

Analysis of the formation of bound poly(dimethylsiloxane) on silica

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The kinetics of adsorption of poly(dimethylsiloxane) (PDMS) on silica particles was studied. A theoretical model was developed and fitted to different sets of experimental data to investigate the dependence of model parameters upon polymer and filler characteristics. In the model, the formation of bound polymer was pictured as a second-order reaction process with a rate proportional to both the number of available binding sites on the filler surface (silanol groups) and the number of free (unbound) polymer chains surrounding silica particles. The assumption was made that these two limiting factors had the same effect on the adsorption rate of bound rubber. This model proved to be well adapted to a wide range of material parameters for mixtures containing less than 30 wt% of silica. © 1998 Elsevier Science Ltd. All rights reserved.

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INTRODUCTION

To compensate for their poor mechanical properties, silicone rubbers have to be reinforced by incorporation of particulate materials. Fumed silica is the most commonly used reinforcing filler for silicone polymers. Strong polymer–filler interactions are responsible for the improvement of mechanical properties of silica-filled silicone rubber. These interactions lead to the adsorption of polymer molecules on the filler surface and the formation of ‘bound rubber’ which consists (by definition) of polymer molecules resisting extraction by a good solvent at room temperature. The quantity of bound polymer was shown to be much higher for silica-filled silicone rubber than for carbon-black-filled natural rubber^{1,2}. This was correlated with the formation of more bonds between silica and silicone polymers than between carbon black and hydrocarbon polymers^{2,3}. Various authors have investigated the nature of polymer–filler interactions in PDMS–silica mixtures. Their contributions to the subject were reviewed in depth by Warrick *et al.*⁴. It is generally considered that the adsorption of PDMS on silica particles occurs through hydrogen bonding between silanol groups (SiOH) of the silica surface (proton donor) and oxygen atoms of the PDMS backbone (proton acceptor)⁵. These conclusions have been supported by the work of Berrod *et al.*⁶. Silanol groups are naturally present at the surface of fumed silica in concentrations ranging between 2 and 6 groups per nm², depending on the hydration level of the powder⁴. A distinction can be made between ‘isolated’ silanol groups, prone to interaction with silicone polymers, and ‘vicinal’ silanol groups (adjacent hydroxyl groups hydrogen-bonded to one another) that are presumably less reactive³. Surface treatments such as alkoxylation or organosilylation (e.g. replacement of

hydroxyl by trimethylsilyl groups) have been reported to lower the hydrophilic character of the powder and reduce polymer–filler interactions^{2,3,7,8}. As a direct consequence, surface-modified silicas yield less bound rubber.

The formation of bound polymer proceeds upon ageing of the uncured mixture and saturation of the surface is reached after generally long storing times, up to several years at room temperature⁹. The kinetics of adsorption of PDMS on silica has been studied thoroughly by Cohen-Addad and co-workers^{9–15}. The formation of bound rubber was found to be well described by the following law¹⁰:

$$Q(t) = Q_{\max} - [Q_{\max} - Q(t=0)] e^{-\sqrt{t/\tau}} \quad (1)$$

where $Q(t)$ is the amount of rubber bound to silica at time t , Q_{\max} is the equilibrium amount of bound rubber (limit of $Q(t)$ when t goes to infinity) and τ is a time constant. A derivation of equation (1) was proposed in a later paper¹³. The silanol groups of the filler surface were thought to be initially blocked by small molecules (referred to as ‘poison’) which progressively left the silica by diffusion. A relationship was established between the amount of bound rubber and the fraction of adsorbing sites on the silica surface (silanol groups liberated from the ‘poison’). This relationship (based on the statistical number of contact points between a single chain and silica) was shown to be approximately linear when the fraction of adsorbing sites was close to unity. This was expected to occur after long contact times, when t exceeded τ . Equation (1) appeared to correspond to this temporal regime. In the derivation of the model, the factor $e^{-\sqrt{t/\tau}}$ arises from the surface concentration of the ‘poison’, which was assumed to be governed by diffusion. In subsequent papers, the ‘poison’ was identified as water molecules hydrogen-bonded to the hydroxyl groups of the filler surface^{14,15} but the authors did not provide undeniable evidence that the adsorption process was

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indeed controlled by the displacement of water molecules off the surface of silica.

The purpose of our study is to propose a kinetic model based on a more general concept of the adsorption process and to specify the sensitivity of model parameters on characteristics of the compound, such as polymer molecular weight and silica content of the mixture.

EXPERIMENTAL

Materials

A low-molecular-weight, methyl-terminated PDMS (Dow Corning 200®, viscosity 50 cSt) was chosen for this study. It is characterized by a number-average molecular weight of approximately 3800 g mol^{-1} and a density of 0.96 g cm^{-3} .

Fumed silica (Aerosil 300) was used as received, without any surface treatment or additional drying. According to the manufacturer, the specific surface area measured by the BET method is around $300 \text{ m}^2 \text{ g}^{-1}$. Primary particles are about 10 nm in size but are covalently associated into aggregates. The density of primary particles is 2.2 g cm^{-3} . The concentration of free silanol groups on the silica surface is approximately 1.8 per nm^2 .

Preparation of the mixture

A PDMS-silica compound was prepared by adding progressively 9 wt% of silica into the liquid polymer and stirring mechanically. After 15 min of stirring, the mixture was placed in an oven at 100°C . At given times (counted from zero right after mixing), up to three samples (a few mm^3) of the mixture, chosen at random, were taken out of the oven. These small quantities of the mixture were diluted in a large excess of heptane in order to remove free (unbound) polymer chains. The solvent was renewed twice over one week. The samples were then dried for 24 h in a vacuum oven at 100°C , prior to the determination of bound polymer.

Determination of bound polymer

Thermogravimetric analysis was used to determine the bound rubber content. Samples were heated from 25°C to 950°C at a rate of $35^\circ\text{C min}^{-1}$ under nitrogen purge; experiments performed with PDMS only showed that the polymer was decomposed and volatilized at around 450°C while pure silica was observed to remain unaffected by the heating process. It was also verified that the weight ratio of polymer to silica of the initial mixture could be predicted accurately by thermogravimetric analysis. Thus, the thermogravimetric technique could be used conveniently to determine the weight ratio of bound polymer to silica at time t , $Q(t)$. These values were then converted into an average number of bound polymer molecules per unit surface area of silica:

$$BR(t) = \frac{Q(t) N_A}{A M_n} \quad (2)$$

where A is the specific surface area of silica, N_A the Avogadro number and M_n the polymer number-average molecular weight. This expression implies that the number-average molecular weight of the adsorbed PDMS is identical to that of the matrix. Thus, we disregarded the possibility of preferential adsorption of shorter or longer chains. In natural rubber/carbon black systems a slight preference toward adsorption of longer chains was observed¹.

KINETIC MODEL

In the case of low silica loading (more specific values are given in the following), each silica particle is surrounded by a relatively large number of polymer molecules. Therefore the diffusion of polymer chains in the melt is not believed to be the limiting factor in the formation of bound silicone rubber. Of all the molecules surrounding silica particles, some are permanently bound to silica whereas others are attached to silica by an insufficient number of hydrogen bonds and can be extracted by a good solvent. All the polymer molecules neighbouring silica particles (either 'bound' or 'free') are forming new hydrogen bonds with the filler and some formerly created bonds are severed in order to allow polymer chains to adopt conformations of lower energy. However, the overall trend (driven by the interaction between siloxane and free silanol groups) is an increase in the number of hydrogen bonds and, as new bonds are created, more polymer molecules become bound to silica.

Experimentally, the rate of formation of the bound polymer layer has been observed to decrease with time^{9-12,14}. Our model accounts for two main factors controlling the rate of formation of bound rubber:

- as the amount of bound polymer increases, a significant number of silanol groups of the filler surface become unavailable for new links, either because they are hydrogen-bonded to polymer chains or because they are 'hidden' by bound polymer chains; and
- steric crowding near the polymer/filler interface is the other limiting factor. As the adsorbed polymer layer is building up, it becomes more and more difficult for free polymer chains to get close enough to the filler surface to form hydrogen bonds.

In our model, following the initial mixing time where some bound rubber is formed, the adsorption process proceeds as a second-order reaction occurring at the polymer/filler interface. The rate of formation of bound rubber is assumed to be proportional to both the concentration of available reactive silanol groups on the silica surface and the concentration of free polymer molecules surrounding silica:

$$\frac{dBR}{dt} = k[\text{PDMS}]_s[\text{SiOH}]_s \quad (3)$$

where $[\text{PDMS}]_s$ is the surface concentration of free polymer chains and $[\text{SiOH}]_s$ the surface concentration of reactive silanol groups available on the silica surface. The latter concentration can be approximated by considering that each newly bound polymer molecule blocks on average N binding sites on the silica surface. N can be defined as the average number of silanol groups bonded to (or hidden by) one bound polymer chain. $[\text{SiOH}]_s$ is readily derived from N , $BR(t)$ and $[\text{SiOH}]^0$ (initial free silanol surface concentration):

$$[\text{SiOH}]_s = [\text{SiOH}]^0 - N BR = [\text{SiOH}]^0(1 - N BR^*) \quad (4)$$

in which BR^* is the quantity of bound rubber made dimensionless on the initial free silanol surface concentration.

The surface concentration of free polymer molecules, $[\text{PDMS}]_s$, is assumed to decrease linearly with the amount of bound rubber, reflecting an increasing steric hindrance near the filler surface:

$$[\text{PDMS}]_s = [\text{PDMS}]^0 \left(1 - \frac{BR^*}{BR_{\text{max}}^*} \right) \quad (5)$$

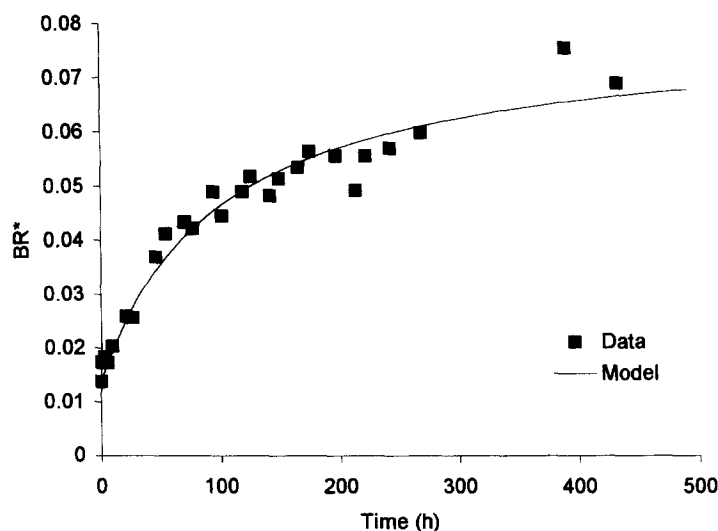


Figure 1 Adsorption kinetics (own data) of methyl-terminated PDMS on fumed silica ($M_n = 3800 \text{ g mol}^{-1}$; $A = 300 \text{ m}^2 \text{ g}^{-1}$; $C_{\text{Si}} = 9 \text{ wt\%}$; $T = 100^\circ\text{C}$)

Table 1 Parameters of the adsorption kinetics of methyl-terminated PDMS

C_{Si} (wt%)	A ($\text{m}^2 \text{ g}^{-1}$)	M_n (g mol^{-1})	I_p	N (sites/chain)	$10^4 \times k[\text{PDMS}]^0$ (h^{-1})
9	150	227 000	2.1	25.6	6.5
17	150	227 000	2.1	35.6	12.2
29	150	227 000	2.1	51.7	12.2
29	50	230 000	1.9	30.7	5

Experimental data from Refs 10 and 11; $T = 70^\circ\text{C}$

where BR_{max}^* is the equilibrium amount of bound rubber (limit of $BR^*(t)$ when t goes to infinity) and $[\text{PDMS}]^0$ is defined such that the quantity $[\text{PDMS}]^0 \{1 - [BR^*(t = 0)/BR_{\text{max}}^*]\}$ stands for the surface concentration of free polymer chains at time zero (right after mixing). The rate of formation of bound rubber can therefore be expressed as:

$$\frac{dBR^*}{dt} = k[\text{PDMS}]^0 \left(1 - \frac{BR^*}{BR_{\text{max}}^*}\right) (1 - N BR^*) \quad (6)$$

In order to reduce the number of model parameters, the assumption is made that N and BR_{max}^* can be linked by the following formula:

$$N = \frac{1}{BR_{\text{max}}^*} \quad (7)$$

This amounts to assuming that when the quantity of bound rubber reaches its equilibrium (BR_{max}^*) there are no binding sites left on the filler surface: all the silanol groups are bonded or hidden. Taking this assumption into account, the adsorption rate becomes:

$$\frac{dBR^*}{dt} = k[\text{PDMS}]^0 (1 - N BR^*)^2 \quad (8)$$

This second-order differential equation is readily integrated:

$$BR^* = \frac{1}{N} \left(1 - \frac{1}{\frac{1}{1 - N BR^*(t=0)} + Nk[\text{PDMS}]^0 t} \right) \quad (9)$$

In the case where $N = 1/BR_{\text{max}}^*$ can be determined experimentally, the only parameter is a reaction rate constant, $k[\text{PDMS}]^0$. The model is otherwise a two-parameter

model. The rate constant $k[\text{PDMS}]^0$ has the dimension of number of chains bound per silanol site per unit time.

RESULTS AND DISCUSSION

The kinetic model was fitted to our own experimental data as well as to different sets of data published by Cohen-Addad and co-workers^{10-12,14}. As shown in *Figure 1* (own data) and *Figures 2-4* (literature data), the model correctly predicts the trends of the adsorption process for a wide variety of PDMS-silica compounds.

Influence of the initial silica concentration in the system

The first three rows of *Table 1* correspond to experimental data reported in the literature on the adsorption kinetics of methyl-terminated PDMS on silica¹⁰. The polymer, characterized by a number-average molecular weight of $227\,000 \text{ g mol}^{-1}$ and a polydispersity index $I_p = 2.1$, was mixed with fumed silica Aerosil 150 ($A = 150 \text{ m}^2 \text{ g}^{-1}$). Initial silica concentration in the system, C_{Si} , was varied between 9 and 29% by weight. The mixtures were kept in an oven at 70°C . According to the manufacturer, the initial concentration of free silanol groups per unit surface area of silica is 1.8 per nm^2 . The experimental data are plotted in *Figure 2*, along with the theoretical curves from our kinetic model.

Since the values of BR_{max}^* can be easily predicted from the data, the rate constant $k[\text{PDMS}]^0$ is the only parameter to be fitted. A good agreement is found between the theoretical curves and the experimental data, showing that the model can be successfully applied to siloxane-silica compounds in which the silica loading is less than 30 wt%, when the silica surface area is equal to or less than $150 \text{ m}^2 \text{ g}^{-1}$. The increase of N (average number of

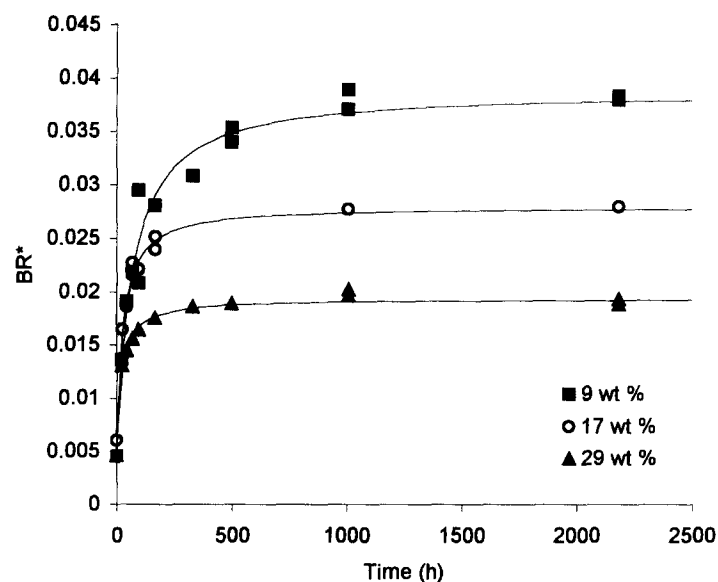


Figure 2 Influence of initial silica concentration on the adsorption kinetics of methyl-terminated PDMS on fumed silica (experimental data from Ref. 10; $M_n = 227\,000\text{ g mol}^{-1}$; $A = 150\text{ m}^2\text{ g}^{-1}$; $T = 70^\circ\text{C}$)

Table 2 Parameters of the adsorption kinetics of hydroxyl-terminated PDMS

C_{Si} (wt%)	M_n (g mol ⁻¹)	N (sites/chain)	$10^4 \times k[\text{PDMS}]^0$ (h ⁻¹)
17	12 000	7.4	367
17	24 000	9.4	182
17	36 000	10.4	140
17	54 000	12.5	140

Experimental data from Ref. 12; $A = 150\text{ m}^2\text{ g}^{-1}$, $T = 70^\circ\text{C}$

sites occupied per bound polymer chain) with silica content reflects the formation of more polymer bridges between particles at higher silica concentration, as a result of a smaller average interparticle distance.

The fourth row of *Table 1* shows the results obtained by applying our model to another set of data published on methyl-terminated PDMS¹¹. The polymer under consideration in that study was very similar ($M_n = 230\,000\text{ g mol}^{-1}$; $I_p = 1.9$) to the one used for the previous set of data, but fumed silica Aerosil 150 was replaced by fumed silica OX 50 ($A = 50\text{ m}^2\text{ g}^{-1}$). It was assumed that the initial surface concentration of free silanol groups remained unchanged compared with silica Aerosil 150. As previously, the experiment was carried out at 70°C and the silica content in the mixture was 29 wt%. The value of BR_{max}^* was calculated from the limit amount of bound rubber reported by the authors (1.1 g of bound polymer per g of silica).

From the results presented in *Table 1*, it can be noted that the rate constant $k[\text{PDMS}]^0$ in the case of the PDMS-silica mixture with 29 wt% silica of surface area $50\text{ m}^2\text{ g}^{-1}$ is very close to that of the mixture with 9 wt% silica of surface area $150\text{ m}^2\text{ g}^{-1}$ (5×10^{-4} versus $6.5 \times 10^{-4}\text{ h}^{-1}$). Interestingly enough, the number of silanol groups per g of mixture is similar in both cases. For the two other compounds (17 and 29 wt% silica of surface area $150\text{ m}^2\text{ g}^{-1}$), the reaction rate constant is higher ($12.2 \times 10^{-4}\text{ h}^{-1}$). It is envisioned that this might be correlated with the extent of formation of polymer bridges between filler particles, which is increasing with silica concentration in the system. When particles are closer to each other, each polymer chain can be in contact with a larger area of the filler (through bridging) and

consequently has the ability to form more hydrogen bonds per unit time with silica. Hence the rate of attachment of polymer molecules on silica increases.

Influence of polymer molecular weight

The dependence of the adsorption kinetics on polymer chain length was assessed for two different types of PDMS fluid differing by their end functionality, namely hydroxyl-terminated PDMS and methyl-terminated PDMS.

The model was first fitted to a set of experimental data published on mixtures of hydroxyl-terminated PDMS and fumed silica (Aerosil 150)¹². Experiments were performed at a temperature of 70°C and the silica content was 17 wt% in all cases. As previously, the values of BR_{max}^* can be determined unambiguously from the adsorption curves. The only unknown parameter is the reaction rate constant $k[\text{PDMS}]^0$. Results for hydroxyl-terminated PDMS are reported in *Table 2* and the theoretical adsorption curves are drawn in *Figure 3*.

The equilibrium amount of bound rubber, Q_{max} , was found¹² to vary proportionally with the square root of the polymer number-average molecular weight, $\sqrt{M_n}$. It can be shown from equations (2) and (7) that N (the number of sites blocked per bound chain) is a multiple of the ratio M_n/Q_{max} . Therefore, as can be seen in *Table 2*, N is proportional to $\sqrt{M_n}$. This dependence arises from the Gaussian nature of the adsorbed polymer molecules. The fact that macromolecules are able to maintain a Gaussian statistics in the adsorbed layer is strongly backed by experimental observations¹⁶.

Table 2 shows that the rate constant $k[\text{PDMS}]^0$ decreases with an increase in molecular weight, consistent with an expected reduction in the mobility of the polymer chains.

The model was also applied to data published on methyl-terminated PDMS of different molecular weight¹⁴. The number-average molecular weights selected in that study were 43 000, 73 000 and 180 000 g mol⁻¹. These polymers were characterized by a polydispersity index of 1.9. The experiments were carried out at 70°C with mixtures containing 29 wt% of silica. Since the experimental adsorption data were reported in a dimensionless form¹⁴, they had to be fitted here to a modified version of

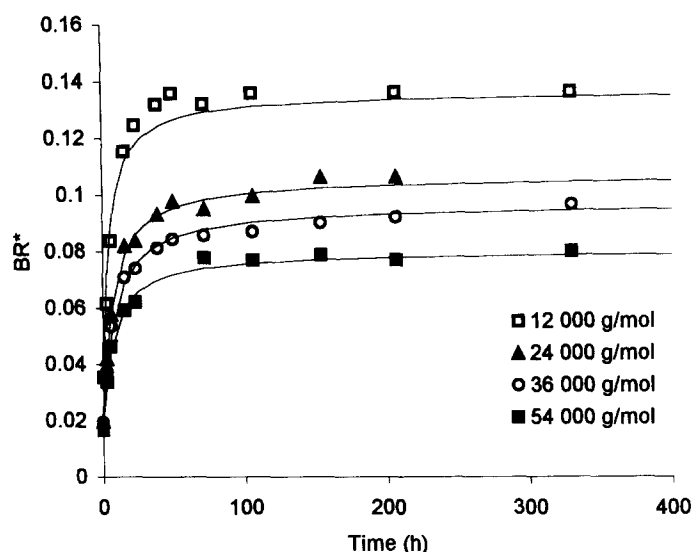


Figure 3 Influence of polymer molecular weight on the adsorption kinetics of hydroxyl-terminated PDMS on fumed silica (experimental data from ¹²; $C_{Si} = 17$ wt%; $A = 150$ m² g⁻¹; $T = 70^\circ\text{C}$)

Table 3 Parameters of the adsorption kinetics of methyl-terminated PDMS

C_{Si} (wt%)	M_n (g mol ⁻¹)	$10^2 \times K$ (h ⁻¹)	$10^4 \times K/\sqrt{M_n}$ (h ⁻¹ g ^{-1/2} mol ^{1/2})
29	43 000	4.6	2.24
29	73 000	7.4	2.75
29	180 000	8.3	1.96

Experimental data from ¹⁴; $T = 70^\circ\text{C}$

equation (9):

$$\Delta q = 1 - \frac{1}{1 + Kt} \quad (10)$$

in which

$$\Delta q = \frac{Q - Q(t=0)}{Q_{\max} - Q(t=0)} = \frac{BR^* - BR^*(t=0)}{BR^*_{\max} - BR^*(t=0)} \quad (11)$$

and

$$\begin{aligned} K &= N(1 - N BR^*(t=0))k[\text{PDMS}]^0 \\ &= N\left(1 - \frac{Q(t=0)}{Q_{\max}}\right)k[\text{PDMS}]^0 \end{aligned} \quad (12)$$

The ratio of $Q(t=0)$ to Q_{\max} is believed to be a very weak function of polymer molecular weight, since both quantities scale roughly with the square root of the polymer number-average molecular weight^{15,16}, $\sqrt{M_n}$. As discussed above, N varies proportionally with $\sqrt{M_n}$. Hence the rate constant $k[\text{PDMS}]^0$ is expected to be proportional to the ratio $K/\sqrt{M_n}$. The best fit values of the rate constant K and the values of the ratio $K/\sqrt{M_n}$ are reported in *Table 3* for the three polymers and the adsorption kinetics curves are shown in *Figure 4*. It should be noted that the value of K was determined less accurately for the PDMS fluid of lowest molecular weight ($M_n = 43\,000$ g mol⁻¹) than for the other two polymers. The correlation coefficient was around 0.976 in the former case as compared with more than 0.993 for the longest chains ($M_n = 73\,000$ and $180\,000$ g mol⁻¹). Overall, it can be concluded that the ratio $K/\sqrt{M_n}$ is decreasing slightly with polymer molecular weight and consequently so is the rate constant $k[\text{PDMS}]^0$.

This means that the number of polymer molecules bound to silica per unit time is less for long chains than for short ones.

Thus, for both hydroxyl and methyl-terminated molecules, long chains lead to a reduced reaction rate constant $k[\text{PDMS}]^0$ compared with short chains. This tendency may be explained by the fact that short chains need not be held to silica as tightly as long chains to resist solvent extraction. If a short chain and a long one form the same number of hydrogen bonds on the filler surface, the solvent more easily extracts the long chain because of a more favorable balance of free energy. The long chain has more monomeric units, therefore it interacts more extensively with the solvent (lower enthalpy) and has more conformational states in solution than the short chain (higher entropy). If the rate of formation of hydrogen bonds is similar whatever the chain length, the rate of adsorption of polymer molecules is thus expected to be higher for short chains for which fewer hydrogen bonds are required to resist solvent extraction. However, one can also imagine that long chains are likely to form more hydrogen bonds with silica per unit time than short chains. Indeed, in the random coil state, long chains can 'cover' more surface on one silica particle, and hence can presumably establish more hydrogen bonds with the filler in a given time. Besides, bridging possibilities are enhanced for long chains which have therefore access to more silica particles. In summary, long chains require more bonds than short ones to resist solvent extraction but most likely exhibit higher rates of formation of hydrogen bonds. These two properties have antagonistic effects on the reaction rate constant $k[\text{PDMS}]^0$. As a result, the dependence of the adsorption kinetics on polymer molecular weight is observed to be rather weak. The effect of chain length is more significant for hydroxyl-terminated PDMS for which the role played by chain ends also has to be taken into consideration.

Influence of polymer end functionality

By comparing the results of *Table 1* with those of *Table 2* it appears clearly that the adsorption kinetics is strongly dependent on polymer end functionality. The rate constant of the adsorption process, $k[\text{PDMS}]^0$, is at least one order of magnitude higher for hydroxyl-terminated chains (*Table 2*) than for methyl-terminated chains (*Table 1*). This difference

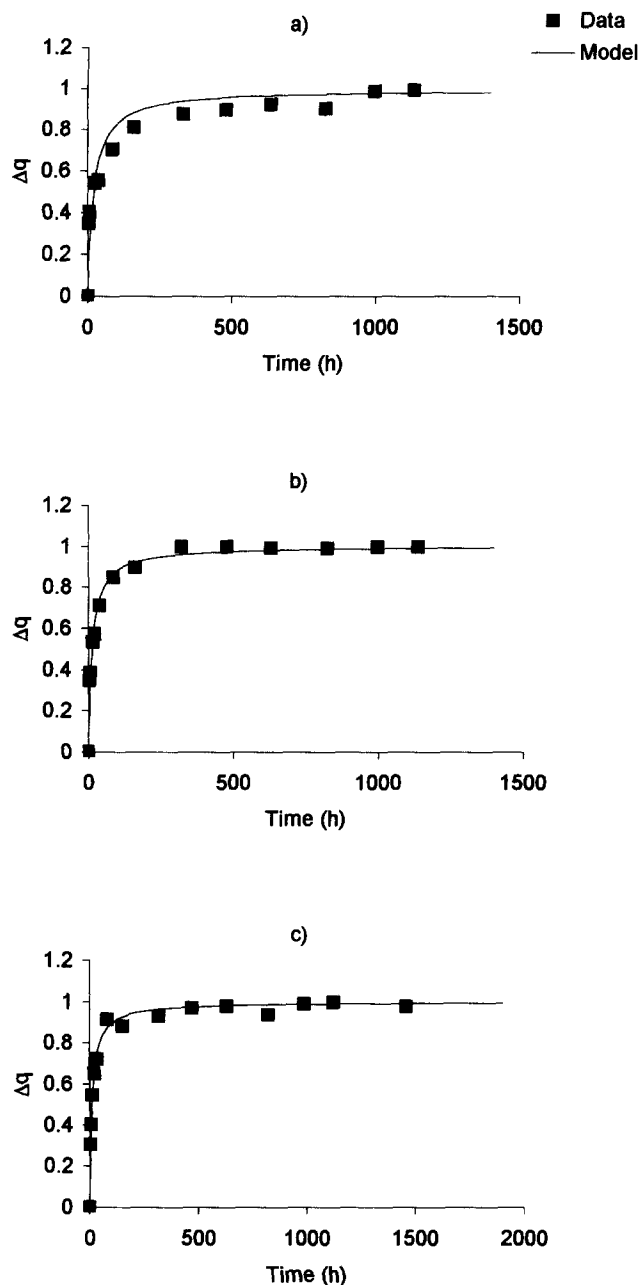


Figure 4 Influence of polymer molecular weight on the adsorption kinetics of methyl-terminated PDMS on fumed silica: (a) $M_n = 43\,000\text{ g mol}^{-1}$, (b) $M_n = 73\,000\text{ g mol}^{-1}$, (c) $M_n = 180\,000\text{ g mol}^{-1}$ (experimental data from ¹⁴; $C_{Si} = 29\text{ wt\%}$; $T = 70^\circ\text{C}$)

can be accounted for by the role played by chain ends in the adsorption process of hydroxyl-terminated PDMS. Terminal hydroxyl groups of the molecules are engaged in double hydrogen bonds with silanol groups of the silica surface³. It is considered that bonds between polymer silanol groups and their counterparts on the silica surface are stronger than the single hydrogen bonds involving polymer siloxane groups. In the case of end-hydroxylated PDMS, the process of formation of bound rubber is accelerated by the adsorption of chain ends: once a chain end is attached to silica, the number of additional bonds needed to anchor the whole chain permanently on the filler surface is lowered,

perhaps to nil. Therefore, the adsorption kinetics is increased since it is mainly governed by chain ends. Moreover, it has been shown that in a melt, chain ends are likely to be drawn to an interface¹⁷. This suggests that, in the case of hydroxyl-terminated PDMS, the adsorption kinetics could be enhanced by the attraction of terminal groups towards the polymer/filler interface.

Furthermore, chain ends could also be responsible for the differences in adsorption kinetics observed between the polymers of different molecular weight in the series of hydroxyl-terminated PDMS. Relative to the total number of monomeric units per chain, short chains have proportionally more chain ends than long chains. This could explain why the rate constant $k[\text{PDMS}]^0$ is significantly higher for short chains.

CONCLUSIONS

The adsorption kinetics of silicone polymer on silica is well predicted by our model for silica loadings of less than 30% by weight. The second-order reaction process we proposed appears to apply to a wide variety of material characteristics (silica surface area, polymer molecular weight and end functionality). The reaction rate constant, $k[\text{PDMS}]^0$, shows a weak dependence on silica concentration and on polymer molecular weight. However, $k[\text{PDMS}]^0$ is very sensitive to polymer end functionality. Hydroxyl-terminated molecules exhibit a much higher reaction rate, which can be related to the strength of the interactions between chain ends and filler silanol groups.

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