# Silica–siloxane mixtures: surface saturation process of particles. Kinetics

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The kinetics of adsorption of poly(dimethylsiloxane) chains on silica particles is observed from end-methylated chains at room temperature and several silica concentrations and from hydroxyl-terminated chains at several temperatures. The kinetics is interpreted as a progressive surface saturation process. The time constant of adsorption of methylated chains was found to be $\tau = 144$, 52 and 39 h for silica concentrations equal to 0.09, 0.17 and 0.29 (w/w), respectively. For hydroxylated chains, $\tau$ was found to be equal to 124, 30 and 2 h at 323, 353 and 373 K, respectively. The activation energy of the process is 18 kcal mol$^{-1}$.

**(Keywords: silica; siloxane; adsorption; kinetics)**

## INTRODUCTION

This work deals with the kinetics of adsorption of poly(dimethylsiloxane) (PDMS) chains on the surface of silica particles. This adsorption process was observed in silica–siloxane systems obtained from the mechanical mixing of mineral particles added to a polymer melt. Polymer chains are adsorbed through the formation of hydrogen bonds; each hydrogen bond is supposed to link one silanol group of the surface to one oxygen atom of the skeleton of a PDMS chain. Several hydrogen bonds can be formed between the silica surface and one chain. End-methylated chains undergo a uniform adsorption while end-hydroxylated chains can form one double hydrogen bond between one silanol group and one chain end, in addition to other hydrogen bonds associated with the chain itself.

Two main features characterize the adsorption effect resulting from the full immersion of mineral particles in a polymer melt.

(i) It is well known that chains in a melt obey Gaussian statistics; consequently, any polymer chain formed from $N$ skeletal bonds is swollen by a number of other chains equal to $\sqrt{N}$, on average. Similarly, at any time that one chain is in contact with the silica surface, the number of other chains also in contact with the same part of the surface is about equal to $\sqrt{N}$. All polymer chains compete with one another to be adsorbed upon the silica surface. This corresponds to a multiple-chain adsorption. As a result specific to this adsorption effect, the residual amount of polymer $Q_r^1$ left bound to silica after removing all free chains is a function of the square root of the chain molecular weight $M_n$:

$$Q_r^1 = \chi_a M_n^{1/2} \tag{1}$$

The order of magnitude of the experimental value of $\chi_a$ is $10^{-3}$ g$^{-1/2}$ mol$^{1/2}$.

This property has recently been given an interpretation by showing that the average number of contact points of one chain with the surface is proportional to the square root of the number $N$ of skeletal bonds:

$$\langle r_c \rangle = \varepsilon_a N^{1/2} \tag{2}$$

Then:

$$Q_r^1 = \frac{A m_b^{1/2}}{\sigma_e \varepsilon_a \mathcal{A}} M_n^{1/2} \tag{3}$$

where $A$ is the specific area of silica, $\sigma_e = 55$ Å$^2$ is the mean area associated with one active silanol group, $\mathcal{A}$ is the Avogadro number and $m_b$ is the average molar weight of one bond[1,2]. For PDMS chains:

$$Q_r^1 \simeq 2.8 \times 10^{-3} (M_n/\varepsilon_a)^{1/2} \tag{3a}$$

$\varepsilon_a$ is about equal to one.

(ii) The other feature concerns the effect of progressive saturation of the surface of mineral particles. At the end of the mechanical mixing most of the surface is covered by adsorbed chains. They represent an initial amount of polymer hereafter called $Q_r(0)$. The surface is nearly saturated. Nevertheless, the adsorbed layer is not at equilibrium. For example, chain segments defining loops may be too stretched because of the presence of constraints exerted during the mechanical mixing. The residual amount of polymer $Q_r(t)$ bound to silica is thus an increasing function of time, until the limit $Q_r^1$ is reached, at equilibrium. The structure of the binding site of any given chain is supposed to vary with time, until an equilibrium between retractive forces and hydrogen bonds is obtained. This also corresponds to the completion of surface saturation.

It has already been shown that the progressive saturation of the surface can be described by a diffusion formula:

$$Q_r(t) = Q_r^1 - [Q_r^1 - Q_r(0)] \exp[-(t/\tau)^{1/2}] \tag{4}$$

The time constant $\tau$ can be expressed as a conventional ratio of a mean-square length $\xi^2$ over a diffusion constant $D$. The large values of $\tau$ ($\tau \simeq 10^2$ h) clearly showed that the limiting process is not chain diffusion in the melt but

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**Table 1** Characteristic parameters and experimental results concerning silica–siloxane mixtures

| Sample ref. | $M_w$ ($10^3$ g mol$^{-1}$) | $I_p$ | $C_{Si}$ (w/w) | $T$ (K) | $Q_r^l$ | $\tau$ (h) |
|---|---|---|---|---|---|---|
| A | 476 | 2.1 | 0.09 | 343 | 4.0 | 144 |
| B | | | 0.17 | | 2.85 | 52 |
| C | | | 0.29 | | 2.0 | 39 |
| D | 41 | 1.7 | 0.30 | 323 | 1.2 | 124 |
| | | | | 353 | 1.18 | 30 |
| | | | | 373 | 1.29 | 2 |
| E | 119 | 2.2 | 0.29 | 343 | 2.05 | 34 |

slow diffusion of chains on the surface[3]. The above formula was shown to apply to end adsorption (hydroxyl-terminated chains) as well as to uniform adsorption (end-methylated chains); the concentration of silica was $C_{Si} \simeq 0.30$.

The purpose of the present work was twofold. Considering end-methylated chains, the kinetics of the surface saturation of particles, resulting from the adsorption process, was investigated as a function of the concentration of silica. More precisely, it was intended to analyse the effect of bridging between particles, induced by polymer chains, upon the kinetics of adsorption. Then, considering hydroxyl-terminated chains, attention was focused upon the effect of temperature variations on the kinetics of surface saturation.

## EXPERIMENTAL

### *Materials*

Poly(dimethylsiloxane) and α,ω-dihydroxypoly(dimethylsiloxane) samples are commercially available polymers. The corresponding weight-average molecular weights and polydispersity indices are reported in *Table 1*.

Fumed silica was bought from Degussa (West Germany) under the tradename Aerosil 150. The surface area, determined by the Brunauer–Emmett–Teller (BET) method, is 150 m$^2$ g$^{-1}$, and there are about 1.8 free silanol groups per 100 Å$^2$ of silica surface. The ultimate particle size is about 140 Å$^2$, but aggregates are formed from the association of particles by covalent links.

### *Sample preparation*

Silica-filled polymers were prepared by mechanical mixing on a two-roll stainless mill at room temperature; homogeneous samples were obtained when the duration of the milling operation was about 15 min. Five different mixtures were studied, corresponding to different initial silica concentrations or to different polymers. Samples A, B and C were obtained by mixing a high-molecular-weight poly(dimethylsiloxane) with different amounts of silica. They were shaped into a plate 2 mm thick, with the help of a calender, immediately after the milling operation. Hydroxyl-terminated poly(dimethylsiloxane) was used to prepare samples D and E. Only sample E was shaped into a plate 2 mm thick.

Then, the initial samples were divided into small pieces (a few cubic millimetres) and put in a glass vessel. It was assumed that all these portions of the sample were evolving simultaneously and under identical external conditions. At this stage, samples were placed in an oven regulated at higher temperature than room temperature, to shorten the duration of the adsorption observations. This time corresponded to the starting point ($t = 0$) of the study.

The effect of temperature variations on the adsorption was investigated in sample D; different pieces were kept at 323, 353 or 373 K; while samples A, B, C and E were studied at 343 K.

### *Polymer extraction*

Methylcyclohexane was used to remove the free polymer chains from silica–siloxane mixtures. At a given time $t$, a piece of the sample was put in a glass vessel with a large excess of solvent at room temperature. The solvent was renewed three or 10 times, over 30 days, for samples consisting of low- or high-molecular-weight polymer, respectively. Then, the product was vacuum dried at 360 K for 48 h to eliminate traces of solvent. After removal of all free polymer chains, $Q_r(t)$, the residual amount of polymer still bound per unit mass of silica, was determined by a microanalysis measurement of carbon content.

## EFFECT OF PARTICLE BRIDGING: END-METHYLATED CHAINS

### *Description*

Following ref. 3, the expression for the equation of progressive saturation relies upon two hypotheses:

(i) The adsorption of chains is described as a conventional diffusion process occurring in the presence of an absorbing screen[4].

(ii) There is an excluded-surface effect; namely, the adsorption process occurs on free parts of the surface only.

In addition to these two hypotheses, it is now proposed to consider that, at any time $t$, the mean surface, per unit mass of silica, covered by adsorbed chains is $A(t)$ in the absence of any bridging effect. Accordingly, the mean number of adsorbed chains is:

$$\nu_c(t) = A(t)/\varepsilon_a \sigma_e N^{1/2} \tag{5}$$

while the amount of adsorbed polymer is:

$$Q_r(t) = A(t) m_b^{1/2} M_n^{1/2}/\varepsilon_a \sigma_e \mathscr{A} \tag{5a}$$

Taking the bridging effect induced by the presence of polymer chains into consideration, the area actually associated with the number $\nu_c(t)$ of adsorbed chains is expressed as:

$$A^*(t) = A(t)[1 + \mu(t)] \tag{6}$$

where $\mu(t)$ describes the extent of the bridging effect at time $t$. The surface available to further adsorption is then:

$$A_T - A(t)[1 + \mu(t)]$$

$A_T$ is the total silica surface in the mixture. At equilibrium, the bridging function reaches the limit value $\mu_l$ and the amount of adsorbed polymer is:

$$Q_r^l = Q_r^m/(1 + \mu_l) \tag{7}$$

where $Q_r^m$ corresponds to the maximum amount of polymer adsorbed on $A_T$, without any effect of bridging. Then, the equation for progressive saturation is written

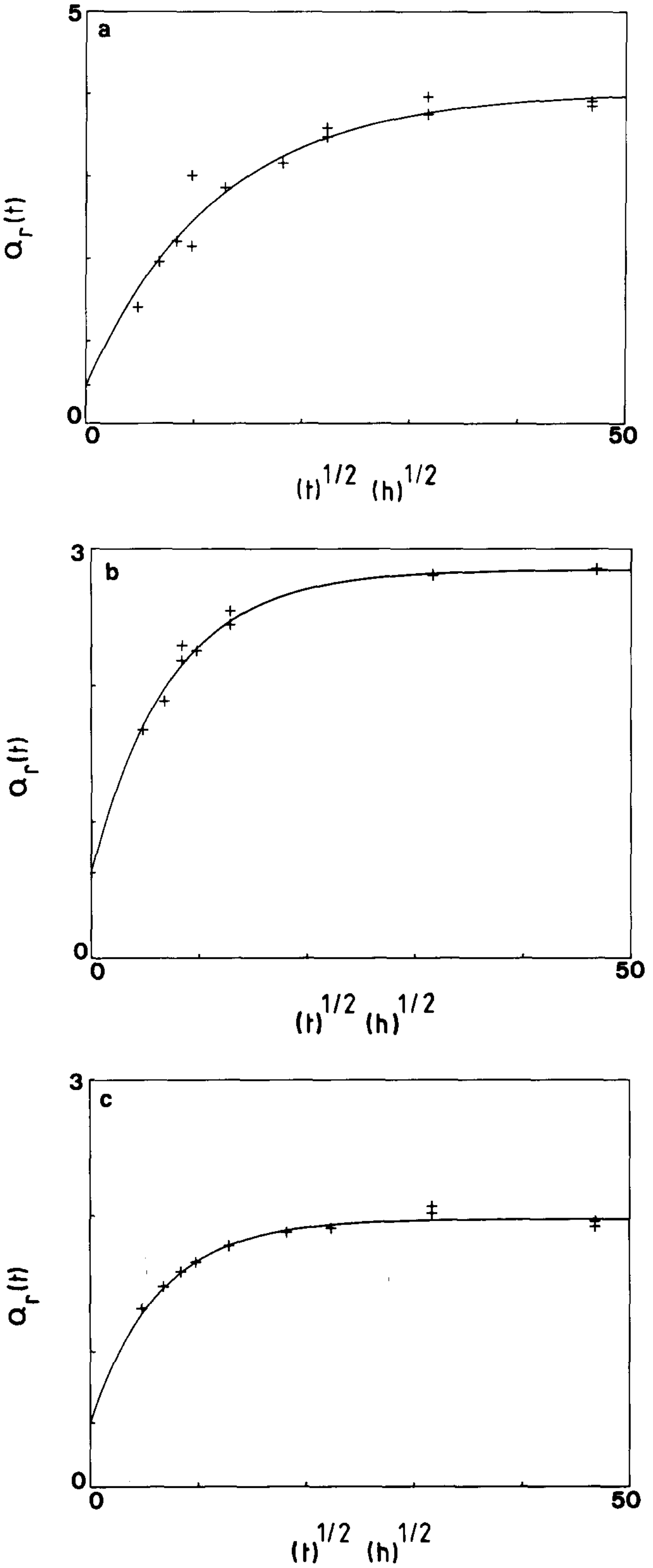

**Figure 1** Amount of methyl-terminated PDMS chains adsorbed on the silica surface as a function of time ($T = 343$ K, $M_w = 476 \times 10^3$). Full curves represent the theoretical variations determined from a least-mean-square procedure with $Q_r^l$ and $\tau$ as adjustable parameters. (a) $C_{Si} = 0.09$, (b) $C_{Si} = 0.17$, (c) $C_{Si} = 0.29$ (w/w)

as:

$$dQ_r(t)/dt = \{Q_r^l(1 + \mu_l) - Q_r(t)[1 + \mu(t)]\}(1/\tau t)^{1/2} \quad (8)$$

This is not easily solved because of the presence of the bridging function $\mu(t)$.

For the sake of simplicity, the bridging function $\mu(t)$ is supposed to be a constant: $\mu(t) = \mu_l$. Then:

$$Q_r(t) = Q_r^l - [Q_r^l - Q_r(0)] \exp\{-[(1 + \mu_l)t/\tau]^{1/2}\} \quad (9)$$

The time constant is divided by $(1 + \mu_l)^2$:

$$\tau(\mu_l) = \tau/(1 + \mu_l)^2 \quad (10)$$

The parameter $\mu_l$ is expected to depend upon the concentration of silica. Combining formulae (7) and (10), the value of the ratio:

$$[\tau(\mu_l)]^{1/2}/Q_r^l$$

should be independent of the concentration of silica.

### *Observations*

Theoretical curves were drawn according to formula (9) to fit experimental results in the best way (*Figure 1*). Three concentrations of silica $C_{Si}$ were observed. Theoretical curves were found to be characterized by the following parameters: $Q_r^l = 4.0$, 2.85 and 2.0 g/g and $\tau(\mu_l) = 144$, 52 and 39 h, for $C_{Si} = 0.09$, 0.17 and 0.29 w/w, respectively. Corresponding values of the ratio $[\tau(\mu_l)]^{1/2}/Q_r^l$ were found to be equal to 3.0, 2.5 and 3.1, respectively (*Table 1*). These three values are in reasonable agreement with one another. The present model shows that the adsorption process of polymer chains can be pictured as the progressive saturation of the silica surface. The increase of the rate of adsorption upon addition of silica results mainly from the bridging of particles induced by polymer chains.

## HYDROXYL-TERMINATED CHAINS

The progressive saturation of the silica surface was also investigated as a function of the temperature of the silica–siloxane system, considering hydroxyl-terminated chains. The concentration of silica was $C_{Si} = 0.30$ (w/w). Theoretical curves drawn from formula (9) and corresponding experimental points are shown in *Figure 2*. The value of the time constant $\tau$ was found to be equal to 2, 30 and 124 h at 373, 353 and 323 K, respectively. A strong variation of the rate of adsorption is observed over a temperature range equal to 50 K. The limit value of adsorbed polymer $Q_r^l$ hardly varies with the temperature increase. An activation energy $E = 18$ kcal mol$^{-1}$ can be assigned to the rate of saturation (*Figure 3*). It corresponds to the formation of about 10 hydrogen bonds. It must be emphasized that the progressive surface saturation is still reasonably described by formula (9): the excluded-surface effect is associated with the random diffusion occurring in the presence of an adsorbing screen.

Finally, the effect of chain length variations was also investigated by considering the rate of adsorption of hydroxyl-terminated chains characterized by a molecular weight $M_w = 119 \times 10^3$ g mol$^{-1}$. Measurements were performed at 343 K. The time constant $\tau$ was found to be equal to 34 h, instead of 30 h for a molecular weight $M_w = 41 \times 10^3$ g mol$^{-1}$ at 353 K. Clearly, the rate of adsorption hardly depends upon the chain molecular weight (*Table 1*). The adsorption process is limited by chain diffusion upon the surface of particles rather than by diffusion through the polymer melt surrounding particles.

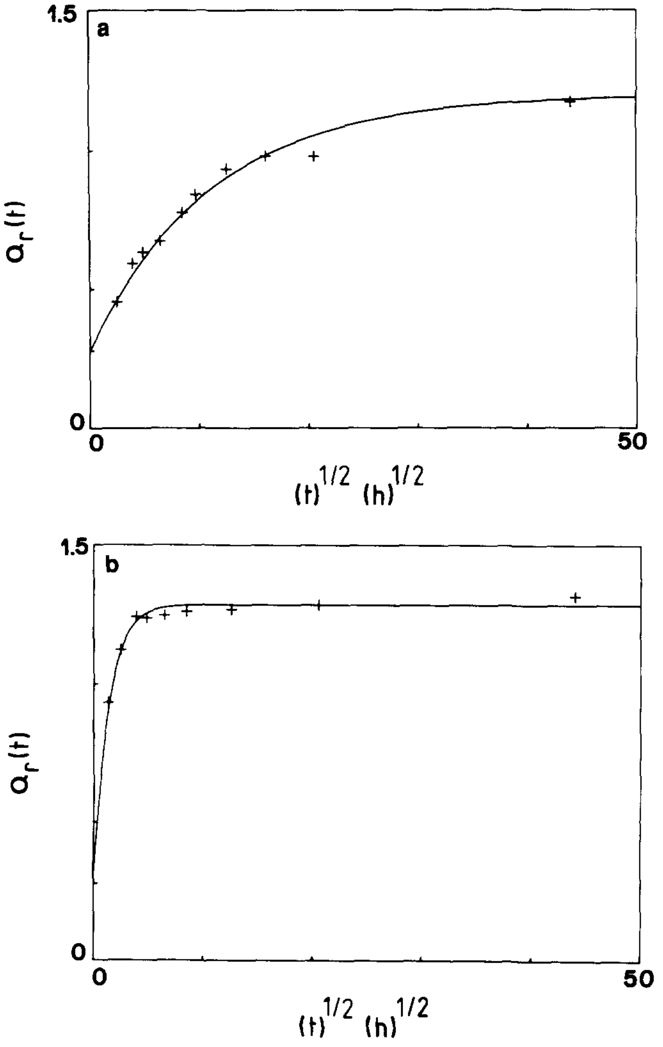

**Figure 2** Amount of hydroxyl-terminated PDMS chains adsorbed on silica as a function of time (sample D). Full curves represent the theoretical variations determined from a least-mean-square procedure with $Q_r^l$ and $\tau$ as adjustable parameters. (a) $T = 323$ K, $Q_r^l = 1.2$ g/g, $\tau = 124$ h; (b) $T = 373$ K, $Q_r^l = 1.3$ g/g, $\tau = 2$ h

## CONCLUSIONS

The kinetics of polymer adsorption, observed after mixing siloxane chains and silica particles, reflects a progressive saturation of the silica surface. It is proposed to picture this process in the following way. One loop of a given adsorbed chain is considered; it is formed from $n_{ij}$ skeletal bonds, joining two contact points $i$ and $j$, on the silica surface. A retractive force can be associated with the distance $r_{ij}$ between these two points. An estimate of the corresponding energy of elasticity is given by:

$$\varepsilon_r = 3kTr_{ij}^2/2n_{ij}b^2$$

where $b$ is the average length of one skeletal bond. Such a loop may be strongly stretched during mechanical mixing. The consequence of this stretching is twofold. The loop may cover several silanol groups and it prevents hydrogen bonds from being formed. Also, the free energy of elasticity may be higher than the strength of one hydrogen bond; therefore, this is broken. The distance between the two considered contact points is shortened, until an equilibrium is reached; this corresponds to $r_{ij} < an_{ij}^{1/2}$. The rate of adsorption corresponds to the rate of increase of entropy of the polymer system.

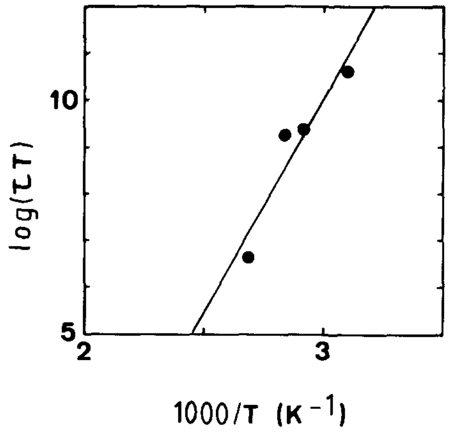

**Figure 3** Effect of temperature variations upon the adsorption rate of hydroxyl-terminated PDMS chains

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