Paper No. 3

EFFECTS OF FUMED SILICA TREATED WITH FUNCTIONAL DISILAZANES ON SILICONE ELASTOMERS PROPERTIES*

BY

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INTRODUCTION

Fumed silicas are excellent reinforcing fillers for fluid silicone polymers and high viscosity silicone gums.[1,2,3] The reinforcing ability of fumed silica is due to its high degree of structuring, large surface area, and active surface chemistry (silanol sites). The silica filler also can associate with polysiloxane chains through the surface silanol site on the silica aggregate prior to curing.[4,5,6] This filler polymer association begins to take place immediately after the fumed silica and polymer are combined and becomes continually stronger as the compound ages. This interaction is referred to as "Crepe Aging". The crepe aging process can result in continual viscosity increases for flowable silicone compositions, even to the point of gellation. Higher consistency compositions become increasingly nervy or rubbery and eventually become no longer extrudable. Reshearing the compound can reverse temporarily the effects of crepe aging, however, once the shearing stops the material beings to crepe again.

The use of disilazanes such as $(RR'R''Si)_2NH$ where R, R' and R" are saturated or unsaturated aliphatic or aromatic substituents, can prevent or reduce the interaction between the highly reactive silanol on the fumed silica surface and silicone polymers.[6,7,8] This allows for incorporating higher filler loading levels, thereby increasing the extent of reinforcement as well as the shelf stability of the unvulcanized stock.

The incorporation of a small amount of vinyl functional disilazane $(ViMe_2Si)_2NH$ along with $(Me_3Si)_2NH$ [major treating agent] can significantly increase the modulus and durometer of the cured elastomer. Curing takes place by a platinum catalyzed hydrosilation reaction, i.e. $\equiv SiH + \equiv SiVi \rightarrow \equiv SiCH_2CH_2Si\equiv$. Properties of the cured elastomer were found to be dependent upon (a) the degree of filler treatment, (b) ratio of vinyl to non-vinyl treating agent, and (c) the type of disilazane which was incorporated with the $(Me_3Si)_2NH$. For example, $[ViMe_2Si(OMe_2Si)_3]_2NH$, (designated as $(ViMD_3)_2NH$ hereafter) gave higher modulus and durometer, whereas $(HMe_2Si)_2NH$ gave lower modulus and durometer values than $(ViMe_2Si)_2NH$. It was also found that the distribution of the vinyl functional group on the silica surface was important. Random distribution resulted in greater changes on cured elastomer properties than did heterogenous treatment at the same treatment level.

EXPERIMENTAL

Materials

Polymers. - The polymers used in this study were all phenylmethylvinyl terminated polydimethylsiloxane, $ViØSiO(Me_2SiO)_xSiMeØVi$. Polymers were prepared by the base catalysis of dimethyl cyclics siloxane and and phenylmethylvinyldisiloxane. All polymers were vacuum stripped at 185°C to remove low molecular weight species. Final polymer viscosities varied from 20,000 to 40,000 centistokes depending upon endblocker concentration.

Filler. - The fumed silica used was commercial grade Cab-O-Sil® MS-75 obtained from Cabot Corp.

Crosslinker. - The crosslinker used was a multi functional silicone compound containing ≡SiH functional groups.

Platinum Catalyst. - Dow Corning plant grade platinum catalyst was employed.

Disilazanes. - All disilazanes were made by reacting the appropriate chlorosilane with gasous ammonia in the presence of an acid acceptor (triethylamine). For example to prepare $(ViMe_2Si)_2NH$ the following reaction was carried out

$$ViMe_2SiCl + NH_3 \xrightarrow[R.T.]{Et_3N} (ViMe_2Si)_2NH + salt$$

The reaction was monitored by GLC to insure that the product was the disilazane and not the monosilazane which forms first.

Filler Treatment

Cab-O-Sil® MS-75 (a fumed silica) was treated by placing the silica in a large 3-neck flask, adding dry toluene, enough to cover the silica, then 5 parts per hundred water followed by the slow addition of the disilazane. The mixture was stirred at room temperature for 24 hours followed by drying at room temperature and devolatilization at 150°C for 4 hours. This step was eliminated if treatment was done during compounding.

Compounding

Compounding was done by first hand mixing all ingredients followed by several passes over a 3-roll high speed mill. After compounding, the stock was press cured 15 minutes at 170°C and if desired a hot air oven post cure at 200°C.

Some samples were prepared by replacing the separate filler treatment step and milling operation described above by in situ treating and compounding in one operating. This was done by first adding the polymer, disilazane, and water to a small one quart Baker Perkins dough mixer, then slowly adding the fumed silica. The materials were mixed cold followed by mixing hot (150-170°C) under vacuum. After cooling, catalyst and crosslinker were added.

RESULTS AND DISCUSSION

$(Me_3Si)_2NH$ As A Treating Agent

Hexamethyldisilazane is an effective treating agent for fumed silica.[6,7,8] The reaction between the disilazane and silica silanol can occur in either of the following ways

$$(1)\quad (Me_3Si)_2NH + HO\{Silica) \rightarrow Me_3SiNH_2 + Me_3Si\text{-}O\{Silica)$$

$$Me_3SiNH_2 + HO\{Silica) \rightarrow NH_3\uparrow + Me_3Si\text{-}O\{Silica)$$

$$(2)\quad (Me_3Si)_2NH + 2\,HOH \rightarrow 2Me_3SiOH + NH_3\uparrow$$

$$Me_3SiOH + HO\{Silica) \rightarrow HOH + Me_3Si\text{-}O\{Silica)$$

The result of both routes is a silica that has a large precentage of its surface silanol groups converted to trimethylsilyl groups.

In addition to the silanol group, fumed silica can have strained siloxane sites on its surface.[6,7] These strained siloxane sites will react with water forming adjacent silanol sites. Therefore, the presence of a small amount of water is beneficial during filler treatment, as it allows for treatment of the strained siloxane site.

Effects on Elastomer Properties. - The use of a fumed silica which has been treated with $(Me_3Si)_2NH$ is compared to (1) a partically treated fumed silica, and (2) an untreated fumed silica in Table 1. The fully treated silica provided a much more extrudable, shelf stable base and also allows for a much higher filler loading level, therefore, providing improved reinforcement.

The conversion of the silica silanol site to the non functional trimethylsilyl group reduces filler-filler association and filler-polymer reaction. Thus at a given filler loading, the elastomer reinforced with timethylsilyl treated filler gives a lower durometer and modulus than that reinforced with untreated filler.

Functional Disilazanes

$(ViMe_2Si)_2NH$. - If the silica is treated with a mixture of $(Me_3Si)_2NH$ (major component) and $(ViMe_2Si)_2NH$ (minor component 2-10 mole %), the resulting silica will contain a small amount of functional $ViMe_2Si$- groups on its surface, as well as the non functional Me_3Si- group. The base compounded with this type of filler has the same improved resistance toward crepe aging as that compound with 100% Me_3Si- treated silica.

During the vulcanization (either addition cured or peroxide cured), the dimethylvinyl group on the silica surface reacts with ≡SiH of the crosslinker, thus chemically linking the silica into the elastomer network. This is schematically shown in Figures 1 and 2. Bonding the filler to the elastomer network can significantly change the mechanical properties of the elastomer.[8,9] A very small amount of polymer-silica bond introduced by this approach dramatically increase both hardness and modulus. Figure 3 shows the stress-strain curve for two identical formulations except that in one the filler is treated with 100% $(Me_3Si)_2NH$ and the other uses a mixture of 95% $(Me_2Si)_2NH$ and 5% $(ViMe_2Si)_2NH$. Generally speaking, percent elongation decreases while tensile can remain unchanged but usually decreases slightly. Tear strength can increase with an increase in $ViMe_2Si/Me_3Si$ ratio and then decrease rapidly if the $ViMe_2Si/Me_3Si$ ratio is too high.

More Effective Vinyl Disilazane

It was found that if the silica was treated with a mixture of $(Me_3Si)_2NH$ (major component) and $(ViMD_3)_2NH$ that the elastomer reinforced with this silica showed higher modulus and durometer values than that with a silica treated with $(ViMe_2Si)_2NH$ and $(Me_3Si)_2NH$. (See Table 2). The higher modulus and durometer obtained with $(ViMD_3)_2NH$ treated silica can be attributed to the increased reactivity of the $ViMe_2Si(OMe_2Si)_3$- group on the silica surface compared to $ViMe_2Si$-. This is illustrated in Figure 4. The steric hinderance induced by adjacent Me_3Si- groups is less severe if the vinyl group is located a few siloxane units away from the silica surface. Such a vinyl group obviously is more efficient in linking the silica to the elastomer network, leading to higher modulus and hardness.

Functional Group Distribution

To study the effect of the distribution of $ViMe_2Si$ groups on the silica surface upon the elastomer properties, we prepared two silicas, one treated exclusively with $ViMe_2Si$- (Silica A) and the other treated with Me_3Si- (Silica B). These silicas were then blended in various ratios, A/B = 10/0, 1/1, 1/2, 1/3, 1/5, 1/7, and 1/10. The properties of the elastomers thus obtained are shown in Table 4, sample 1 through 7. As the proportion of Silica A increases, the crosslinking density increases as evidenced by the decrease in elongation and increase in durometer and modulus.

Shown also in Table 4, sample 8 is the elastomer containing the filler treated with a mixture of $(Me_3Si)_2NH$ and $(ViMe_2Si)_2NH$. The distribution of $ViMe_2Si$- on the silica surface is random, whereas that described in the preceeding section is heterogeneous as illustrated schematically in Figure 6. The content of $ViMe_2Si$ functional group on silica surface in Sample 3 and 8 is identical. Yet the former (heterogeneous Vi distribution) gives a lower durometer and modulus than the latter (random Vi distribution). Obviously randomly distributed $ViMe_2Si$ is more efficient in linking all of the treated silica into the elastomer network than the heterogeneously distributed $ViMe_2Si$ group.

Other Disilazanes

Table 3 also shows the effectiveness of other silica treated agents, $[RR'R'']_2SiNH$. Whenever one of the R group on silicon is H, the resulting elastomer has a lower modulus and hardness than a similar formulation reinforced with silica treated with 100% $(Me_3Si)_2NH$. At first thought one would think that addition of functional $-SiMe_2H$ or $-SiPhMeH$ groups on the silica surface would increase the modulus of the vulcanized elastomer as these groups could react with the silicone polymer,

$$-SiCH{=}CH_2 + HMe_2Si\text{-(silica)} \rightarrow -SiCH_2CH_2SiMe_2\text{ -(silica)}$$

and this bonding would increase modulus over a non-functional silica. In our sample we feel that the lower modulus is due to reduced crosslink density. Figure 5 shows the comparison of a Me_3Si-, $ViMe_2Si$ and HMe_2Si treated fumed silica. In the case of HMe_2Si treated silica, the vinyl endblocked polymer reacts with $\equiv SiH$ on the silica surface. As a result the bulky dynamic sphere of the polymer chain will immediately cover the silica surface. Some of the $\equiv SiH$ functional group will be buried underneath and unaccessible for reaction. The efficiency of linking the silica decreases, leading to a lower crosslinking density of the network system.

CONCLUSIONS

The reinforcement obtained with disilazane treated silica in the platinum catalyzed silicone elastomer was found to be dependent upon not only the amount of disilazane empolyed but also the structure of the disilazane and its distribution on the silica surface. Incorporation of a small amount of vinyl functional disilazane such as $(ViMe_2Si)_2NH$ along with $(Me_3Si)_2NH$ (major treating agent) can significantly increase the modulus and durometer of the resulting elastomer. $[ViMe_2Si\ (OMe_2Si)_3]_2NH$ gives higher modulus and durometer, whereas $(HMe_2Si)_2NH$ gave lower modulus and durometer values than $(ViMe_2Si)_2NH$. The random treatment resulted in greater reinforcement on cured elastomer properties than the heterogenous treatment at the same treatment level.

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Table I

ELASTOMERIC PROPERTIES vs. DEGREE OF FILLER TREATMENT

Sample	Compound	Moles Compound Per 100g Filler	Base Extrusion Rate	Tensile MPa	% Elongation	100% Modulus MPa	Die B Tear KN/m	Shore A Durometer
1	$(Me_3Si)_2NH$	.015	1.6 g/min	6.29	750	.69	29	38
2		.031	61.0	8.69	876	.69	26.9	32
3		.062	149.0	8.95	976	.41	20.3	26
4		.124	162.0	7.72	911	.35	13.1	23
5		.062	399.0	2.50	560	.37	4.5	20
6	No Treatment	–	Nil	3.01	466	.62	5.4	31
7	$(Me_3Si)_2NH$	.015		4.29	385	1.39	18.9	55
8		.031		6.82	455	1.34	20.8	50
9		.062		8.75	680	.89	27.5	40
10		.124		7.68	690	.69	37.6	34
11		.062		2.64	420	.47	4.7	23
12	No Treatment	–		2.57	363	.82	5.9	36

Formulation (Sample # 1–4 & 7–10)

100 Parts By Weight Polymer
30 Parts Treated CAB-O-SIL® MS-75
1.11 Parts Polyorganosiloxane Crosslinker
.20 Parts Platinum Catalyst

Samples 5, 6, 11, 12 Contain Only 15 pph Filler

Cure Condition: Sample 1–6 = 15 Min. @ 170°C, 7–8 = 15 Min. @ 170°C + 20 Hrs. @ 200°C

Table II

ELASTOMERIC PROPERTIES AS A FUNCTION OF FILLER TREATMENT

Sample	Compound	Ratio*	Tensile MPa	Elongation %	100% Modulus MPa	Die B Tear KN/m	Shore A Durometer
1	$(ViMe\phi Si)_2NH$	1/23	7.65	595	0.96	45.5	40
2	"	1/11.5	8.16	725	0.93	51.6	40
3	$(ViMe_2Si)_2NH$	1/23	9.30	550	1.41	26.2	42
4	"	1/11.5	9.80	410	2.31	35.0	53
5	$[ViMe_2Si(OSiMe_2)_3]_2NH$	1/23	9.03	472	2.07	34.1	59
6	"	1/11.5	8.06	427	2.62	24.8	60
7	$(Me_3Si)_2NH$	–	8.41	735	.86	31.0	35
8	$(ViMe\phi Si)_2NH$	1/23	10.06	500	1.72	35.9	54
9	"	1/11.5	9.40	531	1.58	34.3	53
10	$(ViMe_2Si)_2NH$	1/23	10.09	430	2.07	35.9	52
11	"	1/11.5	9.03	321	3.00	26.4	60
12	$[ViMe_2Si(OSiMe_2)_3]_2NH$	1/23	9.59	445	2.34	29.8	63
13	"	1/11.5	7.94	340	3.28	10.8	72
14	$(Me_3Si)_2NH$	–	8.77	442	1.72	23.1	47

*Mole Ratio = Moles Vinyldisilazane/Moles Hexamethyldisilazane

Formulation
100 Parts Polymer
40 Parts CAB-O-SIL® MS-75
.054 Moles Total $(R\ R'\ R''\ Si)_2NH$
2 Parts Water
2.3 Parts Polyorganosiloxane Crosslinker
.2 Parts Platinum

Table III

ELASTOMERIC PROPERTIES SiH SILICA TREATMENT

Sample	Compound	Ratio*	Tensile MPa	Elongation %	100% Modulus MPa	Die B Tear KN/m	Shore A Durometer
1	$(Me_3Si)_2NH$	–	8.41	735	.86	31.0	35
2	$(HMe_2Si)_2NH$	1/23	6.10	755	.34	44.6	27
3	$(H\phi MeSi)_2NH$	1/23	8.65	895	.41	32.4	32
4	$(Me_3Si)_2NH$	–	8.77	442	1.72	23.1	47
5	$(HMe_2Si)_2NH$	1/23	9.38	650	.72	36.7	41
6	$(H\phi MeSi)_2NH$	1/23	9.69	730	.59	38.5	36

*Moles Functional Disilazane/Moles Hexamethyldisilazane

Formulation
100 Parts Polymer
40 Parts CAB-O-SIL® MS-75
.054 Moles Total $(R\ R'\ R''\ Si)_2NH$
2 Parts Water
2.3 Parts Polyorganosiloxane Crosslinker
.2 Parts Platinum Catalyst

Cure Condition: Sample 1–3 = 15 Min./175°C, Samples 4–6 = 24 Hrs./200°C

Table IV

ELASTOMERIC PROPERTIES AS A FUNCTION OF FILLER VINYL CONTENT AND DISTRIBUTION

Sample	Wt. Ratio Base A/B	Measured Weight % Vinyl Base	Measured Weight % Vinyl On Silica	Tensile MPa	Elongation %	100% Modulus MPa	Die B Tear KN/m	Shore A Durometer
1	1/10	.23	.05	10.31	535	1.22	36.75	47
2	1/7	.26	.08	9.48	550	1.09	36.75	48
3	1/5	.28	.10	8.37	475	1.13	38.50	48
4	1/3	.33	.15	9.29	487	1.35	32.21	53
5	1/2	.39	.21	7.70	402	1.72	31.32	61
6	1/1	.50	.32	6.73	344	1.90	24.3	67
7	1/0	.81	.63	4.89	155	3.25	6.4	81
8	Base C	~.28	~.10	9.03	321	3.00	29.92	60

	Base A	Base B	Base C
Weight Polysiloxane	100	100	100
Weight CAB-O-SIL® S-17	40	40	40
Weight $(Me_3Si)_2NH$	—	8.0	8.0
Weight $(Vi\ Me_2Si)_2NH$	8.0	—	.8
Water	2.0	2.0	2.0
Polyorganosiloxane Crosslinker	6.93	1.54	2.3
Platinum Catalyst	.20	.20	.20

Cure Condition: 15 Min./175°C Plus 24 Hrs./200°C

Table V

ELASTOMERIC PROPERTIES vs. FILLER VINYL CONTENT RANDOM DISTRIBUTION

Sample	Mole Ratio $(Me_3Si)_2NH$ $(ViMe_2Si)_2NH$	Moles $(ViMe_2Si)_2NH$	Tensile MPa	Elongation %	100% Modulus MPa	Die B Tear KN/m	Shore A Durometer
1	100% Me_3	–	8.41	735	.86	30.9	35
2	20/1	.0019	7.01	312	2.50	20.1	58
3	10/1	.0038	6.55	271	2.77	13.4	61
4	100% Me_3	–	8.77	442	1.72	23.1	47
5	20/1	.0019	7.18	260	3.10	10.1	63
6	10/1	.0038	5.26	162	3.43	6.8	66

Formulation	Sample # 1	Sample # 2	Sample # 3
Polymer (Grams)	100	100	100
CAB-O-SIL® MS-75 (Grams)	40	40	40
$(Me_3Si)_2NH$ (Grams)	7	6.64	6.30
$(ViMe_2Si)_2NH$ (Grams)	–	.36	.70
H_2O	2	2	2
Polyorganosiloxane Crosslinker	1.9	2.7	3.5
Note: Moles SiH/SiVi = 1.75			
Plantium Catalyst	.2	.2	.2

Cure Condition: Samples 1–3 = 15 Min./175°C, Samples 4–6 = 24 Hrs./200°C

Figure 1. – POLYMER FILLER BONDING

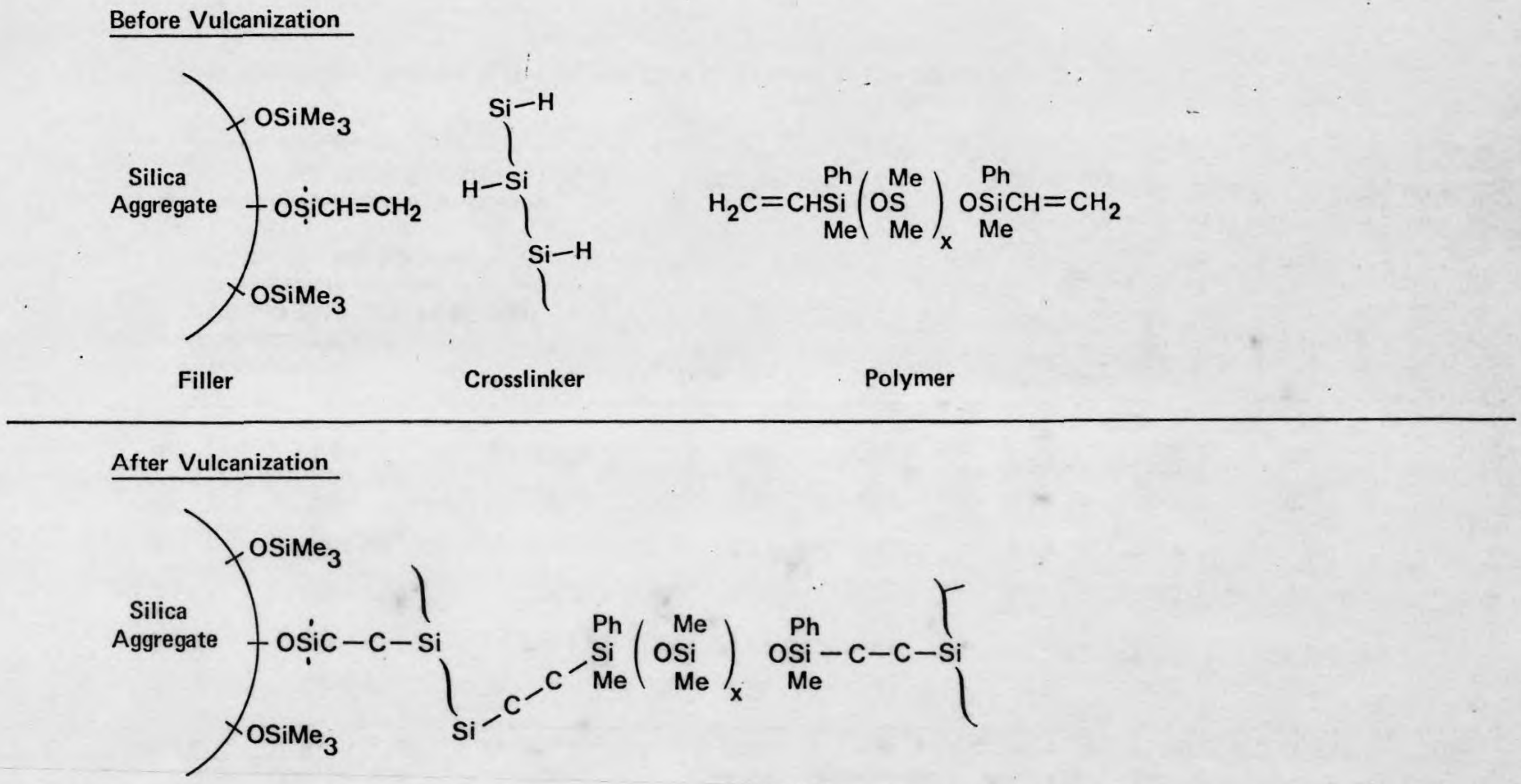
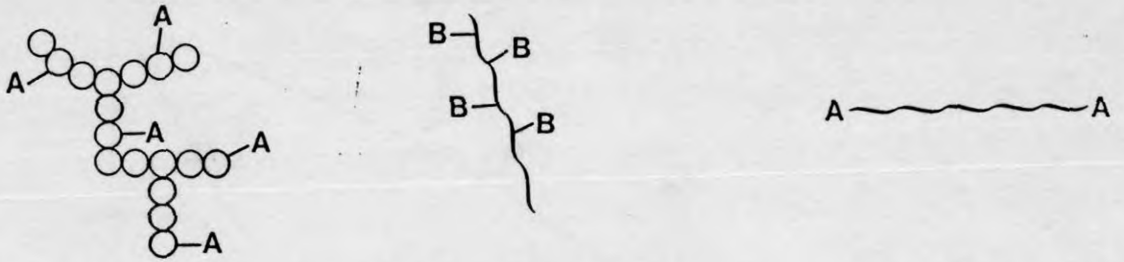


Figure 2. – POLYMER FILLER BONDING

Before Vulcanization

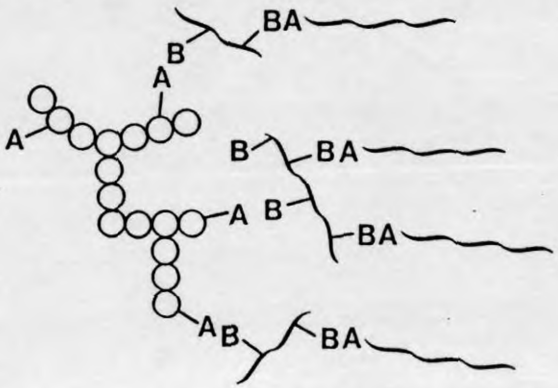


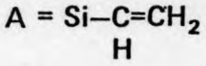
Silica Aggregate

Polysiloxane Crosslinker

Polysiloxane Polymer

After Vulcanization





$$A = Si{-}\underset{H}{C}{=}CH_2$$

B = Si–H

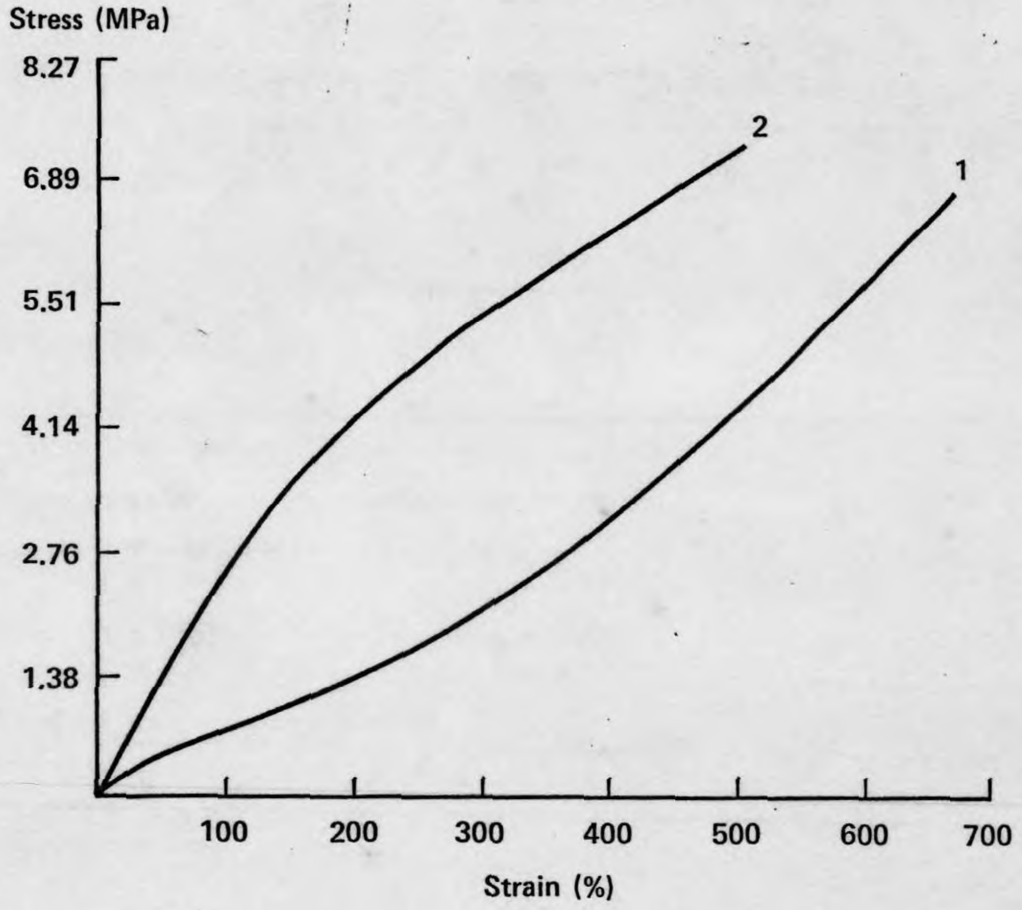
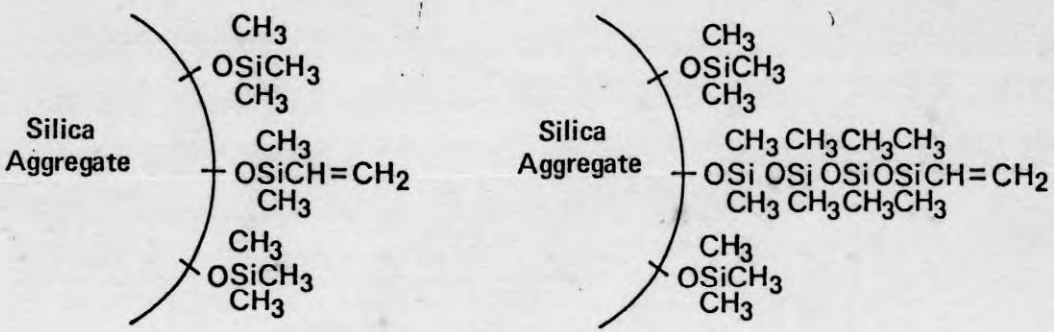


Figure 3. — STRESS STRAIN CURVES FOR ELASTOMERS WITH VINYLATED (2) AND NON VINYLATED FILLERS (1)

Figure 4. – $ViMe_2Si$ – TREATED SILICA vs. $ViMe_2Si(OSiMe_2)_3$ -



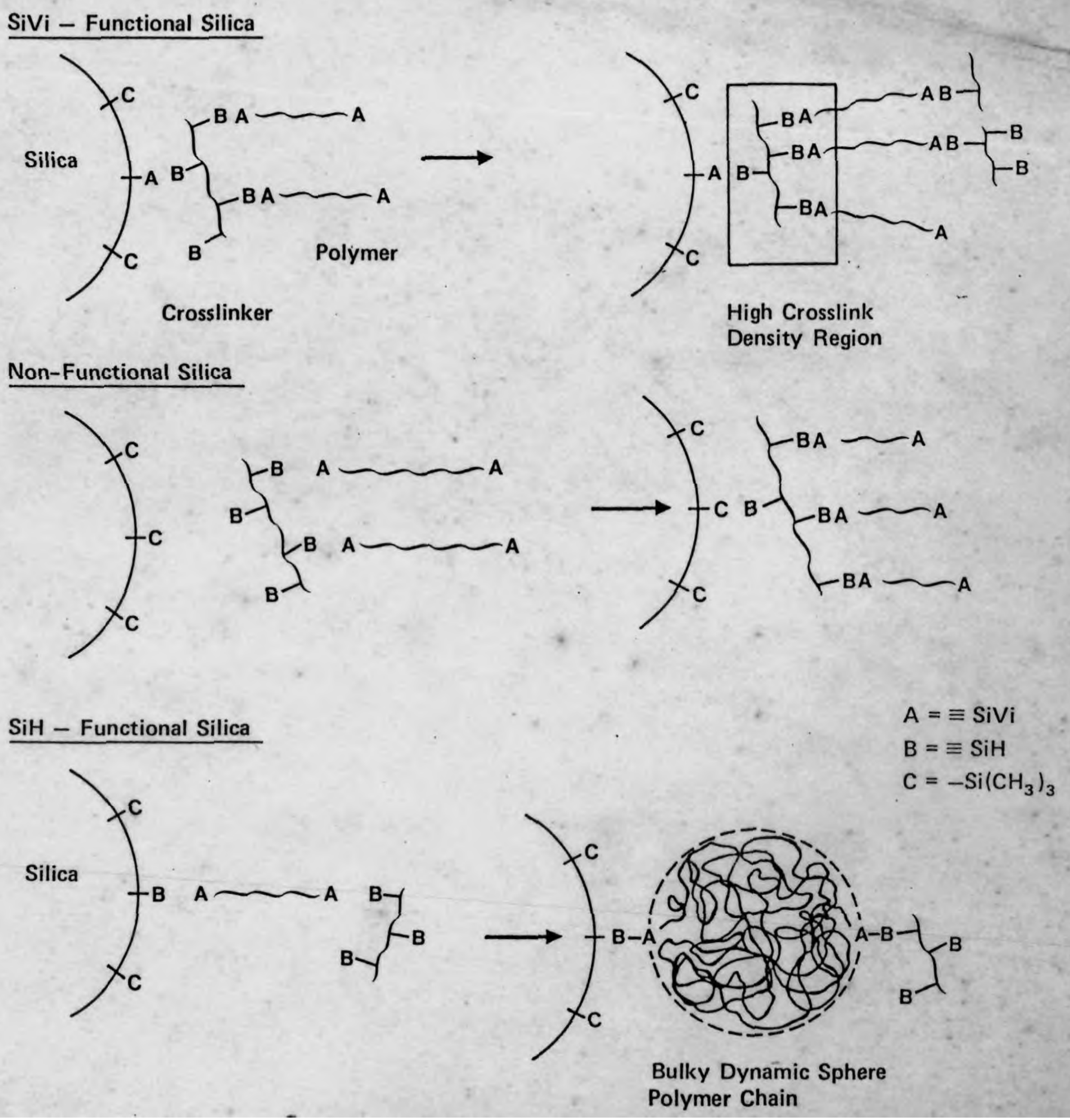
$$\frac{(Vi\,Me_2Si)_2\ NH}{(Me_3\,Si)_2\ NH}$$

Treatment

$$\frac{\left[Vi\,Me_2\,Si(OSi\,Me_2)_3\right]_2 NH}{(Me_3Si)_2\ NH}$$

Treatment

Figure 5. POLYMER FILLER INTERACTIONS AS A FUNCTION OF FILLER SURFACE TREATMENT



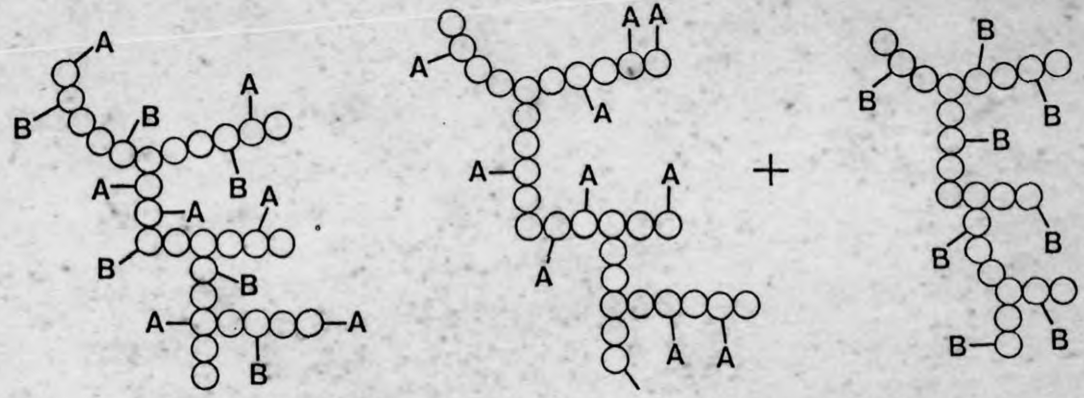
SiVi – Functional Silica

Non-Functional Silica

SiH – Functional Silica

A = ≡ SiVi
B = ≡ SiH
C = $-Si(CH_3)_3$

Figure 6. RANDOM AND HETEROGENEOUS $ViMe_2Si$ – TREATED SILICA AGGREGRATES



Random

Heterogeneous

A = $\equiv$ SiVi

B = $-SiMe_3$