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Mechanical properties and structural characterization of poly(dimethylsiloxane) elastomers reinforced with zeolite fillers

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Poly(dimethylsiloxane) elastomers were filled with two zeolites which were both silicates of sodium and aluminum, but which had different cavity sizes. The reinforcement of the particles provided was characterized by stress–strain measurements in elongation at room temperature. The results indicated that the ultimate properties of the networks were increased by both types of zeolites, but that the increase was larger in the case of the zeolite with the larger cavity size. Small-angle-neutron-scattering results confirmed that the interface between the elastomeric phase and the zeolite particles was smooth, but gave no evidence for increased polymer penetration into the larger-cavity zeolite. Transmission electron microscopy (TEM) showed that the zeolite with a larger pore size also had a smaller particle size, and this is probably the origin of its superior reinforcing ability.

1. Introduction

The polysiloxanes are the most important class of high-performance elastomers, and poly(dimethylsiloxane) (PDMS), with a repeat unit $[-Si(CH_3)_2O-]$, is by far the most commonly used member of this class [1–3]. It remains rubbery and amorphous to very low temperatures because of its exceptionally low values for the glass-transition temperature ($T_g = -123\,°C$) and the crystallization temperature ($T_c = -40\,°C$). Unfortunately, however, PDMS elastomers have very poor mechanical properties, with particularly low tensile strengths. Hence, they require reinforcement to exhibit the improved mechanical properties required in almost all commercial applications [1–3].

Published studies on the reinforcement of PDMS have concentrated on the use of high-surface-area silica, which is much used commercially because of the excellent reinforcement it provides [4–6]. This material is amorphous, as is the carbon black used in the reinforcement of other classes of elastomers. In order to obtain a better molecular understanding of reinforcement mechanisms, however, it may also be useful to study crystalline fillers, preferably of known structures. An example of a class of such inorganic substances are the zeolites, which are hydrated silicates of aluminium and sodium of general formula $Na_2O \cdot Al_2O_3 \cdot nSiO_2 \cdot xH_2O$ [7, 8]. Their structures have been extensively studied largely because they are novel (with one or more cavities), and they have important applications as catalysts, sorption agents, ion-exchange resins and so on [7–10]. Zeolites were therefore used in the present investigation of reinforcement in PDMS elastomers, which is an extension of a previous preliminary study [11]. Two types of zeolites of different cavity size were employed, and the reinforcement they provided compared by stress–strain measurements on the elastomers in elongation. The structures of the filled networks were investigated by means of small-angle-neutron-scattering and transmission electron microscopy (TEM), for correlation with the amounts of reinforcement obtained.

2. Experimental details

2.1. Materials

The polymer utilized (two hydroxyl-terminated PDMS samples having quoted number-average molecular weights corresponding to $M_n = 18$ and $26\,kg\,mol^{-1}$) were obtained from the Huls America Company. The values of the weight-averaged molecular weight, M_w, of M_n, and of the polydispersity index, M_w/M_n, were obtained using a Waters 746 gel-permeation chromatography (GPC) instrument. The results are listed in Table I.

Tetraethoxysilane (TEOS) and stannous hexanoate, used in the network preparations, were supplied by the Petrach Systems Company and the Aldrich Chemical Company, respectively. The two zeolites were the

TABLE I Molecular weights of the PDMS chains

Petrach designation	Quoted M_n ($g\,mol^{-1}$)	GPC results		
		M_n ($g\,mol^{-1}$)	M_w ($g\,mol^{-1}$)	M_w/M_n
PS 343	26 000	22 100	34 600	1.57
PS 342.5	18 000	15 600	27 900	1.79
PS 340	500	344	408	1.20

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same as those used in the previous study [11], and they were obtained from Amresco, Inc. Their chemical formulas and structural parameters are given in Table II.

2.2. Preparation of the filled PDMS elastomers

The samples of hydroxyl-terminated PDMS were blended with the desired amount of zeolite in a dry-nitrogen bag. In some cases, an unfilled sample was prepared to serve as a reference material. In other cases, a mixture of short and long PDMS chains were used, so as to obtain a bimodal distribution [12] of network chain lengths. The mixture in this sample consisted of a 9:1 molar ratio of short chains of molecular weight 500 to long chains of molecular weight 26 000 g mol^{-1}. After incorporation of the zeolite, the PDMS chains were endlinked with TEOS, with stannous hexanoate as a catalyst, in the usual manner [12–14]. The cross-linking reaction was allowed to proceed at room temperature for 3 days. The resulting filled networks were not extracted prior to use.

2.3. Stress–strain measurements

Stress–strain isotherms of uniaxial extension were obtained in the usual manner [12, 15, 16]. The force and elongation measurements were made by using a sequence of increasing values of the elongation or relative length of the sample, $\alpha = L/L_0$. The reduced nominal stress or modulus was calculated from the following equation [12, 17–20]

$$[f^*] \equiv f^*/(\alpha - \alpha^{-2}) \qquad (1)$$

where $f^* = f/A$ is the nominal stress, f is the equilibrium force, and A is the area of the initial cross-section. All measurements were conducted at room temperature, and the elongation was generally increased to the rupture point of the sample.

2.4. Swelling measurements

Swelling measurements in toluene at room temperature were carried out on portions of the unfilled and filled PDMS networks, with several days being allowed for the attainment of equilibrium. The extent of equilibrium swelling was characterized by the volume fraction, v_{2m}, of polymer present in the network. It was calculated assuming simple additivity of volumes.

2.5. Small-angle-neutron-scattering (SANS)

The small-angle-neutron-scattering (SANS) data were obtained at the high-flux isotope reactor (HFIR) at Oak Ridge National Laboratory (ORNL), and the low-Q diffractometer (LQD) at the Los Alamos Neutron Scattering Center. In the scattering experiment, the incident beam of neutrons impinges on the sample and the angular dependence of the scattering intensity is measured. The scattered intensity, $I(Q)$, is parameterized by the momentum transfer or scattering wave vector Q, which for elastic scattering is simply proportional to $\sin(q/2)$, where q is the angle of the scattering intensity with respect to the transmitted beam.

TABLE II Structural information for the zeolites employed

Sample	Zeolite 4A	Zeolite 13x
Formula	$Na_{12}[(AlO_2)_{12}$ $(SiO_2)_{12}]\cdot xH_2O$	$Na_{86}[(AlO_2)_{86}$ $(SiO_2)_{106}]\cdot xH_2O$
Pore diameter	0.4 nm	1.0 nm
Particle size	< 10 μm	< 10 μm

2.6. Transmission electron microscopy (TEM)

Specimen slices with thicknesses of the order of 100 nm were obtained using a diamond knife in an ultramicrotome (Dorter-Blum MT-2) at − 130 °C. Specimens were examined in transmission with a Philips CM 20 electron microscope operating at 200 kV.

3. Results and discussion

3.1. Mechanical properties

3.1.1. Reinforcement effects

The stress–strain isotherms obtained on the unfilled and filled networks were first represented as plots of stress against strain. The area under each such stress–strain curve corresponds to the energy of rupture, E_r, which is a standard measure of elastomer toughness [14]. Typical isotherms for different amounts of filler, 13x and 4A, are shown in Figs 1 and 2, respectively. The same data were analysed in plots of modulus against reciprocal elongation, as suggested by the Mooney–Rivlin equation [12, 19–21].

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

These representations are shown elsewhere [17]. The isotherms were found to be nearly reversible, which is unusual for filled elastomers [5]. Values of the ultimate properties, specifically the ultimate strength, maximum extensibility, and energy of rupture, taken from these plots are given in Table III. They indicate that the nominal stress, modulus, and energy for

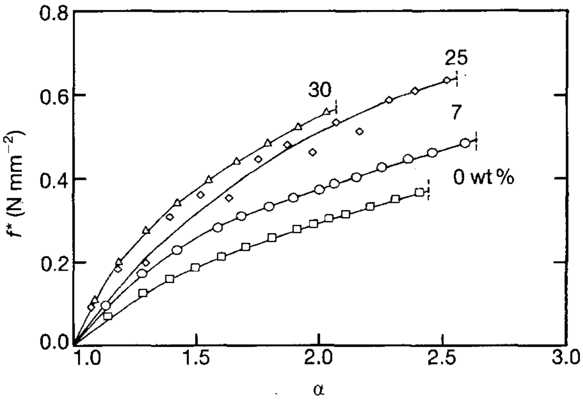

Figure 1 Stress–strain isotherms at 24 °C for the PDMS networks filled with zeolite 13x, represented as the dependence of the nominal stress on elongation. Each curve is labelled with the weight percentage of filler present in the network, and the value of M_c for the PDMS network is 18 000 g mol^{-1}.

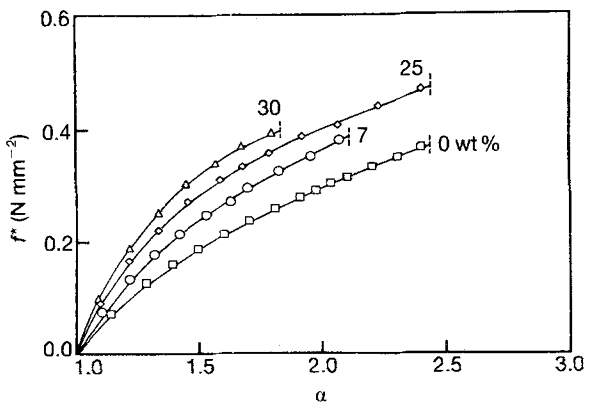

Figure 2 Stress–strain isotherms at 24 °C for the PDMS networks filled with zeolite 4A (see the caption for Fig. 1).

TABLE III Ultimate properties of the filled PDMS networks

Zeolite type	Filler (wt %)	α_r[a]	(f/A^*)[b] (N mm^{-2})	$10^3 E_r$[c] (J mm^{-3})
13x	0	2.41	0.369	0.298
	7	2.59	0.485	0.479
	25	2.52	0.635	0.604
	30	2.03	0.562	0.351
4A	7	2.08	0.383	0.256
	25	2.41	0.470	0.439
	30	1.80	0.395	0.220

[a] Elongation at rupture.
[b] Nominal stress at rupture.
[c] Energy required for rupture.

rupture of the PDMS networks are generally significantly increased by both types of zeolite fillers. Of the two zeolites, 13x gave larger increases in ultimate strength and toughness.

3.1.2. Relaxation effects

Stress–relaxation measurements can often give useful information on the interaction between polymer networks and filler surfaces. Here, stress relaxation was characterized by Δf^*, the difference in nominal stress between the value taken immediately after the deformation and the value close to equilibrium. Fig. 3 shows values of Δf^* as a function of elongation for some of the filled and unfilled networks. The stress relaxation for the filled networks was found to be small at low elongations and it increased gradually with increasing elongation. These changes are similar to, but much smaller than, those observed for silica-filled PDMS networks [22]. They are thought to result from the adsorption of polymer chains onto the filler surfaces, and their partial desorption in response to the applied stresses [22]. In the present case, however, the fact that the stress–strain isotherms were found to be nearly reversible suggests that the effect was simply due to the retarded motions of the chains in the viscous elastomeric matrix.

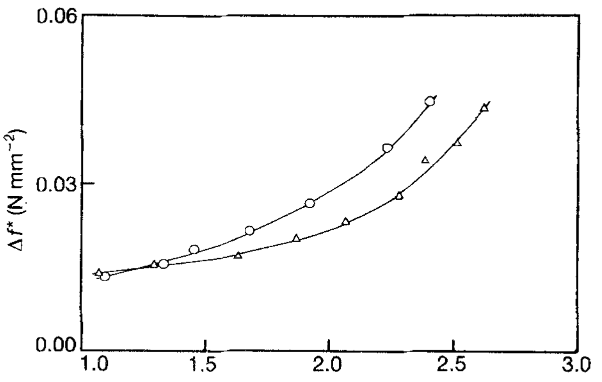

Figure 3 Dependence of stress relaxation on elongation for 18000 g mol^{-1} PDMS networks: (○) zeolite 4A, and (△) zeolite 13x.

3.2. Structural characterization

3.2.1. Swelling equilibrium

Filled elastomers can also be characterized by measurements of their swelling behaviour [23]. For example, Kraus's theory [24] indicates that the effect of fillers on swelling can be used to distinguish between those that give good adhesion to the elastomer and those that do not. It can thus give insight into the reinforcement mechanism. The quantity of interest is V_{ro}/V_{rf}, where V_{rf} is the ratio of the volume of the elastomer in the filled, dry network to its volume in the swollen network, again neglecting the volume of the filler. The quantity V_{ro} is the value of V_r in the case of the unfilled network. Fig. 4 shows values of V_{ro}/V_{rf} as a function of filler loading expressed as a volume fraction ratio, $\phi/(1-\phi)$, of filler to rubber (where ϕ is the volume fraction of filler).

If the filler is of the non-adhering type, the theory [24] predicts that the ratio V_{ro}/V_{rf} will increase as the filler loading increases. If the filler is of the adhering type, however, the elastomer is restricted by attachments on the filler surface, and the ratio should increase with increasing loading. In both cases, V_{ro}/V_{rf} should vary linearly with $\phi/(1-\phi)$:

$$V_{ro}/V_{rf} = 1 - m\phi/(1-\phi) \qquad (3)$$

with the slope m characterizing the extent of the dependence [24]. As can be seen from Fig. 4, the

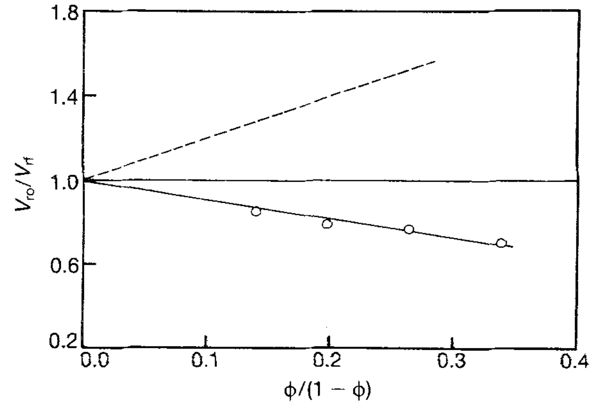

Figure 4 Volume-fraction ratio, V_{ro}/V_{rf} of unfilled to filled networks shown as a function of filler loading (expressed as the volume ratio of filler to rubber, $\phi/(1-\phi)$, where ϕ is the volume fraction of filler): (- - -) non-adhering filler, and (—○—) zeolite 13x. The filled network contained zeolite 13x.

relationship between V_{ro}/V_{rf} and $\phi/(1-\phi)$ was linear, and V_{ro}/V_{rf} did decrease as the filler loading increased. Interaction between the zeolite filler and the PDMS elastomer was therefore of the adhering type.

3.2.2. Neutron scattering

Small-angle scattering plays an important role in the understanding of the structure in disordered systems in general; its application here is to determine whether there was any difference in interaction between the PDMS chains and the two types of zeolites. Zeolite 4A has a pore size (with a diameter of 0.4 nm) too small to accommodate any part of a polymer chain, while zeolite 13x has a 1.0 nm pore size which is possibly large enough for a PDMS chain to penetrate, as was conjectured earlier [11]. Penetration in one case and not in the other would result in different scattering profiles.

Generally, a qualitatively distinct scattering profile is observed from fractal objects. In this case, a featureless power-law scattering is observed, indicating a continuum of Fourier components. From the slope, s, of log–log plots of I versus Q, smooth surfaces ($s = -4$) can be distinguished from fractally rough surfaces ($s = -3$ to -4), from a branched or linear polymer ($s = -1$ to -3).

Fig. 5 shows some typical neutron-scattering profiles for unimodal PDMS networks filled with zeolites 4A and 13x. The fact that the profiles for the 4A and 13x samples are nearly the same argues against chain interpenetration in the large-pore zeolite and not in the small-pore one. Since, statistically, penetration by *loops* would be much more likely than by ends, it may be necessary to have zeolite pore diameters more than twice the diameter of the potentially penetrating chain. In any case, the scattering profiles were found to be independent of the pore size, and also of the molecular weight of the PDMS chains and its distribution (unimodal versus bimodal). Considering a ± 0.2 margin of error in determining values of the terminal slope, s, all samples gave approximately -4, which confirms the expectation of smooth interfaces between filler and elastomer. This is rather different from the diffuse interfaces frequently observed in the case of fillers generated *in situ* by the hydrolysis of metalo-organic compounds [12].

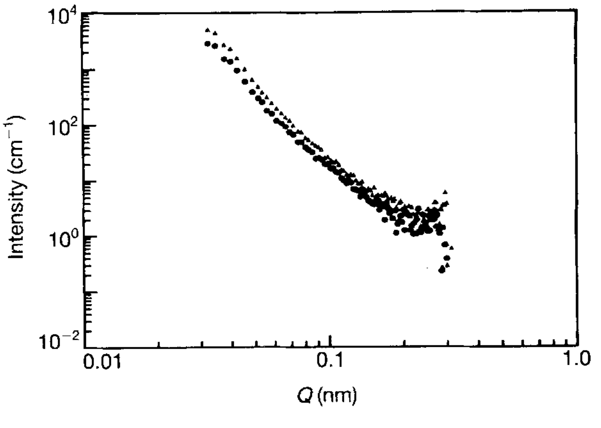

Figure 5 Neutron-scattering profiles for 18 000 g mol^{-1} PDMS networks filled with: (●) 20.8 wt % zeolite 4A, and (▲) 40 wt % zeolite 13x. The results for zeolite 4A gave a terminal slope of -4.0, and those for zeolite 13x gave essentially the same result, -4.2.

3.2.3. Electron microscopy

The fact that the zeolite pore size did not account for the difference in reinforcing ability of the two types of filler places the focus on filler-particle size. Specifically, smaller particle sizes in the case of adhering fillers

Figure 6 A transmission-electron micrograph for an 18 000 g mol^{-1} PDMS network filled with 30 wt % zeolite 4A.

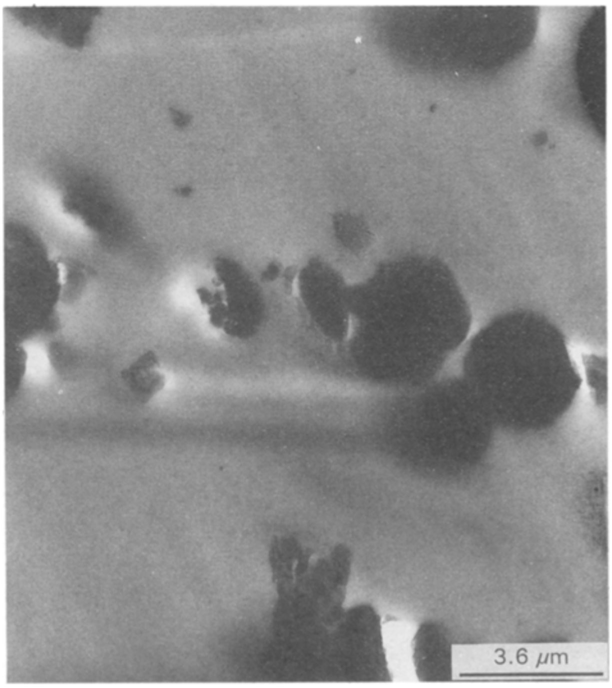

Figure 7 Transmission electron micrograph for an 18 000 g mol^{-1} PDMS network filled with 30 wt % zeolite 13x.

generally give greatly improved reinforcement because of the increased surface area per unit weight or volume of filler [4–6]. The required estimates of the particle sizes were obtained from the transmission electron micrographs, such as the one shown for zeolite 4A in Fig. 6, and for zeolite 13x in Fig. 7. These and other micrographs [17] indicated that zeolite 13x had an average particle size which was only about half that of zeolite 4A. This is presumably the origin of its better reinforcing ability.

It is possible to design other important experiments on the use of zeolites as reinforcing fillers in elastomers. For example, the likelihood of chain interpenetration should greatly increase if a *monomer* is absorbed into the zeolite prior to its polymerization. Such experiments are in progress.

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