Effect of Filler Type on the Response of Polysiloxane Elastomers to Cyclic Stress at Elevated Temperatures

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ABSTRACT: A variety of inorganic fillers are investigated to determine their impact on the response of filled polysiloxane elastomers to cyclic stress in hot air and in hot poly(dimethylsiloxane) PDMS fluid environments. Three fillers stabilize the polysiloxane networks to cyclic stress: zinc oxide, tin oxide, and copper oxide. Four fillers enhance network degradation: aluminum oxide, calcium oxide, titanium oxide, and tungsten oxide. The roles of testing environment, of diphenylsiloxane content of the polysiloxane network, of filler loading, of the stoichiometric balance of network precursors, and of molecular weight between cross-links are investigated. Although each influences the response of the elastomer to cyclic stress at elevated temperature, filler type exerts the primary influence. Silane-treated fillers are used to demonstrate that differences based on filler type do not arise because of changes in the strength of polymer–filler interactions. No correlation between stability of the filled elastomer to cyclic stress in hot air and filler particle size distribution, filler surface acid/base character, or the presence of specific inorganic contaminants in the filler is observed. It is proposed that the intrinsic ability of certain inorganic oxides to catalyze and/or inhibit polysiloxane degradation reactions determines the response of the filled elastomers to cyclic stress at elevated temperature. © 1997 John Wiley & Sons, Inc. J Appl Polym Sci **63:** 1805-1820, 1997

Key words: poly(dimethylsiloxane); inorganic filler; cyclic stress; dynamic creep

INTRODUCTION

The superior thermal stability of silicone elastomers, demonstrated in vacuum[1] and under heat aging in air,[2] permits their use in a wide variety of high-temperature applications. Many of these applications require enhancement of the mechanical properties of the elastomers through incorporation of inorganic fillers. Filler incorporation can impact not only the mechanical properties of silicone elastomers but also the thermal stability of the materials.

Metal-containing additives are known for their ability to interact with the silicone elastomer network and change its thermal stability. Elliot was the first to show that iron and other redox metal salts can stabilize poly(dimethylsiloxane) PDMS fluids above 200°C.[3] The catalytic effect of metal salts on oxidative degradation of hydrocarbons also has been reported.[4] Nielsen[5] and Ishida and Dunkers[6] demonstrated that iron octoate acts to both catalyze and inhibit various degradation reactions in polysiloxanes, depending on the temperature and the environment in which the elastomers are tested. The solubility or chelation state of the metal ions can influence their catalytic activity.[7]

Metal and metal oxide surfaces also display catalytic activity for siloxane degradation reactions. Cuprous oxide surfaces catalyze the cleavage of the Si—C bond in PDMS fluids,[8] and various metal surfaces induce cleavage of the Si—C bond and subsequent crosslinking of PDMS fluids.[9,10] Certain rare earth metal oxides, especially cerium oxide and red iron oxide, were reported to

stabilize vulcanizates of methylvinylsilicones to heat aging.[11] Yang[12] has reported changes in the heat aging response of cured PDMS elastomers through incorporation of different iron oxide, zinc oxide, or graphite fillers. For all fillers, the Young's modulus of the aged filled elastomers first decreased then increased with filler fraction. This behavior was postulated to arise from behavior of the particles as secondary antioxidants, blocking the local reactions of free-radical cross-links and producing locally soft layers around the particles that reduced the modulus of the elastomer. As filler loading increased, the decrease in interparticle spacing allowed the hydrodynamic effect of the rigid fillers to overcome the softening effect introduced by the soft layers around the particles, resulting in an increase in modulus with filler loading. This hypothesis suggests that both particle size and shape should influence the heat aging response of the materials.

Filler type also influences the degradation rate of a filled PDMS elastomer in a PDMS fluid environment.[13] The combination of iron oxide (8 wt %) and aluminum oxide fillers gave higher rates of reduction in effective chain concentration than either an iron oxide (2 wt %)/silica combination or a pure silica filler. The ability of iron oxide to inhibit oxidative crosslinking and catalyze siloxane rearrangement reactions was postulated to explain the differences.

The addition of cyclic stress to thermal stress further enhances the degradation of filled silicone elastomers.[14] Previous studies of the response of filled polysiloxane elastomers to cyclic stress at elevated temperature examined the impact of filler type,[14–17] filler concentration,[16–18] and network curing chemistry[15] on the degradation of the materials. Only a limited number of filler types have been examined; and of those, only zinc oxide[17] produced a filled elastomer that was stable to cyclic stress at elevated temperature.

In this work, a wider range of filler types is examined. In order to derive a more detailed understanding of the various factors influencing the stability of the filled elastomers to cyclic stress at elevated temperature, the influences of a PDMS fluid environment, of filler concentration, of network crosslinking chemistry, of filler surface treatment, and of filler particle size are studied.

EXPERIMENTAL

Sample Preparation

Addition-cured, filled PDMS elastomers were prepared by combining a network-forming polymer, a crosslinking polymer, filler, and catalyst. Network forming polymers used were one of two dimethylvinyl-terminated PDMS polymers, PS442 (M_W = 25,000) or PS445 (M_w = 74,200), or one of two dimethylvinyl-terminated poly(diphenylsiloxane-co-dimethylsiloxane)s (PDPSDMS), PS782 (16 mol % diphenylsiloxane, M_w = 14,100) or PS793 (24 mol % diphenylsiloxane, M_w = 13,000). The network-forming polymers were purchased from United Chemical Technologies and were used as received.

The crosslinking polymers were trimethylsilyl-terminated poly(methylhydro-co-dimethylsiloxane)s. The methylhydrosiloxane content was 30 wt % for PS123, 50 wt % for PS122.5, and 75 wt % for NM203. The catalyst PC075, obtained from United Chemical Technologies, 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 also were used as received.

Addition-cured samples were prepared by blending the crosslinking polymer, network-forming polymer, and filler in the ratios specified in Table I on a three-roll mill. Amounts of crosslinking polymer are indicated as parts crosslinking polymer per hundred parts by weight (pph) network-forming polymer. A catalyst mixture consisting of a 10% solution of PC075 in PS441.2 was used, and a small amount of inhibitor was added to prevent gelation at room temperature. Some formulations also contained a trimethylsiloxy-terminated PDMS (linear PDMS) additive (DC200, Dow Corning, 0.6 Pa-s viscosity at 25°C), as noted in Table I. The additive was blended into the formulation during roll milling. Fillers examined were zinc oxide (Zinc Corporation of America, XX503R), aluminum oxide (Alcoa, T64), tin oxide (Magnesium Elektron, Inc., G2 grade), iron oxide (Mapico Red 297), calcium oxide (Eastman Kodak Company), titanium dioxide (Aldrich), and tungsten oxide (Aldrich). The filled elastomers were cured at 200°C.

The condensation-cured samples were prepared by blending 100 parts by weight silanol-terminated PDMS (DC3-0133, Dow Corning, M_w = 43,400), five parts by weight tetraethylorthosilicate (TEOS; Silbond Corporation), and filler on a three-roll mill. Dibutyltin diacetate catalyst was added at 0.5 wt % of the filled mixture. The materials were cured in 12.7 × 12.7 × 0.2 cm molds overnight at room temperature. The materials were removed from the mold and postcured

Table I   Formulations of Addition-cured Elastomers

Formulation	Polymer	Cross-linker	Filler	Additive
1	PS442	5 pph PS123	35 vol % ZnO	none
2	PS782	5 pph PS123	35 vol % ZnO	none
3	PS793	5 pph PS123	35 vol % ZnO	none
4	PS442	5 pph PS123	30 vol % ZnO/5 vol % iron oxide	none
5	PS442	5 pph PS123	10 vol % CuO	none
6	PS442	5 pph PS123	20 vol % CuO	none
7	PS442	5 pph PS123	30 vol % CuO	none
8	PS442	5 pph PS123	40 vol % CuO	none
9	PS445	5 pph PS123	40 vol % CuO	none
10	PS445	10 pph PS123	35 vol % CuO	none
11	PS445	5 pph PS122.5	35 vol % CuO	none
12	PS445	5 pph NM203	35 vol % CuO	none
13	PS442	5 pph PS123	30 vol % Al_2O_3	none
14	PS442	5 pph PS123	30 vol % CaO	none
15	PS442	5 pph PS123	30 vol % TiO_2	none
16	PS442	5 pph PS123	30 vol % WO_3	none
17	PS442	5 pph PS123	30 vol % SnO_2	none
18	PS445	5 pph PS123	35 vol % SnO_2 (G2 grade)	none
19	PS445	5 pph PS123	35 vol % SnO_2 (G2 grade)	1% linear PDMS
20	PS445	5 pph PS123	35 vol % SnO_2 (G2 grade)	3% linear PDMS
21	PS445	2 pph PS123	35 vol % SnO_2 (G2 grade)	none
22	PS445	2 pph PS123	35 vol % HMDS-treated SnO_2 (G2 grade)	none
23	PS445	2 pph PS123	35 vol % TMCS-treated SnO_2 (G2 grade)	none
24	PS445	2 pph PS123	35 vol % VDCS-treated SnO_2 (G2 grade)	none

through a 12 h ramp to 205°C and an 18 h hold at 205°C. Tin oxide fillers were obtained from Magnesium Elektron, Inc., in four grades: G2, CS3, SV5, and Superlite C. Their particle size distributions were measured with a Coulter counter (aperture 70). Fillers used in each formulation are listed in Table II. Silane-treated fillers were blended into the PDMS/TEOS blend after the final drying step of the silane treatment described below.

Silane treatment of tin oxide fillers was per-

formed by dispersing 1500 g tin oxide (Magnesium Elektron, Inc., G2 grade) in 1500 mL anhydrous tetrahydrofuran (THF) under an inert gas purge. The dispersion was stirred at 60°C overnight. A solution of 150 mL silane and 300 mL THF was added to the filler dispersion dropwise over 2 h, after which the mixture was stirred at 60°C overnight. The treated filler was collected by filtration and dried overnight at 100°C. Silanes used to treat the tin oxide were hexamethyldisilazane (HMDS), trimethylchlorosilane (TMCS),

Table II   Fillers Used in Condensation-cured Formulations

Formulation	Filler	Silane User for Filler Treatment
25	35 vol % SnO_2 (G2 grade)	none
26	35 vol % SnO_2 (G2 grade)	HMDS
27	35 vol % SnO_2 (G2 grade)	TMCS
28	30 vol % SnO_2 (G2 grade)	none
29	30 vol % SnO_2 (CS3 grade)	none
30	30 vol % SnO_2 (SV5 grade)	none
31	30 vol % SnO_2 (Superlite C grade)	none

and vinyldimethylchlorosilane (VDCS). They were obtained from United Chemical Technologies and were used as received.

Cyclic Stress/Dynamic Creep Testing

Cyclic stress data were collected using a dynamic mechanical analyzer (also known as a Mechanical Energy Resolver or MER),[19] as described previously.[14] 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 rms was superimposed on the static load. The samples were run in ambient air atmosphere for 60 h, except where noted otherwise. Corrected storage moduli were calculated as described elsewhere.[14]

Some samples, as indicated, were run while immersed in 0.35 Pa-s (viscosity at 25°C) trimethylsiloxy-terminated PDMS (DC200, Dow Corning). In this case, the static load on the cyclic stress test was decreased to 4 kg, and the dynamic load was 2 kg rms. Testing temperature and frequency were maintained at 218°C and 30 Hz.

Toluene Swell and Effective Cross-link Density Measurements

The method outlined by Bueche[20] and Bobear[21] 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 $\chi_{PDMS\text{-}toluene}$[13] for filled elastomers of PDMS and $\chi_{P(16\%\ DPS/84\%\ DMS)\text{-}toluene}$[15] for filled elastomers of poly(diphenylsiloxane-*co*-dimethylsiloxane). The calculation details and caveats inherent in the use of effective χ values for the PDPSDMS systems are discussed elsewhere.[15] Flory–Rehner theory[22] for determining the crosslink density of elastomers from swelling data, as

Table III Response of Zinc Oxide-filled Polysiloxanes to Cyclic Stress at Elevated Temperature in a PDMS Fluid Environment

Formulation	Weight Loss (%)
2	0
3	0.28
4	−0.39

modified by Henry for filled systems,[13] was used to calculate effective crosslink densities. It should be noted that this method gives a measure of the effective crosslink density that comprises both the true crosslink density from rubber elasticity theory and the apparent increase in crosslink density resulting from network-filler interactions. This has been discussed elsewhere.[17]

Tensile Testing

Tensile testing and Young's modulus determination were performed at room temperature on dog-bone-shaped specimens according to ASTM D412.

Inorganic Contaminant Measurement

The amount of trace contaminants present in the inorganic oxide fillers was determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES) following digestion of the filler samples with nitric, hydrochloric, sulfuric, and/or hydrofluoric acids.

RESULTS AND DISCUSSION

Zinc Oxide-filled Polysiloxanes: Influence of a PDMS Fluid Environment

A number of practical applications of filled PDMS elastomers require that they have the ability to withstand the dual stresses of high temperature and cyclic stress. In addition, certain applications also require that the elastomers maintain stability while in continuous contact with a PDMS fluid. Henry examined the stability of filled PDMS elastomers to heat aging in a PDMS fluid and concluded that the fluid increased the extent of degradation of the elastomers.[13] Since zinc oxide-filled polysiloxane elastomers display stability to cyclic stress at elevated temperatures,[17] the additional stress of a PDMS fluid environment was added to determine if the stability could be maintained.

The results of cyclic stress testing of zinc oxide-filled polysiloxane elastomers are shown in Figure 1 and Table III. As seen for zinc oxide-filled PDMS
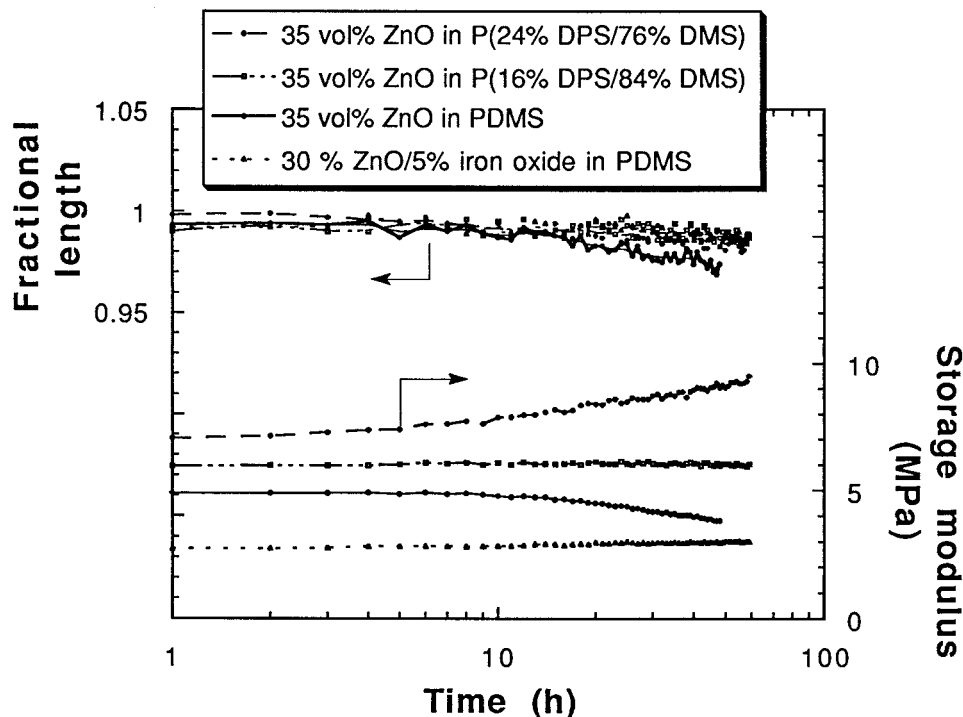
Figure 1 Cyclic stress testing response of zinc oxide-filled polysiloxane (formulations 1–4) tested in a hot PDMS fluid environment. Formulation 1: 35 vol % ZnO in PDMS. Formulation 2: 35 vol % ZnO in P(16% DPS/84% DMS). Formulation 3: 35 vol % ZnO in P(24% DPS/16% DMS). Formulation 4: 30 vol % ZnO/5 vol % iron oxide in PDMS.

elastomers subjected to cyclic stress testing in a hot air environment, the zinc oxide-filled PDMS elastomer (Formulation 1) in the PDMS fluid environment displayed almost no creep during cyclic stress testing. A slight decrease in storage modulus occurs as a result of cyclic stress in a PDMS fluid environment that is not observed in the air environment, indicating a participation of the PDMS fluid in the degradation reactions.

Changing the elastomer type to a poly(diphenylsiloxane-*co*-dimethylsiloxane) (PDPSDMS) changes the response to cyclic stress in a PDMS fluid environment. The storage modulus remains constant when the elastomer contains 16% DPS (Formulation 2); whereas, the storage modulus increases during the course of the testing with 24% DPS in the elastomer (Formulation 3). Little evolution of low molecular weight degradation products is evidenced by the insignificant weight losses measured for these samples.

The differences in final storage moduli for the different polysiloxane elastomers may result from differences in the initial moduli of the materials. Higher modulus materials may have lower levels of stress transmitted to the network chains, resulting in lower levels of degradation.

The differences also may arise from the differences in compatibility of the elastomers with PDMS fluid. Swell of filled polysiloxane elastomers containing greater than 10% DPS units with 0.35 Pa-s viscosity PDMS is negligible.[23] Very little diffusion of the PDMS fluid into the 16 and 24% DPS-content elastomers would be expected compared to the amount of diffusion expected for the PDMS elastomer. Thus, participation of PDMS fluid in interchain bonding reactions with the elastomer is expected to decrease with increasing DPS content. Assuming an equivalent number of interchain bonding reactions are occurring in the three elastomer types, a larger number of effective crosslinks should be formed in the higher DPS-content elastomers because of the absence of participation in the reaction by PDMS fluid. Therefore, an increase in storage modulus should be observed.

Stabilization of the PDMS network is achieved through inclusion of iron oxide filler with the zinc oxide filler (Formulation 4). The storage modulus of the PDMS elastomer filled with zinc oxide and iron oxide remains nearly constant during the cyclic stress testing in the PDMS fluid environment. Virtually no creep or weight loss is observed. The
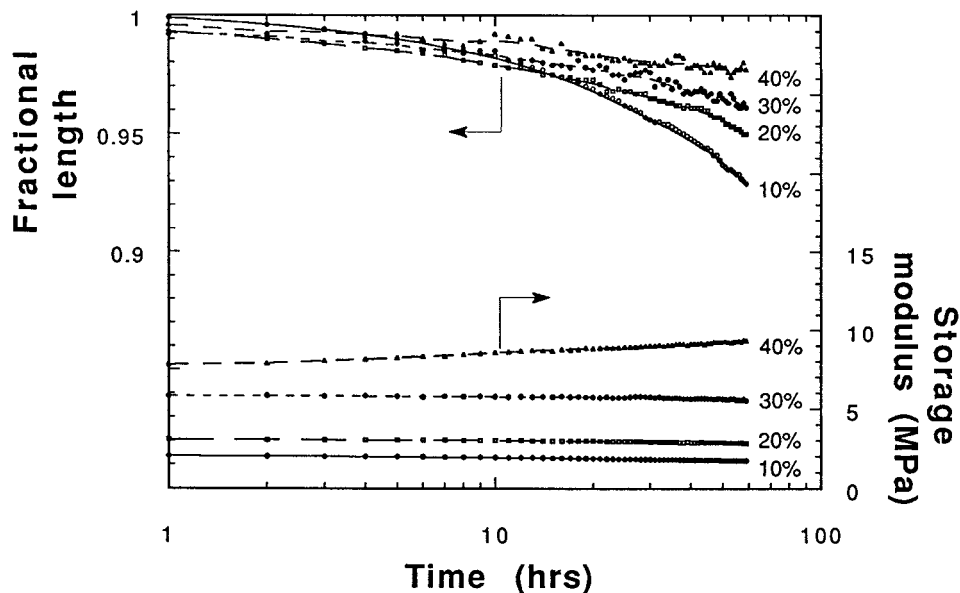
Figure 2 Influence of copper oxide loading on the cyclic stress testing response of PDMS elastomers tested in air at 218°C. Formulations 5–8 correspond to 10, 20, 30, and 40 vol % copper oxide loading, as indicated in the figure.

stability and lower modulus of this material compared to those of the zinc oxide-filled polysiloxanes indicates that modulus alone does not control the response of these materials to cyclic stress at elevated temperature, supporting the hypothesis that interaction of the elastomer with the PDMS fluid strongly influences its response to cyclic stress.

Copper Oxide-filled PDMS: Influence of Filler Concentration and Elastomer Stoichiometry

Although several fillers have been examined for their impact on the response of filled elastomers to cyclic stress at elevated temperature, only zinc oxide fillers have been shown to improve the stability of the elastomers to cyclic stress. The literature suggests that cuprous oxide (Cu_2O) catalyzes the degradation of PDMS.[8] Here, copper oxide (CuO) is examined for its ability to stabilize PDMS elastomers subjected to cyclic stress at elevated temperatures in air.

The response of PDMS elastomers filled with varying concentrations of copper oxide to cyclic stress at elevated temperature is shown in Figure 2. Unlike the aluminum oxide-filled PDMS elastomers examined elsewhere,[15] the copper oxide-filled elastomers (formulations 5–8) display almost no change in storage modulus and minimal creep. As seen with zinc oxide fillers,[17] increasing

the filler loading decreases the creep of the copper oxide-filled elastomer. Comparing the elastomers at equivalent filler loadings, however, the copper oxide-filled elastomers display less creep than the zinc oxide-filled elastomers. They also have higher storage moduli, indicating again that a higher storage modulus or hardness material is not necessarily less stable under conditions of high temperature and cyclic stress. The weight loss of the copper oxide-filled elastomers, shown in Table IV, also attests to the ability of copper oxide to stabilize the elastomers. Decreasing weight loss with increasing filler loading is observed.

In order to examine the influence of changes

Table IV   Influence of Filler Concentration and Elastomer Stoichiometry on the Response of Copper Oxide-filled PDMS to Cyclic Stress at Elevated Temperature

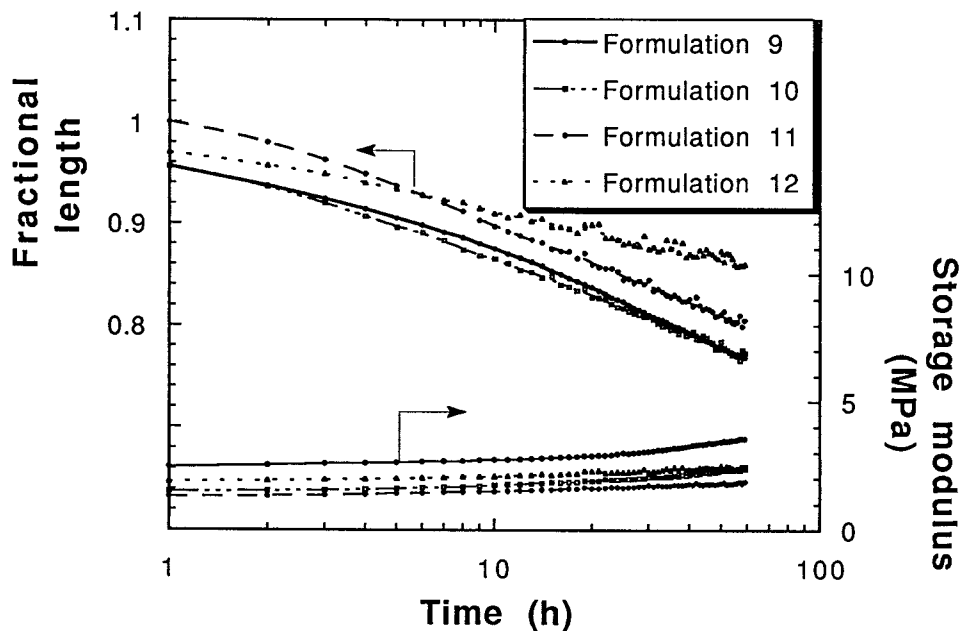| Formulation	Weight Loss (%)
5	1.1
6	0.95
7	0.75
8	0.23
9	0.51
10	0.95
11	0.79
12	0.67

Figure 3 Influence of elastomer structure and network perfection on the cyclic stress testing response of copper oxide-filled PDMS.

in the network structure on the dynamic creep response of filled PDMS elastomers, variations in the network-forming polymer molecular weight and in the Si—H content of the crosslinking polymer were explored. The results are shown in Figure 3 and Table IV. Comparing Formulation 8 to Formulation 9, it can be seen that increasing the network-forming polymer molecular weight without changing the crosslinking polymer concentration decreases the stability of the network to cyclic stress. This behavior also was observed in zinc oxide-filled PDMS elastomers, where it was attributed to both network imperfections resulting from excess crosslinking moiety (Si—H) being present and to the higher molecular weight be-

tween crosslinks requiring fewer chain scission reactions before measurable creep occurs.

When the crosslinking polymer concentration is increased further, however (Formulation 10), the stability of the elastomer to cyclic stress is unaffected, even though the filler concentration has been decreased slightly. Increasing the reactive hydrosiloxane content of the crosslinker (formulations 11 and 12) stabilizes the elastomers slightly, but the effect is small. Further, the weight loss in each of these elastomers is small and similar, regardless of changes in network chemistry. Thus, changes in network crosslink distribution, concentration of dangling ends, or other network parameters are not as important

Table V Influence of Filler Type on the Cyclic Stress Response and Properties of PDMS Elastomers Containing 30 Vol % Filler

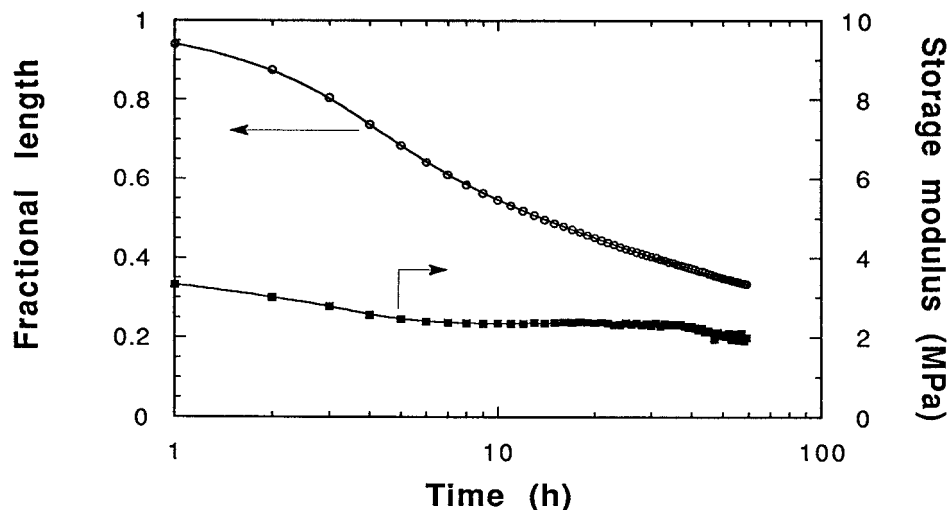| Formulation	Filler	Weight Loss During Cyclic Stress Testing (%)	Crosslink Density (μmol/cm^3)	Young's Modulus (MPa)
13	aluminum oxide	9.75	223	2.5
14	calcium oxide	4.43	ND	5.7
15	titanium oxide	2.25	338	7.1
16	tungsten oxide	6.27	101	4.7
17	tin oxide	0.98	484	6.7

[a] ND = no data.

Figure 4 Cyclic stress testing results for an addition-cured PDMS elastomer containing 30 vol % aluminum oxide (Formulation 13).

in determining response to cyclic stress as is the filler type and loading.

Influence of Different Filler Types

Filler loading strongly influences the response of PDMS elastomers to cyclic stress at elevated temperature. Therefore, a series of elastomers were prepared at identical filler loadings in order to isolate the influence of filler type.

An addition-cured PDMS elastomer containing 30 vol % aluminum oxide was prepared (Formulation 13), and its effective crosslink density and Young's modulus are reported in Table V. Its response to cyclic stress testing is shown in Figure 4 and Table V. The effective crosslink density of this elastomer is comparable to those measured elsewhere for PDMS elastomers containing 30 vol % zinc oxide[17] or 35 vol % aluminum oxide.[15] The Young's modulus is similar to the initial storage modulus measured during cyclic stress testing. The aluminum oxide-filled PDMS experienced a 67% length change during the cyclic stress testing and a weight loss of nearly 10%. Compared to the copper oxide-filled elastomers examined above or the zinc oxide-filled materials examined above and elsewhere,[17] the aluminum oxide-filled elastomers undergo significantly greater degradation.

The results for a calcium oxide filler (Formulation 14) are shown in Figure 5 and Table V. In this case, little creep of the material is observed, but a large increase in storage modulus occurs during the cyclic stress testing. The weight loss during cyclic stress testing is also significantly

greater for the calcium oxide-filled elastomer than for the elastomers filled with zinc oxide or copper oxide. However, it is lower than that seen for aluminum oxide.

Evaluation of a titanium oxide-filled elastomer (Formulation 15) gave the results shown in Figure 6 and Table V. Again, although the creep of the elastomer is not excessive, the titanium oxide filler causes a large increase in the storage modulus of the elastomer in the later stages of the cyclic stress experiment. Also, the weight loss remains relatively high.

The results of changing the filler to tungsten oxide (Formulation 16) are shown in Figure 7 and Table V. The elastomer displays a creep of about 23% during the cyclic stress experiment, as well as an increase in storage modulus at long times and a high weight loss, corresponding to loss of volatile cyclics formed during the degradation reactions.

In contrast, tin oxide filler stabilizes the network to degradation (Formulation 17), as shown in Figure 8 and Table V. The tin oxide-filled elastomer displays virtually no creep, change in storage modulus, or weight loss throughout the 60 h cyclic stress test.

Inclusion of linear PDMS in the PDMS network does not degrade the stability of tin oxide-filled elastomers (formulations 18–20), as shown in Figure 9 and Table VI. A slight decrease in the Young's modulus of the elastomer occurs upon linear PDMS incorporation, but no significant change in creep, storage modulus stability, or weight loss during cyclic stress testing is ob-
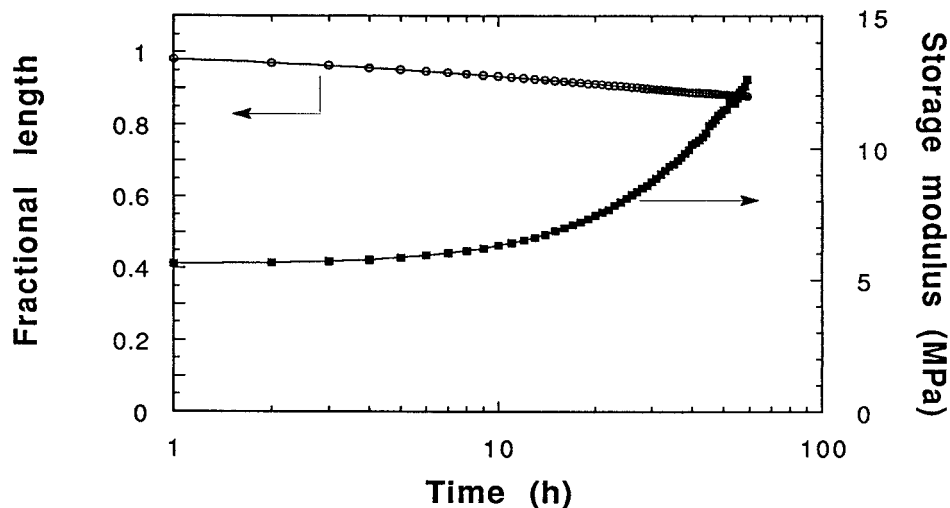
Figure 5 Cyclic stress testing results for an addition-cured PDMS elastomer containing 30 vol % calcium oxide (Formulation 14).

served. This suggests that there is little interchain reaction occurring during the cyclic stress testing of the tin oxide-filled elastomer and that tin oxide may be acting as an inhibitor of degradation reactions.

It has been suggested that the creep and storage modulus changes exhibited by certain filled PDMS elastomers subjected to cyclic stress at elevated temperatures results from sliding of the polymer along the filler surface, causing frictional heat generation and degradation.[14] A correlation between strength of polymer–filled interactions and the response of the elastomer to cyclic stress would be expected if this hypothesis completely explained the experimental observations. One measure of the strength of polymer–filler interactions is the modulus of the filled elastomer at identical filler loadings. As the Young's moduli data in Table V demonstrate, however, there is no correlation between modulus and the stability of the elastomer to cyclic stress. Both tin oxide and titanium oxide give high modulus elastomers; yet one
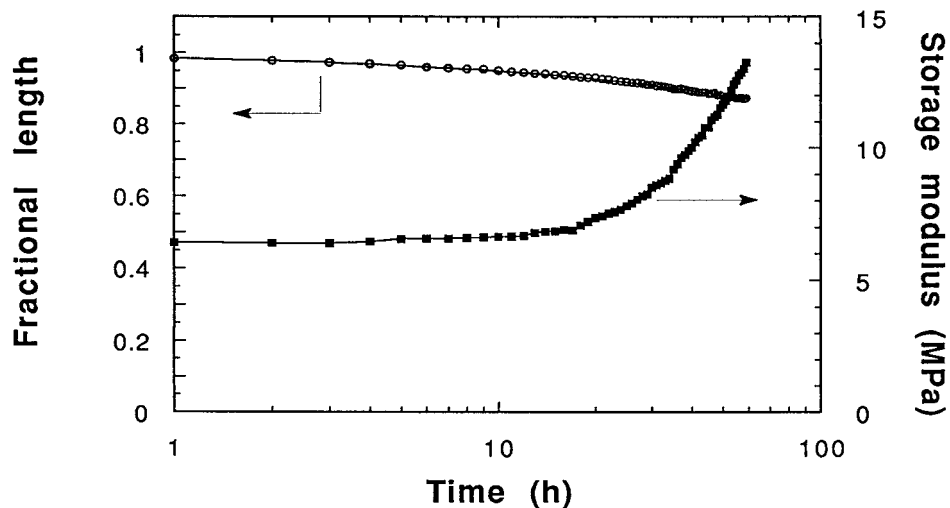
Figure 6 Cyclic stress testing results for an addition-cured PDMS elastomer containing 30 vol % titanium oxide (Formulation 15).
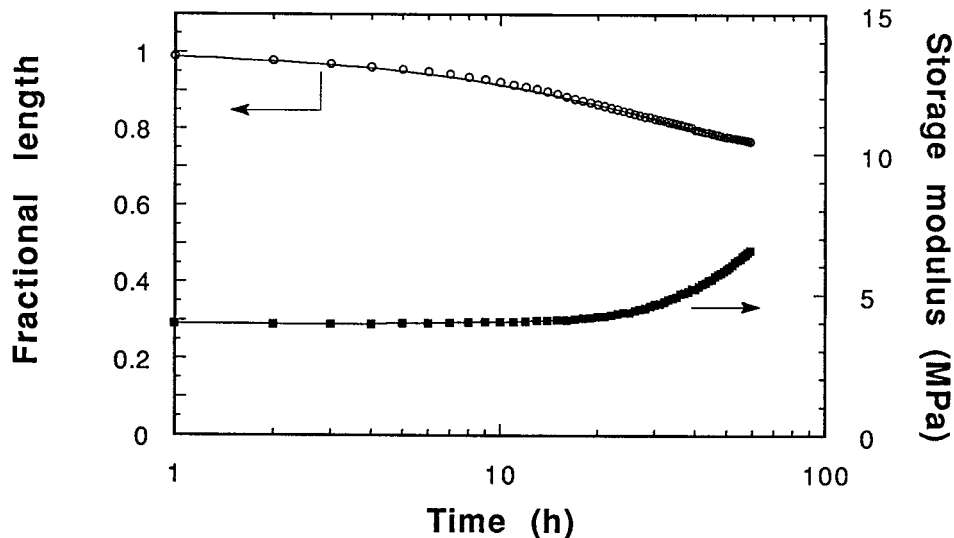
Figure 7 Cyclic stress testing results for an addition-cured PDMS elastomer containing 30 vol % tungsten oxide (Formulation 16).

stabilizes the elastomer, while the other gives a high level of degradation. The modulus of the 30 vol %-loaded copper oxide elastomer is quite similar to that of the calcium oxide-filled elastomer, yet their stabilities to cyclic stress in hot air are quite different.

The effective crosslink density is another indirect measure of the strength of polymer–filler interactions. If it is assumed that the networks formed are independent of the type of filler in the elastomer, differences in effective crosslink density can be attributed to differences in polymer–filler interactions. Higher effective crosslink densities result from stronger polymer-filler interactions. Again, no correlation is seen between effective crosslink density and response to cyclic stress. Aluminum oxide displays the highest level of degradation in the cyclic stress experiment, yet it has the same effective crosslink density as the stable zinc oxide-filled elastomer examined else-
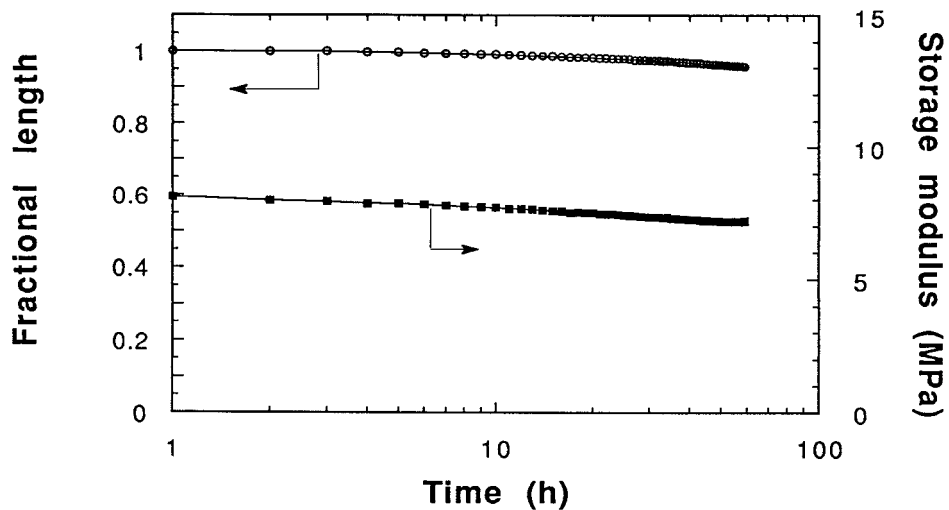

Figure 8 Cyclic stress testing results for an addition-cured PDMS elastomer containing 30 vol % tin oxide (Formulation 17).
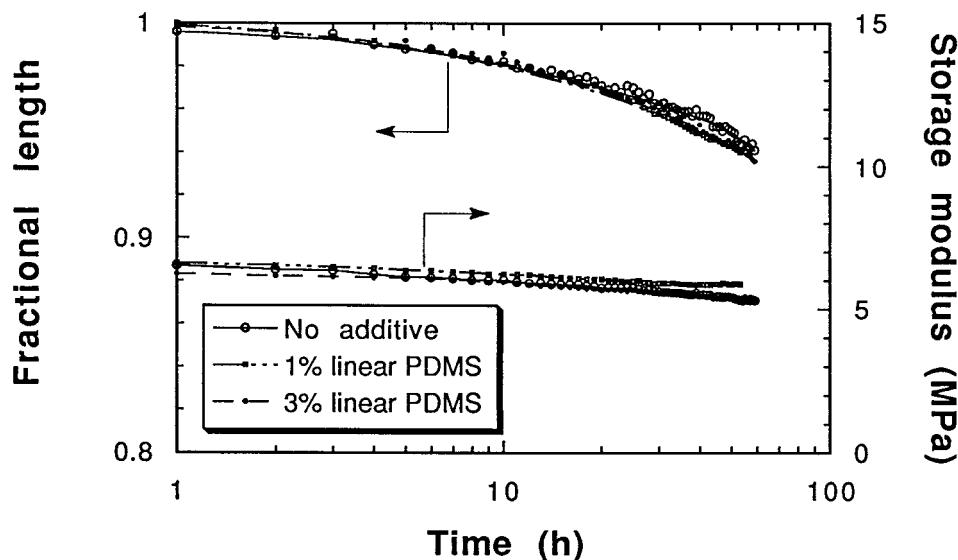
Figure 9 Influence of inclusion of linear PDMS in the addition-cured PDMS elastomer filled with 35 vol % tin oxide. Formulation 18: no additive. Formulation 19: 1% linear PDMS. Formulation 20: 3% linear PDMS.

where.[17] Elastomers with both lower (tungsten oxide-filled) and higher (titanium oxide-filled) effective crosslink densities also display high levels of instability to cyclic stress at elevated temperature.

The strength of polymer-filler interactions also can be altered without changing filler type through silane surface treatment of the fillers. Silanes for filler treatment were selected to either increase or decrease the strength of the interaction between the polymer network and the filler. HMDS and TMCS should decrease polymer-filler interaction, while vinylmethylchlorosilane (VMCS) should increase polymer-filler interaction in addition-cured elastomers through possible participation in the network formation reac-

tions. X-ray photoelectron spectroscopic (XPS) analysis of the treated filler surfaces confirm that monolayer coverage of the filler surfaces with the silanes was achieved (data not shown).

Results of using treated tin oxide fillers compared to the untreated tin oxide are shown in Figure 10 and Table VII for an addition-cured PDMS elastomer (formulations 21−24). Some variation in initial storage modulus is observed based on the silane used for filler treatment. As expected, the VMCS-treated filler gave a higher storage modulus elastomer, indicating enhanced strength of polymer-filler interactions. The VMCS-treated filler also gave an elastomer with a higher effective crosslink density. HMDS decreased the strength of the polymer-filler interactions, resulting in a lower effective crosslink density. Despite these changes in the strength of the polymer-filler interactions, however, no significant differences in response of the elastomers to cyclic stress testing at elevated temperature were observed. The elastomers remained stable.

Because some sensitivity to the curing chemistry used to form the elastomer had been demonstrated previously,[15] the influence of filler treatment on the response to cyclic stress also was investigated in a condensation-cured system filled with tin oxide. Results for untreated (Formulation 25), HMDS-treated (Formulation 26), and TMCS-treated (Formulation 27) tin oxide in a

Table VI   Influence of Linear PDMS Addition on the Young's Modulus and the Response of Tin Oxide-filled PDMS Elastomers to Cyclic Stress at Elevated Temperature

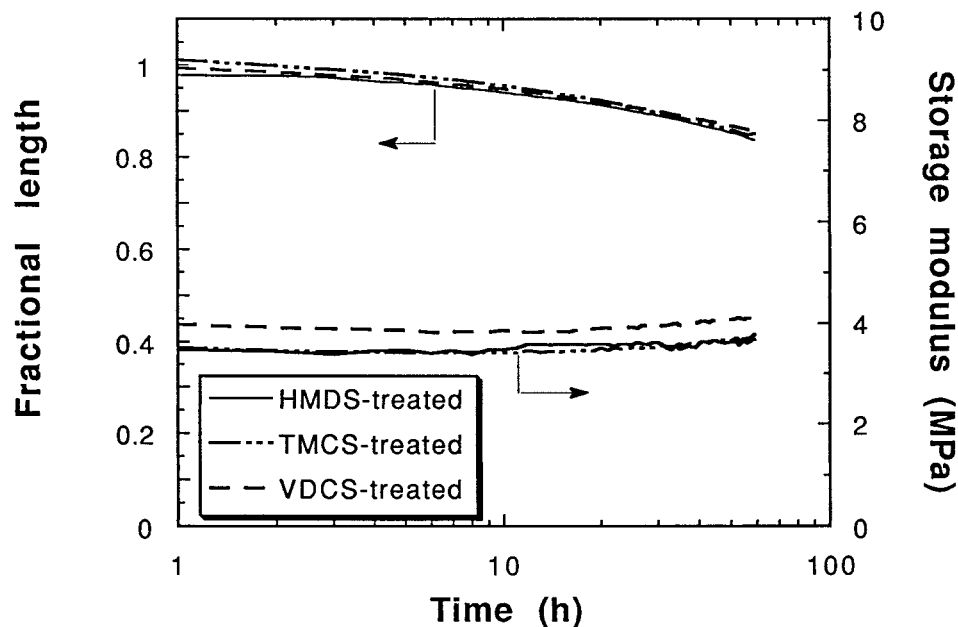| Formulation	Weight Loss During Cyclic Stress Testing (%)	Young's Modulus (MPa)
18	0.83	6.1
19	0.91	5.6
20	0.53	5.7

Figure 10 Cyclic stress testing response of addition-cured PDMS elastomers filled with 35 vol % silane-treated tin oxide. Formulation 22: HMDS-treated tin oxide. Formulation 23: TMCS-treated tin oxide. Formulation 24: VDCS-treated tin oxide.

condensation-cured PDMS elastomer subjected to cyclic stress at elevated temperature are shown in Figure 11 and Table VIII. Changes in the initial storage modulus confirm that the silane filler treatments are decreasing the strength of polymer-filler interactions. The decrease in effective crosslink density for the sample containing TMCS-treated filler (Formulation 27) also indicates a significant decrease in polymer-filler interactions. Again, however, no change in the stability of the elastomer, expressed as low weight loss, almost no creep, and stable storage modulus, is

observed when the strength of the polymer-filler interactions is varied. Comparing the addition-cured elastomers to the condensation-cured elastomers, a slightly lower level of creep is seen in the condensation-cured samples. However, the low level of creep in any of the tin oxide-filled elastomers, regardless of elastomer curing chemistry, suggests that these differences may arise from network imperfections rather than from differences in curing chemistry.

In addition to variations in the strength of polymer-filler interactions, the particle size of the fillers varies with filler type in this study. In order to determine if this is a controlling factor in the response of the elastomers to cyclic stress, a series of condensation-cured PDMS elastomers were filled with tin oxide fillers with different mean particle sizes and widely varying particle size distributions. The size distributions of the fillers are shown in Figure 12, and the volume mean particle sizes are listed in Table IX. The cyclic stress testing results for these materials are shown in Figure 13 and Table IX. The data clearly show that particle size does not influence the response of the materials to cyclic stress at elevated temperature. Further, the fact that some of these tin oxides were formed through a pyrolysis process while others were formed through a chemical process

Table VII Influence of Silane Surface Treatment on the Properties of Tin Oxide-filled, Addition-cured PDMS

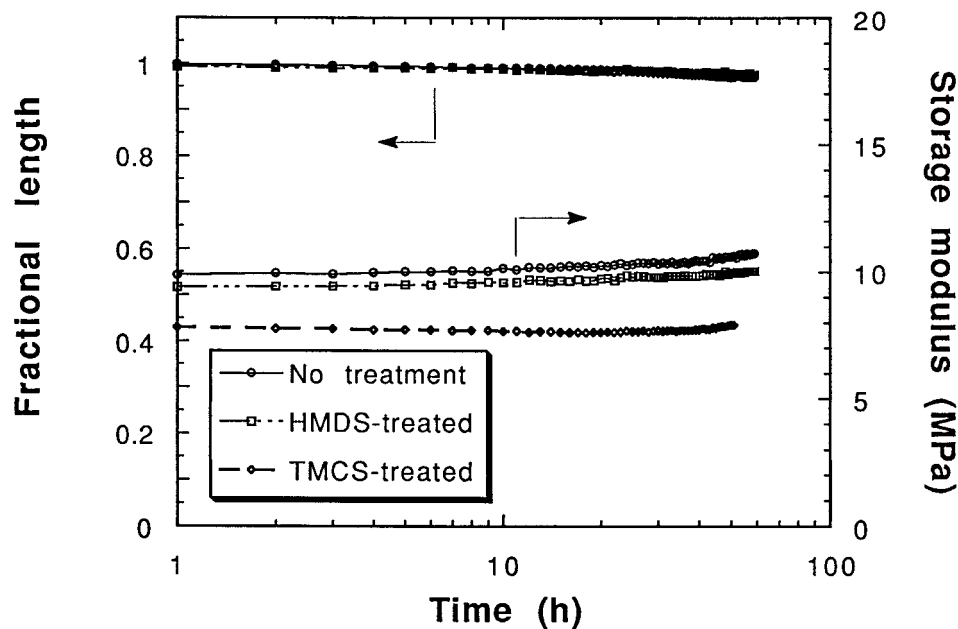| Formulation	Filler treatment	Cross-link Density (μmol/ cm^3)	Weight Loss During Cyclic Stress Testing (%)
21	none	175	1.22
22	HMDS	154	0.4
23	TMCS	182	1.27
24	VMCS	191	0.29

Figure 11 Cyclic stress testing response of condensation-cured PDMS elastomers filled with 35 vol % silane-treated tin oxide. Formulation 25: untreated tin oxide. Formulation 26: HMDS-treated tin oxide. Formulation 27: TMCS-treated tin oxide.

also suggests that residuals from the oxide manufacture do not control the ability of fillers to influence the response of filled elastomers to cyclic stress.

Another possible explanation for the effect of filler type on the cyclic stress testing response is that the acidic or basic character of the filler surface influences the degradation reactions or that there are impurities in the fillers that impart an acidic or basic character to the filler. The reported isoelectric points of the fillers and the results of analyses for trace contaminants are presented in Table X. As the data show, there

is no correlation between stability of a filled elastomer to cyclic stress at elevated temperature and the isoelectric point or trace contaminants of the filler.

The absence of mechanical or external factors to explain the influence of filler type on cyclic stress response leads to the conclusion that the inherent properties of the particular inorganic oxide are the controlling factors. The ability of certain metal oxides, for example, zinc oxide[24] and copper oxide,[25] to catalyze siloxane reactions supports the hypothesis that a fuller understanding of the ability of inorganic oxides to catalyze siloxane scission and crosslinking reactions will permit prediction of the affect of fillers on the stability of polysiloxane elastomers to cyclic stress at elevated temperature.

CONCLUSIONS

The interactions of fillers with a polymer network are important in determining the fitness for use of filled elastomers in both static and dynamic loading applications. Evaluation of a variety of fillers for their impact on the stability of filled elastomers to cyclic stress at elevated temperature has been completed. Zinc oxide, previously
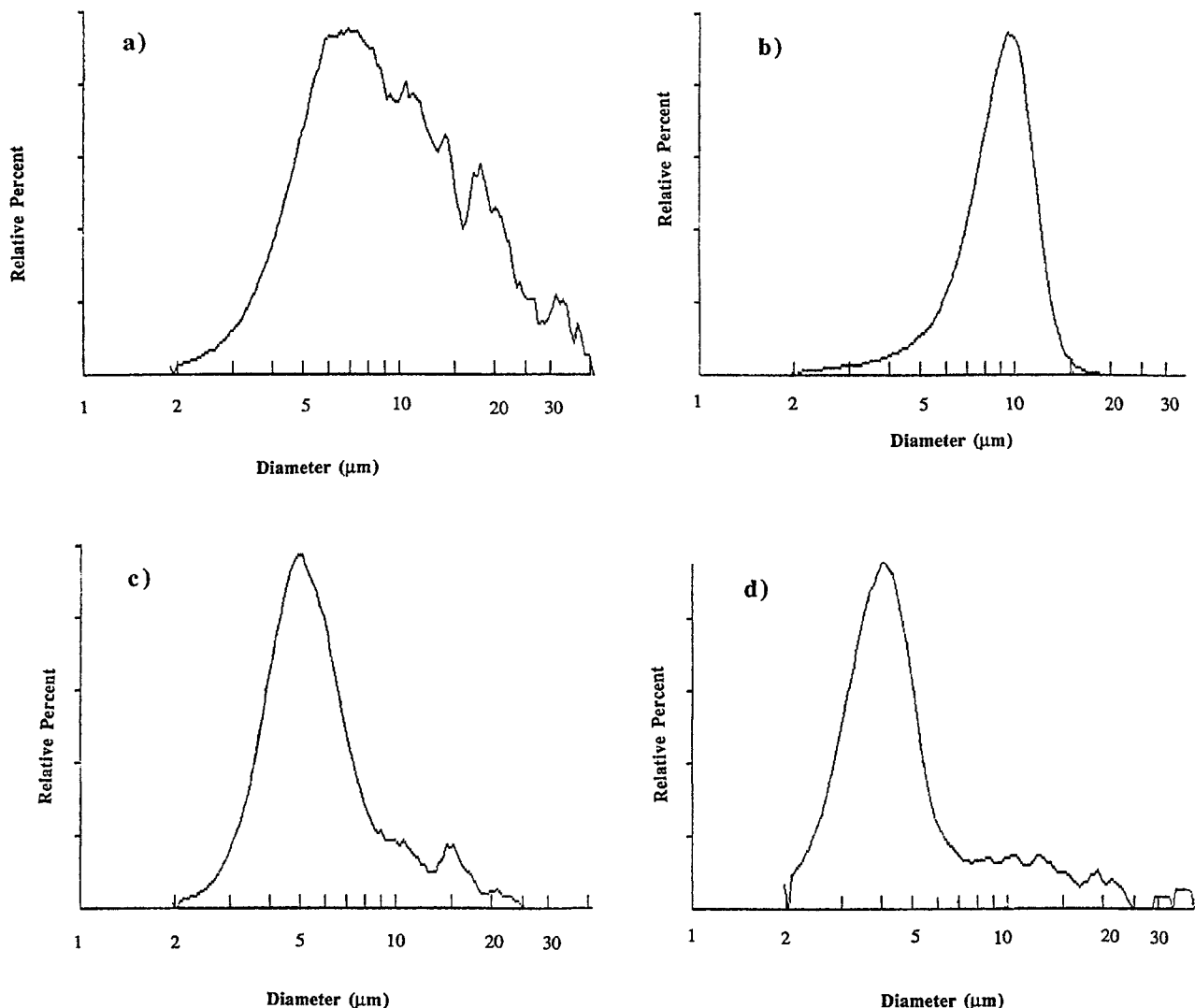
Table VIII   Influence of Silane Surface Treatment on the Properties of Tin Oxide-filled, Condensation-cured PDMS

Formulation	Filler Treatment	Cross-link Density (μmol/ cm^3)	Weight Loss During Cyclic Stress Testing (%)
25	none	506	0.57
26	HMDS	503	0.28
27	TMCS	478	0.41

Figure 12 Particle size distributions of tin oxide fillers: (a) G2 grade; (b) CS3 grade; (c) SV5 grade; (d) Superlite C grade.

shown to stabilize polysiloxane elastomers to cyclic stress in a hot air environment,[17] also stabilized elastomers subjected to cyclic stress in a hot

Table IX   Influence of Filler Particle Size on the Response of Tin Oxide-filled Condensation-cured PDMS Elastomers to Cyclic Stress at Elevated Temperature

Formulation	Filler Volume Mean Particle Size (μm)	Weight Loss During Cyclic Stress Testing (%)
28	8.7	0.34
29	9.1	0.56
30	5.4	0.28
31	4.2	0.16

PDMS fluid environment. Some dependence on diphenylsiloxane content of the elastomer was observed and was hypothesized to arise from incompatibility of the DPS units with the PDMS fluid. Less PDMS fluid permeation into the network resulted in more crosslinks forming between network chains and an increase in storage modulus during cyclic stress testing.

For elastomers subjected to cyclic stress in a hot air environment, two new fillers were identified that stabilized the elastomers: tin oxide and copper oxide. In addition, a number of fillers were identified that imparted varying degrees of instability to the network: aluminum oxide, calcium oxide, titanium oxide, and tungsten oxide. No correlations between strength of polymer-filler interactions, filler isoelectric point, or presence of trace
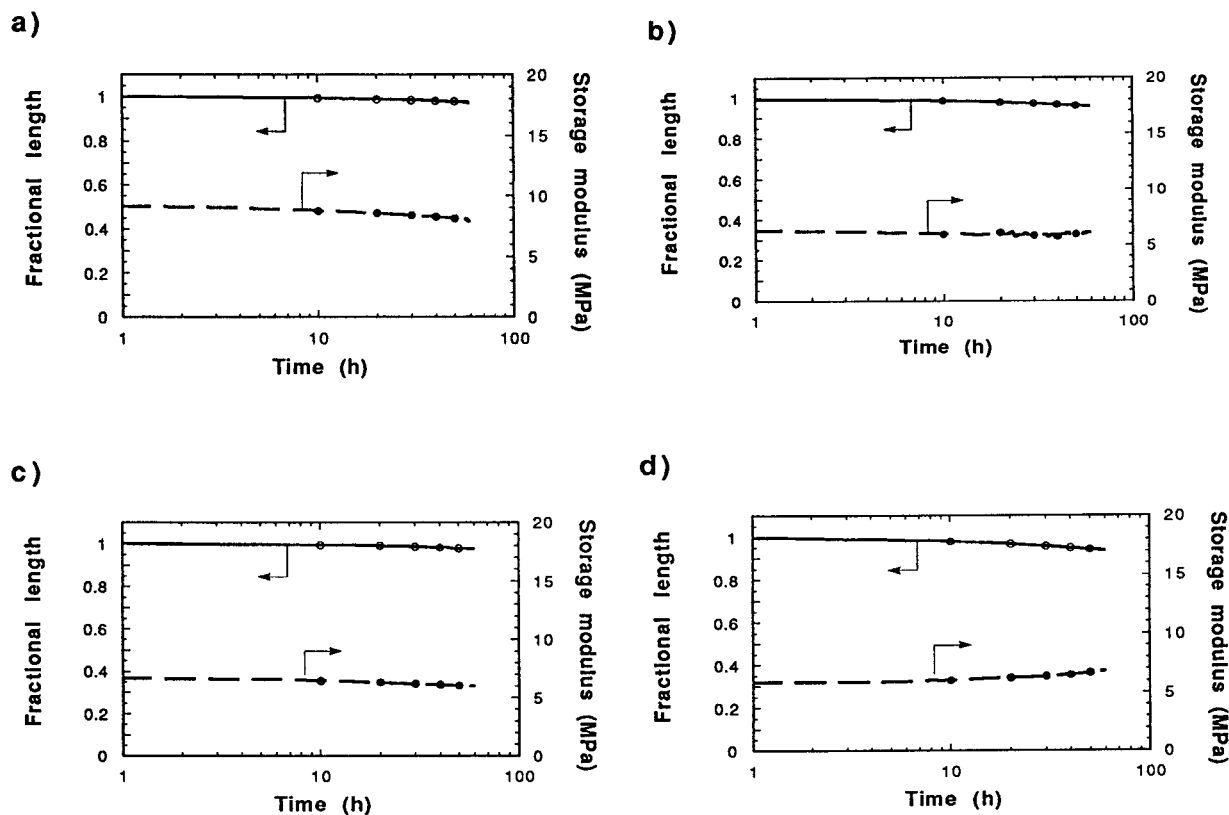
a)

b)

c)

d)

Figure 13 Cyclic stress testing results for condensation-cured PDMS elastomers filled with various grades of tin oxide at 30 vol % loading: (a) G2 grade tin oxide (Formulation 28); (b) CS3 grade tin oxide (Formulation 29); (c) SV5 grade tin oxide (Formulation 30); (d) Superlite C grade tin oxide (Formulation 31).

contaminants in the fillers and ability of the fillers to stabilize the PDMS elastomer to cyclic stress were observed.

Studies of silane-treated tin oxides and of tin oxides of varying particle size distributions fur-

ther confirmed that the strength of polymer-filler interactions and the size of the particles are not responsible for the differences observed with different fillers. Imbalances in the chemistry used to form the elastomer network also showed only a

Table X   Properties of Fillers

Filler	Isoelectric Point[a]	Trace Contaminants (ppm)					
		Ca	Na	Mg	Fe	Ni	Zn
Al_2O_3	9.1	250	1200	220	210	33	<20
CaO	—	MC[b]	190	5500	490	<20	<20
TiO_2	6.0	<20	760	<20	<20	25	<20
WO_3	—	<20	<100	<20	<20	<20	<20
SnO_2	4.5	200	1800	49	33	<20	41
CuO	9.1	76	<100	22	120	31	2600
ZnO	9.2	<20	<100	<20	40	<20	MC

[a] Measured by IEPS in Plueddemann.[26]
[b] MC = major constituent.

minor impact on the stability of the filled elastomers to cyclic creep.

Thus, it is suggested that the ability of a particular inorganic oxide to stabilize a filled polysiloxane elastomer to cyclic stress at elevated temperature is directly related to its ability to participate in the network degradation reactions. Acting as a catalyst or an inhibitor of selected degradation reactions, either chain scission or chain crosslinking reactions, the inorganic oxides control the extent of creep, of weight loss through evolution of volatile cyclics, and of modulus change in polysiloxane elastomers subjected to the combined stresses of cyclic loading and high temperature.

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