Elasticity measurements on bimodal networks in elongation and compression: networks crosslinked in solution and studied unswollen, and networks crosslinked in the undiluted state and studied swollen

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Polydimethylsiloxane (PDMS) bimodal networks were prepared by tetrafunctionally end-linking very short and relatively long hydroxyl-terminated chains, both in solution and in the bulk state. A constant weight fraction of short chains, 30 wt%, was employed. The networks were studied with regard to their stress–strain isotherms, covering the entire range from high elongations to high compressions. In the first type of experiment, the bimodal networks crosslinked in solution were studied in the unswollen state. The dependence of the elastic properties of the networks on the volume fraction v_{2s} of polymer chains in the solution being crosslinked was determined. In particular, as v_{2s} increases, the modulus was found to go through a pronounced maximum with increase in deformation. In the second type, the bimodal networks crosslinked in the undiluted state were studied swollen. Decrease in the volume fraction v_2 of polymer network present during the stress–strain measurements was found to *increase* the modulus, which is the opposite of that invariably found for unimodal networks. This effect of swelling on the elastic properties of bimodal networks confirmed that the self-reinforcement they exhibit is due to the limited extensibility of short chains.

(Keywords: polysiloxanes; elastomers; bimodal distributions; elongation; compression; ultimate properties; solution crosslinking; swelling)

INTRODUCTION

Model networks have now been extensively used for studying rubber-like elasticity[1]. The main advantage of these materials is their known structure, in particular their values of the molecular weight between junction points and its distribution. They can be made by anionic block copolymerization, anionic deactivation cross-linking, or end-linking. In the end-linking technique, the first step is to prepare a linear precursor polymer having a number-average molecular weight M_n and two functionally reactive ends. Reaction of these chain ends with an end-linking agent of functionality ϕ produces a network having this junction functionality and a molecular weight M_c between crosslinks of M_n. The distribution of molecular weights between junctions is also, of course, the same as that of the starting chains.

The most important example of this approach[1] involves hydroxyl-terminated polydimethylsiloxane (PDMS) $[-Si(CH_3)_2O-]_x$ end-linked with tetraethoxysilane (TEOS) $Si(OC_2H_5)_4$. Obviously, the described end-linking technique can be used to prepare bimodal elastomeric networks that consist of mixtures of very short and relatively long chains. In fact, considerable experimental and theoretical interest has recently been focused on this type of elastomeric network[1–17]. The impetus for these studies of bimodal networks was the very unusual elastomeric properties they exhibit, in particular the large increases in their moduli at both high elongations and large compressions[17]. This type of self-reinforcement has been demonstrated to result from the limited extensibility of the short chains in the network structure[4], rather than from strain-induced crystallization.

The present investigation was carried out to determine the effect of diluent on these increases in modulus at high deformations. In the first part, the networks were prepared by end-linking in solution. Previous experimental studies showed that unimodal elastomeric networks crosslinked in solution and subsequently dried have lower values of the modulus, which suggests less chain-junction entangling[18]. It is of obvious interest to determine the effects of diluent present during the preparation of *bimodal* networks, particularly since their stress–strain isotherms are much more complex than those of simple unimodal networks. The second part was essentially the reverse of the first: the networks were prepared in the undiluted state, and the diluent introduced into the network by swelling and kept there during the stress–strain measurements. Stress–strain isotherms in elongation have, in fact, been reported[19] for swollen bimodal PDMS networks that had been end-linked in the bulk state. For completeness, however,

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the stress–strain measurements in both types of experiments to be conducted will include measurements in elongation as well as in compression. Also, the investigations will cover as wide a range in deformation as possible, i.e. the elongations and compressions will both be carried out to the respective rupture points.

EXPERIMENTAL

Preparation of bimodal elastomers

The linear hydroxyl-terminated PDMS samples utilized in this study had number-average molecular weights corresponding to $M_n = 880\ \mathrm{g\ mol^{-1}}$ (obtained from the Dow Corning Corp.) and $22\,600\ \mathrm{g\ mol^{-1}}$ (Petrarch Systems Co.). The two samples were tetrafunctionally end-linked either in the undiluted state or in solution with the stoichiometrically required amounts of TEOS (Aldrich Chemical Co.) using 0.6 wt% stannous-2-ethyl hexanoate (Aldrich Chemical Co.) as a catalyst. A constant weight fraction of short chains (30 wt%) was employed. The preparative procedure is described elsewhere[18]. Briefly, the reactions were run in Teflon moulds at room temperature for three days. The resulting network sheets were extracted with toluene for three days, then deswelled with methanol, and finally dried under vacuum. The fraction of soluble polymer thus removed amounted to approximately 2.5 wt%.

For the bimodal networks crosslinked in solution, the diluent employed was a linear dimethylsiloxane (DMS) oligomer ($M_n = 1250\ \mathrm{g\ mol^{-1}}$) with unreactive chain ends. The amounts that were present are specified in the first column of *Table 1*. The same diluent was used to swell the networks that had been end-linked in the undiluted state. This particular solvent was chosen because the close match between its structure and that of the PDMS network chains would minimize any possible specific solvent effect on elastomeric properties[1]. Also, because of its low volatility, the swollen samples could be suspended in air during the mechanical property measurements without being subject to significant evaporative losses. The diluent was incorporated into the networks by absorption to various extents. The swollen networks were placed into sealed jars and, after sufficient time had elapsed (~72 h) to assure swelling uniformity, they were considered ready for the stress–strain measurements described in the following section.

Uniaxial extension and compression measurements

Uniaxial extension measurements were carried out on sample strips in the usual manner[20,21]. The compressions were imposed by biaxial extensions, which were produced by inflation of circular sheets of the networks. The apparatus and procedure are described in detail elsewhere[22]. Both types of samples were taken from the same sheet. All measurements were carried out at 25°C, in the direction of increasing deformation, but with some data taken out of sequence to test for reversibility. The elongations or compressions were generally increased to the rupture points of the sample.

RESULTS AND DISCUSSION

The stress–strain isotherms were interpreted in terms of the reduced nominal stress or modulus defined by[23,24]:

$$[f^*] \equiv (f/A_d)v_2^{1/3}/(\alpha - \alpha^{-2}) \qquad (1)$$

where f is the equilibrium elastic force, A_d the cross-sectional area of the dry undeformed sample, v_2 the volume fraction of polymer in the stretched network, and $\alpha = L/L_{i,V}$ the extension ratio relative to the length $L_{i,V} = L_0(V/V_0)^{1/3}$ of the unstretched (isotropic) specimen at the volume V prevailing in the elongated state. The values of $[f^*]$ were plotted against reciprocal deformation, as suggested by the semi-empirical equation of Mooney[25] and Rivlin[26]:

$$[f^*] = 2C_1 + 2C_2\alpha^{-1} \qquad (2)$$

where $2C_1$ and $2C_2$ are constants independent of deformation.

Dry bimodal networks that had been crosslinked in solution

The two polymer samples described above had been tetrafunctionally end-linked in solutions with the DMS oligomer at different degrees of dilution ($v_{2s} < 1$) and, for reference purposes, in the undiluted state ($v_{2s} = 1$) as well. The results of the stress–strain measurements on them, carried out on the samples after drying, are given in *Table 1*.

Figure 1 represents the stress–strain isotherms obtained from the elongation and biaxial extension measurements. The vertical broken line divides the experimental curves into two regions, elongation ($\alpha^{-1} < 1$) and compression ($\alpha^{-1} > 1$). Each curve is labelled with the volume fraction v_{2s} of polymer chains in the solution during crosslinking. The results for the data taken out of sequence show the curves to have good reversibility.

Table 1 Preparative conditions and elastomeric properties of the unswollen PDMS bimodal networks[a] crosslinked in solution

v_{2s}[b]	$2C_1$ ($\mathrm{N\ mm^{-2}}$)	$2C_2$ ($\mathrm{N\ mm^{-2}}$)	$2C_2/2C_1$	$\alpha_{e,u}$[c]	$\alpha_{c,u}$[d]	$\Delta[f^*]_e$[e] ($\mathrm{N\ mm^{-2}}$)	$\Delta[f^*]_c$[f] ($\mathrm{N\ mm^{-2}}$)	$[f^*]_{e,r}$ ($\mathrm{N\ mm^{-2}}$)	$[f^*]_{c,r}$ ($\mathrm{N\ mm^{-2}}$)
1.0	0.245	0.254	1.04	1.23	0.794	0.0490	0.108	0.516	0.564
0.8	0.200	0.208	1.04	1.42	0.714	0.0855	0.153	0.445	0.503
0.6	0.175	0.117	0.669	1.47	0.407	0.0748	0.0830	0.338	0.387
0.5	0.162	0.0683	0.422	1.61	0.317	0.0202	0.0230	0.211	0.256
0.4	0.120	0.0421	0.351	1.84	–	0.00230	–	0.147	0.163

[a] 30 wt% short chains of molecular weight $880\ \mathrm{g\ mol^{-1}}$, in mixtures with relatively long chains of $22\,600\ \mathrm{g\ mol^{-1}}$
[b] Volume fraction of polymer present during network formation
[c] Deformation at the upturn in the modulus in elongation
[d] Deformation at the upturn in the modulus in compression
[e] Difference between the modulus at rupture and the modulus at upturn, in elongation
[f] Difference between the modulus at rupture and the modulus at upturn, in compression

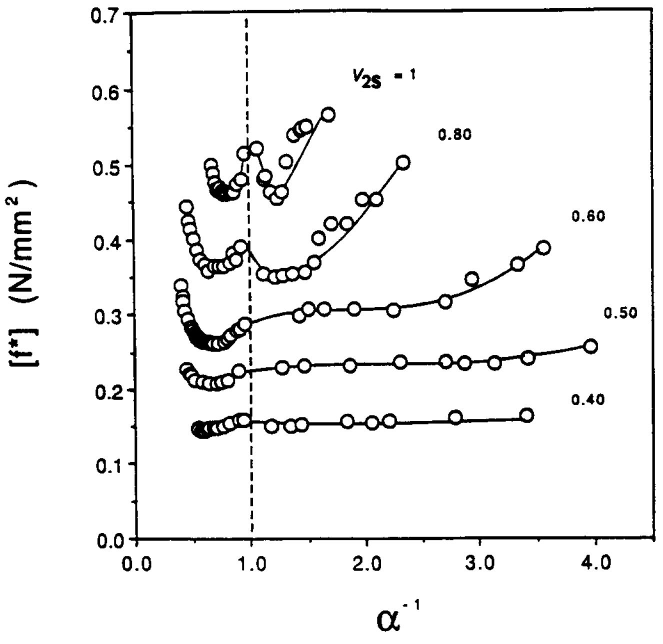

Figure 1 Stress–strain isotherms at 25°C for dry (unswollen) bimodal PDMS networks that had been crosslinked in solution, along with a reference isotherm for one network that had been prepared in the undiluted state. Each curve is labelled with the volume fraction v_{2s} of polymer present during network formation, and the filled symbols (within the overlapping points) locate results taken out of sequence to test for reversibility

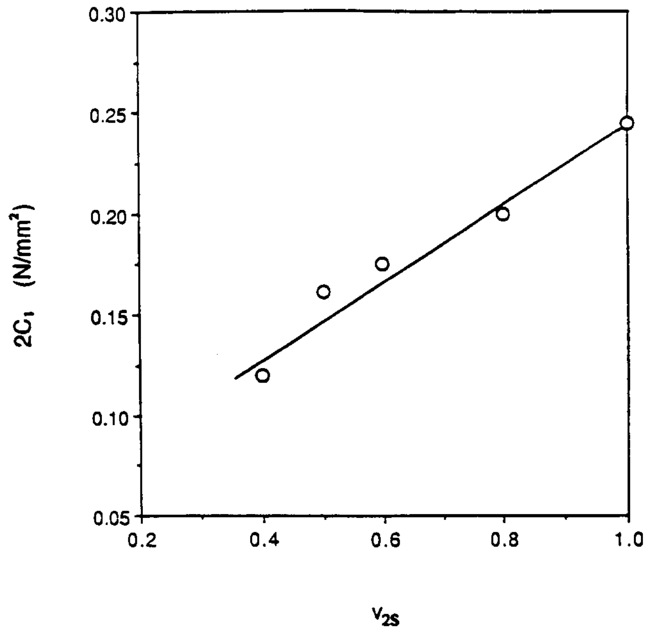

Figure 2 Dependence of $2C_1$ on v_{2s} for the bimodal PDMS networks that had been crosslinked in solution

Values of $2C_1$, $2C_2$ and $2C_2/2C_1$ obtained from the relatively linear portions of the isotherms are given in columns two to four of *Table 1*. The constant $2C_1$ depends primarily on the crosslink density[27]. Obviously, $2C_1$ should be a function of v_{2s}, as illustrated in *Figure 2*, since the crosslink density of a network prepared in solution is lower than that of a network prepared in the undiluted state[18]. The other constant, $2C_2$, depends on the conditions of network formation. For example, a network crosslinked in solution, i.e. at $v_{2s} < 1$, has fewer chain-junction entanglements than one crosslinked in the undiluted state[18]. Hence, the mobility of the network chains increases, as do the fluctuations of the network junctions. Thus, $2C_2$ and its modulus-normalized ratio $2C_2/2C_1$ should decrease with decrease in such entangling, and thus decrease with decrease in v_{2s}. The results in *Figures 3* and *4* show the expected dependence of these quantities on v_{2s}. It can be seen that $2C_2$ itself decreases linearly with decrease in v_{2s}, while the ratio $2C_2/2C_1$ decreases most at the smaller values of v_{2s}.

The deformations at which the upturn in modulus first becomes discernible are given in columns five and six of *Table 1*, and in *Figure 5*. The increases in these quantities are presumably due to the fact that drying a solution-

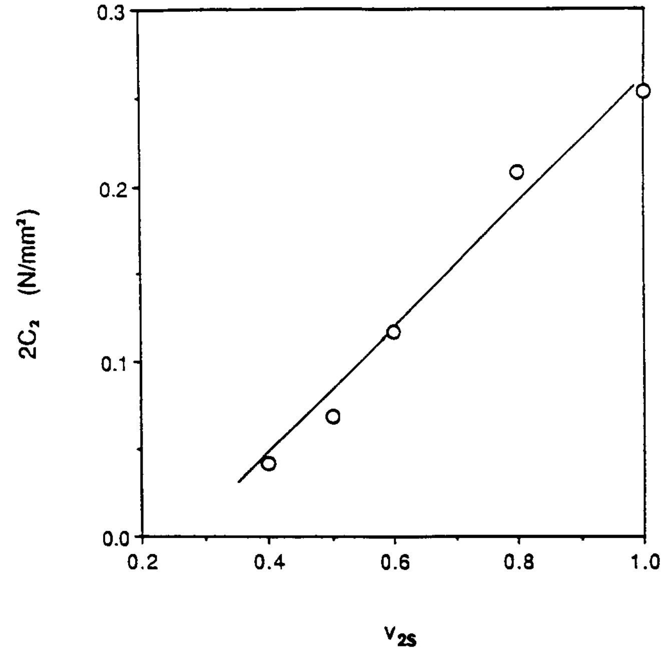

Figure 3 Dependence of $2C_2$ on v_{2s} for the bimodal PDMS networks that had been crosslinked in solution

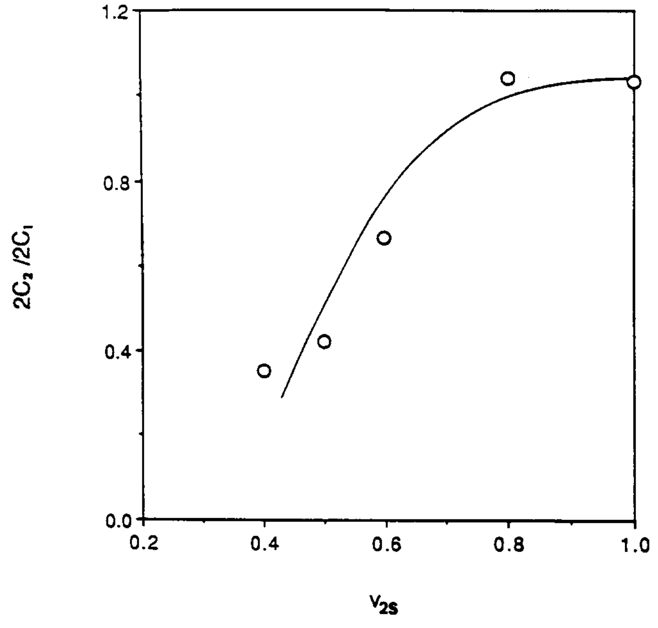

Figure 4 Dependence of $2C_2/2C_1$ on v_{2s} for the bimodal PDMS networks that had been crosslinked in solution

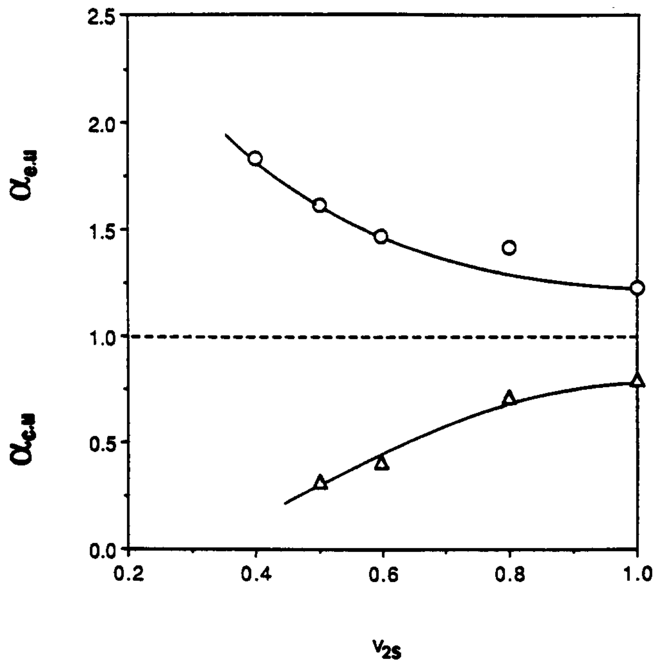

Figure 5 Effect of v_{2s} on the deformation at which the upturns in the modulus are discernible, in elongation, $\alpha_{e,u}$ (○), and in compression, $\alpha_{c,u}$ (△). Taken from *Figure 1*

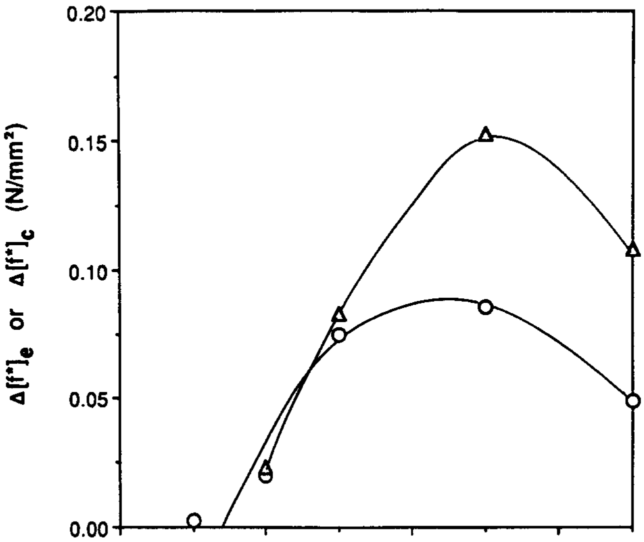

Figure 6 Concentration dependence of the magnitude of the increase in modulus, for elongation, $\Delta[f^*]_e$ (○), and compression, $\Delta[f^*]_c$ (△), taken as the difference between the modulus at rupture and the modulus at the upturn. Taken from *Figure 1*

crosslinked sample partially collapses the chains, thereby giving the network higher extensibility.

In general, the curves have upturns in the modulus at large deformations, both in elongation and in compression, as was found previously for PDMS networks prepared in the undiluted state[17]. One interesting difference, however, is the magnitude of the upturns in the modulus (i.e. the difference between the modulus at rupture and the modulus at upturn). The magnitude first increases with decrease in v_{2s}, and then decreases. The maximum in this quantity is shown more clearly in *Figure 6*. The initial increase could be due to the higher extensibility and thus larger values of the modulus at rupture. This effect could be overcome at higher dilutions, however, by the generation of larger numbers of imperfections such as loops and dangling chains, which are not elastically effective. They could decrease the extensibility and thus the magnitudes of the upturns, as observed.

Figure 7 shows the v_{2s} dependence of the rupture moduli, $[f^*]_{e,r}$ for elongation and $[f^*]_{c,r}$ for compression. As can be seen from these results, decrease in v_{2s} decreases the values of these ultimate properties, as

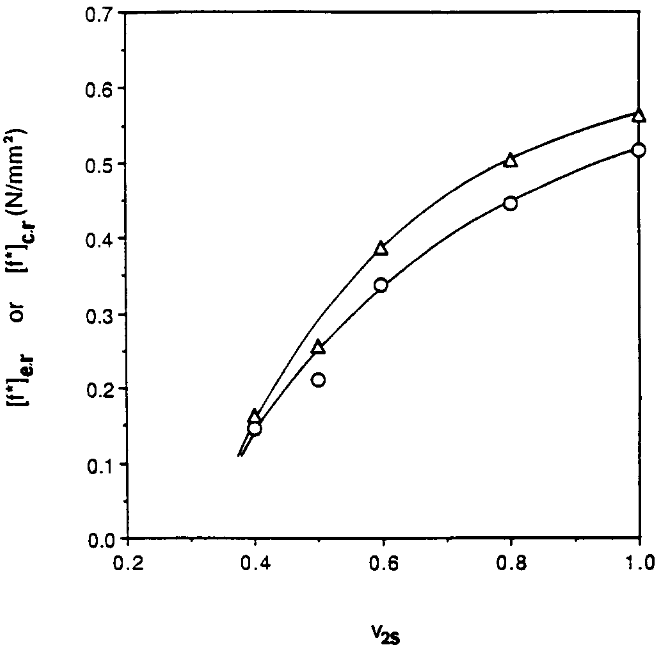

Figure 7 Effect of v_{2s} on the ultimate strength in elongation, $[f^*]_{e,r}$ (○), and in compression, $[f^*]_{c,r}$ (△). Taken from *Figure 1*

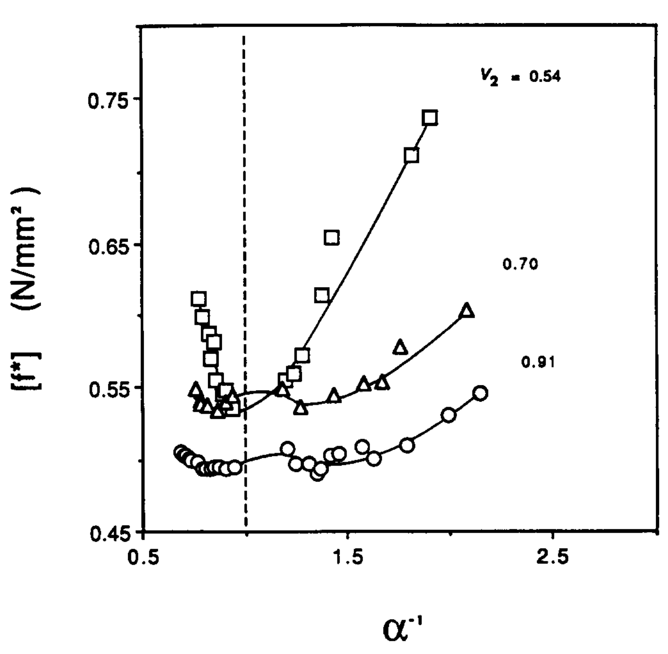

Figure 8 Stress–strain isotherms at 25°C for the swollen PDMS bimodal networks that had been crosslinked in the undiluted state. Each curve is labelled with the volume fraction v_2 of polymer present in the swollen networks during the stress–strain measurements

Table 2 Degrees of swelling and elastomeric properties of the swollen PDMS bimodal networks[a] crosslinked in the bulk (undiluted) state

v_2[b]	$\alpha_{e,u}$	$\alpha_{c,u}$	$\alpha_{e,r}$[c]	$\alpha_{c,r}$[d]	$[f^*]_{e,r}$ (N mm^{-2})	$[f^*]_{c,r}$ (N mm^{-2})
0.91	1.27	0.738	1.46	0.466	0.505	0.546
0.81	1.24	0.758	1.37	0.472	0.516	0.564
0.70	1.20	0.786	1.31	0.480	0.549	0.603
0.54	1.06	0.934	1.30	0.525	0.612	0.736

[a] 30 wt% short chains of molecular weight 880 g mol^{-1}, in mixtures with relatively long chains of 22 600 g mol^{-1}

[b] Volume fraction of polymer present during the stress–strain measurements

[c] Deformation at rupture in elongation

[d] Deformation at rupture in compression

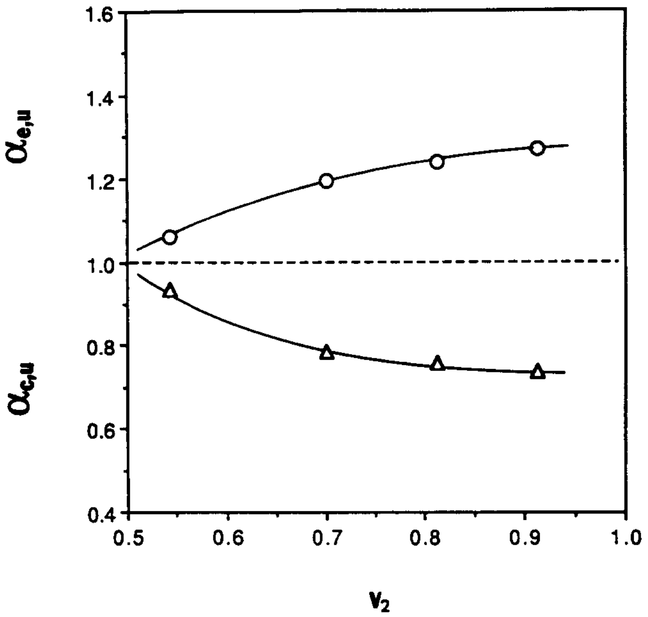

Figure 9 Effect of v_2 on the deformation at which the upturns in the modulus are discernible, in elongation, $\alpha_{e,u}$ (○), and in compression, $\alpha_{c,u}$ (△), for the swollen PDMS bimodal networks that had been crosslinked in the undiluted state

expected, with the curves for elongation and compression having very similar shapes.

Swollen bimodal networks that had been crosslinked in the undiluted state

The stress–strain measurements reported here were carried out on the second set of samples, as swollen with the DMS oligomer. The resulting isotherms are shown in *Figure 8*, and their most important characteristics are summarized in *Table 2*. The effect of swelling on the isotherms for the bimodal networks is very different from that observed for the unimodal networks (consisting of all long chains)[28]. In the usual case of unimodal networks, increase in swelling (decrease in v_2) causes a decrease in the modulus. However, the opposite effect is seen to occur with these bimodal networks: as v_2 *decreases*, the modulus *increases*! In particular, there is a very large increase in the modulus at high swelling, so that the upturn in the modulus appears at lower deformations. In fact, the upturn appears to be immediate for values of v_2 below a critical value, as can clearly be seen from *Figure 9*. These enhanced upturns are apparently due to the diluent stretching the short chains closer to the limits of their extensibility[1]. The results presented here for the elongation region are similar to those also obtained on bimodal PDMS networks in elongation by Clarson *et al.*[19].

Thus, the marked improvement in reinforcement does not result from strain-induced crystallization, but from the very limited extensibility of the short network chains. The deformations at rupture would be expected to decrease with swelling, and this is shown by the results in columns four and five of *Table 2*, and by the lines in *Figure 10*. The increases in the magnitudes of the upturns

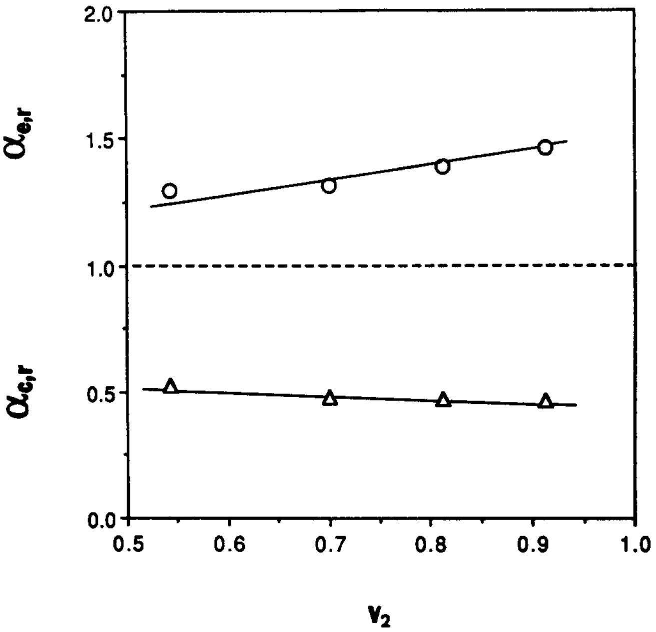

Figure 10 Effect of v_2 on the deformation at rupture in elongation, $\alpha_{e,r}$ (○), and in compression, $\alpha_{c,r}$ (△), for the swollen PDMS bimodal networks that had been crosslinked in the undiluted state

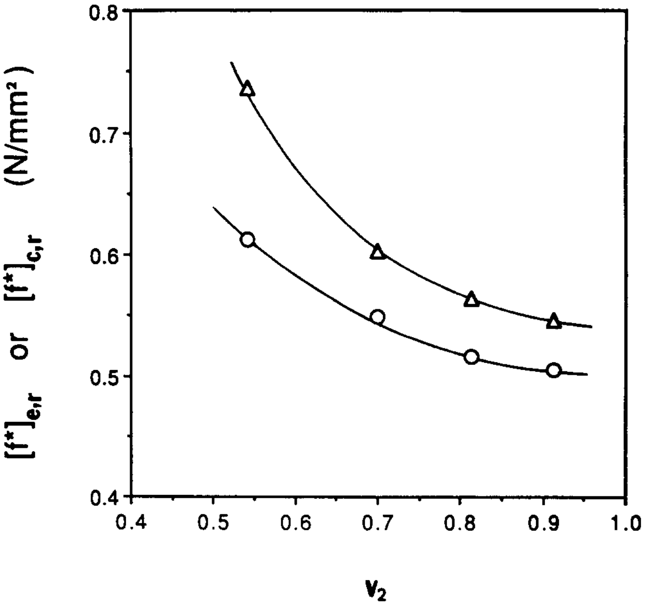

Figure 11 Effect of v_2 on the ultimate strength in elongation, $[f^*]_{e,r}$ (○), and in compression, $[f^*]_{c,r}$ (△), for the swollen PDMS bimodal networks that had been crosslinked in the undiluted state

should give substantial increases in ultimate strength with increased swelling. This was indeed found to be the case, as is shown in the last two columns of *Table 2*, and by the curves presented in *Figure 11*.

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