

Mechanically induced sorption of siloxane on silica: Experimental and theoretical investigations of chain binding, collective behaviour and multiple-aggregate processes

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The purpose of the present paper is to propose a two-parameter model to describe the sorption of siloxane chains onto silica particles immersed in the polymeric liquid at room temperature. Random adsorbed systems were obtained from mechanical mixing. One parameter of the model is the probability ρ_B that a polymer chain is simultaneously bound to two silica particles; the other one, π , attempts to describe the possible collective character of the binding of a single chain. The model was compared with values of the residual amount of polymer Q_r measured siloxane-silica mixtures after removal of all free polymer chains. The number of available chain binding sites per unit mass of silica was varied by using a silica surface treated to a variable extent. Typical relative numbers of silicon chains ($M_n \approx 3.6 \times 10^5$) simultaneously bound to two or three particles were found to be 0.21 and 0.49, respectively, in a mixture determined from an initial siloxane-silica weight-to-weight ratio equal to 2.5. Also, it was shown that a chain binding site can be divided into four subsites; on average, any chain is torn off from the surface whenever it occupies less than two subsites.

(Keywords: siloxane; silica; treated silica; adsorption; mechanical mixing)

INTRODUCTION

This work deals with the description of a model attempting to characterize the non-covalent adsorption of poly(dimethyl siloxane) (PDMS) chains upon aggregates of silica, in systems prepared from mechanical mixing.

Investigations of PDMS-silica interactions so far reported have mostly been developed from the interface obtained from solutions of siloxane in suspensions of silica¹. In that case, PDMS chain binding is expected to result from a thermodynamic field of forces only. The order of magnitude of the free enthalpy² involved in such a process is probably much smaller than the work transfer to the siloxane-silica system occurring during mechanical mixing. Furthermore, in the systems studied in the present paper, silica aggregates are completely immersed in a polymer liquid; consequently the whole surface of the silica must be covered by polymer. Also, macromolecules are strongly entangled with one another in the polymeric liquid part of the mixture; accordingly, they cannot be fully adsorbed upon the silica surface. Any macromolecule must be assumed to undergo partial adsorption only; the remaining part of the chain is considered to be embedded in a temporary network structure built up from all the other silicon chains. Therefore, systems resulting from such mechanical mixing must be carefully distinguished from the usual adsorbed polymer layers^{3,4}.

Although the sample preparation is quite complex, it is worth having a deep insight into such a totally random medium, which results from the mixture possessing a wide

distribution of silica aggregate sizes and a high polydispersity I of silicon chains ($I \lesssim 2$).

In a recent paper⁵, hereafter referred to as I, it has been shown that siloxane adsorption upon silica occurs through a chain binding site involving about 100 hydrogen bonds established between monomeric units and silica. Two thermodynamic variables were used to obtain such a result: the residual amount of polymer Q_r bound to silica and the average chain molecular weight M_n .

The purpose of the present paper is to investigate the multiple-link structure of chain binding sites by considering two additional thermodynamic variables: the concentration of silica aggregates in the mixture C_{Si} and the concentration of active silica bonds, which is controlled by chemical treatment of the surface of the aggregates. More precisely, this study aims to determine the possible collective character of link formation within a chain binding site. The proposed model will attempt to predict variations in the residual amount of polymer bound to silica, after removal of all free siloxane chains, taking both the chemical treatment of the silica surface and a possible multiple-particle chain binding process into consideration.

EXPERIMENTAL

Materials

The poly(dimethyl siloxane) samples were commercially available polymers; the corresponding number-

average molecular weights are reported in Table 1. Fumed silica was bought under the trade name Aerosil 150, with a surface area, determined by the BET method, of $150 \pm 15 \text{ m}^2 \text{ g}^{-1}$. The ultimate particle size is about 140 \AA but the particles are covalently associated with one another into aggregates. There are about 1.8 free silanol groups per 100 \AA^2 .

Sample preparation

A two-roll stainless-steel mill was used to incorporate the mineral into the bulk polymer at room temperature. The mixing was performed up to the formation of homogeneous samples; after full incorporation of the filler into the polymer, the duration of the milling was about 15 min. Two types of mixtures were studied; they were characterized by initial siloxane-silica weight-to-weight ratios equal to 5 and 2.5, respectively.

Silica treatment

Hexamethyldisilazane has been widely used for deactivating chromatographic materials; silica silanol sites are converted to non-functional trimethylsilyl groups. The treatment used here was performed in a gently stirred reactor. Previously humidified silica (200 g) was in suspension in methylcyclohexane (260 cm^3). When the suspension was seen to be homogeneous, hexamethyldisilazane was introduced drop by drop. The suspension was stirred for 1 h before eliminating the solvent under vacuum. Then the treated silica was dried at 378 K under vacuum for about 24 h. The silica surface was analysed in two ways: the first was a microanalysis of carbon content; the second was based on measurements of free silanol absorbances using infra-red spectroscopy⁶. Considering that the area of a trimethylsilyl group^{7,8} is about 35 \AA^2 the fraction of converted free silanols and the surface average ratio are compared with each other in Table 2. The two determinations are in reasonable agreement with each other.

Polymer extraction

The solvent used to remove the free polymer from siloxane-silica mixtures was RP Normapur chloroform (99.2 to 99.6% CHCl_3 , 0.0005% acidity in HCl , 0.05% H_2O). The mixture was divided in small amounts (a few cubic millimetres in size); these were kept in a glass vessel along with a large amount of solvent. After 12 h the

Table 1 Number-average molecular weights of polymer samples and polydispersity *I*

$\bar{M}_n \times 10^{-5}$	<i>I</i>
3.6	1.7
1.3	1.8
0.9	1.8
0.4	1.9

Table 2 Comparison of surface coverage ratios and converted free silanol fractions

Surface coverage ratio	Fraction of converted free silanols
0.22	0.17
0.28	0.22
0.58	0.59
0.84	0.74

Table 3 Experimental results: residual amount of polymer Q_r measured from mixtures characterized by several initial ratios Q_i , several average molecular weights \bar{M}_n and several surface coverage ratios *q*

$\bar{M}_n \times 10^{-5}$	3.6		1.3	0.9	0.4
	5	2.5	5	2.5	5
Q_i	a		b		
	0.15	} Q_r	1.33	1.5	0.87
0.3	1.20		1.4	0.6	0.21
0.6	0.87		1.15	0.4	0.55
0.75	0.5		0.67	0.23	

(a) Samples are three months old
(b) Samples are nine months old

polymer solution was removed and the sample was immersed in pure solvent. This procedure was cautiously applied to avoid any partial damage to the sample. This operation was repeated twice a day for five days. Then, the product was vacuum dried at 360 K for 36 h to eliminate the remaining solvent. The final product was characterized by the residual amount of polymer Q_r left bound to the surface per unit mass of silica; Q_r was determined from microanalysis measurements of the carbon content.

EXPERIMENTAL RESULTS

Measurements of Q_r were first performed on siloxane-silica mixtures characterized by a low silica concentration; the initial siloxane-silica weight-to-weight ratio Q_i was equal to 5.0. Three different chain molecular weights were considered: $\bar{M}_n = 0.4 \times 10^5$, 1.3×10^5 and 3.6×10^5 , respectively. Four different surface coverage ratios were prepared to analyse silica treatment effects on the chain binding process: $q = 0.15, 0.3, 0.6$ and 0.75 , respectively. Then, the residual amount of polymer Q_r obtained after removal of all free chains was measured from mixtures characterized by $Q_i = 2.5$. Two different number-average chain molecular weights were considered: $\bar{M}_n = 0.9 \times 10^5$ and 3.6×10^5 , respectively. Surface coverage ratios had values identical with those corresponding to the first series of experiments. Furthermore, the sorption equilibrium of samples with a low Q_i value ($Q_i = 2.5$) and a high chain molecular weight ($\bar{M}_n = 3.6 \times 10^5$) was known to be reached within nine months; consequently, some Q_r values were measured before the achievement of adsorption (samples were only three months old). All experimental results are reported in Table 3.

STRUCTURAL INVESTIGATION OF THE CHAIN BINDING SITE

Untreated silica

It has been shown in paper I that the residual amount of polymer Q_r^0 bound to silica after removal of free chains is a linear function of the number-average molecular weight \bar{M}_n of PDMS macromolecules⁵. This striking result has been interpreted by assuming that the average number $n_f^0 = 2.82 \times 10^{18} \text{ g}^{-1}$ of bound macromolecules per unit mass of silica is independent of the chain molecular weight. The surface area of the adsorbent is $150 \text{ m}^2 \text{ g}^{-1}$; therefore, the average area of a chain binding site, whatever its detailed structure, is $\sigma_f \approx 5.4 \times 10^3 \text{ \AA}^2$.

Finally, the average number f of hydrogen bonds involved in the chain binding process can be derived from an estimate of the number $\nu_1 = 1.8 \times 10^{-2} \text{ \AA}^{-2}$ of free silanol groups per unit area of silica^{9,10}:

$$f = \nu_1 \sigma_f \approx 97$$

The above description was shown to hold in the case of siloxane-silica mixtures characterized by a PDMS molecular weight \bar{M}_n lower than about 4×10^5 and polymer-silica weight-to-weight ratio Q_i higher than or equal to 5.

This basic result stresses the need to investigate the possible collective character of the hydrogen bonding mechanism responsible for the adsorption process. Such an investigation necessitates varying the number of available silanol groups forming hydrogen bonds with oxygen atoms of chain skeletons. Partly treated siloxane was assumed to present a surface with non-active silanol groups distributed in a random way. The surface coverage ratio q of treated silica was assumed to be varied by changing the concentration of available silanol groups C_B . This section aims to propose a simple model to describe possible collective aspects of the chain binding process onto silica. The parameter $q(C_B)$ will be considered as a variable in addition to the other variable Q_r already used in paper I.

It is assumed that any chain binding site can be divided into several groups of hydrogen bonds, which we call subsites of coordination. Any subsite is assumed to correspond to silanol groups forming hydrogen bonds with oxygen atoms attached to a short segmental part of the polymer skeleton. When any of the hydrogen bonds located within a given subsite is broken, the whole corresponding segmental part of the chain is assumed to break away from the silica surface because of a collective effect induced by the linkage of monomeric units. Let z denote the average number of subsites of coordination within the binding site of a single chain. The average number of hydrogen bonds determining a subsite is $\nu_s = f/z$. Also, it is assumed that there is a threshold of adsorption defined by a number ζ_s ; it is considered that no polymer chain can be bound to the silica surface whenever it occupies a number of subsites lower than or equal to $z - \zeta_s$.

Treated silica

Let $p(q)$ denote the probability that a short segmental part of a siloxane chain cannot be attached to a subsite because of the partial treatment of the silica surface. The probability that m subsites are non-active among z subsites of a chain binding site is written as:

$$P(m) = \frac{z!}{m!(z-m)!} p(q)^m [1-p(q)]^{z-m} \quad (1)$$

Consequently, the probability that a PDMS chain is attached to a site is equal to the sum of the probabilities of finding a number of non-active subsites lower than the threshold number ζ_s :

$$\Pi = \sum_{m=0}^{\zeta_s-1} P(m) \quad (2)$$

Therefore, Πn_f^0 is the number of available chain binding

sites per unit mass of treated silica. The residual amount of polymer bound to treated silica is expressed as:

$$Q_r = \Pi \frac{n_f^0 \bar{M}_n}{N_A} = \frac{n_f \bar{M}_n}{N_A} = \Pi Q_r^0 \quad (3)$$

with $n_f = \Pi n_f^0$ and $N_A = \text{Avogadro's number}$.

Figure 1 illustrates variations in the ratio Q_r/Q_r^0 drawn for several values of the parameters z and ζ_s . Clearly, the calculated curves exhibit sharp variations whenever z is given values higher than about 20 whatever the value of $\zeta_s < z$; while smooth variations characterize the ratio Q_r/Q_r^0 when z is lower than 10. Effects of variations of the threshold value ζ_s are also presented in Figure 1.

Comparison with experimental results

The comparison of properties predicted from the proposed model with experimental results requires expressing the probability p as a function of the coverage ratio q of treated silica surface. For the sake of simplicity p was set equal to q . Calculated curves were first compared with experimental results obtained from a mixture defined by an initial polymer-silica weight-to-weight ratio Q_i equal to 5 and a chain molecular weight $\bar{M}_n = 3.6 \times 10^5$. The curve fitting the experimental results in the best way is shown in Figure 2; adjusted values of the parameters are $z=4$ and $\zeta_s=3$. Then, the chain molecular weight was varied while the initial ratio Q_i was kept constant ($\bar{M}_n = 0.4 \times 10^5$, $\bar{M}_n = 1.3 \times 10^5$). Experimental results for the mixture with an initial ratio $Q_i = 2.5$ and a chain molecular weight $\bar{M}_n = 0.9 \times 10^5$ are compared with the calculated curve in Figure 2; adjusted values of the parameters are again $z=4$ and $\zeta_s=3$.

The reasonable agreement of experimental data with theoretical curves suggests that the chain binding site on silica is probably divided into about four subsites of coordination. Each subsite corresponds to the binding of one segmental part of a siloxane chain determined from about 25 monomeric units. However, this approach does not give any details about the conformational structure of chain segments adsorbed onto silica. Such a structure could be either fully ordered as a helical segment in a crystal (about 10 monomeric units are necessary to build a helical turn) or completely disordered. A siloxane chain is broken away from the surface or at least it is easily torn off from silica whenever three-quarters of the subsites are

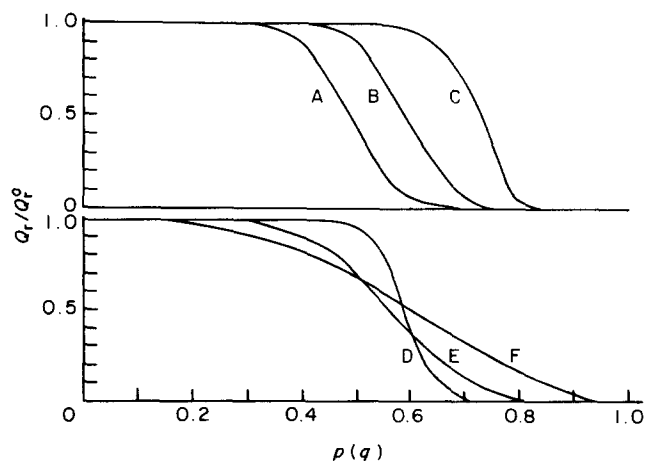


Figure 1 Theoretical variations in the ratio Q_r/Q_r^0 as a function of the probability p : A, $z=50$, $\zeta_s=25$; B, $z=50$, $\zeta_s=30$; C, $z=50$, $\zeta_s=37$; D, $z=100$, $\zeta_s=60$; E, $z=15$, $\zeta_s=9$; F, $z=5$, $\zeta_s=3$

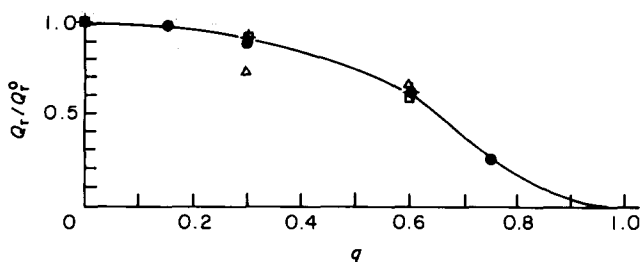


Figure 2 Experimental variations in the ratio Q_r/Q_r^0 as a function of the surface coverage ratio, and the theoretical curve: +, $\bar{M}_n = 3.6 \times 10^5$; □, $\bar{M}_n = 1.3 \times 10^5$; △, 0.4×10^5 (the initial siloxane-silica weight-to-weight ratio is $Q_i = 5$); ●, $\bar{M}_n = 0.9 \times 10^5$ ($Q_i = 2.5$)

rendered unavailable because of surface treatment. Finally, the probability that a siloxane chain can be attached to the silica surface is written as a simple function of the coverage ratio q :

$$\Pi(q) = 1 - 4q^3 + 3q^4 \quad (4)$$

Formula (4) may be considered as a series expansion of the probability $\Pi(q)$.

MULTIPLE-PARTICLE CHAIN BINDING

The main hypothesis underlying the model proposed in the foregoing section was to consider that any poly(dimethyl siloxane) chain is attached to a single silica particle, because the average distance between centres of silica particles is longer than the average size of macromolecules. Roughly:

$$C_{Si}^{-1/3} < \langle R^2 \rangle^{1/2} \quad (5)$$

where C_{Si} is the average number of silica aggregates per unit volume of polymer in the initial silica-siloxane mixture, and $\langle R^2 \rangle$ is the mean square end-to-end distance of a siloxane chain.

The purpose of this section is to analyse binding properties of siloxane chains under the condition where the average distance $C_{Si}^{-1/3}$ becomes shorter than the average chain dimension $\langle R^2 \rangle^{1/2}$. In that case a multiple-aggregate chain binding process is expected to occur.

The residual amount of polymer Q_r left bound to silica after removal of all free chains should exhibit a strong deviation from a value observed at low silica particle concentrations because the number of available chain binding sites is larger than the number of polymer chains linked to the silica surface. In addition to Q_r and Π a new variable p_B is introduced to describe properties of siloxane-silica mixtures: p_B denotes the probability that a siloxane chain is simultaneously bound to two silica aggregates. The value of p_B is given by $0 \leq p_B \leq 1$ and p_B is probably a function of the ratio $C_{Si}^{-1/3}/\langle R^2 \rangle^{1/2}$.

Untreated silica

A typical situation where $C_{Si}^{-1/3}$ and $\langle R^2 \rangle^{1/2}$ obey inequality (5) is encountered in a mixture defined by an initial polymer-silica weight-to-weight ratio Q_i equal to 2.5 and a number-average molecular weight of silicon chains $\bar{M}_n = 3.6 \times 10^5$. In that case, the experimental value of Q_r is 1.6 while Q_r is equal to 2.0 in mixtures defined by $Q_i = 5.0$ or $Q_i = 10$ and $\bar{M}_n = 3.6 \times 10^5$ (paper I).

Two-aggregate chain binding. Let us first consider an initial siloxane-silica mixture characterized by a moderately high concentration of silica aggregates; namely the residual amount of polymer linked to silica after removal of free chains is assumed to consist of two kinds of chains only. The total number N_2 of linked chains per unit mass of silica is divided into two parts:

- (i) $N_2(1 - p_B)$ is the number of chains bound to one particle only;
- (ii) $N_2 p_B$ is the number of chains simultaneously linked to two particles.

Since the total number of chain binding sites occupied by the polymer is n_f^0 :

$$n_f^0 = N_2(1 - p_B) + 2N_2 p_B \quad (6)$$

or

$$n_f^0 = N_2(1 + p_B) \quad (7)$$

Therefore, the number of chains linked per unit mass of silica is:

$$N_2 = n_f^0 / (1 + p_B) = N_1 / (1 + p_B) \quad (8)$$

N_1 is the number of linked chains in the absence of a two-particle binding process.

Three-aggregate chain binding. Let us now consider an initial siloxane-silica mixture characterized by a high concentration of aggregates; namely the residual amount of polymer linked to the silica surface consists of three kinds of siloxane chains. The total number N_3 of linked chains per unit mass of silica is now divided into three parts:

- (i) $N_3(1 - p_B)$ is the number of chains linked to one particle only;
- (ii) $N_3(1 - p_B)p_B$ is the number of chains linked to two particles only;
- (iii) $N_3 p_B^2$ is the number of chains simultaneously bound to three particles.

Since the total number of chain binding sites occupied by the polymer is n_f^0 :

$$n_f^0 = N_3(1 - p_B) + 2N_3(1 - p_B)p_B + 3N_3 p_B^2 \quad (9)$$

and

$$N_3 = N_1 / (1 + p_B + p_B^2) \quad (10)$$

Treated silica

In the case where the silica is treated, the probability Π that a chain can be linked to the surface must be included in the description of the multiple-aggregate binding process. The total number of available binding sites is now Πn_f^0 .

Two-aggregate chain binding. The number of chains $N_2(1 - p_B)$ initially linked to a single silica aggregate (corresponding to untreated silica) is now split into two parts:

- (i) $\Pi N_2(1 - p_B)$ is the number of siloxane chains bound to a single aggregate;

- (ii) $(1 - \Pi)N_2(1 - p_B)$ is the number of chains that are now broken away from the aggregate surface.

Also, the number of chains N_2p_B initially linked to two aggregates is now divided into three parts:

- (i) $\Pi^2 N_2 p_B$ is the number of chains still bound to the silica surface;
 (ii) $2\Pi(1 - \Pi)N_2 p_B$ is the number of chains now bound to a single particle; and
 (iii) $(1 - \Pi)^2 N_2 p_B$ is the number of chains torn out from the silica surface because of the treatment.

The total number of siloxane chains $N_{2,t}$ bound to the treated silica surface is now:

$$N_{2,t}/N_2 = 1 + p_B(1 - \Pi) \quad (11)$$

On inspection of formulae (2) and (11) it is clearly seen that the number of linked chains varies strongly with the coverage ratio of treated silica surface.

Three-aggregate chain binding. The total number of siloxane chains $N_{3,t}$ still bound to silica after surface treatment is calculated in the same way as above (see Appendix):

$$N_{3,t}/N_3 = \Pi[1 + p_B(1 - \Pi) + p_B^2(1 - \Pi)^2] \quad (12)$$

By taking the polydispersity of polymer chains into consideration, the residual amount of siloxane bound to silica should actually be expressed as:

$$Q_t(3,t) =$$

$$\frac{mp \int dN f(N) N \Pi [1 + (1 - \Pi)p_B(N) + (1 - \Pi)^2 p_B^2(N)]}{\int f(N) dN}$$

where $f(N)$ is the chain length distribution number; p_B obviously depends upon chain length. Again, for the sake of simplicity, the residual amount of polymer $Q_t(3,t)$ per unit mass of silica is written as:

$$Q_t(3,t)/Q_t(3) = \Pi[1 + (1 - \Pi)p_B + (1 - \Pi)^2 p_B^2] \quad (13)$$

where $Q_t(3)$ is the residual amount of polymer measured from untreated silica. Calculated curves are reported in Figure 3 for $p_B = 0.3, 0.5$ and 0.6 , respectively ($z = 4, \zeta_s = 3$).

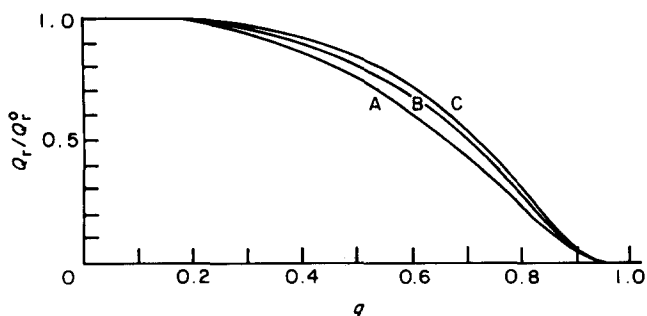


Figure 3 Theoretical variations in the ratio Q_t/Q_t^0 as a function of the surface coverage ratio q (curves are calculated according to formula (13); $z = 4, \zeta_s = 3$): A, $p_B = 0.3$; B, $p_B = 0.5$; C, $p_B = 0.6$

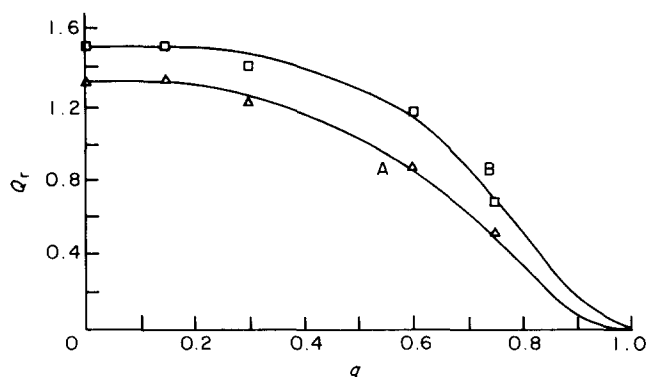


Figure 4 Comparison of experimental results (points) with theoretical variations (curves) in the residual amount of polymer per unit mass of silica as a function of the surface coverage ratio q : \triangle , samples three months old, $p_B = 0.4, Q_t^0 = 1.32$; \square , samples nine months old, $p_B = 0.7, Q_t^0 = 1.5$; A, $z = 4, \zeta_s = 3, p_B = 0.4$; B, $z = 4, \zeta_s = 3, p_B = 0.7$

Comparison with experimental results

Theoretical curves were compared with results concerning mixtures characterized by an initial polymer-silica weight-to-weight ratio $Q_i = 2.5$ and a number-average chain molecular weight $\bar{M}_n = 3.5 \times 10^5$. Assuming that the shape of any silica aggregate is a sphere with an average diameter equal to 700 \AA , the average distance between centres of aggregates in the initial mixture is $C_{Si}^{-1/3} \approx 10^3 \text{ \AA}$ (for $Q_i = 5, C_{Si}^{-1/3} \approx 1.25 \times 10^3 \text{ \AA}$). Also, the average dimension of a siloxane chain corresponding to a molecular weight $M = 3.6 \times 10^5$ is:

$$\langle R^2 \rangle^{1/2} \approx (C_x \times 2 \times 5 \times 10^3)^{1/2} \times 1.5 \text{ \AA} \approx 360 \text{ \AA}$$

(the characteristic ratio of PDMS chains is known to be $C_x \approx 6$).

Theoretical curves $Q_t(3,t)/Q_t(3)$ were drawn by adjusting the parameter p_B of formula (13) to experimental results. Figure 4a illustrates the theoretical curve drawn for a mixture where the adsorption is supposed to be in the process of completion. Experimental points are also reported in this figure; corresponding values of the parameters are $z = 4, \zeta_s = 3$ and $p_B = 0.4$. The relative number of chains bound to a single aggregate is 0.6, while the number of macromolecules undergoing a three-aggregate binding process is about four times smaller than 0.6. Figure 4b shows the theoretical curve drawn for a mixture observed after completion of the adsorption process. Corresponding values of the parameters are $z = 4, \zeta_s = 3$ and $p_B = 0.7$. Most siloxane chains are now bound to two aggregates (relative number: 0.21) or to three aggregates (relative number: 0.49). Finally, the relative number of chains that do not participate in a multiple-aggregate binding process can easily be calculated from formula (13) for any value of the coverage ratio q . For example, this relative number is equal to 0.6 after completion of the adsorption process, while it is equal to 0.8 during partial adsorption.

CONCLUSION

Siloxane-silica systems resulting from mechanical mixing of silica aggregates immersed in siloxane exhibit saturated sorption properties. By varying the area of treated silica surface, the binding site of a siloxane chain can be reasonably shown to consist of four subsites containing

about 25 silanol groups; this partition is defined on average. However, no characterization has yet been obtained about the average distance between subsites. Evidence for a collective property of the chain binding process was also given from the use of treated silica surface. This collective effect was assumed to be induced by the linear structure of siloxane macromolecules.

The totally random mixture determined from silica particles immersed in siloxane is characterized by a very high functionality. However, aggregates are not necessarily connected with one another in systems defined from a low chain molecular weight and a high initial siloxane-silica weight-to-weight ratio $Q_i \gtrsim 5$. In that case, some clusters probably exist but their fractal nature is not yet known. When the initial ratio Q_i is lower than or equal to 2.5 and the chain molecular weight is higher than about 10^5 , there is probably a permanent network structure organized throughout the whole mixture. About half of the chains are involved in a three-particle binding process when the molecular weight is about 4×10^5 . This result suggests investigating both the gel-like behaviour of the mixture and the percolation nature of its organization in space¹¹. However, it must be emphasized that the siloxane-silica mixture is swollen by free chains and by chains bound to one particle only (dangling chains); consequently, it is not exactly a dry gel. Also, the probability p_B that a polymer bond is formed randomly between two nearest silica particles is an unknown function of the chain molecular weight and the actual distribution of particles in space. It probably smears the usually observed sharpness of percolation processes. Again, it would be worth characterizing the fractal nature of the mixture¹².

It is believed that the two-parameter model proposed to describe the mechanically induced sorption of siloxane upon silica is not oversimplified. It is a convenient approach appropriate to the understanding of statistical properties of a medium characterized by a broad distribution of silica particle sizes and a high chain polydispersity.

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APPENDIX A

The number of chains $N_3(1 - p_B)$ initially linked to a single silica aggregate is split into two parts:

- (i) $\Pi N_3(1 - p_B)$ is the number of chains still bound to a single aggregate;
- (ii) $(1 - \Pi)N_3(1 - p_B)$ is the number of chains torn off from the aggregate surface.

Also, the number of chains $N_3 p_B(1 - p_B)$ initially bound to two silica aggregates is divided into three parts:

- (i) $\Pi^2 N_3 p_B(1 - p_B)$
- (ii) $2\Pi(1 - \Pi)N_3 p_B(1 - p_B)$
- (iii) $(1 - \Pi)^2 N_3 p_B(1 - p_B)$

Finally, the initial number of chains $N_3 p_B^2$ simultaneously bound to three silica aggregates is divided into four parts:

- (i) $\Pi^3 N_3 p_B^2$
- (ii) $3\Pi^2(1 - \Pi)N_3 p_B^2$
- (iii) $3\Pi(1 - \Pi)^2 N_3 p_B^2$
- (iv) $(1 - \Pi)^3 N_3 p_B^2$

The total number of attached chains is:

$$N_{3,u}/N_3 = \Pi[1 + (1 - \Pi)p_B + (1 - \Pi)^2 p_B^2] \quad (\text{A1})$$

This corresponds to formula (12).