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Effect of Composition and Cross-Link Functionality on the Elastomeric Properties of Bimodal Networks

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ABSTRACT: Hydroxyl-terminated poly(dimethylsiloxane) chains were tetrafunctionally and trifunctionally end-linked to give bimodal elastomeric networks in which the short chains had a number-average molecular weight of 660 and the long chains 21.3×10^3. Elongation measurements were carried out at 25 °C to obtain the stress–strain isotherms for these materials up to their rupture points. Decrease in the mol % of short chains was found to cause an increase in the elongation at which the modulus shows a strong upturn because of limited chain extensibility and also an increase in maximum extensibility. The ultimate strength and energy for rupture increase with cross-link functionality and go through a maximum upon changes in composition, with approximately 95 mol % short chains giving the largest values for these two properties.

Introduction

Elastomeric networks of known structure may be prepared by reacting suitably terminated polymer chains with an end-linking agent of functionality three or greater.[1] If a mixture of very short and relatively long chains is treated in this way, the resulting (unfilled) elastomer has a bimodal distribution of network chain lengths. Networks of this type have been prepared from chains of poly(dimethylsiloxane) (PDMS) [$-Si(CH_3)_2O-$] and were found to have unusually good ultimate properties.[1-3] The present investigation explores in detail the way in which the elastomeric properties of trifunctional and tetrafunctional bimodal networks of PDMS depend on the relative proportions of short and long chains.

Experimental Details

The two polymers employed were hydroxyl-terminated PDMS chains having number-average molecular weights M_n of 660 and 21.3×10^3, respectively. They were generously provided by Dow Corning Corp. of Midland, MI. After careful drying, these two components were mixed to give the compositions listed in columns three and four of Table I. One series of mixtures was tetrafunctionally end-linked by using $Si(OC_2H_5)_4$, and two other series were trifunctionally end-linked by using the corresponding vinyl and phenyl derivatives $ViSi(OC_2H_5)_3$ and $PhSi(OC_2H_5)_3$, respectively. The reactions were run in the usual manner,[1,4,5] with the end-linking agents present in amounts stoichiometrically equivalent to the number of polymer chain ends and the catalyst (stannous 2-ethyl hexanoate) present to the extent of 1.7 wt. % of the polymer mixture. The ingredients were thoroughly mixed to give perfectly clear solutions, which were then poured into glass molds. The reaction was allowed to proceed at room temperature for 2 days, with the molds covered during the first part of the process to prevent volatility losses of the end-linking agents.

The bimodal networks thus prepared were extensively extracted as described elsewhere.[4-6] Specifically, tetrahydrofuran and toluene were used as solvents (with stirring), at room temperature, for a period of several days. Values of the amount of soluble (un-cross-linked) polymer extracted, given in column five of Table I, are seen to be quite small. Strips having the approximate dimensions 1 mm × 3 mm × 30 mm were cut from each unswollen network sheet and then used in elongation experiments to obtain the stress–strain isotherms at 25 °C.[1,4-6] The elastomeric properties of primary interest are the nominal stress $f^* \equiv f/A^*$ (where f is the equilibrium elastic force and A^* the undeformed cross-sectional area) and the reduced stress or modulus[1,4,7] $[f^*] \equiv f^*/(\alpha - \alpha^{-2})$ (where $\alpha = L/L_i$ is the elongation or relative length of the strip). All stress–strain measurements were carried out to the rupture points of the samples and were generally repeated in part to test for reproducibility.

Results and Discussion

The first representation of the stress–strain data was based on the Mooney–Rivlin equation[7,8]

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

where $2C_1$ and $2C_2$ are constants. These plots, of the

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Table I
Network Characteristics and Stress-Strain Results

end-linker		short chains[b]						
molecule	ϕ[a]	mol %	wt %	sol fraction, %	α_u[c]	α_r[d]	$(f/A^*)_r$,[e] N mm^{-2}	10^3E_r,[f] J mm^{-3}
$Si(OC_2H_5)_4$	4	100.0	100.0	4.4		1.12	0.568	0.039
		99.9	96.7	4.7	1.15	1.20	0.856	0.082
		99.7	90.0	4.1	1.13	1.17	0.719	0.061
		99.4	83.3	4.1	1.17	1.21	0.695	0.068
		98.5	66.7	4.6	1.22	1.33	0.774	0.133
		97.0	50.0	4.9	1.23	1.66	1.45	0.397
		95.1	40.0	5.3	1.30	2.24	3.19	1.17
		94.2	33.3	5.4	1.41	2.27	2.45	0.963
		92.1	26.7	5.3	1.39	2.19	1.40	0.623
		90.8	23.3	5.2	1.55	2.42	1.64	0.769
$ViSi(OC_2H_5)_3$	3	100.0	100.0	3.9		1.17	0.557	0.052
		99.9	96.7	3.0	1.18	1.23	0.656	0.087
		99.7	90.0	3.2	1.24	1.27	0.700	0.105
		99.4	83.3	3.3	1.23	1.29	0.655	0.117
		98.5	66.7	3.6	1.29	1.58	0.834	0.256
		97.0	50.0	4.0	1.39	1.96	1.33	0.572
		94.2	33.3	4.1	1.38	2.19	1.29	0.640
		90.8	23.3	4.5	1.53	2.23	0.933	0.512
$PhSi(OC_2H_5)_3$	3	100.0	100.0	3.3		1.15	0.560	0.044
		99.9	96.7	3.5		1.25	0.658	0.082
		99.7	90.0	3.5	1.17	1.25	0.626	0.071
		99.4	83.3	3.7	1.23	1.40	0.935	0.195
		98.5	66.7	4.4	1.26	1.35	0.622	0.116
		97.0	50.0	4.7	1.31	1.78	1.08	0.397
		94.2	33.3	4.7	1.41	2.47	1.79	0.858
		90.8	23.3	4.6	1.45	2.40	1.30	0.710

[a] Junction functionality. [b] Having a number-average molecular weight of 660, in mixtures with long chains having 21.3 × 10^3. [c] Elongation at upturn in the modulus. [d] Elongation at rupture. [e] Ultimate strength, as represented by the nominal stress at rupture. [f] Energy required for rupture.

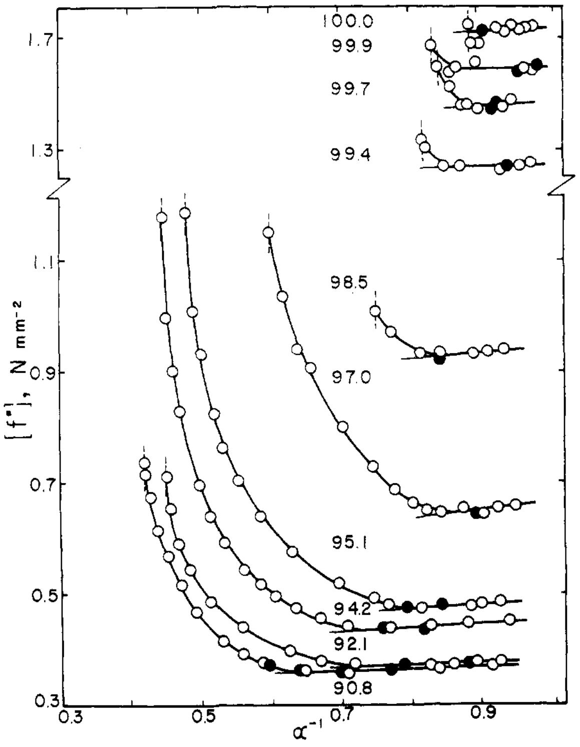

Figure 1. Stress–strain isotherms at 25 °C for the networks prepared by tetrafunctionally end-linking the chains with $Si(OC_2H_5)_4$ plotted as suggested by the Mooney–Rivlin representation of the reduced stress or modulus. Each curve is labeled with the mol % of short chains (M_n = 660) mixed with the much longer chains (21.3 × 10^3). The open circles locate the results obtained by using a series of increasing values of the elongation α and the filled circles the results obtained out of sequence to test for reversibility. The short extensions of the linear portions of the isotherms help locate the values of α at which the upturn in [f^*] first became discernible. These linear portions were located by least-squares analysis.

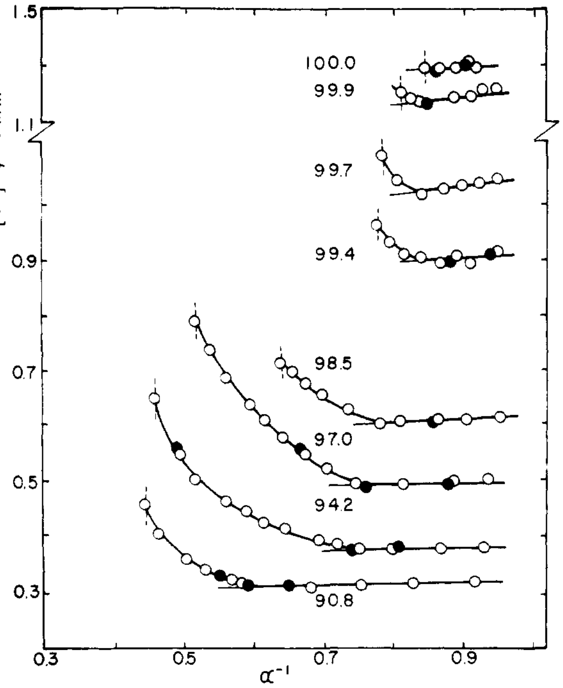

Figure 2. Stress–strain isotherms for the trifunctional networks prepared by using $ViSi(OC_2H_5)_3$; see legend to Figure 1.

reduced stress against reciprocal elongation, are shown in Figures 1–3. Figure 4, which is illustrative, shows some of the data of Figure 1 plotted in such a way that the area under each stress–strain curve corresponds to the energy E_r of rupture,[1,5] which is the standard measure of elastomer toughness. The very large increases in [f^*] and f/A^* observed at the higher elongations are due to the limited extensibility of the short network chains.[1,9,10] This is consistent with the values, presented in Figure 5 and in

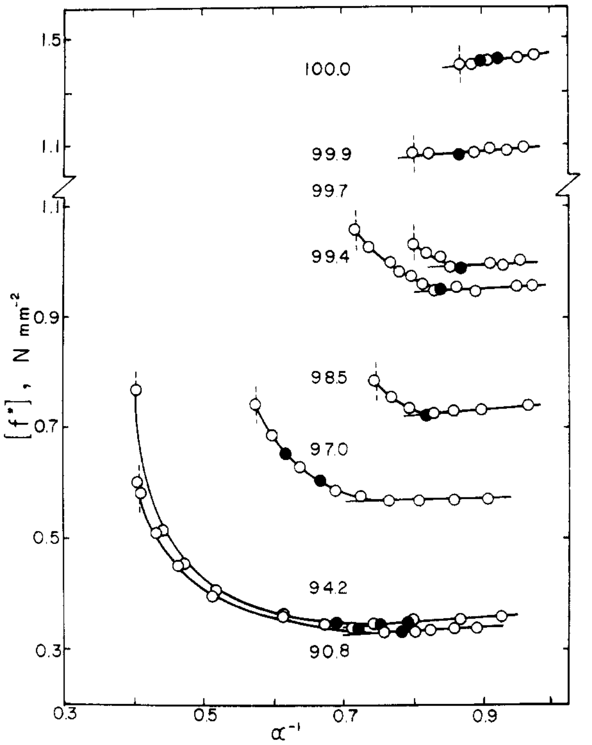

Figure 3. Stress–strain isotherms for the trifunctional networks prepared by using $PhSi(OC_2H_5)_3$; see legend to Figure 1.

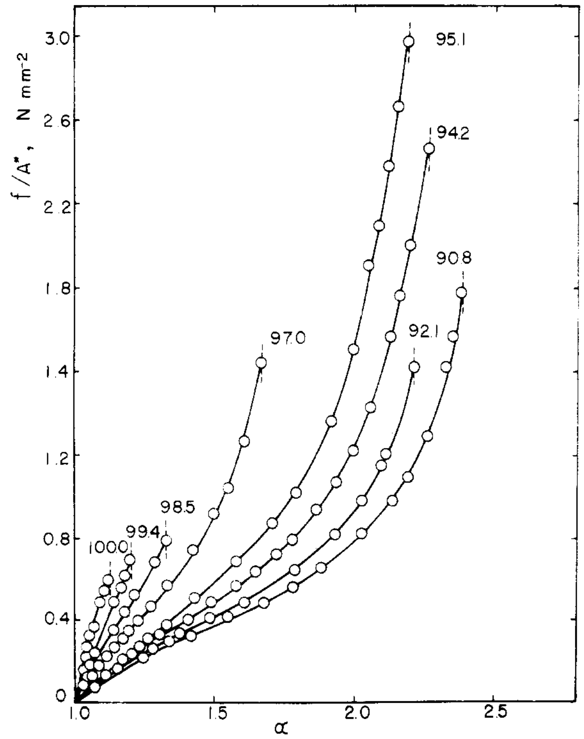

Figure 4. Illustrative results from Figure 1 plotted so that the area under each curve represents the energy E_r required for rupture.

column six of the table, of the elongation α_u at which the upturn in $[f^*]$ becomes discernible. The two series of networks prepared from $ViSi(OC_2H_5)_3$ and $PhSi(OC_2H_5)_3$ seemed to give equivalent results, as expected. Values of α_u should increase as the number of short chains is decreased and should be essentially independent of cross-link functionality ϕ. This is found to be the case.

Also, as demonstrated by the results in Figure 5 and column seven, the elongation α_r at rupture shows the expected increase with decrease in the mol % of short chains,

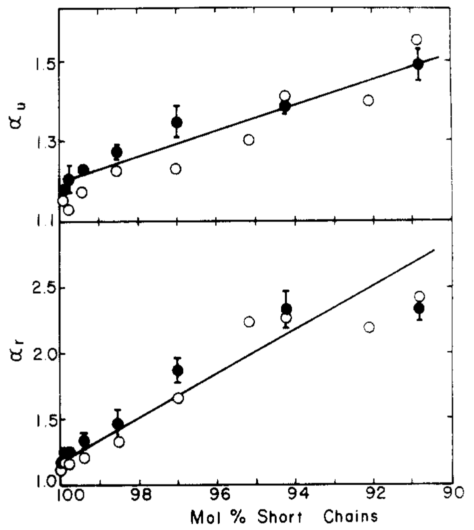

Figure 5. Effect of composition on the elongation at which the upturn in modulus becomes discernible and the elongation at rupture (maximum extensibility). The open circles locate results for the tetrafunctional networks and the filled ones the results for the trifunctional networks [averaged over the $ViSi(OC_2H_5)_3$ and $PhSi(OC_2H_5)_3$ series].

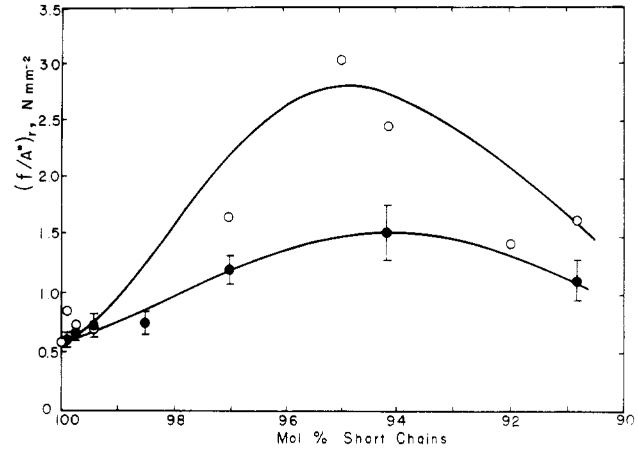

Figure 6. Effect of composition on the ultimate strength, as represented by the nominal stress at rupture; see legend to Figure 5.

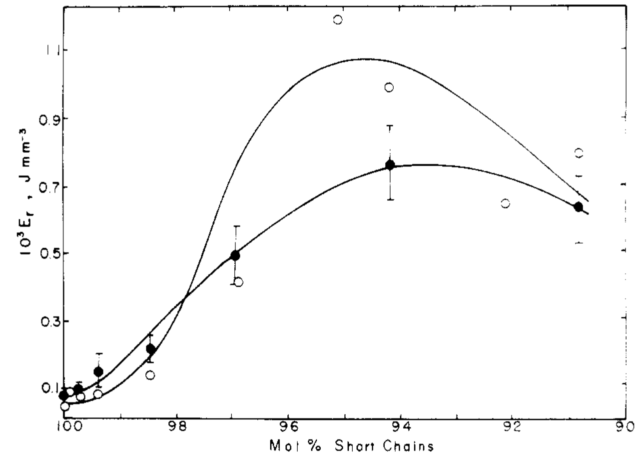

Figure 7. Effect of composition on the energy of rupture; see legend to Figure 5.

without any obvious dependence on ϕ. Values of the ultimate strength, as represented by the nominal stress $(f/A^*)_r$ at rupture, and the energy E_r required for rupture are given in the final two columns of Table I and are shown as a function of composition in Figures 6 and 7, respec-

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tively. The values of $(f/A^*)_r$, and thus also E_r, are somewhat higher for the tetrafunctional networks, which is consistent with the expectation that the stress should increase with increase in junction functionality. The larger the number of chains emanating from a junction, the more firmly embedded it is within the network structure, and this partially suppresses the fluctuations which diminish the stress.[11]

Both $(f/A^*)_r$ and E_r are seen to go through a maximum with decrease in the number of short chains. A composition of approximately 95 mol % short chains avoids excessive brittleness from having too few long chains and also having so many long chains as to preclude reinforcing effects from the limited extensibility of the short chains.[3] At this composition, which corresponds to 35–40 wt % short chains, the ultimate properties are apparently as high as can be achieved in an unfilled PDMS network.

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Synthesis of Polyacetylene Block/Graft Copolymers

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ABSTRACT: Graft/block copolymers of polyacetylene and polyisoprene or polystyrene have been prepared by intercepting a growing polyacetylene chain with a polymer-bound ketone or epoxide, thus forming a new carbon–carbon bond. The catalyst employed is a modification of the Shirakawa catalyst for acetylene polymerization. The molecular weight of the polyacetylene block was varied by changing the ratio of monomer to graft sites in the polymerization, thus generating a series of samples of increasing polyacetylene block lengths. These samples exhibit visible absorption spectra ranging from that characteristic of low molecular weight *trans*-polyenes to that of conventional *trans*-polyacetylene. Graft copolymers in which the polyacetylene block length is relatively long were shown in solution to form aggregates which appear to be amorphous. When longer block lengths were prepared, the polyacetylene blocks formed crystalline domains with a characteristic *trans*-polyacetylene structure. The graft copolymers contain unusually low spin densities (<1/300 000 polyacetylene C atoms). Addition of bromine to graft copolymer solutions initially results in the formation of a charge-transfer complex and subsequently bromination. The formation of these complexes could be partially reversed (compensated) by the addition of ammonia.

Conducting polymers have been the focus of considerable research in recent years due to their electrical and electronic properties.[1-4] Polyacetylene is the most widely studied of this class of polymers and serves as the prototype for other conducting polymers. In order to unravel the complicated problem of electrical conduction in the bulk material, it is first necessary to better understand the intrinsic electronic properties of polyacetylene. This requires the separation of intrachain properties from those induced by chain–chain interactions or defect sites. Unfortunately, such effects are complicated by the fact that polyacetylene is insoluble and decomposes prior to melting.

One solution to this problem has been to prepare random copolymers of acetylene with other acetylenic monomers,[5-7] which can yield a more tractable material. These copolymers not only exhibit inferior electrical properties but also are inadequate models for the electronic properties of polyacetylene due to their greatly altered chemical structure. An alternative approach to synthesizing random copolymers is to prepare a block copolymer from acetylene and a suitable comonomer. With this method, the integrity of the polyene chain is maintained, allowing studies of the electronic properties of individual polyacetylene chains. Block copolymers exhibit phase diagrams characterized by elevated critical points[8] and phase structures which are limited to a microregime (e.g., 10–10^3 Å).[9,10] Thus, block and graft copolymers potentially offer a method by which the intrinsic properties of polyacetylene can be retained in an experimentally tractable form.

The combination of a highly crystalline and inherently insoluble polymer (e.g., polyacetylene) with an amorphous, soluble polymer in the form of a block or graft copolymer should result in a spectrum of phase states which is strongly dependent on composition. When the polyacetylene segment represents a minor fraction of the polymer, the block copolymer solubility should be dictated by the solubility characteristics of the "carrier" block. In the limit of a low carrier polymer composition, the phase behavior of the composite should be similar to that of pure polyacetylene, which has been shown to form a fibrous

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