Reinforcement from alumina-type fillers precipitated into an elastomer

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Summary

The in-situ precipitation of alumina-type fillers into poly(dimethylsiloxane) is achieved by the hydrolysis of an aluminate, aluminum tri-sec-butoxide, in a reaction paralleling the preparation of silica and titania from silicates and titanates. Both HCl and NH_4OH were found to be good catalysts, but the latter produced particles which gave larger increases in ultimate strength of the reinforced elastomers.

Introduction

A very general way of reinforcing an elastomer while avoiding the problems of polymer-filler blending techniques involves the mixing or absorption of a suitable organometallic substance into a polymer or cross-linked network (1-9). Such a substance can frequently be hydrolyzed, thermolyzed, or photolyzed to give hard, frequently ceramic-type, particles having considerable reinforcing ability. Most studies of this type to date have involved hydrolysis of an alkoxysilane or silicate to provide silica particles, specifically in poly(dimethylsiloxane) (PDMS) (1-3), poly(methylphenylsiloxane) (4), and polyisobutylene (5). Several additional studies, however, have involved the hydrolysis of a titanate to titania (6,7), and ferric chloride to iron oxide (8,9).

The present investigation extends this in-situ technique to the formation of alumina-type particles, by the hydrolysis of an aluminate absorbed into PDMS networks. The nature and extent of the reinforcement obtained is gauged by stress-strain measurements, carried out in elongation, on the resulting filled elastomers.

Experimental Details

Preparation of elastomers. Hydroxyl-terminated PDMS chains having a number-average molecular weight of 18.0×10^3 g mol^{-1} were end linked with tetraethylorthosilicate, in the undiluted state, in the usual manner (10). The resulting network sheets were extracted with tetrahydrofuran (THF) for three days, thereby extracting a few wt % of soluble material.

Precipitation of alumina. The extracted strips were weighed and then placed into the aluminate aluminum tri-sec-butoxide $[C_2H_5CH(CH_3)O]_3Al$ until they swelled sufficiently to give the desired values of the volume fraction v_1 of butoxide in the network. The specific values of v_1 obtained are given in column two of Table I. The

Table I Results of Filler Precipitations and Stress-Strain Measurements

Hydrolysis Catalyst	Precipitation Results[a]		Stress-Strain Results[b]				
	v_1	Al_2O_3 Content (Wt %)	$2C_1$ ($N mm^{-2}$)	$2C_2$ ($N mm^{-2}$)	α_r	$(f/A^*)_r$ ($N mm^{-2}$)	$10^3 E_r$ ($J mm^{-3}$)
--	0.000	0.0	0.379	0.064	1.66	0.422	0.162
HCl	0.085	2.6	--	1.19	1.33	0.382	0.0784
	0.216	7.5	0.135	0.638	1.23	0.372	0.0549
	0.233	8.4	--	2.56	1.25	0.435	0.0569
	0.325	14.5	--	1.61	1.49	0.735	0.244
NH_4OH	0.135	2.2	0.236	0.223	1.67	0.503	0.206
	0.172	4.2	0.417	0.115	1.68	0.665	0.275
	0.230	7.4	0.235	0.422	1.59	0.631	0.189
	0.329	18.5	--	35.9	1.12	1.10	0.089

[a]Networks were swollen with $[C_2H_5CH(CH_3)O]_3Al$, which was then hydrolyzed to Al_2O_3 at room temperature in a 2.0% aqueous HCl or NH_4OH solution.

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

swollen strips were then immersed in aqueous catalyst solutions of either HCl or NH_4OH for 24 hrs, as specified in the Table.

The hydrolysis reaction of aluminum tri-sec-butoxide is very complicated (11-13), but in its overall form is simply

$$2[C_2H_5CH(CH_3)O]_3Al + 3H_2O \longrightarrow Al_2O_3 + 6 C_2H_5CH(CH_3)OH \qquad (1)$$
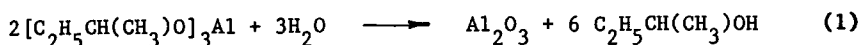
The strips, thus treated, generally turned very cloudy because of the precipitated alumina. They were first dried in air, extracted in THF for four days, and then re-dried under vacuum at 60-80°C to constant weight. They remained very cloudy. The increase in dry weight gave the amount of alumina precipitated, relative to the total weight of sample, in the allotted time. The data are given in the third column of the Table.

Stress-strain measurements. Equilibrium stress-strain data were obtained in elongation in the usual manner (10,14), on some of the (unswollen) 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. 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 (14-16) by $[f^*] \equiv f^*/(\alpha - \alpha^{-2})$.

Results and Discussion

Some of the results bearing on the amount of filler precipitated at various values of the volume fraction v_1 of aluminate present in the network are given in the third column of the Table. The complete set of results is shown in Figure 1. The amount precipitated is seen to

increase significantly with increase in v_1, as expected, and there is little difference between the HCl and NH_4OH as catalysts in this regard. This contrasts to hydrolysis of a titanate, where the NH_4OH was significantly more efficient.

One unfilled sample and eight samples filled using either catalyst were studied in the stress-strain experiments. The stress-strain isotherms obtained were first represented as plots of the modulus against reciprocal elongation, as suggested by the Mooney-Rivlin equation (3,14,17,18)

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

The results are shown in Figures 2 and 3, and the values of the constants $2C_1$ and $2C_2$ obtained from the linear portions of the isotherms are given in columns four and five of the Table. The former is an approximation to the high-deformation modulus (18), and the latter is a measure of the increase in non-affineness with increase in elongation (15,16,19). The in-situ filled networks are seen to have
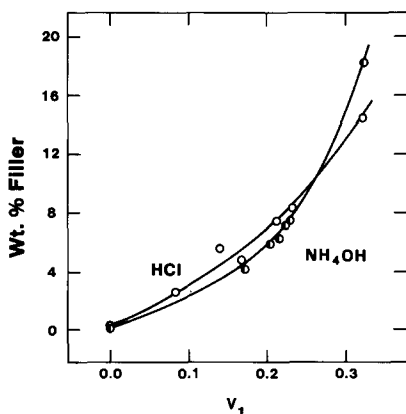

Figure 1. The amount of alumina precipitated shown as a function of the volume fraction of aluminate present in the network, for the two catalysts investigated.
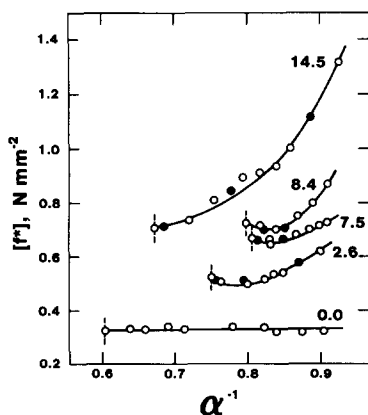

Figure 2. Stress-strain isotherms at 25°C for the alumina-filled PDMS networks obtained using HCl as catalyst, represented as the dependence of the reduced stress or modulus on reciprocal elongation. The open circles locate the results gotten using a series of increasing values of elongation α, and the filled circles 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.
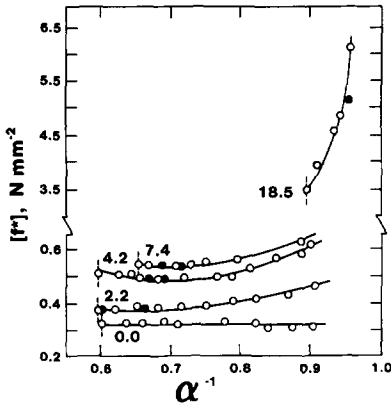
Figure 3. Stress-strain isotherms for the PDMS networks obtained using NH_4OH as catalyst; see legend to Figure 2.
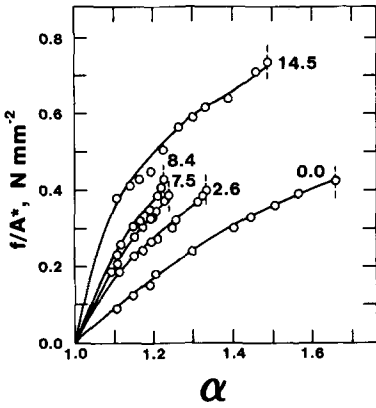

Figure 4. The stress-strain isotherms of Figure 2 now represented as the dependence of the nominal stress on elongation.
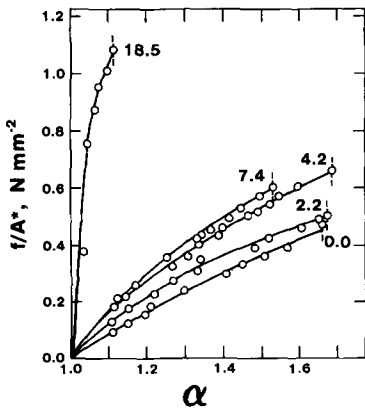

Figure 5. The stress-strain isotherms of Figure 3 now represented as the dependence of the nominal stress on elongation.

values of the modulus which are much higher than those of the corresponding unfilled network. Furthermore, the upturns in $[f^*]$ observed at higher elongations clearly demonstrate the desired reinforcing effects.

The same stress-strain data are shown as plots of the nominal stress against elongation in Figures 4 and 5. The advantage of this

representation is the fact that the area under each curve represents the energy E_r required for rupture (20), which is a standard measure of toughness. Values of the elongation α_r and nominal stress $(f/A^*)_r$ at rupture, and E_r, all obtained from the isotherms, are given in the last three columns of the Table.

The presence of the fillers is seen to decrease the maximum extensibility α_r, and these decreases frequently predominate over the increases in ultimate strength $(f/A^*)_r$. As a consequence, the energy E_r required for rupture is frequently decreased. On the positive side, however, some of the increases in $(f/A^*)_r$ are very large indeed, with the NH$_4$OH catalyst being better than the HCl in this regard. This could be due to the fact that, at least in the case of silicates, basic catalysts give much better defined particles (21). In any case, the in-situ precipitated alumina filler is seen to be quite effective as a reinforcing agent in these elastomers.

Acknowledgement

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