

# Reinforcement of elastomeric poly(dimethylsiloxane) by glassy poly(diphenylsiloxane)

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Some novel approaches were taken to provide the improvements in mechanical properties that are almost always necessary to prepare a commercially useful elastomer from poly(dimethylsiloxane) (PDMS)  $[-\text{Si}(\text{CH}_3)_2\text{O}-]$ . The reinforcement was provided by poly(diphenylsiloxane) (PDPS)  $[-\text{Si}(\text{C}_6\text{H}_5)_2\text{O}-]$ , a hard glassy polymer, which was introduced into the PDMS by two rather different techniques. In the first, the PDPS was prepared separately by condensation polymerization of diphenylsilanediol and then solution-blended into the PDMS. In the second, it was generated by *in situ* polymerization of the same monomer absorbed into the PDMS network. The resulting materials were characterized by scanning electron microscopy and by stress-strain isotherms in elongation. At least under some conditions both techniques were found to be successful, leading to increases in ultimate strength by a factor of two or more.

## 1. Introduction

One unusual way of reinforcing an elastomer is to polymerize within it a monomer that will produce a polymer that is relatively hard, either because of its glassiness or partial crystallinity. The result of this *in situ* polymerization can be thought of as either a novel filled elastomer [1-10], or a semi-interpenetrating network (IPN) [11, 12]. Specific examples are the *in situ* polymerization of styrene within networks of poly(dimethylsiloxane) (PDMS)  $[-\text{Si}(\text{CH}_3)_2\text{O}-]$  [13] or polyisobutylene  $[-\text{C}(\text{CH}_3)_2\text{CH}_2-]$  [14]. The polystyrene thus introduced was found to give considerable reinforcement. It has the disadvantage, however, of having a relatively low glass transition temperature  $T_g$  ( $\sim 100^\circ\text{C}$ ) [15], above which it would soften and presumably lose its reinforcing capability.

An attractive alternative is poly(diphenylsiloxane) (PDPS)  $[-\text{Si}(\text{C}_6\text{H}_5)_2\text{O}-]$  [16, 17], which, for a polysiloxane, has a relatively high value of  $T_g$  ( $49^\circ\text{C}$ ) [17], at least one liquid-crystalline transition temperature, and an extraordinarily high melting point ( $550^\circ\text{C}$ ) [17]. The present investigation was therefore undertaken to determine the extent of reinforcement provided by PDPS in PDMS networks, particularly when the PDPS is introduced by means of *in situ* polymerizations.

## 2. Experimental details

### 2.1. Preparation of PDMS networks

The PDMS sample employed was hydroxyl-terminated, had a number-average molecular weight  $M_n$  of  $18.0 \times 10^3 \text{ g mol}^{-1}$ , and was obtained from the Petrarch Systems Co. One sample of PDPS was also obtained

from Petrarch as an already-polymerized commercial material having an  $M_n$  of approximately  $1.2 \times 10^3 \text{ g mol}^{-1}$ . In some cases the PDMS was used in the pure state, and in others it was first solution-blended with either the commercial sample of PDPS or with PDPS synthesized as described in the following section. For the solution blending, tetrahydrofuran (THF) and chlorobenzene were used as solvents. In either case the PDMS was end-linked with tetraethoxysilane (Petrarch) in the absence of solvent, in the usual manner [18], using stannous 2-ethyl hexanoate obtained from the Sigma Chemical Co. as catalyst. The networks were extracted with toluene for four days, and the amount of soluble material thus determined was found to be approximately 8 wt %. The resulting sheets were cut into samples suitable for electron microscopy and stress-strain measurements in elongation. For reference purposes, one network strip was not given any further treatment, and another was simply swelled with monomer.

### 2.2. Preparation of PDPS

The monomer, diphenylsilanediol  $[\text{Si}(\text{C}_6\text{H}_5)_2(\text{OH})_2]$ , was also obtained from the Petrarch Systems Co. 65 parts of it were blended into 20 parts of THF as solvent, and 1 part of stannous 2-ethyl hexanoate as catalyst. The THF was then removed under reduced pressure; for one portion the temperature for this drying step was  $25^\circ\text{C}$ , and for the other  $95^\circ\text{C}$ . Thereafter, both samples were heated to  $150^\circ\text{C}$  for 40 h, extracted with boiling toluene, dissolved and recrystallized from boiling chlorobenzene, and then finally

TABLE I Compositions and ultimate properties of the poly(dimethylsiloxane) networks

Filler			Ultimate properties		
Type	Introduction	Concentration (wt %)	$(f/A^*)_r$ ( $\text{N mm}^{-2}$ )	$\alpha_r$	$10^3 E_r$ ( $\text{J mm}^{-3}$ )
None	–	0.00	0.25	2.7	0.243
DPS*	Swelling	26.8	0.12	1.9	0.0615
Comm PDPS*	Blending, 25°C†	24.4	0.21	3.1	0.261
PDPS	Blending, 25°C	26.8	0.39	1.9	0.188
	Blending, 95°C	29.6	0.10	1.8	0.0392
PDPS	<i>In situ</i> polymerization	6.50	0.23	1.7	0.0882
		17.0	0.29	2.0	0.168
		21.0	0.37	1.4	0.0802
		31.0	0.63	1.4	0.151

\*DPS is the monomer diphenylsilanediol, and PDPS is the corresponding polymer poly(diphenylsiloxane).

†Solution blending, followed by drying at the specified temperature.

held at 200°C for 24 h under reduced pressure [19]. Since the material obtained using the first drying procedure seemed to have a higher molecular weight, it was characterized using a Knauer vapour pressure osmometer. Its value of  $M_n$  was thus found to be  $5.5 \times 10^3 \text{ g mol}^{-1}$ . Both samples were solution-blended into PDMS samples, as described in the preceding section.

### 2.3. *In situ* polymerization of PDPS

Monomer and catalyst in the 65:1 ratio mentioned above were dissolved in various amounts of THF. PDMS network strips not filled by the solution-blending technique were then swelled in one of these solutions. A decrease in THF concentration was found to cause a decrease in the extent of swelling, and this causes the amount of monomer introduced in this way to reach a maximum at around 30 wt %. The THF in the swollen strips was removed by drying at 25°C, and the diphenylsilanediol then polymerized *in situ* as described in the preceding section [19].

The compositions of the network samples prepared by all of these techniques are given in the third column of Table I.

### 2.4. Extraction measurements

The strips of filled PDMS were extracted using toluene at room temperature for seven days. They were then

deswollen in methanol and dried, first in air and then under reduced pressure. Values of the percentage of soluble material were calculated from changes in the dry weights of the samples. In those cases where only a small fraction of the PDPS was removed, additional extractions were carried out for three days using chlorobenzene, first at 130°C and then at 80°C.

### 2.5. Scanning electron microscopy (SEM)

Some of the filled networks were fractured under liquid nitrogen and the parts mounted in suitable sample holders as to display their cross-sectional regions. They were then coated with gold and examined with a Cambridge Stereoscan 600 scanning electron microscope at a magnification of  $10^3$  to  $10^4$ .

### 2.6. Stress–strain measurements

Equilibrium stress–strain data in elongation at 25°C were obtained on the samples in the usual manner [18, 20]. The nominal stress was given by  $f^* \equiv f/A^*$ , where  $f$  is the elastic force and  $A^*$  the cross-sectional area of the undeformed sample, 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 [20–23].

## 3. Results and discussion

The PDPS which had been introduced by solution

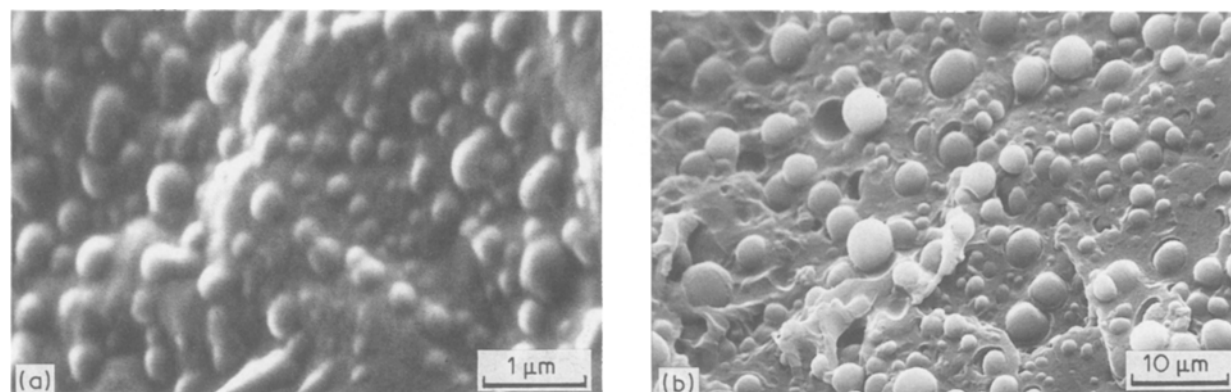


Figure 1 Scanning electron microscopy results for two of the filled poly(dimethylsiloxane) (PDMS) networks. (a) Network filled by solution-blending into it 24.4 wt % of commercial poly(diphenylsiloxane) (PDPS). (b) Network in which 31.0 wt % PDPS was introduced by *in situ* polymerization.

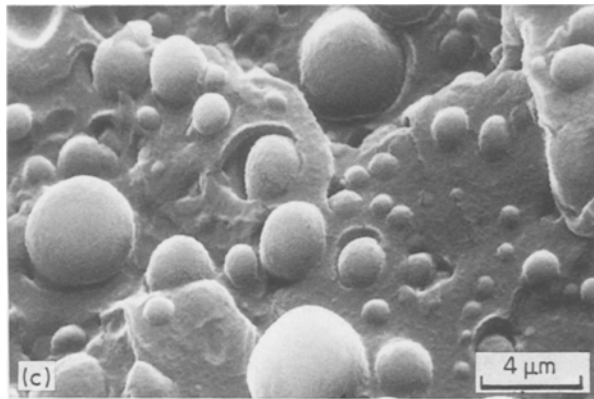
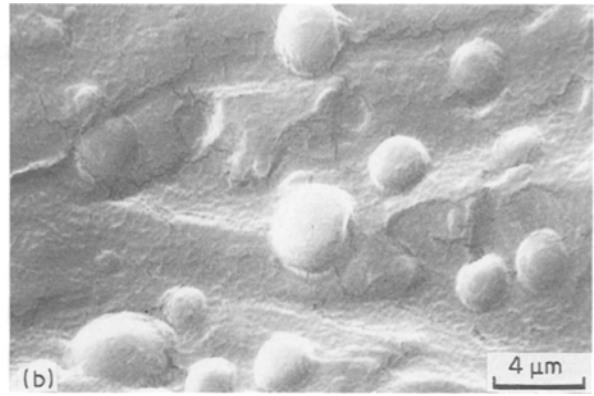
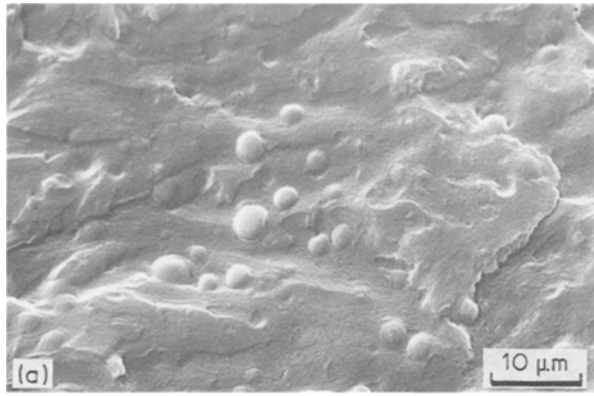


Figure 2 Scanning electron micrographs at different magnifications for two of the PDMS networks containing *in situ* polymerized PDPS to the extent of (a, b) 14.0 wt % and (c) 31.0 wt % (see also Fig. 1b).

Some typical SEM results are shown in Figs 1 and 2. Fig. 1 shows that the particles obtained by the solution-blending technique are somewhat smaller to those obtained in the *in situ* polymerizations (0.1 to 0.5 compared with 0.5 to 4.0  $\mu\text{m}$ ). The latter particles appear to be more homogeneous in size, however. Fig. 2 indicates that in the case of the *in situ* polymerized particles, an increase in the weight percentage of PDPS increases the number density of particles without much change in particle size.

blending was found to be entirely removed by the simplest of the extraction techniques employed. On the other hand, only about 10% of the PDPS introduced in the *in situ* polymerizations could be removed, even after the more extensive of the extractions described above. This clearly demonstrates the achievement of superior elastomer–filler bonding in the case of the *in situ* technique.

The stress–strain results were first represented in the usual manner [3, 20, 23, 24], as the dependence of the reduced stress on reciprocal elongation. Typical results are shown in Fig. 3. An alternative representation of the same results, specifically the nominal stress as a function of elongation, is shown in Fig. 4. Values of the ultimate strength, as measured by the nominal stress ( $f/A^*$ ), at rupture obtained from these curves, are given in the fourth column of Table I. The

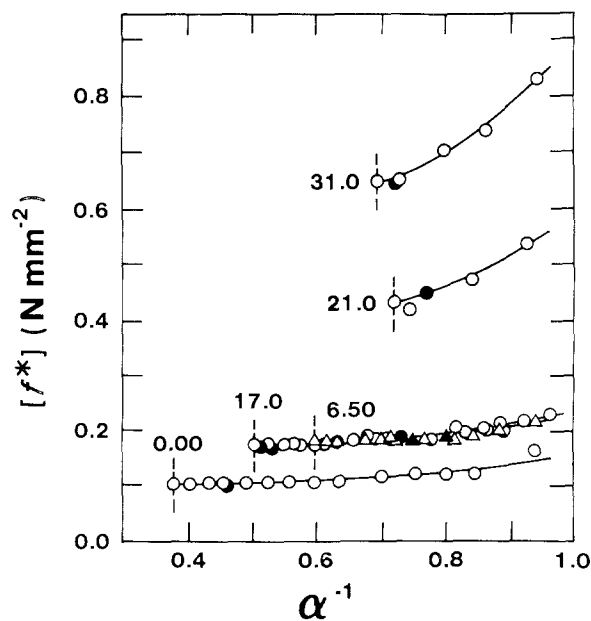


Figure 3 Stress–strain isotherms in elongation at 25°C for PDMS networks containing *in situ* polymerized PDPS, represented as the dependence of the modulus on reciprocal elongation. Each curve is labelled with the PDPS present in the network (wt %), and the dashed vertical lines locate the rupture points of the networks.

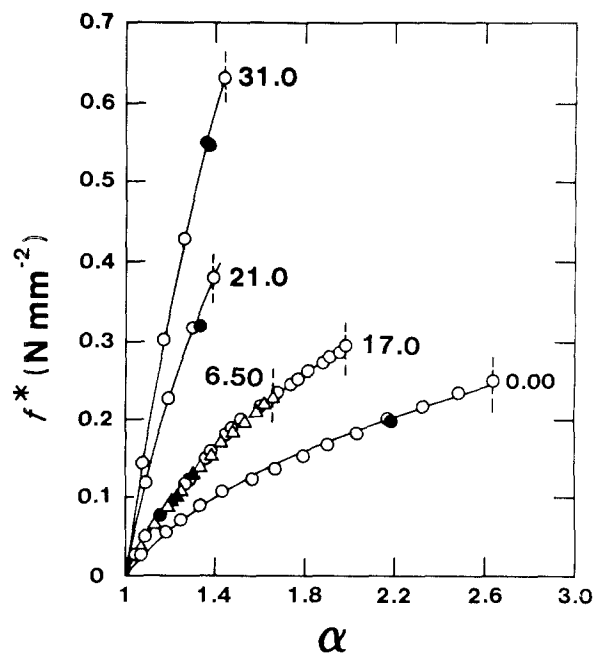


Figure 4 The stress–strain results of Fig. 3 now represented as the dependence of the nominal stress on elongation. The area under each curve corresponds to the energy  $E_r$  required for rupture.

corresponding values of the maximum extensibility  $\alpha_r$  or elongation at rupture are given in the next column. The area under each curve in Fig. 4 represents the energy  $E_r$  required for rupture, a standard measure of toughness [25]. These results are given in the final column of Table I.

The stress-strain results obtained indicate that the largest values of the reduced stress are obtained in the case of the solution-blended samples containing non-commercial PDPS and dried at 25°C, and the *in situ* polymerized samples having relatively high concentrations of PDPS. The main advantage of these samples might well involve high-temperature stability, since the silica typically used to reinforce PDMS can cause extensive high-temperature degradation through its high concentration of surface silanol groups [26]. Experiments relevant to this issue are in progress.

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