Comparisons among the reinforcing effects provided by various silica-based fillers in a siloxane elastomer

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(Received 9 May 1988; accepted 1 July 1988)

Filled networks of poly(dimethyl siloxane) (PDMS) were prepared using the following wide variety of materials and techniques: (1) incorporating a commercial silica which had been treated with hexamethyldisilazane; (2) incorporating 'wet-process' silica which had been precipitated from a silicate in an aqueous dispersion with PDMS; (3) precipitating silica directly into PDMS during its curing; (4) precipitating silica directly into a swollen PDMS network after it was cured; (5) incorporating silica prepared from tetraethoxysilane (TEOS) and containing some PDMS, and (6) incorporating silica prepared from partially hydrolysed TEOS and also containing some PDMS. The resulting filled elastomers showed the largest values of the ultimate strength in the case of methods (4) and (6), and the largest value of the rupture energy for method (4).

(Keywords: poly(dimethyl siloxane); fillers; siloxane elastomer)

INTRODUCTION

The usual way of 'filling' an elastomer in order to reinforce it involves blending finely divided carbon black or silica into high molecular weight polymer prior to curing[1-3]. In the case of the silica fillers, the surfaces are generally highly reactive and must usually be partially pre-reacted with a hydrophobic material to prevent premature gelation of the polymer. In any case, the techniques are relatively cumbersome, in part because of the high viscosities of the high molecular weight polymers typically employed.

A variety of alternative techniques and modified fillers have recently come under investigation. Some have the potential of simplifying the process, or improving reinforcement capability. For example, it may be possible to improve the bonding to a commercial filler by using hydroxyl-terminated PDMS and tetraethoxysilane (TEOS). As another example, 'wet-process hydrophobic' silica has been prepared by precipitating silica from a silicate in an aqueous dispersion with poly(dimethyl siloxane) (PDMS)[4]. The advantage here is the combination of the generation of the filler and the coating of it with a hydrophobic material. Even more novel is the precipitation of silica into a polymer prior to its curing, or into a swollen network after curing[5-8]. Finally, polymer-modified silica particles[9,10] can be prepared by simultaneously hydrolysing a mixture of TEOS and triethoxysilyl-terminated PDMS. These materials can be blended into hydroxyl-terminated PDMS, and then bonded to it using a condensation reaction. Similar fillers can be obtained using partially hydrolysed TEOS. One possible advantage of these fillers would be increased deformability resulting from the polymer they contain[11,12].

The purpose of the present investigation was to prepare such materials and to compare their reinforcing capabilities in networks of PDMS in a preliminary manner, using stress–strain measurements in elongation.

EXPERIMENTAL

Materials

Two samples of hydroxyl-terminated PDMS having a number-average molecular weight M_n of 1.70 and 18.0 × 10^3 g mol^{-1}, respectively, were obtained from Petrarch Systems of Bristol, PA. Two samples of vinyl-terminated PDMS having $M_n = 0.392$ and 17.3×10^3 g mol^{-1} were obtained from the McGhan NuSil Corporation of Carpinteria, CA.

Triethoxysilyl-terminated PDMS was prepared by reaction of the vinyl-terminated PDMS samples with a small excess of triethoxylsilane (Petrarch). Chloroplatinic acid was used as catalyst and the reactions were run in sealed flasks at 70°C for 24 h. Removal of unreacted triethoxylsilane under reduced pressure gave the desired polymers as colourless, viscous liquids. A small portion of each was characterized by standard chemical titration. The revised values of M_n were 0.720 and 17.6 × 10^3 g mol^{-1}, respectively.

TEOS and a sample of hexamethyldisilazane-treated commercial silica (SS 0216) were also obtained from Petrarch.

Incorporation of fillers

Commercial silica. Enough of the commercial silica sample described above was added to the high molecular weight hydroxyl-terminated PDMS to make up 20 wt % of the mixture. TEOS in an amount sufficient to react with all of the PDMS hydroxyl groups was then added, along with 1 wt % stannous-2-ethyl hexanoate as catalyst.

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0032-3861/89/010104-03$03.00

Table 1 Filler characteristics and network ultimate properties

Filler characteristics		Ultimate properties		
Type	Wt% introduced	f_r^* (N mm^{-2})	α_r	10^3E_r (J mm^{-3})
None	0.00	0.45	3.10	0.54
COMM[a]	20.00	0.38	1.48	0.10
WPH[b]	10.00	0.67	1.93	0.38
	20.00	0.72	1.83	0.36
ISPD[c]	8.50	0.45	2.20	0.27
ISPA[d]	19.20	1.32	2.25	0.85
PMT[e]	10.00	0.62	1.56	0.19
	20.00	0.98	1.59	0.30
PMHT[f]	20.00	1.01	1.43	0.25

[a] Commercial, surface-treated silica

[b] Wet-process hydrophobic silica

[c] *In situ* precipitated during curing

[d] *In situ* precipitated after curing

[e] Polymer-modified silica from TEOS (tetraethoxysilane)

[f] Polymer-modified silica from hydrolysed TEOS

The mixtures were poured into moulds to a height of 1 mm, and the reaction was permitted to proceed at room temperature for 3 days.

Wet-process hydrophobic silica. This material was made by first mixing the low molecular weight hydroxyl-terminated PDMS with appropriate amounts of ethanol, concentrated NH_4OH and water[4]. After 10 min of mixing, the desired amount of TEOS was added. Stirring was stopped when gelation started, and the resulting gel was aged at room temperature for 24 h. It was then blended into the high molecular weight hydroxyl-terminated PDMS at room temperature, and volatiles removed under vacuum at 80°C for 4 h. Stannous-2-ethyl hexanoate was again used as catalyst for the condensation reaction with the polymer, using the same reaction conditions as described above.

Silica precipitated in situ during curing. The high molecular weight PDMS was mixed with a 50-fold excess of TEOS, which serves simultaneously to tetrafunctionally end-link some of the chains and to act as a source of silica upon hydrolysis[5–8]. These reactions were run as already described, with the required water being absorbed simply from the humidity in the air. Volatiles were then removed under vacuum.

Silica precipitated in situ after curing. A PDMS network was first prepared by end linking the same high molecular weight chains with TEOS. The network was then swelled to the equilibrium extent with excess TEOS, and placed into water containing 2 wt% ethylamine as hydrolysis catalyst for 2 h[5–8]. It was then dried to constant weight.

Polymer-modified silica from TEOS. The short and long triethoxysilyl-terminated PDMS chains were added to TEOS to give a 17.8/2.2/80.0 wt% mixture. This bimodal mixture[5] was added to a water solution of NH_4OH and TEOS in which the molar ratio of NH_4OH to TEOS was 0.1 (ref. 10). The entire system was then held at 60°C, with agitation, and then allowed to further react at room temperature, without agitation. The resulting gel was mixed into the high molecular weight PDMS and the mixture dried under vacuum at 80°C for 4 h. Catalyst was then added and the condensation reaction carried out as described in the preceding sections.

Polymer-modified silica from hydrolysed TEOS. A sample of partially hydrolysed TEOS was prepared by reacting it with distilled water, in an isopropanol solution, in the presence of tetrahydrofuran (THF). Acetic acid was used as catalyst, and the reaction was carried out at 60°C, with agitation, for 2 h. The resulting material was washed with distilled water, and then dried to constant weight. It was then used to prepare PDMS-modified silica, as described above.

Extraction of soluble material

Each of the filled networks thus prepared was extracted in stirred THF for 3 days, at room temperature. They were then deswelled in a series of THF–methanol solutions of increasing methanol content, and then dried to constant weight. Suitable strips were then cut from the unswollen sheets for the elasticity parts of the experiments.

Stress–strain measurements

The stress–strain isotherms were obtained on these strips, at 25°C in the usual manner[13–15]. Measurements were made using a sequence of increasing values of the elongation or relative length of the sample $\alpha = L/L_i$, with frequent inclusions of values out of sequence to test for reversibility. Two elastomeric properties were of interest. The nominal stress was given by $f^* \equiv f/A^*$ (where f is the elastic force and A^* the undeformed cross-sectional area) and the reduced stress or modulus by $[f^*] \equiv f^*/(\alpha - \alpha^{-2})$[15,16]. The measurements were carried out to the rupture points of the samples.

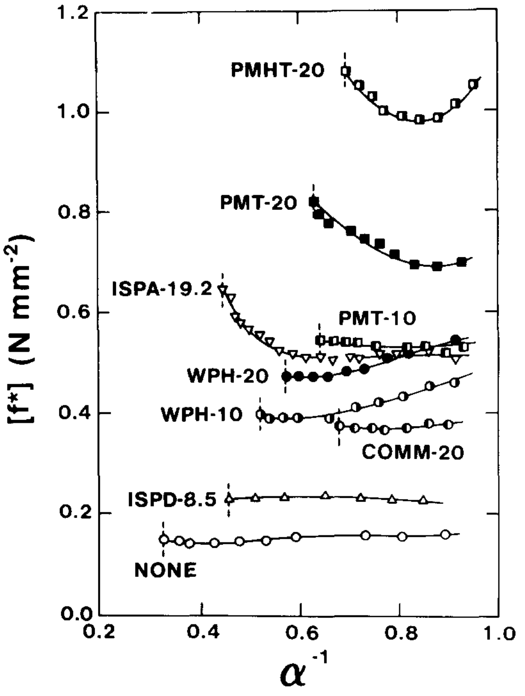

Figure 1 Reduced stress or modulus shown as a function of reciprocal elongation for the poly(dimethyl siloxane) networks at 25°C. The vertical broken lines locate the rupture points of the networks. Each curve is identified with its designation in *Table 1*, and with the wt% filler it contains

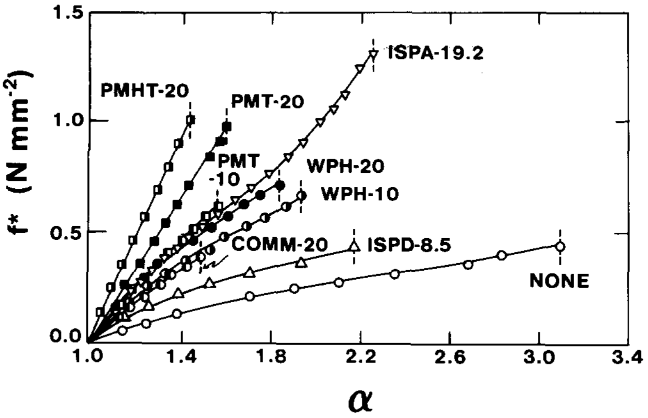

Figure 2 Results of *Figure 1* in the alternative representation of nominal stress against elongation. The area under each curve corresponds to the energy E_r required to rupture the network

RESULTS AND DISCUSSION

The wt% filler introduced into the various networks is given in *Table 1*. In the two cases involving polymer-modified silica, the values are based on the assumption that the reactions generating the filler went essentially to completion.

The first representation of the stress–strain results was in terms of the Mooney–Rivlin relationship[8,16,17]

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

where $2C_1$ and $2C_2$ are constants independent of elongation. These results are shown in *Figure 1*. The same results, but now in terms of the nominal stress as a function of elongation, are shown in *Figure 2*. The values of the ultimate strength (nominal stress f_r^* at rupture), and the maximum extensibility (elongation α_r at rupture) obtained from *Figure 2* are given in *Table 1*. The area under each of these curves corresponds to the energy E_r (ref. 18) required for rupture (see *Table 1*).

The average value of $[f^*]$ exhibited by a network is probably the most reliable estimate of its extent of reinforcement since values of the ultimate properties generally scatter considerably because of adventitious rupture. Even so, quantitative comparisons are difficult, particularly since commercial filled elastomers can be prepared by means not generally described in the literature. In any case, it can be seen that all of the filled elastomers studied have values of the modulus significantly higher than those of the reference, unfilled elastomer. Also, most of the new techniques and materials yield elastomers with moduli at least as large as those filled in the more customary manner. If the results are held to have at least semi-quantitative significance, then the elastomers having the largest values of the ultimate strength are those prepared by precipitating silica into the already-formed network and those containing polymer-modified silica prepared from partially hydrolysed TEOS. The one having the largest value of the rupture energy was that prepared by precipitating silica into the already formed network.

Although such comparisons are difficult, it would be very worthwhile to investigate further the variety of materials which can be used to reinforce elastomers.

ACKNOWLEDGEMENT

It is a pleasure to acknowledge the financial support provided by the Army Research Office through Grant DAAL03-86-K0032 (Materials Science Division).

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