high mobility. Therefore, a practically complete reticulation was possible.

Rheological behavior of the silicon networks

Linearity

First, the linearity field was determined (see Fig. 4). The experiments consisted of a strain sweep test at a given temperature and frequency while the torque was measured. We then deduced the limit of the linearity field, which was given by the end of the plateau of G' . The experiments were performed at -125 , 25 , and 175°C at 0.05 and 50 Hz.

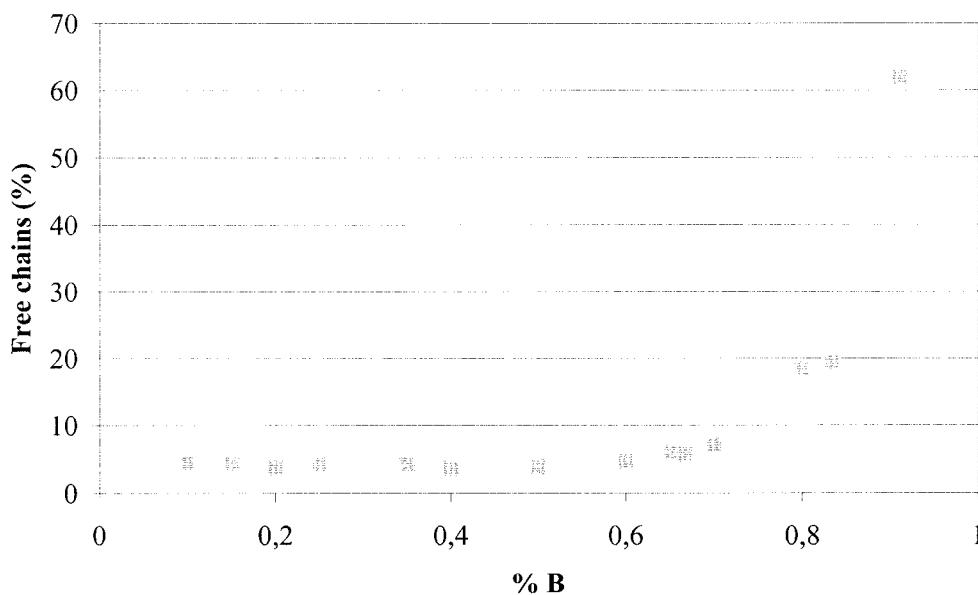


Figure 3 Amount of free chains as a function of the formulation.

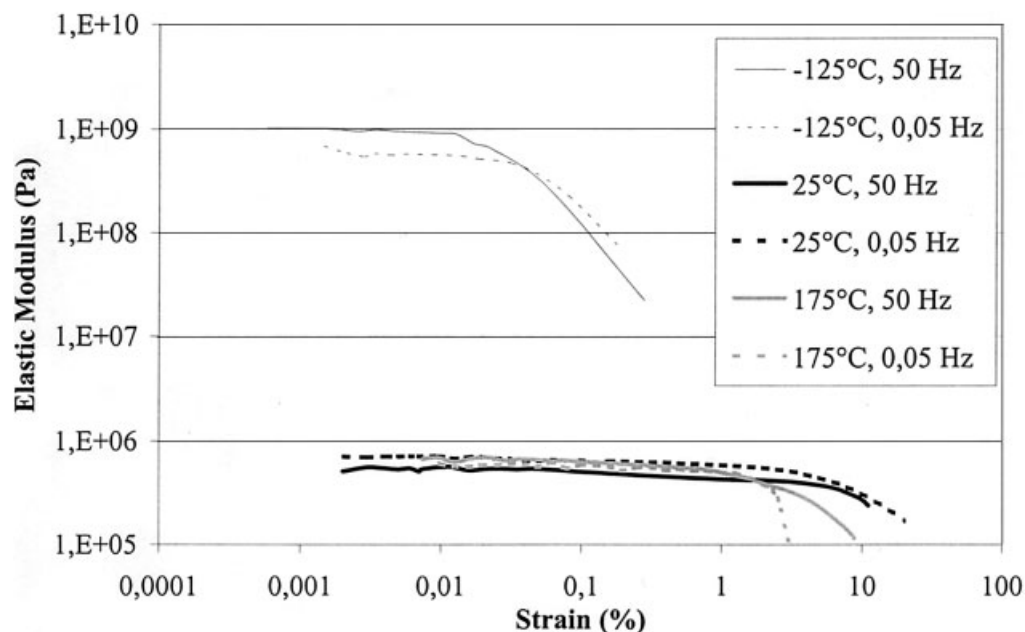


Figure 4 Linearity test for the 50% formulation.

On the different curves, when the strain reached a characteristic value called *critical strain*, G' decreased. As the latter represented the order and elasticity of the network, this decrease could be explained by a partial destruction of the network or by a loss of elasticity.^{13,14} In Figure 5, the critical strain was plotted in relation to the formulation of the network. The critical strain was always reduced when the strength of the network was increased, independently of the studied temperatures and frequencies.

As previously mentioned, the loss of linearity (above the critical strain) might have been due to a partial destruction of the polymer network. Therefore, an increasing crosslink density of the network led to a decrease in the critical strain to break the first chain, as observed in Figure 5: the critical strain had its lowest value near the stoichiometric composition, a slight shift beyond this one (for networks still well reticulated, see the Microstructural Characteristics of the Silicon Networks section), and, at the reverse, a dramatic increase above this for weak networks.

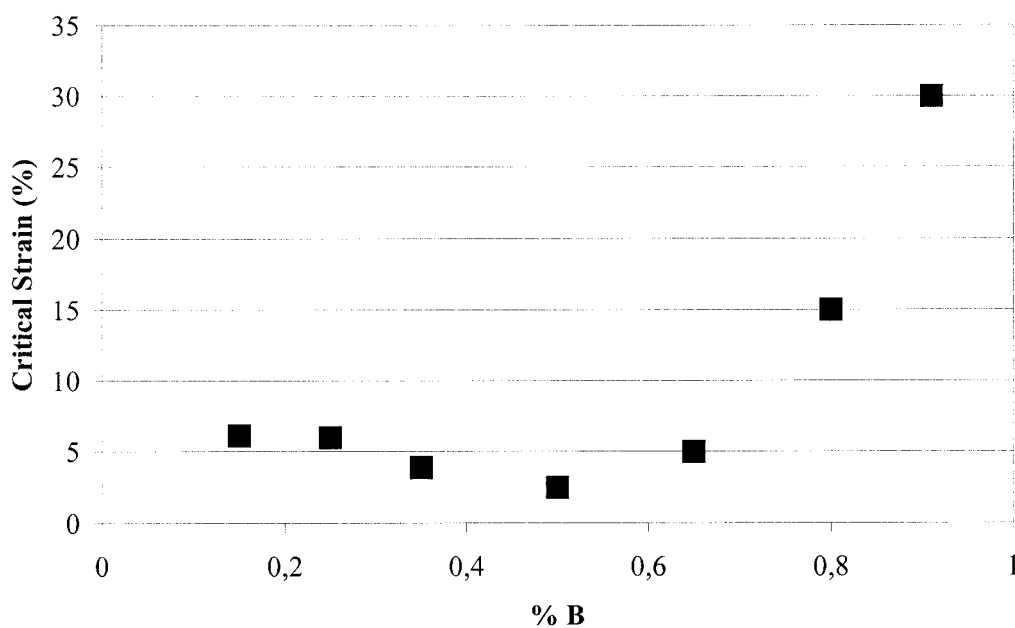


Figure 5 Evolution of the critical strain with the formulation at 25°C and 50 Hz.

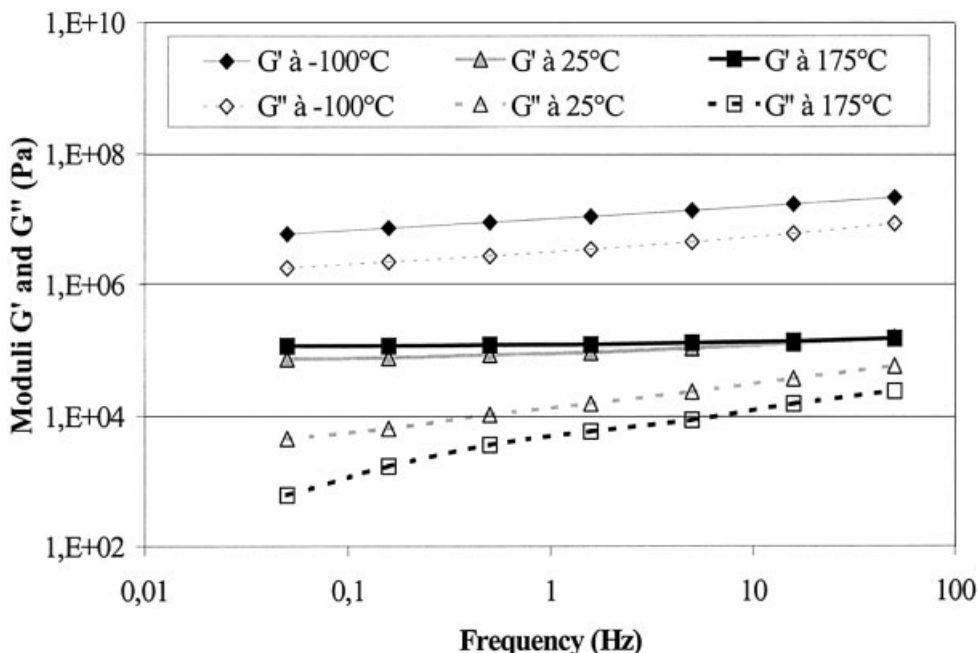


Figure 6 Evolution of G' and G'' as a function of the frequency for the 80% B silicon network.

Influence of the frequency on G' , G'' , and the loss tangent ($\tan \delta$)

Tests were performed for seven frequencies in the range of 0.05–50 Hz, at ideal strains to be in the linearity field and to reach the highest sensibility of the torque. Seven formulations were tested: 15, 25, 35, 50, 65, 80, and 91% B.

Figure 6 shows some typical evolutions obtained with the 80% B silicon network. G' increased with the frequency over the whole temperature range. Nevertheless, it was more sensible at low temperatures ($< -100^\circ\text{C}$) than for higher ones: at 175°C , G' was almost independent of the frequency.¹⁵ G'' also increased with the frequency over the whole temperature range. This behavior is typical for polymers: when they are submitted to a mechanical solicitation, there are movements between the polymer chains. If sufficient time allows the chains to reorganize themselves, the polymer appears soft, and the modulus is low. However, for a shorter time, which means a higher frequency, the material appears stiff, and the modulus is higher.

Influence of temperature

The general evolutions of G' , G'' , and $\tan \delta$ were similar for all the formulations of the silicon networks. Some representative curves are given below for the 80% B formulation. The evolution of G' could be divided into two regions. First, there was a large decrease when the material passed the α -transition temperature (associated with the glass-transition temperature, this was a transition field between glassy behavior and caoutchoutic behavior); the material pre-

sented a viscoelastic behavior. Second, the modulus became independent of the temperature (or even increased slightly), this being characteristic of the caoutchoutic plateau. The realized tests did not allow us to reach the glassy region plateau (at really low temperatures), for which the expected modulus would be 10^9 Pa.

The α -transition temperature could also easily be determined by a $\tan \delta$ curve: it was characterized by the presence of a peak. Four characteristic values were defined to allow us to compare the different formulations: the α -transition temperature and the height of the associated peak; the onset temperature of the caoutchoutic plateau (see Fig. 7), which we defined as the temperature above which G' changed less than 5% for every 5°C ; and the value of G' at this temperature. The influence of the frequency on these values was investigated. Figure 8 presents the results for the 80% B formulation.

Both the α -transition and onset temperatures shifted with the frequency approximately 30°C toward the high temperatures when the frequency increased from 0.05 to 50 Hz. The behavior was similar for all the formulations. Moreover, the frequency had no influence on the height of the peak associated with the α -transition temperature or on G' at the onset temperature of the caoutchoutic plateau.

This behavior could be related to the time–temperature equivalence proposed by Williams, Landel, and Ferry: a polymer submitted to a solicitation at a given frequency and temperature will present the same behavior if both the frequency and the temperature are increased (or decreased).¹⁶ Another possible formula-

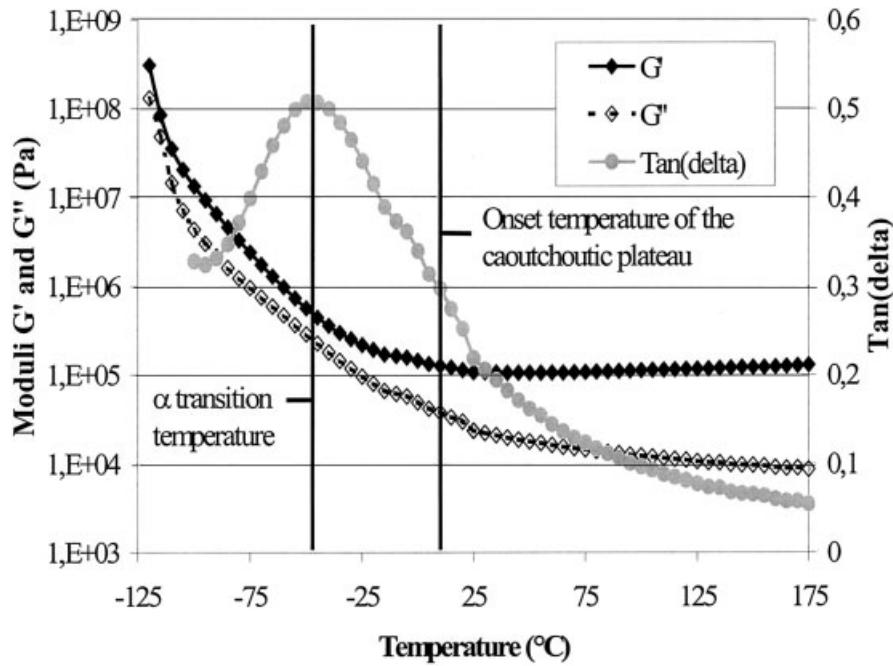


Figure 7 Evolution of G' , G'' , and $\tan \delta$ with temperature for the 80% B silicon network at a frequency of 5 Hz.

tion is that increasing the frequency is equivalent to decreasing the temperature.

The behavior of the studied silicon networks could be explained by microstructural considerations. An increase in the temperature induced an increase in the Brownian movement and, therefore, in the mobility of the polymer chains; during a sollicitation at a given frequency, the answer was, therefore, faster, and the mobility of the chains was enhanced. If, at a lower

temperature, the frequency of the imposed sollicitation was itself lower, although the chains were less mobile, they had more time to be rearranged, and the macroscopic behavior was identical. However, the amplitude of the peak of $\tan \delta$ and G'' at the onset temperature of the caoutchoutic plateau practically did not vary because intrinsically the material remained the same; only the external conditions of the sollicitation changed.

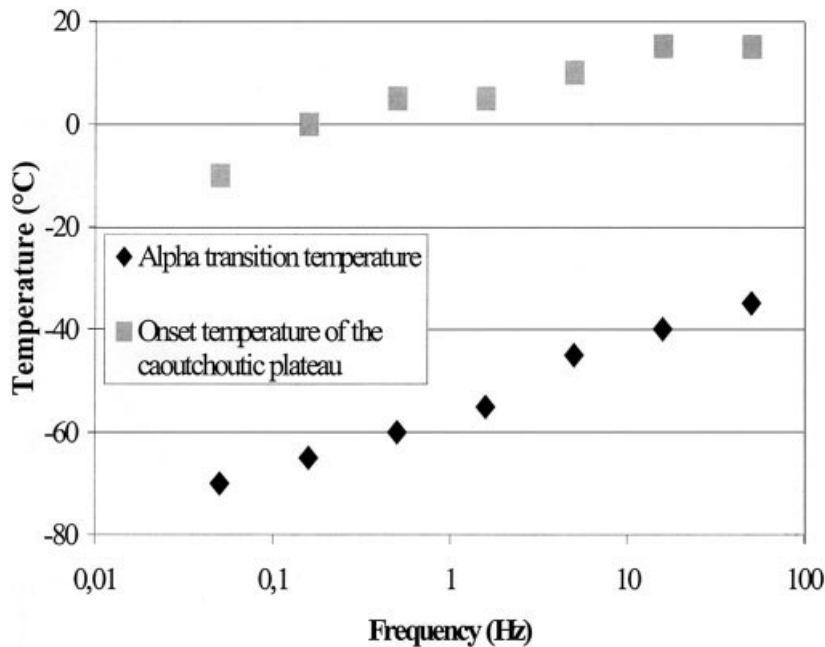


Figure 8 Influence of the frequency on the characteristic temperatures of the 80% B silicon network.

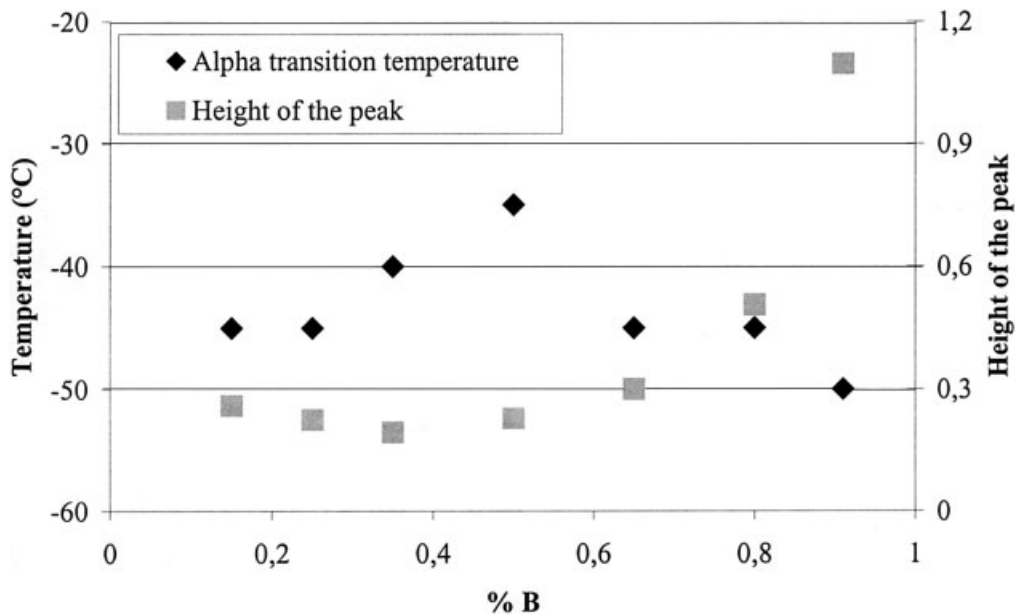


Figure 9 Evolution according to the formulation of the α -transition temperature and the height of the associated peak

Influence of the formulation

Figures 9 and 10 present the evolution of the α -transition temperature and the onset temperature of the caoutchoutic plateau according to the formulation of the silicon network and the amplitude of the peak of $\tan \delta$ and G' at the onset temperature of the caoutchoutic plateau according to the formulation of the silicon network. The values are given for a frequency of 5 Hz; the evolution of these four characteristic values according to the frequency has already been discussed.

We found temperatures associated with the passage of the α transition and the caoutchoutic plateau, which

presented a maximum near the stoichiometric composition. The amplitude of the peak of $\tan \delta$ also presented a minimum connected to the stoichiometric composition. Finally, G' at the onset temperature of the caoutchoutic plateau was maximal around the stoichiometric composition and decreased toward large proportions of the B component. The experiments that we performed to characterize the three-dimensional network helped us to understand these results.

We pointed out that the reticulation was not total; that is, not all the hydrogen and vinyl functions

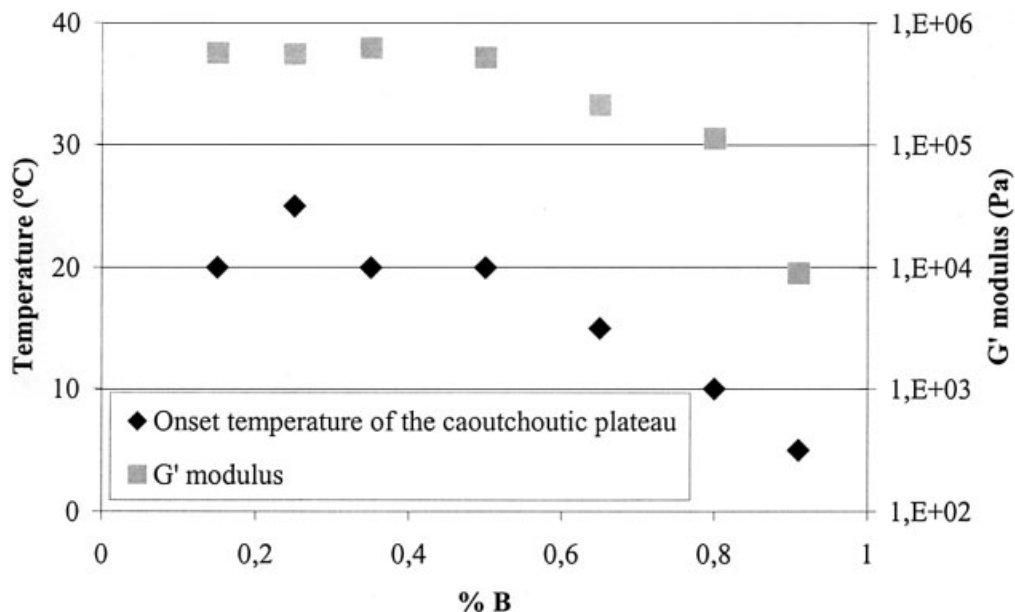


Figure 10 Evolution according to the formulation of the onset temperature of the caoutchoutic plateau and the associated G' value.

formed crosslinks. In addition, we also observed that a liquid phase could exist within the network. This phase could represent more than one-third of the total mass of silicone when the compositions were far from the stoichiometric proportions (Table IV, Fig. 3).

The behavior on a macroscopic scale could be attributed to several phenomena that could happen together.¹⁷ First, the liquid phase acted as a plasticizer. The presence of free and very mobile chains increased the average distance between the chains and consequently facilitated their mobility; this involved a shift of the α transition and the caoutchoutic plateau toward the low temperatures, and less energy was necessary to obtain the same mobility level. Second and simultaneously, when the stoichiometric proportions were approached, the quantity of the liquid phase decreased, as well as M_c ; this increase in the reticulation was an obstacle to the flow of the chains and involved an increase in G' at the onset temperature of the caoutchoutic plateau. It also involved a reduction in the amplitude of the peak associated with the α -transition temperature; these two characteristic values were indeed linked by a relation of proportionality:

$$\text{Heights of } \tan(\delta) \text{ peak} \propto \frac{G_{\text{Glass}} - G_{\text{Caoutchoutic}}}{G_{\text{Caoutchoutic}}}$$

and

$$\text{Height of } \tan(\delta) \text{ peak} \propto \frac{G_{\text{Glass}}}{G_{\text{Caoutchoutic}}}$$

because

$$G_{\text{Glass}} \gg G_{\text{Caoutchoutic}}$$

Finally, dangling chains, connected to the network at only one end, could also act as plasticizers of the silicon network.^{18,19}

CONCLUSIONS

First, we showed the influence of the formulation and crosslink density on the critical strain, a strain beyond which the network was modified and presented a nonlinear behavior: the higher the crosslink density was, the lower the critical strain was.

The influence of the frequency was then studied, and we highlighted a strong dependence of G' on the frequency at the low temperatures, a dependence that was reduced as the temperature increased. We observed that, for its part, G'' also increased with the frequency but over the whole temperature range.

Finally, we showed that the formulation notably influenced the four characteristic values of the silicone behavior. That is, the α -transition temperature and the onset temperature of the caoutchoutic plateau shifted toward higher temperatures as the crosslink density increased; the amplitude of the peak associated with the α -transition temperature decreased; and, finally, G' at the onset temperature of the caoutchoutic plateau increased.

The simultaneous reductions of the amount of the liquid phase trapped in the network and of M_c involved a decrease in the mobility of the chains and could, therefore, explain the behavior observed.

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