

Stabilization of Filled Polysiloxane Elastomers to Cyclic Stress at Elevated Temperature Through Use of Zinc Oxide Fillers

SUSAN A. VISSER

Eastman Kodak Company, Rochester, New York 14650-2129

Received 6 May 1996; accepted 13 October 1996

ABSTRACT: The susceptibility of filled polysiloxane elastomers to cyclic stress at elevated temperatures is investigated. It is shown that zinc oxide fillers, unlike other fillers examined previously, can produce filled elastomers with remarkable stability to combined mechanical and thermal stresses. The influences of filler concentration, diphenylsiloxane incorporation, and molecular weight between network crosslinks are examined. The data demonstrate that the elastomer stability to cyclic stress at elevated temperature increases with increasing filler content and does not correlate with diphenylsiloxane content. It is suggested that chemical interactions between the polysiloxane network and the filler surfaces control the response to cyclic stress at elevated temperature and that the response strongly depends on the type of filler selected. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **64**: 1499–1509, 1997

Key words: polydimethylsiloxane; poly(dimethylsiloxane-*co*-diphenylsiloxane); metal oxide filler; cyclic stress

INTRODUCTION

The excellent thermal stability of polysiloxane elastomers makes them useful for high temperature applications. However, their low mechanical strength often necessitates the incorporation of inorganic fillers. Although fillers can improve the mechanical properties of a polysiloxane elastomer, they can also change the thermal stability of the materials.

Catalysis of degradation or stabilization of silicones by metal-containing additives is well known. Yang demonstrated that certain fillers can significantly influence the heat aging response of polydimethylsiloxane (PDMS) elastomers.¹ Willis and Shaw² demonstrated catalysis of Si—C bond scission in PDMS fluids by cuprous oxide surfaces with an activation energy much less than the 33–36 kcal/mol reported for the un-

catalyzed reaction. Formation of crosslinked PDMS films on aluminum, cadmium, and zinc surfaces in heated PDMS fluids has been observed,³ and Si—C bond cleavage and subsequent crosslinking induced by metal surfaces has been reported.⁴ Stabilization of vulcanizates of methylvinylsilicones to heat aging by certain rare earth metal oxides, especially cerium oxide and red iron oxide, has been reported.⁵ Nielsen demonstrated that iron octoate inhibits a free radical oxidative degradation of PDMS fluids above 150°C and catalyzes a non free radical oxidation of PDMS fluids below and above 150°C,⁶ which is consistent with earlier reports on the catalytic effect of metal salts on oxidative degradation of hydrocarbons.⁷ As noted in Shelton's review⁸ of oxidation processes in elastomers, rendering metal salts insoluble or fully chelating the metal ion can neutralize its catalytic activity. However, for certain metals, partial chelation can enhance activity.

An additional element to the long-term stability of polysiloxane elastomers is added when cyclic

stress is applied in addition to elevated temperature. Aluminum oxide fillers incorporated into a PDMS elastomer subjected to cyclic stress at elevated temperature accelerate the degradation of the elastomer.^{9,10} Certain *in situ* precipitated fillers have been identified that decrease the creep of PDMS elastomers subjected to cyclic stress at elevated temperature,¹¹ but no blended filler has been identified that stabilizes the polysiloxane network. However, incorporation of diphenylsiloxane groups into the elastomer backbone has been shown to stabilize the network in the presence of an aluminum oxide filler.¹⁰

In this report zinc oxide filled polysiloxanes containing 0–24 mol % diphenylsiloxane (DPS) units are examined for their response to cyclic stress at elevated temperature. Contrary to predictions derived from earlier reports in the literature on the effect of zinc-containing fillers on network stability,³ it is shown that zinc oxide stabilizes the elastomer to combined mechanical and thermal stresses. The effects of DPS incorporation, filler concentration, and molecular weight between crosslinks in the elastomer are examined. Further, the addition of iron oxide or tin oxide to the zinc oxide filler is also shown to give a polysiloxane elastomer that is stable to cyclic stress at elevated temperature.

EXPERIMENTAL

Sample Preparation

Filled polysiloxane elastomers were prepared by combining a network-forming polymer, a crosslinking polymer, filler, and catalyst. The network-forming polymers were dimethylvinyl-terminated PDMS or poly(diphenylsiloxane-*co*-dimethylsiloxane) (PDPSDMS). The molar content of DPS and dimethylsiloxane (DMS) units in the PDPSDMS are indicated by percentages preceding the three letter abbreviations: *P*(16% DPS/84% DMS) is a copolymer containing 16 mol % DPS and 84 mol % DMS. The copolymers were random. All polymers except the *P*(11% DPS/89% DMS), PLY-7630, were purchased from United Chemicals. PLY-7630 was purchased from Nusil Technologies, Inc. The polymers were used as received. Their DPS contents and weight average molecular weights (M_w) are listed in Table I. Molecular weights are reported relative to polystyrene standards. The molecular weight data

Table I Characteristics of Polysiloxanes

Polymer	DPS Content (mol %)	DMS Content (mol %)	M_w
PS442	0	100	25,200
PS732	3	97	23,000
PLY-7630	11	89	40,000
PS782	16	84	14,100
PS793	24	76	13,000
PS784	16	84	44,800
PS785	16	84	68,200

Weight average molecular weights (M_w) were measured using size exclusion chromatography. Results are presented relative to polystyrene standards.

were collected by size exclusion chromatography in toluene for PDMS and in THF for PDPSDMS.

The crosslinking polymer was a trimethylsilyl-terminated poly(methylhydro-*co*-dimethylsiloxane), sold as PS123 by United Chemicals. The methylhydrosiloxane content is 40 mol %. The catalyst PC075, obtained from United Chemicals, was composed of 2–3% platinum concentration in vinyl-terminated PDMS. It was diluted with the dimethylvinyl-terminated PDMS PS441.2, also sold by United Chemicals. These materials were also used as received.

Addition-cured, zinc oxide filled samples were prepared by blending 5 parts by weight crosslinking polymer PS123 to 100 parts network-forming polymer. Network-forming polymers used to prepare these samples were PS442 (0% DPS), PS732 (3% DPS), PLY-7630 (11% DPS), PS782 (16% DPS), and PS793 (24% DPS). Zinc oxide filler (Zinc Corporation of America, XX503R; volume mean particle size 8 μ m) was added to the required concentration by blending the mixture on a three-roll mill. A catalyst mixture containing 2.2 g PC075 platinum catalyst dispersion in 100 g PS441.2 vinyl-terminated PDMS was added to the filled polymer/crosslinker at the ratio of 1 mg catalyst mixture to 1 g of filled polymer/crosslinker. The catalyzed material was mixed, degassed, and injected into a mold, where it was cured at 175°C for 10 min. The material was removed from the mold and cured as a free slab through a 2-h ramp-up to 200°C and holding for an additional 8 h at 200°C.

Materials were prepared from combinations of zinc oxide filler with other fillers using procedures similar to those described above. Other fillers used were tin oxide (MEI Corporation, G2 grade; volume

mean particle size 9 μm) and iron oxide (Mapico Red 297; volume mean particle size $< 1 \mu\text{m}$).

Cyclic Stress/Dynamic Creep Testing

Cyclic stress data were collected using a dynamic mechanical analyzer (also known as a mechanical energy resolver or MER)¹² as described previously.⁹ For each material a cylindrical sample 1.27 cm in diameter and 1.2 cm in thickness was placed in the dynamic mechanical analyzer, and the sample was exercised under compression at a frequency of 30 Hz at 218°C. The static load was maintained at 8 kg, and a sinusoidally varying load of 4 kg root mean square (RMS) was superimposed on the static load. The samples were run in ambient air atmosphere for 60 h. Corrected storage moduli were calculated as described elsewhere.⁹

Toluene Swell and Effective Crosslink Density Measurements

The method outlined by Bueche¹³ and Bobear¹⁴ was used to extract and swell the samples. Initially the samples were extracted with toluene by placing them in a vial with an excess of toluene for 24 h at 50°C. The toluene was then discarded; fresh toluene was added and the samples were allowed to equilibrate an additional 24 h at room temperature. The samples were removed from the toluene and blotted to remove excess toluene. Then their swollen weights were measured. The samples were dried to a constant weight at 110°C in a vacuum oven and weighed to the closest milligram. Finally, the sample's specific gravity was measured using ASTM Standard D297 15.1.2.

Effective crosslink density calculations were completed using $\chi_{\text{PDMS-toluene}}$ ¹⁵ for filled elastomers of pure PDMS and of P(3% DPS/97% DMS) and $\chi_{\text{P(16% DPS/84% DMS)-toluene}}$ ¹⁰ for filled elastomers of P(16% DPS/84% DMS) and P(24% DPS/76% DMS). The calculation details and caveats inherent in the use of effective χ values for the PDPSDMS systems are discussed elsewhere.¹⁰

RESULTS AND DISCUSSION

Addition-cured, aluminum oxide filled PDMS and PDPSDMS elastomers exhibit extreme susceptibility to degradation under conditions of cyclic stress at elevated temperatures.¹⁰ It was suggested that the degradation resulted from surface

chemical properties of the aluminum oxide filler. Here, the use of a different filler type was explored to determine if this chemical argument is valid or if a purely mechanical argument arising from the incompressibility of the filler is required to understand the degradation phenomena.

Zinc Oxide Filled PDMS: Effect of Filler Content

The dynamic creep testing results obtained for zinc oxide filled, addition-cured PDMS are shown in Figure 1. The sample shows almost no dimensional change or creep and no change in storage modulus throughout the 60-h experiment. In contrast, a comparable aluminum oxide filled sample, shown in Figure 1(b), displayed a 60% reduction in the height (length) and a 27% decrease in storage modulus under identical conditions.¹⁰ Further, the zinc oxide filled PDMS displayed a weight loss of only 1.1% compared to 6% for the aluminum oxide filled PDMS.¹⁰

The apparent reduction in degradation of the zinc oxide filled sample suggests a difference in either the interaction of the filler surface with the PDMS matrix or in the chemical composition of the filler surface that alters the balance of degradation reactions. Degradation of a PDMS network proceeds as a result of chain scission and crosslinking reactions. At temperatures in excess of 400°C, polysiloxanes undergo these reactions without requiring a catalyst.¹⁶ The presence of external factors can cause the degradation reactions to proceed at lower temperatures.¹⁷ The role of metal-containing fillers in catalyzing degradation reactions of polysiloxanes was discussed above. Changes in the rates of those reactions or inhibition of the reactions, induced by the chemical nature of the filler surface, could produce the observed resistance to creep under cyclic stress.

In addition to chemical interaction, a mechanical origin for PDMS degradation under cyclic stress conditions was suggested.⁹ The model postulated that weak polymer–filler interactions allow slippage of polymer chains along the filler surface during a cyclic stress experiment. Friction generated by the chain slippage provides the heat required to enable the Si—O bond cleavage, a chain scission reaction, causing creep. The reactive ion fragments generated by the chain scission participate in chain crosslinking reactions, causing an increase in storage modulus.

The difference in the initial storage moduli of the zinc oxide versus the aluminum oxide filled PDMS at 35 vol % filler loading (6.5 MPa for zinc

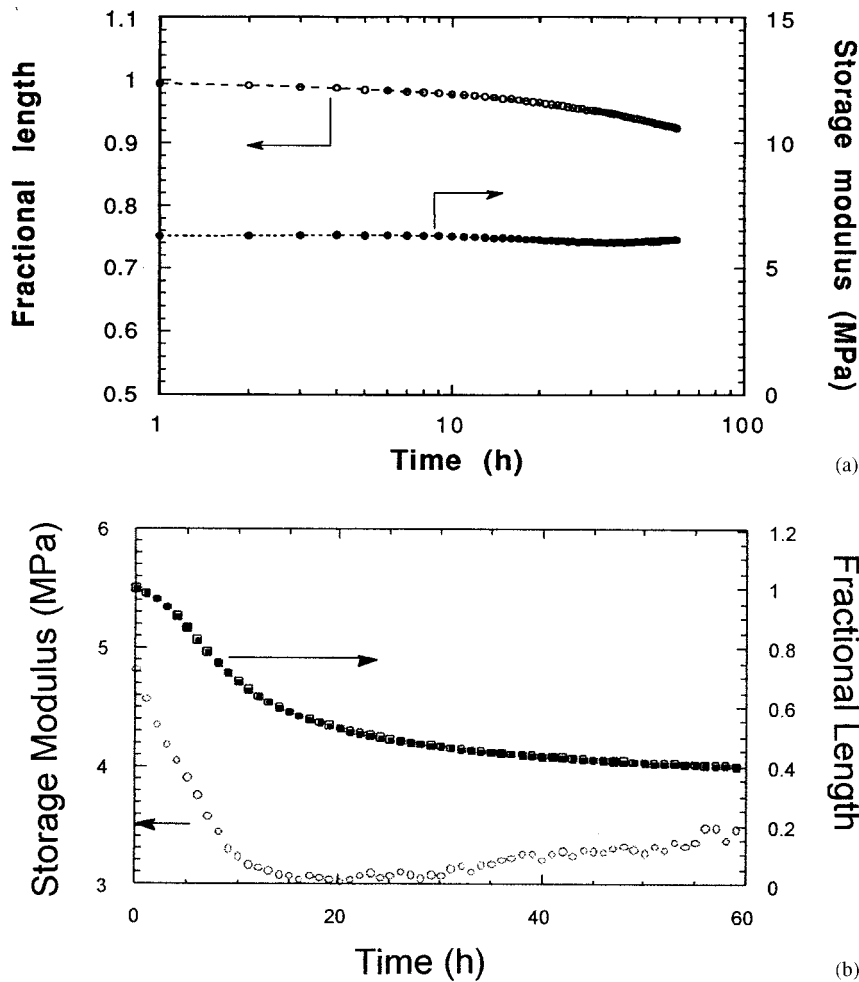


Figure 1 Dynamic creep testing results for PDMS filled with (a) 35 vol % zinc oxide and (b) 35 vol % aluminum oxide (data from Visser et al.¹⁰).

oxide filler and 4.8 MPa for aluminum oxide filler) suggests a slightly stronger polymer–filler interaction for the zinc oxide filler. In the mechanical model stronger polymer–filler interactions result in lower chain slippage and frictional heat generation. Less chain scission and creep result. Therefore, the stability of the zinc oxide filled PDMS compared to the aluminum oxide filled PDMS might be predicted by the mechanical model. A chemical catalysis role played by the filler cannot be dismissed on the basis of these data, however.

To further evaluate the influence of zinc oxide filler on the stability of filled PDMS to cyclic stress at elevated temperature, the effect of changing filler concentration was investigated. The cyclic stress testing results appear in Figure 2. Creep of the zinc oxide filled PDMS decreases as filler content increases. Similar behavior was observed for aluminum oxide filled PDMS previously¹⁸;

however, the extent of the creep was much larger for the aluminum oxide filled PDMS. At 20 vol % filler loading, the aluminum oxide filled PDMS exhibited a 60% change in length¹⁸ versus a 13% change for the zinc oxide filled sample examined here. At 40 vol % filler loading, the aluminum oxide filled PDMS sample length¹⁸ changed by 50% whereas the zinc oxide filled sample changed only 8%.

According to Oberth's model¹⁹ of the effect of filler concentration on the properties of filled elastomers, an increase in filler content results in a decrease in the stress concentration factor and decreased stress on the polymer matrix. Previous work has shown that decreasing the applied stress in a dynamic creep experiment results in less creep of the elastomer. Therefore, decreasing creep with increasing filler content is expected. However, Oberth's model would not predict the

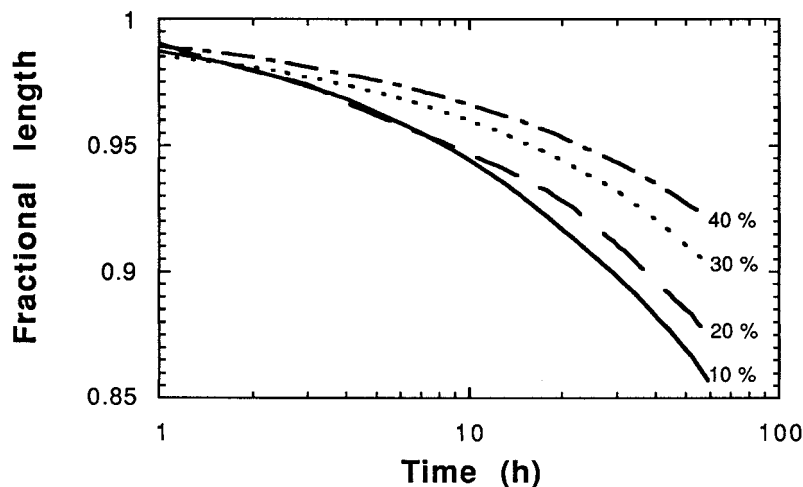


Figure 2 Influence of zinc oxide filler concentration on dynamic creep testing results of PDMS.

differences observed between the two different filler types. The significantly smaller change in the amount of creep with filler concentration for the zinc oxide filled PDMS suggests that zinc oxide has the ability to stabilize the PDMS elastomer, that the aluminum oxide filler catalyzes the degradation of the elastomer, or that both effects are occurring.

Variation of the storage modulus of the zinc oxide filled PDMS during the cyclic stress experiment for various filler loadings is shown in Figure 3. The zinc oxide filled materials display nearly

constant storage moduli during cyclic stress testing, independent of filler concentration. In contrast, the aluminum oxide filled samples examined previously had storage moduli that remained nearly constant for only 20 and 30 vol % filler; at 40 vol % filler, the storage modulus of the sample changed by 107% during the course of the experiment.¹⁸ The consistency of the storage moduli for the zinc oxide filled materials is further evidence of resistance of these materials to degradation under cyclic stress.

The weight loss experienced by the zinc oxide

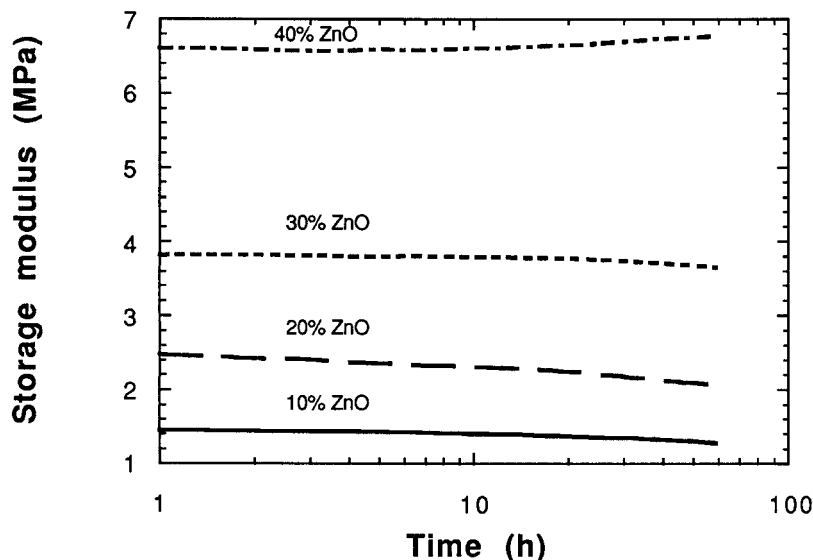


Figure 3 Dependence of storage modulus on time in dynamic creep experiments on PDMS elastomers containing various amounts of zinc oxide. Filler amounts indicated are in volume percent.

Table II Effect of Filler Concentration on Weight Loss of PDMS Elastomers Subjected to Cyclic Stress Testing

Filler Amount (vol %)	Zinc Oxide Filler		Aluminum Oxide Filler ^a	
	Weight Loss ^b (%)	Polymer Loss ^c (%)	Weight Loss ^b (%)	Polymer Loss ^c (%)
10	1.2	4.0	—	—
20	0.8	1.3	10.8	18.6
30	0.9	1.1	8.6	21.6
40	0.7	0.7	8.5	13.8

^a Data from Fitzgerald and Nielsen¹⁸ for PDMS filled with aluminum oxide.

^b Weight loss of filled elastomer after 60-h dynamic creep experiment.

^c Weight loss normalized for amount of polymer in the sample, assuming entire weight loss results from loss of volatile cyclic siloxanes.

filled PDMS is also quite low compared to aluminum oxide filled PDMS. Weight loss data appear in Table II. Weight loss during the cyclic stress experiment is postulated to result from reaction of the ionic fragments with their polymer chains in a backbiting or a random chain scission reaction.^{20,21} The reaction results in the formation of volatile cyclic species that are lost during the cyclic stress experiment. Assuming that the weight loss is entirely attributable to loss of the polymer matrix and not of the filler, the polymer loss results of Table II were calculated. A decrease in polymer loss with increasing zinc oxide content is observed, suggesting that zinc oxide may be playing an active role in changing the relative rates of the PDMS degradation reactions rather than only the passive role envisioned by the mechanical frictional heat generation argument. Further, the weight loss of an unfilled PDMS elastomer subjected to cyclic stress testing at loads only half of those used here showed a weight loss of 5.58%.¹¹ Because network degradation and weight loss are expected to increase with increasing load in cyclic stress testing, the lower weight losses exhibited by the zinc oxide filled elastomers clearly demonstrate the stabilizing effect of the filler.

An enhanced understanding of the network structure and polymer–filler interactions can be obtained through swelling studies of the filled elastomers. Extensive use has been made of the Flory–Rehner network theory of swelling²² to estimate the crosslink density of elastomers. However, there are limitations to the theory when it is applied to filled elastomers. Bueche assumed that the equilibrium modulus and equilibrium volume swelling of a filled network in a solvent

may be analyzed by relationships applicable to unfilled networks of identical composition and that apparent increases in the number of network branches results from network–filler interactions.¹³ Henry followed Bueche's assumption and used Flory–Rehner theory to analyze the crosslink density of filled PDMS networks with the introduction of a correction for the network volume occupied by filler particles.²³ The effective crosslink density comprises both the true crosslink density from rubber elasticity theory and the apparent increase in crosslink density resulting from network–filler interactions.

Kraus noted that the degree of interaction of the filler with the elastomer will influence the degree of swelling of a filled network, potentially leading to erroneous calculations of crosslink density in Flory–Rehner calculations.²⁴ Adherent fillers that exhibit strong polymer–filler interactions will swell in a manner consistent with Bueche's assumptions, permitting calculation of effective crosslink densities completed with Flory–Rehner theory. Nonadherent fillers will swell with vacuole formation around the filler surfaces, resulting in an increase in the apparent swelling of the rubber and in erroneously low crosslink densities calculated with Flory–Rehner theory.

According to Kraus' theory, polymer–filler adhesion can be estimated in a filled elastomer system by determining the relationship between the swell ratio Q of a filled elastomer in a good solvent to the filler/polymer ratio $\varphi/(1 - \varphi)$, where φ is the volume fraction of filler. If Q decreases as $\varphi/(1 - \varphi)$ increases, the filler is adherent and Flory–Rehner theory may be applied for crosslink density calculations.

Table III Influence of Filler Concentration on Swelling of Zinc Oxide Filled PDMS

Filler Concn (vol %)	Swell Ratio Q	$\varphi/(1 - \varphi)$
10	2.3	0.11
20	1.8	0.25
30	1.4	0.43
40	1.1	0.67

The results for swelling of the zinc oxide filled PDMS networks in toluene are shown in Table III. As the data demonstrate, Q decreases with increasing $\varphi/(1 - \varphi)$, indicating that zinc oxide is an adherent filler. The presence of the filler does not permit calculation of absolute crosslink densities, but effective crosslink densities may be calculated. Therefore, the Flory–Rehner theory,²² as modified for filler concentration by Henry,¹⁵ was used to calculate the effective crosslink densities of the filled systems before and after dynamic creep testing.

The effective crosslink densities of the zinc oxide filled PDMS samples are shown in Figure 4. An increase in effective crosslink density with increasing filler content is observed, consistent with the assumption of slight reinforcement of the PDMS network by polymer–filler interactions. At low filler loadings, no change in effective crosslink

density occurs as a result of cyclic stress testing whereas a small increase in effective crosslink density is seen for higher filler loadings. The increasing change in effective crosslink density with increasing filler loading matches the dynamic creep results in which less creep was observed for materials with higher filler loading. The increase at higher filler loadings is not accompanied by an increase in storage modulus, however. Either other changes in network structure, such as the presence of a higher concentration of dangling ends, or changes in polymer–filler interactions that are not considered in the theory could explain the experimental observations.

Zinc Oxide Filled PDPSDMS: Effect of DPS Content

Incorporation of DPS units into a PDMS elastomer increases its thermal stability.^{25,26} DPS incorporation also improves the stability of aluminum oxide filled polysiloxanes subjected to cyclic stress at elevated temperatures.¹⁰ The response of zinc oxide filled polysiloxanes with varying DPS content to cyclic stress at elevated temperatures is shown in Figure 5. The response of two aluminum oxide filled polysiloxanes¹⁰ is shown for comparison. The zinc oxide filled polysiloxanes display very little creep (dimensional change) compared to the aluminum oxide filled samples and little

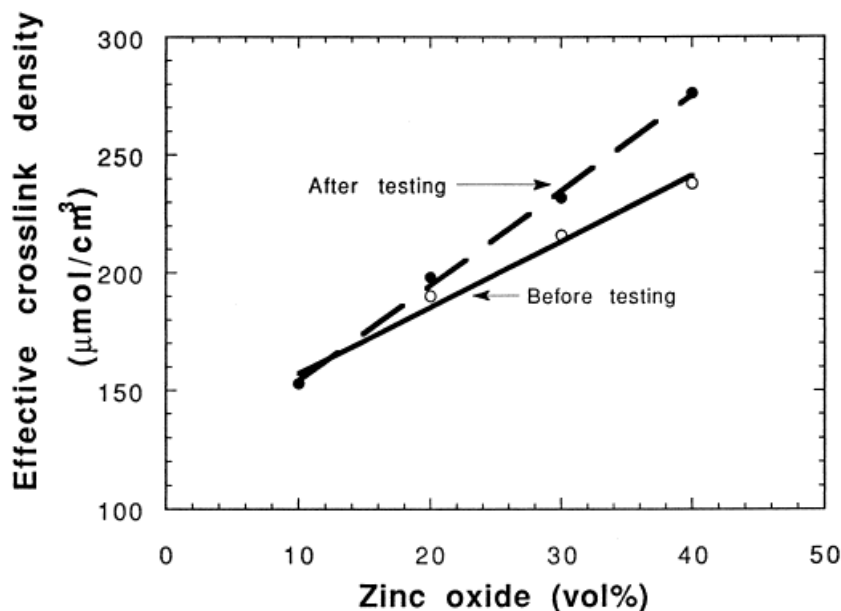


Figure 4 Effective crosslink density as a function of zinc oxide loading for PDMS elastomers before and after dynamic creep testing.

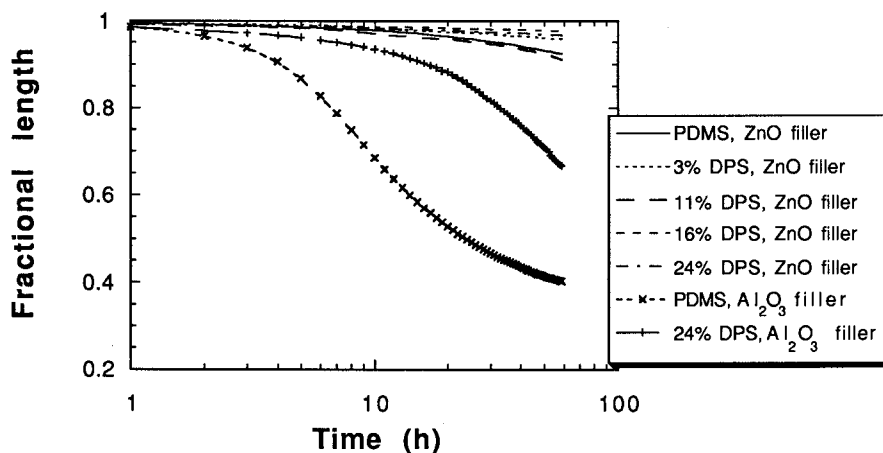


Figure 5 Influence of DPS content on the dynamic creep response of zinc oxide and aluminum oxide filled polysiloxanes. Filler loading is 35 vol % for all samples.

variation based on DPS content. No correlation between extent of creep and DPS content is observed.

The dynamic creep data summarized in Table IV show that the storage moduli of the zinc oxide filled PDPSDMS samples remain virtually invariant during the cyclic stress test. Weight loss also remains low and independent of DPS content for the zinc oxide filled elastomers. This contrasts sharply with the behavior of the aluminum oxide filled elastomers examined elsewhere.¹⁰

Influence of Network-Forming Polymer Molecular Weight on Properties of Filled PDPSDMS Elastomers

The influence of the molecular weight of the PDPSDMS network-forming polymer used to

form the elastomer network on the cyclic stress testing response is shown in Figures 6 and 7. Increasing the network-forming polymer molecular weight at constant DPS content increases the creep of the materials, and it causes a slight increase in storage modulus during the 60-h experiment. Two causes may account for these differences.

First, the elastomers were prepared at constant crosslinker concentration. As network-forming polymer molecular weight increases, an excess of crosslinker would be present, giving a less fully crosslinked network that would be more susceptible to change during the dynamic creep experiment.

Second, a higher molecular weight prepolymer translates to a higher molecular weight between crosslinks. Because only a single chain scission

Table IV Summary of Dynamic Creep Responses of 35 vol % Zinc Oxide or 35 vol % Aluminum Oxide Filled Polysiloxanes Containing Varying DPS Contents

DPS Content (mol %)	Filler	Storage Modulus (MPa)		Creep (%)	Weight Loss (%)
		Initial	Final		
0	ZnO	6.5	6.1	7.6	1.1
3	ZnO	7.2	7.4	4.0	1.1
11	ZnO	4.0	3.4	8.8	0.3
16	ZnO	6.3	6.3	2.3	1.2
24	ZnO	9.3	10.1	3.3	0.8
0	Al ₂ O ₃ ^a	4.8	3.5	60.0	6.0
3	Al ₂ O ₃ ^a	4.8	5.1	55.4	5.1
16	Al ₂ O ₃ ^a	4.1	7.0	51.9	6.5
24	Al ₂ O ₃ ^a	4.8	6.3	33.3	4.4

Data from Visser et al.¹⁰

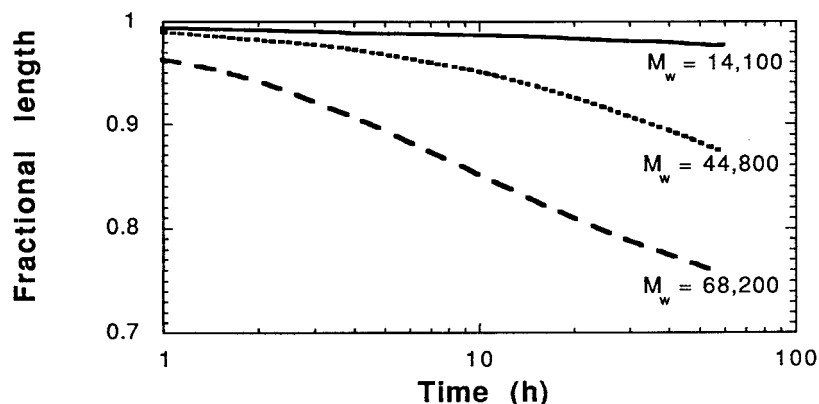


Figure 6 Influence of prepolymer molecular weight on dynamic creep response of *P*(16% DPS/84% DMS) filled with 35 vol % zinc oxide.

between crosslinks is necessary for creep of the elastomer, a higher molecular weight between crosslinks means fewer chain scission reactions are necessary before measurable creep occurs in the cyclic stress experiment. Therefore, although the rate of chain scission may be constant for the varying molecular weights, the creep will increase with network-forming polymer molecular weight.

PDPSDMS with Mixed Fillers

Mixing filler types in polysiloxane elastomers can improve the performance in certain cases. For example, in condensation-cured PDMS, mixing zinc oxide and tin oxide gives enhancements in resis-

tance to creep under cyclic stress and in thermal conductivity compared to the fillers taken singly.²⁷ A condensation-cured PDMS containing 17.5 vol % zinc oxide and 17.5 % aluminum oxide showed good stability to cyclic stress and enhanced thermal conductivity.²⁸ Mixed fillers were examined in the addition-cured PDPSDMS elastomers to determine if additional benefits could be derived for the zinc oxide filled systems.

The dynamic creep response and properties of *P*(16% DPS/84% DMS) filled with zinc oxide and tin oxide (17.5%/17.5% v/v) is shown in Figure 8. Almost no change in length or in storage modulus is observed in the mixed filler system. Weight loss for this material was 1.0%, indicating that

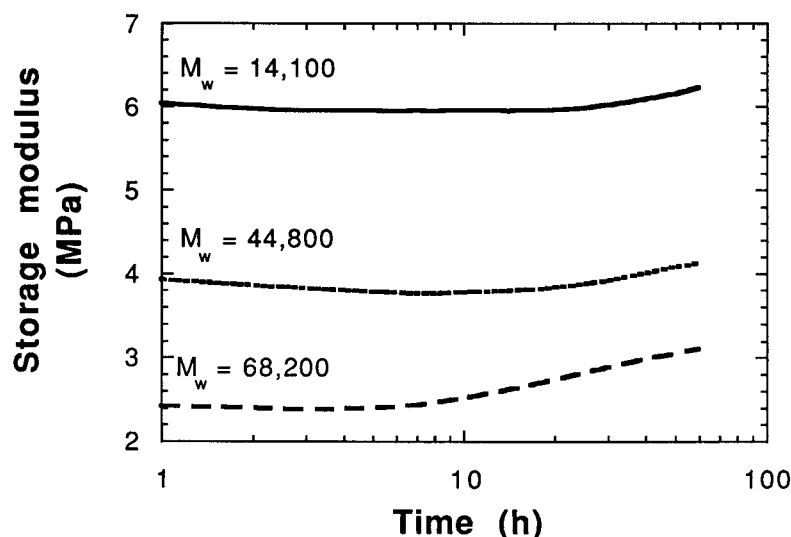


Figure 7 Influence of network-forming polymer molecular weight on response of *P*(16% DPS/84% DMS) filled with 35% zinc oxide to cyclic stress at elevated temperature.

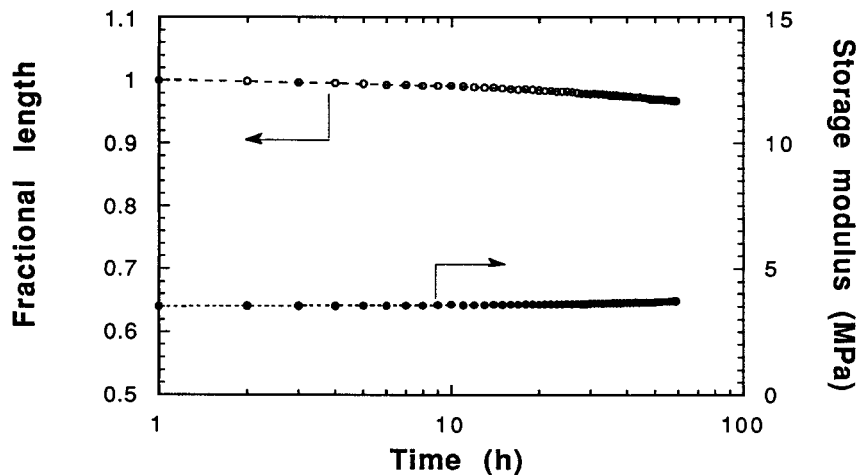


Figure 8 Response of *P*(16% DPS/84% DMS) filled with 17.5 vol % tin oxide and 17.5 vol % zinc oxide to cyclic stress at elevated temperature.

the elastomer with the combined fillers retains resistance to degradation under cyclic stress at elevated temperature. Another literature article shows that tin oxide alone can also prevent elastomer degradation.²⁹

The cyclic stress testing results for *P*(16% DPS/84% DMS) filled with 30 vol % zinc oxide and 5 vol % iron oxide are shown in Figure 9. The weight loss for this sample was 0.5%. As can be observed, this material is stable to cyclic stress at elevated temperature. The well-known ability of iron oxides to improve the heat aging properties of polysiloxanes suggests that this material should offer advantages for nonloading and loading applications at elevated temperature.

CONCLUSIONS

The response of filled polysiloxane elastomers to cyclic stress at elevated temperature is influenced strongly by the type of filler. Whereas aluminum oxide filled polysiloxanes show high susceptibility to degradation under cyclic stress conditions, zinc oxide filled polysiloxanes, as demonstrated here, do not. Although the data show that zinc oxide interacts more strongly with the siloxane network than aluminum oxide, it is apparent that not only the polymer–filler interaction but also the chemical nature of the filler influences the dynamic creep behavior. The degradation reactions that give rise to the creep and storage modulus

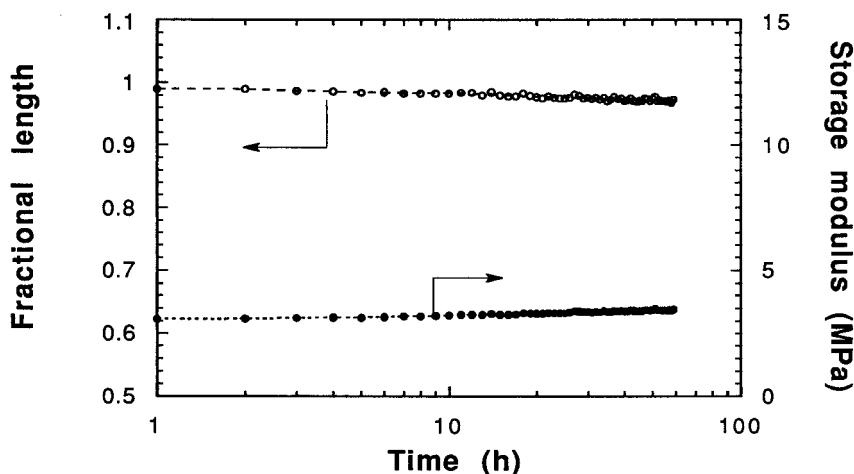


Figure 9 Response of *P*(16% DPS/84% DMS) filled with 30 vol % zinc oxide and 5 vol % iron oxide to cyclic stress at elevated temperature.

changes in aluminum oxide filled polysiloxanes must be assigned both mechanical and chemical origins.

The ability of zinc oxide to moderate or inhibit the degradation reactions occurring under conditions of cyclic stress at elevated temperature is dependent on the amount of zinc oxide in the network. Increasing zinc oxide loading decreased the creep of filled PDMS in the cyclic stress experiments. No additional increase in the stability of the siloxane network to cyclic stress at elevated temperatures was observed with increasing levels of DPS incorporation, unlike the response of the aluminum oxide filled elastomers examined previously.¹⁰ Inclusion of tin oxide or iron oxide fillers with the zinc oxide did not affect the stability of the elastomers to cyclic stress at elevated temperature.

The results of this article are consistent with a filler surface catalysis mechanism controlling the elastomer stability to combined mechanical and thermal stresses. Further work is required to fully understand the chemical reactions occurring at the surface of each type of filler.

The author sincerely thanks Chip Hewitt and Tonya Binga for their help in preparing the samples and collecting the data presented here.

REFERENCES

1. A. C. M. Yang, *Polymer*, **35**, 3206 (1994).
2. R. F. Willis and R. F. Shaw, *J. Colloid Interface Sci.*, **31**, 397 (1969).
3. R. F. Willis, *Nature*, **221**, 1134 (1969).
4. D. Tabor and R. F. Willis, *Wear*, **2**, 145 (1968).
5. I. N. Kas'yamova, F. A. Galil-Ogly, L. V. Kireeva, and A. S. Shapatin, *Int. Polym. Sci. Technol.*, **2**, 5 (1975).
6. J. M. Nielsen, *J. Polymer Sci.: Polym. Symp. Ed.*, **40**, 189 (1973).
7. J. Chalk and J. F. Smith, *Trans. Faraday Soc.*, **53**, 1214 (1957).
8. J. R. Shelton, *Rubber Chem. Technol.*, **45**, 359 (1972).
9. J. J. Fitzgerald, A. C. Martellock, P. L. Nielsen, and R. V. Schillace, *Polym. Eng. Sci.*, **32**, 1350 (1992).
10. S. A. Visser, C. E. Hewitt, and T. D. Binga, *J. Polym. Sci. B: Polym. Phys. Ed.*, **34**, 1679 (1996).
11. J. Wen, J. E. Mark, and J. J. Fitzgerald, *Macromol. Reports*, **A31**(Suppl. 3-4), 429 (1994).
12. R. A. Heinrich, *Measurements Control*, **September**, 1985.
13. A. M. Bueche, *J. Polym. Sci.*, **15**, 105 (1955).
14. W. J. Bobear, *I&EC Prod. Res. Dev.*, **3**, 277 (1964).
15. A. W. Henry, *Rubber Chem. Technol.*, **56**, 83 (1982).
16. N. Grassie and I. G. MacFarlane, *Eur. Polym. J.*, **14**, 875 (1978).
17. P. R. Dvornic and R. W. Lenz, *High Temperature Siloxane Elastomers*, Hüthig & Wepf, New York, 1990.
18. J. J. Fitzgerald and P. L. Nielsen, *Polym. Mater. Sci. Eng.*, **66**, 63 (1992).
19. A. E. Oberth, *Rubber Chem. Technol.*, **40**, 1337 (1967).
20. N. Grassie and I. G. MacFarlane, *Eur. Polym. J.*, **14**, 875 (1978).
21. T. H. Thomas and T. C. Kendrick, *J. Polym. Sci. A2*, **7**, 537 (1969).
22. P. J. Flory, *Principles of Polymer Chemistry*, Cornell University Press, Ithaca, NY, 1953, Chap. XIII.
23. A. W. Henry, *Rubber Chem. Technol.*, **56**, 83 (1982).
24. G. Kraus, *J. Appl. Polym. Sci.*, **7**, 861 (1963).
25. N. Grassie, K. F. Francey, and I. G. MacFarlane, *Polym. Degrad. Stabil.*, **2**, 67 (1980).
26. N. Grassie and K. F. Francey, *Polym. Degrad. Stabil.*, **2**, 53 (1980).
27. S. A. Visser, W. B. Vreeland, and C. E. Hewitt, U.S. Pat. Application 60/001,679 (1995).
28. J. J. Fitzgerald, U.S. Pat. 5,292,606 (1994).
29. S. A. Visser, *J. Appl. Polym. Sci.*, to appear.