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Morphology

Comparisons Between Poly(Dimethylsiloxane) Networks Filled with Particles of Poly(Dimethylsiloxane) Thermosets and Unfilled Bimodal Networks Prepared from the Same Components

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Summary

Very short, non-elastomeric chains of poly(dimethylsiloxane) (PDMS) were incorporated in samples of a long-chain PDMS elastomer in two ways: (i) end linking the short chains into a thermoset, cryoscopically grinding it into fine particles, and then mixing them into much longer PDMS chains which were then also end linked, and (ii) end linking mixtures of the short and long chains simultaneously. The short chains introduced by the first method do give some increases in ultimate strength, but these increases are more than offset by decreases in maximum extensibility and the resulting filled elastomers are very weak. On the other hand, end linking the short chains directly into the long-chain network gives much larger increases in ultimate strength and smaller decreases in maximum extensibility; as a result these bimodal elastomers are much tougher than the corresponding filled networks.

Introduction

In two earlier studies (1,2), attempts were made to form spatially heterogeneous bimodal networks by end linking very short and relatively long chains of poly(dimethylsiloxane) (PDMS) in a two-step reaction. Specifically, the short chains were partially prereacted and then mixed with the much longer chains for the second step in the curing process. Essentially, the goal was to achieve deformable filler particles. The ultimate properties of the networks were not significantly improved, however, but this could conceivably have been due to the segregation technique being only partially successful.

The present study carries these ideas to the extreme of totally prereacting the short chains into what is essentially a thermoset, and cryoscopically grinding it into fine particles which are then used to fill elastomeric PDMS networks. The ultimate properties of these filled networks are then compared with the properties of bimodal networks prepared using the same amounts of the same components.

Experimental Details

The polymers employed were hydroxyl-terminated PDMS chains, with the two samples of short chains having number-average molecular weights M_n of 220 and 660 g mol^{-1}, respectively, and the single sample of long chains having M_n = 21.3 x 10^3 g mol^{-1}. They were generously provided by the Dow Corning Corporation of Midland, MI.

Portions of each of the two short-chain samples were tetrafunctionally end linked using the stoichiometrically required amounts of tetraethylorthosilicate (TEOS) [$Si(OC_2H_5)_4$]. The reactions were run in the usual manner (3-5), with 1.6 wt % stannous-2-ethylhexanoate as catalyst. The resulting networks, which were nearly thermosets, were cryoscopically ground in a Janke & Kunkel model A-10S grinder with liquid nitrogen as coolant. Scanning electron microscopy indicated that the average diameter of the particles obtained was approximately 30 µm for both samples. The two types of particles were thoroughly mixed with portions of the long-chain PDMS to give the compositions listed in the two upper sections of column three in Table I.

Table I

Network Characteristics and Ultimate Properties

	Short Chains			Ultimate Properties		
Type of Network	$10^{-3}M_n$, g mol^{-1}	Wt %	v_{2C}	α_r	$(f/A^*)_r$, N mm^{-2}	10^3E_r, J mm^{-3}
Filled	220	0.0	0.963	3.15	0.311	0.403
		2.4	0.942	2.01	0.281	0.155
		4.0	0.940	2.08	0.308	0.178
		8.5	0.967	1.60	0.323	0.100
		16.4	0.969	1.56	0.354	0.101
		25.0	0.974	1.50	0.423	0.107
		37.0	0.963	1.42	0.413	0.090
		50.0	0.978	1.42	0.553	0.118
Filled	660	0.0	0.963	3.15	0.311	0.403
		4.4	0.946	1.97	0.248	0.108
		5.0	0.953	1.90	0.249	0.111
		6.7	0.979	1.77	0.283	0.110
		11.0	0.954	1.71	0.270	0.111
		23.3	0.960	1.77	0.405	0.139
		37.1	0.965	1.42	0.422	0.104
		50.0	0.978	1.45	0.541	0.108
Bimodal	660	0.0	0.963	3.15	0.311	0.403
		4.4	0.971	3.17	0.540	0.608
		6.7	0.970	3.24	0.890	0.885
		11.0	0.973	2.98	1.06	0.830
		23.3	0.948	2.42	1.64	0.769
		33.3	0.946	2.27	2.45	0.963
		37.1	0.947	2.34	3.19	1.17
		50.0	0.950	1.66	1.45	0.397

The mixtures were poured into glass molds approximately 1 mm deep, and were then briefly degassed. The long chains were then end linked as described above and the resulting networks exhaustively extracted and dried (3,4,6). The amounts of soluble material thus determined were used to calculate values of v_{2C}, the volume fraction of polymer successfully incorporated in the network. Values are given in column four of the Table; they are seen to be quite close to unity, as they typically are for this type of cross-linking reaction (3,4,6). They confirm the expectation that the filler particles are rather firmly bonded to the network chains.

Another series of samples, useful for purposes of comparison, consisted of bimodal networks prepared by directly adding short chains (660 g mol^{-1}) to the long chains and then end linking the mixture. The compositions employed were very close to those used for the filled networks; specific values and the corresponding values of v_{2C} are given in columns three and four, respectively, in the lower portion of the Table.

Strips having the approximate dimensions 1 mm x 3 mm x 30 mm were cut from each unswollen network sheet and then used in elongation experiments to obtain the stress-strain isotherms at 25°C (3-6). The elastomeric properties of primary interest are (i) the maximum extensibility or elongation at rupture, (ii) the ultimate strength, and (iii) the energy required for rupture.

Results and Discussion

Some typical isotherms obtained on the thermoset-filled networks are shown in Figure 1. The results are represented in the usual manner (7,8), as the reciprocal-elongation dependence of the reduced stress $[f^*] \equiv f/[A^*(\alpha - \alpha^{-2})]$, where f is the equilibrium value of the force, A^* is the undeformed cross-sectional area, and $\alpha = L/L_i$ is the elongation (where L and L_i are the stretched and unstretched sample lengths, respectively). The corresponding results for the bimodal networks are shown in Figure 2. An alternative representation, in which the areas under the curves correspond to the energy E_r of rupture are shown in Figures 3 and 4. The resulting values of the maximum extensibility α_r, the ultimate strength as represented by the nominal stress $(f/A^*)_r$ at rupture, and the rupture energy E_r are listed in the last three columns of the Table. As can be seen, there is essentially no difference between the two types of fillers.

As Figures 1 and 3 illustrate, addition of the thermoset filler particles does increase somewhat the ultimate strength of the networks, but at the expense of decreasing the maximum extensibility. Accordingly, E_r is small and the networks are weak. In the case of the corresponding bimodal networks, the values of the ultimate strength are much higher, because of upturns in f/A^* arising from the limited extensibility of the short chains. As a result, these networks are much tougher. Apparently, segregating the short chains into filler particles precludes this type of reinforcement; the alternative explanation of insufficient bonding of the filler particles to the network is contradicted by the observation (9) that irradiating the filled networks with γ radiation (which should

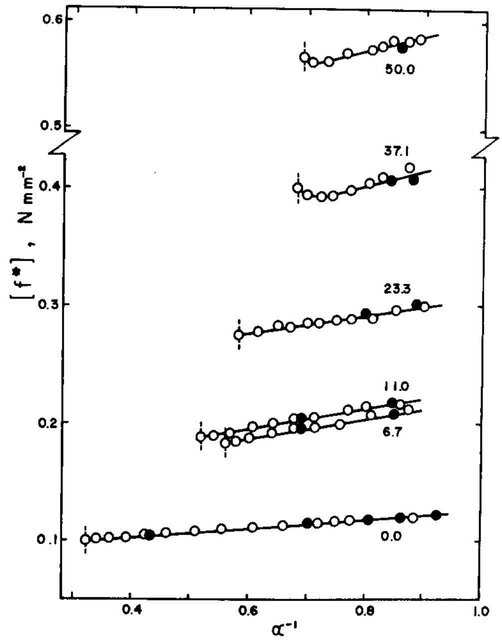

Figure 1. Stress-strain isotherms (25°C) for the networks containing filler prepared from short chains having a number-average molecular weight of 660 g mol^{-1}. Each curve is labelled with the wt % of filler present in the network. The open circles locate the results gotten using a series of increasing values of the elongation α, and filled circles the results obtained out of sequence to test for reversibility. The dashed vertical lines locate the rupture points of the networks.

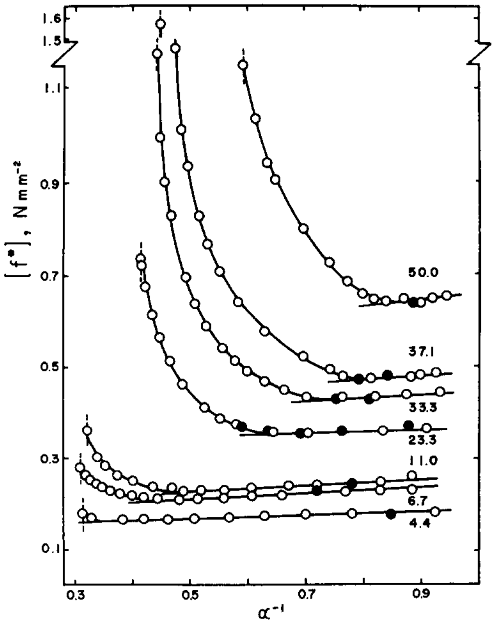

Figure 2. Stress-strain isotherms for the bimodal networks, each of which is identified by the wt % of the short chains (660 g mol^{-1}) present in the network. The short extensions of the linear portions of the isotherms help locate the values of α at which the upturn in $[f^*]$ first becomes discernible. The linear portions of the isotherms were located by least-squares analysis. See legend to Figure 1.

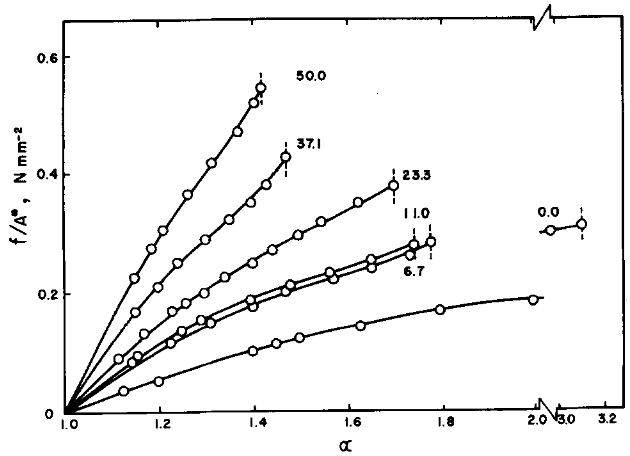

Figure 3. The results of Figure 1 represented so that the area under each curve corresponds to the energy required for rupture.

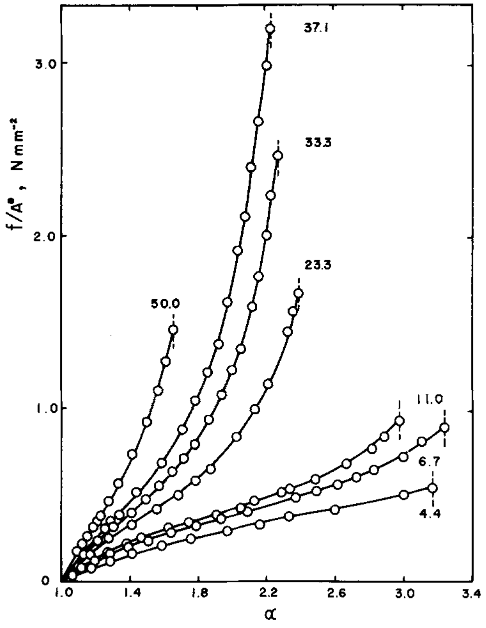

Figure 4. The results of Figure 2 represented so that the area under each curve corresponds to the rupture energy.

increase such bonding) has relatively little effect on their ultimate properties.

The present results thus demonstrate that short chains segregated into filler particles can not reinforce an elastomeric network the way they do when dispersed to give a true bimodal distribution of network chain lengths. This is of course consistent with the intramolecular nature of the reinforcing effect, namely the extremely limited extensibility of very short network chains (5,10).

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