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Some reinforcing characteristics of iron-based fillers

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SUMMARY

Thermolysis of iron carbonyl dissolved in poly(dimethylsiloxane) (PDMS) networks was found to greatly increase the modulus and toughness of the elastomers. Similarly good reinforcement was obtained in other PDMS networks filled with a ferrite, when it was coated with a silane, for example one of the coupling agents commonly used to improve adhesion in composites.

INTRODUCTION

Although carbon black and silica are by far the most commonly used fillers to reinforce elastomers (1-5), other finely-divided particles can also be used for this purpose. Metal and metal oxide particles are examples of particular interest since there is then the possibility of using a magnetic field to manipulate the particles, during curing in the case of an elastomer (6-8), or during solidification in the case of a thermoplastic (9). It has thus been possible to obtain materials having structures (9), and mechanical (6-8), thermal, and electrical properties (9) that are highly anisotropic, even when the particles are spherical. When fillers of any type are generated in-situ (8,10,11), there is the additional possible advantage that their bonding to the elastomeric matrix will be extraordinarily good. For example, iron particles generated by the thermolysis of iron carbonyl [$Fe(CO)_5$] within a matrix of poly(vinylidene fluoride) (a very stable thermoplastic) are apparently sufficiently reactive to abstract fluorine atoms from the polymer backbone (12). The achievement of such strong interactions in a filled elastomer should give unusually good reinforcement.

Incorporating already-formed iron-based fillers into an elastomer is also of interest (6,7). In this case, it would be of considerable importance to determine whether surface treatment (13) of such particles would improve particle-elastomer bonding and thus increase the desired reinforcement.

These two issues are addressed in a preliminary manner in the present study. First, $Fe(CO)_5$ is dissolved into a matrix of poly(dimethylsiloxane) (PDMS), and then thermolyzed in-situ. Second, particles of a ferrite (which can be considered a mixed metal oxide containing iron) are coated with a silane and then used as a filler in a PDMS

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elastomer. In both cases, the extent of reinforcement obtained is determined by means of stress-strain measurements in elongation.

EXPERIMENTAL DETAILS

Iron Carbonyl Thermolysis

The sample of PDMS employed consisted of hydroxyl-terminated chains having a number-average molecular weight of 2.6 x 10^4 g mol^{-1}. Liquid $Fe(CO)_5$ was filtered and then added to four portions of the PDMS sample. Initial concentrations were in the range 4-21 wt %. Thermolyses of the $Fe(CO)_5$ within the PDMS were carried out under nitrogen, at 150°C, for a period of 24 hrs. Values of the concentration of filler thus produced are given in the first column of Table I.

Table I

Ultimate Properties of the PDMS Networks Treated with Iron Carbonyl

Wt % filler[a]	α_r[b]	f_r^*,[c] N mm^{-2}	$10^3 E_r$,[d] J mm^{-3}
0.00	3.4	0.24	0.27
0.22	2.6	0.62	1.3
0.35	1.9	0.43	1.79
0.53	2.4	0.62	1.58
0.75	2.2	0.64	1.28

[a] Present in the network after thermolysis.

[b] Elongation at rupture.

[c] Nominal stress at rupture.

[d] Energy required for rupture.

The PDMS samples thus prepared were end linked using tetraethoxysilane (TEOS), in the usual manner (14), to give network sheets approximately 1 mm thick. Test strips cut from the sheet were approximately 4 mm wide and 50 mm long.

Ferrite Reinforcement

The ferrite employed was a "Magnoflux" sample obtained from the SCM Corporation, and had an average particle size of 10 μm. Three silanes were chosen to coat these particles; two are ones commonly used to improve adhesion in composites (13) and the third was TEOS. All were obtained from Petrarch Systems, Inc., and were used as received. The coating process was carried out in a 2 wt % solution of each silane in a 95/5 wt % solution of ethanol/water, the pH of which was adjusted to 4.5 -5.5 by addition of acetic acid. The desired amount of the ferrite was dipped into one of the solutions, agitated gently for 5 min., removed, rinsed twice with ethanol, and then dried in air (first at room temperature for 24 hrs. and finally at 60°C for 5 hrs.)

The particles thus coated were mixed into portions of the PDMS described above, which was then end linked with TEOS (14). The amounts of filler and the specific silanes used are described in the first two columns of Table II. The resulting network sheets, approximately 1 mm thick, were extracted with toluene and methanol. Test strips cut from the sheets were similar to those already described.

Table II

Ultimate Properties of the PDMS Networks Filled With a Silane-Coated Ferrite

Wt % Ferrite	Silane	α_r	f_r^*, N mm^{-2}	$10^3 E_r$, J mm^{-3}
0.0	--	3.4	0.24	0.27
5.0	--	2.0	0.14	0.20
5.0	MPES[a]	1.9	0.45	0.70
5.0	APMS[b]	2.0	0.48	0.86
5.0	TEOS[c]	2.2	0.53	1.0

[a] 3-Mercaptopropylethoxysilane.

[b] 3-Aminopropylmethoxylsilane.

[c] Tetraethoxylsilane.

Stress-Strain Measurements

Equilibrium stress-strain data were obtained in elongation in the usual manner (14), on the (unswollen) samples at 25°C. 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

Iron Carbonyl Thermolysis

The stress-strain isotherms for the PDMS samples reinforced using the $Fe(CO)_5$ treatment are shown in the Mooney-Rivlin representation (15) in Figure 1. Values of the elongation α_r at rupture (maxium extensibility) and nominal stress f_r^* at rupture (ultimate strength) obtained from these curves are given in columns two and three, respectively, of Table I. The same stress-strain results, shown as the elongation dependence of the nominal stress, are presented in Figure 2. Values of the energy E_r of rupture, a standard measure of toughness, are given in the final column of Table I. The degree of reinforcement, as judged by the substantial increases in f_r^* and E_r with relatively small decreases in α_r, is seen to be remarkably high for the amount of $Fe(CO)_5$

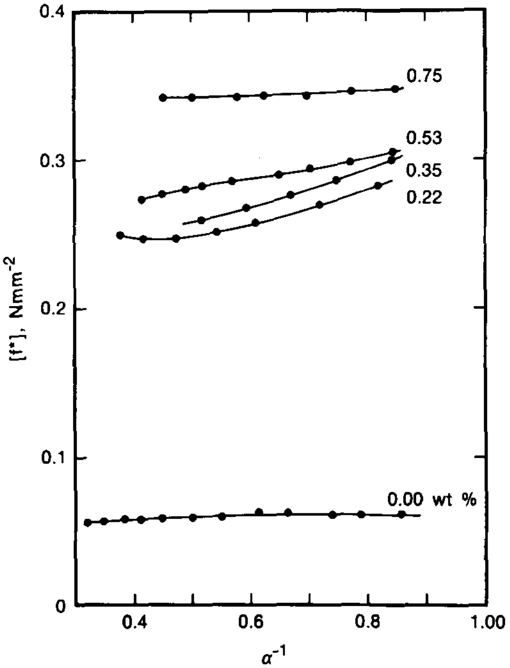

Figure 1. The reduced stress shown as a function of reciprocal elongation at 25°C for the (unswollen) PDMS samples treated with iron carbonyl. Each curve is labelled with the wt % filler present in the elastomer after the thermolysis reaction. See Table I.

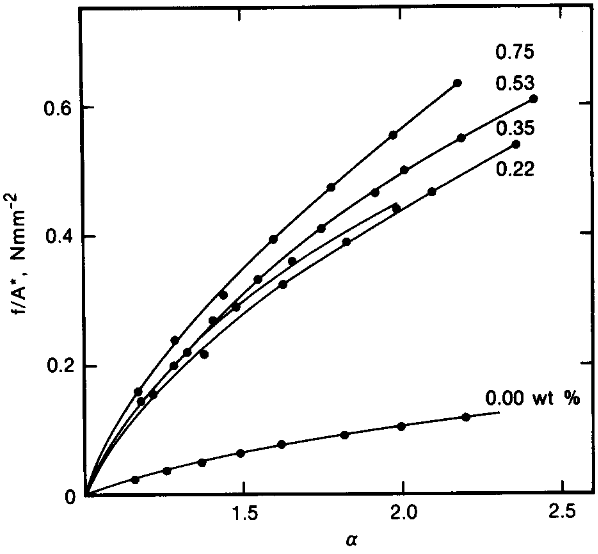

Figure 2. The results of Figure 1 plotted so that the area under each curve corresponds to the energy E_r required for rupture.

employed. Since the $Fe(CO)_5$ may decompose by a free-radical mechanism, the observed increases could be due to increases in (covalent) degree of cross linking as well as to the expected filler effect.

Ferrite Reinforcement

The Mooney-Rivlin representations (15) of the results obtained on the ferrite-filled PDMS elastomers are shown in Figure 3, and the values of α_r and f_r^* obtained therefrom are presented in columns three and four of Table II. The alternative representation of the results is given in Figure 4, and the corresponding values of E_r are presented in the final column of this table. The results show that very little reinforcement is obtained from the uncoated filler particles. All of the silanes, however, appear to be efficient at greatly increasing f_r^* so that even though α_r decreases somewhat, E_r increases substantially. Of the silanes studied, TEOS seems to be the most effective.

This technique, and the preceding one, for preparing novel fillers could be of considerable interest with regard to the reinforcement of elastomeric materials. Additional experiments to characterize such fillers and their effects on elastomers are in progress.

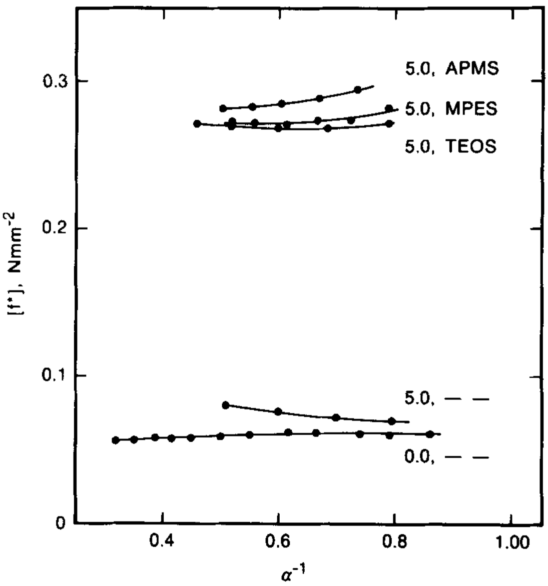

Figure 3. Reduced stress reciprocal-elongation curves for the PDMS elastomers filled with ferrite particles. The labels give the wt % ferrite present and specify the silane, if any, used to coat it. See Table II.

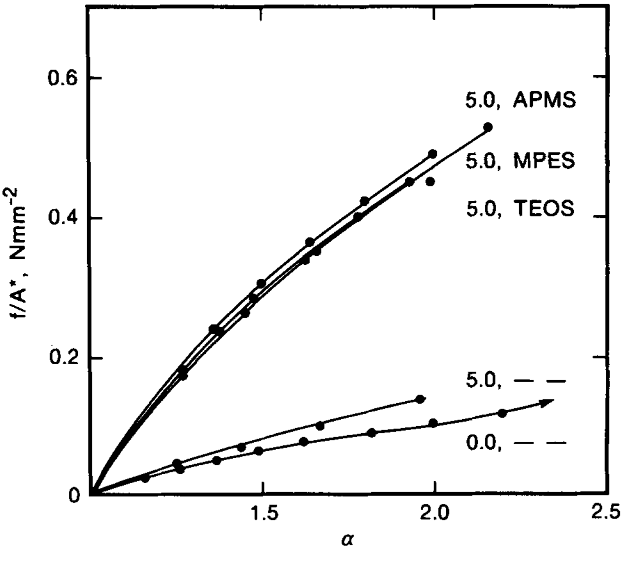

Figure 4. The results of Figure 2 plotted so that the area under each curve corresponds to the energy of rupture.

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