Thermal Stability of *In Situ* Filled Siloxane Elastomers

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SYNOPSIS

Poly(dimethylsiloxane) elastomers that had been filled with *in situ* precipitated silica were studied by thermogravimetric analysis, under nitrogen and in air. Both types of measurements indicated that the filler raises the temperature of thermooxidative degradation of the polymer, possibly by inactivating the terminal —OH groups on the chains. Commercial fume silica was found to cause more severe degradation problems than did the *in situ* precipitated silica. In all cases, the degradation was more pronounced in air than in the inert atmosphere provided by nitrogen. © 1992 John Wiley & Sons, Inc.

INTRODUCTION

The need for elastomeric materials in a variety of applications has resulted in the development of high-performance materials that can be used over a wide range in temperature and under different environmental conditions, some of which are quite hostile. Organosiloxane polymers, of repeat unit [— SiRR'O —], have long been known to be very good materials in this regard[1] because of their low glass transition temperatures and high thermal stabilities compared with those of most carbon-based elastomers.[2,3] Among these, elastomers of poly(dimethylsiloxane) (PDMS) are by far the most used.

Thermal effects on elastomers can be either reversible or irreversible.[4] More specifically, raising the temperature of an elastomer generally affects it in two ways: There is an immediate effect, which is reversible, followed by a long-term effect known as "heat-aging," which is irreversible. The reversible effects of temperature are physical in origin, for example, changes in the nature or degree of polymer crystallinity. Examples of irreversible change would be additional (inadvertent) curing, and degradative interactions with oxygen or ozone.

Siloxane vulcanizates are extremely stable thermally, frequently to temperatures as high as 250°C. Above this temperature, the heat-aging process gradually reduces the highly elastic rubber to a useless material of a crumbly nature.[5] The changes during heat aging can be caused by a variety of chemical processes, depending on the environmental conditions.[5,6] Among these are siloxane-bond exchange, hydrolysis of siloxane bonds, oxidation of hydrocarbon groups making up cross-links, oxidation of hydrocarbon side groups, depolymerization or reversion, and condensation of hydroxyl groups.[5,7–10]

Of all the siloxane elastomers studied with regard to thermal degradation, PDMS has received the most attention. More specifically, several groups of workers have carefully analyzed PDMS depolymerization products under various degradation conditions. *In vacuo,* PDMS has been known to undergo depolymerization to low molecular weight cyclic siloxanes.[9,11–19] Thomas and Kendrick[9] accounted for the low activation energy of depolymerization (40 kcal mol^{-1}) compared with the energy of the siloxane bond (108 kcal mol^{-1}) by proposing a less energetic mechanism for bond dissociation. They suggested a randomly initiated process that involves the formation of an intramolecular, cyclic, four-centered transition state followed by a siloxane-bond rearrangement.

The cyclic trimer [(CH$_3$)$_2$SiO]$_3$ is reported to be the most abundant product, with decreasing amounts of cyclic tetramer, pentamer, hexamer, and higher oligomers. Hydroxyl-terminated PDMS is

less stable thermally than is PDMS end-blocked with trimethylsilyl [(CH_3)$_3$Si—] groups. Isothermal investigations on hydroxyl-terminated PDMS fractions have shown the presence of a chain-lengthening process *in vacuo* below the depolymerization temperature[9] that is attributed to intermolecular condensation of terminal hydroxy groups. Clarson and Semlyen[20] investigated the high-temperature behavior of cyclic PDMS and attributed the depolymerization process to the ring-opening polymerization of cyclic siloxanes, catalyzed ionically by the surfaces of the vessels, and not to the bond-interchange reactions suggested earlier.[9,21]

PDMS elastomers are known to have a very low melting point ($-40°C$)[22] and therefore cannot readily undergo strain-induced crystallization. This makes them very weak in the unfilled state.[23-26] As a result, most applications require that these elastomers be filled with a "high-structure" particulate silica (SiO_2) in order to improve their mechanical properties.[6,27-29] Under some conditions, they can also improve thermal stability. These silica fillers, however, can also have deleterious effects that promote heat aging.[5] The silanol groups ($\equiv$SiOH) on the surface of the filler are acidic and can not only react with $\equiv$SiOH groups at the end of the siloxane chains, but can also cause cleavage of their Si—O skeletal bonds.[30,31] In the presence of oxygen, the pendant methyl groups on the PDMS chain are first oxidized to hydroperoxide groups, which then eliminate formaldehyde to yield silanol side groups.[6,32] Differential scanning calorimetry measurements, in fact, show exotherms near 250°C in oxygen, but not in nitrogen.[20] In addition, volatile siloxanes can be formed by reaction of either type of $\equiv$SiOH group (along the chain or at its ends) with the siloxane bonds in the chain.[18,30] As mentioned above, the silica surface can also function advantageously, in the present context, by retarding this process through chemisorption or physisorption of $\equiv$SiOH groups.[30]

Apart from the disadvantages that silica fillers can cause in thermal stability, their incorporation in high molecular weight PDMS can be a difficult, time-consuming, and energy-intensive process.[6,27-29] It can also cause premature gelation ("crepe hardening"), which interferes with subsequent processing steps.[33] For these and other reasons primarily concerned with the control of particle size and its distribution,[34] new techniques were developed for precipitating reinforcing silica into an already-cured network by the catalyzed hydrolysis of an alkoxysilane absorbed into it.[34-41]

The present investigation was therefore undertaken in order to study the high-temperature sta-

bility of PDMS elastomers reinforced with such *in situ* precipitated silica. Specifically, two series of PDMS elastomers with different cross-link densities were prepared either by random, peroxide cures of high molecular weight PDMS or by end-linking of relatively short, functionally terminated PDMS. Silica filler was precipitated into both types by the hydrolysis of tetraethyl orthosilicate (TEOS) [Si(OC_2H_5)$_4$]. Another series, closely related to commercial materials, was prepared by blending fume silica into some of the high molecular weight PDMS, which was then cured with peroxide. Both dynamic and isothermal thermogravimetric analyses (TGA) were performed on the various elastomers, either under nitrogen or exposed to air. Comparisons among the results were used to evaluate the effects of the two types of fillers on the thermal properties of PDMS elastomers.

EXPERIMENTAL

Materials

The three PDMS polymers employed consisted of hydroxyl-terminated chains having number-average molecular weights M_n of 3.0×10^5 g mol^{-1} and 18 $\times 10^3$ and 26×10^3 g mol^{-1}. The high molecular weight sample was generously provided by the Dow Corning Corporation of Midland, MI, and the two low molecular weight samples were purchased from the Petrarch Systems Company of Bristol, PA.

Two fume silica samples, Aerosil A130 and MOX80, were obtained from the Degussa Corporation of Teterboro, NJ. Such silicas are obtained by hydrolysis of silicon tetrachloride in a hydrogen-oxygen flame[42]:

$$2H_2 + O_2 + SiCl_4 \xrightarrow{1000°C} SiO_2 + 4HCl \quad (1)$$
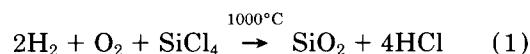
They are hydrophilic because of the chemical nature of the groups present on their surfaces and are nonporous (in contrast to the generally porous particles of precipitated silicas).[43] According to the manufacturer, the two samples have very nearly the same surface concentration of $\equiv$SiOH groups, but the MOX80 sample was co-fumed so as to contain 1.3 wt % Al_2O_3.

Network Preparation

Randomly Cross-linked Networks

The PDMS with the higher molecular weight (3.0 $\times 10^5$ g mol^{-1}) was first dissolved in ethyl acetate

to yield a 10 wt % solution. To this was added the desired amount of benzoyl peroxide (1.5, 2.5, or 4.0% relative to the weight of the polymer). The solutions were then poured into shallow trays and most of the solvent permitted to evaporate. Complete removal of the solvent was ensured by subsequently subjecting the samples to vacuum. The resulting polymer–peroxide mixtures, of high viscosity, were then placed into Teflon-lined aluminum molds. They were cross-linked under pressure (15,000 psi), at 120°C for 1 h, in a Carver Laboratory Press (Model C). The pressure was released when the mold had cooled to room temperature, after which the cross-linked sheets were carefully removed from the molds.

End-linked Networks

The two PDMS samples having lower molecular weights (18 and 26 × 10^3 g mol^{-1}) were dried using molecular sieves (type 4A, Fisher) having a pore size of approximately 4 Å. A weighed amount of each polymer was mixed with an amount of TEOS corresponding to that required for exact stoichiometric balance between its ethoxy groups and the hydroxyl groups present on the ends of the PDMS chains. About 0.5 wt % of stannous-2-ethyl hexanoate catalyst was added to each mixture, which was then poured into a Teflon-lined glass mold. The samples were then end-linked with the TEOS in the usual manner,[35] the reaction occurring in a dry nitrogen atmosphere at reduced pressure (10 mmHg). After 24 h, the network sheets thus formed were turned over (to facilitate removal of the volatile ethanol byproduct) and then allowed to react for an additional 24 h.

Network Extraction

To remove any soluble material that they may have contained, both sets of networks thus-prepared were extracted at room temperature in tetrahydrofuran for 5 days and then deswollen in a series of tetrahydrofuran–methanol mixtures of increasing methanol content. Approximately 5% polymer was thus found to be removable.

Precipitation of SiO$_2$ into the Networks

The silica was *in situ* precipitated into the PDMS elastomers by the following procedure: The sheets of extracted elastomer were cut into small strips that were weighed and then immersed in TEOS for times ranging from 10 min to 22 h to introduce varying amounts of it. The strips were removed and placed into an aqueous solution of 3% by weight of diethylamine catalyst (Matheson), and the hydrolysis of the silane was permitted to proceed for 24 h at 25°C. The networks, which turned cloudy after the reaction, were taken out and dried in air and, finally, in a vacuum oven to constant weight, from which the weight of filler introduced in each case was determined.

Networks with Fume Silica

Some of the high molecular weight PDMS (3 × 10^5 g mol^{-1}) was dissolved in benzene and 1.5 wt % of the cross-linking agent benzoyl peroxide was added to it. When the peroxide had dissolved, 4.9% (by weight of PDMS) of Aerosil A130 or MOX80 fume silica was well mixed into it. (This amount is comparable to the amounts, by volume, of *in situ* precipitated silica in the other samples). The solution was stirred continuously overnight to promote uniform dispersion of the particles and was then evaporated to dryness under vacuum. The polymer-filler blend was finally squeezed repeatedly through a two-roll laboratory mill to further promote homogeneous distribution of the silica particles. Cross-linking of the polymer was then achieved by the benzoyl peroxide cure described above.

Thermogravimetric Analysis (TGA) Measurements

These measurements were carried out on a Perkin-Elmer thermogravimetric analyzer (Model TGA-7) installed in line with a PE 7500 professional computer for data acquisition. The temperature scale of the balance was calibrated prior to use with inorganic thermal standards as recommended in the instrument handbook.[44] All samples were studied both under prepurified nitrogen and in air. Both gases were dried by passing them through a gas purifier before they entered the sample chamber.

The samples, typically 10–20 mg, were placed in platinum pans and were weighed directly on the thermogravimetric balance to within ±1 μg. Both dynamic and isothermal heating studies were carried out, and in either case, the samples were maintained at 50°C for 10 min before the experiments were begun. In the dynamic heating experiments, a heating rate of 10°C min^{-1} over a temperature range of 50–800°C was employed. In the isothermal experiments, the samples were heated to the desired temperature using the maximum heating rate allowed by the furnace, which was 200°C min^{-1} and then held at this chosen temperature. The resulting data were trans-

ferred to a plotter at the end of each experiment to produce the desired thermogram.

RESULTS AND DISCUSSION

Dynamic TGA Results under Nitrogen for *In Situ* Precipitated Silica

The preparative details for the *in situ* filled elastomers are summarized in Table I. The designations for the elastomers prepared by the random peroxide cures consist of the wt % peroxide used followed by either the letter U for the unfilled reference material or letters A–D to specify the increasing amounts of TEOS absorbed into the network for the generation of the silica. The designations for the elastomers prepared by end-linking are obtained by replacing the wt % peroxide by the molecular weight of the chains that were end-linked. The first is a direct measure of the degree of cross-linking, and the latter,

an inverse measure. The wt % silica introduced by the *in situ* precipitation in each of the networks is given in the final column of the table.

Figure 1 presents typical results obtained from the TGA measurements under nitrogen, showing % weight loss over the temperature range 50–800°C for the lightly cross-linked networks (1.5 wt % benzoyl peroxide). The corresponding results for the series of end-linked elastomers $M_n = 18,000 \text{ g mol}^{-1}$ are shown in Figure 2. The curves for the other thermograms under nitrogen were very similar and can be found elsewhere.[10] Interestingly, most of the samples containing *in situ* precipitated silica show small weight losses at relatively low temperatures, well below the temperature at which the pure PDMS begins to degrade. This could possibly be due to the loss of organic groups not hydrolyzed from the TEOS. There are, of course, other reactions that could be occurring below approximately 350°C that would not involve any weight losses at all; for example, the oxidative cross-linking of the chains.[20]

Table I   Preparative Details for Elastomers Filled with *in Situ* Precipitated Silica

Network Designation	$10^{-3} M_n$ g mol^{-1}	Type of Cross-linking	Wt % Benzoyl Peroxide[a]	Wt % Silica
1.5%-U	310	Random	1.5	0.0
1.5%-A				6.1
1.5%-B				19.8
1.5%-C				55.4
1.5%-D				75.3
2.5%-U	310	Random	2.5	0.0
2.5%-A				8.9
2.5%-B				20.4
2.5%-C				49.9
2.5%-D				68.0
4.0%-U	310	Random	4.0	0.0
4.0%-A				10.6
4.0%-B				20.5
4.0%-C				47.3
4.0%-D				71.3
18K-U	18	End-linked	—	0.0
18K-A				4.4
18K-B				20.0
18K-C				50.5
18K-D				57.2
26K-U	26	End-linked	—	0.0
26K-A				3.9
26K-B				17.2
26K-C				44.1
26K-D				52.2

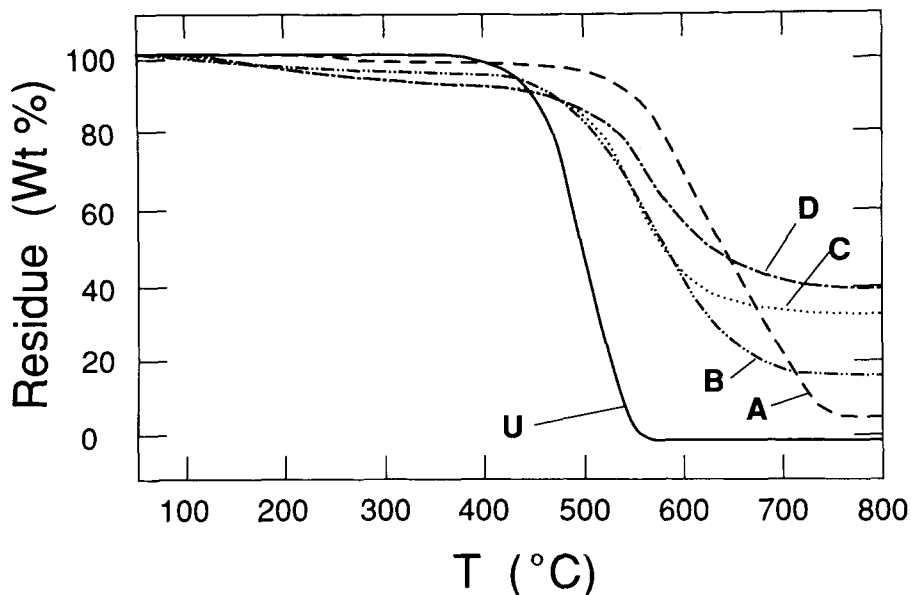[a] Relative to the weight of polymer.

Figure 1   TGA thermograms for networks cross-linked with 1.5% benzoyl peroxide and heated under nitrogen. Each thermogram is labeled with part of the network designation used in Table I.

The most important other features of the thermograms for all five series of samples under nitrogen are given in Table II. Of particular interest is the onset of degradation, observed by the more marked weight loss, presumably due to the formation of volatile cyclic oligomers. This is seen to occur at a lower temperature ($\sim 400°C$) for the unfilled elastomers. Thus, the presence of small amounts of silica in-

creases this degradation onset temperature significantly. As the amount of silica is increased, however, this degradation temperature decreases somewhat before leveling off, with quite a bit of scatter in the results. In any case, the presence of the *in situ* precipitated silica does seem to retard the process of PDMS degradation, at any filler concentration.

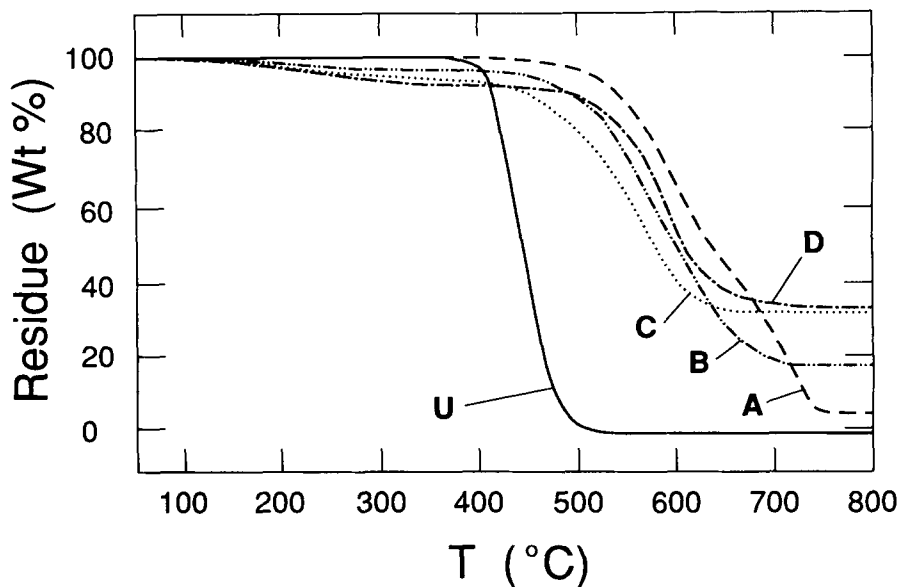While decomposition occurred by a single-step

Figure 2   TGA thermograms for end-linked networks having $M_n = 18,000$ g mol^{-1} and heated under nitrogen. See legend to Figure 1.

process for the unfilled elastomers, the *in situ* filled elastomers degraded by a two-step process. The weight loss during the first step of gradual degradation is very small and slow. Therefore, all the temperatures for onset of degradation reported in this investigation were for the second step, where most of the decomposition (weight loss) occurs. Also, as shown in Figures 1 and 2, the wt % remaining in the filled elastomers is entirely silica. (Although it might seem, e.g., that the network which contained 75.3 wt % silica has more polymer remaining than does the network that contained 6.1 wt % silica, both networks show the expected 100% weight loss when the losses were calculated for polymer alone [assuming no loss of silica]. This representation was used for all the networks in the study.)

Depolymerization of PDMS is a reaction involving the siloxane bond. In the present case, the process could be complicated if the reaction is catalyzed by residual diamine bonded to the surfaces of the *in*

situ precipitated particles. Any residual tin present could also cause complications. In any case, a weight loss is observed if low molecular weight, usually cyclic, volatile polysiloxanes are formed during the depolymerization. This can occur at constant molecular weight of the (remaining) polymer, but under certain conditions, decreases in molecular weight have also been observed.[45] Siloxane-bond exchange, hydrolysis of siloxane bonds, and condensation of hydroxyl groups[10] can lead to a decrease in molecular weight or, in the case of networks, a decrease in effective cross-link density. These changes, however, cannot be measured by TGA, which primarily detects only weight losses due to the formation of cyclics resulting from depolymerization or reversion and to the oxidation of hydrocarbon groups in the cross-links.[10] In the case of elastomers heated under nitrogen, the second effect is presumably absent.

In the case of hydroxyl-terminated PDMS, one of the mechanisms for the formation of cyclics in-

Table II   TGA Results under Nitrogen for Elastomers Filled with *In Situ* Precipitated Silica[a]

Network	Wt % Silica	Onset of Degradation (°C)	Temp for 50% Wt. Loss (°C)	End of Degradation (°C)
1.5%-U	0.0	404	500	566
1.5%-A	6.1	475	636	753
1.5%-B	19.8	424	568	716
1.5%-C	55.4	440	546	755
1.5%-D	75.3	453	562	770
2.5%-U	0.0	412	522	572
2.5%-A	8.9	467	615	757
2.5%-B	20.4	420	555	692
2.5%-C	49.9	440	545	720
2.5%-D	68.0	446	568	751
4.0%-U	0.0	415	516	572
4.0%-A	10.6	447	606	768
4.0%-B	20.5	424	557	711
4.0%-C	47.3	426	546	708
4.0%-D	71.3	452	564	752
18K-U	0.0	383	443	538
18K-A	4.4	460	632	751
18K-B	20.0	445	584	730
18K-C	50.5	412	542	676
18K-D	57.2	466	579	739
26K-U	0.0	386	490	572
26K-A	3.9	459	639	755
26K-B	17.2	410	555	681
26K-C	44.1	419	554	690
26K-D	52.2	467	580	722

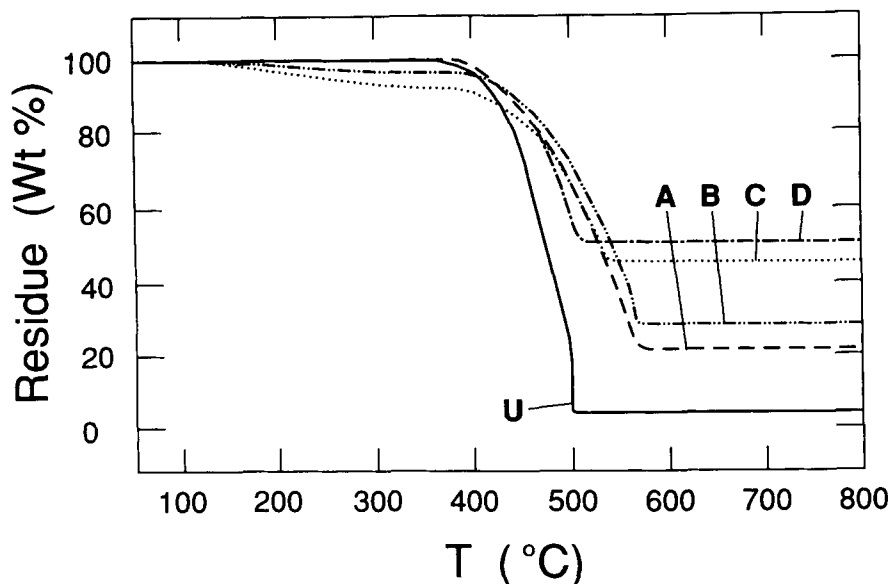[a] Measured at a heating rate of 10°C min^{-1}.

Figure 3   TGA thermograms for networks cross-linked with 1.5 wt % benzoyl peroxide and heated in air. See legend to Figure 1.

volves the hydroxyl chain ends "biting" into the chain a few units back.[9,10,15] Since the addition of *in situ* precipitated silica retards the depolymerization process, it appears that the filler blocks these terminal hydroxyl groups. Presumably, the silica surface has hydroxyl groups that can hydrogen bond with those at the ends of the polymers, resulting in their deactivation. Metal oxides,[45] amphoteric hydroxides,[46] and silica gels[30] have, in fact, been re-

ported to stabilize PDMS elastomers by such deactivation of hydroxyl chain ends.

The acidic $\equiv$SiOH groups on the surface of the silica can themselves cause chain cleavage.[31] Thus, at low concentrations of silica, most of the $\equiv$SiOH groups on the surface of the silica seem to have been used up in binding the polymer chain ends. As the concentration of silica is increased, the number of $\equiv$SiOH groups exceeds the number of PDMS chain

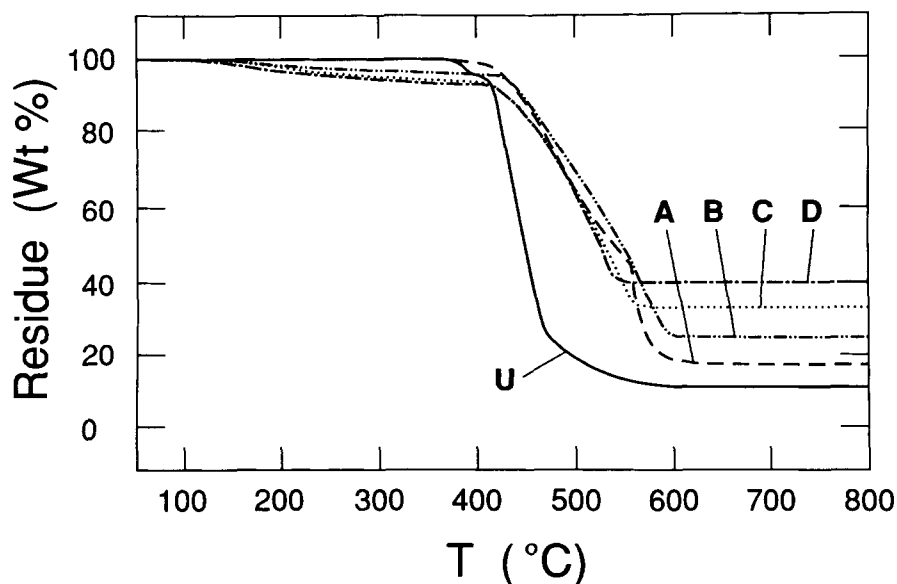**Figure 4**   TGA thermograms for end-linked networks having M_n = 18,000 g mol^{-1} and heated in air. See legend to Figure 1.

ends. The excess $\equiv$SiOH groups on the filler can now cause cleavage of the PDMS chains. This would explain the observation that the effect of this stabilization is most pronounced at the lower concentrations of filler. As another complication, the water formed during the heating of the filler and during the interaction of silanol groups could possibly cause hydrolysis of the elastomer and this effect would be increased at higher filler concentrations.

The TGA thermograms for the networks that were more heavily cross-linked, with 2.5 and 4.0 wt % benzoyl peroxide, show the same trends as the elastomers that were comparatively lightly cross-linked.[10] This supports the expectation that in the presence of an inert atmosphere the only weight loss is due to the formation of cyclic oligomers; that is, there is no significant oxidation of hydrocarbon groups in the cross-links. The major weight losses for all the elastomers examined occurred in the temperature range 404–770°C. Within this range, however, there were quite substantial differences in the

temperature for various stages of breakdown. The differences in temperatures for onset of degradation for the unfilled elastomers and the filled ones are smaller than the differences in temperatures for 50% weight loss, which, in turn, are smaller than those of temperatures for termination of degradation. This indicates that not only does the presence of silica postpone the onset of degradation, it also slows down the rate for complete degradation.

In all the thermogravimetric traces recorded, the temperature at which thermal depolymerization commences was found to be greater than 350°C. Since any residual basic catalysts remaining from the polymerization process would have had a deleterious effect on the thermal stability of the polymer,[13,14,45-48] this observation confirms the catalyst-free nature of the elastomers[9] (the catalyst having been removed during the extraction process).

Since the hydroxyl end groups of PDMS are responsible for its depolymerization, polymers end-blocked with trimethylsilyl [$(CH_3)_3Si$—] groups

Table III   TGA Results in Air for Elastomers Filled with *In Situ* Precipitated Silica[a]

Network	Wt % Silica	Onset of Degradation (°C)	Temp for 50% Wt. Loss (°C)	End of Degradation (°C)
1.5%-U	0.0	371	475	515
1.5%-A	6.1	381	525	582
1.5%-B	19.8	381	528	577
1.5%-C	55.4	390	500	549
1.5%-D	75.3	395	483	521
2.5%-U	0.0	368	496	526
2.5%-A	8.9	401	547	634
2.5%-B	20.4	381	539	588
2.5%-C	49.9	389	508	555
2.5%-D	68.0	409	517	596
4.0%-U	0.0	378	511	546
4.0%-A	10.6	402	545	615
4.0%-B	20.5	387	540	581
4.0%-C	47.3	387	517	571
4.0%-D	71.3	409	500	580
18K-U	0.0	374	450	580
18K-A	4.4	403	533	615
18K-B	20.0	424	530	607
18K-C	50.5	418	496	565
18K-D	57.2	414	494	558
26K-U	0.0	375	450	581
26K-A	3.9	411	523	579
26K-B	17.2	424	529	579
26K-C	44.1	418	499	569
26K-D	52.2	419	494	597

[a] Measured at a heating rate of 10°C min^{-1}.

Table IV Comparison of TGA Results under Nitrogen for Elastomers Filled with *In Situ* Precipitated Silica or Commercial Fume Silica

Network	Type of Silica	Wt % Silica	Onset of Degradation (°C)		Temp for 50% Wt Loss (°C)		End of Degradation (°C)	
			N_2	Air	N_2	Air	N_2	Air
1.5%-U	—	0.0	404	371	500	475	566	515
1.5%-A	*In situ* precipitated	6.1	475	381	636	525	753	582
1.5%-AE	Fume (A130)	4.9	458	372	527	477	600	511
1.5%-MO	Fume (MOX80)	4.9	418	361	514	462	603	508

are of considerable interest and have, in fact, been prepared.[9] In the present investigation, an attempt was made to eliminate such hydroxyl groups by preparing the networks using an end-linking technique. Specifically, the PDMS terminal hydroxyl groups are reacted with TEOS, which in this context serves as a multifunctional end-linking agent.[35,49] Typical results of TGA analysis on PDMS elastomers prepared in this way, using polymer with molecular weight of 18×10^3 g mol^{-1}, are presented in Figure 2. The corresponding results for those having a molecular weight of 26×10^3 g mol^{-1} are presented elsewhere.[10] Preparative details for both series of samples are given in Table I, and the most important features of their thermograms under nitrogen are given in Table II. From these results, it can be seen

that the molecular weight of the end-linkable chains has very little effect on the depolymerization temperatures, which is in agreement with the results on the peroxide-cured samples mentioned above.

On the basis of the previous discussion of the peroxide cross-linked elastomers, it would seem that if the PDMS hydroxyl end groups were blocked, all the hydroxyl groups on the silica surface would be free and able to depolymerize the PDMS even faster. However, this was not found to be the case. The filled elastomers exhibit the same behavior as that of the peroxide cross-linked elastomers in that the presence of silica retarded the depolymerization. This could possibly be explained by incomplete end-linking of the PDMS chains, which is consistent with the elastomers containing approximately 5%
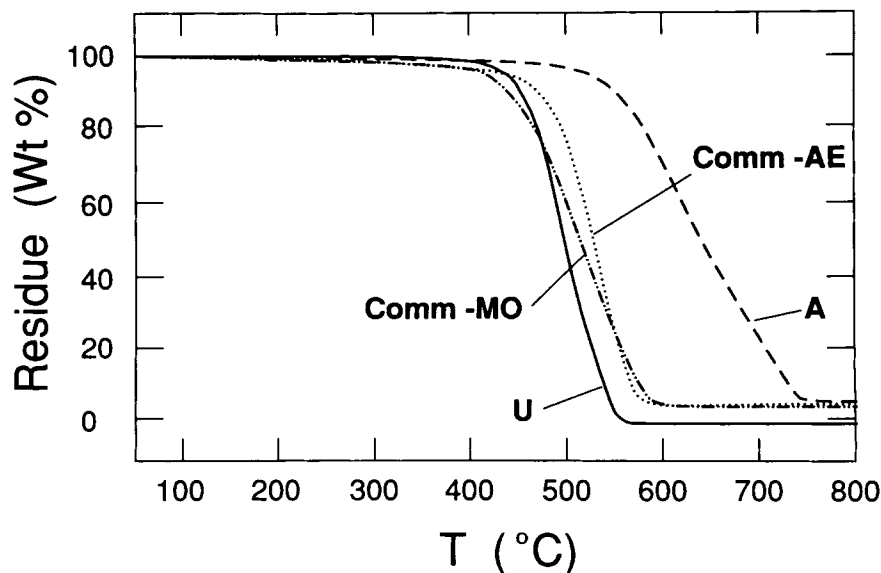

Figure 5 Comparison of TGA thermograms for networks containing either *in situ* precipitated silica or commercial fume silica (COMM-AE for sample A130 and COMM-MO for MOX80). Networks had been cross-linked with 1.5 wt % benzoyl peroxide, the samples were heated under nitrogen, and each curve is labeled with part of the network designation used in Table IV.

soluble polymer. This implies the presence of some free PDMS hydroxyl groups that could have bonded to and deactivated the hydroxyl groups on the silica surface, thereby again improving the thermal stability.[10]

Dynamic TGA Results in Air for *In Situ* Precipitated Silica

In the case of an oxidizing environment such as air, the aging of PDMS becomes much more complex. The production of volatile material is accelerated[15] and there can be considerable oxidation of hydrocarbon groups in cross-links and even the formation of silica.[5] Typical TGA data for both the peroxide cross-linked and end-linked elastomers are shown in Figures 3 and 4, respectively. The complete set of thermograms in air is given elsewhere,[10] and their most important features are summarized in Table III. One of the most striking features indicated by these results involves the degradation temperature, which decreased markedly. This suggests that the filler was unable to deactivate the large number of depolymerization sites that apparently appear as a result of the oxidative rupture of the chains.[30] As a result, the increases in depolymerization temperature provided by the filler are smaller in the case of heating in air compared with heating under nitrogen. Nonetheless, the filler is apparently still effective in blocking the hydroxyl chain ends and retarding the depolymerization process, even though to a lesser extent.

It might be expected that an increase in cross-link density would decrease the thermal stability,[10] but the relevant results in Table III do not demonstrate such an effect. The results also show that $-CH_3$ groups on the Si atoms are eliminated in some way, and Andrianov et al.[50] and Aleksandrova et al.[51] have, in fact, found methane among the degradation products of hydroxyl-terminated PDMS. Grassie and MacFarlane[15] have proposed a mechanism for such formation of methane through an intermediate siloxy ion in the presence of oxygen, thus explaining the accelerated formation of volatile material. In any case, during the degradation in air, all the elastomers lost all of their organic groups with only silica remaining as the final product.

Comparisons between *In Situ* Precipitated Silica and Commercial Fume Silica

Dynamic TGA Results

Networks cross-linked with 1.5 wt % benzoyl peroxide were chosen to compare the relative effectiveness of *in situ* precipitated and fume silica (Aerosil A130 and MOX80) on thermal stability. Comparable amounts of silica (by volume) were used, as shown in the third column of Table IV.

The results of the TGA analysis under nitrogen are shown in Figure 5. It can be seen that the fume silica did not increase the degradation temperature nearly as much as did the *in situ* precipitated silica. Somehow, the $\equiv$SiOH groups on the surface of the
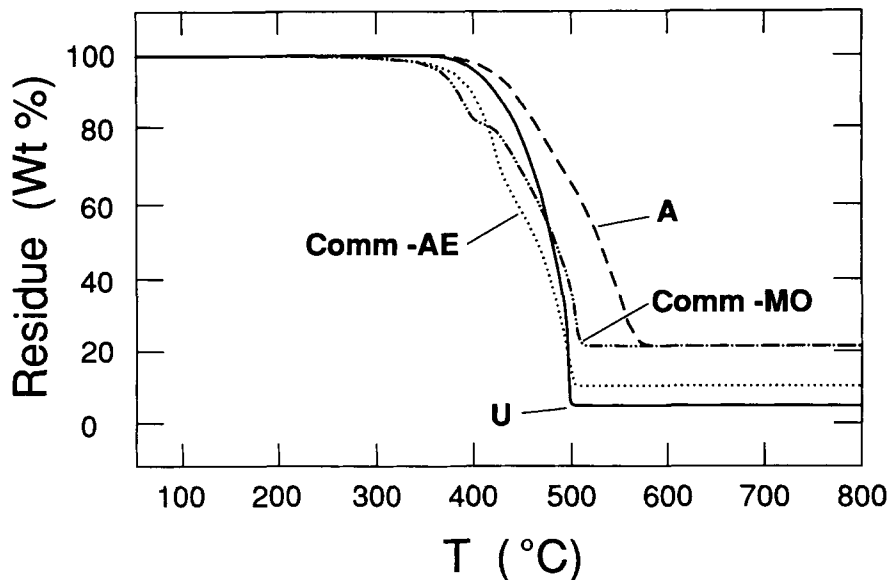
Figure 6   Comparison of TGA thermograms for the same samples characterized in Figure 5, but now having been heated in air.

Table V   Isothermal Degradation Results for *In Situ* Filled Elastomers under Nitrogen for 1 h

Network	Wt % Silica	Temp (°C)	Wt Loss (%)	TGA Wt Loss (%)
1.5%-U	0.0	300	0.8	0.1
		350	5.2	0.1
		400	48.1	0.8
		450	87.9	8.5
		500	100.0	50.6
		600	100.0	100.0
		700	100.0	100.0
1.5%-A	6.1	300	1.3	0.7
		350	2.2	0.9
		400	5.5	0.9
		450	30.5	1.3
		500	32.5	3.1
		600	88.8	29.7
		700	98.9	80.3
1.5%-B	19.8	300	3.7	4.3
		350	5.7	4.7
		400	17.0	5.1
		450	40.7	7.8
		500	95.1	18.9
		600	95.0	67.5
		700	97.9	98.8
1.5%-C	55.4	300	9.9	9.7
		350	12.0	10.9
		400	25.3	11.5
		450	53.6	13.4
		500	99.6	22.1
		600	100.0	87.1
		700	100.0	100.0
1.5%-D	75.3	300	13.1	12.2
		350	15.8	14.4
		400	30.1	15.5
		450	54.8	16.8
		500	91.7	22.1
		600	100.0	74.1
		700	100.0	100.0

fume silica particles are less able to inactivate all the hydroxyl groups on the PDMS chains. A definitive explanation would require very careful measurements of ≡SiOH group concentrations on the two types of particles and their relative reactivities.

Figure 6 shows the analogous TGA data for the samples in air, and the most pertinent features of the thermograms are given in Table IV. Under these conditions, the beneficial effect of the *in situ* precipitated silica is much reduced, and the effect of the fume silica is actually detrimental.

Isothermal TGA Results

To investigate the long-term thermal degradation behavior of the filled elastomers, selected samples were exposed to isothermal heating for 1 h at different temperatures in a nitrogen atmosphere. The ones containing *in situ* precipitated silica were 1.5%-U, 1.5%-A, 1.5%-B, 1.5%-C, and 1.5%-D, along with the elastomers containing the two types of fume silica. The results for the former series are shown in Table V, and for the latter, in Table VI. The trends

Table VI **Isothermal Degradation Results for Elastomers Filled
with Commercial Fume Silica**[a]

Network	Type of Silica	Wt % Silica	Temp (°C)	Wt Loss (%)	TGA Wt Loss (%)
1.5%-AE	Fume (A130)	4.9	300	3.2	1.7
			350	4.4	2.5
			400	29.2	3.4
			450	63.4	6.2
			500	99.5	23.9
			600	100.0	99.6
			700	100.0	100.0
1.5%-MO	Fume (MOX80)	4.9	300	3.2	1.6
			350	10.6	2.4
			400	40.0	4.0
			450	64.6	13.0
			500	99.9	39.3
			600	100.0	99.6
			700	100.0	100.0

[a] Heated under nitrogen for 1 h.

in the results were found to be very similar to those found in the dynamic experiments, in particular the presence of silica did seem to retard the depolymerization proc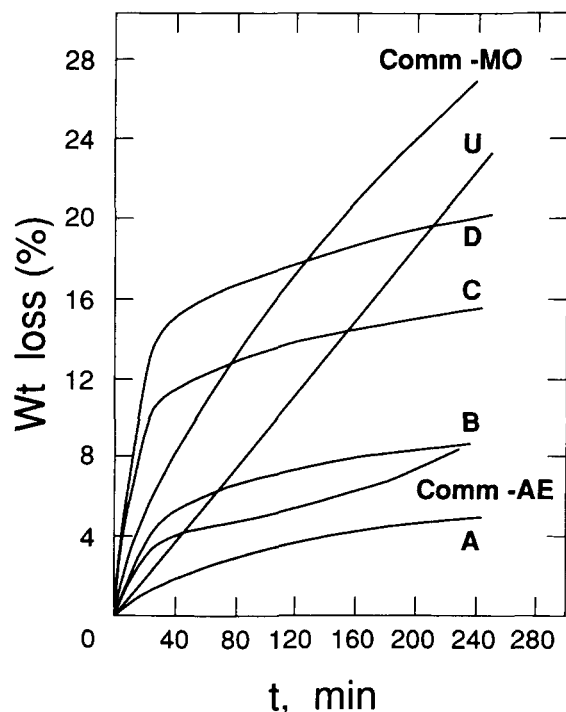ess. Also, the weight loss was seen to be higher during isothermal heating, compared to that at the same temperature in the dynamic experiments. Figure 7 shows the % weight loss as a function of time for these samples heated at 350°C in nitrogen. The reason the MOX80 fume silica causes such a pronounced increase in the degradation of PDMS is not known, but could conceivably be related to the Al_2O_3 it contains. In any case, there do appear to be considerable advantages to using *in situ* precipitated silica for improving the thermal stability of PDMS elastomers.

It may be possible to carry out additional experiments to elucidate the detailed mechanisms of the degradation process for various types of fillers, under different environmental conditions.

Figure 7 Isothermal heating results, taken at 350°C and under nitrogen, for the networks cross-linked with 1.5 wt % benzoyl peroxide. Each curve is labeled with part of the network designation used in Tables V and VI.

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