Reinforcing Fillers

Hydrolysis of Several Ethylethoxysilanes to Yield Deformable Filler Particles

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Summary

A technique is devised for incorporating organic groups in filler particles, thus giving them some deformability. Hoped-for increases in toughness were not obtained, presumably because of replacement of some surface silanol groups by less reactive organic groups, thus decreasing filler-matrix bonding and elastomer reinforcement.

Introduction

A series of recent experimental investigations (1-9) has focused on the hydrolysis of tetraethoxysilane (TEOS) $[Si(OC_2H_5)_4]$ to give filler particles capable of reinforcing elastomeric networks. The reactions are typically carried out within a TEOS-swollen network of poly(dimethylsiloxane) (PDMS) and yield essentially unagglomerated particles with diameters of 150-250 Å (7). The reinforcing effects of these fillers have been clearly demonstrated by measurements of stress-strain isotherms in elongation (1-5,8,9), and by falling-dart impact tests (6).

It is conceivable that the reinforcing effect could be enhanced if the filler particles could be given some degree of deformability or toughness. This could be accomplished by the retention of organic groups in the particles, for example by including some silanes of the type $(C_2H_5)_{4-x}Si(OC_2H_5)_x$ in the hydrolysis reaction. Of primary interest would be hydrolysis of mixtures of TEOS with silanes of lower functionality (x = 3 and 2). It would be hoped that the effects of the particle deformability thus obtained would predominate over the effects of the diminished filler-PDMS bonding caused by the decreased number of silanol groups on the particle surfaces.

The present study addresses these questions, using the hydrolysis of TEOS, $C_2H_5Si(OC_2H_5)_3$, $(C_2H_5)_2Si(OC_2H_5)_2$, and mixtures thereof. Measurements of the elongation moduli and ultimate properties of the PDMS networks filled in this way are used to evaluate the effectiveness of the reinforcement obtained.

Some Experimental Details

The network was prepared from vinyl-terminated poly(dimethylsiloxane (PDMS) chains obtained from the McGhan NuSil Corporation; they had a

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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 (10), and the resulting network extracted with tetrahydrofuran and then toluene for a total of six days to remove soluble material (found to be present to the extent of 5.2 wt %). Strips cut from the network sheet were then dried, and one was set aside as a reference material (0 wt % filler).

The three ethoxysilanes investigated were obtained from the Fisher Scientific Company. They are listed in the first two columns of Table I,

Table I

Reaction Conditions and Amount of Filler Precipitated

Reaction Conditions				
Silane A	Silane B	Wt A/Wt B	Reaction time, hrs.	Wt % filler
--	--	--	0.0	0.0
$Si(OC_2H_5)_4$	--	100/0	0.6	7.7
			1.0	11.6
			2.7	34.4
			4.9	53.0
$C_2H_5Si(OC_2H_5)_3$	--	100/0	8.0	2.5
			17.0	4.8
$(C_2H_5)_2Si(OC_2H_5)_2$	--	100/0	5.0	2.7
			8.0	5.2
			17.0	8.6
$Si(OC_2H_5)_4$	$C_2H_5Si(OC_2H_5)_3$	90/10	1.5	15.3
			5.0	43.7
			7.0	44.6
			22.5	38.1
		70/30	1.5	10.5
			5.0	35.4
			7.0	39.3
			22.5	29.3
$Si(OC_2H_5)_4$	$(C_2H_5)_2Si(OC_2H_5)_2$	90/10	1.5	14.8
			5.0	48.4
			7.0	48.0
			22.5	37.0
		70/30	1.5	10.3
			5.0	37.2
			7.0	41.1
			22.5	30.5

and the compositions employed are given in the following column. The network strips to be filled were swelled with the specified ethoxysilanes to the maximum extent attainable, which corresponded to a volume fraction of polymer of 0.21 - 0.23. The swollen strips were then placed into a 2.0 wt% aqueous solution of ethylamine. The hydrolysis of the ethoxysilanes was permitted to occur at room temperature for the periods of time specified in the fourth column of Table I. Values of the wt % filler incorporated, obtained from the weights of the dried strips, are given in the final column.

Portions of each of the networks were used in elongation experiments to obtain the stress-strain isotherms at $25^{\circ}C$ (11-14). 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 (14-17) $[f^*] \equiv f^*/(\alpha - \alpha^{-2})$ (where $\alpha = L/L_i$ is the elongation or relative length of the strips). 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

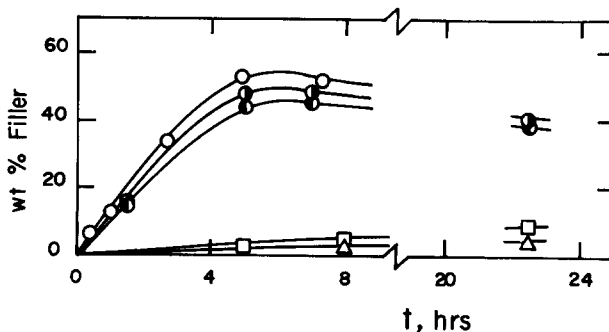Figure 1 shows the amount of filler precipitated as a function of

Figure 1. Time dependence of the wt % filler precipitated by the hydrolysis of $Si(OC_2H_5)_4$ (O), $C_2H_5Si(OC_2H_5)_3$ (△), $(C_2H_5)_2Si(OC_2H_5)_2$ (☐), weight ratio 90/10 of $Si(OC_2H_5)_4/C_2H_5Si(OC_2H_5)_3$ (◐), and weight ratio 90/10 of $Si(OC_2H_5)_4/(C_2H_5)_2Si(OC_2H_5)_2$ (●).

time for the five systems investigated. The rate of hydrolysis is seen to be largest for the TEOS. The curves for both the TEOS and its mixtures go through a maximum, the origin of which is probably loss of colloidal silica. The rates of hydrolysis of the pure $C_2H_5Si(OC_2H_5)_3$ and $(C_2H_5)_2Si(OC_2H_5)_2$ are seen to be very small.

This was confirmed in separate tests in which the hydrolysis of the pure silanes was observed using acetone as a cosolvent for the silanes

and the ethylamine solution. Whereas the product of hydrolysis of the
TEOS was a particulate silica, the hydrolysis of $C_2H_5Si(OC_2H_5)_3$ resulted
in a mixture of a viscous liquid and a waxy solid.[5] The product of the
hydrolysis of $(C_2H_5)_2Si(OC_2H_5)_2$ was a liquid. These cannot, of course,
be considered to be particulate fillers in themselves, and their primary
role is to add deformability when used in mixtures with TEOS.

Some typical stress-strain isotherms obtained as described above are
presented in Figure 2. The data are shown in the usual way (15-17), as
the dependence of the reduced stress on reciprocal elongation. As is
frequently the case for filled elastomers (18-20), some of the isotherms
did not exhibit complete reversibility. Figure 3 shows the data of
Figure 2 plotted in such a way that the area under each stress-strain
curve corresponds to the energy E_r of rupture (12), which is the standard
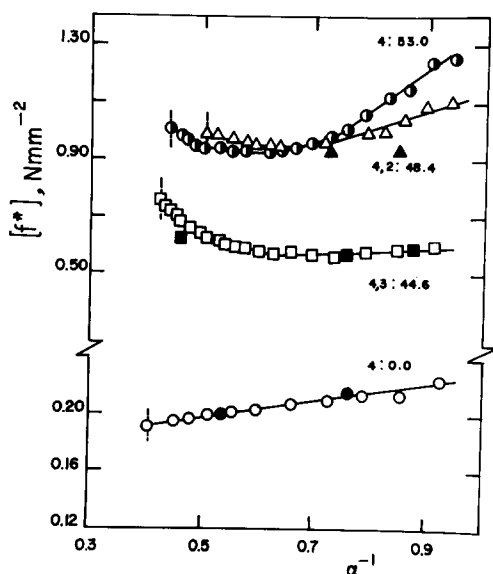measure of elastomer toughness. Its values, along with values of the

Figure 2. The reduced stress as a function of reciprocal
elongation for several filled PDMS networks at $25^{\circ}C$. Each
curve is labelled with the number of ethoxy groups in the
silane or silane mixture being hydrolyzed, followed by the wt %
filler thereby precipitated into the PDMS network. Filled
symbols are for results obtained out of sequence to test for
reversibility, and the vertical dashed lines locate the rupture
points.

maximum extensibility α_r and ultimate strength f_r^* are given in the last three columns of Table II. Reference to the values of the extensibility

Table II

Ultimate Properties of the Filled Networks

Filler Characteristics			Ultimate Properties		
Silane A	Silane B	Wt A/Wt B	α_r [a]	$f_r^*,$ [b] N mm^{-2}	$10^3 E_r,$ [c] J mm^{-3}
--	--	--	2.48	0.422	0.394
$Si(OC_2H_5)_4$	--	100/0	--	--	--
			--	--	--
			--	--	--
			2.37	2.09	1.55
$C_2H_5Si(OC_2H_5)_3$	--	100/0	--	--	--
			2.60	0.421	0.394
$(C_2H_5)_2Si(OC_2H_5)_2$	--	100/0	--	--	--
			--	--	--
			2.83	0.495	0.601
$Si(OC_2H_5)_4$	$C_2H_5Si(OC_2H_5)_3$	90/10	1.89	0.565	0.288
			--	--	--
			2.40	1.94	1.09
			--	--	--
		70/30	1.87	0.525	0.258
			--	--	--
			2.24	1.46	0.858
			--	--	--
$Si(OC_2H_5)_4$	$(C_2H_5)_2Si(OC_2H_5)_2$	90/10	2.26	0.831	0.571
			1.94	1.67	0.918
			--	--	--
			--	--	--
		70/30	2.37	0.776	0.539
			--	--	--
			1.85	1.16	0.541
			--	--	--

[a] Elongation at rupture.

[b] Ultimate strength, as represented by the nominal stress at rupture.
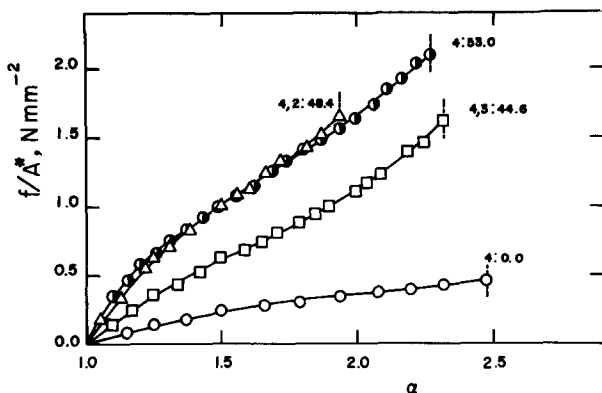
[c] Energy required for rupture.

Figure 3. The nominal stress as a function of elongation for the same networks characterized in Figure 2. The area under the curves corresponds to the energy required for network rupture.

indicates that the products of the hydrolysis of the pure lower silanes act more as plasticizers for the network polymer than as reinforcing fillers.

The TEOS hydrolysis is seen to give the strongest reinforcement, with the other two pure ethoxysilanes being essentially ineffective in this regard. In the case of the particles formed from the silane mixtures, the loss of silanol groups on the filler surfaces is presumably the origin of the decreased reinforcement. The concept of creating deformable filler particles giving improved reinforcement, however, does seem to have merit and other approaches to achieve this goal will be attempted.

Acknowledgements

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