Sol or gel-like behaviour of ideal silica–siloxane mixtures: percolation approach

Jean-Pierre Cohen-Addad
Laboratoire de Spectrométrie Physique associé au C.N.R.S., Université Joseph Fourier, Grenoble I, B.P. 87, 38402 St Martin d'Hères Cedex, France
(Received 8 May 1991; revised 10 September 1991; accepted 2 October 1991)

Properties of idealized silica–siloxane mixtures are described within the framework of a percolation process. Polymer chains are considered as bifunctional units of percolation. Silica particles are considered as units of percolation with a high functionality, f_c ($f_c \simeq 10^2$); f_c is determined by the process of chain adsorption which results from the formation of hydrogen bonds with the silica surface. The state of gelation of a given mixture is characterized by using three variables: the initial specific amount of polymer Q_i, the specific amount of adsorbed polymer Q_r, and the chain molecular weight $\bar{M}_n$. A diagram is proposed to distinguish domains where an infinite cluster is formed from domains in which the clusters formed have a finite size. Expressions of the modulus of elasticity above the threshold of percolation are proposed.

(Keywords: silica; percolation; adsorption; poly(dimethylsiloxane))

INTRODUCTION

It is now well established that silica–siloxane systems obtained by mechanical mixing behave like permanent gels. They can be reversibly swollen by using a good solvent and they exhibit elasticity. However, the cohesion of the permanent network structure depends strongly upon two main variables: the initial concentration of silica C^i_{Si} in the mixture and the chain molecular weight $\bar{M}_n$ of the polymer. It is shown experimentally that a gel structure can be formed by using a silica concentration as low as 0.05 g g^{-1}; however, in this case the silica–siloxane mixture is easily broken into small microscopic grains under the action of a weak shear. There exists a threshold of mechanical constraint; above this threshold, creep of the polymer system is induced. The size of clusters resulting from the flow is closely related to the amplitude of the shear rate applied to the mixture. When the concentration of silica is too low, no infinite gel can be formed; all clusters which are observed have a finite size. These observations stress the need to define an equation associated with the physical state of a given mineral-filled polymer. This equation must relate three main variables to one another; the silica concentration C^i_{Si}, the molecular weight $\bar{M}_n$ and the specific amount of adsorbed polymer Q^i_r on the silica surface.

The purpose of this work is to propose a simple framework to describe the state of gelation of silica–siloxane mixtures by considering that this state arises from a percolation process of silica particles connected to one another by polymer chains.

0032-3861/92/132762–06

LAW OF ADSORPTION

The crucial problem encountered in describing physical properties of silica-filled polymers concerns the law of adsorption of siloxane chains upon the surface of particles. The mechanism of adsorption relies upon the formation of hydrogen bonds between oxygen atoms of chain skeletons and silanol groups located on the silica surface. The amount of polymer Q^i_r left bound to 1 g silica is measured after washing silica–siloxane mixtures several times; a good solvent is used to eliminate all free chains. The process of adsorption observed by fully immersing particles in a melt is contrasted to that resulting from the presence of polymer chains in a suspension of particles. It has been well established experimentally that the specific amount of polymer Q^i_r which forms the adsorbed layer obeys the relation:

$$Q^i_r = \chi_a \sqrt{\bar{M}_n} \qquad (1)$$

within the range $2 \times 10^3 \leqslant \bar{M}_n \leqslant 3.6 \times 10^5$ g mol^{-1}; the numerical value of the factor $\chi_a \simeq 3 \times 10^{-3}$ (g mol^{-1})$^{-1/2}$ is determined[1] from the slope of the representation of Q^i_r as a linear function of $\bar{M}_n^{1/2}$.

This empirical law has been interpreted as the result of the following simple effect concerning polymer chains which obey Gaussian statistics[2]. Considering that the end of one chain is anchored in one plane, there is a probability distribution function of the number of contact points of this chain with the silica surface; the chain which has only one end attached to the surface is part of the distribution. Then, the average number $\langle r_c \rangle$ of returns of this chain to this plane can be expressed as:

$$\langle r_c \rangle = \varepsilon_a \sqrt{N} \tag{2}$$

where N is the number of skeletal bonds in one chain and the numerical factor $\varepsilon_a \simeq 1$ accounts for the chain stiffness and surface coverage[2]. Formula (2) essentially assumes that the chain is just an unperturbed random coil. The average number of chains adsorbed per unit mass of silica is:

$$\langle \nu_c(N) \rangle = A_T / \sigma_e \varepsilon_a \sqrt{N} \tag{3}$$

where A_T is the specific area of silica and σ_e is the average area associated with the formation of one hydrogen bond. The specific amount of adsorbed polymer is written as:

$$Q_r^1 = \langle \nu_c \rangle \bar{M}_n / \mathscr{A} \tag{4}$$

and

$$\chi_a = A_T \sqrt{M_b} / \sigma_e \mathscr{A} \varepsilon_a \tag{5}$$

where $\mathscr{A}$ is the Avogadro number and M_b is the average weight of one skeletal bond. Numerical values are $A_T = 150\ \mathrm{m^2\ g^{-1}}$, $\sigma_e = 55\ \text{Å}^2$ and $M_b = 37\ \mathrm{g\ mol^{-1}}$; then, the numerical value of χ_a is 2.8×10^{-3}, in accordance with the order of magnitude of experimental values. However, the above description does not take the initial concentration of silica into consideration; in this case the quantity Q_r^1 represents only the maximum specific amount of polymer which can be adsorbed upon the whole silica surface.

KINETICS OF SURFACE SATURATION

The foregoing description applies to the case where the adsorbed layer is at equilibrium. Then, the specific amount Q_r^1 corresponds to the maximum weight of adsorbed polymer, given specific initial conditions used to form a silica–siloxane mixture. At the end of a mechanical mixing the silica surface is not saturated. The process of surface saturation lasts over about 3 years at room temperature when polymer chains are end-methylated, and 3 months at room temperature when polymer chains are end-hydroxylated. The process of saturation is conveniently described according to the expression:

$$Q_r^1 - Q_r(t) = [Q_r^1 - Q_r(o)] \exp(-\sqrt{t/\tau}) \tag{6}$$

The specific amount of polymer adsorbed at a time t is $Q_r(t)$; $Q_r(o)$ is measured immediately after the mechanical mixing[3]. The time constant τ depends upon the temperature according to an Arrhenius law.

PERCOLATION FRAMEWORK OF DESCRIPTION

The description of silica–siloxane mixtures starts from the following assumption. Whatever the procedure used to form a mixture and whatever the time of observation of this mixture, the mineral-filled polymer which is obtained consists of particles connected to one another by links defined by polymer chains; consequently, any silica–siloxane mixture is considered as the result of a percolation process; the state of percolation is characterized by measuring the specific amount of adsorbed polymer $Q_r(t)$ or Q_r^1. An infinite cluster or clusters of finite size can be formed; the state of gelation depends upon the initial concentration of silica and the length of polymer chains.

The analysis of the state of gelation observed at any time t parallels that proposed by Flory to describe the gelation process involving small molecules[4].

Units of percolation

For the sake of simplicity, polymer chains are considered as bifunctional units: they can connect only two particles to each other. The chain functionality may be a point of discussion; however, it is assumed that polymer chains are attached to two aggregates at most, except for very high silica concentrations. Let $M_{\mathrm{Si}}^{\mathrm{i}}$ denote the initial amount of silica in the mixture; $M_{\mathrm{p}}^{\mathrm{i}}$ is the initial amount of polymer. The ratio $Q_{\mathrm{i}} = M_{\mathrm{p}}^{\mathrm{i}} / M_{\mathrm{Si}}^{\mathrm{i}}$ is the initial specific amount of polymer. The initial number of chains is $\mathscr{N}_{\mathrm{p}}^{\mathrm{i}} = M_{\mathrm{p}}^{\mathrm{i}} \mathscr{A} / \bar{M}_n$ and the initial number of functions is $2\mathscr{N}_{\mathrm{p}}^{\mathrm{i}}$. Then, at a time t, it is considered that there is a fraction $\phi_{\mathrm{p}}(t)$ of functions involved in the percolation process. Therefore, the number of chains which connect two particles is $\mathscr{N}_{\mathrm{p}}^{\mathrm{i}}(\phi_{\mathrm{p}})^2$ while the number of chains attached to only one particle is $2\mathscr{N}_{\mathrm{p}}^{\mathrm{i}}[\phi_{\mathrm{p}}(1-\phi_{\mathrm{p}})]$. Finally, the number of chains which are not adsorbed on the silica surface is $\mathscr{N}_{\mathrm{p}}^{\mathrm{i}}(1-\phi_{\mathrm{p}})^2$. The specific amount $Q_r(t)$ of adsorbed polymer is thus expressed as:

$$Q_r = Q_{\mathrm{i}}[1 - (1-\phi_{\mathrm{p}})^2] \tag{7}$$

Therefore:

$$\phi_{\mathrm{p}}(t) = 1 - [1 - Q_r(t)/Q_{\mathrm{i}}]^{1/2} \tag{8}$$

The maximum value of the specific amount of polymer adsorbed on silica is called Q_r^m for convenience (Q_r^m is equal to the quantity Q_r^1 already defined); this corresponds to the case where particles are fully covered by the adsorbed layer but no particles are connected to one another. Schematic variations of ϕ_{p} are shown as a function of Q_r in *Figure 1*. For $Q_{\mathrm{i}} < Q_r^m$, the silica surface cannot be saturated (*Figure 1a*); then, some particles may be completely free.

Functionality of silica particles

It is assumed that silica particles have a uniform size; let $\bar{m}_{\mathrm{Si}}^{\mathrm{o}}$ denote the average mass of one particle. The average area of the surface of one particle participating in the percolation process is $\bar{m}_{\mathrm{Si}}^{\mathrm{o}} A_T$. Considering that the average number of links formed by one chain with the silica surface is $\langle r_c \rangle = \varepsilon_a N^{1/2}$, the functionality f_c of one particle is defined by:

$$f_c = \bar{m}_{\mathrm{Si}}^{\mathrm{o}} A_T / \sigma_e \varepsilon_a \sqrt{N} \tag{9}$$

The order of magnitude of $\bar{m}_{\mathrm{Si}}^{\mathrm{o}}$ is 3.3×10^{-17} g; then, the order of magnitude of f_c is $9 \times 10^3 / \varepsilon_a \sqrt{N}$ with $N \simeq 10^4$ for long chains ($\bar{M}_n = 3.7 \times 10^5\ \mathrm{g\ mol^{-1}}$) or $N \simeq 10^2$ for short chains ($\bar{M}_n = 3.7 \times 10^3\ \mathrm{g\ mol^{-1}}$) and $\varepsilon_a \simeq 1$. Thus, the functionality is supposed to depend upon the law of adsorption, i.e. upon the chain molecular weight. More generally, let the function $\psi(N)$ denote the number of links formed by one chain with the silica surface, then:

$$f_c = \bar{m}_{\mathrm{Si}}^{\mathrm{o}} A_T / \sigma_e \psi(N) \tag{10}$$

The total number of functions associated with the silica surface is:

$$\mathscr{N}_{\mathrm{Si}}^{\mathrm{i}} = M_{\mathrm{Si}}^{\mathrm{i}} A_T / \sigma_e \psi(N) \tag{11}$$

At a given time t, the number of functions participating in the percolation process is a fraction $\phi_{\mathrm{Si}}(t)$ of the initial

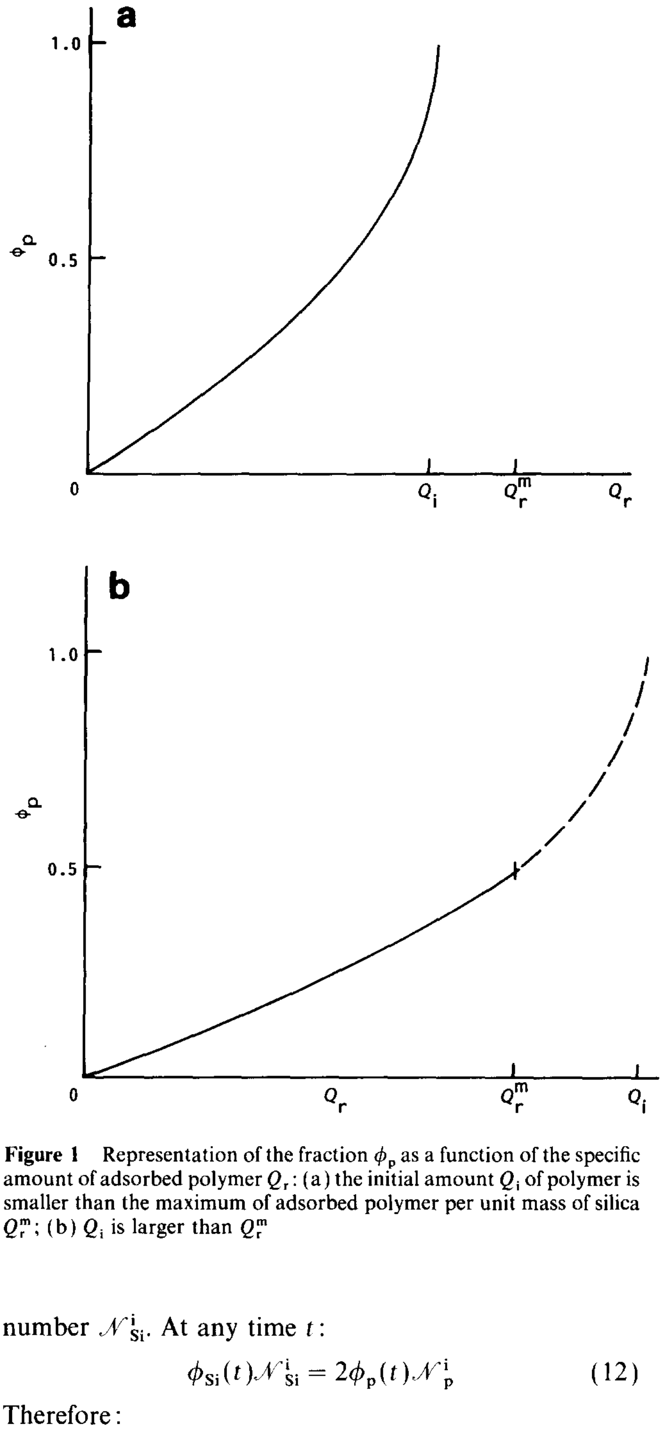

Figure 1 Representation of the fraction ϕ_p as a function of the specific amount of adsorbed polymer Q_r: (a) the initial amount Q_i of polymer is smaller than the maximum of adsorbed polymer per unit mass of silica Q_r^m; (b) Q_i is larger than Q_r^m

number $\mathcal{N}_{Si}^i$. At any time t:

$$\phi_{Si}(t)\mathcal{N}_{Si}^i = 2\phi_p(t)\mathcal{N}_p^i \qquad (12)$$

Therefore:

$$\phi_{Si}(t) = 2\phi_p(t)\frac{Q_i}{Q_r^m} \qquad (13)$$

or

$$\phi_{Si}(t) = 2[1 - \sqrt{1 - Q_r(t)/Q_i}]\frac{Q_i}{Q_r^m} \qquad (14)$$

Equation (14) shows that three key variables are used to determine the fraction of surface covered by polymer chains. In addition to the initial specific amount of polymer Q_i used to form a mixture, it is necessary to take the specific amount of adsorbed polymer $Q_r(t)$ and the maximum amount of adsorbed polymer Q_r^m into consideration. The quantity Q_r^m is closely related to the law of adsorption while the measured quantity $Q_r(t)$ characterizes the state of a given silica–siloxane mixture. To avoid any assumption about the law of adsorption, an attempt can be made to measure the quantity Q_r^m, directly.

The two conditions $\phi_{Si}(t) \leqslant 1$ and $\phi_p(t) \leqslant 1$ are associated with equation (13) to lead to the two limiting values:

$$\phi_p(t) \leqslant Q_r^m/2Q_i$$

for $Q_r^m \leqslant 2Q_i$ with $\phi_{Si} \leqslant 1$ and

$$\phi_{Si}(t) \leqslant 2Q_i/Q_r^m$$

for $2Q_i \leqslant Q_r^m$ with $\phi_p \leqslant 1$.

State of gelation

The probability $p(t)$ of observing two silica particles which have been connected to each other is given by:

$$p(t) = \phi_{Si}(t)\phi_p(t) \qquad (15)$$

or

$$p(t) = 2[1 - \sqrt{1 - Q_r(t)/Q_i}]^2\frac{Q_i}{Q_r^m} \qquad (16)$$

The state of gelation of a silica–siloxane mixture, observed at any time t, is determined by the variable:

$$\varepsilon(t) = [p(t) - p_c]/p_c \qquad (17)$$

with $p_c = 1/(f_c - 1)$ or $p_c = 1/f_c$. Then,

$$\varepsilon(t) = p(t)f_c - 1 \qquad (18)$$

or

$$\varepsilon(t) = 2[1 - \sqrt{1 - Q_r(t)/Q_i}]^2\frac{Q_i\mathscr{A}\bar{m}_{Si}^o}{\bar{M}_n} - 1 \qquad (19)$$

The law of adsorption does not appear explicitly in equation (19), but the size of particles plays a crucial role. The numerical value of the ratio $(Q_i\mathscr{A}\bar{m}_{Si}^o)/\bar{M}_n$ is equal to 2×10^3, for $Q_i = 10$ and $\bar{M}_n = 10^5$ g mol^{-1}; this ratio represents an estimate of the number of polymer chains per silica aggregate. It is also convenient to express $\varepsilon(t)$ as:

$$\varepsilon(t) = 2\frac{Q_r^2(t)\mathscr{A}\bar{m}_{Si}^o}{Q_i[1 + \sqrt{1 - Q_r(t)/Q_i}]^2\bar{M}_n} - 1 \qquad (20)$$

Given $\bar{M}_n$ and $Q_r(t)$, the variable $\varepsilon(t)$ decreases when Q_i is increased whatever the law of adsorption which gives rise to the specific amount $Q_r(t)$ measured at a time t.

Threshold of percolation

The threshold of percolation is defined by $\varepsilon(t) = 0$. This corresponds to the specific amount of adsorbed polymer:

$$Q_r^c(t) = \sqrt{Q_i}\sqrt{2\bar{M}_n/m_{Si}^o\mathscr{A}}\,(1 - \sqrt{\bar{M}_n/8Q_im_{Si}^o\mathscr{A}}) \qquad (21)$$

or

$$Q_r^c(t) \simeq \sqrt{Q_i}\sqrt{\bar{M}_n}\,(3.3 \times 10^{-4})$$

for small values of $\bar{M}_n$ and large values of Q_i. For example, $Q_r^c(t) = 0.33$ g g^{-1} when $Q_i = 10$ and $\bar{M}_n = 10^5$ g mol^{-1}; $Q_r^c(t)$ is independent of the law of adsorption. The quantity Q_r^c may also be expressed as a function of the variable Q_r^m instead of $\bar{M}_n^{1/2}$:

$$Q_r^c(t) = (Q_i/\kappa)^{1/2}Q_r^m(1 - Q_r^m/4\sqrt{Q_i}\kappa) \qquad (22)$$

with the following definition of the parameter κ:

$$\kappa = M_b m^o_{Si}(A_T/\sigma_e)^2/2\mathscr{A}\varepsilon_a^2 \qquad (23)$$

It may be more convenient to express the variable $\varepsilon(t)$ as a function of Q_i, Q^c_r and $Q_r(t)$:

$$\varepsilon(t) = (1 - \sqrt{1 - Q_r/Q_i})^2/(1 - \sqrt{1 - Q^c_r/Q_i})^2 - 1 \qquad (24)$$

for $Q_r > Q^c_r$.

SATURATED ADSORPTION

Silica–siloxane mixtures are usually studied in the case where the saturation of the silica surface is completed. Then, at equilibrium, the fraction $\phi_{Si}(t \to \infty)$ is set equal to unity. Thus, according to equation (12):

$$\phi_p(t \to \infty) = Q^m_r/2Q_i \qquad (25)$$

Since ϕ_p is smaller than or equal to unity, Q_i must obey the condition $Q^m_r/2 \leqslant Q_i$ to obtain a saturated adsorption. Considering also equation (8), the specific amount Q^s_r of polymer adsorbed when the silica surface is saturated is expressed as:

$$Q^s_r/Q_i = [1 - (1 - Q^m_r/2Q_i)^2] \qquad (26)$$

or

$$Q^S_r = Q^m_r(1 - Q^m_r/4Q_i) \qquad (27)$$

As is expected, the highest value of Q^S_r is Q^m_r while the lowest value is $Q^m_r/2$ because polymer chains are considered as bifunctional units; in this last case, all particles are connected by polymer chains.

Comparison with experimental results

According to equation (27), the specific amount of adsorbed polymer is a function of the initial amount Q_i. Experimental values of Q^S_r range from 0.5 to 2.5 g g^{-1}. Variations of Q^S_r are shown as a function of Q^m_r in *Figure 2*; they are drawn according to equation (27). The quantity Q^m_r is expressed according to:

$$Q^m_r = A_T\sqrt{M_b}\sqrt{M_n}/\sigma_e\varepsilon_a\mathscr{A} \qquad (28)$$

by applying the law of adsorption $\langle r_c \rangle = \varepsilon_a\sqrt{N}$; Q^m_r is equal to the quantity Q^l_r defined by equations (4) and (5). Then, equation (27) becomes analogous to the empirical equation (1) when the ratio $Q^m_r/4Q_i$ is given small values. There is no more saturation of the surface when the inequality $Q^m_r > 2Q_i$ is satisfied ($\phi_{Si} < 2Q_i/Q^m_r$).

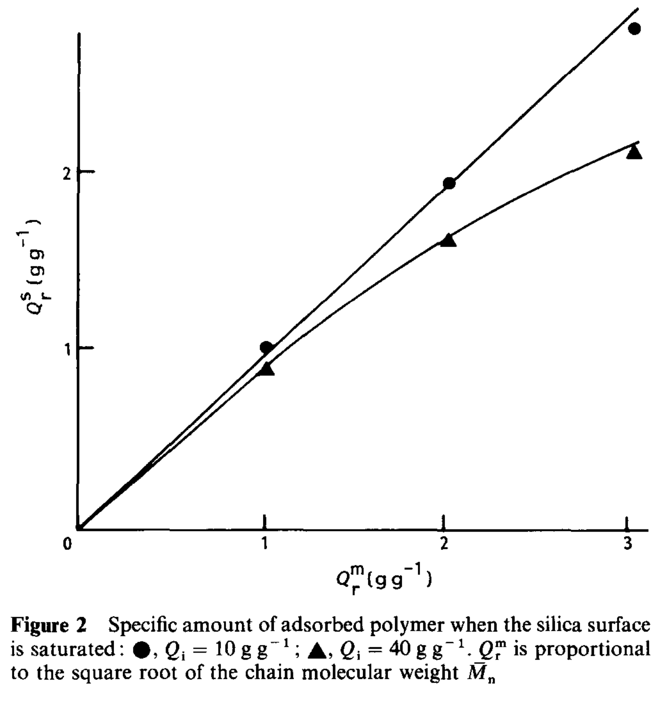

Figure 2 Specific amount of adsorbed polymer when the silica surface is saturated: ●, $Q_i = 10$ g g^{-1}; ▲, $Q_i = 40$ g g^{-1}. Q^m_r is proportional to the square root of the chain molecular weight $\bar{M}_n$

PERCOLATION THRESHOLD AND SATURATED ADSORPTION

It is of interest to determine values of parameters which correspond to both a saturated adsorption and the threshold of percolation. The fraction $\phi_p(t)$ obeys both of the following relations:

$$\phi_p = Q^m_r/2Q^c_i \qquad \text{and} \qquad \phi_p = 1/f_c$$

It determines the value of the initial specific amount of polymer necessary to reach the percolation threshold and to obtain a saturated adsorption. These relations are combined to give:

$$\frac{Q^m_r}{2Q^c_i}f_c = 1 \qquad (29)$$

or

$$(A_T/\sigma_e\varepsilon_a)^2 M_b \bar{m}^o_{Si}/2\mathscr{A}Q^c_i = 1 \qquad (30)$$

This relation is independent of the chain molecular weight because the law of adsorption is given by $\langle r_c \rangle = \varepsilon_a N^{1/2}$; it leads to the numerical value of $Q^c_i = \kappa$.

Experimental result

If the average mass $\bar{m}^o_{Si}$ is set equal to 3.2×10^{-17} g, then the initial specific amount Q^c_i obeys the relation:

$$Q^c_i \simeq 70/\varepsilon_a^2 \qquad (31)$$

It is usually observed[5] that an infinite cluster is formed for $Q^c_i \simeq 20$; this result gives an estimate of the value of ε_a: $\varepsilon_a \simeq 1.9$. Correspondingly, the specific amount of adsorbed polymer is written as:

$$Q^{s,c}_r = Q^m_r(1 - Q^m_r/Q^c_i) \qquad (32)$$

and it is a function of the chain molecular weight. In the case where Q_i is smaller than Q^c_i the variable $\varepsilon(t)$ is expressed as:

$$\varepsilon(t) = Q^c_i/Q_i - 1 \qquad (33)$$

SOL–GEL AND GEL–SOL DIAGRAM

A diagram can be drawn to distinguish domains where a mixture forms an infinite cluster from domains in which the clusters formed have a finite size (*Figure 3*). To draw the diagram a value is given to the quantity Q^m_r by choosing a chain molecular weight M_n. For $Q_i < Q^m_r$, the specific amount of adsorbed polymer Q_r cannot be larger than Q_i (curve A) while in the case where $Q_i > Q^m_r$, the quantity Q_r cannot be larger than Q^m_r (curve B). Then, specific domains are defined in the following way (*Figure 3*).

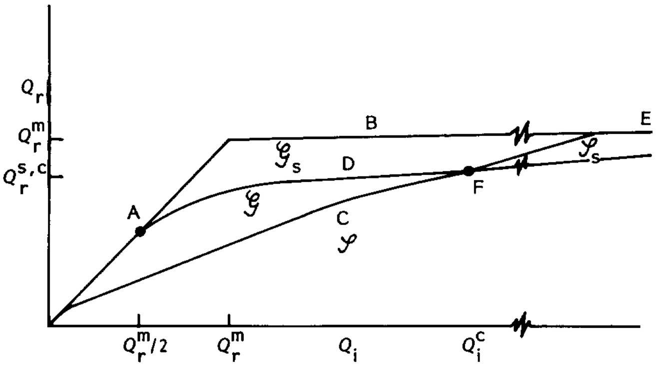

Figure 3 Sol–gel diagram of ideal silica–siloxane mixtures. Domain $\mathscr{T}$ corresponds to a sol behaviour; in domain $\mathscr{G}$ an infinite cluster is formed. Domain $\mathscr{G}_s$ corresponds to a gel behaviour and a saturated adsorption while domain $\mathscr{T}_s$ corresponds to a sol behaviour and a saturated adsorption. See text for discussion of curves A–D and point F. Along the curve E silica particles are fully coated

Domain $\mathscr{T}$. The function Q_r^c (Q_i, Q_r^m) determines the domain $\mathscr{T}$: $0 \leqslant Q_r^c \leqslant Q_r$ (curve C); in this domain, a given mixture behaves like a sol.

Domain $\mathscr{G}$. The function $Q_r^s(Q_i, Q_r^m)$ determines the domain $\mathscr{G}$: $Q_r^c \leqslant Q_r \leqslant Q_r^s$ (curve D); in this domain a given mixture behaves like a gel. The silica surface is not saturated. The upper limit of the values of Q_i corresponding to this domain is Q_r^c; the amount of adsorbed polymer is given by $Q_r^{s,c}(Q_i, Q_r^m)$.

Domain $\mathscr{G}_s$. For values of Q_r larger than Q_s^r and smaller than Q_r^m (or Q_i), a given mixture does not result from a simple percolation process. Particles are fully coated when $Q_r^m = Q_r$; they behave like a liquid.

Domain $\mathscr{T}_s$. This domain is defined for Q_i values larger than Q_i^c and values of Q_r in the range $Q_r^s \leqslant Q_r < Q_r^c$ (*Figure 3*). When the silica surface is saturated, it is impossible to create an infinite cluster; then a mixture behaves like a sol.

The point F, $[Q_r^c(Q_i, Q_r^m), Q_i^c]$, plays a crucial role in the diagram.

MODULUS OF ELASTICITY

An attempt may be made to give a qualitative expression of the contribution of linked chains to the modulus of elasticity by using quantities defined in the foregoing sections. The number ν_p of all chains which have two functions involved in the percolation process is expressed as:

$$\nu_p = Q_i \mathscr{A} \phi_p^2 / M_n \tag{34}$$

for 1 g silica. In the case of a saturated adsorption and without extracting any free chain, this number of chains in the reaction bath is:

$$\nu_p = (Q_r^m)^2 \mathscr{A} / 4 M_n Q_i \tag{35}$$

By taking the law of adsorption $\varepsilon_a N^{1/2}$ into consideration, the number ν_e of active segments per unit volume of polymer is supposed to be defined by:

$$\nu_e = \nu_p \varepsilon_a N^{1/2} \rho_p / Q_i \tag{36}$$

where ρ_p is the pure polymer density. According to the simplest model describing the property of elasticity of polymeric gels, the modulus E of elasticity should be written as[4]:

$$E/kT \propto A_T Q_r^m \rho_p / 4\sigma_e Q_i^2 \tag{37}$$

or

$$E \propto 54 \times 10^5 / \varepsilon_a Q_i^2 \tag{38}$$

in which E is expressed in dyne cm^{-2}, for $M_n = 3.6 \times 10^5$ g mol^{-1}.

Experimental result

The experimental value of E reported[5] for a silica–siloxane mixture characterized by $Q_i = 5$ is 4.5×10^5 dyne cm^{-2}; equation (38) gives 2.5 dyne cm^{-2} for the estimate of E. The value of E is increased by decreasing the initial specific amount of polymer in a mixture ($Q_i > Q_i^c$ with $Q_i^c = Q_r^m f_c / 2$). It is also increased by increasing Q_r^m, i.e. the chain molecular weight. However, within the framework of description of classical percolation, the modulus of elasticity should be expressed[6] as a function of the variable of gelation ε:

$$E \propto \varepsilon^3 \tag{39}$$

with

$$\varepsilon = (Q_i^c / Q_i - 1) \tag{40}$$

for a saturated adsorption and small values of ε. Thus, E is a function of $Q_r^m f_c$ which is independent of the chain molecular weight and the power of Q_i is three instead of two in equation (37). This expression of E is in great contrast to that predicted by equation (37). The property of elasticity will be analysed experimentally in a subsequent study to discriminate between these two expressions. More generally, the modulus of elasticity is a universal function of ε. The general expression (24) of ε must be used when the surface is not saturated.

VISCOSITY

Below the threshold of percolation, a given mixture can flow. Near the threshold the viscosity η_0 is expected to vary as:

$$\eta_0 \propto \varepsilon^{-s} \tag{41}$$

with $s = 0.75$ for a gel described in the critical domain and a logarithmic dependence of η_0 for a gel described in the classical range. The coefficient of viscosity can be measured from a creep compliance experiment.

The infinite cluster which is formed above the threshold of percolation cannot flow unless the external stress applied to the mixture is strong enough. The contribution to the enthalpy of cohesion due to the formation of hydrogen bonds between the silica surface and siloxane chains is estimated in the following way. For 1 g silica in a given mixture, the number of all chains which have their two functions involved in the percolation process is equal to $\mathscr{N}_p^i \phi_p^2$. In the case of a saturated adsorption the corresponding number of formed hydrogen bonds is expressed as:

$$\nu_B = (A_T/\sigma_e)^2 \sqrt{M_b} \sqrt{M_n} / 4\sigma_e \varepsilon_a \mathscr{A} Q_i \tag{42}$$

The corresponding enthalpy is equal to:

$$\Delta H_B = 4.5/330 \varepsilon_a Q_i \tag{43}$$

ΔH_B is expressed in J m^{-2}; $\bar{M}_n$ is set equal to 3.6×10^5 g mol^{-1}. No quantitative experimental results concerning the energy of cohesion of silica–siloxane mixtures have been reported until now.

TREATED SILICA SURFACE

When a partial chemical treatment is applied to the silica surface the quantity Q_r^c is unchanged. The quantity Q_i^c is a function of the extent τ of the treatment:

$$Q_i^c(\tau) = (1 - \tau)^2 Q_i^c \qquad (44)$$

Then, for a given initial amount of polymer Q_i, the modulus of elasticity is written as:

$$E \propto [Q_i^c(1 - \tau)^2/Q_i - 1]^3 \qquad (45)$$

The ratio may become smaller than unity when the extent τ of the treatment is increased; then, no infinite cluster is created.

CONCLUSION

Gel-like structures which arise from the mechanical mixing of silica with siloxane chains are induced by a well defined elementary mechanism of adsorption; this corresponds to the formation of hydrogen bonds. The full immersion of silica particles in a siloxane melt leads to a specific law of polymer adsorption when the mineral surface is saturated. The quantitative description given to the kinetics of surface saturation also results from this well defined elementary mechanism. This work shows that a percolation framework can be used to attempt to describe gel-like properties of silica–poly(dimethylsiloxane) mixtures. Although the possible formation of large loops is ignored, this classical description of percolation permits relevant variables to be related to one another: the initial amount of polymer, the amount of adsorbed layer and the chain molecular weight. The main features predicted by this model will be compared with new experimental results concerning swelling and elasticity properties in a subsequent work.

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