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Silica concentration dependence of the kinetics of polydimethylsiloxane adsorption on aggregates

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Summary

The kinetics of adsorption of pure polydimethylsiloxane or of bimodal mixtures, onto silica aggregates, was observed from the melt as a function both of polymer weight fraction (2.5 to 20 g/g) and of the specific area (50, 150 and 300 m^2/g). Attention was focused on filled polymers wherein silica aggregates are connected to one another by adsorbed chains to form a network. Results were analysed according to a molecular approach. All observed kinetics curves were found to obey a property of superposition by using a suitable reduced time variable defined as : $t\overline{M}_n/Q_i$; $\overline{M}_n$ is the number average molecular weight and Q_i is the initial amount of polymer per unit mass of silica. The rate of adsorption is proportional to $1/Q_i$.

I. Introduction

The understanding of the effect of reinforcement of rubbers is partly based on the analysis of the properties of networks which result from polymeric bridging of mineral aggregates (1). The formation of physical networks can be described in terms of a bond percolation process that takes place when adsorbed polymer chains can bridge percolation units (mineral aggregates) to one another. Clusters can form and at some suitable filler concentration and suitable chain length, one of the clusters may span the whole sample so that a physical network is established; the threshold of bond formation of the network is revealed, for example, from the possible observation of a swelling effect, induced by a good solvent of the polymer (2).The existence of a network is also detected from the observation of a low frequency plateau in which the storage modulus exhibits behavior similar to that of a crosslinked rubber (3). The estimate of the functionality of percolation units is determined by the mean number of chains that can be adsorbed on one aggregate; it requires to know the specific area of the mineral filler, the mean size of aggregates and the law of chain adsorption onto aggregates, fully immersed in the molten polymer.

The formation of polymeric layers on solid or liquid surfaces has received a lot of attention in recent years mostly due to the use of scaling concepts and of a continuous chain description (4-8). In the melt, the adsorption per unit area is proportional to the square root of the chain molecular weight, assuming Gaussian statistics (9).

With regard to fumed silica, it is well known that the adsorption of polydimethylsiloxane (PDMS) chains occurs through the formation of hydrogen-bonds between oxygen atoms attached to chain skeletons and silanol groups located on the surface of the filler. The free enthalpy of monomeric desorption is thus higher than the thermal energy at room temperature. Consequently, monomers adsorb almost irreversibly when aggregates are fully immersed in the molten polymer, at this temperature. Then, the distribution of loops in the layer arises from the distribution of loops in the melt; this distribution is frozen when macromolecules are in contact to the silica surface. Correspondingly, it is now well established that the adsorption of pure PDMS on silica aggregates obeys Gaussian statistics notwithstanding the geometrical nature of the surface which cannot be considered as an infinite plane (10, 11). The surface of any aggregate can be pictured as an ensemble of finite planes, the area of each plane is usually much larger than the square of the radius of gyration of chains which are in contact to the surface. According to the molecular approach briefly outlined here, the mean number of contact points of one chain with the silica surface is proportional to the square root of the number of skeletal bonds, N; the resulting amount of PDMS, Q_m, adsorbed per unit mass of silica when aggregates are fully coated and well separated from one another is expressed

as a function of the square root of the number average molecular weight $\overline{M}_n$, according to the equation

$$Q_m = \beta_m (\overline{M}_n)^{1/2} \quad (1)$$

with

$$\beta_m = A_T (M_m)^{1/2} / \sigma_e \mathcal{A} \quad (2)$$

in which M_m is the molar weight of one monomeric unit and $\mathcal{A}$ is the Avogadro number; A_T is the specific area and σ_e, is the mean area associated with one hydrogen-bond participating in the adsorption process (12). However, in most loaded systems prepared from a mechanical mixing, the amount of adsorbed polymer per gram of silica, Q_B^s, measured at equilibrium, is smaller than Q_m. Q_B^s obeys the following equation

$$Q_B^s = Q_m \left(1 - \frac{Q_m}{4Q_i}\right) \quad (3)$$

where Q_i is the initial amount of polymer per unit mass of silica, used to make a mixture (12). The difference Q_m - Q_B^s accounts for the effect of bridging. Equation (3) has been derived from the simple numbering of chains which are adsorbed on one aggregate or which bridge two aggregates. It is supposed that one chain can connect, at most, 2 aggregates, with each other.

Furthermore, it has been also shown that the amount of adsorbed polymer per gram of silica, Q_B^0, measured right after the end of the mechanical mixing and after eliminating free chains, is smaller than Q_B^s; Q_B^0 has been found to vary as the square root of the chain molecular weight according to the equation

$$Q_B^0 = \beta_o (\overline{M}_n)^{1/2} \quad (4)$$

with an experimental value of β_o lower than that of β_m. Equation (4) shows that the law of adsorption is still Gaussian; however, strongly linked chains occupy only a fraction of the silica surface. This property is related to the existence of two types of sites of adsorption of monomeric units on aggregates (13,14). One type corresponds to free silanol groups which have been shown experimentally to cover about 25% of the silica surface while the other type corresponds to vicinal silanol groups. Furthermore, it has been shown that water molecules which are hydrogen-bonded to silica are easily removed from free silanol groups upon heating whereas water molecules which interact with vicinal silanol groups are tightly bound through 2 hydrogen-bonds.

It has been already established both experimentally and theoretically that the kinetics of adsorption of the amount of polymer, determined by the difference Q_B^s- Q_B^0, strongly depends on the chain molecular weight. In contrast to most dynamic phenomena observed in molten polymers, an increasing rate of adsorption is measured when the chain molecular weight is increased. This result has been interpreted by considering that after the mechanical mixing there is a slow release of water molecules tightly bound to vicinal silanol groups. The probability $\pi(t)$ that one poison molecule occupies one adsorption site on the silica surface has been shown to be expressed as

$$\pi(t) = \exp(-\sqrt{t/\tau_0}) \qquad (5)$$

τ_o is a time constant specific to the release and to the diffusion of water molecules through PDMS (15). Considering any given adsorbed chain, the mean number of contact points to the surface is equal to $\sqrt{N}$ (Gaussian statistics). Then, the probability that one chain cannot bind to silica is expressed as $(\pi(t))^{\sqrt{N}}$ and the fraction of chains that can be bound at time t is (16)

$$\Delta q_{Bound}(Nt/\tau_0) = 1 - (\pi(t))^{\sqrt{N}} \qquad (6)$$

This fraction is represented by the experimental value of the ratio

$$\Delta q_{Bound}(Nt/\tau_0) = (Q_B(t) - Q_B^0)/(Q_B^s - Q_B^0) \qquad (7)$$

$Q_B(t)$ is the amount of adsorbed polymer per gram of silica, at time t. From equation (6), the time constant associated with Δq_{Bound} (t) is predicted to depend on N as τ_o/N.

In this work, attention was focused on the kinetics of polymer adsorption, considering variations of the silica concentration; both the polymer molecular weight and the specific area of silica were varied to provide a broad characterization of the adsorption process. The study was also extended to a bimodal polymer. In a previously reported work, the study has been only qualitative because the specific area of silica was not varied and a too narrow range of silica concentrations was considered; it was not possible to propose a quantitative analysis of results (17). In this work, three specific areas were considered (50, 150 and 300 m^2/g), the initial amount of polymer Q_i per gram of silica was varied from 2.5 to 20 g/g. The question which was addressed here concerned the role of the silica concentration when the filled polymer forms a network.

Experimental

Materials

Filled polymers were prepared using a Haake Rheomix 610 with sigma blades ; the chamber capacity was 69 cm^3. After full incorporation of the filler into the polymer, the duration of the milling was about 90 minutes. Fumed silica was bought from Degussa ; the specific area was equal to 300 or 150 or 50 $m^2.g^{-1}$ (B.E.T. measurements). No chemical treatment was applied to the surface. Polymers were kindly supplied by Rhône-Poulenc (St Fons, France). Values of the weight ratio of PDMS, Q_i, of the specific area, of the number-average molecular weights and of the polydispersity indices are reported in Table 1.

The bimodal mixtures consisted of two chemically identical polymers with different molecular weights (43 10^3 and 300 10^3 g/mol). The polymer species were premixed in the Rheomix during 10 minutes before the addition of silica. All filled bimodal polymers were prepared using a silica with a specific area equal to 50 $m^2.g^{-1}$. Bimodal mixtures are described in Table 2. After the milling, samples were placed in an oven regulated at 343K. This time was chosen as the starting point (t = 0) of the kinetics study of the polymer adsorption on silica.

polymer weight fraction : Q_i (g/g)	A_T (m^2/g)	$\overline{M_n}$ (g/mol)	I_p
20.0 12.5 10.0 5.0	150	43 000	2.5
5.0 2.5	50	43 000	2.5
5.5	300	43 000	2.5
16.6 12.5 10.0 6.6 5.5 5.3	150	73 000	2.6
4.8 2.5	50	73 000	2.6
16.6 10.0 5.0	150	300 000	2.7
5.0 3.3 2.5	50	300 000	2.7
5.5 3.8	300	300 000	2.7

Table 1 : Initial weights of polymer per gram of silica Q_i, specific areas (A_T), chain molecular weights (M_n) and polydispersity indices (I_p).

weight concentration of long chains (g/g)	Q_i (g/g)
0.5	5.0
0.5	2.6
0.75	5.5
0.75	2.4

Table 2: Bimodal systems; Q_i is the total weight of PDMS per gram of silica.

Polymer extraction

At a given time t, a small cubic part ($\approx$ 0.125 cm^3) of mixture was taken out of the oven and immersed in a large excess of good solvent (methylcyclohexane) at room temperature during three days. The solvent was renewed after one day. This procedure eliminates all free chains. After the extraction, the sample was dried under air and the weight fraction $Q_B(t)$ of polymer left bound to the silica surface was determined from the mass fraction of carbon obtained from chemical microanalysis measurements performed at the Laboratoire Central d'Analyse (Solaize, France).

Results and discussion

To provide a base for an accurate characterization of the kinetics, the adsorption process was first observed right after the mechanical mixing and then at equilibrium.

Initial state of adsorption

The amount of adsorbed polymer per gram of silica, Q_B^0, was measured right at the end of the mechanical mixing and after eliminating all free chains ; studied mixtures characterized by the chain molecular weight and the silica concentration are listed in Table I. Considering the fraction of bound PDMS, given by the ratio Q_B^0/Q_i, experimental points were found to lie on a straight line drawn as a function of the reduced variable $\sqrt{Mn}/Q_i$ (Fig. 1) ; Q_B^0 obeys equation (4) (β_o = 1.4 10^{-3} or 4.8 10^{-4} $(g/mol.)^{-1/2}$ with a specific area equal to 150 $m^2.g^{-1}$ or 50 $m^2.g^{-1}$, respectively). The scale of the reduced variable $\sqrt{Mn}/Q_i$ was divided by 3 for the specific area equal to 50 $m^2.g^{-1}$. It is worth noting that experimental results obtained from the specific area equal to 300 m^2/g are not different from those obtained from the specific area equal to 150 m^2/g.

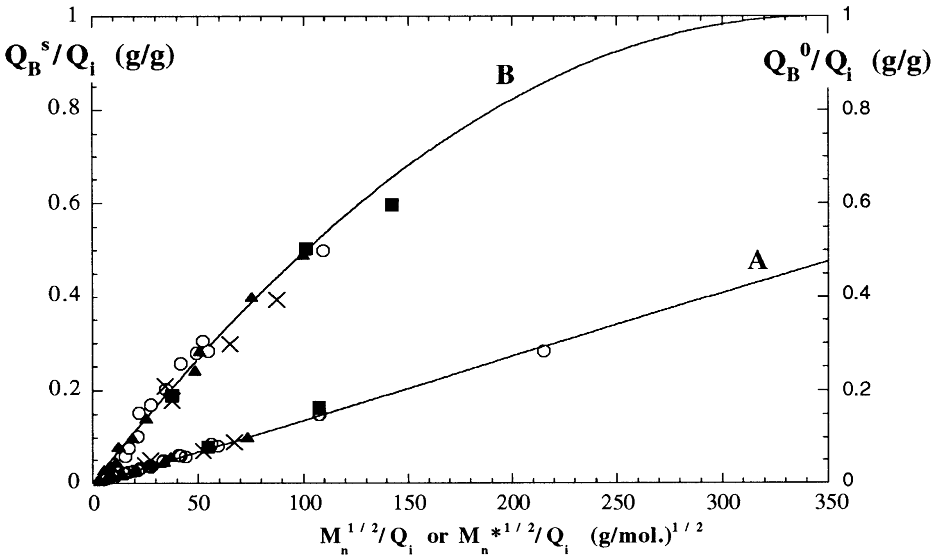

Fig. 1. Fraction of bound polymer.
Pure polymer; specific area : 300 m^2/g (■), 150 m^2/g (○) and 50 m^2/g (▲) (the scale of $M_n^{1/2}/Q_i$ was divided by 3). × : bimodal polymer (specific area : 50 m^2/g ; the scale of $M_n^{*1/2}/Q_i$ was divided by 3).
A : fraction measured right after the mechanical mixing of PDMS with silica.
B : fraction measured at equilibrium.

Considering the bimodal polymer, the amount of adsorbed polymer per gram of silica, measured right after the mechanical mixing, was found to vary as a linear function of the mean chain molecular weight M_n^* defined as follows

$$(M_n^*)^{1/2} = c(\bar{M}_n^L)^{1/2} + (1-c)(\bar{M}_n^S)^{1/2} \quad (8)$$

c is the weight concentration of long chains in the mixture; $\bar{M}_n^L$ and $\bar{M}_n^S$ are the molecular weights of long and short chains, respectively. Experimental points corresponding to several concentrations of silica and two values of c (Table 2) are plotted in Fig. 1 ; they lie on the straight line already drawn from experimental results corresponding to the pure polymer. The interpretation of equation (8) is based on the assumption that in the case of a bimodal polymer, the probability of adsorption of one monomeric unit is weighted using the molar fraction of each chain species. Then, the total amount of the long polymer, adsorbed on aggregates, is expressed, in accordance with Eq. (4), as

$$Q_m^L(0) = c\beta_0(\bar{M}_n^L)^{1/2} \quad (9)$$

A similar equation applies to short chains, with a weight factor equal to 1-c. The total amount of adsorbed polymer, per gram of silica, is thus expressed as

$$Q_B^0 = \beta_0\, c(\bar{M}_n^L)^{1/2} + \beta_0\,(1-c)(\bar{M}_n^S)^{1/2} \quad (10)$$

This is a new result about silica filled PDMS; with regard to the adsorption of a bimodal polymer, the silica surface is occupied according to the weight fraction of each chain species.

Equilibrium state of adsorption

The amount of adsorbed polymer per unit mass of silica, Q_B^s, measured at equilibrium, after eliminating free chains, is a function of both the square root of the chain molecular weight and the initial weight fraction of polymer in the mixture. Considering the weight fraction of bound PDMS, given by the ratio Q_B^s/Q_i, experimental points are plotted in Fig. 1; the reduced variable is $\sqrt{Mn}/Q_i$. The fit to experimental results provides experimental values of the adsorption constant β_m introduced in equation (2) ; ($\beta_m = 5.8\ 10^{-3}$ and $2.6\ 10^{-3}$ (g/mol.)$^{-1/2}$ for the specific area equal to $A_T = 150$ and 50 m^2/g, respectively). The experimental values of β_m call for two remarks.

i) The fraction of the silica surface offered to chains adsorbed during the mechanical mixing is given by the ratio β_o / β_m ; it is equal to 25% and 18% for the specific areas equal to 150 and 50 m^2/g, respectively.

ii) The estimate of the total number of silanol groups n_c which participate in the full polymeric adsorption is represented by the ratio A_T/σ_e ; it is equal to 4×10^{20} and 1.8×10^{20} g^{-1} for specific areas equal to 150 and 50 m^2/g, respectively.

Again, experimental results obtained from a specific area equal to 300 m^2/g do not differ from those obtained from a specific area equal to 150 m^2/g. These results show that the number of sites of chain adsorption is given by $150/\sigma_e \sqrt{N}$ g^{-1} for both types of silica while the specific areas measured from small molecules may have different values (150 and 300 m^2/g, respectively).

Fractions of adsorbed polymer, measured when the equilibrium state of adsorption is reached are also found to lie on the experimental curve drawn in Fig. 1 provided the mean variable M_n^* is used.

Kinetics of PDMS adsorption

A close attention to experimental values of β_o and β_m shows that the kinetics of PDMS adsorption corresponds to the coverage of about 114 m^2/g and 41 m^2/g, considering either the specific area equal to 150 m^2/g or the specific area equal to 50 m^2/g.

Experimental results about Δq_{Bound} (t) were first plotted as a function of the reduced variable $\sqrt{tMn}$. Considering, then, each silica filled PDMS system described in Tables 1 and 2, an empirical curve was drawn through experimental points to serve as a guide for eyes. The system prepared from the initial weight fraction of polymer, $Q_i^R = 5.5$ g/g, was arbitrarily chosen as a reference (specific area of silica, A_T : 150 m^2/g). All other kinetics curves that were observed were then put into coincidence with the reference curve by multiplying the $\sqrt{tMn}$ scale of each curve by a suitable factor $s(Q_i)$. The result of the superposition is illustrated in Fig. 2A. The same analysis was applied to the bimodal polymer; the result is shown in Fig. 2B. Variations of the factor $s(Q_i)$ are shown in Fig.3 ; s is proportional to the square root of the initial weight fraction of polymer (the experimental slope is 2.3 instead of 2.35). Taking measurement uncertainties into consideration, this result shows that any kinetics curve can be derived reasonably from the reference curve according to the simple relationship

$$\Delta q_{Bound}\left(\frac{\overline{M_n}t}{\tau_o Q_i}\right) = \Delta q_{Bound}\left(\frac{\overline{M_n}ts^2}{\tau_o Q_i^R}\right) \qquad (11)$$

with s^2 defined from the ratio Q???/Q_i. The mathematical expression for the Δq_{Bound} function can be considered as invariant. According to equation (11) the time constant depends linearly on the initial amount of polymer per gram of silica, used to make each filled polymer. This result requires to analyze the predicted expression of the rate τ_o^{-1},

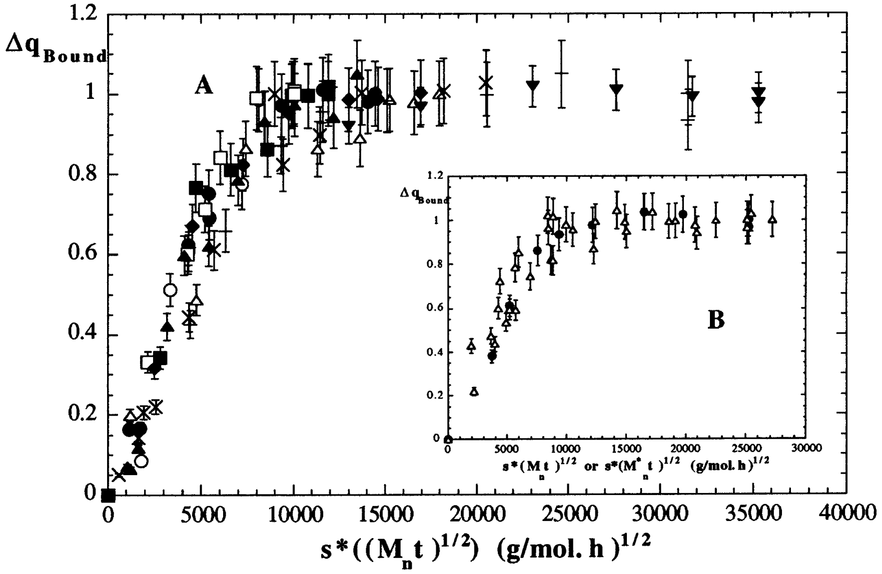

Fig. 2 Property of superposition of curves of kinetics of adsorption. ● Reference curve (specific area 150 m^2/g, $M_n = 73\ 10^3$ g/mol and $Q_i^R = 5.5$ g/g). **A**. **Specific area** : 150 m^2/g. $M_n = 73\ 10^3$ g/mol, $Q_i = 16.6$ g/g (○); $M_n = 43\ 10^3$ g/mol, $Q_i = 5.0$ (■) and 10.0 g/g; $M_n = 300\ 10^3$ g/mol, $Q_i = 5.0$ (◆) and 10.0 g/g (Δ). **Specific area** : 50 m^2/g. $M_n = 73\ 10^3$ g/mol, $Q_i = 4.8$ (▲) and 2.5 g/g (X); $M_n = 300\ 10^3$ g/mol, $Q_i = 3.3$ (+) and 2.5 g/g (▼). **B**. Kinetics of adsorption (specific area 50 m^2/g). ● pure polymer : Mn = 300 10^3 $g.mol^{-1}$ and $Q_i = 5.0$ g/g. Δ Bimodal polymer : weight concentrations of long chains : c = 0.5g/g, Q_i =2.6 and 5.0 g/g ; c= 0.75g/g, $Q_i = 2.4$ and 5.5 g/g .

used in equation (5), for the probability of release of a water molecule (15) ; τ_o^{-1} ($\approx 10^{-7}$s) is equal to the ratio $D\kappa^2/\mathbf{a}^2$ in which **a** ($\approx$2 Å) is the thickness of the monolayer of adsorbed water, κ gives the fraction of free water molecules, near the surface and in equilibrium with adsorbed water molecules and D is the diffusion constant of water molecules leaving the surface. It is considered that the only parameter which may depend on the silica concentration in τ_o is the diffusion coefficient D; it is assumed that D depends on the free volume of the system which in turn is closely related to the texture of the mixture. The compactness of these systems results only from the mechanical mixing since no high pressure treatment was applied to the samples; the compactness decreases upon silica addition and D increases. The estimate of $D \approx 10^{-7}$ cm^2/s gives $\kappa \approx 10^{-8}$.

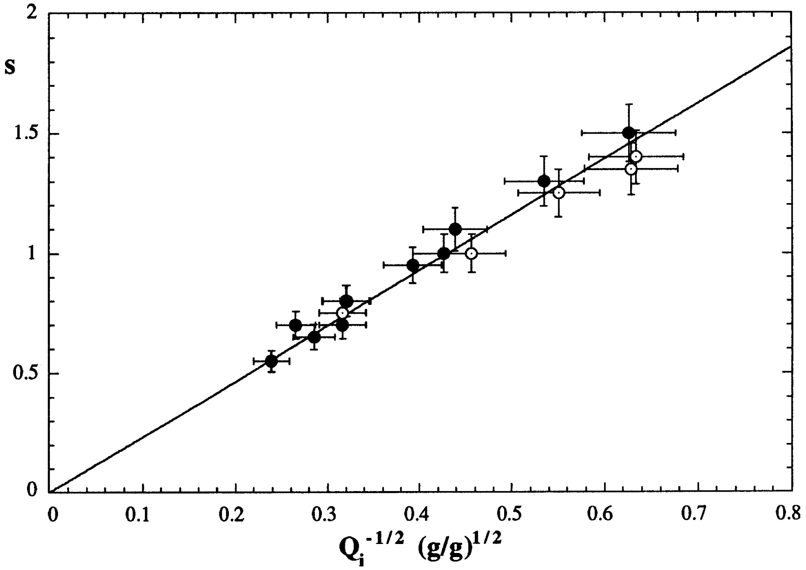

Fig.3 Scale factor $s(Q_i)$ used to put all kinetics curves into coincidence with the reference curve; specific area 150 m^2/g (●) and specific area 50 m^2/g (○).

Conclusion

The PDMS adsorption on aggregates is supposed to be related to the release of water molecules from the surface. The adsorption rate is increased upon addition of silica. It is assumed that this effect is due to the texture of mixtures; the higher the concentration of silica, the lower the compactness resulting from the spacial arrangement of hard objects (silica aggregates) and the higher the rate of release of water molecules.

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