

Ultimate Properties of Filled Bimodal Networks Containing a Nonvolatile Diluent

Networks of poly(dimethylsiloxane) (PDMS) [$-\text{Si}(\text{CH}_3)_2\text{O}-$] are generally very weak in the unfilled state,^{1,2} because the low melting point (-40°C)³ of the polymer prevents reinforcement from strain-induced crystallization^{4,5} under most conditions. The ultimate properties of PDMS networks, however, were found to be considerably better in the case of a bimodal distribution of network chain lengths.^{6,7} The major effect is an upturn in the modulus at high elongation, thus resulting in relatively large values of the ultimate strength and energy required for rupture. The short chains are thought to increase the ultimate strength because of their limited extensibility, and the long chains to increase the maximum extensibility by retarding the growth of rupture nuclei.

Equally interesting is the observation⁸ that swelling such bimodal networks has a relatively small effect on the ultimate properties, which is, of course, consistent with the intramolecular interpretation mentioned above. If this retention of good ultimate properties also occurs upon swelling bimodal networks that are filled, this could also be of commercial importance through reduction in cost of an elastomeric material by incorporation of a relatively inexpensive nonvolatile diluent. The present investigation was carried out to explore this possibility.

EXPERIMENTAL

The three PDMS polymers employed had hydroxyl end groups. The first was unimodal with a number-average molecular weight corresponding to $10^{-3}M_n = 21.3 \text{ g} \cdot \text{mol}^{-1}$, and the second and third were (bimodal) mixtures of this polymer with a short-chain PDMS ($10^{-3}M_n = 0.860 \text{ g} \cdot \text{mol}^{-1}$), as described in the first column of Table I. The filler employed was a proprietary fume silica which had a surface area of $275 \text{ m}^2 \text{ g}^{-1}$ prior to being partially capped with $(\text{CH}_3)_3\text{SiO}-$ groups. It was mixed into each sample in amounts corresponding to 15 phr (parts per hundred parts of polymer, by weight). The end-linking agent⁷ employed was tetraethyl orthosilicate (TEOS) [$\text{Si}(\text{OC}_2\text{H}_5)_4$] having a purity in excess of 99%, according to gas-liquid chromatography (GLC). Since the presence of filler capable of reacting with the TEOS makes it very difficult to carry out the desired PDMS end-linking reaction stoichiometrically, a series of preliminary experiments were carried out to determine the optimal amounts of TEOS for network formation. These amounts, given in column two, exceeded the amounts required for stoichiometric equivalence with the hydroxyl ends of the three bimodal mixtures (0.0, 90.0, and 95.0 mol % short chains) by 35, 12, and 14 wt %, respectively.

One portion of each of the three samples was used without further treatment, but other portions were diluted with *n*-hexadecane (at least 99% pure according to GLC). The amounts employed are given in the third column of the table. Approximately 1% of the catalyst, dibutyltin diacetate, was mixed into each of the six samples. They were then centrifuged to remove bubbles and spatulated into glass molds. The molds were sealed for the first day of the 3-day room-temperature cure, the molds being open the rest of the time to permit escape of the ethanol appearing as byproduct in the end-linking reaction.⁷ No extractions were performed, and thus the designations U and S were applied to the unswollen networks and *n*-hexadecane-swollen networks, respectively.

Equilibrium stress-strain data were obtained on these six samples in elongation in the usual manner,^{9,10} at 25°C . The nominal stress was given by $f^* \equiv f/A^*$, where f is the elastic force and A^* the unelongated (but swollen) cross-sectional area, and the reduced stress or modulus⁹⁻¹² by $[f^*] \equiv f^*/(\alpha - \alpha^{-2})$, where $\alpha = L/L_0(\text{swollen})$ is the elongation or relative length of the sample. The dimensions of a typical test strip were $1 \times 3 \times 20 \text{ mm}$.

TABLE I
Compositions and Ultimate Properties of the Filled^a PDMS Networks

Mol %	Composition		Ultimate properties		
	phr Si(OC ₂ H ₅) ₄	phr <i>n</i> -hexadecane	f_r^* ^c (N mm ⁻²)	α_r^d	$10^3 E_r^e$ (J mm ⁻³)
0.0	0.638	0.0	1.01	4.83	2.96
	0.683	34.6	0.53	5.35	1.64
90.0	3.96	0.0	2.72	2.19	2.49
	4.00	35.5	1.36	2.19	1.03
95.0	6.16	0.0	2.96	1.80	1.64
	6.34	36.2	1.27	1.73	0.66

^a Fume silica, present to the extent 15 phr (parts per hundred parts of polymer, by weight).

^b $10^{-3}M_n = 0.860$ g mol⁻¹, mixed with long chains having $10^{-3}M_n = 21.3$ g mol⁻¹.

^c Ultimate strength, as represented by the nominal stress at rupture.

^d Maximum extensibility or elongation at rupture.

^e Energy required for rupture.

RESULTS AND DISCUSSION

The stress-strain isotherms obtained on the unswollen and swollen networks were first represented as plots of the modulus against reciprocal elongation, as suggested by the Mooney-Rivlin equation^{13,14}

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

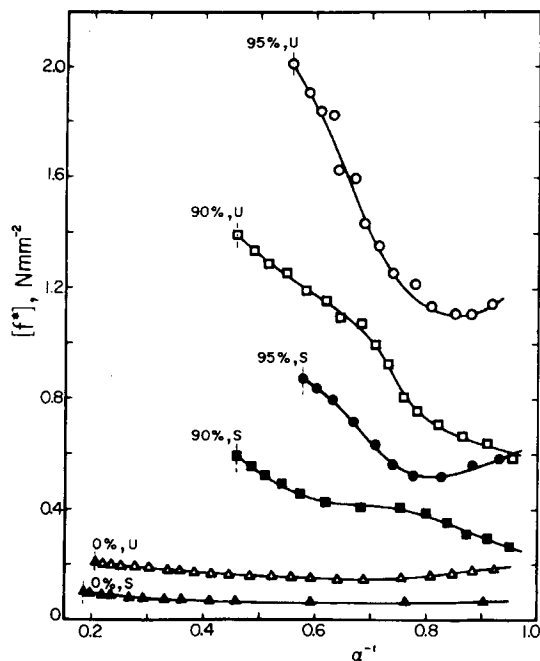


Fig. 1. The reduced stress or modulus shown as a function of reciprocal elongation at 25°C for the unswollen (U) and hexadecane-swollen (S) poly(dimethylsiloxane) networks. Each curve is identified with the mol % short chains ($10^{-3}M_n = 0.860$ g mol⁻¹) mixed with long chains ($10^{-3}M_n = 21.3$ g mol⁻¹), and the vertical dashed lines locate the rupture points.

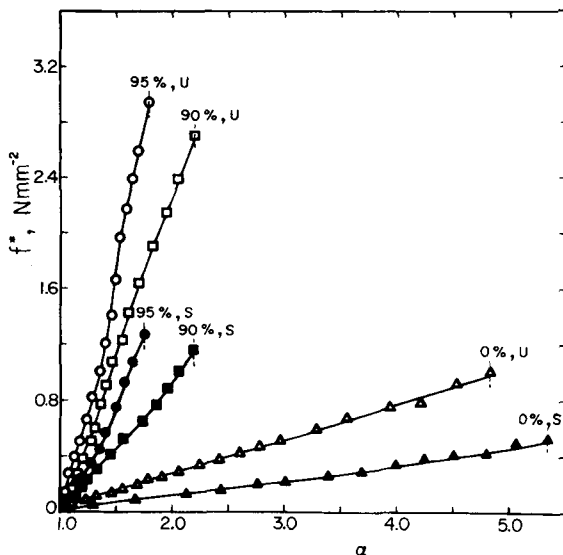


Fig. 2. The results of Figure 1 plotted so that the area under each curve corresponds to the energy E_r of rupture of the sample.

The results are shown in Figure 1. The values of the ultimate strength and maximum extensibility thus obtained are given in columns four and five of the table. Figure 2 shows 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,¹⁵ which is the standard measure of elastomer toughness. The specific values of E_r are given in the final column of the Table.

The values of the ultimate strength increase with fraction of short chains, as expected.⁷ Most relevant, however, is the observation that the bimodal filled networks show strong reinforcing upturns in the modulus and nominal stress even after swelling, whereas the unimodal networks do not, in either the unswollen or swollen states. Although the ultimate strength, maximum extensibility, and energy for rupture are decreased by the diluent, the swollen bimodal networks, nevertheless, are seen to retain excellent mechanical properties. They certainly do not have the fragility usually associated with highly swollen materials, and this could be highly advantageous in applications in which costs are of crucial importance or in which exposure to solvents is unavoidable.

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