Anisotropic Reinforcement in Elastomers Containing Magnetic Filler Particles

G. B. SOHONI and J. E. MARK, *Department of Chemistry and the Polymer Research Center, The University of Cincinnati, Cincinnati, Ohio 45221*

Synopsis

Magnetic particles of iron oxide were blended into portions of a high molecular weight sample of poly(dimethylsiloxane) which were then peroxide cured in a magnetic field. Strips cut from the resulting elastomers parallel and perpendicular to the magnetic lines of force were studied with respect to their equilibrium swelling and their stress–strain isotherms in elongation. Both resistance to swelling (as measured by the volume fraction of polymer in the network) and the elongation modulus increased with increase in the amount of filler. They were also generaly larger in the direction parallel to the field, and the differences increased both with increase in the amount of filler and with increase in the strength of the magnetic field. Stress relaxation also increased with amount of filler and field strength, thus illustrating the importance of adsorption of the polymer onto the filler particles, and its subsequent desorption under stress.

INTRODUCTION

Most elastomeric materials are reinforced with hard mineral fillers to improve their mechanical properties.[1] Such fillers are typically introduced by mechanically blending them into the polymer, which is then cured using any of a variety of crosslinking techniques.[2] Although fibrous fillers are much used in thermoplastic and thermosetting composites,[3] they are seldom used in elastomers. Here the particles are typically spherical and even though they are generally agglomerated as prepared and as present in the cured elastomer,[1] the blending process yields an isotropically reinforced material.

A recent study,[4] however, demonstrated that even spherical particles can be used to achieve anisotropic reinforcement of an elastomer. The polymer was poly(dimethylsiloxane) (PDMS) [—$Si(CH_3)_2O$—], and the filler was a ferrite, which was manipulated in a magnetic field applied during the crosslinking process. The reinforcement obtained parallel to the magnetic lines of force was found to be significantly larger than that obtained perpendicularly. The present study extends this work by using asymmetric magnetic particles and by investigating how the anisotropy in mechanical properties depends on amount of filler and magnetic field strength.

EXPERIMENTAL

The polymer employed, PDMS having a number-average molecular weight of 3.0×10^5 g mol^{-1}, was generously provided by Dow Corning Corporation. The filler, cobalt surface-treated iron oxide (Pferrico 3070), had a specific magnetization of 76 emu/g, and was donated by Pfizer Pigments, Inc. The

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TABLE I
Preparative Details and Characteristics and Elastic Properties of the Networks

Wt% filler[a]	Magnetic field: Strength (Gauss)	Magnetic field: Orientation	Soluble fraction	Swelling equilibrium: v_{2m}^b	Swelling equilibrium: L/L_i	Elongation moduli[c]: $[f^*]_{1.5}$ (N mm^{-2})	Elongation moduli[c]: $[f^*]_r$ (N mm^{-2})	$10^3 E_r^d$ (J mm^{-3})
0.0	0	—	0.079	0.172	1.80	0.128	0.101	0.0250
30.0	0	—	0.072	0.198	1.73	0.130	0.107	0.0310
	300	∥	0.046	0.217	1.63	0.170	0.143	0.0350
		⊥	0.045	0.221	1.69	0.170	0.140	0.0320
	525	∥	0.039	0.250	1.56	0.231	0.205	0.0273
		⊥	0.036	0.257	1.58	0.221	0.185	0.0233
	1100	∥	0.037	0.267	1.48	0.283	0.276	0.0266
		⊥	0.036	0.264	1.63	0.196	0.165	0.0444
60.0	0	—	0.028	0.318	1.45	0.404	0.373	0.0423
	525	∥	0.029	0.320	1.38	0.454	0.479	0.0512
		⊥	0.029	0.337	1.48	0.396	0.419	0.0665
	1100	∥	0.030	0.349	1.33	0.540	0.615	0.0472
		⊥	0.028	0.338	1.51	0.366	0.362	0.0236

[a] Relative to the weight of polymer.
[b] Volume fraction of polymer present at swelling equilibrium in benzene at room temperature.
[c] Determined at an elongation α of 1.5 and at the rupture point.
[d] Energy required for rupture.

particles were asymmetric with an average length of 0.35 μm and an acicularity ratio of 6:1.

A solution of the PDMS in ethyl-acetate was prepared and Pferrico 3070 amounting to 30 and 60 wt% of the polymer was mixed into two portions of it, along with a suitable amount (1.3 wt%) of benzoyl peroxide. Both mixtures were poured into shallow trays, allowed to dry in air, and finally subjected to vacuum to remove all solvent. The mastics obtained were then repeatedly squeezed through a roll mill to ensure homogeneous distribution of the filler and peroxide within the two samples. Portions of both were then placed into Teflon-lines aluminum molds, and crosslinked in a press at 120°C for one hour. The entire cure took place in a magnetic field. Field strengths of 300 and 525 G were obtained using Alnico permanent magnets, while a 1,100 G field was obtained from an electromagnet. No postcuring treatment was given any of the samples.

A number of sheets using different amounts of filler and field strengths were thus prepared. Specific values are given in the first two columns of Table I. The densities of the PDMS, Pferrico filler, and 30 and 60 wt% filled elastomers were 0.95, 4.75, 1.17, and 1.36 g cm^{-3}, respectively. Thus, 30.0 and 60.0% filler by weight correspond to 6.00 and 12.0% by volume, respectively. The values of the wt% filler relative to the total weight of sample were 23.1 and 37.5, respectively; the corresponding values of the volume percent were 5.66 and 10.7, respectively.

The cured sheets were allowed to relax for 7 days, after which rectangular strips were cut from them parallel and perpendicular to the direction of the magnetic field. Some of these were extracted in benzene in the usual manner[5] to determine soluble fractions. Swelling equilibrium measurements in benzene at room temperature were also carried out, using portions of the extracted

samples. Other (unextracted and unswollen) portions were used in elongation experiments carried out to obtain stress–strain isotherms at 25°C, as described elsewhere.[5-7] Preliminary stress measurements showed considerable relaxation under tension, especially in the case of the higher concentration of filler. Therefore, the force f was read after 10 min for the 30 wt% filled samples and after 30 min for the samples with 60 wt%. In some cases, values of f were recorded as a function of time in order to characterize the stress relaxation.

There are two elastomeric properties of interest. The nominal stress is given by $f^* = f/A^*$, where A^* is the undeformed cross-sectional area, and the reduced stress or modulus[8] $[f^*] = f^*/(\alpha - \alpha^{-2})$, where $\alpha = L/L_i$ is the elongation or relative length of the sample.

RESULTS AND DISCUSSION

The values of the soluble fraction obtained from the extractions are given in Table I. It is interesting to note that the amount of extracted polymer

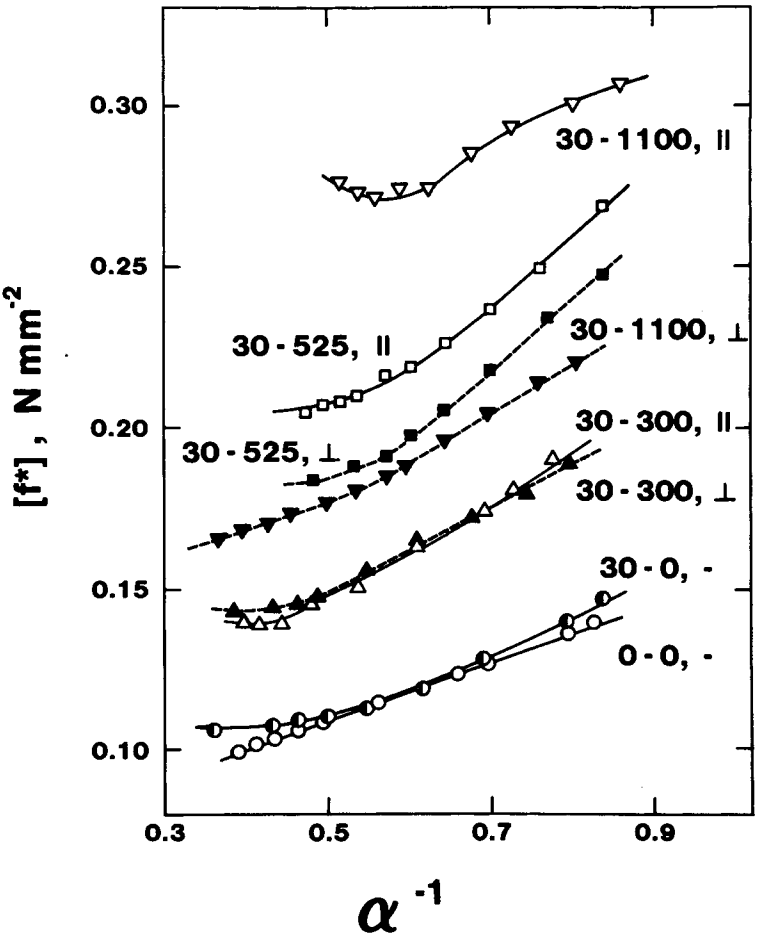

Fig. 1. Stress–strain isotherms in elongation at 25°C for the lightly filled poly(dimethylsiloxane) elastomers. In this and the following two figures, each curve is identified by the wt% of filler present, the strength of the magnetic field in Gauss, and the orientation (parallel or perpendicular) of the sample strip relative to the lines of force of the magnetic field.

decreases sharply from 7.9 wt% for the unfilled polymer to 2.8 wt% for polymer loaded with 60 wt% filler. This of course confirms physisorption of some of the polymer chains onto the filler surface, thus preventing them from being extracted by the solvent. Moreover, as expected, the soluble fraction decreases with increase in filler concentration.

The swelling equilibrium results are given in terms of the volume fraction v_{2m} of polymer in the swollen network. The values, given in Table I, show that the resistance to swelling increased with an increase in concentration of filler and with increase in field strength. Apparently, movement of the particles by interaction with the magnetic field aids slightly in the sorption process. The swelling is anisotropic in the case of the filled elastomers cured in the magnetic field. The anisotropy can be characterized by the swelling-induced increases L/L_i in length of the sample parallel and perpendicular to the field, which are given in Table I. The resistance to swelling is larger parallel to the field, which is the opposite of that shown by some very limited measurements[4] using magnetic manipulation of spherical filler particles. Earlier experiments

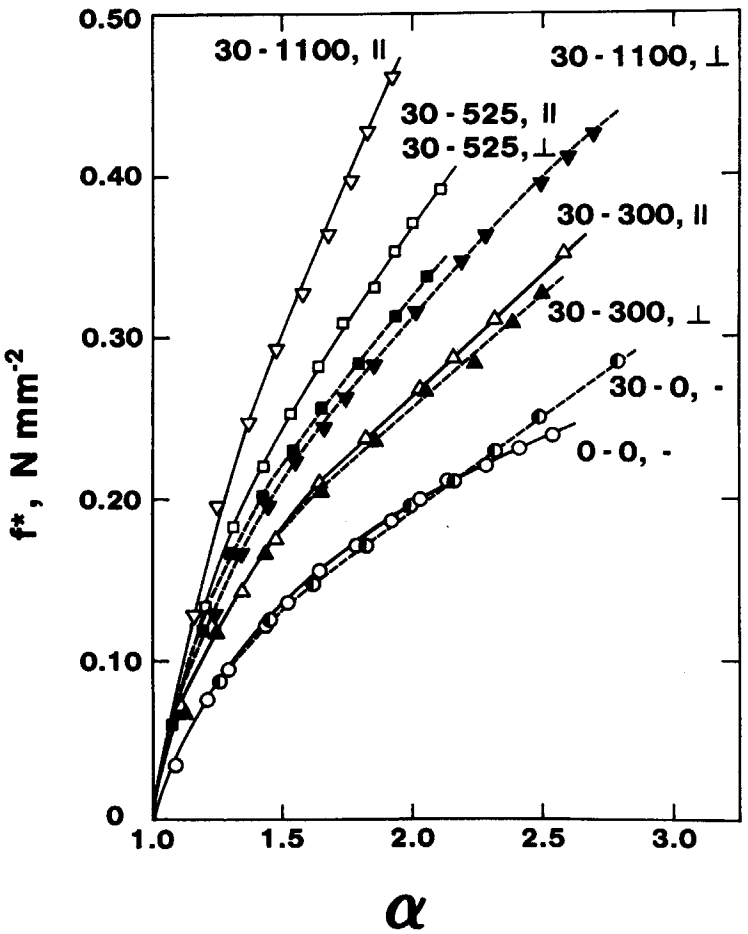

Fig. 2. The data of Figure 1 so represented that the area under each curve corresponds to the energy E_r required to rupture the network.

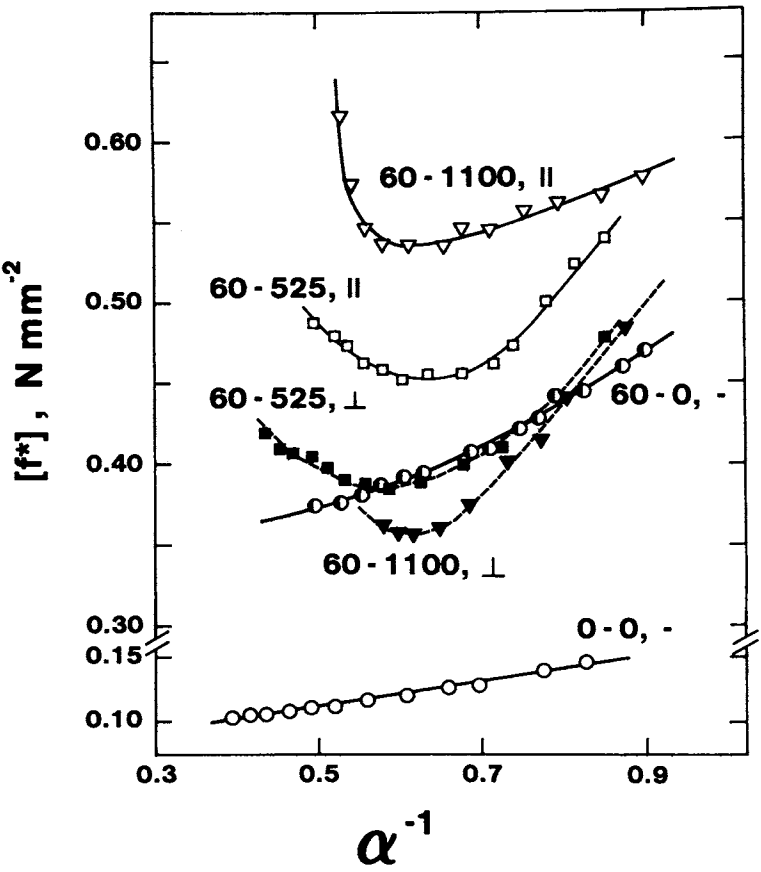

Fig. 3. Stress–strain isotherms for the more heavily filled networks.

would have to be repeated in greater detail to determine whether or not this difference is significant.

The stress–strain isotherms obtained on the unfilled network, and on the filled networks cured in the absence and presence of the magnetic field are shown in Figures 1 to 3. Figure 1 includes the results on the samples containing 30 wt% filler, in the Mooney-Rivlin representation[9-11]

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

where $2C_1$ and $2C_2$ are constants. The same data are shown in an alternative plot of nominal stress against elongation in Figure 2. The advantage of this type of display is the fact that the area under each curve corresponds to the energy E_r required for rupture, and this is a standard measure of toughness. Figure 3 includes the results on the networks containing 60 wt% filler, in the Mooney-Rivlin representation.

Isotherms were first obtained for strips cut in different directions from the two filled elastomers which were crosslinked in the absence of the field. Such strips cut from the same elastomer were found to be identical. This indicates that the geometric asymmetry of the particle alone was insufficient to induce any detectable anisotropy in the mechanical properties.

As shown in Figures 1-3, increase in filler content causes a significant increase in modulus. Specific values of $[f^*]$ at an elongation of 1.5 are given in Table I. The upturns in $[f^*]$ at high elongations are relatively small at the lower filler concentrations, and are very pronounced at the higher concentrations. The desired reinforcing effect is thus clearly in evidence.[12,13]

These three figures and the tabulated values of $[f^*]$ at $\alpha = 1.5$ also demonstrate the anisotropy achieved by use of the magnetic field. The values of $[f^*]$ and f^* (and thus the reinforcement) obtained parallel to the field are larger than those obtained perpendicular. This is consistent with the nature of the anisotropy observed in the swelling results. Furthermore, the differences generally increase with increase in the amount of filler and with increase in field strength. It is also interesting to note that for the elastomers containing 30 wt% filler, the reinforcement in both directions is larger than that obtained in the absence of the field. In any case, the differences in $[f^*]$ are as large as 50%.

The values of the modulus at rupture and the energy required for rupture, given in Table I, characterize the ultimate properties of the elastomers. The

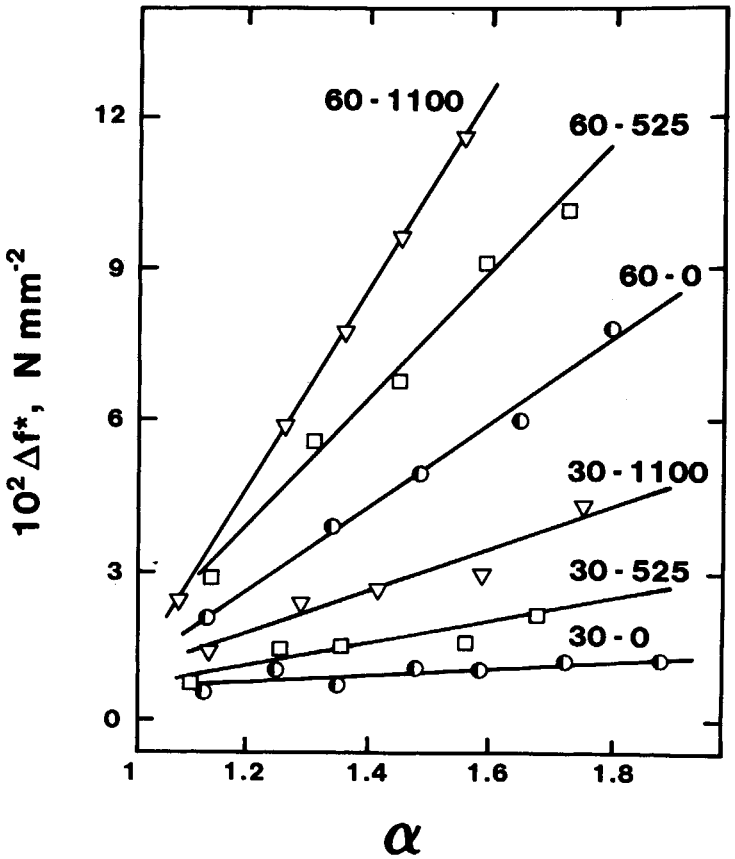

Fig. 4. The dependence of stress relaxation on elongation and the constitution of the elastomers, for strips cut parallel to the magnetic field. Each curve is labelled by the wt% of filler present and the strength of the magnetic field.

results show that the main advantage of the fillers is the marked increases in modulus; since the extensibility is generally decreased by the presence of the filler, E_r and the toughness are not necessarily increased.

Stress relaxation was characterized by the difference Δf^* between the value of the nominal stress immediately after the deformation and that close to elastic equilibrium. Figure 4 shows this quantity as a function of elongation for some of the samples cut parallel to the field. The most important observation is the increase in Δf^* with increase in filler content and with field strength. It illustrates the importance of the adsorption of the polymer chains onto the filler surface, and their partial desorption in response to the imposed stresses.

Additional experiments using other types of magnetic fillers are in progress.

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