

The Effect of Fumed Silica upon the Reaction of Iron Octoate and Polysiloxanes

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SYNOPSIS

Silica is a common component in silicone elastomer formulations. Silica is known to have surface hydroxyl groups and the reactions and interactions of these surface groups with various materials have been studied extensively in the past. It is believed that the iron octoate used to combat oxidative embrittlement in silicone elastomer formulations may also react with the surface of silica, specifically fumed silica. Dynamic mechanical spectroscopy (DMS), Fourier Transform Infrared Spectroscopy (FT-IR), Electron Scanning for Chemical Analysis (ESCA), and Gel Permeation Chromatography (GPC) were used to study the influence of untreated fumed silica and silica treated with dimethylsiloxane species on the iron octoate reaction. The rate of reaction was studied as a function of loading of silica. From analyzing rates of backbone scission and salt consumption, it is found that the iron octoate reacts preferentially with the surface of untreated fumed silica. Conversely, iron octoate appears to have no preferential reaction with the surface of the treated fumed silica.

INTRODUCTION

Silicones are damaged at elevated temperatures by oxidative crosslinking. Oxidative crosslinking causes embrittlement of the silicone leading to shrinkage, cracking, and eventual failure. It has been shown that the addition of metallic salts slows the viscosity increase of linear siloxanes caused by oxidative crosslinking.¹ Temperature stabilization of silicone elastomers can be improved since metallic salts react to cleave the siloxane backbone. This backbone scission softens the elastomer which counteracts embrittlement caused by oxidation, thereby extending the life at elevated temperatures (200–400°C). At higher temperatures, degradation of the siloxane chain itself occurs due to chain unzipping; this severely limits the life of the elastomer.²

One limitation of this reaction is that it is not catalytic in the absence of oxygen radicals. Previous work has postulated that in an oxygen-rich atmosphere, the iron reacts to cleave the siloxane backbone and is converted to ferrous iron. Subsequent

reaction of the ferrous iron with oxygen regenerates the ferric iron.³ The formation of M—O—Si structures was inferred. Other transition metals found to be effective were copper, cobalt, nickel, cerium, and manganese.

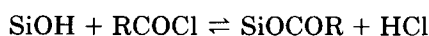
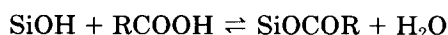
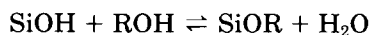
In the previous paper, a fundamental study of the reaction of iron octoate and polysiloxanes was undertaken.⁴ The reaction was performed under an inert atmosphere and the reaction products were identified as cyclic siloxane distillates with a repeat unit of three and higher, a black precipitate identified as an iron (III) silicate, and hexanoic acid which is partially converted into the anhydride. The reaction is believed to proceed by electrophilic attack of the iron upon the oxygen of the siloxane backbone with subsequent ligand exchange. The result is cleavage of the siloxane backbone and formation of Fe—O—Si bonds, leaving one silicon atom adjacent to the oxygen with an orbital available for bonding. This reactive end then undergoes cyclization, but the exact mechanism is not as yet known.

Since the siloxane backbone cleavage is thought to occur through attack on the oxygen by the ferric iron, it is thought that the introduction of other oxygen-containing species might have an influence upon the rate of reaction of the iron octoate. Silica

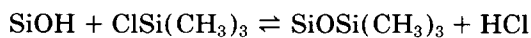
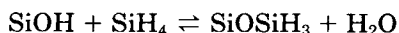
is an important component in elastomeric formulations. It provides improved tensile strength, as well as tear and abrasion resistance. Silica has a hydroxyl oxygen that could react with the metallic salt. The influence of untreated fumed silica is assessed and compared with the influence of surface-treated silica upon the rate of reaction of the iron octoate with the polysiloxanes.

Amorphous silicas have a high specific surface area. The accepted method for calculating surface area is the Bruman, Emmett, and Teller (BET) method.⁵ Specific surface area is calculated from an adsorption isotherm of N₂ gas. The BET method provides the same results whether the surface is hydroxylated or dehydrated. Lowen and Broge⁶ calculated the surface area of amorphous silica that was dehydrated at 120°C to be 182 m²/g. It is generally agreed that on a smooth, nonporous, heat-stabilized amorphous silica, dried at 120°C, there are 4–5 Si—OH groups/nm².

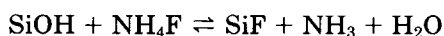
Since the beginning of this century, there have been many studies concerning reactions on the silica surface. In an excellent review, reactions are categorized by the nature of bonds formed with the silicon atom, and important reactions are summarized below.⁷ Examples of reactions that form Si—O—C bonds are shown:



Reactions of silanol groups that can form Si—O—Si bonds are as follows:



Silicon halogen bonds, although subject to hydrolysis, can be formed through these reactions:



Reaction of silanols with Grignard reagents produces Si—C bonds. There are various reactions of silanol with boron, sulfur, phosphorous, aluminum, titanium, tin, molybdenum, vanadium, and chromium that form M—O—Si bonds. Adsorption of various organic cations and bases, inert gases (argon and nitrogen), and hydrocarbon groups through poly-

valent metals have been studied. Lastly, adsorption of polymers such as polyethylene oxide, polyvinyl alcohol, polyethylene glycol, and proteins have been documented. Thus, the presence of the silica surface is expected to have some influence upon the reaction of iron octoate and the siloxane.

The influence of the addition of the silica can be monitored by Fourier transform infrared spectroscopy and dynamic mechanical analysis. Dynamic mechanical analysis was used to evaluate empirically the influence of untreated and surface-treated fumed silica on the rate of siloxane backbone cleavage. The use of mechanical analysis is common to monitor degradation of crosslinked elastomers, and the word “chemorheology” was coined to describe such work. Chain scission (random and chain-end induced), depolymerization, oxidation, and cleavage of crosslinks were investigated using stress relaxation of rubber materials. The theory of rubber elasticity was applied to describe quantitatively the decay of stress as a result of these processes.⁸ It was possible to describe the effect of temperature as follows:

$$f(t) = \phi(k', t)$$

The functional dependence was found to be given by the Arrhenius equation:

$$k = k_0 \exp(\Delta E/RT)$$

The data in this study follow the same functional dependence as in the elastomeric studies. However, theoretical analysis is complicated by the fact that the system is analyzed in the dynamic mode, consists of linear chains with no crosslinks, and is plasticized by the presence of small cyclic species from depolymerization, as was shown in the previous paper. Thus, the equations applied to study this system are empirical in nature; however, they are a valuable tool for comparison of samples within this study.

EXPERIMENTAL

Trimethylsilyl end-blocked polydimethylsiloxane (PDMS) gum, oligomeric trimethylsilyl end-blocked poly(*co*-dimethyl-methylphenyl) siloxane and oligomeric PDMS were used as received from Rhone Poulenc. Iron octoate, untreated fumed silica, and treated fumed silica were also used as received from Rhone Poulenc. Iron octoate is a solution of mineral spirits and the salt of 2-ethylhexanoic acid and 6% ferric iron. Phenyltrimethoxysilane was used as received from Petrarch Systems.

Reactions of 3 mL poly(*co*-dimethyl-methyl-phenyl)siloxane and iron octoate mixture were performed at 230°C under inert conditions. Samples were taken every 15 min for FT-IR analysis. The *co*-oligomer was chosen for its resistance to oxidation at this temperature and its ability to disperse the iron octoate homogeneously.

The iron octoate and fillers were incorporated into the siloxane gum (40 g) by mixing in a sigma blade mixer which is coupled with a Brabender Plasticorder, for 20 min, at room temperature and 20 rpm.

A Rheometrics RMS-800 dynamic mechanical spectrometer equipped with a 2000 g cm force rebalance transducer was used for the rheological measurements. A 50 mm cone with an angle of 0.039 rad was used with a 55 mm stainless steel cup. Samples were pressed flat into the cup. The strain and rate at which the experiments were done were 7% and 5 rad/s, respectively. These parameters were chosen to insure that the material remained between the plates, and that adequate torque was maintained throughout the experiment. All measurements were performed under flowing nitrogen to minimize oxidation of exposed material.

A Michelson 110 single beam FT-IR spectrometer equipped with a liquid-nitrogen-cooled mercury-cadmium-telluride (MCT) detector was used at a resolution 4 cm⁻¹. The specific detectivity of the MCT detector was 1 × 10¹⁰ cm Hz^{1/2}/W. Samples were purged by nitrogen gas for 20 min to minimize atmospheric moisture. One hundred coadded scans were taken. Samples for transmission spectra were placed between two KBr plates and referenced to

$$\eta^* = \eta_1^* e^{-kt}$$

$$\frac{d\eta^*}{dt} = -k\eta_1^* e^{-kt}$$

$$\ln \frac{d\eta^*}{dt} = \ln(-k\eta_1^*) - kt$$

$$\Downarrow$$

$$k = k_0 e^{\frac{\Delta E}{RT}}$$

$$\ln k = \ln k_0 - \frac{\Delta E}{R} + \frac{1}{T}$$

Figure 1 Calculation of empirical front factor (k_0) as a criterion for comparing the influence of various fillers on the rate of siloxane backbone scission.

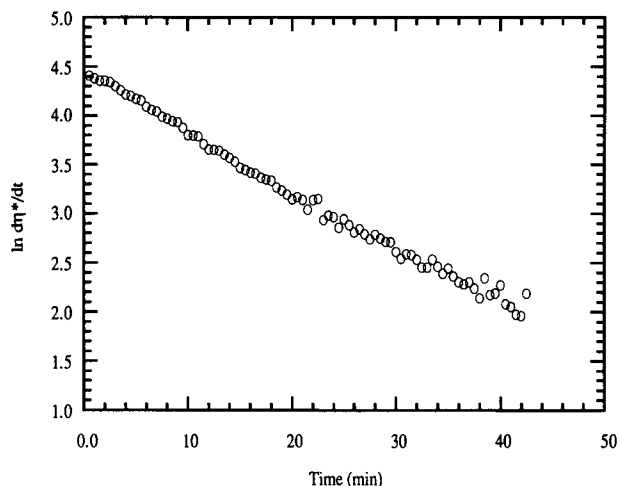


Figure 2 Natural log of the first derivative of the complex viscosity versus time for 1% by weight iron octoate in trimethyl end-blocked PDMS gum at 190°C. Empirical rate constant k is the slope of this curve.

an empty chamber with attenuator. Diffuse reflectance samples (DRIFT) were referenced to ground KBr. The sample was ground 1–2% in KBr.

Electron spectroscopy for chemical analysis (ESCA) was performed using a Perkin Elmer ϕ -5400 with an Omni focus lens. The source was magnesium K α radiation. The power was 400 W, and the vacuum was 10⁻⁹ torr. The powder sample was placed on a copper tape before placing in the sample holder. An argon ion source was used for sputtering and the sputtering rate was 3.0–3.5 nm/min.

RESULTS AND DISCUSSION

One of the useful methods for evaluating the performance of an elastomer at elevated temperatures is to investigate its mechanical properties under these conditions. At elevated temperatures, the iron octoate cleaves the siloxane backbone leading to a drop in viscosity and an increase in $\tan \delta$ over time. A method was developed to describe quantitatively the reaction of the iron octoate and linear siloxanes, and the influence of the addition of any fillers, by following the change in these properties.

Figure 1 provides a method for calculating an empirical rate constant of the rate of siloxane backbone cleavage. Complex viscosity, which is defined as $\eta^* = \eta' - i\eta''$, has an exponential dependence (e^{-kt}) upon the initial complex viscosity (η_1^*). By plotting the natural log of the viscosity derivative versus time, errors from differences in initial viscosity of

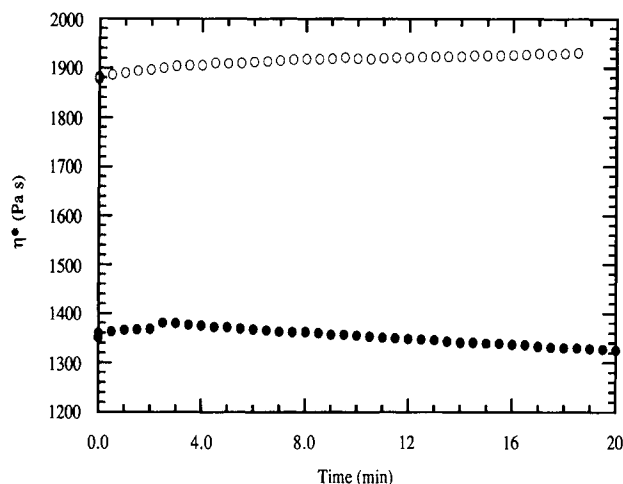


Figure 3 Plot of the complex viscosity versus time for pure PDMS gum at 190°C and 230°C: (○) 190°C; (●) 230°C.

the samples are eliminated and errors from thermal equilibration are minimized. The viscosity derivative at any data point is determined by plotting the difference between the data points before and after any one data point. Since the time interval is 30 s between measurements, the denominator of the equation is equal to 1. Thus, the slope is simply calculated by the difference of the two viscosities. The empirical rate constant k is taken from the slope of the viscosity derivative curve. An example of this plot is shown in Figure 2. An overall rate constant is calculated by assuming an Arrhenius temperature de-

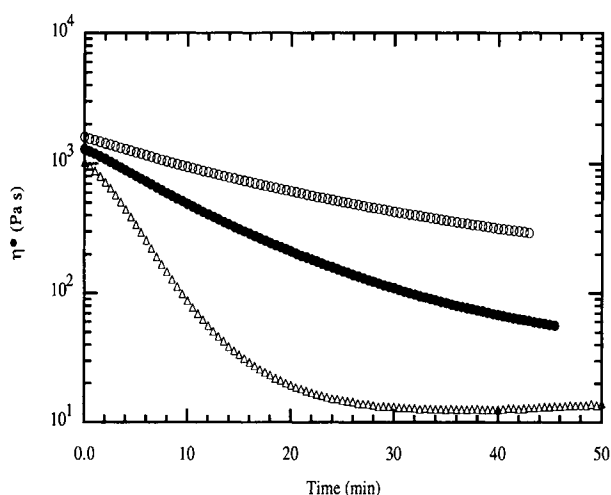


Figure 4 The effect of the 1% by weight iron octoate in PDMS is shown by the decrease of the complex viscosity over time for 189°C, 209°C, and 229°C: (○) 189°C; (●) 209°C; (△) 229°C.

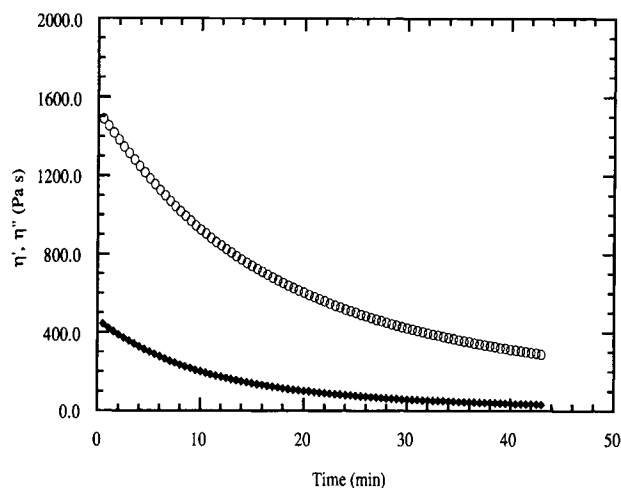


Figure 5 The decrease of storage (η') and loss (η'') viscosities as a function of time for 1% by weight iron octoate at 190°C; (○) η' ; (◆) η'' .

pendence and plotting the natural log of the empirical rate constant ($\ln k$) versus the inverse of the temperature ($1/T$). The front factor (k_0) is calculated by extrapolation to the y axis. This rate constant is valid only for the temperature range studied since the iron octoate is known to catalyze oxidation below 150°C.⁹ Since the material is viscoelastic, the rate constant is also dependent upon the rate and strain applied to the sample. The value of the activation energy (ΔE) calculated from the slope of the plot is dubious. However, by comparison of front factors (k_0), the effect of various fillers upon the rate of reaction may be evaluated.

Figure 3 displays the complex viscosity of pure PDMS as a function of time at typical experimental temperatures, 190 and 230°C. The complex viscosities are essentially constant, showing that thermal equilibration has occurred and that the material remains between the plates throughout the course of the experiment. This is essential for correct interpretation of the phenomena. The chain scission is reflected in the rheological properties in Figure 4. The rate of chain scission, as reflected with the

Table I Calculation of Front Factor (k_0) for Various Loadings of Untreated Fumed Silica

Percentage Silica	$\ln k_0$	Error
0.0	15.0	± 1.0
2.0	14.2	± 1.0
3.5	9.8	± 1.0
5.0	8.5	± 1.0

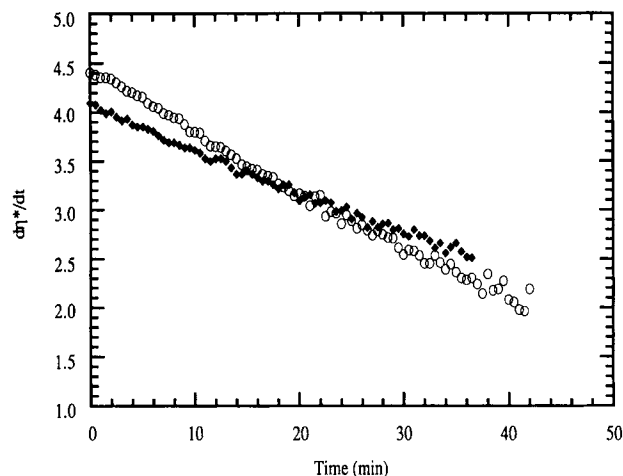


Figure 6 The first derivative for complex viscosity versus time for various loadings of silica: (○) 0% silica; (◆) 3.5% silica.

changing slope, increases with increasing temperature. Eventually, the viscosity reaches a plateau as is seen at 229°C. This reflects the noncatalytic nature of the reaction of the iron octoate and the polysiloxanes. The storage (η') and loss (η'') viscosity in Figure 5 both exhibit an exponential decrease upon time. The contribution of η'' is large since the polymer is linear. Thus, η^* is used for calculations since η' and η'' are comparable in magnitude.

The relative rates of reaction between different concentrations of treated fumed silica for 5% by weight iron octoate is summarized in Table I. The front factor decreases with increasing loading of untreated fumed silica. Also, if the rates of degradation with different loadings of silica are compared at the same temperature as in Figure 6, the same trend is seen: a decreasing slope with increased loading of untreated fumed silica. A more thorough understanding of the phenomena at hand warranted a molecular study with the following hypothesis.

If the reaction of iron octoate and polysiloxanes involves attack of the iron upon the oxygen of the siloxane, then addition of oxygen-containing species should have an effect upon the rate of reaction. Since the oxygen of the hydroxy species on the surface of the silica has a more negative charge than the oxygen in a siloxane backbone, the electrophilic attack by the iron should be accelerated by the presence of such species. If the iron preferentially reacts with the hydroxyl oxygen, then less iron is available for reaction with the siloxane matrix. Consequently, the rate of siloxane backbone cleavage should slow with increased loading of silica. This is indeed what we observe. This hypothesis was further investigated

by monitoring salt consumption as a function of loading for untreated fumed silica.

Preferential reaction of iron with the silica was tested. FT-IR was used to follow the reaction of the iron octoate. The $-\text{CH}_2$ stretching mode at 2859 cm^{-1} of the salt was followed and the $-\text{CH}_3$ stretching mode of the methyl group on the silicon atom of the siloxane matrix at 2905 cm^{-1} was used as an internal standard. The areas of these two bands were compared from data obtained through curve resolution of this region. Analysis of the reaction in the infrared through any other species is virtually impossible. Although some siloxane is lost through volatilization of low molecular weight species from the siloxane gum after reaction with the iron octoate, the siloxane is present in such an excess that such a small loss makes little difference in the 2905 cm^{-1} band. Figure 7 shows the reaction of the salt as a function of loading for fumed silica with 5% by weight iron octoate in poly(*co*-dimethyl-methyl-phenyl)siloxane at 230°C. As the loading of silica is increased, so is the rate of reaction of the salt, as reflected by the increasing slope. The disappearance of the salt, as indicated by the decrease in the 2859 cm^{-1} band, originates from the conversion of the salt to hexanoic acid. Subsequent evaporation of the hexanoic acid product controls the decrease in the 2859 cm^{-1} band. The rate of evaporation is assumed to be the same for all loadings of silica and differences in the slopes of the 2859 cm^{-1} peaks are attributed to the effect of the silica.

Table II displays the slopes of Figure 7. The slope indicates of the rate of reaction. The higher the

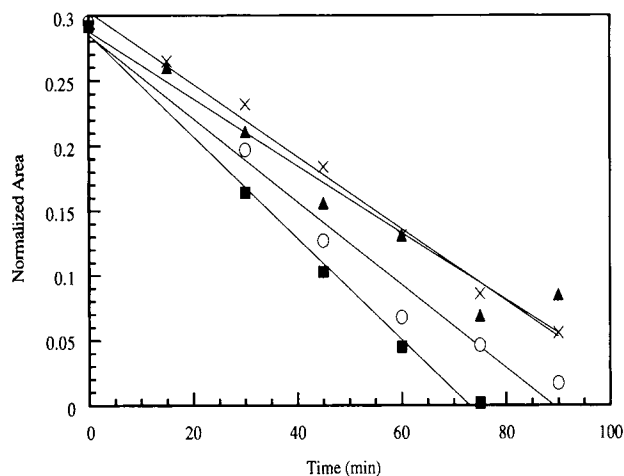


Figure 7 Kinetics of salt consumption for 5% iron octoate in PMPS at 230°C as a function of loading of untreated fumed silica: (▲) 0% silica; (X) 1% silica; (○) 5% silica; (■) 10% silica.

Table II Slope of Salt Consumption Curves as a Measure of the Rate of Reaction of Iron Octoate for Various Loadings of Untreated Fumed Silica

Percentage Silica	Slope $\times 10^{-4}$	Error $\times 10^{-4}$
0	25.8	± 2.4
1	28.0	± 1.3
5	32.0	± 1.5
10	39.2	± 1.5

* 5% by weight iron octoate PMPS at 230°C.

slope, the faster the reaction. As the silica content increases, so does the rate of reaction. Linear regression was performed and the standard error was calculated. The differences in the slopes are real, except where the errors overlap between 0% and 1% silica content. The increase in rate can be explained only if the iron has reacted with the hydroxyl species on the silica surface. The rate of reaction was accelerated by the presence of a hydroxyl oxygen, which has a greater electronegativity than an oxygen in the siloxane backbone.

It is interesting to understand further the reaction of iron and surface hydroxyl groups. Grafting of siloxane molecules through reaction with the iron at the surface of the silica was investigated. Silica reacted with the iron octoate and siloxane for 105 min at 23°C was extracted with THF and centrifuged for 10 min. After centrifuging, the THF was discarded. This process was repeated three times to insure removal of species not bound to the silica surface. The silica was air dried overnight. Figure 8 shows the DRIFT spectra of the silica (A), reacted

silica (B), the difference spectrum B-A, and poly(*co*-dimethyl-methylphenyl)siloxane (C). The broad band from 1300 to 1000 cm^{-1} in spectrum A is assigned to the antisymmetric Si—O—Si stretching mode whereas the symmetric Si—O—Si stretching mode gives rise to the band at 800 cm^{-1} . The peak at 950 cm^{-1} is assigned to the Si—O stretching mode of the surface hydroxy species. Clearly, the subtracted spectrum, comparing the subtracted spectrum with the transmission spectrum of the siloxane, shows the existence of the copolymer on the silica surface. Judging from these spectral features, plus the difficulty of further solvent extraction of physically adsorbed siloxane, the observed copolymer is probably chemically bound to the surface.

It is desirable to further verify that the siloxane seen on the surface of the silica had actually reacted with the surface and was not merely physically adsorbed. The silica was mixed as 10% by weight in the siloxane oligomer and underwent the same washing procedure as did the previous sample. The DRIFT spectrum was taken and subtracted from the spectrum of the as received silica and the presence of the siloxane species was not detected. Thus, four washings were deemed sufficient to remove all physically adsorbed siloxane and it was assumed that the remaining siloxane seen on the surface is chemically grafted.

It is known that Si—O—Si bonds undergo exchange reactions catalyzed by the presence of acids or bases or even water.¹⁰ An experiment was performed to determine whether these interchange reactions and subsequent recondensation with surface

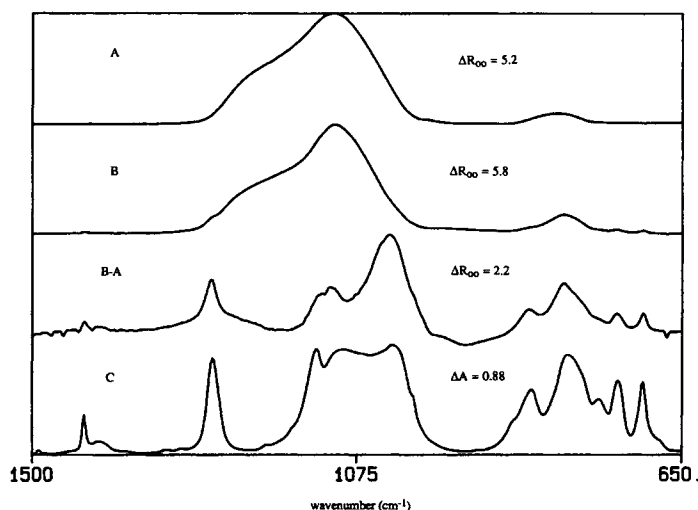


Figure 8 DRIFT spectra: (A) as received untreated fumed silica; (B) reacted untreated fumed silica; B-A; (C) transmission spectrum of PMPS.

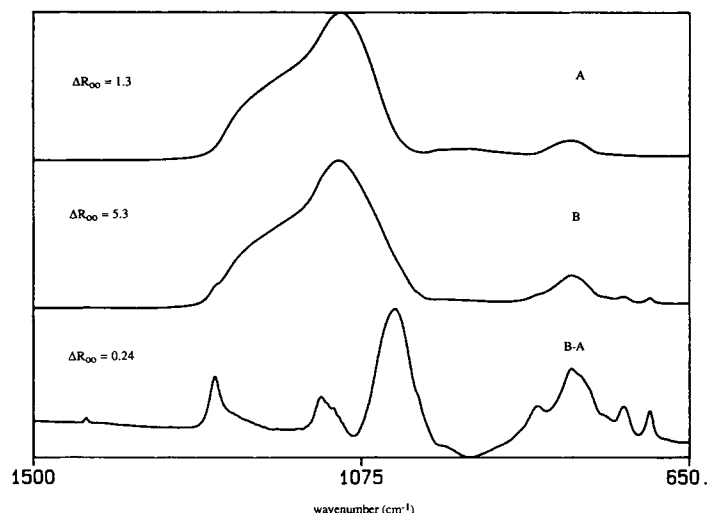


Figure 9 DRIFT subtraction spectrum of untreated fumed silica 10% by weight in PMPS heated at 230°C for 90 min minus untreated fumed silica. Grafting of the siloxane oligomer onto the silica surface occurs without iron octoate.

hydroxyl species could influence chemical grafting of the siloxane onto the surface of the silica. The silica was mixed as 10% by weight of the siloxane oligomer and heated at 230°C for 90 min. The silica underwent washing and drying and a DRIFT spectrum was taken. A subtraction was performed with the as received silica (Fig. 9). The presence of silox-

ane molecules on the surface of the silica suggests that these interchange reactions could occur causing the siloxane to graft onto the surface of the silica. This could be a contributing reason as to why the siloxane is present on the surface of the silica from the reaction of the siloxane and iron octoate. It is concluded that through both exchange reactions and

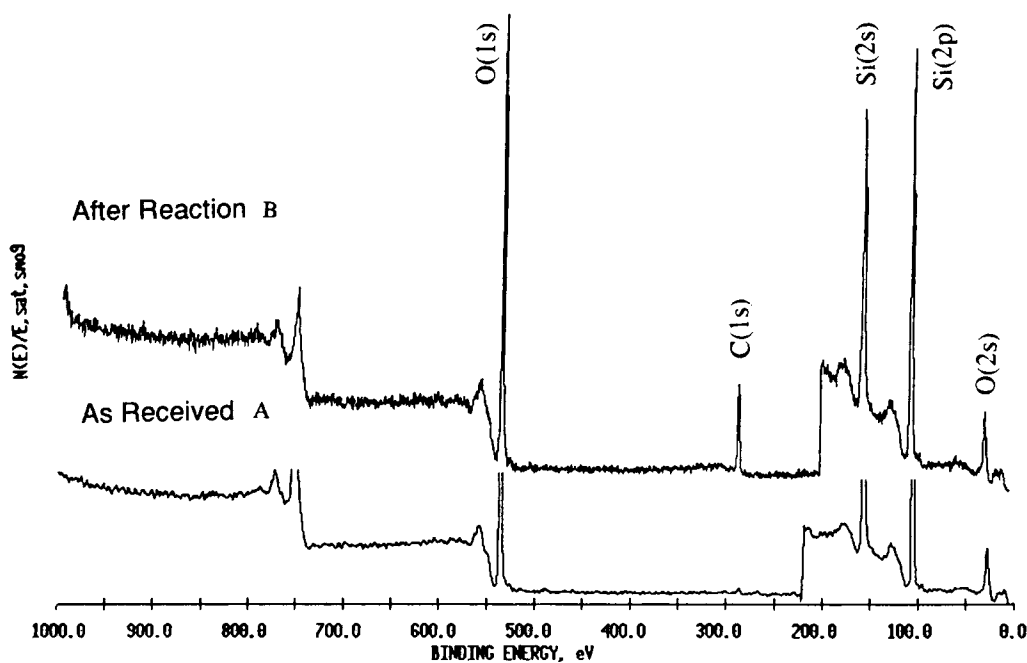


Figure 10 ESCA survey scans: (A) untreated fumed silica as received; and after reaction (B) with 5% iron octoate in PMPS at 230°C, 90 min.

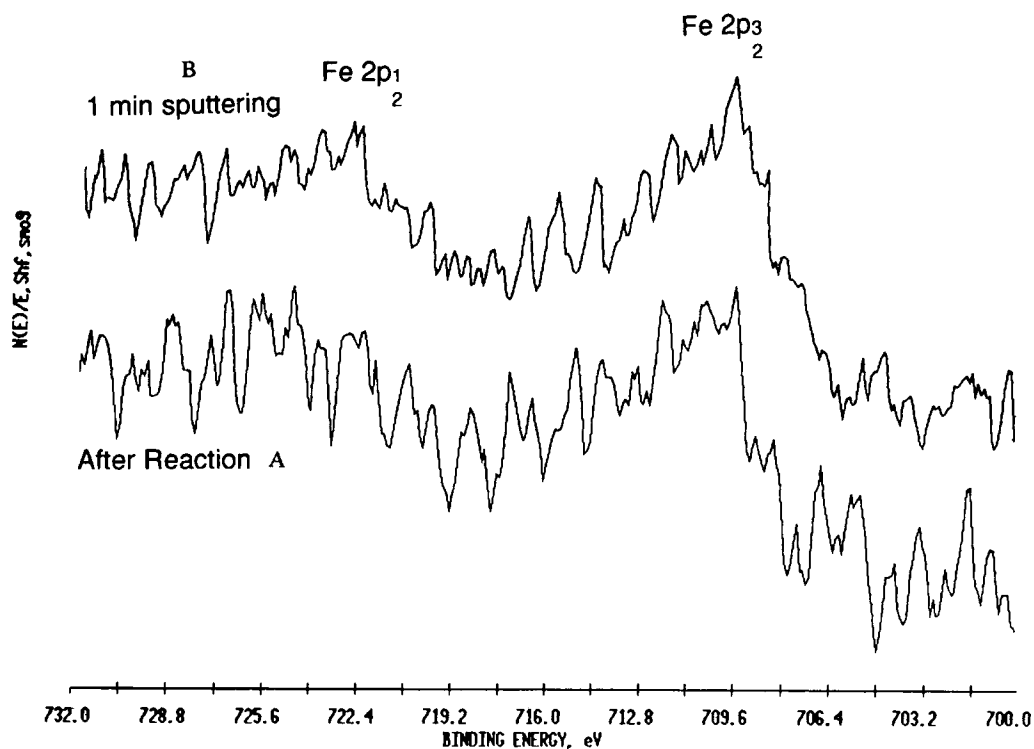


Figure 11 (A) ESCA multiplex scan of the iron region of untreated fumed silica after reaction (B) after 1 min sputtering time to increase signal.

grafting via the iron atom the siloxane is chemically bound to the surface.

Reaction of the iron octoate with the silica surface was inferred from the presence of iron in the silica after washing and drying of material that was reacted with 5% iron octoate for 90 min at 230°C. Detection of iron species upon the surface of the

silica was done by ESCA. Figure 10(A) is a survey scan of the fumed silica as received. Peaks due to oxygen 1s and 2s and silicon 2s and 2p electrons are identified. Figure 10(B) shows the silica after the reaction with iron octoate and siloxane. The silica is now medium brown in color, in contrast to its white color before the reaction. A new peak due to

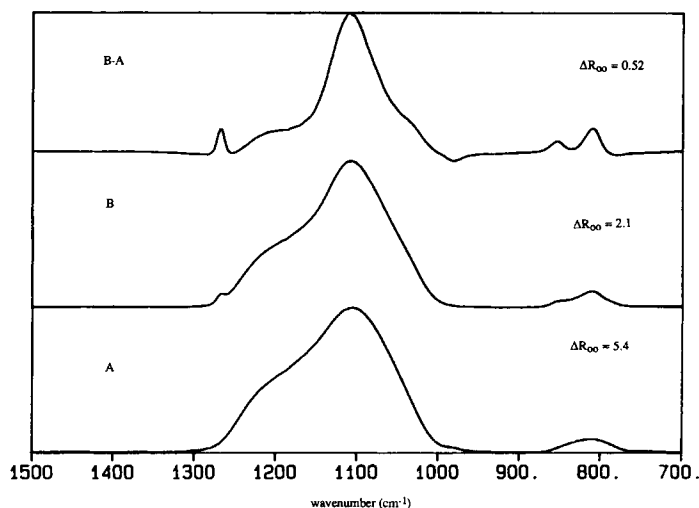


Figure 12 DRIFT spectra: (A) untreated fumed silica as received; (B) fumed silica treated with small dimethylsiloxane oligomers; and B-A.

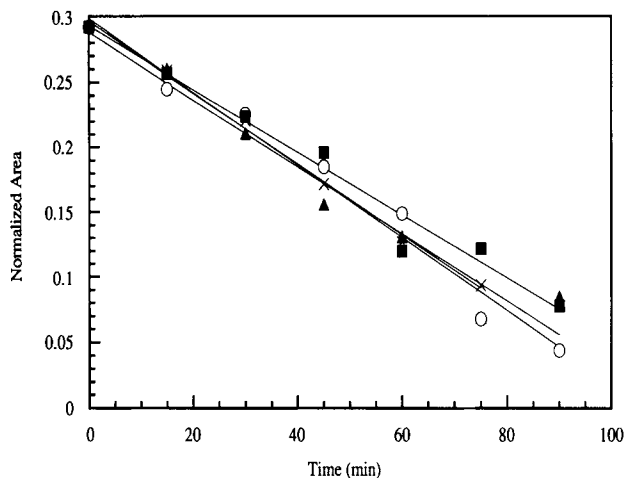


Figure 13 Kinetics of salt consumption for 5% iron octoate in PMPS at 230°C as a function of loading of surface-treated fumed silica: (▲) 0% silica; (X) 0.67% silica; (○) 1.7% silica; (■) 2.7% silica.

carbon 1s electrons is clearly visible at 275 eV. However, no new information is found in the iron region (700–735 eV). Thus, a multiplex scan of the iron region was performed to increase the sensitivity of analysis by taking more data points within a region and by lowering the analyzer energy. The results are shown in Figure 11(A). The peaks at 725 eV and 711 eV are due to the $2p_{1/2}$ and $2p_{3/2}$ electrons of the iron atom, respectively. Figure 11(B) shows more clearly the presence of the iron on the silica surface after the sputtering. To verify that the iron on the surface of the silica was a result of reaction

Table III Slope of Salt Consumption Curves as a Measure of the Rate of Reaction of Iron Octoate for Various Loadings of Surface Treated Fumed Silica

Percentage Silica	Slope $\times 10^{-4}$	Error $\times 10^{-4}$
0.0	25.8	± 2.4
0.67	27.3	± 0.8
1.7	28.0	± 2.0
2.7	26.6	± 4.5

* 5% by weight iron octoate in PMPS at 230°C.

and not merely physical adsorption, a sample of silica was taken from a mixture of 5% iron octoate, 5% untreated fumed silica, and poly(co-dimethylmethylphenyl)siloxane (PMPS) which was allowed to stand for 60 days. The same washing procedure was performed as with the reacted silica. After drying, the color of the reacted fumed silica and the silica in the mixture of iron octoate and siloxane were examined. The silica washed after the reaction had a medium brown color compared to the off-white color of the mixture. Accordingly, it is proposed that the iron underwent the same electrophilic attack on the oxygen as was proposed in the previous paper, expelling the positively charged hydrogen atom and forming Fe—O—Si bonds.

A similar reaction of ferric iron with polymeric silica of varying degrees of polymerization has been studied.¹¹ Ferric iron reacted with polymerized silica to form Si—O—Fe bonds according to the reaction described below:

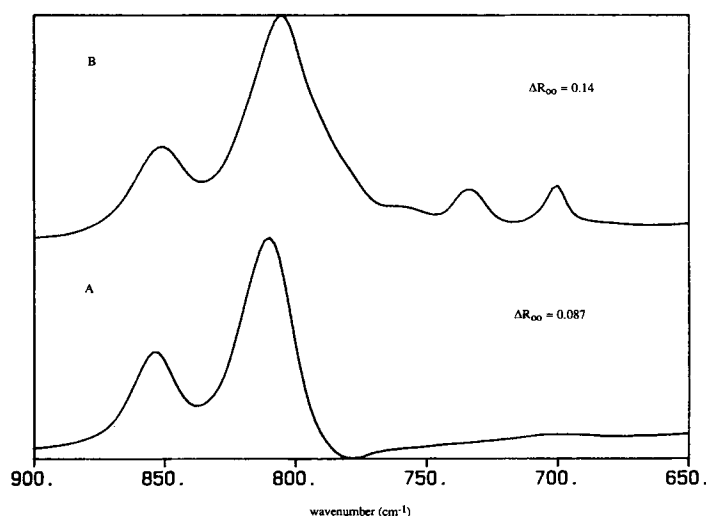
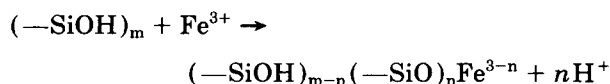


Figure 14 DRIFT spectra: (A) surface treated fumed silica with small dimethylsiloxane molecules; after reaction (B) of the silica with 5% iron octoate in PMPS at 230°C for 90 min.



The adsorption of metallic ions onto silica takes place with many ions of varying valencies. Also, the adsorption occurs at different pH values for specific ions.

The effect of the fumed silica treated with small dimethylsiloxane molecules was assessed in the same manner as the untreated fumed silica. Figure 12 displays the FT-IR spectra of untreated fumed silica (A), treated fumed silica (B), and their subtraction spectrum (B-A). The presence of the dimethylsiloxane species is evident from the band at 1270 cm^{-1} which is the methyl C—H bending mode, the band from 1150 to 1000 cm^{-1} which is the Si—O—Si asymmetric stretching mode, and the bands at 854 and 810 cm^{-1} which are the Si—C stretching mode of the difunctional surface treatment.

FT-IR was used to follow the reaction of the iron octoate, polysiloxane, and the treated fumed silica. The $-\text{CH}_2$ stretching mode of the salt at 2859 cm^{-1} was followed and the $-\text{CH}_3$ stretching mode of the siloxane at 2905 cm^{-1} was used as an internal standard as with the untreated silica. The influence of the surface species upon the rate of salt consumption is shown in Figure 13. The slopes of the lines and standard errors are shown in Table III. The presence of the treated silica has no effect upon the rate of salt consumption. This is reasonable since attack of the iron on either the surface of the silica or on the siloxane backbone would involve reaction with oxygen of essentially the same electronegativity, an oxygen within an Si—O—Si bond. The loadings of the untreated and surface treated fumed silica are comparable on a volume basis since the density of the untreated fumed silica is approximately twice that of the surface treated fumed silica.

Reaction of the iron octoate with the treated surface would cause some grafting of the siloxane, but not a preferential reaction as with the untreated silica. Figure 14 shows preliminary evidence of reaction of iron octoate and subsequent grafting of the siloxane onto the surface of the silica. After washing the silica as previously described, it was dried, and a DRIFT FT-IR spectrum was taken. The Si—C stretching region of the reacted silica (B) is compared to the as received material (A). The appearance of the Si—C mode of the phenyl functionality at 734 and 710 cm^{-1} suggests reaction of the siloxane onto the surface of the silica.

The results from the empirical rheological evaluation of the rate constant are shown in Table IV.

Table IV Calculation of Front Factor (k_0) for Various Loadings of Surface Treated Fumed Silica

Percentage Silica	$\ln k_0$	Error
0.0	15.0	± 1.0
1.0	14.9	± 1.0
2.0	18.3	± 1.0
3.0	19.1	± 1.0
4.0	17.9	± 1.0

There is no observable trend in the rate constants up to 4% by weight treated fumed silica. These results, like the IR data, indicate that there is little effect of the treated fumed silica upon the rate of backbone cleavage. This phenomenon is in contrast to the influence found with the untreated fumed silica which slowed the rate constant when it was added as a the filler. This is due to the fact that there is no preferential reaction of the iron octoate with the surface-treated fumed silica since Si—O—Si bonds are present on both the silica surface and in the bulk siloxane.

CONCLUSIONS

An empirical method for evaluating the effect of fillers and additives upon the rate of siloxane backbone cleavage by dynamic mechanical analysis was developed. The complex viscosity of a system of PDMS gum and iron octoate was found to have an exponential dependence as reaction time proceeds. Both the storage and loss viscosities contributed significantly to the complex viscosity. The front factor k_0 was used as a measure of the rate of siloxane backbone cleavage.

The addition of untreated fumed silica accelerates the consumption of the iron octoate salt, as shown by infrared analysis. The rheological analysis shows a decrease in the rate of siloxane backbone cleavage with increased loading of silica. After the washing of reacted silica, ESCA shows the presence of iron on the surface which is not attributed to physical adsorption. These results are consistent with the reaction of the ferric iron with the hydroxy species on silica. Preferential reaction of the iron with the surface of the silica leaves less iron to react with the siloxane backbone and this translates into a decrease in the rate of reaction with increased loading of untreated fumed silica. Also, siloxane molecules can

be grafted onto the surface since the ferric iron has other ligands available for reaction and is sterically restricted so as to react with any other surface oxygens.

The addition of silica treated with small dimethylsiloxane molecules has a very different effect. There is little or no effect of the treated silica on the rate of siloxane backbone cleavage as monitored rheologically. Also, there is no change in the rate of salt consumption as monitored by FT-IR. This is because the ferric iron has the same affinity for the surface grafted small poly(dimethylsiloxane) molecules as with the siloxane matrix since Si—O—Si bonds are present in both cases.

From an application point of view, the treated fumed silica is a better choice than silica without surface treatment for use as a filler in a high temperature silicone elastomer because it does not appear to interfere with the rate of reaction of the iron octoate and polysiloxanes.

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