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Elastomers

Treatment of Filler-Reinforced Silicone Elastomers to Maximize Increases in Ultimate Strength

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Summary

Model elastomers prepared by end linking poly(dimethylsiloxane) chains were filled in-situ by the ethylamine-catalyzed hydrolysis of tetraethylorthosilicate. The increases in modulus and ultimate strength obtained from the presence of filler were enhanced by a swelling-extraction treatment of the elastomers with tetrahydrofuran. The effect may be due to hydrolytic formation of additional particle surface silanol groups or removal of adsorbed small molecules, thereby increasing the number of sites for particle-polymer bonding.

Introduction

It has recently been demonstrated that it is possible to reinforce already cross-linked elastomers by the in-situ precipitation of silica particles generated in the hydrolysis of tetraethylorthosilicate (TEOS) [$Si(OC_2H_5)_4$] (1-10). The reactions are typically carried out with a TEOS-swollen network of poly(dimethylsiloxane) (PDMS) and yield essentially unagglomerated particles with diameters of 150-250 Å (7). The reinforcing effects of these fillers have been demonstrated by measurements of ultimate properties in elongation (1-5,8-10) and in impact tests (6).

The efficacy of any filler depends on the strength of the particle-elastomer interactions, which in turn depend on the number and types of groups on the particle surface. Silanol groups are thought to be particularly effective in this regard. Thus, it is of interest to try to hydrolyze any surface ethoxy groups occurring because of only partial hydrolysis of some of the TEOS. Similarly, it would be important to try to extract any adsorbed small molecules such as water, or the hydrolysis catalyst and byproduct, ethylamine and ethanol. The present investigation was carried out to ascertain whether it is in fact possible to obtain increased reinforcement in in-situ filled PDMS networks by means of an extended swelling-extraction technique.

Some Experimental Details

The PDMS network employed was prepared by tetrafunctionally end linking (11) vinyl-terminated chains which had a number-average molecular weight of 13.0 x 10^3 g mol^{-1}, and were obtained from the McGhan NuSil Corporation. Strips were cut from the network sheet and several were swelled in TEOS to the maximum extent attainable, which corresponded to a volume fraction of polymer of approximately 0.26. The swollen strips were then placed into a 2.0 wt % aqueous solution of ethylamine (2,10), and the hydrolysis permitted to occur at room temperature. Values of the wt % filler incorporated, obtained from the weights of the dried strips, are given in the first column of Table I. Portions of each strip were

TABLE I

Ultimate Properties of the Elastomers

Wt % filler	Elastomer treatment[a]	α_r[b]	f_r^*,[c] N mm^{-2}	$10^3 E_r$,[d] J mm^{-3}
0.0	--	3.07	0.293	0.372
33.0	--	2.93	0.92	0.866
	T	2.68	1.99	1.42
62.0	--	2.33	2.15	1.61
	T[e]	>1.77	>2.28	>0.99
63.0	--	1.81	2.30	1.14
	T	1.70	2.54	1.27

[a] T specifies treatment with THF at room temperature for two days.

[b] Elongation at rupture.

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

[d] Energy required for rupture.

[e] Premature rupture because of imperfection in strip.

then swelled at room temperature for two days in tetrahydrofuran (THF), chosen because it is a good, hydrogen-bonding solvent for PDMS. The strips were then dried under vacuum for ten hours; they were found to have lost only 0.8 - 1.4 % by weight.

Both untreated and THF-treated filled strips were used in elongation experiments to obtain the stress-strain isotherms at 25°C (12-15). An unfilled and untreated sample was included for purposes of comparison. The elastomeric properties of primary interest were 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 (15-18) $[f^*] \equiv f^*/(\alpha - \alpha^{-2})$ (where $\alpha = L/L_i$ is the elongation or relative length of the strip). All stress-strain isotherms were tested for reproducibility, with the measurements eventually carried out to the rupture points of the samples.

Results and Discussion

The stress-strain isotherms obtained as described above are presented in Figure 1. The data are shown in the usual way (16-18), as the dependence of the reduced stress on reciprocal elongation. As is frequently the case for filled elastomers, some of the isotherms did not exhibit complete reversibility, with repeat determinations giving values of the modulus lying below the previous values. 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 (13), which is the standard measure of elastomer toughness. Its values, along with values of the maximum extensibility α_r and ultimate strength f_r are given in the last three columns of the Table.

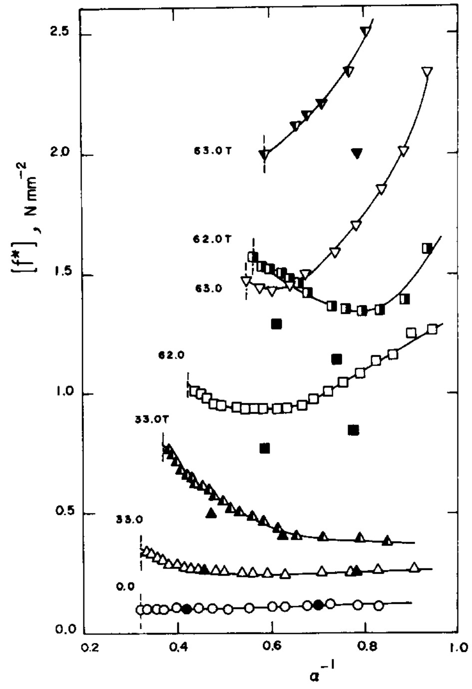

Figure 1. The reduced stress shown as a function of reciprocal elongation for the unfilled and filled PDMS networks at 25°C. The numbers correspond to the wt % filler in the network, and the letter T specifies treatment with THF. Filled symbols are for results obtained out of sequence to test for reversibility, and the vertical dashed lines locate the rupture points.

The in-situ filled but untreated networks are seen to be very superior to the unfilled network with regard to values of the modulus $[f^*]$ and ultimate strength f_r^*. This is, of course, at the expense of

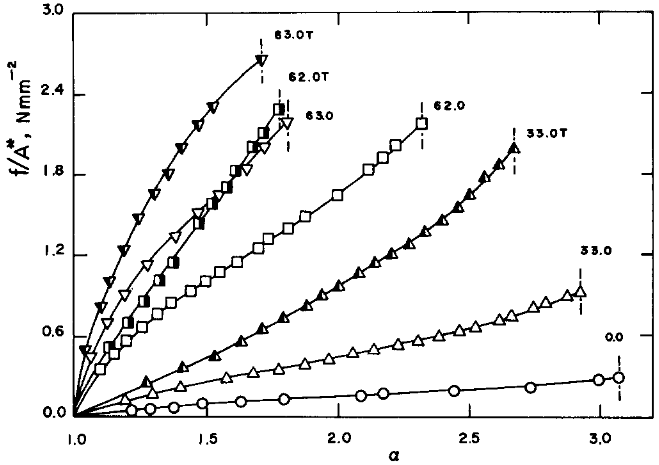

Figure 2. The nominal stress shown as a function of elongation for the same networks characterized in Fig. 1. In this representation, the area under each curve corresponds to the energy required for network rupture.

somewhat reduced values of the maximum extensibility. The subsequent THF swelling-extraction treatment of the filled elastomers is seen to give significant additional increases in $[f^*]$ and f_r^*. The technique thus clearly improves the particle-polymer bonding and could therefore be of practical as well as fundamental interest.

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