

Hydroxyl or methyl terminated poly(dimethylsiloxane) chains: kinetics of adsorption on silica in mechanical mixtures

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The kinetics of adsorption of siloxane chains on silica aggregates was observed in mechanically induced mixtures. The amount of polymer $Q_r(r)$ bound, to silica per unit mass, was found to obey the time dependence: $Q_r^1 - Q_r(t) = (Q_r^1 - Q_r(0)) \exp(-\sqrt{t/\tau})$; Q_r^1 is the limit amount of adsorbed polymer and $Q_r(0)$ represents the initial adsorption resulting from the mechanical mixing. Two polymer species were structured: hydroxyl terminated chains ($\bar{M}_n = 2.4 \times 10^4$) or methyl terminated ones ($\bar{M}_n = 2.9 \times 10^5$). Values of the characteristic time τ were 7.1×10^7 s and 6.2×10^8 s, respectively. The silica concentration was 0.29 (w/w) for both species.

(Keywords: siloxane chains; kinetics; adsorption; mechanical mixtures)

INTRODUCTION

This work deals with the process of adsorption, of poly(dimethylsiloxane) chains, induced by a mechanical mixing of the pure molten polymer with fumed silica aggregates. This sorption results from the migration of chains from the polymer melt surrounding particles towards the silica surface. It is a saturated adsorption since all aggregates are fully immersed in a polymer melt. It occurs through hydrogen bonding. Two species of chains are currently used to form silica-siloxane mixtures. The first one concerns methyl terminated chains: the adsorption occurs from skeletal oxygen atoms, only. It may be worth emphasizing that a striking feature characterizes the process of adsorption of methyl terminated poly(dimethylsiloxane) chains: the average number n_f of monomeric units involved in trains formed on the surface of particles is a constant, whatever the chain length; $n_f \approx 60$ monomeric units¹. Accordingly, the average number v_c of chains adsorbed per unit mass of silica is a constant: $v_c = 4.6 \times 10^{18} \text{ g}^{-1}$. This number has been shown to be invariant within a broad chain molecular weight range: $10^4 \lesssim \bar{M}_n \lesssim 3.5 \times 10^5$. This is very different from the effect resulting from the binding of chains to mineral particles of a large size ($\approx 10^{-6}$ m in diameter) in suspension in a polymer solution. More precisely, in this last case, the average number v_1 of monomeric units associated with trains formed onto the surface of particles is usually proportional to the chain length². Poly(dimethylsiloxane) (PDMS) chains and silica particles can form clusters. When the silica concentration is high enough and PDMS chains are long enough, an infinite cluster appears. Then the silica-siloxane mixture behaves

like any gel; it can be reversibly swollen by a good solvent³.

The other species of chains, mechanically mixed with silica, concerns hydroxyl terminated poly(dimethylsiloxane) molecules. In this case the adsorption also occurs from skeletal oxygen atoms and from chain ends. No investigations about lengths of trains induced from hydroxyl terminated chains have been reported so far. These silica filled polymers can also behave like gels when they are formed from silica particles with a suitable concentration (> 0.17 w/w) and chains with appropriate lengths ($\bar{M}_n \gtrsim 3 \times 10^4$). Whether they are formed from hydroxyl terminated chains or from methyl terminated chains, siloxane-silica mixtures exhibit a strong time evolution long after their mechanical mixing. More precisely, the amount of polymer left bound to silica particles after eliminating all unattached chains increases as a function of time. The purpose of the present work is to give a framework of analysis of the kinetics of adsorption of PDMS chains onto the silica surface. The kinetics were observed from two mixtures formed from a silica concentration equal to 0.286 (w/w). Two polymer species were used: hydroxyl terminated PDMS chains ($\bar{M}_n = 2.4 \times 10^4$; $\bar{M}_w = 4.1 \times 10^4$) and methyl terminated PDMS chains ($\bar{M}_n = 2.9 \times 10^5$; $\bar{M}_w = 5.4 \times 10^5$).

EXPERIMENTAL

Mixtures used throughout this investigation were silica filled siloxane systems. The surface area of fumed silica (Aerosil 150), determined by the BET method is $150 \text{ m}^2 \text{ g}^{-1}$. Silica aggregates were used without any

chemical treatment and the chemical nature of the silica surface was that of the commercially available product. A two roll stainless steel mill was used to incorporate the mineral into the bulk polymer at room temperature. The milling was performed as long as needed to form a sample of homogeneous appearance, i.e. a material without any trapped air bubbles. Fifteen minutes was an average duration for this operation. The mixture was characterized by an initial concentration $C_{\text{Si}} = 0.29$ (w/w). The time of milling was precisely known and corresponded to the starting point of the study ($t=0$). Then, the initial sample of hydroxyl terminated chains was divided into 25 small pieces. These were supposed to evolve simultaneously under identical external conditions, at room temperature. The amount of polymer $Q_r(t)$ left bound to silica at a given time, t , was determined from the irreversible analysis of a single piece, chosen at random. Therefore, the time dependence of $Q_r(t)$ was defined from 25 different time values. The same experimental procedure was applied to methyl terminated chains using 9 pieces instead of 25. The removal of free polymer chains was performed by using methylcyclohexane (C_7H_{14}) as solvent¹. A piece of mixture chosen at random at a given time, t , was kept in a flask at room temperature along with 60 ml of solvent for 12 h. Then, the liquid phase was gently pumped out with a small pipette. This set of operations was repeated once. The product was vacuum dried at 90°C for 48 h. After removal of all free polymer chains, $Q_r(t)$, the residual amount of polymer still bound per unit mass of silica was defined by microanalysis measurements of carbon-silicon ratio. From experiments performed on other similar systems, it can be assumed that the sol fraction does not have the original distribution of molecular weight. Some fractionation has actually occurred leading to a slight shift towards shorter chains.

HYDROXYL TERMINATED CHAINS: KINETICS OF ADSORPTION

Observation

Considering a silica-siloxane mixture made from hydroxyl terminated chains and silica particles (10^3 Å in average size), the time variation of the amount of polymer $Q_r(t)$ left bound to silica after removing all free chains was measured over six months. The variable $Q_r(t)$, determined per unit mass of silica, is represented in Figure 1 as a time function. The limit of $Q_r(t)$ is $Q_r^1 = 0.95$. The difference $Q_r^1 - Q_r(t)$ was found to obey an exponential dependence upon the square root of time. The corresponding semi-logarithmic plot is shown in Figure 2.

Qualitative description of the mixture

Estimates of parameters characterizing this silica filled polymer are given in this section.

Number of silanol groups involved in chain binding. The number of silanol groups, per unit area of silica surface, possibly involved in hydrogen bonding is 1.8×10^{-2} Å⁻². Furthermore, the average number of chains bound to silica is 1.9×10^{19} per unit mass of silica. Taking the specific area of the silica into consideration, the average area associated with a given chain is $s_a = 7.9 \times 10^2$ Å². Therefore, the number of silanol groups involved in the binding of one chain is about 14. This number does not

necessarily correspond to the formation of hydrogen bonds; it only indicates that, whenever a PDMS chain is fixed, 14 silanol groups, on average, become unavailable for the adsorption of other chains.

Average chain size. Assuming, for the sake of simplicity, that any PDMS chain is described by a Gaussian random walk, although it is bound to silica, its root mean square end-to-end distance $\sqrt{\langle R^2 \rangle}$ is 120 Å. It corresponds to an average cross-section equal to 1.2×10^4 Å². About 15 chains bound to silica can be associated with such a cross-section. If a given chain is imagined as a sphere, it is swollen by about 20 other chains.

Model of kinetics of adsorption

Diffusion law. The description of the kinetics of adsorption relies upon the following hypothesis.

(i) It is assumed that the sorption process of a given chain is entirely controlled by chain ends. In other words, even though skeletal oxygen atoms are involved in the adsorption mechanism, it is considered that the chain binding effect becomes permanent only in the case where one of the two chain-ends is bound to silica. It corresponds to a double H bond formed with a silanol, on the surface. Therefore, the adsorption is pictured as

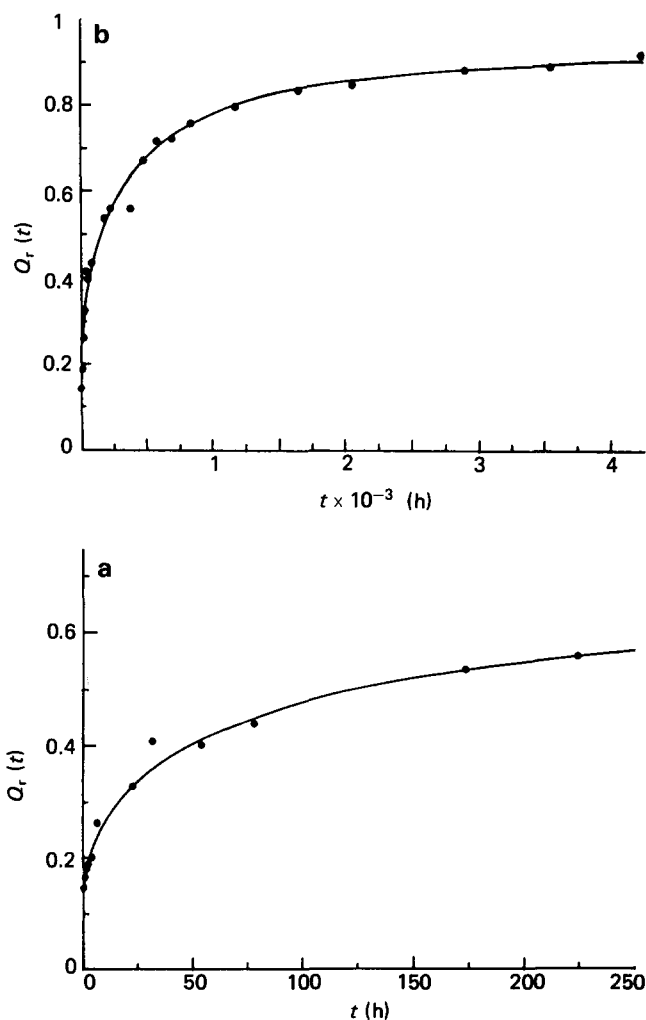


Figure 1 Amount of hydroxyl terminated PDMS chains adsorbed on silica as a function of time. ($\overline{M}_n = 2.4 \times 10^4$; initial silica concentration: $C_{\text{Si}} = 0.30$ (w/w)). (a) Variations observed over 10 first days. (b) Variations observed over six months

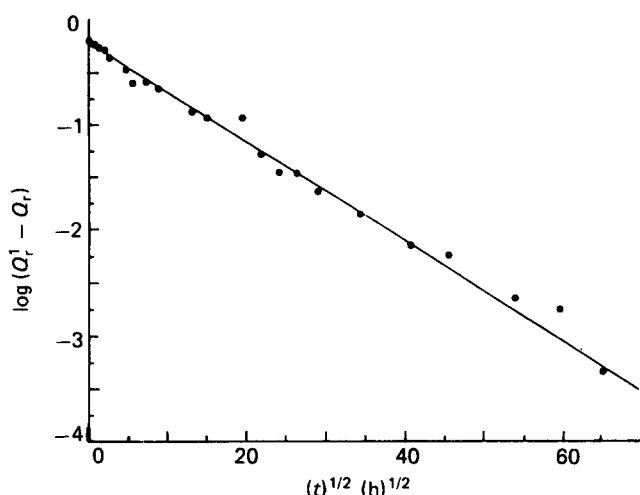


Figure 2 Semi-logarithmic plot of $(Q_r^1 - Q_r(t))$ as a function of the square root of time. Hydroxyl terminated PDMS chains: $\bar{M}_n = 2.4 \times 10^4$; initial silica concentration: $C_{Si} = 0.30$ (w/w); $Q_r^1 = 0.95$

an irreversible process.

(ii) To describe the saturated adsorption effect, it is supposed that the probability of binding of a chain is proportional only to the area of the silica surface still available at a time, t .

Then, any chain end is pictured as a particle and it is possible to calculate the probable rate at which it deposits itself on an adsorbing screen. Assuming, for the sake of simplicity, that the silica surface is an infinite plane, the z axis is perpendicular to this plane. The probability of presence of chain ends along this z direction is $2/\sqrt{\langle R^2 \rangle}$. The probability that a given chain end initially at z is adsorbed on the silica surface, per unit time, at time t is:

$$\sigma(z, t) = \frac{2}{\sqrt{\langle R^2 \rangle}} \times \frac{z}{t} \times \frac{1}{\sqrt{4\pi Dt}} e^{-z^2/4Dt} \quad (1)$$

The whole rate of adsorption of chain-ends is defined by:

$$\sum(t) = \int_0^\infty \sigma(z, t) dz \quad (2)$$

or

$$\sum(t) = 2 \sqrt{\frac{D}{\pi \langle R^2 \rangle t}} \quad (3)$$

The amount of polymer left bound to silica, as a function of time, simply obeys the following equation:

$$Q_r^0(t) = \sum(t)(Q_r^1 - Q_r(t)) \quad (4)$$

or

$$Q_r(t) = Q_r^1 - (Q_r^1 - Q_r(0)) e^{-4\sqrt{(Dt)/\pi \langle R^2 \rangle}} \quad (5)$$

$Q_r(0)$ represents the amount of polymer left bound to silica right after the mechanical mixing.

Discussion. The slope of the straight line, drawn in Figure 2, is equal to $5 \times 10^{-2} \text{ H}^{-1/2}$; it is determined by $4\sqrt{D/\pi \langle R^2 \rangle}$. It corresponds to a diffusion constant D equal to $2 \times 10^{-20} \text{ cm}^2 \text{ s}^{-1}$. This very low value of the diffusion parameter D indicates that it does not correspond to a chain migration process through the melt part of

the mixture. It can be associated with a chain diffusion mechanism occurring near the surface of silica. Several H bonds must be simultaneously severed to allow such a chain diffusion. Considering the usual formula defining the rate of molecular processes⁴:

$$\tau^{-1} = \frac{kT}{h} \exp\left(-\frac{\Delta H}{RT}\right) \quad (6)$$

ΔH represents the free enthalpy necessary to break H bonds; the value $\tau^{-1} = D/\langle R^2 \rangle = 1.4 \times 10^{-8} \text{ s}^{-1}$ leads to an estimate of ΔH : $\Delta H \approx 28 \text{ kcal mol}^{-1}$. This corresponds to about 10–14 H bonds to be broken to let polymer chains move onto the silica surface.

The following interpretation is suggested for the results. As an effect of the mechanical mixing, silica aggregates are completely immersed in the polymer melt. There is a temporary saturated adsorption of siloxane chains onto the silica surface. More precisely, some chains are already permanently bound to particles while other chains are not tightly attached to the surface: these correspond to a weak adsorption and they are eliminated by gently washing the silica–siloxane mixture. Most chains must undergo a rotational diffusion to let the ends form double H bonds with silica. Also some chains must probably leave the surface before neighbouring chains can be firmly attached to particles. It is this rotational diffusion process of chains on silica which is finally perceived. The binding rate of chain ends is controlled by the dynamics of random motions occurring on the surface.

METHYL TERMINATED CHAINS: KINETICS OF ADSORPTION

Observation

Considering now a silica–siloxane mixture made from methyl terminated chains and silica particles, the time variation of the residual amount of polymer $Q_r(t)$ was observed over three years. Experimental results are reported in Figure 3, using a semi-logarithmic plot. A linear variation is observed as a square root of time. The time scale of adsorption is divided by nine compared with that of hydroxyl terminated chains. This leads to the value

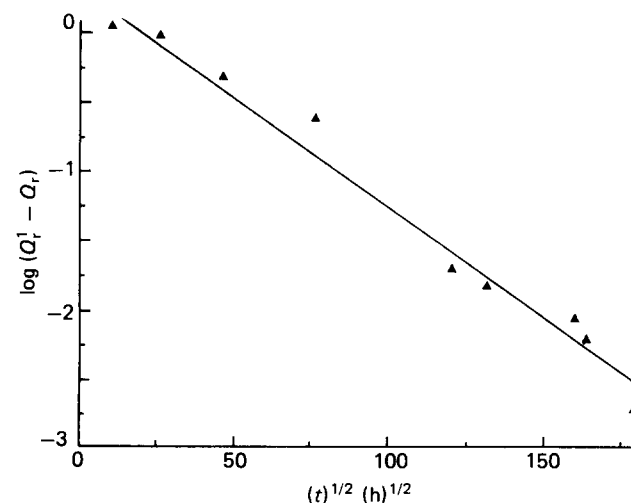


Figure 3 Semi-logarithmic plot of $(Q_r^1 - Q_r(t))$ as a function of the square root of time. Methyl terminated PDMS chains: $\bar{M}_n = 2.9 \times 10^5$; initial silica concentration: $C_{Si} = 0.286$ (w/w); $Q_r^1 = 1.85$

$D'/\langle R'^2 \rangle = 1/\tau' = 1.6 \times 10^{-9} \text{ s}^{-1}$. The diffusion constant D' is equal to $3.4 \times 10^{-20} \text{ cm}^2 \text{ s}^{-1}$ with $\sqrt{\langle (R')^2 \rangle} = 460 \text{ \AA}$. D' does not characterize the diffusion of a chain in the melt part of the mixture. It must correspond to random motions occurring on the silica surface.

Discussion

It must be emphasized that the adsorption process only occurs through H bonding with skeletal oxygen atoms. Chain ends are not involved in this mechanism: there are no double hydrogen bonds. About 60 silanol groups become unavailable on the silica surface whenever the bonding of any given chain occurs. Although the number of hydrogen bonds formed between a siloxane chain and a particle is probably smaller than 60, the permanent sorption must correspond to a high number of monomeric units ($\lesssim 50$) attached to the surface. The absence of double H bonds due to chain ends is compensated by a large number of single H bonds. Furthermore, the elongation of chain segments connecting two consecutive monomer units bound to silica must be small enough to avoid any effect of strong retractive forces which are entropic in origin. Otherwise, the binding of chain segments cannot be considered as permanent. The minimum number of H bonds formed and the state of weak stretching of chain segments probably determine the conditions of sorption. It is supposed that the stable organization of trains on the particles necessitates a rotational diffusion of chains occurring onto the silica surface. It corresponds to a free enthalpy $\Delta H' = 30 \text{ kcal mol}^{-1}$; this is associated with about 10–15 H bonds to be broken to let polymer chains move along the surface of particles. However, it is probably more realistic to consider that characteristic times τ and τ' are

associated with the diffusion of chain segments rather than that of a whole chain whether it is hydroxyl terminated or not. Chain segments at most contain 15 monomeric units. Also, the ratio $\tau/\tau' = 9$ could be associated with an entropic contribution $\Delta s = R \log 9 = 4.5 \text{ cal mol}^{-1}$, which takes the collective behaviour of chain binding into consideration. These collective aspects have been already described elsewhere⁵. Evidence for a binding process occurring according to four separated groups of bonds has been given with an estimate of about 20 bonds per group.

CONCLUSION

A saturated adsorption process of siloxane chains on fumed silica aggregates occurs in systems obtained from a mechanical mixing. It is suggested that its time dependence may be pictured as a diffusion process toward an absorbing screen. The kinetics of adsorption are controlled by the rate at which chain segments of about 15 monomeric units are randomly removed from the surface to allow hydroxylated chain ends or more organized chain skeleton parts of end methylated chains be attached to silica.

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