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In-situ precipitation of reinforcing titania fillers

S.-B. Wang and J. E. Mark

Department of Chemistry and the Polymer Research Center, University of Cincinnati,
Cincinnati, OH 45221, USA

Summary

The technique developed for precipitating reinforcing silica into an elastomer is extended to titania fillers by hydrolyzing a titanate instead of a silicate. Of the three catalysts studied, namely HCl, NH_4OH, and $(C_2H_5)_2NH$, the NH_4OH was the most efficient, introducing as much as 65 wt % titania into a poly(dimethylsiloxane) network in twelve hours. Stress-strain measurements in elongation showed the nature and extent of the reinforcement to be very similar to that obtained from in-situ precipitated silica.

Introduction

A series of previous investigations (1-20) has shown the feasability of precipitating silica (SiO_2) into a polymer or cross-linked elastomer by the catalyzed hydrolysis of an alkoxysilane or silicate. The in-situ generated particles give reinforcement comparable to that obtained in the usual technique (21,22) of blending already-formed filler into a polymer prior to its being cured or cross linked.

At least in the latter case, the silica is known (23-27) to have a detrimental effect on the high-temperature properties of poly(dimethylsiloxane) (PDMS), an elastomer in which silica is almost always employed to improve its mechanical properties (21,27,28). This is particularly unfortunate since PDMS itself has such superb thermal stability (27,28). It is therefore much used for high-temperature applications and, of course, even in low-temperature environments there can be considerable heat build-up from hysteresis in the case of cyclic deformations. Specifically, it is thought (26) that acidic SiOH groups on the silica surface can cause PDMS chain cleavage. The results can be unpredictable since the cleavage itself would decrease the modulus, but attachment of the newly-formed chain ends onto the particle surface could cause a net increase in the number of elastically effective chains and thus increase the modulus. Fumed titania (TiO_2) is known (27,29) to improve the compression set of PDMS elastomers and also their heat stability above 300°C, presumably by not having silica's ability to cleave the PDMS chain.

The present investigation was therefore undertaken to determine whether or not in-situ precipitated TiO_2 is on effective reinforcing agent for PDMS elastomers in elongation at 25°C. If it is, it would be very worthwhile to initiate a long-term study comparing the high-temperature stabilities of unfilled, SiO_2-filled, and TiO_2-filled PDMS elastomers using several types of deformation, under a variety of environmental conditions.

Experimental Details

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 (30). The resulting network sheets were extracted with gently-stirred tetrahydrofuran (THF) for three days.

The extracted strips were weighed and then placed into n-propyl titanate [$(C_3H_7O)_4Ti$] until the desired amount was incorporated, as specified by the volume fraction v_2 of polymer present in the network. The swollen strips were then immersed in one of the aqueous catalyst solutions, at room temperature, for 12 hrs. The details are given in the first three columns of Table I. The titanate hydrolysis reaction is

Table I

Effect of Precipitation Conditions on TiO_2 Content

Precipitation Conditions			
Hydrolysis Catalyst	Cat. Conc. (wt %)	v_2[a]	TiO_2 Content (wt %)
HCl	2.0	0.812	2.7
		0.692	5.2
		0.655	6.9
		0.615	7.8
		0.597	11.9
		0.307	42.8
NH_4OH	2.0	0.812	7.1
		0.716	7.5
		0.709	12.0
		0.615	23.0
		0.361	55.1
		0.307	65.0
$(C_2H_5)_2NH$	2.4	0.615	30.8
		0.307	55.8

[a] The volume fraction of polymer in the $(C_3H_7O)_4Ti$-swollen network.

very complicated (31), but in its overall form is simply (15,31)

$$(C_3H_7O)_4\,Ti + 2H_2O \longrightarrow TiO_2 + 4C_3H_7OH \qquad (1)$$

The strips, thus treated, generally turned very cloudy because of the precipitated TiO_2. 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.

Equilibrium stress-strain data were obtained in elongation in the usual manner (30,32), 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. 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 (32-34) by $[f^*] \equiv f^*/(\alpha - \alpha^{-2})$.

Results and Discussion

The amounts of TiO_2 precipitated using the three catalysts and different degrees of swelling with $(C_3H_7O)_4Ti$ are given in the last column of Table I. The NH_4OH was the most efficient catalyst, introducing 65 wt % TiO_2 during the 12-hr. hydrolysis period. The acidic HCl catalyst, however, gave reactions that were easier to control.

One unfilled sample and four samples filled using HCl as catalyst were used in the stress-strain experiments. Their TiO_2 contents are given in the second column of Table II. The stress-strain data were first represented as the dependence of the modulus on reciprocal elongation as suggested by the Mooney-Rivlin equation (32,35,36)

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

where $2C_1$ and $2C_2$ are constants independent of elongation. The former is an approximation to the high-deformation modulus (36), and the latter is a measure of the increase in non-affineness with increase in elongation (33,34,37). 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 Table II. The modulus is seen to be greatly increased by the filler, by a factor of up to six for the sample having the largest TiO_2 content (11.9 wt %). This is similar to the amount of reinforcement obtained from in-situ precipitated SiO_2 (1-20). Similar upturns at high α are also seen in some of these isotherms.

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 (38), which is a standard measure of

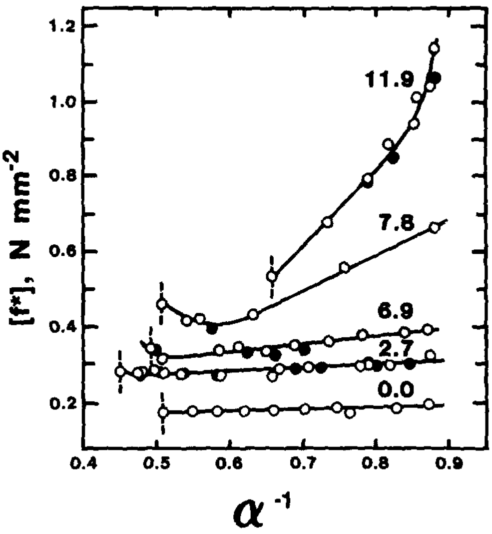

Figure 1. Stress-strain isotherms at 25°C for the titania-filled PDMS networks, represented as the dependence of the nominal stress or modulus on reciprocal elongation. The open circles locate the results gotten using a series of increasing values of elongation α, and the filled circles the results obtained 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.

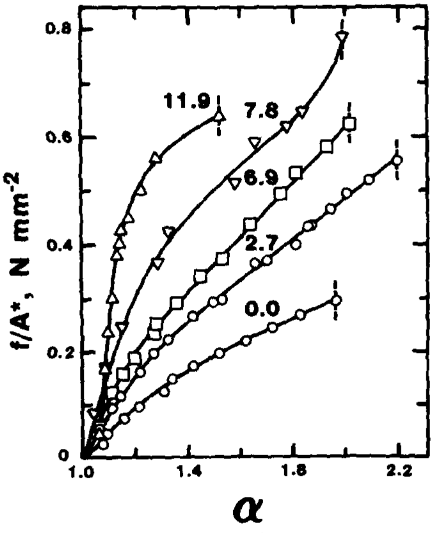

Figure 2. The stress-strain isotherms represented as the dependence of the nominal stress on elongation. See legend to Figure 1.

Table II

Results of Filler Precipitations and Stress-Strain Measurements

Precipitation Results[a]		Stress-Strain Results[b]				
v_2	TiO_2 Content (Wt %)	$2C_1$ ($N\ mm^{-2}$)	$2C_2$ ($N\ mm^{-2}$)	α_r	$(f/A^*)_r$ ($N\ mm^{-2}$)	10^3E_r ($J\ mm^{-3}$)
1.000	0.0	0.163	0.022	1.97	0.294	0.0210
0.812	2.7	0.226	0.087	2.21	0.552	0.0393
0.655	6.9	0.266	0.128	2.03	0.608	0.0373
0.615	7.8	0.044	0.682	1.96	0.785	0.0470
0.597	11.9	--	1.47	1.52	0.638	0.0241

[a] Networks were swollen with $(C_3H_7O)_4Ti$, which was then hydrolyzed to TiO_2 at room temperature in a 2.0% aqueous HCl solution.

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

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 Table II. Although α_r is relatively constant, both $(f/A^*)_r$ and E_r increase significantly with increase in TiO_2 content up to a factor of approximately 2.5. The in-situ precipitated TiO_2 is thus seen to be a good reinforcing agent for PDMS elastomers.

Additional studies, some addressed to the question of thermal stability, are in progress.

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