Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

Reinforcing Zirconia Particles Precipitated into an Elastomeric Material

S. B. Wang[a][b]; J. E. Mark[a]
[a] Department of Chemistry and the Polymer Research Center, The University of Cincinnati, Cincinnati, OH, USA [b] Polymer Technologies, Inc., a subsidiary of the University of Detroit, Detroit, MI

To cite this Article Wang, S. B. and Mark, J. E.(1991) 'Reinforcing Zirconia Particles Precipitated into an Elastomeric Material', Journal of Macromolecular Science, Part A, 28: 11, 185 — 192
To link to this Article: DOI: 10.1080/00222339108054400
URL: http://dx.doi.org/10.1080/00222339108054400

MACROMOLECULAR REPORTS, A28(SUPPL. 3), 185-192 (1991)

REINFORCING ZIRCONIA PARTICLES PRECIPITATED INTO AN ELASTOMERIC MATERIAL

S. B. Wang* and J. E. Mark
Department of Chemistry and the Polymer Research Center,
The University of Cincinnati, Cincinnati, OH 45221 USA

ABSTRACT

Particles of ZrO_2 were precipitated into a polysiloxane elastomer by the hydrolysis of zirconium n-propoxide, using NH_4OH or HCl as catalyst. Transmission electron micrographs of the resulting in-situ filled elastomers indicated that the particle diameters were similar to those obtained in silica precipitations, but with broader distributions of particle size. Stress-strain isotherms obtained on the elastomers in elongation showed that the particles obtained from either catalyst gave good reinforcement, but those prepared using HCl gave larger increases in ultimate strength and higher maximum extensibilities.

INTRODUCTION

In the in-situ technique for reinforcing an elastomer, a metallo-organic substance is typically absorbed into a polymer network, and then hydrolyzed to give hard, ceramic-like particles having considerable reinforcing ability (1-12). Previous investigations of this type have generally involved the hydrolysis of silicates to silica (SiO_2) (4-6,8-10,12), but extensions of this work have involved hydrolyses of titanium tri-n-propoxide [$(C_3H_7O)_4Ti$] to titania (TiO_2) (1,2,7,11), and aluminum tri-sec-butoxide [$(C_2H_5CHCCH_3O)_3Al$] to alumina (Al_2O_3) (3).

The present investigation extends this technique to the formation of ZrO_2 particles, by the hydrolysis of zirconium tri-n-propoxide [$(C_3H_7O)_4Zr$] absorbed into poly(dimethylsiloxane) (PDMS) networks. The particles thus precipitated will be characterized by electron microscopy, and the nature and extent of the reinforcement obtained will be gauged by stress-strain measurements on the resulting materials in elongation.

---

* Permanent address: Polymer Technologies, Inc., a subsidiary of the University of Detroit, 4001 West McNichols Road, Detroit, MI 48221.

Table I

Results of Filler Precipitations and Stress-Strain Measurements

Precipitation Results[a]			Stress-Strain Results[b]				
Hydrolysis Catalyst	v_1	ZrO_2 Content (Wt %)	$2C_1$ ($N\ mm^{-2}$)	$2C_2$ ($N\ mm^{-2}$)	α_r	$(f/A^*)_r$ ($N\ mm^{-2}$)	$10^3\ E_r$ ($J\ mm^{-3}$)
None	0.000	0.0	0.311	0.0318	1.66	0.421	0.164
NH_4OH	0.070	2.0	0.145	0.657	1.22	0.266	0.0309
	0.118	4.1	–	1.83	1.21	0.256	0.0340
	0.185	7.5	–	3.83	1.25	0.424	0.0667
	0.232	10.7	–	1.20	1.32	0.622	0.134
None	0.000	0.0	0.326	0.0081	2.16	0.643	0.421
HCl	0.133	3.2	0.306	0.184	1.75	0.639	0.275
	0.207	6.0	0.384	0.0800	2.07	0.874	0.926
	0.241	7.4	0.389	0.279	2.31	1.11	0.896
	0.365	13.0	0.220	0.597	2.67	1.32	1.27

[a] Networks were swollen with $(C_3H_7O)_4Zr$, which was then hydrolyzed to ZrO_2 at room temperature in a 2.0% aqueous NH_4OH or HCl solution.

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

EXPERIMENTAL DETAILS

Preparation of Elastomers

Hydroxyl-terminated chains of PDMS having a number-average molecular weight of 18.0×10^3 g mol^{-1} were end linked with tetraethylorthosilicate (TEOS), in the undiluted state, in the usual manner (13). The resulting network sheets were extracted with tetrahydrofuran (THF) for three days, thereby extracting any soluble (uncross-linked) material.

Precipitation of ZrO_2

The extracted strips were weighed and then placed into the zirconium propoxide. Swelling was permitted to continue until the desired values were obtained for the volume fraction v_1 of $(C_3H_7O)_4Zr$ present in the network. The specific values of v_1 thus obtained are given in column two of Table I. The swollen strips were then immersed in aqueous solutions of either NH_4OH or HCl as catalyst, for 24 hrs.

As is the case with other metal alkoxides, the hydrolysis reaction of zirconium propoxide is very complicated (14-16), but in its overall form is simply

$$(C_3H_7O)_4Zr + 2H_2O \longrightarrow ZrO_2 + 4C_3H_7OH \qquad (1)$$

The strips exposed to this hydrolysis procedure generally turned very cloudy because of the precipitated ZrO_2. In a final series of steps, 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.

Electron Microscopy

A piece of each filled network approximately 1 mm x 1 mm x 5 mm was mounted in an appropriate specimen holder, which was then placed into the cryostatic chamber (Sorvall FS 1000) of an ultramicrotome (Sorvall MT 6000). The entire area to be sectioned was cooled to -140°C. It was maintained at this temperature with a device controlling the delivery of the precise amounts of liquid nitrogen or heat necessary for this thermostatting. A diamond knife was used to obtain specimen slices having a thickness the order of 1,000 Å . They were collected on carbon-coated grids, and then examined in transmission with a Hitachi HS-7 electron microscope operating at 100 kV.

Strain-Strain Measurements

Equilibrium stress-strain data were obtained in elongation in the usual manner (13.17), 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. There were two elastomeric properties of primary interest. Specifically, they were the nominal stress (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) [given by $[f^*] \equiv f^*/(\alpha - \alpha^{-2})$]. The values of either of these quantities at rupture represent the ultimate strength of the material, and the value of the elongation at rupture represents the maximum extensibility.

RESULTS AND DISCUSSION

Amounts of Filler Precipitated

The amounts of ZrO_2 precipitated at various values of the volume fraction v_1 of zirconium propoxide present in the network are given in the third column of the Table. These results are also shown graphically in Figure 1. The amount precipitated is seen to increase significantly with increase in v_1, as expected. There is seen to be a significant difference betweeen the NH_4OH and HCl as catalysts, however, in this regard. The NH_4OH is the more effective of the two, and can introduce as much as 56 wt % ZrO_2 into a PDMS network in 24 hrs.

Particle Sizes

Some typical transmission electron micrographs obtained for both types of materials are given in Figures 2 and 3. Particle diameters were in the range 160-320 Å ,

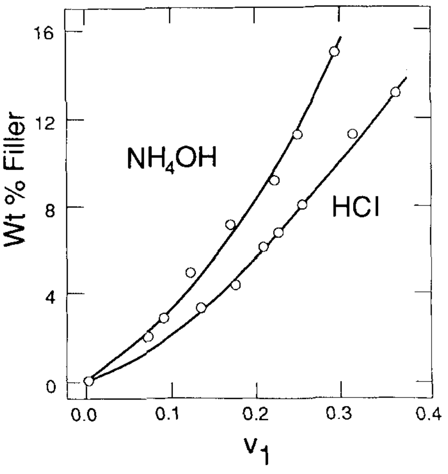

FIG. 1. The amount of ZrO_2 precipitated shown as a function of the volume fraction of zirconium propoxide present in the network, for the two catalysts investigated.

and were generally smaller when prepared using the HCl catalyst. They also appeared to have rougher surfaces, as was also found to be the case in comparisons of acid-catalyzed and base-catalyzed silica particles (4,6,9). In both cases, the particle size distribution seems significantly broader than those obtained in in-situ precipitations of silica (4,6,9). If large amounts of zirconia are precipitated, aggregation becomes more pronounced, as should be expected. The aggregation seemed to be less pronounced in the case of the particles produced using HCl.

Mechanical Properties

As described in Table I, two unfilled samples and eight filled samples were studied in the stress-strain experiments. The data were first represented as the dependence of the modulus on reciprocal elongation as suggested by the Mooney-Rivlin equation (4,17,20,21)

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

where $2C_1$ is an approximation to the high-deformation modulus (21), and $2C_2$ is a measure of the increase in non-affineness with increase in elongation (18,19,22). The isotherms thus obtained using the NH_4OH and the HCl are shown in Figures 4 and 5, respectively. The isotherms are seen to have good reversibility, as was also found to be the case with titania (2,7), and alumina (3), but not with silica (4,6,9). The values of the elasticity constants $2C_1$ and $2C_2$ obtained from the low-elongation, relatively linear portions of the isotherms are given in columns four and five of the Table. The in-situ filled

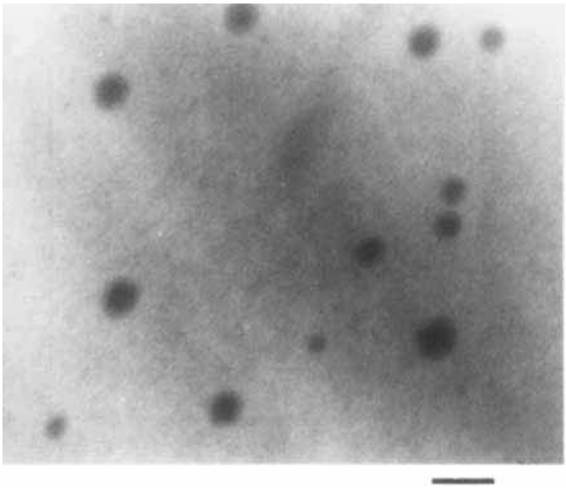

Fig. 2. Micrograph of the PDMS elastomer filled with 14.3 wt % zirconia from a 2% aqueous NH_4OH solution. In this and the following figure, the magnification is 10,000 x and the length of the bar corresponds to 1,000 Å.

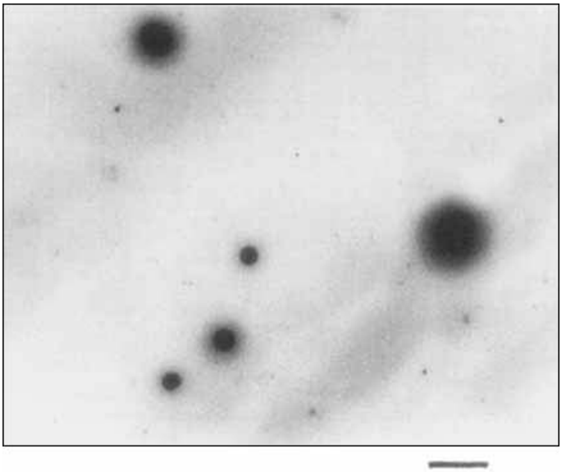

Fig. 3. Micrograph of the PDMS elastomer filled with 13.0 wt % zirconia from a 2 % aqueous HCl solution.

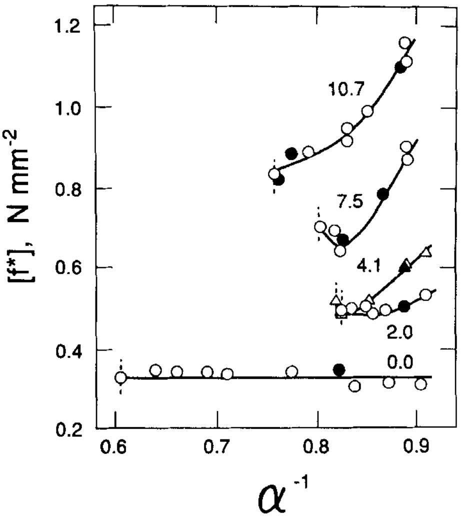

Fig. 4. Stress-strain isotherms at 25°C for the ZrO_2-filled PDMS networks obtained using NH_4OH as catalyst, represented as the dependence of the reduced stress or modulus on reciprocal elongation. The open symbols locate the results gotten using a series of increasing values of elongation α, and the 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.

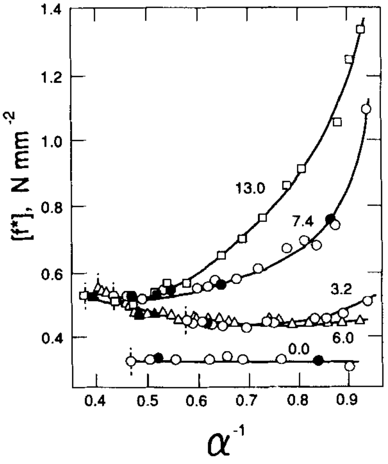

Fig. 5. Stress-strain isotherms for the filled PDMS networks obtained using HCl as catalyst; see legend to Figure 4.

networks are seen to have values of the modulus which are much higher than those of the corresponding unfilled network. Also, the upturns in $[f^*]$ observed at higher elongations in both types of networks clearly demonstrate the desired reinforcing effects.

The same stress-strain data were also represented in terms of the nominal stress against elongation. The advantage of this representation is the fact that the area under each curve represents the energy E_r required for rupture (23), which is a standard measure of toughness. Values of the elongation α_r and nominal stress $(f/A^*)_r$ at rupture and values of E_r, all obtained from the isotherms, are given in the last three columns of the Table. Although both catalysts are seen to give particles with good reinforcing ability, those prepared using the HCl are significantly better than those prepared using the NH_4OH. At approximately the same concentration of filler, the acid-catalyzed samples have values of the maximum extensibility and ultimate strength approximately twice those of the base-catalyzed samples. This could be due to the surface of the acid-catalyzed particles being larger due to smaller particle size and increased roughness, which could improve the bonding between the filler particles and the elastomeric matrix.

ACKNOWLEDGEMENT

It is a pleasure to acknowledge the financial support provided by the National Science Foundation through Grant DMR 89-10002 (Polymers Program, Division of Materials Research).

REFERENCES

(1) G. S. Sur and J. E. Mark, Eur. Polym. J., **21**, 1051 (1985).

(2) S.-B. Wang and J. E. Mark, Polym. Bulletin, **17**, 271 (1985).

(3) J. E. Mark and S.-B. Wang, Polym. Bulletin, **20**, 443 (1988).

(4) J. E. Mark and B. Erman, "Rubberlike Elasticity. A Molecular Primer", Wiley-Interscience, New York, 1988.

(5) P. Calvert and S. Mann, J. Mat. Sci., **23**, 3801 (1988).

(6) J. E. Mark, CHEMTECH, **19**, 230 (1989).

(7) S. J. Clarson and J. E. Mark, Polym. Comm., **30**, 275 (1989).

(8) C.-C. Sun and J. E. Mark, Polymer, **30**, 104 (1989).

(9) J. E. Mark and D. W. Schaefer, in "Polymer-Based Molecular Composites", ed. by D. W. Schaefer and J. E. Mark, Materials Research Society Symposium Volume, Pittsburgh, PA, 1990.

(10) D. W. Schaefer, J. E. Mark, D. McCarthy, L. Jian, C.-C. Sun, and B. Farago, in "Polymer-Based Molecular Composites", ed. by D. W. Schaefer and J. E. Mark, Materials Research Society Symposium Volume, Pittsburgh, PA, 1990.

(11) K. A. Mauritz and C. K. Jones, J. Appl. Polym. Sci., **40**, 1401 (1990).

(12) P. Xu, S. Wang, and J. E. Mark, in "Better Ceramics Through Chemistry, IV", ed. by B. J. J. Zelinski, C. J. Brinker, D. E. Clark, and D. R. Ulrich, Materials Research Society Volume, Pittsburgh, PA, 1990.

(13) J. E. Mark and J. L. Sullivan, J. Chem. Phys., **66**, 1006 (1977).

(14) D. C. Bradley, R. C. Mehrotra, and D. P. Gaur, "Metal Alkoxides", Academic Press, New York, 1978.

(15) B. E. Yoldas, J. Mat. Sci., **21**, 1080 (1986).

(16) A. Ayral, T. Assih, M. Abenoza, J. Phalippou, A. Lecomte, and A. Dauger, J. Mat. Sci., **25**, 1268 (1990).

(17) J. E. Mark and P. J. Flory, J. Appl. Phys., **37**, 4635 (1966).

(18) J. P. Queslel and J. E. Mark, Adv. Polym. Sci., **65**, 135 (1984).

(20) L. R. G. Treloar, "The Physics of Rubber Elasticity", Oxford University Press, Clarendon, 1975.

(21) J. E. Mark, Rubber Chem. Technol., **48**, 495 (1975).

(22) P. J. Flory, Polym. J., **17**, 1 (1985).

(23) M. A. Llorente, A. L. Andrady, and J. E. Mark, J. Polym. Sci., Polym.Phys.Ed., **19**, 621 (1981).