Fatigue-Resistant Silicone Elastomer Formulations

J. J. FITZGERALD,* W. T. FERRAR, T. D. BINGA

Office Imaging Research and Technology Development, Eastman Kodak Company, Rochester, New York 14650-2129

Received 5 October 1997; accepted 17 May 1998

ABSTRACT: Fatigue-resistant elastomers have been prepared using various metal oxides as fillers in poly(dimethylsiloxane) (PDMS)-based elastomers. The judicious choice of inorganic fillers produced elastomers that were stable under cyclic testing at elevated temperatures. These experiments were carried out using the Mechanical Energy Resolver, an instrument modified to reduce testing time from approximately 6 weeks to 60 h. Four elastomers showed stable storage moduli, were creep resistant, and showed less than 1% weight loss after 60 h. By comparison, a formulation prepared with alumina as the filler showed high rates of creep and greater than 10% weight loss. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 70: 1633–1641, 1998

Key words: poly(dimethylsiloxane); silicone; PDMS elastomer; cyclic stress; fatigue

INTRODUCTION

The design of elastomers whose properties are resistant to change when subjected to cyclic stress is of paramount importance in applications ranging from automotive tires to keypads. While the influence of cyclic stress on carbon-based elastomers has been widely studied by the automobile industry, only a few reports have been published that discuss the influence of cyclic stress on poly-(dimethylsiloxane) (PDMS).^{1–5}

The influence of cyclic stress on the mechanical properties of fumed silica-filled PDMS elastomer was studied by Bjork et al.⁶ These studies were done in tension at room temperature and showed that changes in the physical properties of the elastomer occurred that were related to the surface treatment of the filler. Fitzgerald et al. studied the influence of cyclic stress on aluminum oxide-filled PDMS samples in compression and at elevated temperature.⁷ The results showed that cyclic stress and elevated temperature caused the

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degradation of the filled PDMS elastomer. Due to the degradation of the elastomer there were changes in storage modulus, specific gravity, and height of the elastomer. More recent work has extended these findings to include copolymers containing poly(diphenylsiloxane) segments in PDMS.⁸

As expected, the rate of creep was highly dependent on the temperature and the applied force. The creep rate (change in height of the sample) was higher for a sample subjected to the sinusoidal loading compared to a sample held at a constant static load. The weight loss after a 60-h dynamic experiment was nearly an order of magnitude higher than for a sample quiescently heated at a similar temperature.

Speculation was that because of the high forces and temperature, scission of the Si—O bond was occurring. Once scission occurred there were a number of competing reactions that could take place. A typical reaction scheme might involve the "back-biting" of the ion resulting in the formation of cyclic products. Some of the cyclics formed were volatile. The loss of the polymer would be consistent with the observed loss of weight of the sample and the increase in the specific gravity of the sample. Another opportunity is for the reactive

Correspondence to: W. T. Ferrar.

^{*} Current address: GE Silicones, Waterford, NY 12188. Journal of Applied Polymer Science, Vol. 70, 1633–1641 (1998)

ions to form new bonds, thereby relieving the mechanical stress placed on the elastomer. This would be consistent with the observation that samples creep.

In this article we wish to further extend our studies to understand not only how the role of filler concentration influences the chemical changes occurring in the elastomer, but also determine how changes in the applied stress influences the degradation of the material. The majority of the work is with condensation-cured PDMS, but also includes elastomers prepared from diphenylsiloxane–PDMS copolymers via condensation and addition cure. Finally, we wish to consider how extremes in acidity/basicity of the filler surface influences the elastomers resistance to cyclic stress.

EXPERIMENTAL

Sample Preparation via Condensation Cure

Poly(dimethylsiloxane)-filler (Alcoa T-61 aluminum oxide) composites were prepared by mixing 5 pph of tetraethoxysilane (TEOS) with condensation curable PDMS purchased from Huls (unless otherwise noted PS342.5 was used as the base polymer), followed by the addition of the oxide filler. PS342.5 is a silanol-terminated PDMS with a molecular weight of 18,000. Condensation-crosslinked (diphenyl)(dimethyl)siloxane elastomers were also prepared from silanol-terminated (diphenyl)(dimethyl-)siloxane polymer, but were compression molded due to the higher viscosity. PS086 (Huls) is a silanol-terminated (diphenyl)(dimethyl)siloxane copolymer, and is specified by the manufacturer to contain 14 mol % of the diphenylsiloxane repeat units, although we found 18 mol % by ¹H-NMR spectroscopy. The polymer is specified by Huls to have a viscosity between 8000–12,000 centistokes, but no molecular weight information was given. We found the molecular weight by size exclusion chromatography to be very broad, with a number average (M_n) of 14,000 and a weight average (M_w) of 92,300, both in polystyrene equivalents. To ensure intimate mixing, the fillers were dispersed in the elastomer via a three-roll milling process. To the dispersion, 0.50 pph of dibutyl tin diacetate catalyst was added. The sample was stirred for 5 min before being transferred to a Semco tube. The sample was degassed for 5 min, and subsequently injected into a mold by turning the screw on the Semco tube. The sample was left at room temperature for 12 h, removed

from the mold, placed in an oven, and the temperature ramped to 65° C over 2 h and held at this temperature for 48 h. The oven was then ramped to 205° C over 20 h, and the sample was postcured for 16 h at this temperature.

Sample Preparation via Addition Cure

Sample slabs of tin oxide-filled, addition-crosslinked siloxane elastomer were prepared by mixing siloxane, the crosslinking agent, and filler on a three-roll mill. Catalyst was then stirred into the mixture. The mixture was compression molded using a hydraulyic press and allowed to crosslink at room temperature. The sample was removed from the mold after about 3 h. The sample was then placed in an oven at 175°C for 11 h.

The siloxane was PS784 (Huls) a vinyl-terminated, 16 mol % diphenyl-84 mol % dimethylsiloxane copolymer having a molecular weight of about 35,000. This material has a viscosity of 5000 centistokes. The siloxane was added so as to provide a final concentration of 60.52 vol % (19.16 wt %).

The crosslinking agent used was a trimethylsilyl-terminated poly(methylhydrosiloxane) PS123 (Huls). This material has a viscosity of 25 to 30 centistokes, a molecular weight of 2000 to 2500, and a methylhydro mole percentage of 30 to 35 (with the remainder dimethyl). The crosslinker was added to provide a volume percentage of 3.0 (0.96 wt %). Tin oxide particles were added to provide a concentration of 35 vol % (79.4 wt %).

The catalyst used was added to provide a volume percentage of 1.51 (0.48 wt %) of a catalyst solution. The catalyst solution was prepared by mixing 0.10 g of product PC075 and 10 g of product PS441.2 (Huls). Product PC075 is a neutral platinum divinyl complex (2–3% platinum concentration) of chloroplatinic acid and vinyl-terminated poly(dimethylsiloxane). PS441.2 is a vinyldimethyl-terminated poly(dimethylsiloxane) having a viscosity of 200 centistokes.

Mechanical Energy Resolver

Normally, six samples were stacked in the mechanical energy resolver (MER) (the individual samples were approximately 1.27 cm in diameter and 0.2 cm thick) such that the overall height of the sample was approximately 1.2 cm. The samples were run at constant force or constant strain in compression, with a frequency of 30 Hz at 218°C. Under constant force conditions the static load was maintained at 8 kg, and superimposed



Figure 1 Influence of cyclic stress under constant force on PDMS elastomer containing 35 vol % aluminum oxide: (A) storage modulus; (B) fractional length.

on this was a sinusoidally varying load of 4 kg rms. The samples were run in an ambient atmosphere.

Surface pH of Fillers

Fillers were slurried in an aqueous solution. The electrodes were placed in the slurry and the pH obtained.

RESULTS AND DISCUSSION

Fatigue of Alumina-Filled PDMS

A sample containing 35 vol % aluminum oxide was subjected to a 60-h isothermal fatigue experiment. These conditions caused a 60% change in height and a 30% increase in the storage modulus of the elastomer (Fig. 1), as well as a 9% wt loss of the elastomer (Table I). Based on changes in specific gravity of the elastomer, all the weight loss can be accounted for by assuming there is no filler loss, but volatilization of the PDMS.

A series of samples was prepared that contained from 10-50 vol % aluminum oxide. This was to address whether the changes in physical properties is the result of the high concentration of the aluminum oxide present in the sample. Under conditions of constant force, larger changes in the storage modulus are observed for samples containing higher concentrations of aluminum oxide (Fig. 2). However, the rate of creep is observed to increase as the concentrations of the aluminum

Table IWeight Loss of Condensation CuredElastomers During MER Testing

	Volume Percent Filler				
Filler type	20	25	30	35	40
Aluminum oxide	10.8		10.0	8.6	8.5
Tin oxide	1.0	0.7	—	0.3	0.3
Zinc oxide	_	0.3	0.4	0.2	0.3
Chromium oxide	_	1.1	1.0	0.8	0.4
Copper oxide		0.5	0.5	—	0.9

oxide decreases (Fig. 3). Both results can easily be explained. As the concentration of aluminum oxide increases, there is a corresponding increase in the storage modulus of the elastomer. When the sample is subjected to constant force, the strain experienced by the sample under these conditions decreases as the concentration of the aluminum oxide increases. Therefore, in a sense, the reduction in the rate of creep at the higher concentrations of the aluminum oxide is an artifact of the experimental conditions chosen to study the samples. In fact, it is probably better to compare the materials at constant strain.

If the strain experienced by the samples containing more filler is smaller, why is the change in storage modulus more pronounced at the higher concentrations as seen in Figure 2? To understand this result, we first considered the storage



Figure 2 Storage modulus versus time under constant force for samples of PDMS containing various amounts of aluminum oxide. (A) 50; (B) 45; (C) 40; (D) 35; (E) 30; (F) 20 vol % filler.



Figure 3 Fractional length versus time for samples under constant force of PDMS containing various amounts of aluminum oxide. (A) 20; (B) 30; (C) 35; (D) 40; (E) 45; (F) 50 vol % filler.

modulus of each sample plotted as a function of filler concentration (Fig. 4). These data were obtained from the initial measurement of the storage modulus at the start of the isothermal experiment. The slope on the storage modulus/volume fraction filler curve is steeper at higher concentrations of aluminum oxide (Fig. 4). The line through the data was the best fit obtained using a modified form of the Guth-Smallwood equation [eq. (1)], where E is used to calculate the modulus



Figure 4 Storage volume versus volume fraction filler of aluminum oxide in PDMS. The points represent the experimentally determined storage modulus and the line is the best fit using the modified Guth equation with f = 1.77.



Figure 5 Fractional length versus time under constant strain for PDMS elastomer containing 35 vol % aluminum oxide. (A) 1% constant strain; 0.0845 mm RMS; 1.91% wt loss. (B) 2.5% constant strain; 0.210 mm RMS; 14.17% wt loss. (C) 3% constant strain; 0.2586 mm RMS; 22.84% wt loss. (D) 5% constant strain; 0.4402 mm RMS; 39.40% wt loss (norm). (E) 7% constant strain; 0.619 mm RMS; 30.55% wt loss (norm).

of the filled elastomer, E_0 is the modulus of the unfilled elastomer, ϕ is the volume fraction of filler, and *f* is a shape factor related to the ratio of the anisotropy of the filler.⁹

$$E = E_0 (1 + 2.5f\phi + 141f^2\phi^2) \tag{1}$$

A good fit to the data is obtained with f = 1.77. However, the fatigue experiment results must also include a consideration of the weight loss from the elastomer. The results shown in Table I indicate that there is a substantial weight loss after 60 h for all samples filled with aluminum oxide. Therefore, even small weight losses at the higher concentrations of filler will result in large changes in the storage modulus of the elastomer.

The question still remains as to whether the large amount of degradation observed is the result of mechanical or chemical forces. Perhaps a better way to study these samples is under constant strain. To choose an appropriate strain, samples containing 35 vol % were studied at various initial constant strain (Fig. 5). The results shown in Figure 5 indicate the rate of creep is highly dependent on the strain. To analyze the data, an arbitrary failure point was chosen. The number of cycles required for the sample to creep 60% was calculated. At the lowest applied strains,



Figure 6 Fractional length versus time under 2.5% constant strain for PDMS elastomer containing various levels of aluminum oxide. (A) 20 vol % alumina; 3.96% wt loss. (B) 30 vol % alumina. (C) 35 vol % alumina; 14.17% wt loss. (D) 40 vol % alumina; 7.13% wt loss. (E) 45 vol % alumina; 18.19% wt loss. (F) 50 vol % alumina; 17.43% wt loss.

the sample took nearly ten million cycles to fail. At the highest applied strain ($\approx 7\%$), the sample reached failure in less than one million cycles.

Based on a reasonable time to reach failure, it was decided to study the samples at a constant initial strain of 2.5%. Previous studies have shown that in elastomers, the applied strain is actually amplified, because while the particle is rigid, all the strain is absorbed by the elastomer. The strain amplification factor increases as the concentration of filler increases.¹⁰ Therefore, it would be reasonable to expect that if the rate of creep was reduced as the concentration of filler decreased, that high local strains were initiating the scission of the Si—O bond. However, at constant initial strain the rate of creep is similar at all the concentrations studied (Fig. 6). The rate of creep does not decrease as the concentration of filler increases. The results suggest the initiating event leading to cleavage of the Si—O bond is not driven by mechanical forces.

If not mechanical, possibly the acidity or basicity of the surface of the filler could lead to the degradation of the elastomer. Fumed and precipitated silica are the most common fillers used to reinforce the PDMS elastomers. However, the thermal stability of silica-filled elastomers is thought to be decreased by attack of the surface hydroxyl group of the particle on the siloxane backbone, leading to chain cleavage and depolymerization. Thus, the high acidity of the filler particle results in poor thermal stability of the elastomer.¹¹ A similar tendency for degradation is thought to persist when very basic fillers are used with siloxanes. Basic fillers will attack the polar Si—O backbone, which results in chain cleavage. This sensitivity of the siloxane polymers to acid and base at elevated temperatures is consistent with the facile cleavage of the cyclic siloxane tetramer octamethylcyclotetrasiloxane $[Si_4O_4(CH_3)_8]$ by trace amounts of acid or base at temperatures as low as 100°C to give high molecular weight polymers.¹²

Recently, the *in situ* polymerization of metal alkoxides by the sol-gel process has been used to generate oxides in siloxane networks. This allows the preparation of very pure fillers, and thus comparisons about the mechanical properties can be related to the chemical composition of the filler. Mark and coworkers have shown that siloxane elastomers filled with titanium dioxide generated by a sol-gel process are more thermally stable than elastomers filled with silicon dioxide. The

Oxide (Source)	Measured pH	Particle Size (SEM) Microns	Particle Size (Coulter at 50%) Microns	
Aluminum oxide (Alcoa T-61)	9.2	1–20	9.3	
Tin oxide ^a (Keeling & Walker G2)	8.4	10-20	8.4	
Zinc oxide (Zinc Corp. Am.)	6.9	_	9.8	
Copper oxide (Aldrich)	7.0	1–10	7	
Chromium oxide (Meyers)	8.1	< 1 - 1.5	3.9	
Calcium oxide (Kodak)	12.3	2-15		
Titanium oxide (Kodak)	4.5	< 1 - 5	5	
Tungsten oxide (Aldrich)	5.4	10-100	—	

Table II Condensation Elastomer Formulations

^a Also tested Keeling and Walker CS3 (3 micron average particle size).

increased thermal stability is attributed to the more neutral surface of the titanium oxide compared to the silicon oxide.¹³

Comparison of Condensation-Cured PDMS Elastomers

Using the acid-base properties as a guide, a series of fillers were obtained from various companies. The pH of the fillers were measured using the techniques described in the Experimental section (Table II). The samples had pH values ranging from 3–12, and did not always agree with the expected acid-base properties of the oxides.¹⁴ Various fillers were chosen and formulated with the condensation-cured PDMS elastomer (Table II). The samples were studied under constant force and the creep behavior, changes in storage modulus, and weight loss were compared with samples containing aluminum oxide.

For those fillers that had pH values near neutral we found little or no degradation occurring in MER testing. Examples of MER curves for samples containing tin oxide, zinc oxide, copper oxide, and chromium oxide are shown in Figures 7-10, respectively. The weight losses of these formulations are compared to standard aluminum oxide formulations shown in Table I. The results of the experiments are quite remarkable, because those formulations containing tin oxide, copper oxide, chromium oxide, and zinc oxide exhibit a near zero rate of creep over the composition range studied. Further, the storage modulus typically exhibited no tendency to harden during the 60-h MER experiment (a slight hardening was observed for chromium oxide at 40 vol %). It was interesting that the weight loss of these formulations after the MER experiment were generally below 1%, while alumina-filled systems ranged from 8-15%.

However, not all fillers performed as well. For example, as shown in Figure 11(a,b), calcium oxide, and to a lesser extent titanium and tungsten oxides, exhibit significant hardening during the MER testing. pH measurements failed to predict performance of these latter two fillers. No filler exhibited a higher rate of creep than the aluminum oxide-filled samples (Fig. 1). In fact, even for those samples that hardened significantly, the creep rates were significantly less.

Diphenylsiloxane Condensation-Cured Elastomers

Evaluation of the fatigue properties was carried out for formulations made with the diphenyl-



Figure 7 (a) Storage modulus versus time for PDMS elastomers filled with tin oxide at (A) 20; (B) 25; (C) 30 vol % filler. (b) Fractional length versus time for PDMS elastomers filled with tin oxide at (A) 20; (B) 25; (C) 30 vol % filler (plots offset for clarity).

PDMS copolymer. Mechanical properties comparisons of the elastomers are difficult because of crosslink density differences due to varying molecular weights of the starting siloxanes. However, the same general trends in fatigue resistance were observed for the diphenylsiloxane elastomers as with the PDMS materials. The use of tin oxide or zinc oxide as the filler particle resulted in a material with greater fatigue resistance than a corresponding alumina filler.

A comparison of the fractional length changes with time was made for three elastomers prepared from 14 mol % diphenyl copolymer filled with 35 vol % tin, zinc, and aluminum oxides. The tin and zinc oxide elastomers showed little change in length over the time of the experiment. The



Figure 8 (a) Storage modulus versus time for PDMS elastomers filled with zinc oxide at (A) 40; (B) 35; (C) 30; (D) 25 vol % filler. (b) Fractional length versus time for PDMS elastomers filled with zinc oxide at (A) 40; (B) 35; (C) 30; (D) 25 vol % filler (plots offset for clarity).

alumina formulation showed a large change in length. Additionally, the alumina-filled elastomer had a weight loss of 2.48%, while the weight losses for the tin and zinc oxides were only 0.27 and 0.58%, respectively. A comparison of the storage modulus showed little change in storage modulus over the time of the experiment.

Diphenylsiloxane Addition Cured Elastomers

Addition polymerization was carried out using the vinyl-terminated (diphenyl)(dimethyl)siloxane copolymer containing 16 mol % diphenylsiloxane. As in the experiments described above, tin oxide or zinc oxide as the filler particle resulted in a material with greater fatigue resistance than a corresponding alumina filler. The 35 vol % tin oxide-filled sample had the best characteristics, with both the length and storage modulus virtually unchanged over 60 h at elevated temperature. The weight loss for this sample was 0.24%, also consistent with good fatigue resistance on the formulation. The formation of stable products from both addition and condensation cured elastomers was consistent with filler-induced degradation of the polymer, not an interaction of the filler with the curing catalyst.

Oxide Purity

Additional analysis of the particles that we used was carried out using Atomic Absorption Spec-



Figure 9 (a) Storage modulus versus time for PDMS elastomers filled with copper oxide at (A) 40; (B) 30; (C) 25 vol % filler. (b) Fractional length versus time for PDMS elastomers filled with copper oxide at (A) 40; (B) 30; (C) 25 vol % filler (plots offset for clarity).



Figure 10 (a) Storage modulus versus time for PDMS elastomers filled with chromium oxide at (A) 40; (B) 35; (C) 30; (D) 25 vol % filler. (b) Fractional length versus time for PDMS elastomers filled with chromium oxide at (A) 40; (B) 35; (C) 30; (D) 25 vol % filler (plots offset for clarity).

troscopy to look for impurities in the particles that would raise the pH. Five oxides were examined for sodium, calcium, and magnesium and the results are reported in Table III. Of the five oxides, tin oxide, zinc oxide, and copper oxide showed only trace amounts of basic impurities (less than 5 PPM). All three of these oxides produced fatigue-resistant elastomers. In contrast, oxides that contained the above impurities showed some degree of fatigue by MER testing. The impurities are probably in the oxide form. Titanium dioxide contained significant amount of these impurities, and Figure 11 shows that the corresponding elastomer does show a small



Figure 11 (a) Storage modulus versus time for PDMS elastomers containing 30 vol % filler. (A) calcium oxide; (B) titanium dioxide; (C) tungsten oxide. (b) Fractional length versus time for PDMS elastomers containing 30 vol % filler. (A) Calcium oxide; (B) titanium dioxide; (C) tungsten oxide.

amount of fatigue in the MER testing. The filler with the highest levels of impurities is the aluminum oxide. High levels of sodium, calcium, and

Oxide	Sodium	Calcium	Magnesium
$\begin{array}{c} \mathrm{Al_2O_3}\\ \mathrm{SnO_2}\\ \mathrm{ZnO}\\ \mathrm{CuO}\\ \mathrm{TiO_2} \end{array}$	700 ppm 0 0 0 0	300 ppm 0 5 5 250	300 ppm 10 0 200

magnesium were found in this material. Additionally, the product literature of various aluminas list Na_2O as an impurity in levels as high as 0.5 wt %.

CONCLUSIONS

Cyclic stress, at an elevated temperature, can accelerate the degradation of filled PDMS elastomers either under constant force or constant strain conditions. The results suggest that cleavage of the Si—O bonds occurs and is the initiating event leading to chemical changes in the elastomer. It appears that a significant amount of "back-biting" reactions occur, resulting in oligomers that are volatile. This is evidenced by both the loss of weight of the elastomer and change in specific gravity.^{7,8} Also important is the reaction of ions with other chains in the network. By reaction with other chains, it is possible to relieve the mechanical stress placed on the sample.

The results presented here suggest that the surface properties of the fillers play a role in determining the stability of the elastomers at elevated temperature. In an ideal case, the pH of the filler surface may be the controlling factor. A more thorough analysis suggest that the impurities, possibly from the manufacturing of the oxide, also can play a role in controlling the stability at elevated temperature. The observed fatigue resistance seems general in nature, occurring over a variety of different siloxane polymers and copolymers used as the base polymers. Although other factors such as the curing chemistries may play an important role in the stability of the elastomers, the fatigue resistance was observed in both condensation and addition-cured materials.

This article was based on paper No. 84 presented at the 151st Meeting, Rubber Division, American Chemical

Society, Anaheim, CA, May 6–9, 1997. The authors would like to thank R. J. Patti for help with pH and atomic adsorption measurements on the fillers. The authors are also grateful to J. R. Babiarz and M. W. Fichtner for preparation of the silicone elastomers.

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