Reaction of polysiloxanes and iron 2-ethylhexoate

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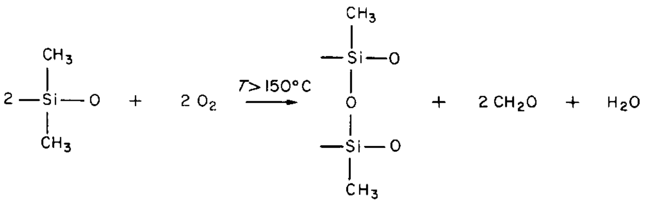
Iron 2-ethylhexoate is a salt of ferric iron and 2-ethylhexanoic acid. It is incorporated into silicone elastomeric formulations to provide high temperature stability by counteracting oxidative embrittlement. Though metallic salts are commonly used, the reaction of the salt with the siloxane is poorly understood. In this paper, the incorporation of iron 2-ethylhexoate as thermal stabilizer in the elastomer is studied with dynamic mechanical spectroscopy, *FT*-i.r. spectroscopy and ^{29}Si n.m.r. The reaction involves conversion of the ferric salt to ferric silicate, volatilization of small, cyclic siloxanes, and reaction of the salt to hexanoic acid with partial conversion to anhydride.

(Keywords: polysiloxanes; stability; elastomer)

INTRODUCTION

The formulation of high temperature silicone elastomer is quite complex, involving a number of gums, fillers and additives. A typical formulation consists of 70 parts polysiloxane gum, 12.5 parts hydroxy terminated poly(dimethylsiloxane) (PDMS), 17.5 parts fumed silica, 8.0 parts titanium dioxide (fumed) and 2.0 parts cerium stannate[1]. The gums are usually mixtures of methyl and vinyl functional poly(dialkylsiloxane)s. Crosslinking occurs using a peroxide catalyst at the vinyl site to provide mechanical integrity. Phenyl functional polysiloxanes give additional heat resistance. Fumed and precipitated silica fillers provide strength as well as tear and abrasion resistance. Titanium dioxide, iron oxide and other metallic oxides are used as pigments. Metallic soaps are often incorporated as heat stabilizers to counteract the embrittlement caused by oxidation through scission of the siloxane backbone.

Oxidation of the silicone elastomer severely degrades its mechanical properties. Degradation by oxidation occurs via the organic functionality attached to the silicon causing embrittlement from crosslinking. Oxidation of the side groups is believed to occur by a free radical mechanism. The rate of oxidation is influenced by the nature of the side group, backbone composition and the content and nature of additives and fillers. The oxidation of silicone fluids, for example PDMS, in air can be represented most simply by[2]:



$$2\,-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{Si}}-O \;+\; 2\,O_2 \xrightarrow{T>150^\circ C} \begin{array}{c} CH_3 \\ | \\ -Si-O \\ | \\ O \\ | \\ -Si-O \\ | \\ CH_3 \end{array} \;+\; 2\,CH_2O \;+\; H_2O$$

The formaldehyde may then undergo polymerization. In addition, other products are formed upon oxidation of PDMS (280°C)[3]. These include H_2O, CO_2, small cyclic siloxanes, methanol, formic acid, CO, H_2 and CH_4.

To protect against thermal oxidation of hydrocarbon polymers, antioxidants are conventionally used. Antioxidants are selected according to the type of protection required[4]. Low molecular weight phenols and diethyldithiocarbanates of zinc and nickel have been found to be effective short term antioxidants. Short term antioxidants provide protection against oxidation during processing and are low molecular weight in nature since they need to migrate freely. In contrast to processing antioxidants, those stabilizers for long term protection are usually large, complex molecules which have less mobility through the polymer and are also less volatile. Antioxidants function by two general mechanisms: preventative and chain breaking. Preventive antioxidants cause hydroperoxides to decompose by a mechanism which does not yield radicals. Chain breaking antioxidants compete with the polymer to trap or react with those radicals which propagate oxidation. Carbon black is perhaps the most versatile additive used to inhibit polymer degradation. It has been shown that carbon black traps free radicals which penetrate into the carbon black structure where most of the unpaired electrons exist. The use of conventional methods for combating oxidation is severely limited with silicones since oxidation begins above the use temperatures of typical antioxidants. Other ways to stabilize silicones were sought.

Metallic soaps were first used as drying agents in paint formulations. Elliott[5] was the first to discover the ability of metallic salts to stabilize polysiloxanes. The compositions that prove to provide the best stability ranged from 0.05 to 1 wt% stabilizer. Higher amounts of stabilizer offer no particular advantage. Among the metallic salts surveyed were iron salts of aliphatic fatty acids, iron salts of aromatic acids, and saturated and unsaturated aliphatic and aromatic polycarboxylic acids.

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Nielsen[6] refined a procedure for incorporating metallic stabilizers. The preparation involves first forming a concentrate of iron 2-ethylhexoate in poly(dialkylsiloxane)s. The resulting mixture was oxygenated by bubbling an oxygen containing gas through the mixture at the temperature at which the fluid was designed to operate. The aerated fluid was cooled to room temperature and the resulting precipitate was filtered out. The concentrate was then added to additional amounts of siloxane for further stabilization of the fluids. When elastomers are needed, the concentrate is incorporated into the siloxane gum using a roll mill.

According to the previous work, the metals found effective are transition metals capable of giving a single electron redox system[7]:

$$M^{x+1} + e^- \rightleftharpoons M^x \qquad (M{=}Fe,Cu,Co,Ni,Ce,Mn)$$

The formation of M–O–Si structures was inferred from the preoxidation of iron soaps in PDMS fluids. In a hot system, M^x can react rapidly with oxygen to regenerate M^{x+1}. As long as this reaction recycles the redox metal and keeps the concentration of M^{x+1} even with the generation of free radicals by oxygen, a low level of metallic soap can provide stabilization. The reaction scheme is excellent for siloxane materials such as low molecular weight fluids and coatings where oxygen can penetrate readily. However, the regeneration of the M^{x+1} species in the bulk silicone elastomer where oxygen cannot penetrate is a major obstacle.

The ability of the metallic salts to stabilize siloxanes depends upon various factors. The effect of aeration on the time to gelation of PDMS for iron stabilization has been investigated[8]. As the amount of aeration is increased, so is the time to gelation. The data support the regeneration reaction proposed above. The effect of iron concentration upon gelation has been investigated and it was found that there is an optimal level of iron for each operating temperature.

However, it was found that at ⩽150°C oxidation is accelerated by the presence of metallic soaps[9]. The reaction observed below 150°C can be described by a catalytic oxidation mechanism in which methyl groups are oxidized as follows:

$$\equiv Si\text{–}CH_3 + Fe^{3+}O\ \text{complex} \rightleftharpoons \equiv Si\text{–}OH + Fe^{2+}\ \text{complex}$$

Then, a silanol condensation takes place:

$$2{\equiv}Si\text{–}OH \rightarrow {\equiv}Si\text{–}O\text{–}Si{\equiv} + H_2O$$

The effect of metal catalyst has a major influence on time to gelation[10]. Copper, iron and cerium metals have been studied. Cerium provides the best protection from oxidation and copper provided the least. Addition of the metal deactivator disalicylalpropylenediamine (DSPD) lengthened the time to gelation up to eight times that of the metal salt alone. The best inhibition came from mixtures of DSPD and cerous salts.

Much of the major research in the field of stabilization of high temperature silicone elastomers was halted in the early 1970s. To date, most of the work that has been performed concentrates on various aspects of the reaction of metallic salts and polysiloxanes. In this work, the high temperature properties of a commercial silicone elastomer were investigated in terms of the effect of iron 2-ethylhexoate upon the elastomer. Then, the reaction between iron 2-ethylhexoate and linear siloxanes is studied using *FT*-i.r. spectroscopy and ^{29}Si n.m.r. spectroscopy. Finally, the reaction products are characterized and a reaction scheme is proposed different from those previously stated involving air and reflects the reaction that would occur in the bulk of the elastomer where little oxygen can penetrate. This reaction is used to explain the rheological results in our subsequent paper published elsewhere[11].

EXPERIMENTAL

Trimethylsilyl end-blocked poly(co-dimethyl-methylphenyl)siloxane (PMPS) and trimethyl end-blocked PDMS and iron 2-ethylhexoate were used as received (Rhone Poulenc). The co-oligomer was chosen for its ability to disperse the iron 2-ethylhexoate, whereas the PDMS oligomer was selected for its simple ^{29}Si n.m.r. spectrum. Iron 2-ethylhexoate is a solution of mineral spirits and the salt of 2-ethylhexanoic acid and 6 wt% ferric iron. The dynamic mechanical samples, cured elastomers and gum stock were used as received (Rhone Poulenc).

The iron 2-ethylhexoate was incorporated under flowing argon in a distillation set-up at various temperatures and concentrations, using a small amount of siloxane as a carrier, with an addition funnel for the model reactions. This was done to ensure that the resulting distillate was truly a reaction product and not volatilized low molecular weight siloxane. The total amount of siloxane reacted was 20 g. The reaction was run until no further distillate was trapped. No distillates were trapped prior to addition of iron 2-ethylhexoate. The amounts of 1% and 10% iron octoate were chosen to verify the presence of the reaction products. The precipitate was collected by extraction with tetrahydrofuran and centrifuged four times before drying.

A Michelson 110 single beam *FT*-i.r. spectrometer equipped with a liquid nitrogen cooled mercury–cadmium–telluride (MCT) detector was used at a resolution of 4 cm^{-1}. The specific detectivity of the MCT detector was 1×10^{10} cm Hz$^{1/2}$ W^{-1}. 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 an empty chamber with attenuator. Diffuse reflectance (DRIFT) samples were referenced to ground KBr. The sample was ground 1–2% in KBr.

A Rheometrics RMS-800 dynamic mechanical spectrometer equipped with a 2000 g cm force rebalance transducer was used for the rheological measurements. Parallel plate (2.5 mm) and cone-and-plate (50 mm) geometries were used. The frequency sweeps of commercial elastomer were studied at 10% strain. All measurements were performed under flowing nitrogen to minimize oxidation except where stated that the measurements were done under atmospheric conditions. Samples were stamped from commercially made compression moulded plaques, and were chosen to illustrate the softening that occurs in the actual sample.

A Varian XL 200 n.m.r. spectrometer was used with gated decoupling to eliminate the nuclear Overhauser effect. The concentration of distillate was 1 ml distillate per 3 ml deuterated acetone, and 20 mg chromium acetylacetonate was added as a paramagnetic relaxation agent. One hundred coadded scans were taken. Tetramethylsilane (TMS) was used as a reference.

RESULTS AND DISCUSSION

The change in properties of a material can be shown by its dynamic mechanical spectrum. *Figure 1* displays a frequency sweep at 10% strain of the commercial silicone elastomer. The elastomer is composed of trimethyl end-blocked dimethyl and methylvinyl functional polysiloxane gums, hydroxy terminated polysiloxanes, fumed and precipitated silicas, titanium dioxide and iron 2-ethylhexoate. The actual effect of iron 2-ethylhexoate upon the as moulded sample after thermal treatment is also illustrated. Shown are frequency sweeps at room temperature of a commercial elastomer containing iron 2-ethylhexoate as received, after exposure to air at 415°C for 30 min, and after exposure to nitrogen at 415°C for 30 min. The embrittlement due to oxidative damage results in an increase in the complex modulus (G^*) compared to the as received sample. The G^* of the elastomer exposed under flowing nitrogen changes very little. This is due to the fact that the strength of the material is in its crosslinks, and the iron 2-ethylhexoate reacts with the siloxane backbone only.

This behaviour is shown better in *Figure 2*. Tan δ, the ratio of the viscous component and the elastic component of the modulus, is a good indicator of embrittlement or softening of a material. The tan δ of the elastomer exposed to nitrogen is increased relative to the as received elastomer indicating a softening of the material. Also, a dependence of tan δ upon frequency is an indication of the viscoelastic nature of the material. The increase of tan δ for the air exposed material is contradictory to the expected behaviour. A material that is embrittled by oxidation should have a decrease in tan δ relative to the as received material reflecting an increase in elasticity. This phenomenon is explained by cracking from stresses induced by shrinkage during oxidation. These cracks act as loss mechanisms through friction when an oscillatory strain is applied to the sample making the material appear to be softer while in fact it is more brittle.

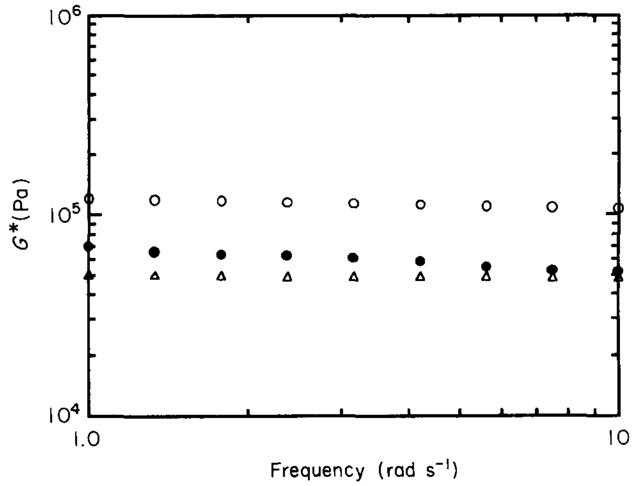

Figure 1 Frequency sweeps at 25°C displaying the complex moduli after heating to 415°C in air (●), after heating in N_2 (○) and for commercial elastomer as received without heating (△)

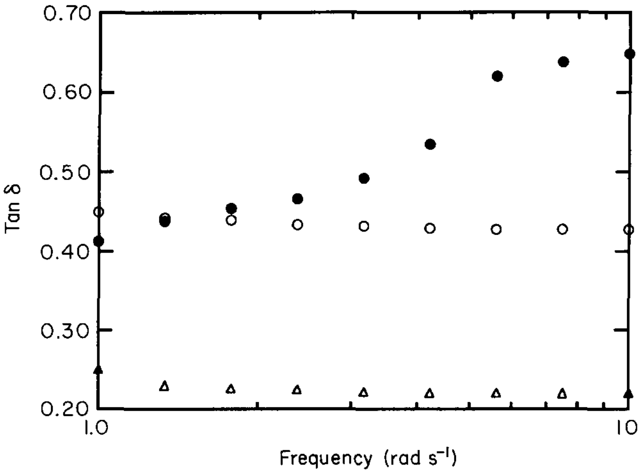

Figure 2 Frequency sweeps at 25°C displaying tan δ after heating in air (●), after heating to 415°C in N_2 (○) and for commercial elastomer as received without heating (△)

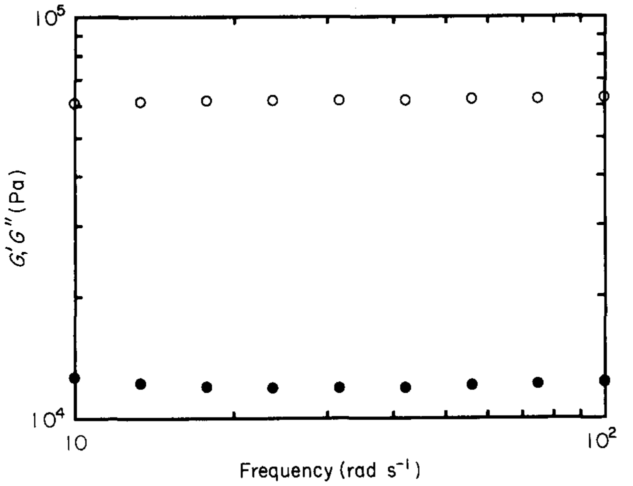

Figure 3 Frequency sweep at 25°C displaying the storage (○) and loss (●) moduli of the crosslinked commercial elastomer as received

Comparison of the material before and after thermal history for crosslinked and uncrosslinked commercial elastomers sheds light on the mechanism that softens the material. *Figure 3* displays the storage modulus (G') and loss modulus (G'') of a frequency sweep of the as received crosslinked elastomer. As expected, G' is much larger than G'' for this crosslinked elastomer. The elastomer was ramped from 250 to 430°C and held there isothermally for 0.5 h under flowing nitrogen. The sample was then cooled down to room temperature and a frequency sweep was performed at 10% strain. The results are shown in *Figure 4*. The magnitude of G' remains virtually constant while there is an increase in G''. This increase in G'' is a result of backbone scission of the siloxane. Since the elasticity is maintained through the crosslinks which are not broken, G' is unaffected.

This hypothesis is confirmed by performing the same experiment with uncrosslinked gum. *Figure 5* displays the frequency sweep of uncrosslinked commercial gum at room temperature. A dependence of the dynamic moduli upon frequency again indicates that this material is viscoelastic. The same thermal history was applied to this sample as was applied to the crosslinked elastomer. A reduction of modulus by one order of magnitude is shown for both G' and G'', as seen in *Figure 6*. Since there are no crosslinks via vinyl sites, both the moduli are affected by the backbone scission.

Iron 2-ethylhexoate is a salt of ferric iron and 2-ethylhexanoic acid. Important features of the *FT*-i.r.

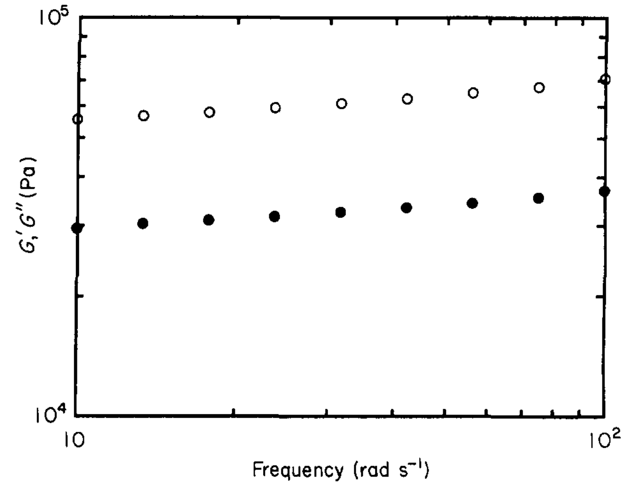

Figure 4 Frequency sweep at 25°C displaying the storage (○) and loss (●) moduli of the crosslinked commercial elastomer after thermal history

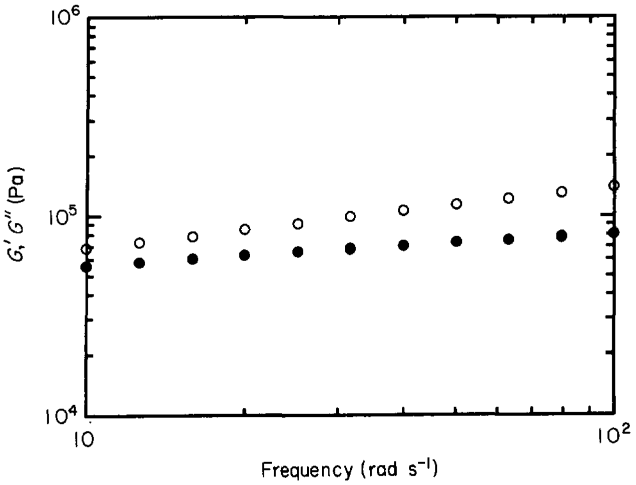

Figure 5 Frequency sweep at 25°C displaying the storage (○) and loss (●) moduli of the uncrosslinked commercial elastomer as received

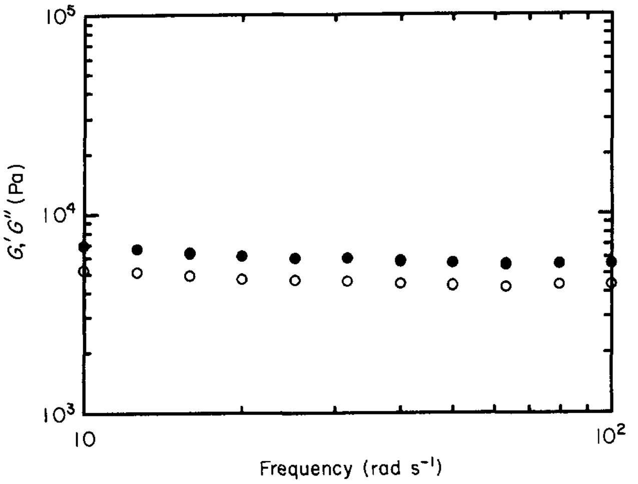

Figure 6 Frequency sweep at 25°C displaying the storage (○) and loss (●) moduli of the uncrosslinked commercial elastomer after thermal history

spectrum of iron 2-ethylhexoate are presented in *Figure 7A*. The peak at 1461 cm^{-1} is the methylene bending mode of the aliphatic backbone and will be used as the fingerprint band for the presence of the 2-ethylhexane moiety in future spectra. The band at 1588 cm^{-1} is assigned to the asymmetric COO$^-$ stretching mode. The peak at 1692 cm^{-1} is due to the carbonyl stretch of hydrogen bonded residual acid. The amount of residual acid was ~12 mol%. (It is general knowledge that a catalytic amount of acid cleaves siloxane bonds. However, the effect of residual acid is unknown since there is competition between volatilization of the acid and catalytic cleavage of the siloxane bond.) The previous assignments of the iron 2-ethylhexoate are compared with the *FT*-i.r. spectrum of hexanoic acid. The methylene assignments agree with the spectrum of iron 2-ethylhexoate. There is no band at 1588 cm^{-1} to which the carboxylic anion is assigned. Model systems of iron 2-ethylhexoate and siloxane were used to probe this reaction.

Model reactions were performed using a commercial poly(co-dimethyl-methylphenyl)siloxane co-oligomer in order to understand thoroughly the reaction pathway and products. The co-oligomer was selected for its ability to disperse the iron 2-ethylhexoate. The siloxane was heated to 230°C under flowing argon and then the iron 2-ethylhexoate was added anaerobically with some siloxane as a carrier. Iron 2-ethylhexoate solution (1 and 10 wt%) was added in the manner described above. The *FT*-i.r. spectra of the volatilized products from the samples with 10 wt% and 1 wt% iron 2-ethylhexoate are displayed in *Figures 8A* and *B*, respectively. The methyl and phenyl groups are present at 1270 and 1430 cm^{-1}, respectively. The siloxane doublet is fully collapsed into a singlet centred at 1080 cm^{-1}. Evolution of 2-ethylhexanoic acid as a reaction product is shown by the appearance of the 1461 cm^{-1} band as a shoulder on the 1430 cm^{-1} band. The presence of the acid is also partly accounted for by the residual acid initially present in the iron 2-ethylhexoate. The presence of hexanoic acid is further substantiated by the carbonyl stretch at 1710 cm^{-1}. The acid is partially converted into anhydride as shown by the bands at 1743 and 1815 cm^{-1}.

The reaction of iron 2-ethylhexoate is demonstrated by the disappearance of the shoulder (1461 cm^{-1}) of the 1430 cm^{-1} band in the starting mixture compared with the siloxane remaining in the flask in *Figure 9*. This supports the conclusion that the salt is converted into the acid and that the presence of the acid is not due to mere evaporation of residual acid present in the as

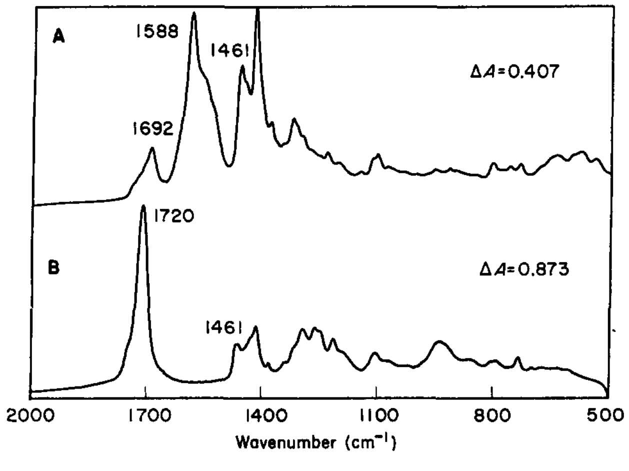

Figure 7 *FT*-i.r. spectra of iron 2-ethylhexoate film (A) compared to hexanoic acid (B)

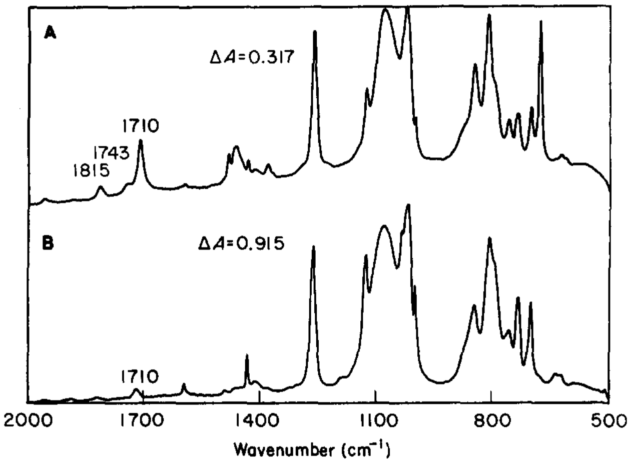

Figure 8 *FT*-i.r. spectra of trapped volatiles from reaction of 10 wt% iron 2-ethylhexoate in PMPS oligomer (A) and 1 wt% iron 2-ethylhexoate in PMPS oligomer (B)

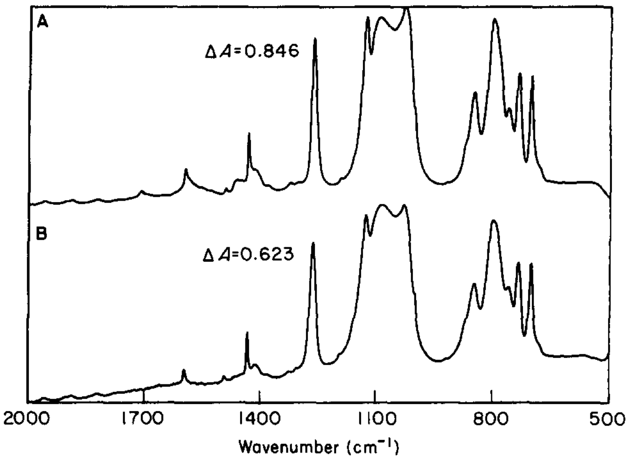

Figure 9 *FT*-i.r. spectra of starting mixture of 10 wt% iron 2-ethylhexoate in PMPS (A) and siloxane after reaction (B)

received material. The liquid siloxane remains spectroscopically the same. From a qualitative comparison of the functional peaks in the i.r. between the unreacted siloxane, distillates and siloxane after reaction, the relative intensities remain the same. This implies that the functional groups are unaffected by the iron salt under these conditions.

However, a black precipitate was formed. This precipitate is insoluble in all organic solvents and soluble in HCl. *Figure 10* shows the DRIFT spectrum of the black precipitate. This spectrum has characteristics of siloxane as is seen by a methyl mode at 1270 cm^{-1}, a phenyl mode at 1430 cm^{-1} and the asymmetric Si–O–Si stretch in the range from 1150 to 1000 cm^{-1}. The presence of Fe–O bonds are indicated by the broad Fe–O stretch centred at 560 cm^{-1}. The shoulder around 950 cm^{-1} is assigned to the asymmetric Fe–O–Si stretch. This shoulder is seen better in the curve resolved spectrum in *Figure 11* where it appears at 1000 cm^{-1}. The broadness of this peak is understandable since iron has multiple ligands. The Fe–O–Si stretch position[12] appears at 947 cm^{-1} for trimethylsiloxy ferrate $\{[(CH_3)_3SiO]_3Fe\}_2$. This is in good agreement with the calculated value of 933 cm^{-1}.

The oxidation state of the iron was determined by chemical means. It is well known that the addition of a potassium thiocyanate solution to ferric iron turns a solution of ferric ions a deep red colour[13]. The red colour is from the ferric ferrithiocyanate species $Fe[Fe(CNS)_6]$. The addition of a potassium thiocyanate solution to ferrous ions results in no colour change. The iron silicate ($\sim$0.2 g) was dissolved in a warm solution (70°C) of HCl (30 ml concentrated HCl in 200 ml distilled H_2O). The reaction was purged with argon since ferrous iron is known to convert slowly to ferric iron in the presence of oxygen when dissolved in acid. The strongly acidic nature acts to hydrolyse the silicate species to siloxane with hydroxy end groups with the chlorine counterion as in ferric chloride. Addition of a solution of potassium thiocyanate (0.5 g) in distilled water (100 ml) turned the solution red. This indicates that ferric iron is present, but does not exclude the presence of ferrous ions. However, the composition is believed to be mostly ferric. This conclusion is reasonable since similar ligand exchange reactions involving ferric iron and silane species are documented where the ferric iron moiety is preserved.

Model reactions were performed for 5 wt% iron 2-ethylhexoate solution as a function of temperature and at 230°C as a function of concentration with PDMS. The PDMS oligomer was selected for the simplicity of the resulting n.m.r. spectra. The volatile products were analysed by ^{29}Si n.m.r. for information pertaining to their structure. TMS was used as an internal standard and

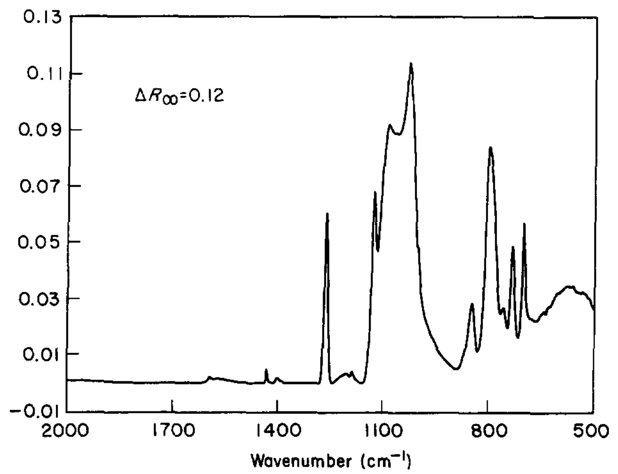

Figure 10 DRIFT spectrum of black precipitate

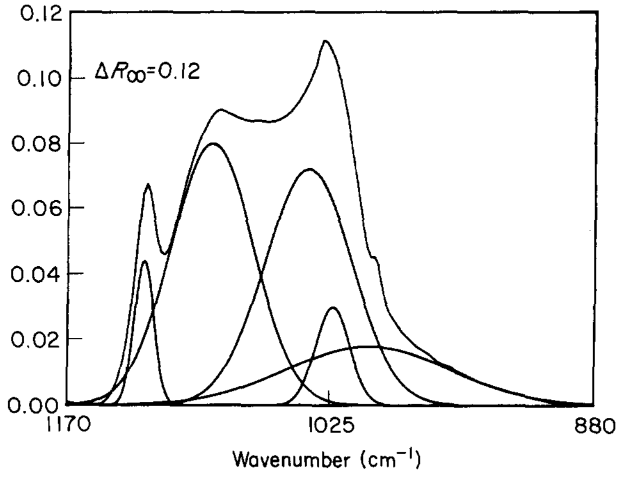

Figure 11 Curve resolved DRIFT spectrum of black precipitate showing the contributions of various bands

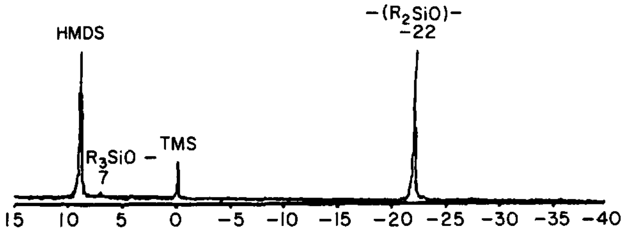

Figure 12 ^{29}Si n.m.r. spectrum of the as received trimethylsilyl end-blocked PDMS with TMS as a reference and hexamethyldisiloxane as a standard

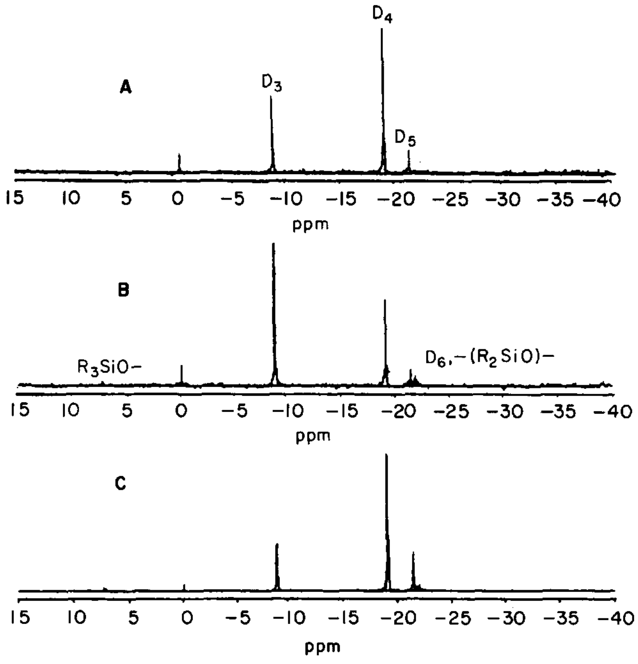

Figure 13 ^{29}Si n.m.r. spectra of trapped distillates from a reaction of 5 wt% iron 2-ethylhexoate in PMPS at 180°C (A), 230°C (B) and 270°C (C)

hexamethyldisiloxane (HMDS) was used as a reference, having a shift of 9.0 ppm downfield from TMS. *Figure 12* displays the ^{29}Si n.m.r. spectra of the starting material, trimethylsilyl end-blocked PDMS. The resonance for linear dimethylsiloxane chains appears in the spectrum at -22.0 ppm. The distillates, however, are distinctly different in structure.

Figure 13 displays the ^{29}Si n.m.r. spectra of volatiles of the reaction of 5 wt% iron 2-ethylhexoate as a function of reaction temperature. The reactions performed were at 180, 230 and 270°C. The resonances that result are assigned[14] exclusively to small cyclic siloxanes: hexamethyltrisiloxane (D_3) at -8.9 ppm, octamethyltetrasiloxane (D_4) at -19.0 ppm and decamethylpentasiloxane (D_5) at -21.4 ppm. Any other small peaks appearing upfield could be due to larger cyclics or linear species present. There is evidence of a small amount of linear siloxanes present from the peak at 7.4 ppm due to the silicon atoms at the end of the molecule. The types of product present over the temperature range are constant although the distribution changes somewhat. The ^{29}Si n.m.r. spectra of volatiles at 230°C as a function of concentration are presented in *Figure 14*. Again, the types of product present are the same as mentioned above, but no conclusions can be drawn about the relative distributions of the products. The species D_3 and D_4 are present in the largest amounts. This suggests that these species are favoured from energetic considerations. The reaction products of poly(dimethylcarboxylate metallosiloxanes) were analysed using gas chromatography[15]. The majority of the products were cyclic D_3 and D_4 species. The investigators postulated a mechanism involving electrophilic attack of the metal upon the oxygen of the siloxane backbone through which a cyclic product is formed.

Using the results from this study, the reaction between iron 2-ethylhexoate and polysiloxanes under anaerobic conditions is postulated in *Figure 15*. Reaction occurs between iron 2-ethylhexoate and siloxane to form a ferric iron silicate which precipitates. Small cyclic siloxanes, 2-ethylhexanoic acid and anhydride are removed as volatiles. The reaction is a simple ligand exchange with cleavage between an oxygen atom and a silicon atom in the siloxane backbone. This pathway is different than the one postulated for the oxygen-rich environment and is not catalytic. The mechanism of this reaction is believed to be a random, electrophilic attack of the iron at the oxygen of the siloxane backbone. Subsequently, Si–O–Fe bonds are formed leaving a reactive silicon atom. Since there is no change in oxidation state of the

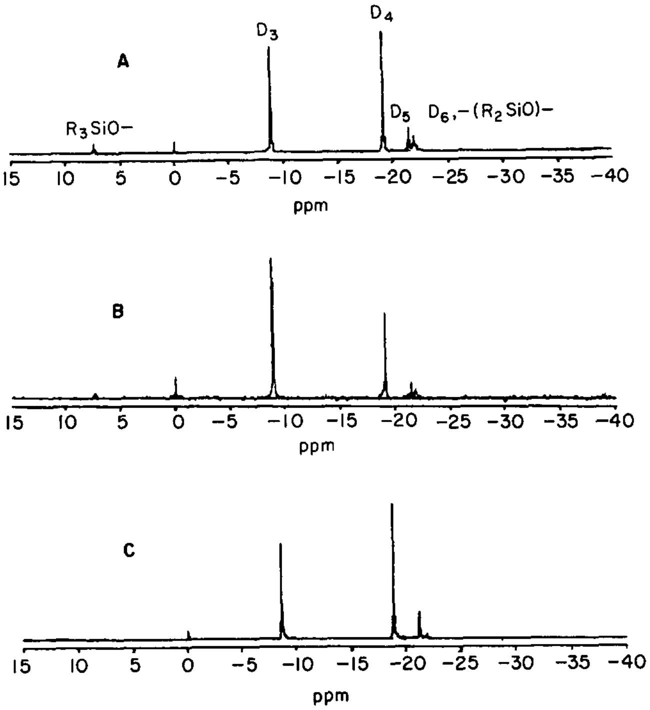

Figure 14 ^{29}Si n.m.r. spectra of trapped distillates from a reaction at 230°C for 1 wt% iron 2-ethylhexoate in PMPS (A), 5 wt% iron 2-ethylhexoate (B) and 10 wt% iron 2-ethylhexoate (C)

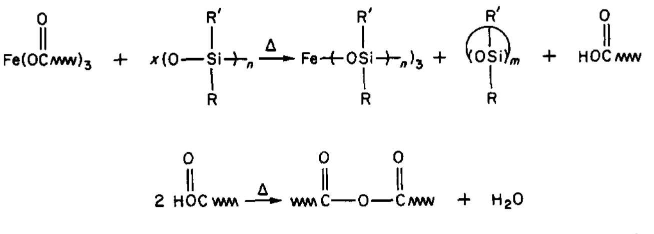

Figure 15 Proposed reaction scheme of iron 2-ethylhexoate and polysiloxanes

iron, the reaction is thought to be free radical in nature. Cyclization and subsequent volatilization of small siloxane molecules occurs through the reactive silicon atom.

CONCLUSIONS

The silicone elastomer is stabilized by the presence of the iron 2-ethylhexoate from oxidative embrittlement at elevated temperatures. Since G' of the crosslinked elastomer does not change very much with heating relative to the as received material, the softening occurs at the siloxane backbone and not as a result of breakage of the crosslinks. After heating the uncrosslinked gum, an order of magnitude drop in both G' and G'' occurred when compared to the as received stock. Clearly, the softening of the polymer occurs from cleavage of the siloxane backbone and not breakage at the crosslinking sites.

Iron 2-ethylhexoate is a salt of ferric iron and 2-ethylhexanoic acid. Through model reactions, the iron 2-ethylhexoate reacts, under an anaerobic environment, to evolve volatiles and a black precipitate. The volatiles are identified as small, cyclic siloxanes with repeat unit of $\geqslant 3$ with a small amount of linear species present. Also, hexanoic acid and anhydride are volatilized. The black precipitate was identified to be a ferric iron silicate.

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