

Silica-filled polydimethylsiloxane: crystallization process of the adsorbed layer

D. Bordeaux and J. P. Cohen-Addad*

Laboratoire de Spectrométrie Physique associé au CNRS, Université Joseph Fourier, Grenoble I, BP 87, 38402 St Martin d'Hères Cedex, France

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Mechanical mixtures of silica particles and molten polydimethylsiloxane give rise to an adsorbed layer. Crystallization properties of this polymeric layer were investigated as a function of the residual amount of polymer Q_r left bound to silica after removing all free chains. The partial crystallinity ρ_c was determined from the measured enthalpy of crystallization divided by the enthalpy of crystallization per monomer unit. No crystallization effect was observed from very short chains ($\bar{M}_n < 6 \times 10^3 \text{ g mol}^{-1}$); accordingly, it was considered that loops formed from the adsorption effect are too short to participate in the crystallization. The partial crystallinity ρ_c associated with longer adsorbed chains was found to vary as $1 - \rho_c \propto Q_r^{-1}$. It is shown that eight monomeric units, on average, are locked in space by the formation of one H bond between a silanol group and a skeleton oxygen atom. The sol-gel transition resulting from the connection of particles by polymer chains is clearly perceived from the state of crystallinity of the adsorbed layer: when all particles and polymer chains form a gel, the resulting adsorbed layer has a constant partial crystallinity $\rho_c = 0.7$, whatever the silica concentration and the amount of adsorbed polymer.

(Keywords: polydimethylsiloxane; silica; adsorption; crystallization)

INTRODUCTION

This work deals with properties specific to polydimethylsiloxane (PDMS) chains adsorbed upon silica particles that were embedded in systems obtained via mechanical mixing. The elementary process of adsorption of polymeric chains occurs through the hydrogen bonds that the oxygen atoms of the siloxane skeleton form with silanol groups located on the silica surface.

It has already been shown that the residual amount of polymer Q_r left bound to silica after removing all free chains depends strongly upon the chain molecular weight \bar{M}_n , on the one hand, and upon the silica concentration C_{Si} on the other¹. The variable Q_r was defined per unit mass of silica; it was measured by chemical analysis. More precisely, variations of Q_r within silica-siloxane mixtures corresponding to three concentrations of silica have been investigated over a wide range of chain molecular weights, from $\bar{M}_n = 0.18 \times 10^4$ to $35 \times 10^4 \text{ g mol}^{-1}$. The residual amount Q_r has been found to obey the characteristic law:

$$Q_r = \chi_a (\bar{M}_n)^{1/2} \quad (1)$$

This dependence has been observed within a good accuracy, with $\chi_a = 3.3 \times 10^{-3}$, 4.3×10^{-3} and $5.3 \times 10^{-3} \text{ g}^{-1/2} \text{ mol}^{1/2}$, for silica concentrations equal to 0.29, 0.17 and 0.09 w/w, respectively. This experimental result has recently been interpreted by describing any polymer chain adsorbed on the silica surface as a random walk colliding with a plane. Thus, the average number $\langle r_c \rangle$ of contact points to the surface can be shown to be proportional to the square root of the number N of skeletal bonds²:

$$\langle r_c \rangle \propto N^{1/2} \quad (2)$$

Formula (1) is closely related to the Gaussian statistics of polymer chains in a melt.

The purpose of the present work was two-fold:

(i) We first attempted to determine the average number γ_a of monomeric units frozen by the formation of one H bond between one silanol group and one oxygen atom of a chain skeleton.

(ii) Attention was then focused upon formulae (1) and (2) by attempting to show that the fraction x_a of monomeric units that do not participate in the crystallization process is proportional to $(\bar{M}_n)^{-1/2}$.

The properties of the adsorbed layer were investigated by inducing a crystallization process affecting loops and tails formed from the adsorption process of polymer chains. The principle of this approach was to determine the polymer crystallinity as a function of the amount of polymer Q_r left bound to silica after removing all free chains. It was considered that monomeric units bound to or very close to the silica surface have a low mobility and cannot be ordered by lowering the temperature. They cannot participate in the crystallization process.

CHARACTERISTIC FEATURES OF THE ADSORPTION PROCESS

It may be worth emphasizing that the adsorption process resulting from the mechanical mixing of silica particles with siloxane chains in a melt is characterized by several features. Fumed silica consists of particles that obey a mass scaling law; the corresponding fractal exponent, equal to 1.9, has been determined from neutron scattering experiments³. The average length of particles ranges from 10^3 to $3 \times 10^3 \text{ \AA}$, while the average diameter may vary from 3×10^2 to about $7 \times 10^2 \text{ \AA}$.

* To whom correspondence should be addressed

Multiple-chain adsorption

Silica particles are fully immersed in a polymer melt, at any time. Consequently, it must be considered that any polymer chain that is in contact with the silica surface is swollen by many other chains, which compete with one another to be adsorbed on the particle: it is a multiple-chain adsorption. Thus, there is a great contrast between this adsorption process and the adsorption occurring on mineral particles in suspension in a polymer solution.

Average area associated with one chain

The average area $\bar{\sigma}_c$ associated with the binding of one chain is derived from the specific area A of silica, by assuming that the whole surface participates in the adsorption effect:

$$\bar{\sigma}_c = A\bar{M}_n/Q_r \quad (3)$$

or

$$\bar{\sigma}_c = A(\bar{M}_n)^{1/2}/\chi_a \quad (4)$$

So $\bar{\sigma}_c$ is also proportional to $(\bar{M}_n)^{1/2}$. At a silica concentration $C_{Si}=0.09$ (w/w), $\bar{\sigma}_c$ is thus found to vary from about $2 \times 10^2 \text{ \AA}^2$ to about $45 \times 10^2 \text{ \AA}^2$ within the range of molecular weights $0.18 \times 10^4 < \bar{M}_n < 35 \times 10^4 \text{ g mol}^{-1}$ ($A=150 \text{ m}^2 \text{ g}^{-1}$). Formulae (2) and (4) are in agreement with each other on assuming that the area associated with one contact point is constant.

Average number of H bonds per chain

The average number of free silanol group per unit area of silica has already been estimated⁴: $v_c = 1.8 \times 10^{-2} \text{ \AA}^{-2}$. This number can be used to derive the average size of trains as a function of the chain molecular weight:

$$\bar{\mu}_t = \bar{\sigma}_c v_c \quad (5)$$

or

$$\bar{\mu}_t = 1.8 \times 10^{-2} A(\bar{M}_n)^{1/2}/\chi_a \quad (6)$$

A typical value of $\bar{\mu}_t$ is 80 for $\bar{M}_n = 3.4 \times 10^5 \text{ g mol}^{-1}$.

Average thickness

The average thickness e of the adsorbed layer is derived from the residual amount of polymer bound to silica and the specific area of silica:

$$\bar{e} = Q_r/\rho_p A \quad (7)$$

where ρ_p is the polymer density. A typical value of \bar{e} is 133 \AA for $Q_r = 2 \text{ g g}^{-1}$ and $A = 150 \text{ m}^2 \text{ g}^{-1}$.

Numerical values of $\bar{\sigma}_c$, $\bar{\mu}_t$ and \bar{e} should be handled with care; they are only estimates of quantities that determine the binding process of one chain.

Site-bond percolation

Mineral particles can be connected to one another when the average size of unstretched chains and the concentration of silica have appropriate values⁵. In other words, a site-bond percolation process may occur either by increasing the chain molecular weight and keeping the silica concentration at a constant value, or by increasing the silica concentration and keeping the chain molecular weight constant. The threshold of the site-bond percolation effect is roughly defined by $\bar{M}_n = 35 \times 10^4 \text{ g mol}^{-1}$ at a silica concentration $C_{Si} = 0.09$ w/w, by $\bar{M}_n = 11 \times 10^4 \text{ g mol}^{-1}$ at $C_{Si} = 0.23$ w/w and by $\bar{M}_n = 8 \times 10^4 \text{ g mol}^{-1}$ at $C_{Si} = 0.29$ w/w. Above the threshold of percolation, an infinite cluster is formed, which behaves like a gel: it can be reversibly swollen and it has a modulus of elasticity⁶. Below the threshold of gelation, finite clusters are formed: they give rise to a coarse powder.

EXPERIMENTAL

Samples

Polydimethylsiloxane (PDMS) samples were commercially available polymers. Number-average molecular weights and corresponding polydispersity indices are reported in Table 1. Silica-PDMS systems were provided by Rhône-Poulenc Recherches (France). Silica-filled polymers were prepared via mechanical mixing. The

Table 1 Calorimetric data concerning pure polymer samples: T is the rate of temperature increase; T_g is the glass transition temperature; T_c is the cold crystallization temperature; T_m^1 , T_m^2 and T_m^3 are three melting temperatures observed, ΔH_f^1 and ΔH_f^2 denote the enthalpies of fusion; $(\tau_c^e)_1$ and $(\tau_c^e)_2$ denote the ratios of crystallinity. The index of polydispersity is $I \approx 2$

PDMS $\bar{M}_n \times 10^{-3}$	T (K min ⁻¹)	T_g (K)	T_c (K)	T_m^1 (K)	T_m^2 (K)	ΔH_f^1 (J g ⁻¹)	$(\tau_c^e)_1$
5.6	20	146	199	227	—	23.0	0.30
5.6	10	145.5	183	222	234	35.5	0.57
42	20	147	191	228	236	33.3	0.40
44.5	10	146	190	229	236.5	30.5	0.39
85	20	147	189	227.5	235	29.7	0.37
250	20	148	182, 195	—	231.5	30.0	0.38
250	10	147	191	228	232.5	30.4	0.38
325	20	149.5	178	224	231	28.5	0.36
325	10	148	172	226	234	30.5	0.39
PDMS $\bar{M}_n \times 10^{-3}$	T (K min ⁻¹)	T_m^1 (K)	T_m^2 (K)	T_m^3 (K)	ΔH_f^2 (J g ⁻¹)	$(\tau_c^e)_1$	
5.6	1.25	231	235	220	47.9	0.61	
42	1.25	225	238	—	33.4	0.42	
44.5	1.25	227	238	—	33.5	0.42	
73	1.25	226	236.5	—	28.7	0.36	
85	1.25	227	237	—	22.7	0.51	
110	1.25	226	234	236	25.8	0.39	
250	1.25	227	235	—	35.0	0.44	
325	1.25	227	236	—	33.2	0.42	

Table 2 Calorimetric data concerning the adsorbed layer, in silica-siloxane mixtures: C_{Si} is initial concentration of silica; Q_r is residual amount of polymer bound to silica; ρ_c is normalized ratio of crystallinity; x_a is fraction of tightly bound monomeric units; T_m^1 and T_m^2 are melting temperatures; ΔH_f is enthalpy of fusion; τ_c^{Si} is ratio of crystallinity without normalization

PDMS $\bar{M}_n \times 10^{-3}$	C_{Si} ($g g^{-1}$)	Q_r ($g g^{-1}$)	ρ_c	x_a	T_m^1 (K)	T_m^2 (K)	T_m^3 ($J g^{-1}$)	τ_c^{Si}
1.8	0.29	0.2	0	1			0	0
5.6	0.29	0.3	0	1			7.4	0
	0.17	0.4	0.15	0.85	wide		15	0.09
	0.09	0.5	0.31	0.69	wide			0.19
42	0.29	0.7	0.56	0.44	228	233	18.9	0.23
	0.09	0.7	0.63	0.37	228	232	21	0.26
44.5	0.17	0.8	0.52	0.49	228.5	232.5	17.1	0.22
85	0.29	1.1	0.68	0.32	230	236	16.6	0.21
	0.09	1.0	0.76	0.32	229	234	18.5	0.23
110	0.29	1.2	0.67	0.33	227.5	233.5	17.3	0.22
250	0.29	1.8	0.66	0.34	228	232.5	23.2	0.29
	0.17	2.3	0.65	0.35	228	234	22.7	0.29
	0.09	2.8	0.65	0.36	228	234	22.6	0.29
325	0.05	3.1	0.66	0.34	230	234.5	22	0.28

Table 3 Calorimetric data concerning silica-siloxane mixtures obtained after a partial treatment of silica surface: t is fraction of silanol sites converted into non-functional trimethylsilyl groups; Q_r is residual amount of polymer; ρ_c is normalized ratio of crystallinity; x_a is fraction of tightly bound monomeric units; T_m^1 and T_m^2 are melting temperatures; ΔH_f is enthalpy of fusion; τ_c^{Si} is crystallinity of the adsorbed layer

PDMS $\bar{M}_n \times 10^{-3}$	t	Q_r ($g g^{-1}$)	ρ_c	x_a	T_m^1 (K)	T_m^2 (K)	ΔH_f ($J g^{-1}$)	τ_c^{Si}
44.5	0.17	0.7	0.32	0.68	229	234	10.6	0.13
	0.50	0.33	0	—	—	—	—	0
	0.75	0.39	0	—	—	—	—	0
73	0.17	1.0	0.65	0.35	wide		18.5	0.23
	0.22	0.9	0.68	0.33	229	234	19.5	0.25
	0.60	0.6	0.57	0.43	231	234.5	16.3	0.21
325	0	2.2	0.72	0.28	229	234.5	24.0	0.30
	0.17	2.0	0.71	0.29	229	234	23.6	0.30
	0.22	1.9	0.67	0.33	228	233	22.4	0.28
	0.60	1.6	0.69	0.31	229	233	22.8	0.29
	0.75	1.0	0.50	0.50	228	233.5	16.7	0.21

fumed silica was bought from Degussa (Aerosil, specific area $150 m^2 g^{-1}$). The mixtures used throughout this study were characterized by initial concentrations of silica $C_{Si} = 0.29, 0.17, 0.09$ and 0.05 w/w. The residual amount of polymer Q_r still bound to silica after removing all free chains was determined from microanalysis measurements of carbon and silicon⁶. Values of Q_r are reported in Table 2.

Investigations were extended to mixtures prepared from silica particles obtained after a chemical treatment of the surface. Silica silanol sites were converted into non-functional trimethylsilyl groups according to an experimental procedure described elsewhere⁴. Fractions of treatment are reported in Table 3.

Differential scanning calorimetry

Samples were submitted to thermal cycles by using the cell of a Perkin-Elmer DSC-2 differential scanning calorimeter. The temperature scale and the standardization were calibrated by using cyclohexane as a reference. The calorimeter was adjusted to its highest sensitivity to operate with small amounts of sample (about 10 mg). The samples were encapsulated in aluminium pans. The baseline was optimized over the whole experimental temperature range: 100 to 300 K. A

consistent thermal treatment was applied to all samples, according to the following conditions. The samples were rapidly cooled to 100 K at a rate of $320 K min^{-1}$. When the system reached thermal equilibrium, the cell was heated to 180 K at a rate of $20 K min^{-1}$ and was held at 180 K for 30 min. Then, it was heated to 280 K at a rate of $1.25 K min^{-1}$. All experimental results are reported in Table 1. The ratios of crystallinity were calculated from the enthalpy of crystallization per monomer Δh_m , determined from the lowering of the melting temperature induced by addition of solvent⁷; $\Delta h_m = 1.4 kcal g^{-1}$.

PARTIAL CRYSTALLIZATION OF THE ADSORBED LAYER

Variations of the partial crystallization τ_c^{Si} of the adsorbed layer were measured as a function of the variable Q_r . They are reported in Figure 1a. The partial crystallization of the adsorbed layer was also compared with the partial crystallization τ_c^p of the corresponding pure polymer melt, measured before any adsorption process^{8,9}. The ratio $\tau_c^{Si}/\tau_c^p = \rho_c$ is called the normalized crystallinity; variations of ρ_c are reported in Figure 1b. The striking feature perceived from Figure 1 concerns the three well defined ranges determined from the variations of τ_c^{Si} or ρ_c .

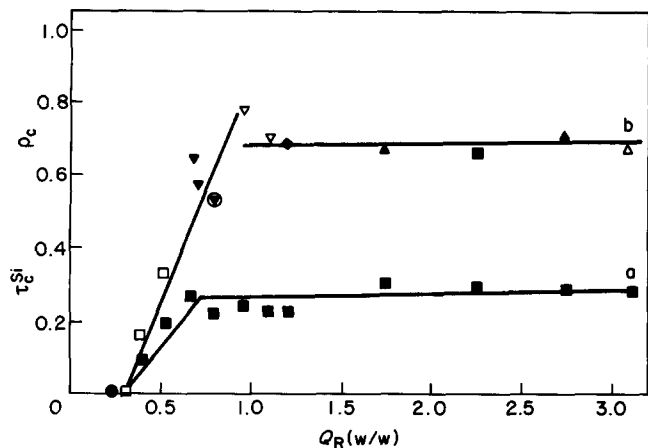


Figure 1 Partial crystallinity of the adsorbed layer. Measurements were performed upon silica-siloxane mixtures after removing all free chains; Q_r is the residual amount of polymer bound to silica. (a) The partial crystallinity ratio ρ_c^{si} observed from bound PDMS chains. (b) The partial crystallinity ρ_c normalized with respect to the crystallinity of the corresponding pure polymer. Number-average molecular weights ($10^{-4}\bar{M}_n$) are: 32.5 (Δ), 25 (\blacktriangle), 11 (\blacklozenge), 8.5 (∇), 4.2 (\blacktriangledown), 0.56 (\square) and 0.18 (\bullet). All silica concentrations are reported in Table 2

Considering the normalized curve in Figure 1a, no crystallization ($\rho_c=0$) was observed within the accuracy of the experiments for Q_r values lower than 0.3 g g^{-1} ; then a sharp increase of the partial crystallization ρ_c , from 0 to 0.7, was observed within the range $0.3 < Q_r < 1.0 \text{ g g}^{-1}$; finally, a plateau value 0.7 was observed for ρ_c , when Q_r varies from 1.1 to 3.1 g g^{-1} . It is worth emphasizing that silica-siloxane mixtures corresponding to values of Q_r higher than 1.0 exhibit a gel behaviour. Consequently, the transition from the sol, where finite clusters are formed, to the gel, where silica particles are connected to one another by chains, is perceived from the state of partial crystallinity of the adsorbed layer.

ADSORPTION OF SHORT CHAINS

Starting from an initial concentration of silica C_{Si} equal to 0.29 (w/w), two chain lengths were found to give rise to the value $\rho_c=0$; they correspond to $\bar{M}_n=1.8 \times 10^3$ and $\bar{M}_n=5.6 \times 10^3 \text{ g mol}^{-1}$. They are associated with residual amounts of polymer equal to 0.23 and 0.30 g g^{-1} , respectively. It is considered that the absence of crystallization shows that all loops that are formed during the adsorption process are too short to participate in the crystallization process. In that case, the fraction x_a of monomeric units tightly bound to the surface is equal to unity. The average number of chains adsorbed on the particles is 7.7×10^{19} for $Q_r=0.23 \text{ g g}^{-1}$ and 3.2×10^{19} for $Q_r=0.30 \text{ g g}^{-1}$, while the number of monomer units frozen by the adsorption effect is 19×10^{20} in the first case and 24×10^{20} in the second one. The number of H bonds available per gram of silica is 2.7×10^{20} . Accordingly, about eight monomer units were frozen by the formation of one H bond between one monomer unit of the chain skeleton and one silanol group of the surface.

FINITE CLUSTERS

A strong increase of the normalized crystallinity was observed within the range $0.3 \text{ g g}^{-1} \leq Q_r \leq 1.0 \text{ g g}^{-1}$. This range is associated with the formation of finite clusters.

Partial crystallinity

Assuming that the whole area of silica particles participates in the adsorption process, the total number of bonds formed with silanol groups is A/σ_e , where A is the specific area of silica and σ_e is the average area associated with a silanol site: $\sigma_e=55 \text{ \AA}^2$. Furthermore, it is considered that the number of monomeric units locked by the effect of adsorption is γ_a per H bond. Then, the total number of locked monomer units is $A\gamma_a/\sigma_e$ per gram of silica. The fraction of bonds participating in the crystallization process is:

$$x_a = 1 - \rho_c = \bar{M}_m A \gamma_a / \sigma_e Q_r \quad (8)$$

where \bar{M}_m is the molecular weight of one monomeric unit. This fraction must be a linear function of Q_r^{-1} . Variations of the experimental quantity $1 - \rho_c$ are reported in Figure 2 as a function of the inverse of the adsorbed amount of polymer. The experimental value of the slope of the straight line drawn in Figure 2 is 0.35 g g^{-1} . The numerical value of γ_a calculated from formula (8) is then equal to 10. This value is in reasonable agreement with the average number obtained in the foregoing section and corresponding to frozen monomer units associated with one H bond formed with a silanol group. The comparison of the two results only shows that the adsorption of short chains does not correspond to the maximum length of loops that are locked as a result of the binding process.

Law of adsorption

A direct experimental approach to the law of adsorption given by formula (1) can be obtained by representing the variations of the inverse of the fraction $x_a = 1 - \rho_c$ as a function of $(M_n)^{1/2}$. The corresponding curve is reported in Figure 3; it is a straight line. The silica concentration was $C_{Si}=0.09$ (w/w). In accordance with the experimental law (1) and the interpretation given in ref. 2, the average number of contact points of one chain with the silica surface is expressed as:

$$\langle r_c \rangle = \epsilon_a (N_n)^{1/2} \quad (9)$$

where N_n is the number average of bonds in one chain

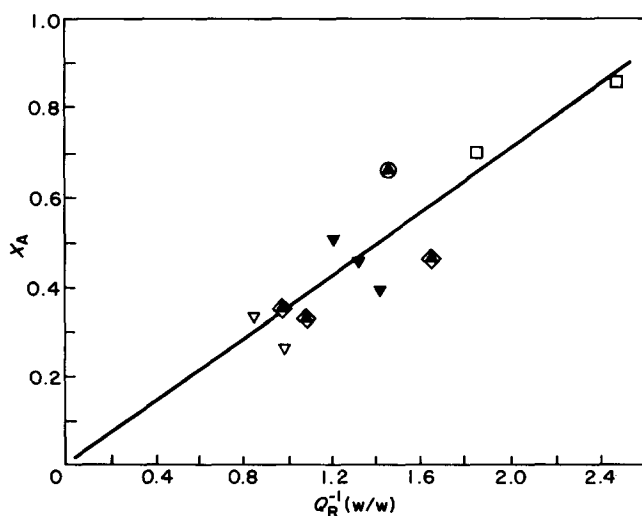


Figure 2 The fraction $x_a = 1 - \rho_c$ of monomeric units tightly bound to the silica surface represented as a function of the inverse of the residual amount of polymer. Key to symbols is given in Figure 1. Measurements corresponding to treated silica are also reported (\blacktriangle within \diamond and \circ)

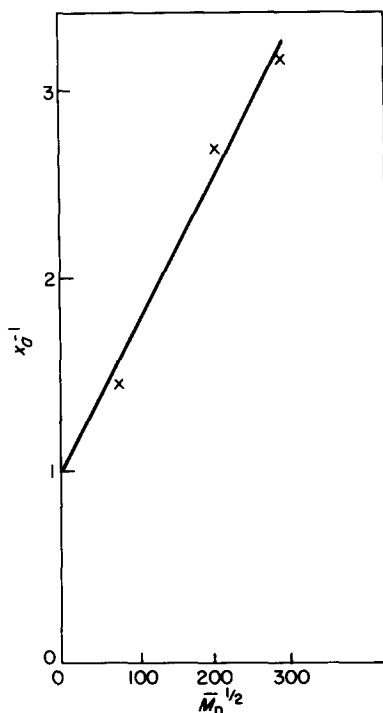


Figure 3 The inverse of the fraction of tightly bound monomeric units reported as a function of the square root of the chain molecular weight (the silica concentration is $C_{Si}=0.29$ w/w)

and ϵ_a is a numerical factor depending upon the silica concentration. Then, the residual amount Q_r of polymer bound to silica is:

$$Q_r = [A(\bar{M}_m)^{1/2}/\sigma_e \epsilon_a \mathcal{A}^{1/2}](\bar{M}_n)^{1/2} \quad (10)$$

Therefore:

$$x_a = A(\bar{M}_m)^{1/2}/\sigma_e \epsilon_a \mathcal{A}^{1/2} \quad (11)$$

where \mathcal{A} is the Avogadro number. Correspondingly, the fraction x_a of monomeric units locked by the adsorption process is expressed as:

$$x_a = \epsilon_a \gamma_a (\bar{M}_m)^{1/2}/(\bar{M}_n)^{1/2} \quad (12)$$

The inverse of the fraction x_a must vary as a linear function of $(\bar{M}_n)^{1/2}$. The slope of the straight line drawn in *Figure 3* leads to a numerical value of the product $\epsilon_a \gamma_a$ equal to 1.4. Considering that $\gamma_a \approx 10$, the value of ϵ_a is about 0.14. This estimate of ϵ_a accounts for stiffness effects concerning real PDMS chains; it represents the deviation from a pure random walk.

INFINITE CLUSTERS: SILICA-SILOXANE GELS

When the concentration of silica C_{Si} and the chain molecular weight M_n reach values higher than those corresponding to the threshold of site-bond percolation, an infinite cluster is formed. Silica aggregates are connected to one another by PDMS chains. The resulting systems can be reversibly swollen by using a good solvent. They also exhibit an elasticity property that can be characterized by a modulus. Swelling properties have already been described elsewhere⁶. The formation of a silica-siloxane gel can be experimentally associated with the range of residual amount of polymer Q_r going from 1.0 to 3.1 g g⁻¹. It is clearly seen from *Figure 1* that this range corresponds to a plateau value of the normalized

partial crystallization of the adsorbed layer. It is worth emphasizing that the site-bond percolation effect is well understood from the ordering properties of the adsorbed layer. Although the amount of polymer Q_r confined between particles varies from 1.0 to 3.1 g g⁻¹, the fraction x_a of monomeric units tightly bound to silica has a constant value. This is also observed by keeping the number-average chain molecular weight constant and varying the silica concentration. It is not the purpose of the present work to give a thorough description of all properties of the adsorbed layer. The observation of a plateau associated with the formation of a gel can be discussed in the following way.

(i) It is first noticed that the law of adsorption (1) concerns all polymer samples studied from the partial crystallization of the adsorbed layer. Consequently, neither the specific area A of silica nor the parameter ϵ_a must be considered as varying with Q_r within the range corresponding to the plateau (formulae (10) and (11)).

(ii) Then, considering formula (8) or (12), it is assumed that the parameter γ_a may depend upon the amount of polymer bound to silica when a gel is formed. Experimentally, it is found that γ_a must be proportional to Q_r .

The residual amount Q_r is increased either by lowering the silica concentration or by lengthening polymer chains. It could be considered that in both cases PDMS chains are given more freedom when Q_r is increased; consequently, they should be more easily ordered during the crystallization process. This is contrary to the experimental result. Thus, it is assumed that additional constraints arise from the increase of Q_r ; these constraints may be identified as entanglements, for example. This will be discussed in a subsequent work.

TREATED SILICA SURFACE

Finally, the threshold of percolation was shifted towards higher silica concentrations at constant chain length or towards higher chain lengths at constant silica concentration by treating the silica surface. Hexamethyldisilazane was used to deactivate a partial number of silanol groups.

Finite clusters

One of the most striking results concerns the mixture made from polymer chains of number-average molecular weight $M_n = 44.5 \times 10^3$ g mol⁻¹. The initial concentration of the mixture was $C_{Si} = 0.17$ (w/w). In the absence of any treatment of the silica surface, the residual amount of polymer Q_r left bound to silica was 0.8 g g⁻¹. Then, the values of Q_r were 0.7, 0.4 and 0.4 g g⁻¹ for converted free silanol fractions equal to 0.17, 0.72 and 0.75, respectively. The corresponding partial crystallinity ratios were $\rho_c = 0.32, 0$ and 0 , respectively (*Table 3, Figure 4*). Therefore, it is considered that loops formed from the adsorption process can collapse onto the silica surface when the density of free silanol groups is smaller than 0.3. Accordingly, they cannot participate in the crystallization process. Mixtures made from polymer chains characterized by a number-average molecular weight $M_n = 7.3 \times 10^4$ were also observed. Ratios of converted silanols were 0.17, 0.22 and 0.60; corresponding amounts of residual polymer were 1.0, 0.9 and 0.6 g g⁻¹, respectively. The partial crystallinity was found to be equal to 0.65, 0.68 and 0.57 (*Table 3, Figure 4*). Corresponding fractions of frozen bonds are reported in *Figure 2*.

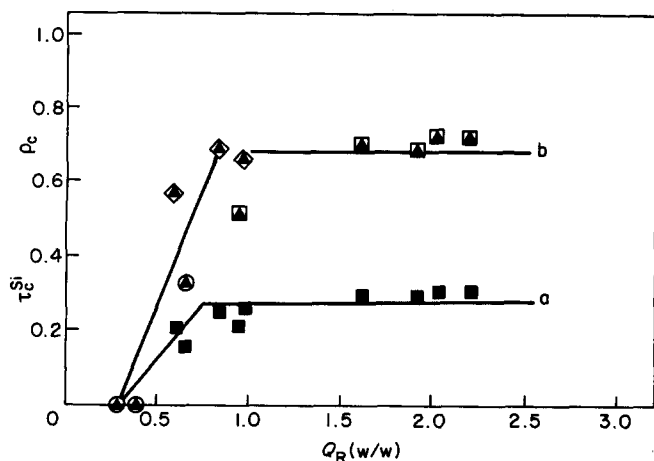


Figure 4 The partial crystallinity observed from mixtures of siloxane and silica with a chemical treatment of the surface. Experimental points are compared with the average curves obtained without any chemical treatment (Figure 1). (a) The ratio of crystallinity ρ_c^s observed on PDMS chains. (b) The crystallinity ρ_c normalized with respect to that of corresponding pure polymer chains. Number-average chain molecular weights ($10^{-4} \bar{M}_n$) are: 32.5 (\blacktriangle within \square), 7.3 (\blacktriangle within \diamond) and 4.45 (\blacktriangle within \circ). Corresponding points without any treatment are also reported in Figure 1. Fractions of treatment are reported in Table 3

Infinite cluster

Treated silica was also used to observe the formation of infinite clusters. The concentration of silica was kept constant, $C_{Si} = 0.17$ (w/w), and the chain molecular weight was $M_n = 3.25 \times 10^5$. As long as an infinite cluster was formed, the partial crystallinity was characterized by $\rho_c \approx 0.7$. Then, for $Q_r < 1$, the partial crystallinity was found to decrease. Figures 1 and 4 clearly show that the crystallinity ratio is a constant in all silica-siloxane mixtures that form a gel although the silica concentration and the chain length may vary from one system to another. The fraction of trains (or of loops and tails) has a constant value whatever the amount of polymer bound per gram of silica. This property will also be discussed in a subsequent work.

CONCLUSIONS

The mechanical mixing of siloxane chains and silica particles induces an adsorption process for which char-

acteristic properties arise mainly from the full immersion effect of particles in the polymer melt: the amount of adsorbed polymer is proportional to the square root of the number-average molecular weight of chains. The purpose of the present work was to give a preliminary investigation of the structure of the adsorbed layers. The degree of freedom of monomeric units is determined by observing the partial crystallinity of the polymeric phase. Differential scanning calorimetry measurements performed after removing all free chains showed that about 10 monomeric units are frozen by the formation of one hydrogen bond between one silanol group and one oxygen atom of a chain skeleton.

The site-bond percolation induced by polymer chains connecting silica particles was perceived from the state of partial crystallinity of the adsorbed layer.

This preliminary study will be extended by an n.m.r. approach to the kinetics of crystallization of the polymeric layer⁷.

Measurements of differential scanning calorimetry performed on the adsorbed layer of silica-siloxane mixtures show clear evidence for the existence of a site-bond percolation transition of silica particles. The percolation process occurs through polymer molecules. The present work also shows that eight monomeric units on average are fixed in space by the formation of one hydrogen bond between a silanol group and a skeleton oxygen atom. The analysis of experimental results suggests that the area of silica surface available to polymer chains might vary the silica concentration.

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