

Reinforcement of Siloxane Elastomers by Silica. Chemical Interactions between an Oligomer of Poly(dimethylsiloxane) and a Fumed Silica

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Synopsis

The study of the interactions between an organosiloxane and a fumed silica was undertaken in order to improve our knowledge of the reinforcement of silicon rubbers by silica. IR spectroscopy, gravimetry, and chromatography techniques were used to characterize the chemical interactions taking place above 150°C between octamethylcyclotetrasiloxane and a fumed silica which yield silicas modified by grafted siloxanes. Reaction mechanisms were proposed for the interpretation of the grafting processes. They were checked by the study of the reaction of water with octamethylcyclotetrasiloxane. The results obtained suggest that the reactions proceed through an attack of the siloxane by the surface free silanol groups of silica, causing an opening of the siloxane cycle and the grafting of the subsequent material on the surface of the filler. It was shown that the siloxane-modified silicas exhibit a high thermal stability.

INTRODUCTION

The study of the adsorption of an organosiloxane onto a fumed silica was undertaken in order to improve our knowledge of the reinforcement of silicon rubbers by silica. Recently we showed,^{1,2} using IR spectroscopy and chromatography techniques, that between 25 and 140°C the adsorption of octamethylcyclotetrasiloxane (D_4) onto a fumed silica (Aerosil 300) was due to hydrogen bonding. The amount of material adsorbed according to this mechanism was shown to be strongly dependent on temperature. Particularly, the adsorption phenomena are reversible at temperatures close to 150°C. From the isotherms plotted at these temperatures it was possible to measure the heats of adsorption at various covering ratios.

This article deals with the processes occurring when the interactions between an oligomer of PDMS and a fumed silica proceed at temperatures higher than 150°C. The characterization of the ensuing materials as well as the study of their properties are considered.

EXPERIMENTAL

Reactants

Studies were performed with a fumed silica, Aerosil 300 (A300, Degussa, specific surface area 300 m²/g).

Octamethylcyclotetrasiloxane (D_4), hexamethylcyclotrisiloxane (D_3), tetramethylethylenedioxymethylsilane, tetradecamethylhexasiloxane (M_2D_4),

and 1,5-hexamethyltrisiloxanediol [$D_3(OH)_2$], used as models for siloxane rubbers, were supplied by Rhône Poulenc Industries and used without further purification.

All chemicals used were reagent grade and were purified by standard procedures.

Gas Phase Chromatography

Equipment and experimental procedures were described previously.^{1,2} Identification of the different compounds resulting from the siloxane-water reaction, performed at 300°C in an autoclave, and determination of their ratios were provided by gas-liquid chromatography analyses. They were performed on the low boiling point fraction of the reaction medium as follows:

The stainless steel columns were 0.32 cm in diameter and 2-3 m long. They were filled with a diatom earth treated with dichlorodimethylsilane (Gas Chrom-Q) and a methylsiloxane (SE 30) as stationary phase. Helium was the carrier gas used at a rate of 20 cm³/min. After 5 min at 90°C, in steps of 7°C/min, the temperature of the column was gradually increased to 300°C. It was kept at this temperature for 5 min. Sample injections were performed at 300°C and a catharometer was used for detection.

IR Spectroscopy

The equipment and devices used for IR spectroscopy were described previously.^{1,2}

The preparation of the chemisorbed material was performed as follows: The silica (A300) degassed 15 hr at 150°C was reacted with D_4 in a quantity ten times bigger than that necessary for the completion of a monolayer on the surface of the adsorbent. Different times of reaction were used. After separation of the excess of D_4 , by filtration and washing with hexane, the modified silica was dried at 150°C for 15 hr. These samples, as well as initial silicas washed with the same solvents, were submitted to elemental analysis for the determination of their carbon content. IR spectroscopy analyses were performed on disc-shaped samples (10 mg) agglomerated under a pressure in the range 10^8 - 5×10^8 Pa, depending on the grafting ratio of the silica. After degassing under vacuum at 150°C, IR spectra were recorded between 2500 and 4000 cm⁻¹.

The thermal stability of the chemisorbed material was investigated under different atmospheres. This study, performed on agglomerated A300 modified by treatment with D_4 , was made on 10-mg disc-shaped samples, heated for 1/2 hr respectively at 150, 250, 400, 500, and 600°C either under vacuum or in the presence of oxygen or at the vapor pressure of water at 20°C (17.4 torr). IR spectra were recorded after each experiment. Quantification of the spectral lines was obtained by reference to master curves obtained as described previously.^{1,2}

IR spectroscopy was also used to study the resulting products of the reaction siloxane-water at 300°C in an autoclave. Using the spectrum of 1,5-hexamethyltrisiloxanediol as reference, and knowing that for this compound the ratio of the absorbance of the 3400 cm⁻¹ band (OH) to that of the 1420 cm⁻¹ line (CH_3), $R = (\text{absorbance } 3400 \text{ cm}^{-1})/(\text{absorbance } 1420 \text{ cm}^{-1})$, is 5.9, it was pos-

sible to evaluate for each product of reaction the average number \bar{n} of dimethylsiloxy groups between two hydroxyl endgroups:

$$\bar{n} = \frac{5.9 \times 3}{R}$$

Gravimetry

A thermobalance Perkin-Elmer TGS 2 was used to study the chemisorption of siloxane onto silica at temperatures higher than 150°C. The balance was fitted with a device allowing on one hand the degassing of silica and on the other hand the admittance of siloxane vapors at known pressures and temperatures (Fig. 1).

The reaction was performed as follows: After degassing silica at the temperature of the experiment, a known pressure of siloxane was admitted in the apparatus. After various times of reaction, the sample was degassed under vacuum and its weight increase, corresponding to the grafted material, recorded.

RESULTS AND DISCUSSIONS

Giving Evidence of Chemisorption by Chromatography and Gravimetry

At 150°C, as shown previously, no chemisorption process seems to take place after treating A300 with D₄. Indeed, a series of identical chromatographic injections is not followed by any variation of the retention times or of the surface area of the peaks.

However, after this treatment, IR examination of silica reveals a new spectral band at 2960 cm⁻¹. This line, attributed to the vibrations of the CH₃ group, could be indicative of the occurrence of a chemical linkage between the siloxane molecule and the surface of the filler. Support of this assumption is provided by elemental analysis, which shows that 0.12 molecule D₄/100 Å² is irreversibly

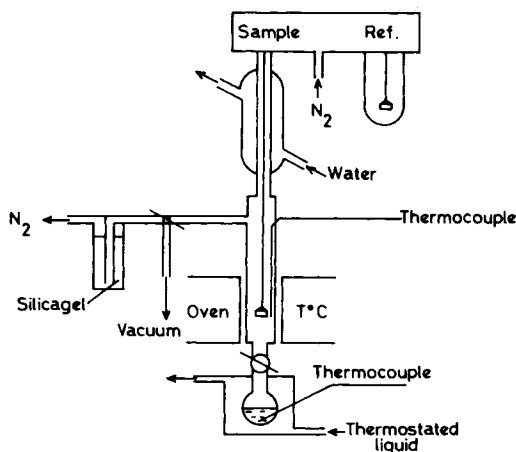


Fig. 1. Thermobalance diagram.

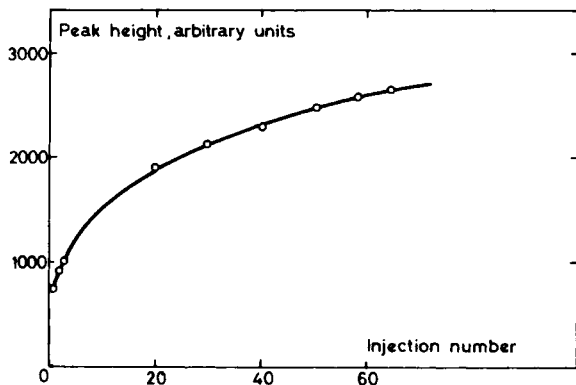


Fig. 2. Variation of peak height vs. number of injections of D_4 at $250^\circ C$.

held on the solid surface at this temperature. Since at $150^\circ C$ a beginning of chemisorption is observed, this process was examined at higher temperature. At $250^\circ C$, a series of identical chromatographic injections yield peaks with increasing heights tending toward a limit (Fig. 2). This limit is obtained when the adsorbent is saturated with chemisorbed material, and it is associated with the complete elution of the D_4 injected. This is in agreement with gravimetric determinations. The latter technique particularly allowed a quantification of the chemisorption process. Study at $250^\circ C$ of the reaction between agglomerated A300 and D_4 shows (Fig. 3) the process to be slow, e.g., only 0.155 molecule $D_4/100 \text{ \AA}^2$ is grafted onto the surface of the silica after treatment of 66 hr, while the maximum amount of D_4 that can be irreversibly held on the surface is 0.5 molecule $D_4/100 \text{ \AA}^2$. IR spectroscopy was used in order to have a better insight into this grafting reaction.

IR Spectroscopy—Quantification of the Grafting Reaction and Possible Reaction Mechanisms

This technique not only allowed the determination of the functional groups involved in the grafting reaction but, by reference to master curves,^{1,2} quantitative interpretations were provided, and therefore reaction mechanisms could be proposed.

Study of the IR spectrum (Fig. 4) of a degassed silica treated with D_4 at $150^\circ C$ reveals a new spectral band at 2960 cm^{-1} , owing to the methyl groups of the sil-

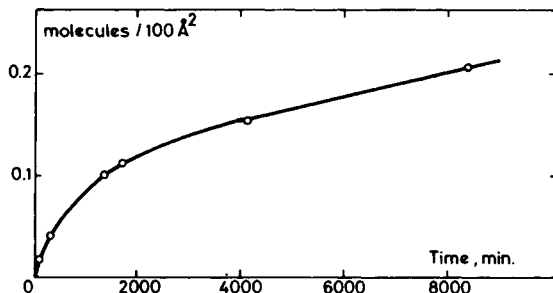


Fig. 3. Number molecules $D_4/100 \text{ \AA}^2$ vs. time of reaction at $250^\circ C$.

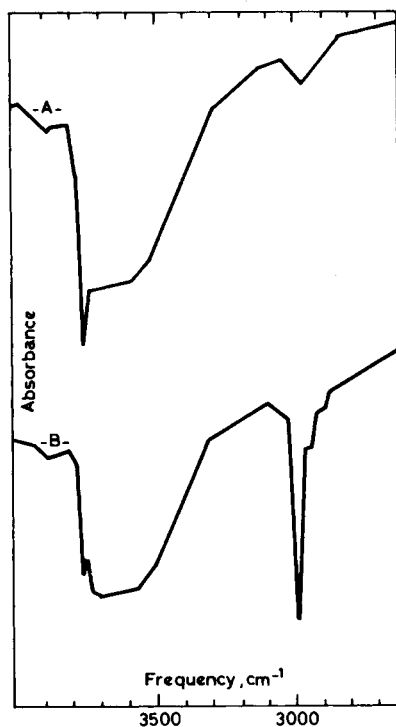
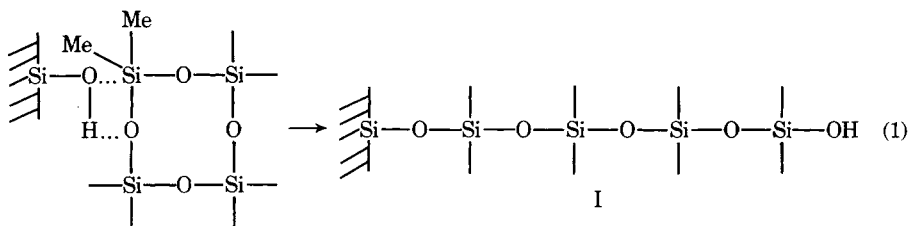
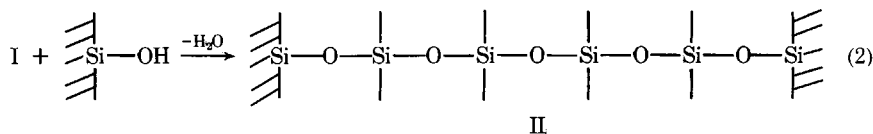


Fig. 4. IR spectra of silica before (A) and after (B) treatment with D_4 .

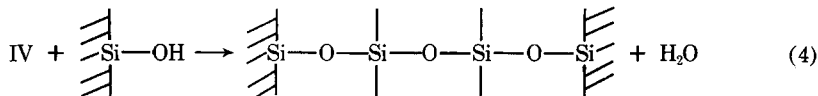
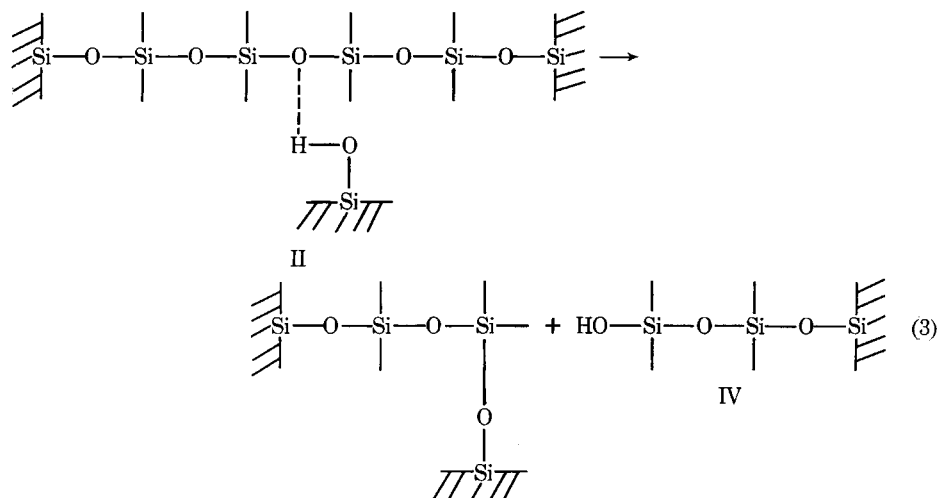
oxane. Moreover, this line is associated with a decrease of the 3750 cm^{-1} band because of the free OH groups of silica (OH_f). Inversely, no evolution of the 3400 cm^{-1} line, attributed to the associated OH groups (OH_{ass}) of A300 can be detected, i.e., no hydrogen bonding is occurring. Such observations are thus indicative of a chemical reaction between the free silanol groups of the filler and the siloxane. By reference to standard curves, it was possible to express the variation of CH_3 and OH_f line intensities respectively in number of molecules of D_4 grafted onto the filler and remaining free OH groups per unit surface area (100 \AA^2).

For the highest degree of reaction (i.e., $0.5\text{ molecule } D_4/100\text{ \AA}^2$), the experimental results indicate that the grafting of 1 molecule D_4 corresponds to the consumption of 2.7 silanols. Such a result suggests that the reaction $D_4\text{-A300}$ is proceeding through the opening of the siloxane cycle according to the following reaction scheme:





In a second step, I can react with another silanol group thus yielding a dimethylsiloxane bridge (II) onto the surface of silica. According to this reactional scheme, grafting of 1 molecule D_4 is associated to the disappearance of 2 OH groups. However, as shown previously, the experimental results indicate 2.7 OH_f to disappear per molecule D_4 . A possible interpretation of such a result could envision the reaction of free silanol groups, close to the grafted siloxane chain, yielding smaller siloxane bridges. The following sequence of reactions, while purely speculative, involves however a number of OH_f higher than 2:

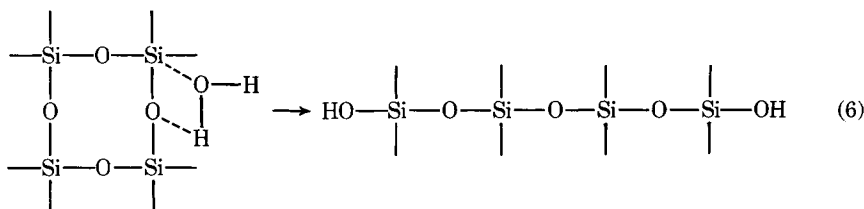


For samples having a smaller surface coverage, i.e., 0.1–0.2 molecule $D_4/100 \text{ \AA}^2$, the ratio D_4/OH_f becomes 1/5. Thus, at the beginning of the reaction, the cyclosiloxane could react selectively with the maximum of attainable and available free OH groups. Later on, it would react with the remaining silanols in the ratio 1–2 and perhaps 1–1 if after the first opening of the cyclosiloxane the intermolecular condensation of two chains with hydroxyl endgroups can be assumed. Such a reaction would provide a dimethylsiloxy bridge with eight $(\text{CH}_3)_2\text{SiO}$ sequences.

According to our hypothesis, D_4 by reaction with the free silanol groups can be opened and thus grafted onto the surface of the filler. Water is formed as a result [see reactions (2), (4), and (5)]. To elucidate the part played by water in this mechanism and thus get confirmation of the proposed reactional scheme, we studied the opening of the D_4 cycle in the presence of H_2O .

Reaction of Water with Octamethylcyclotetrasiloxane

This reaction has been studied under experimental conditions close to those retained when silica is treated with D_4 ($300^\circ C$). It is worth noting that after separation and drying, the IR spectrum of the reaction medium is closely similar to that of 1,5-hexamethyltrisiloxanediol. Such a result suggests the following reaction for the opening of the D_4 cycle:



The influence of reactant concentrations and time of reaction on this process was examined. For comparison, the reactivity of other siloxanes was checked (hexamethylcyclotrisiloxane, D_3 ; and tetradecamethylhexasiloxane, M_2D_4). According to Lagarde,³ in the presence of air, oxidation of D_4 could not be ruled out; thus, we considered the effect of this parameter as well as that of formic acid that could be generated during this oxidation. Results of the analyses (IR spectroscopy and liquid- and vapor-phase chromatography) performed on the reaction medium are reported in Tables I, II, and III.

It appears that water not only reacts with cyclosiloxanes but also reacts with linear chains yielding in both cases hydroxylated compounds. Such behavior is closely similar to that observed when studying the chemisorption of D_4 onto silica, i.e., opening of the D_4 cycle and attack of the ensuing siloxane chain by

TABLE I
Reaction of Water with Siloxanes

Siloxane	H_2O /siloxane	Reaction time, hr	Experimental conditions	\bar{n}^a
D_4	excess	3	air	95
D_4	1/1	3	air	26
D_4	1/1	3	N_2	33
D_4	1/1	6	air	26
D_4	10/1	3	air	10
D_4	1/1	3	air + A300	33
D_4	1/1	3	air + HCOOH	28
D_3	1/1	3	air	30
M_2D_4	excess	3	air	<600
M_2D_4	1/1	3	air	41
M_2D_4	10/1	3	air	14

^a Average number of dimethylsiloxy groups between two hydroxyl endgroups (see experimental part). (From this average number, it is, however, impossible to deduce the composition of the analyzed mixture.)

TABLE II
Low- and High-Boiling-Point Fraction of Products of the Reaction of Siloxanes with Water

Siloxane	D ₄	D ₄	D ₄	D ₄	D ₄	D ₄	D ₃	M ₂ D ₄	M ₂ D ₄
H ₂ O/siloxane	1	1	1	1	1	10	1	1	10
Reaction time hr	3	6	3	3	3	3	3	3	3
Experimental conditions	air	air	N ₂	air + SiO ₂	air + HCOOH	air	air	air	air
Low-boiling-point fraction, %	82.0	64	88.5	87.5	71.0	73.5	18.3	97.0	31.6
High-boiling-point fraction, %	18	36	11.5	12.5	29	26.5	81.7	3	68.4
\bar{M}_w	1850	3240	1740	2520	3850	1240	7620	—	2120
\bar{M}_n	1360	2030	1170	1700	2230	990	3960	—	1480

silanol groups. Moreover, from the variation of \bar{n} versus the different experimental parameters, the tendency of the siloxane–water reaction to reach equilibrium is clear. Indeed, whatever the siloxane used (cyclic or linear) at a given H₂O/siloxane ratio, \bar{n} is constant.

In Table II one can compare, under different experimental conditions, the percentages of the resulting low- and high-boiling-point materials and the average molecular weights (\bar{M}_w, \bar{M}_n) of the latter products.

Comparison of the amount of low-boiling-point materials and of the molecular weights of the high-boiling-point fractions shows clearly, in opposition to what was observed by IR spectroscopy analysis, that the ratio H₂O/siloxane is not the only significant parameter of the reaction. Particularly, a longer reaction time and the presence of formic acid as catalyst contribute to an increase in the amount of high-boiling-point materials. The great reactivity of D₃ should also be underlined.

The composition of the low-boiling-point fraction of the materials resulting from the treatment of siloxane with water at 160°C, under 0.5 torr pressure, was determined by chromatography. The results obtained are reported in Table III as weight percentages.

It appears that the low-boiling-point fraction of each reaction medium is a complex mixture of different siloxanes. The identification of a continuous series of cyclic and linear homologs as well as higher-molecular-weight compounds suggests the occurrence of combinations, rearrangements, and inter- or intramolecular condensation reactions. The amounts of reactants remaining after treatment are in agreement with the conclusions drawn from Table II. Moreover, the increasing amount of hydroxylated compounds obtained for H₂O/siloxane = 10 is in agreement with results of IR analyses in which a decrease of \bar{n} was observed (Table I).

Such results allow the proposition of the following set of reactions which accounts for the obtained products:

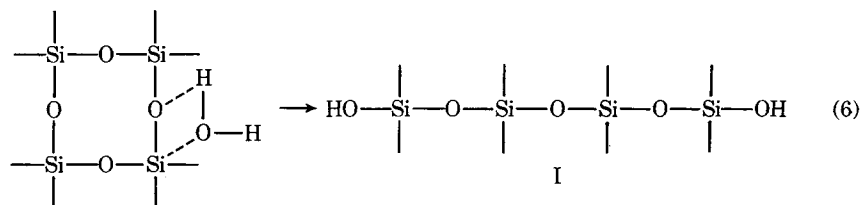


TABLE III
Analysis of the Low-Boiling-Point Fraction of Products of the Siloxane-Water Reaction

Siloxane	D ₄	D ₄	D ₄	D ₄	D ₄	D ₄	D ₃	M ₂ D ₄	M ₂ D ₄
H ₂ O/siloxane	1	1	1	1	1	10	1	1	10
Reaction time, hr	3	6	3	3	3	3	3	3	3
Experimental conditions	air	air	N ₂	air + SiO ₂	air + HCOOH	air	air	air	air
D ₃ , %	2.1	2.0	2.1	2.0	1.9	4.0	2.4	0.9	2.7
D ₄ , %	73	56	83.2	78.3	58.9	47.3	9.4	1.0	15.8
D ₅ , % ^a	1.1	1.1	0.7	0.9	3.7	4.6	2.6	0.9	5.4
D ₆ , % ^b	0.2	0.9	0.3	0.4	1.0	1.1	1.5	0.9	1.8
D ₇ , % ^c	0.9	0.6	0.4	0.9	0.9	0.6	0.5	0.8	0.9
D ₈ , % ^d	0.3	0.6	0.9	1.4	0.6	0.7	0.5	0.8	0.9
D ₉ , % ^e	0.4	0.2	0.2	0.5	0.5	—	—	—	0.3
D ₁₀ , % ^f	0.3	0.2	—	—	—	—	—	—	0.3
M ₂ D ₂ , % ^g	—	0.1	0.1	—	—	0.2	—	4.0	—
M ₂ D ₃ , % ^h	—	0.1	0.1	—	—	0.1	—	4.7	—
M ₂ D ₄ , %	—	—	—	—	—	—	—	72.0	—
M ₂ D ₅ , % ⁱ	—	—	—	—	—	—	—	3.6	—
M ₂ D ₆ , % ^j	—	—	—	—	—	—	—	2.4	—
D ₂ (OH) ₂ , % ^k	—	—	—	—	—	0.8	—	—	—
D ₃ (OH) ₂ , %	0.2	0.2	0.1	0.2	0.2	2.6	—	0.1	0.3
D ₄ (OH) ₂ , % ^l	0.2	0.3	0.1	0.1	0.3	3.1	—	0.1	0.4
D ₅ (OH) ₂ , % ^m	0.2	0.1	0.1	0.3	0.3	2.7	—	—	0.8
D ₆ (OH) ₂ , % ⁿ	0.2	0.2	0.1	—	0.3	1.4	—	—	0.8
D ₇ (OH) ₂ , % ^o	0.2	—	—	—	—	1.0	—	0.5	0.3

^a Decamethylcyclopentasiloxane.

^b Dodecamethylcyclohexasiloxane.

^c Tetradecamethylcycloheptasiloxane.

^d Hexadecamethylcyclooctasiloxane.

^e Octadecamethylcyclononasiloxane.

^f Eicosamethylcyclodecasiloxane.

^g Decamethyltetrasiloxane.

^h Dodecamethylpentasiloxane.

ⁱ Hexadecamethylheptasiloxane.

^j Octadecamethyloctasiloxane.

^k 1,3-Tetramethyldisiloxanediol.

^l 1,7-Octamethyltetrasiloxanediol.

^m 1,9-Decamethylpentasiloxanediol.

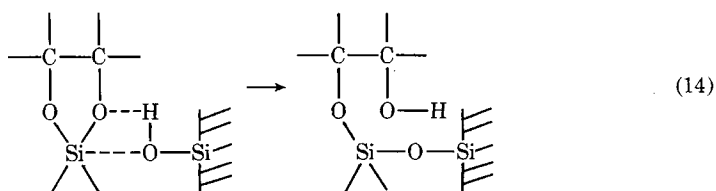
ⁿ 1,11-Dodecamethylhexasiloxanediol.

^o 1,13-Tetradecamethyloctasiloxanediol.

Reaction of Tetramethylethylenedioxydimethylsilane and of 1,5-Hexamethyltrisiloxanediol with Silica

Reaction of Tetramethylethylenedioxydimethylsilane

This compound has alkoxy functions whose reactivity toward silanol groups is well known. Its reactivity with A300 was studied at 150°C after checking its thermal stability. Figure 5 shows that while working at a temperature lower than in the reaction A300-D₄, this silane reacts more rapidly with silica. Moreover, the plot of grafting ratios versus reaction time tends toward a plateau at 1.8 molecule/100 Å², a quantity which corresponds to the amount of free silanol groups available on the surface of silica (1.7 OH_f/100 Å²) and suggests the following reaction scheme:



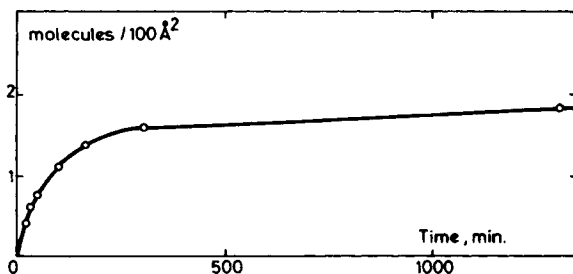


Fig. 5. Number molecules tetramethylethylenedioxidimethylsilane/100 Å² vs. time of reaction at 150°C.

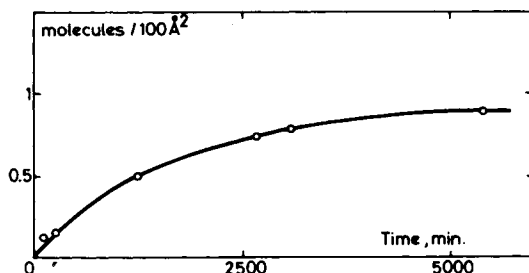
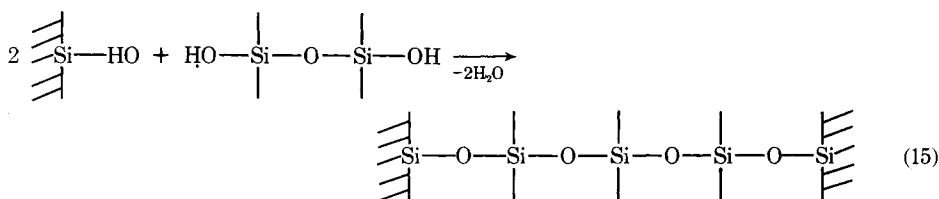


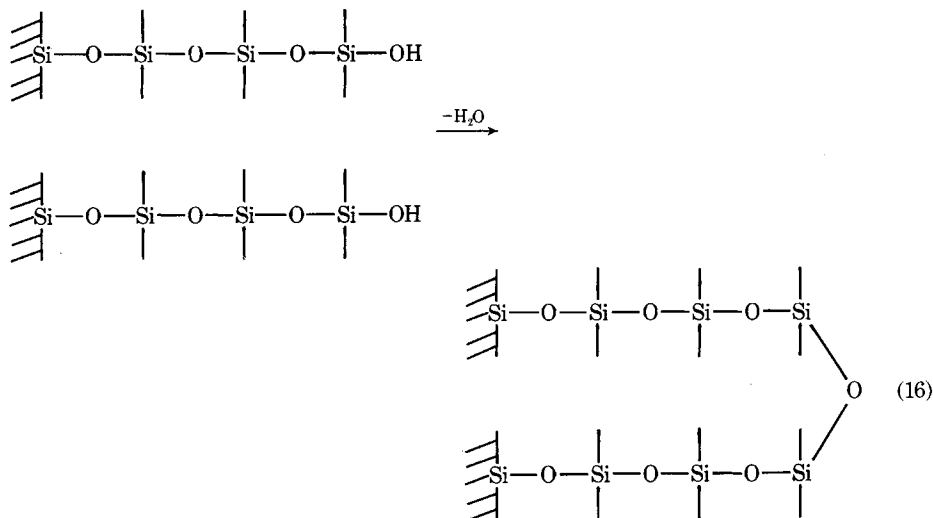
Fig. 6. Number molecules 1,5-hexamethyltrisiloxanediol/100 Å² vs. time of reaction at 75°C.

Reaction of 1,5-Hexamethyltrisiloxanediol

As a consequence of the poor thermal stability of this compound, its reactivity was studied at 75°C (Fig. 6). It appears that in spite of the low temperature at which this reaction was performed, the diol reacts very easily with silica. The curve of grafting ratios versus time tends to flatten out at 0.9 molecule/100 Å². This ratio corresponds to about half the amount of free silanol groups available on the surface of the filler (1.7 OH_f/100 Å²). Interpretation of the grafting process can be provided by the following reaction, which associates the grafting of 1 molecule siloxane to the release of 2 molecules water:



Considering the loss of water, at the end of the reaction, 1 molecule/100 Å² should be grafted onto the surface. It is, however, worth noting that intermolecular condensation could also occur between molecules already grafted through one end, a fact which might account for a ratio of grafted siloxane in excess of the one postulated by reaction (15).



Study of the chemisorption of other siloxanes such as an alkoxy silane and a dihydroxysiloxane shows, as expected, the great reactivity of these materials toward silica. Particularly, the maximum grafting ratios are attained when all the available free silanol groups of silica have reacted. Therefore, this study supports the set of reactions proposed for the interpretation of the chemical interactions taking place between D_4 and a fumed silica.

Having shown the ability of PDMS oligomers to react efficiently with silanol surface groups, we tried to characterize the ensuing materials, particularly by studying the thermal stability of the grafted silica under various atmospheres.

Thermal Behavior of the Modified Silicas

After treatment with D_4 , the modified silicas may be used for the reinforcement of silicon rubbers. It was thus of interest to study their behavior under the conditions used for the preparation of PDMS-silica composites, particularly the effect of heating in the presence of oxygen and water. Such a study was performed by following the evolution of the IR spectral line of the CH_3 group versus temperature, either under vacuum or in the presence of O_2 or H_2O or air. The corresponding results are plotted in Figure 7.

The intensity of the CH_3 line varies slightly upon heating the modified A300 under vacuum to $600^\circ C$ or under controlled atmosphere to $500^\circ C$. This is in agreement with previous observations³ related to the stability of dimethylsiloxy grafts under nitrogen at $600^\circ C$. Inversely between 500 and $600^\circ C$, this adsorption band decreases strongly in the presence of water and nearly disappears in the presence of air or O_2 . Table IV provides not only the observed weight losses of D_4 under the various experimental conditions but also the amount of OH_f groups regenerated per molecule D_4 eliminated (OH_f/D_4).

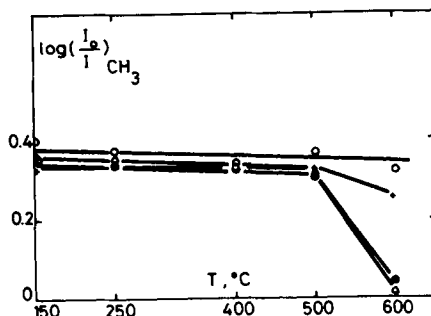


Fig. 7. Log $|I_0/I|_{\text{CH}_3}$ vs. treatment temperature for D₄-modified silica: (—○—) vacuum; (—●—) air; (—△—) oxygen; (—+—) water.

TABLE IV

Experimental conditions	Weight loss upon heating, %		Reappearance of OH _f , OH _f /D ₄
	150°C < T < 500°C	500°C < T < 600°C	
Vacuum	7	11	—
Air	5	72	1
O ₂	9	79	2.4
H ₂ O	9	21	0.17

These results are underlining the outstanding thermal stability of siloxane grafts chemically held onto the surface of silica. Therefore, these materials efficiently contribute to the decrease of interactions between PDMS and silica in a temperature range which is much larger than the one selected for the preparation of the filled PDMS.

CONCLUSIONS

The examination of silica-siloxane interactions by means of IR spectroscopy, gravimetry, and chromatography has shown that above 150°C, chemical interactions take place between D₄ and Aerosil 300. Confirmation of the reaction mechanisms proposed for the interpretation of the grafting processes has been drawn from the study of the D₄-water reaction and from the behavior of PDMS oligomers with reactive groups. Investigation of the thermal properties of the siloxane-modified A300 has shown these materials to exhibit a high thermal stability that is favorable to the limitation of interactions between PDMS and silica in the corresponding vulcanizates.

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