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Effects of Ethylamine Catalyst Concentration in the Precipitation of Reinforcing Silica Filler in an Elastomeric Network

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Summary

Ethylamine is found to be an effective catalyst for the hydrolysis of tetraethylorthosilicate in the in-situ filling of a polymer network. The silica filler thus precipitated strongly reinforces the elastomer, increasing its modulus, ultimate strength, and rupture energy. Increase in ethylamine concentration increases the rate of filler precipitation, and also increases the ultimate properties at constant weight % filler.

Introduction

In a recent study (1), a variety of inorganic and organic acids, bases, and salts were evaluated as catalysts for the hydrolysis of tetraethylorthosilicate (TEOS). When the reaction

$$Si(OC_2H_5)_4 + 2H_2O \longrightarrow SiO_2 + 4C_2H_5OH \qquad (1)$$

is carried out within an elastomeric network, the filler thus precipitated "in-situ" provides considerable reinforcement (1-6).

One of the most promising of the catalysts identified in this survey (1) was ethylamine, which was therefore chosen for the present more detailed investigation. The primary purpose was to determine the effects of the ethylamine catalyst concentration on both the rate of filler precipitation, and the ultimate properties of the resulting filled elastomers in elongation.

Some Experimental Details

The networks were prepared from vinyl-terminated poly(dimethylsiloxane) (PDMS) chains obtained from the McGhan NuSil Corporation; they had a number-average molecular weight corresponding to $10^{-3}M_n = 13.0$ g mol^{-1}. The chains were tetrafunctionally end linked with $Si[OSi(CH_3)_2H)]_4$ in the usual manner (7), and the resulting network extracted with tetrahydrofuran and then toluene for several days to remove soluble material (found to be present to the extent of a few percent). Strips cut from the network sheet were then dried, and one was set aside as a reference material (0 wt % filler).

The other network strips were swelled with TEOS to the maximum extent attainable, which corresponded to a volume fraction of polymer of approximately 0.26. Several strips were placed into one or the other of two aqueous solutions containing 2.0 and 25.0 % by weight of ethylamine, respectively. The hydrolysis of the TEOS was permitted to occur at room temperature for the periods of time specified in the second column of Table I. Values of the weight % filler incorporated, obtained from the weights of the dried strips, are given in the third column of the Table.

TABLE I

Reaction Conditions, Amount of Filler Precipitated, and Ultimate Properties of the Filled Elastomers

Reaction Conditions			Ultimate Properties		
Wt % EA[a]	Time, hrs.	Wt % Filler	α_r[a]	f_r^*[c] $N\ mm^{-2}$	10^3E_r, $J\ mm^{-3}$
2.0	0.0	0.0	3.07	0.293	0.372
	1.5	11.6	3.02	0.504	0.479
	3.0	33.0	2.93	0.919	0.866
	5.2	62.0	2.33	2.15	1.61
	8.0	67.0	2.01	2.16	1.41
	19.0	70.5	2.12	2.82	2.13
	72.0	63.0	1.81	2.30	1.14
25.0	0.0	0.0	3.07	0.293	0.372
	1.0	40.0	2.25	1.80	1.12
	1.5	50.3	2.15	2.92	2.02
	2.0	49.8	2.17	3.25	2.50
	4.0	48.7	2.25	2.71	2.00

[a] Ethylamine, in aqueous solution.

[b] Elongation at rupture.

[c] Ultimate strength, as represented by nominal stress at rupture.

[d] Energy required for rupture.

Portions of each of the networks were used in elongation experiments to obtain the stress-strain isotherms at 25°C (8-11). The elastomeric properties of primary interest were the nominal stress $f^* \equiv f/A^*$ (where f is the equilibrium elastic force and A^* the undeformed cross-sectional area), and the reduced stress or modulus (11-14) $[f^*] \equiv f^*/(\alpha - \alpha^{-2})$ (where $\alpha = L/L_i$ is the elongation or relative length of the strip). All stress-strain measurements were carried out to the rupture points of the samples, and were generally repeated in part to test for reproducibility.

Results and Discussion

As can be seen from Table I, increase in the concentration of the ethylamine greatly increases the rate of precipitation of the filler. For example, after 1.5 hrs. of reaction time, the 25.0 % ethylamine solution has precipitated over four times as much filler as the 2.0 % solution. Also, at the higher concentration the maximum amount precipitated is reached in less than one-tenth of the time.

Typical stress-strain isotherms obtained as described above are presented in Figure 1. The data are shown in the usual way (12-14), as the dependence of the reduced stress on reciprocal elongation. As is frequently the case for filled elastomers (15-18), some of the isotherms did not exhibit complete reversibility. In any case, the presence and efficacy of the filler are demonstrated by the marked increases in modulus, with marked upturns at the higher elongations.

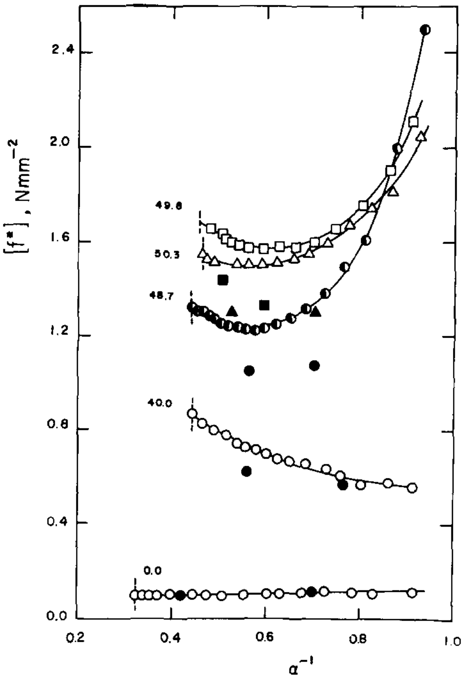

Figure 1. The reduced stress shown as a function of reciprocal elongation for the second series of filled PDMS networks at 25°C. Filled symbols are for results obtained out of sequence to test for reversibility, and each curve is labelled with the weight % filler present in the network. The vertical dashed lines locate the rupture points.

Figure 2 shows the data of Figure 1 plotted in such a way that the area under each stress-strain curve corresponds to the energy E_r of

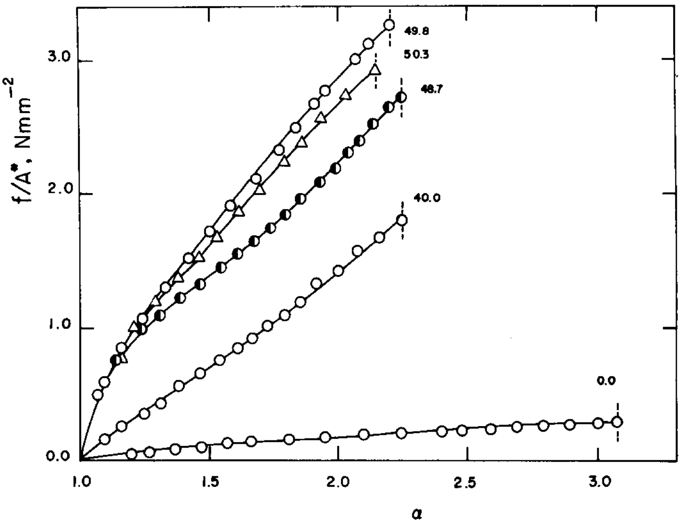

Figure 2. The nominal stress shown as a function of elongation for the same networks characterized in Figure 1.

rupture (9), which is the standard measure of elastomer toughness. Its values, along with values of the maximum extensibility α_r and ultimate strength f_r^* are given in the last three columns of the Table. Increase in % filler decreases α_r but increases f_r^*. The latter effect predominates and E_r increases accordingly.

Of considerable interest is the observation that even at constant weight % filler, the elastomers prepared from the more concentrated ethylamine solution had better ultimate properties. This must be due to differences in the nature of the filler particles, in particular their average size, size distribution, or degree of agglomeration (19). Such differences can, of course, be studied using transmission electron microscopy (19) and light scattering intensities (20).

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