Silica–siloxane mixtures. Structure of the adsorbed layer: chain length dependence

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This work deals with the statistical structure of the adsorbed layer formed in silica–siloxane mixtures. The description relies upon a basic experimental feature: adsorbed poly(dimethylsiloxane) chains obey Gaussian statistics. Two very simple approaches are proposed to picture the adsorbed layer. Firstly, a random walk model is used to evaluate the average number $\bar{\mu}_c$ of points of contact of any given chain to the silica surface; $\bar{\mu}_c$ is shown to be proportional to $N_b^{1/2}$ (N_b is the number of skeletal bonds in one chain). Secondly, a packing condition hypothesis is used to assert that all polymer chains contained in a given volume are bound either to one or two silica particles. In both cases the residual amount of polymer bound to silica is shown to vary as $\bar{M}_n^{1/2}$, where $\bar{M}_n$ is the number average chain molecular weight. Numerical values are in agreement with experimental results.

(Keywords: silica particles; siloxane chains; adsorption; mechanical mixtures)

INTRODUCTION

It is worth emphasizing that silica-filled polymers obtained from a mechanical mixing are characterized by several basic features. A multiple-chain adsorption process occurs from the melt onto the surface of particles. In other words, any chain of N_b skeletal bonds, in contact with the surface of silica, is swollen by about $N_b^{1/2}$ other chains. These compete with one another to be adsorbed. A saturated adsorption necessarily results from the full immersion of particles in a molten polymer. All silica particles are surrounded by polymer chains.

A site-bond pecolation effect may occur; at a given concentration of particles, the formation of an infinite cluster depends upon the length of polymer chains. Short chains give rise to finite clusters. Longer chains join several particles to one another. The resulting infinite clusters exhibit elasticity properties and can be reversibly swollen by a good solvent[1]. In the case of poly(dimethylsiloxane) chains (PDMS), the elementary mechanism of adsorption is well defined. Silanol groups located on the silica surface can form hydrogen bonds with oxygen atoms of chain skeletons. Thus, the free enthalpy of adsorption, U, is larger than the thermal energy kT, at room temperature. It is not a van der Waals type adsorption.

One of the main problems encountered in describing the mechanical behaviour of silica-filled PDMS systems concerns properties of the adsorbed layer. The size of trains and the length of loops are expected to play a crucial role in determining the boundary conditions governing the response of mixtures under external constraints. The purpose of the present work is to propose an approach to the description of the structure of the adsorbed layer obtained after removing all free chains from studied mixtures. This description relies upon a thorough experimental investigation of silica–siloxane systems reported in previous studies[1,2,3].

CHARACTERISTIC PROPERTIES OF MIXTURES

Mechanically induced mixtures of PDMS and silica particles exhibit characteristic properties which will serve as a basis of the present description.

The residual amount of polymer Q_r^l left bound to silica, at equilibrium (after 40 months), after removing all free chains from silica–siloxane mixtures has been found to vary as:

$$Q_r^l \propto \bar{M}_n^{1/2} \tag{1}$$

$\bar{M}_n$ is the number average molecular weight of the initial melt in which particles are immersed[2]. This law is observed not only at equilibrium but even four days after the mechanical mixing. Typical curves are shown in *Figure 1*. They illustrate the $\bar{M}_n^{1/2}$ dependence of Q_r^l observed for three different concentrations of silica.

Curve a in *Figure 1* corresponds to a silica concentration $C_{Si}=0.29$ (w/w). The slope of the straight line is $\gamma_b=3.3\times10^{-3}\,g^{1/2}\,mol^{1/2}$. Curve b in *Figure 1* is associated with a silica concentration $C_{Si}=0.17$ (w/w). The corresponding slope is $\gamma_b=4.3\times10^{-3}\,g^{1/2}mol^{1/2}$.

It is clear that deviations from the $\bar{M}_n^{1/2}$ dependence occur in the range $4\times10^4<\bar{M}_n<10.5\times10^4\,mol\,g^{-1}$. These deviations correspond to polymer chains weakly bound to silica. The free enthalpy of binding of these chains is not low enough compared with the free enthalpy of dilution in the presence of solvents used to extract free polymer chains from the mixtures.

Curve c in *Figure 1* illustrates the $\bar{M}_n^{1/2}$ dependence corresponding to the silica concentration $C_{Si}=0.09$ (w/w). The slope is $\gamma_c=5.3\times10^{-3}\,g^{1/2}\,mol^{1/2}$. Deviations from this dependence occur in a range of molecular weight broader than in the case of the silica concentration $C_{Si}=0.17$ (w/w). No deviations are found to occur when the silica concentration is $C_{Si}=0.29$ (w/w) because infinite clusters are formed. They are slightly swollen by a good solvent and the free energy of chain dilution is not low

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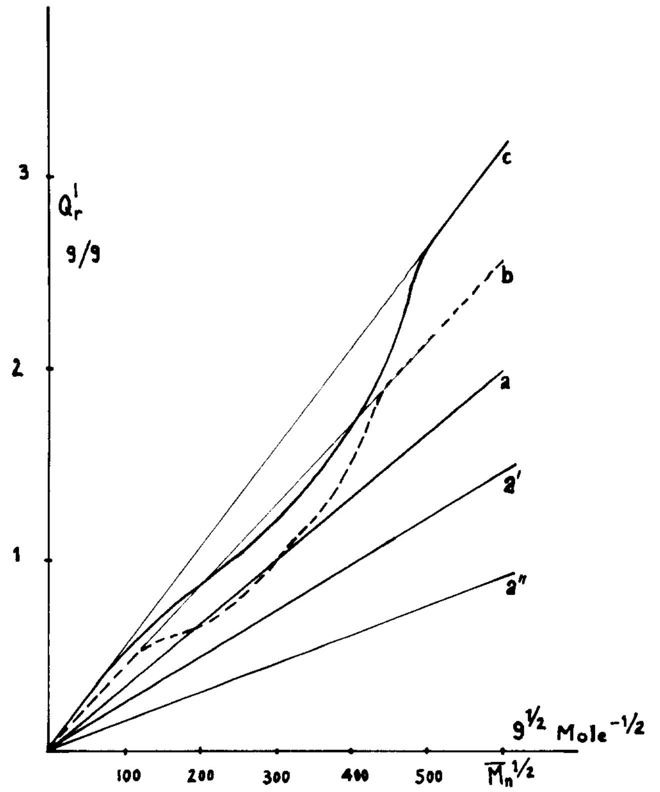

Figure 1 Schematic variations of the residual amount of polymer left bound to silica after removing all free chains from the mixtures. The concentration of silica was: curve a, $C_{Si}=0.29$ (w/w); curve b, $C_{Si}=0.17$ (w/w); curve c, $C_{Si}=0.09$ (w/w). Curves a'', a' and a correspond to measurements performed four days, nine months and forty months after the mechanical mixing

enough to untie polymer chains from the silica surface.

The average number of chains ν^a bound to silica is estimated from the ratio:

$$\nu_c^a = Q_r^1/\bar{M}_n \qquad (2)$$

ν_c^a varies from 7.7×10^{19} ($\bar{M}_n=1800$) to 0.33×10^{19} ($\bar{M}_n=3.25\times10^5$) when the silica concentration is $C_{Si}=0.29$ (w/w).

Assuming that there is a saturated adsorption, the average area of the silica surface covered by one polymer chain is:

$$\bar{\sigma}_c = A\bar{M}_n/Q_r^1 \qquad (3)$$

A is the specific area of silica; $A=150\,\mathrm{m^2\,g^{-1}}$. Typical values of σ_c are 195 Å^2 and 4510 Å^2, which correspond to the above values of ν^a. Equation (3) gives only an upper limit of σ_c because polymer chains may be bound to two or three particles in some cases.

The average area covered by one silanol group has been already estimated[4]: $\sigma_e=55$ Å^2. Therefore, the average number of H bonds formed by the binding of one chain is:

$$\bar{\mu}_c = \bar{\sigma}_c/\sigma_e \qquad (4)$$

For example, $\bar{\mu}_c\simeq4$ and 81 for $\nu_c^a\simeq7.7\times10^{19}$ ($N_B=50$) and 0.33×10^{19} ($N_b=8800$), respectively. These estimates show that the average number of monomeric units participating in the binding process of one chain is much smaller than the average number of skeletal bonds N_b contained in this chain.

The small size of trains or equivalently the small value of the ratio $2\bar{\mu}_c/N_b$ indicates that the adsorption process does not induce any strong deformation of polymer chains.

This is the experimental feature underlying the present description. It shows that polymer chains adsorbed on the silica surface probably maintain a Gaussian character as in a pure melt. Loops are swollen by one another and obey a Gaussian description.

A rough estimate of the average thickness e of the adsorbed layer existing in an infinite cluster is given by:

$$\bar{e} \simeq 2Q_r^1/Ap_p \qquad (5)$$

p_p is the density of the pure polymer ($p_p\simeq1$ g cm^{-3}): $\bar{e}\simeq240$ Å. The radius of gyration R_G of a polymer chain (PDMS) comprising 8800 bonds is 165 Å. The estimate of R_G compared to that of $\bar{e}$ shows that polymer chains are not strongly confined by silica particles. This comparison reinforces the hypothesis of Gaussian chains forming the adsorbed layer.

Finally, it must be noted that the size of polymer chains studied is smaller on average than the mean diameter ($\simeq400$ Å) of silica particles.

A RANDOM WALK APPROACH

Recent investigations of surface and volume properties of fumed silica have been reported from neutron scattering experiments[5]. The mass scaling exponent characterizing the fractal structure of these particles is equal to 1.9. The surface scaling exponent is two over an average area equal to $(10^2)^2$ Å^2. Then, a roughness can be detected over larger areas.

The first approach of the present work is the calculation of the average number $\langle r_d\rangle$ of points of contact that any Gaussian chain may form with a plane surface.

Average number of contact points

For the sake of simplicity but without any loss of generality, the origin of a given polymer chain is assumed to be bound to the plane. Then, the chain can move freely in the x and y directions parallel to the plane picturing the surface of adsorption. The z-axis is perpendicular to this plane. Along the directions x and y, the random flight is classically described according to Gaussian statistics. Along the z-direction, the probability that the r_cth return of the chain to the origin occurs at the N_bth monomeric unit is[6]:

$$\Pi(r_c,N_b)\propto\frac{r_c}{N_b-r_c}\times\frac{(N_b-r_c)!}{(N_b/2)!((N_b-2r_c)/2)!}\times\frac{1}{2^{N_b-r_c}} \qquad (6)$$

N_b is the number of skeletal bonds in one chain.

Equation (7) can be given a more convenient expression because N_b and r_c are large numbers:

$$\Pi(r_c,N_b)\propto r_c(N_b-r_c)^{-3/2}\exp-\{r_c^2/2(N_b-r_c)\} \qquad (7)$$

The calculation of the mean value $\langle r_c\rangle$ of r_c is not easily carried out. Therefore, $\langle r_c\rangle$ is identified with the expression of r_c giving rise to the maximum value of $\Pi(r_c, N_c)$, as is usual. $\langle r_c\rangle$ is thus found to obey the equation:

$$\langle r_c\rangle^3/2N_b^2-\langle r_c\rangle^2/N_b-\langle r_c\rangle^2/2N_b^2-\langle r_c\rangle/2N_b=-1 \qquad (8)$$

The obvious solution of equation (8) is $\langle r_c\rangle=N_b^{1/2}$ within an accuracy given by $1/2N_b$ i.e. 0.02 for shortest chains.

The average number of H bonds in all trains associated with one chain is therefore equal to:

$$\bar{\mu}_c = \varepsilon(N_b)^{1/2} \tag{9}$$

μ_c must be considered as an average calculated over all particles; ε is a factor which takes both the chain stiffness and the number of skeletal oxygen atoms per monomeric unit into consideration.

Average length of loops

The average length κ_1 of loops is estimated by assuming that any contact of a given chain to the silica surface corresponds to a single H bond. Thus:

$$\bar{\lambda}_1 = aN_b/\bar{\mu}_c \tag{10}$$

a is the average skeletal bond length[7]: $a = 1.74$ Å. Also:

$$\bar{\lambda}_1 = a(N_b)^{1/2}/\varepsilon \tag{10a}$$

To estimate the values of $\bar{\lambda}_1$ consider each train to contain only one monomeric unit.

Average area covered by one chain

The average area covered by a given chain is expressed by:

$$\bar{\sigma}_c = \bar{\mu}_c\sigma_e = \varepsilon(N_b)^{1/2}\sigma_e \tag{11}$$

This can be expressed as:

$$\bar{\sigma}_c = \varepsilon(\bar{M}_n)^{1/2}\sigma_e(\bar{M}_b)^{1/2} \tag{11a}$$

where M_b is the average molecular weight associated with a skeletal bond; $M_n = 37\,\mathrm{g\,mol^{-1}}$. Typical experimental values of the slope $\varepsilon\sigma_a(M_b)^{1/2}$ are: 4.5 and 7.6 Å^2 g^{-1} mol$^{1/2}$, for $C_{Si} = 0.09$ (w/w) and 0.29 (w/w), respectively.

Average area associated with one chain

The mean square distance $\bar{d}_c^2$ separating two contact points associated with a given loop is now estimated from the following probability distribution functions:

$$\Pi(x, \bar{\lambda}_1/a) \times \Pi(y, \bar{\lambda}_1/a) \propto (\exp - 3(x^2 + y^2)/2\bar{\lambda}_1 a) \tag{12}$$

Thus:

$$\bar{d}_c^2 = 2\bar{\lambda}_1 a/3 \tag{13}$$

or

$$\bar{d}_c^2 = 2(N_b)^{1/2}a^2/3\varepsilon \tag{13a}$$

Therefore, the mean area associated with a given chain is:

$$\textstyle\sum_c = \Pi(N_b)^{1/2}\varepsilon\bar{d}_c^2/4 \propto \Pi N_b a^2/6 \tag{14}$$

This estimate indicates that about $N_b^{1/2}$ chains are also involved in the single adsorption process of one given chain. This mean square value should actually result from a calculation based on a distribution function of distances between contact points which takes steric hindrance on the silica surface into consideration.

It may be worth emphasizing that the quantity r_{ij}^2/n_{ij}^2 can be measured on average from n.m.r. r_{ij} is the distance between two contact points of a loop comprising n_{ij} bonds.

Residual amount of polymer

The residual amount of polymer left bound to silica after removing all free chains is derived from equation (11a):

$$Q_r^1 = A\bar{M}_n f/\bar{\sigma}_c$$

or

$$Q_r^1 = A\bar{M}_n{}^{1/2}(M_b)^{1/2} f/\varepsilon\sigma_e \tag{15}$$

f accounts for the binding of one PDMS chain to one, two or more silica particles. This formula is in accordance with the experimental equation (1). Experimental values of the ratio f/ε derived from the slopes of *Figure 1* are: 1.22 for $\gamma_a = 3.3 \times 10^{-3}\,\mathrm{g^{1/2}\,mol^{1/2}}$, 1.6 for $\gamma_b = 4.3 \times 10^{-3}\,\mathrm{g^{1/2}\,mol^{1/2}}$ and 1.96 for $\gamma_c = 5.3 \times 10^{-3}\,\mathrm{g^{1/2}\,mol^{1/2}}$.

Conclusion

The conclusion of this random walk approach to the description of the structure of the adsorbed layer existing in silica–siloxane mixtures is that polymer chains obey Gaussian statistics. The calculated average number μ_c of contact points of one chain to the silica surface is the key parameter in the description. This number is found to be proportional to the square root of the number of skeletal bonds N_b in one chain. From this simple dependence upon N_b experimental properties are interpreted in a straightforward way.

A PACKING CONDITION APPROACH

In this section a slightly different approach is proposed. However, both approaches are consistent with each other. This description begins with mixtures formed from a silica concentration $C_{Si} = 0.29$ (w/w). In that case a site-bond percolation effect occurs. Silica particles are connected to one another by polymer chains. It appears that some PDMS chains can join two particles while others are adsorbed once. These are dangling chains. Throughout this section it is assumed that the binding site of any chain on a particle has a constant area σ_c. Accordingly, the binding of one chain to two particles is associated with an area equal to $2\sigma_c$.

Residual amount of polymer

Two silica particles facing each other are now considered. They are separated by polymer chains. A cylinder of polymer is determined by the area $2S$ of its two sections. One section is drawn on each particle and the two sections face each other. The height of the cylinder is equal to the distance e between the two particles. The number of chains filling this cylinder is given, on average, by:

$$v_c^a \equiv 2SQ_r^1/A\bar{M}_n \tag{16}$$

Q_r^1 denotes the residual amount of polymer left bound to silica. Of this number v_c^a, $2\alpha S/\bar{\sigma}_c$ chains are bound once to silica particles, while $(1-\alpha)S/\bar{\sigma}_c$ chains join two particles, the area covered by the v_c^a chains is such that:

$$2(\mathrm{S}/\bar{\sigma}_c)\alpha + (\mathrm{S}/\bar{\sigma}_c)(1-\alpha) = v_c^a \tag{17}$$

and

$$Q_r^1 = A\bar{M}_n(\alpha + 1)/2\bar{\sigma}_c \tag{18}$$

Thus, $\bar{\sigma}_c$ depends upon the chain molecular weight.

Estimate of $\bar{\mu}_c$: packing condition

The average area μ_c covered by the binding site of one chain is estimated by assuming that a polymer chain obeys Gaussian statistics. Then, the number of chains filling the average volume of one given chain is:

$$\nu_v \simeq \Pi N_b^{1/2} C_\infty^{3/2} a^3 / 6\omega_b \qquad (19)$$

C_∞ is the characteristic ratio of PDMS chains; $C_\infty = 7$. The average volume of one skeletal bond is $\omega_b = 62\,\text{Å}^3$. Correspondingly, the mean area associated with one given chain is:

$$\Pi C_\infty N_b a^2 / 4$$

It corresponds to an average area per binding site of one chain equal to:

$$\bar{\sigma}_c = 3 N_b^{1/2} \omega_b / 2 C_\infty^{1/2} a \qquad (20)$$

Combining equations (18) and (20):

$$Q_r^1 = \bar{M}_n^{1/2} A C_\infty^{1/2} a (M_b)^{1/2} (1+\alpha)/3\omega_b \qquad (21)$$

By including numerical values:

$$Q_r^1 = 3.4 \times 10^{-3} (1+\alpha) \bar{M}_n^{1/2} \qquad (21a)$$

This expression is in agreement with equations (5) and (15).

Comparison of this slope with experimental values gives $\alpha \simeq 0$ for γ_a. There are no dangling chains; α is found to be equal to 0.26 for γ_b ($C_{Si} = 0.17$ (w/w)) and $\alpha = 0.56$ for γ_c. In this last case,the presence of dangling chains is not negligible ($C_{Si} = 0.09$ (w/w)). The reasonable order of magnitude of experimental values of α is, of course, not fully significant taking the roughness of the above model into consideration.

Conclusion

The packing condition approach to the description of the structure of the adsorbed layer relies upon the Gaussian character of polymer chains. It is based on a simple assumption: all chains contained in a given volume must be bound to one, two or more particles.

CONCLUSION

The adsorption phenomenon resulting from the immersion of mineral particles in a polymer melt is very different from the binding of polymer chains induced from a suspension of particles dispersed in a polymer solution[8,9]. A multiple-chain adsorption necessarily occurs in the first case. In addition to this feature, the surface of particles available to polymer chains is necessarily saturated at equilibrium. The most important experimental result associated with silica–poly(dimethylsiloxane) mixtures concerns the small number of monomeric units participating in the binding effect of one chain. This number varies from about 1–10% of the number of skeletal bonds, depending upon the chain length. In other words, polymer chains are not strongly deformed by the adsorption effect. They are still Gaussian, as in a pure melt. Consequently, they can be described on the basis of a random flight colliding with the silica surface in a random way. This basic picture leads to the interpretation of the dependence of the amount of polymer Q_r^1 adsorbed on silica upon the chain molecular weight $\bar{M}_n$ in the relationship $Q_r^1 \propto \bar{M}_n^{1/2}$.

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