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Reinforcing Effects from Silica-Type Fillers Containing Hydrocarbon Groups

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Summary

Curing hydroxyl-terminated chains of poly(dimethylsiloxane) is achieved by reacting them with tetraethoxysilane, vinyltriethoxysilane, methyltriethoxysilane, and phenyltriethoxysilane, with excess amounts of the silanes hydrolyzed in-situ to filler particles. When triethoxysilanes are used, the vinyl, methyl, and phenyl groups must be part of the filler particles and, in at least some cases, the resulting reinforcement is better than that given by the silica particles obtained from the (unsubstituted) tetraethoxysilane.

Introduction

In an earlier study (1), an attempt was made to obtain deformable filler particles by hydrolysis of mixtures of tetraethoxysilane (TEOS) with ethyltriethoxysilane and diethyldiethoxysilane. A sequential process was used, with vinyl-terminated chains of poly(dimethylsiloxane) (PDMS) first being end linked into a network structure, followed by its swelling in the silane mixture, and the hydrolysis of the silanes to give filler particles (1-14). The technique was not very successful in that the resulting filled networks did not have unusually good ultimate properties.

This approach is modified in the present investigation. Specifically, the silanes employed are TEOS, vinyltriethoxysilane (VTEOS), methyltriethoxysilane (MTEOS), and phenyltriethoxysilane (PTEOS), and the curing and in-situ precipitation are carried out simultaneously in an attempt to improve the bonding between the filler particles and the elastomeric matrix.

Experimental Details

The polymers employed, two hydroxyl-terminated PDMS samples having number-average molecular weights corresponding to $10^{-3}M_n = 18.0$ and 26.0 g mol^{-1}, respectively, were provided by Petrarch Systems Inc. Portions were mixed with TEOS, VTEOS, MTEOS, and PTEOS in amounts characterized by the molar feed ratio $r = [OC_2H_5]/[OH]$, where the $-OC_2H_5$ groups are on the silanes and the $-OH$ groups appear as chain ends on the PDMS. Specific values of this ratio, which range upward from 1.0 (stoichiometric

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** On leave from Yeungnam University, Daegu 632, Korea balance), are given in the third column of Table I. The catalyst employed, stannous-2-ethylhexanoate, was present in an amount corresponding to 1.0 wt % of the PDMS. Both series of mixtures of these components appeared to be perfectly homogeneous. They were poured into molds to a depth of 1 mm, and the reaction was allowed to proceed at room temperature for two days. The water required for the hydrolysis was simply absorbed from the humidity in the air.

Table I

Preparative Details and Properties of the Filled Networks

$10^{-3}M_n$,[a] g mol^{-1}	Silane	r[b]	Network Designation	Sol Fraction	ρ,[c] g cm^{-3}	Wt% Filler	α_r[d]	$(f/A^*)_r$,[e] N mm^{-2}	10^3E_r,[f] J mm^{-3}
18.0	TEOS	1	T-1	0.058	0.955	0.00	3.48	0.19	0.28
		50	T-50	0.042	0.976	4.42	2.20	0.45	0.61
		100	T-100	0.040	0.990	6.18	2.52	0.55	0.93
	VTEOS	50	V-50	0.036	0.973	4.21	2.85	0.55	1.1
		100	V-100	0.021	1.12	8.15	1.99	0.40	0.39
	MTEOS	50	M-50	0.032	0.961	3.45	2.71	0.79	1.46
		100	M-100	0.045	0.989	5.98	2.42	0.96	1.37
	PTEOS	50	P-50	0.030	0.962	3.54	1.89	0.71	0.69
		100	P-100	0.031	1.34	17.3	1.50	0.59	0.33
26.0	TEOS	1	T-1	0.082	0.955	0.00	3.60	0.17	0.32
		50	T-50	0.075	1.04	6.24	2.34	0.94	1.16
		100	T-100	0.070	1.29	13.8	2.90	1.23	1.94
	VTEOS	50	V-50	0.052	0.984	5.97	2.86	1.03	1.64
		100	V-100	0.049	1.12	7.93	2.86	1.20	2.01
	MTEOS	50	M-50	0.057	1.19	10.3	2.38	0.44	0.57
		100	M-100	0.051	1.23	12.9	2.17	0.45	0.65
	PTEOS	50	P-50	0.078	1.04	6.35	2.37	2.26	1.82
		100	P-100	0.071	1.23	12.7	2.46	3.02	2.51

[a] Molecular weight of the network chains.

[b] Feed ratio of OC_2H_5 groups on the silane to OH groups on the polymer.

[c] Density at room temperature.

[d] Elongation at rupture.

[e] Nominal stress at rupture.

[f] Energy required for rupture.

The resulting networks were extracted in tetrahydrofuran in the usual manner (15,16); the sol fractions thus obtained are small, as can be seen from the values given in column five of the table. The densities ρ of the extracted materials, determined by pycnometry, are reported in column six, and values of the wt % filler, determined from the increases in weight, are given in column seven.

Unswollen portions were used in the elongation experiments carried out to obtain the stress-strain isotherms at 25°C (15-17). 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 $[f^*] \equiv f^*/(\alpha - \alpha^{-2})$, where $\alpha = L/L_i$ is the elongation or relative length of the sample.

Results and Discussion

Typical stress-strain isotherms obtained for the networks having $M_n = 18.0 \times 10^3$ g mol^{-1} are shown in Figure 1, and some for $M_n = 26.0 \times 10^3$ g mol^{-1} in Figure 2. Values of the maximum extensibility or elongation

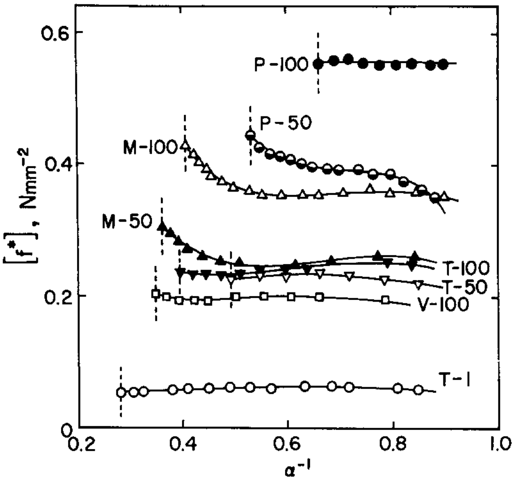

Figure 1. The reduced stress shown as a function of reciprocal elongation at 25°C for typical filled PDMS networks having $M_n = 18.0 \times 10^3$ g mol^{-1}. Each curve is identified by the designation given in column four of the Table, and the vertical dashed lines locate the rupture points.

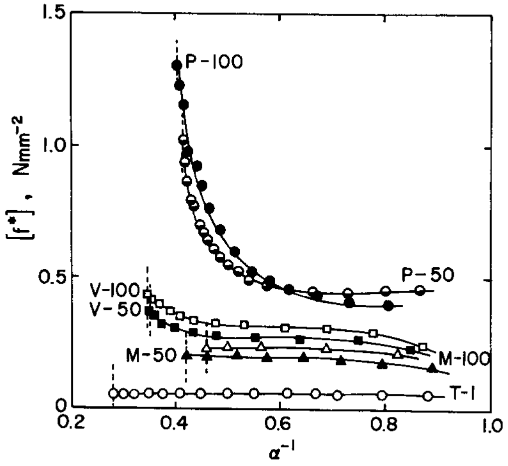

Figure 2. The reduced stress shown as a function of reciprocal elongation for the networks having $M_n = 26.0 \times 10^3$ g mol^{-1}.

at rupture obtained from all the curves of this type are given in column eight of the table. Similarly obtained values of the ultimate strength, as represented by the nominal stress at rupture, are given in the following column.

Figure 3 shows some of the data plotted in such a way that the area under each curve corresponds to the energy E_r required for rupture. Values are listed in the final column of the table.

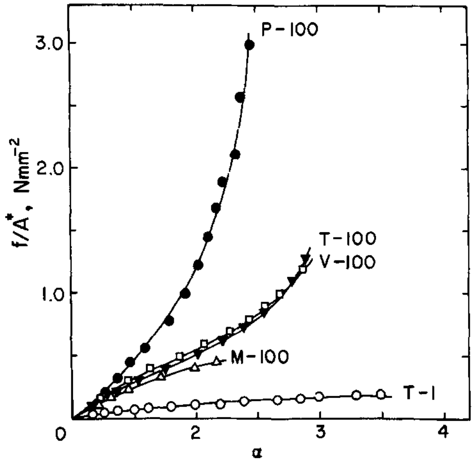

Figure 3. The nominal stress shown as a function of elongation for selected networks having $M_n = 26.0 \times 10^3$ g mol^{-1}.

There are seen to be large increases in modulus in general, and some large upturns in modulus at high elongations as well. The desired reinforcing effects (18) are thus clearly in evidence.

Of considerable interest is the observation that, at comparable wt % filler, the fillers containing vinyl, methyl, or phenyl groups frequently give better reinforcement than that given by the silica particles obtained from the TEOS. The PTEOS system seems particularly interesting in this regard. The improvements could be due to deformability of some of the filler particles. A definite conclusion, however, would require examination of stretched and quenched samples by electron microscopy, a very difficult but conceivably achievable goal.

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