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Zeolites as reinforcing fillers in an elastomer

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Summary

Two zeolites that were both silicates of sodium and aluminum but of different pore size were blended into samples of hydroxyl-terminated poly(dimethylsiloxane), which were then end linked into elastomeric networks. Stress-strain isotherms measured in elongation showed that both types of zeolites increased the ultimate properties of the elastomer and were thus effective reinforcing fillers. The one having the larger pore size gave larger increases in the ultimate strength of the elastomers.

Introduction

One of the standard fillers used to reinforce elastomeric materials is silica (SiO_2) (1-3). It has excellent reinforcing capability, and there is now a great deal of literature on this aspect of its behaviour and on a number of its other physical properties as well. The silica employed is invariably the amorphous variety, however, and this lack of well-defined structure makes it a poor choice for determining how the structure of a filler affects the reinforcement it provides.

A related but more versatile class of inorganic substances are the zeolites, which are metal silicates, either hydrated or anhydrous (4-6). In the latter case, their chemical structures may be represented by

$$xM_2O \cdot yAl_2O_3 \cdot zSiO_2 \tag{1}$$

where M represents an alkali metal cation. Many members of this class are crystalline, and [because of their importance as catalysts, sorptive agents, ion-exchange materials, etc. (4-9)] their structures have been determined and extensively documented. Of particular importance here is their sieve-like structures, the pore sizes of which differ from one zeolite to another, at least to some extent. A range of particle sizes is generally also available. A final, practical advantage is the fact that they are naturally occurring materials, quite easy to procure, and relatively inexpensive.

The present investigation was conducted to obtain some information on the reinforcing capabilities of some typical zeolites. It is part of a general program (10-14) involving structure-property relationships for elastomers containing fillers of known and carefully controlled structure. Of the two zeolites chosen for investigation the first, but not the second, has a pore size too small to accomodate any part of a polymer chain. Both zeolites are used to fill elastomeric networks, and the extent to which they provide reinforcement is gauged by stress-strain measurements on the resulting materials in elongation.

Experimental Details

The two zeolites employed were anhydrous, and were obtained from Alfa Morton Thiokol, Inc. The first (sample 87953, 600 mesh, lot 092386), is of the A type, which has the chemical structure

$$(1.0 \pm 0.2)Na_2O \cdot 1.0\ Al_2O_3 \cdot (1.85 \pm 0.5)SiO_2 \qquad (2)$$

Its pore size is quite small, corresponding to a diameter of only 3 Å. It is herein given the designation "3A". The other (600 mesh, lot C16G), is of the X type, which has the chemical structure

$$(0.9 \pm 0.2)Na_2O \cdot 1.0\ Al_2O_3 \cdot (2.8 \pm 0.5)SiO_2 \qquad (3)$$

Its pore diameter is considerably larger, 13 Å, and is herein designated "13X". Both materials have a cubic crystalline structure, with a particle size of 1-5 μm.

Hydroxyl-terminated PDMS chains having a number-average molecular weight of 18.0×10^3 g mol^{-1} were blended with the desired amount of the zeolite under investigation in a pure, dry nitrogen atmosphere. This was done in a glove-bag from which the air was pumped several times, each time being replaced by the dry nitrogen. After incorporation of the zeolite, the PDMS chains were end linked with tetraethoxysilane, in the usual manner (15). The reaction was allowed to proceed at room temperature, under nitrogen, for 24 hours (16).

Equilibrium stress-strain data were obtained in elongation, in the usual manner (15-17), on the samples at 25°C. Measurements were made using a sequence of increasing values of the elongation or relative length of the sample $\alpha = L/L_i$, with frequent inclusions of values out of sequence to test for reversibility. Two elastomeric properties were of interest. 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 (17-19) by $[f^*] \equiv f^*/(\alpha - \alpha^{-2})$.

Results and Discussion

The amounts of filler introduced as described above are given in the second column of Table I. Only a limited amount of the 13X sample could be incorporated, presumably because of its larger surface area. The stress-strain data were first represented as the dependence of the modulus on reciprocal elongation as suggested by the Mooney-Rivlin equation (17, 20, 21)

Table I

Filler Concentrations and Stress-Strain Results

Zeolite		Stress-Strain Results[a]				
Type	Wt %	$2C_1$ (N mm^{-2})	$2C_2$ (N mm^{-2})	α_r	$(f/A^*)_r$ (N mm^{-2})	10^3 E_r (J mm^{-3})
None	0.0	0.041	0.152	1.92	0.173	0.085
3A	13.8	0.100	0.078	3.04	0.377	0.470
	25.1	0.068	0.110	3.42	0.333	0.524
	36.7	0.079	0.303	2.04	0.406	0.289
	42.2	0.203	0.107	1.44	0.262	0.071
	50.0	--	0.079	1.29	0.373	0.076
13X	12.3	0.140	0.080	2.21	0.351	0.257
	20.3	0.240	0.119	2.29	0.595	0.481

[a] Mooney-Rivlin constants, ultimate properties, and energy required for rupture.

$$[f^*] = 2C_1 + 2C_2\alpha^{-1} \qquad (4)$$

where $2C_1$ and $2C_2$ are constants independent of elongation. The former is an approximation to the high-deformation modulus (20), and the latter is a measure of the increase in non-affineness with increase in elongation (18,19,22). The isotherms thus obtained are shown in Figure 1, and the corresponding values of $2C_1$ and $2C_2$ are given in columns three and four of the Table. The modulus is seen to be greatly increased by the fillers, by a factor of up to nearly seven.

The same stress-strain data are shown as plots of the nominal stress against elongation in Figure 2. The advantage of this representation is the fact that the area under each curve represents the energy E_r required for rupture (23,24), which is a standard measure

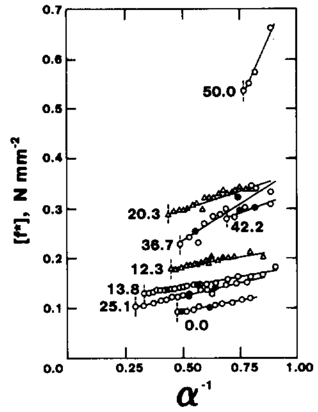

Figure 1. Stress-strain isotherms at 25°C for the zeolite-filled PDMS networks, represented as the dependence of the reduced stress or modulus on reciprocal elongation. The circles and triangles are for zeolites 3A and 13X, respectively. The open symbols locate the results gotten using a series of increasing values of elongation α, and the filled symbols the results obtained out of sequence to test for reversibility. Each curve is labelled with the wt % filler present in the network, and the vertical dashed lines locate the rupture points.

of toughness. Values of the elongation α_r and nominal stress $(f/A^*)_r$ at rupture and E_r, obtained from the isotherms, are given in the last three columns of the Table. As can readily be seen, these qualities are also generally significantly increased by the zeolite fillers.

Of the two zeolites, the 13X sample gave larger increases in ultimate strength. This is presumably due to its larger surface area, and it is tempting to attribute it more specifically to the fact that its pore size is presumably large enough for it to be invaded by the PDMS chains. Additional experiments would, of course, be required to provide a definitive test for conjectures of this type.

Acknowledgement

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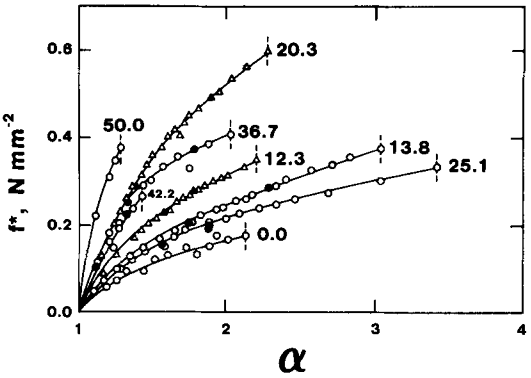

Figure 2. The stress-strain isotherms represented as the dependence of the nominal stress on elongation. See legend to Figure 1.

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