Characterization of chain binding to filler in silicone–silica systems

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(Received 10 December 1984)

Extraction of polymer from mechanically blended poly(dimethylsiloxane)–silica mixtures was conducted at room temperature using chloroform. The amount of silicon still bound to silica after removal of the polymer solution was studied as a function of the average chain molecular weight. A multiple-link structure of binding sites of PDMS chains onto the plain surface of silica is proposed from the analysis of results.

(Keywords: silicone–silica systems; polymer adsorption; poly(dimethylsiloxane)

INTRODUCTION

The mechanical properties of industrially used rubbers are often known to be due to mineral fillers added to the bulk polymer as well as to the viscoelastic behaviour of the organic component. Any bulk silicone, for instance, has a tensile strength much too low to be of much use as a pure gum; hence reinforcement is very important for technological applications of silicone rubbers. However, the use of fillers in the preparation of materials displaying expected mechanical properties is still largely empirical, since interactions involved between the different components are not well understood at the molecular level.

In the case of poly(dimethylsiloxane)–silica mixtures the precise knowledge of the polymer/filler interface is still an open problem. The purpose of this paper is to attempt to characterize silica–silicone interactions; the principle of the experimental approach was to start from a basic silicone–silica system prepared by mechanical mixing; then, a thorough extraction of the free polymer part was conducted with chloroform, at room temperature; finally, the amount of PDMS left bound to silica was determined. An attempt to characterize silica–silicone interactions is developed from the observed dependence of the amount of bound polymer upon the chain molecular weight.

EXPERIMENTAL

Materials

The poly(dimethylsiloxane) samples were commercially available polymers. They were characterized by their weight average molecular weight $\bar{M}_w$ and their number average molecular weight $\bar{M}_n$ (*Table 1*); it must be noted that they have about the same polydispersity index.

Fumed silica was bought under the reference Aerosil 150 and used without any surface treatment. According to the manufacturer, the BET surface area is 150 ± 15 m^2 g^{-1} and there are 1.8 free silanol groups per 100 Å^2. The average primary particle size is said to be 140 Å but these elementary spheres are covalently associated into clusters as soon as they are synthesized; the average equivalent diameter is then about 700 Å. These clusters are possibly linked to one another through hydrogen bonds to form larger particles (up to several dozen microns) which break easily under mechical stress.

A two roll stainless steel mill was used to incorporate the mineral into the bulk polymer at room temperature. The milling was performed as long as needed to form a sample looking homogeneous, i.e. a material without any trapped air bubbles; 15 min was an average order of magnitude of the duration of this operation. The composition of the obtained material was defined by the weight to weight polymer/silica ratio Q_i. For the present study two sets of samples were used, Q_i being equal to 10 and 5 (respectively, 10 and 20 parts of silica per 100 parts of silicone). The solvent was RP Normapur chloroform (99.2 to 99.6% $CHCl_3$, 0.0005% acidity in HCl, 0.0500% H_2O) without further purification.

Polymer extraction

The starting mixtures were divided in pieces of a few millimetres in size whatever their physical aspect; then, 1.5 g of the obtained sample was placed in a glass vessel along with 50 ml of solvent for two weeks; this preparation was kept at room temperature and subjected only to gentle manual agitation several times a day. At the end of this time, the liquid phase (a polymer solution) was pumped out with a pipette as completely as it could be without obviously taking away any part of the 'solid' phase. This set of operations was repeated twice. For the pipette work part it must be noted that the chloroform density is superior to that of the polymer/filler complex in the earlier stages, whereas the later ones display the opposite situation (the pumping of the liquid phase is then easier).

The product obtained after the third extraction was finally vacuum dried at 55°C for 2 days; the constancy of the mass as a function of time was taken as a criterion for the complete elimination of $CHCl_3$.

Residual polymer ratio

The quantitative observation of polymer chain binding was done using a parameter Q_r defined as the amount of residual polymer per unit mass of silica; Q_r was determined from the product obtained after three successive extractions. Two ways were used to determine values of the ratio Q_r of the amount of polymer still bound to mineral particles, after removal of the free polymer part with the solvent, over the initial amount of silica.

0032-3861/85/081231-03$03.00

Table 1 Average molecular weights of polymer samples

Sample reference	M_w	M_n	I_p
V 20	3200	1850	1.73
V 100	9300	5200	1.8
V 6390	75100	38700	1.94
V 6160	76400	43700	1.75
V 73280	155000	90000	1.72
V 89970	159000	89000	1.79
V 500000	236000	130000	1.81
V 884500	291000	156000	1.87
F B	606000	362000	1.67
CMT 580	3.6×10^6		

The first way was based on gravimetric measurements; weights of the samples were measured before and after extractions assuming that no silica was taken away along with the elimination of the polymer solution; this procedure was posteriorly justified in the case of samples keeping a solid shape from the beginning to the end of extractions.

The second way was based on microanalysis used to perform measurements of carbon ratios from final products. The two sets of measurements were in fair agreement with each other; however, the largest discrepancies were mostly observed with the original samples keeping no well defined shape in the solvent (powder or grease); in that case some silica was extracted with the dilute polymer solution and the real amount of silica remaining in the end product was lower than the initial weight introduced in the mixture. It is the reason why the following analysis and interpretation of results will be based on carbon ratio measurements, only.

CHAIN BINDING CHARACTERIZATION

Results

For the two series of experiments ($Q_i = 10$ and $Q_i = 5$), the amount of polymer fixed on one gram of silica is given as a function of the number average chain molecular weight $\bar{M}_n$ in the *Table 2* and illustrated in *Figure 1*. The outstanding feature of this graphic representation is the linear correlation of the experimental points: it is valid over the whole range of chain molecular weights investigated. The parameters of the linear regression done with all the experimental points are: slope $= 4.68 \times 10^{-6}$, origin ordinate $= 0.196$, correlation coefficient $= 0.984$.

Chain binding model

The model proposed to describe the binding of PDMS chains onto the silica surface comes from the observed linear law just described; the increase of the molecular weight of the polymer induces a proportional increase of the amount of adsorbed chains onto the silica surface.

(i) The proportionality between Q_r and $\bar{M}_n$ is interpreted as indicating that the number of PDMS chains n_f bound to one gram of silica is a constant, over the whole molecular weight interval considered in the linear plot; $n_f = 2.82 \times 10^{18}\ \mathrm{g}^{-1}$ is the slope of the straight line. The proportionality property is given further analysis.

(ii) We assume that binding of PDMS macromolecules occurs through a single complex site, only; macromolecules have a uniform probability to be attached to silica whatever the chain molecular weight. The number of available chain binding sites per gram of silica is supposed to be equal to n_f. Let $f(N)$ be the distribution function of PDMS chains in a sample; N is the number of monomeric units in a chain; m_p is the molecular weight of one monomeric unit. Then, the number average molecular weight is known to be defined by:

$$\bar{M}_n = \frac{\int N f(N) m_p \mathrm{d}N}{\int f(N) \mathrm{d}N} \tag{1}$$

and the ratio Q_r of the amount of polymer still adsorbed on silica, after removal of the free polymer part with the solvent, over the initial amount of silica is expressed as:

$$Q_r = \frac{\int n_f N f(N) m_p \mathrm{d}N}{\int f(N) \mathrm{d}N} = n_f \bar{M}_n \tag{2}$$

(iii) The hypothesis of single-site chain binding necessarily implies that the binding site has a multiple-link structure involving numerous monomeric units. From the specific surface area of silica ($150\ \mathrm{m}^2\ \mathrm{g}^{-1}$) it is possible to derive the average area σ_f of one binding site:

$$\sigma_f = 5.4 \times 10^3\ \text{Å}^2$$

Also, the number of possible links per unit area of silica v_l is supposed to be equal to the known number of free silanol groups per unit area:

$$v_l = 1.8 \times 10^{-2}\ \text{Å}^{-2}$$

Accordingly, the possible number of non-covalent bonds f involved in the multiple-link structure of the binding site of a PDMS macromolecule is easily calculated:

$$f = \sigma_f v_l = 97$$

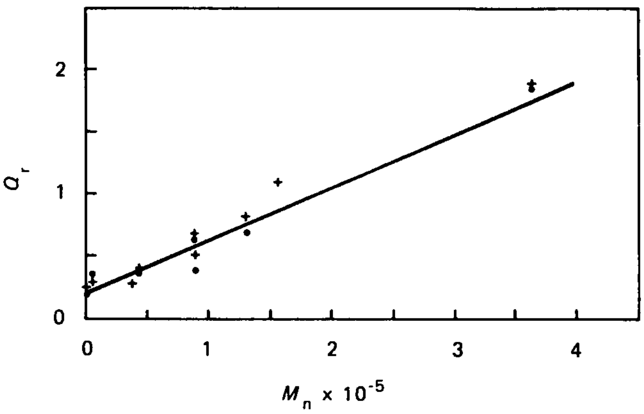

Figure 1 Amount of polymer fixed on silica as a function of the number-average chain molecular weight

Table 2 Residual polymer/silica ratio as a function of chain length

$\bar{M}_n$	Q_r ($Q_i = 10$)	Q_r ($Q_i = 5$)
1850	0.22	0.23
5200	0.36	0.30
38700		0.28
43700	0.38	0.39
89000	0.64	0.68
90000	0.39	0.53
130500	0.69	0.82
156000		1.10
362000	1.86	1.92

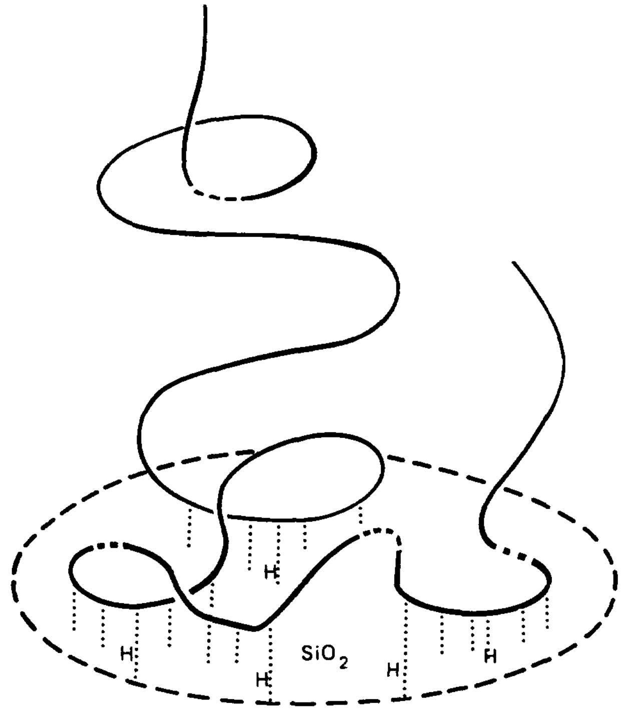

Figure 2 Schematic representation of the single-site chain binding model

(iv) It is worth pointing out that the average number of monomeric units N_e in a PDMS viscoelastic submolecule is about equal to 10^2; while the average size of this submolecule is:

$$R_S \simeq \sqrt{C_\infty \times 10^2 \times 2} \times 1.5\ \text{Å} \simeq 52\ \text{Å}$$

(the characteristic ratio of PDMS chains is known to be $C_\infty \simeq 6$); therefore, f is not very different from N_e, and the average size R_S is not very different from the linear size of the chain binding site $\sigma_f{}^{1/2} = 73$ Å. Therefore, it turns out from the foregoing estimates that silicon macromolecules are attached onto the silica surface through a chain segment comparable in size with a viscoelastic submolecule, with a probable slight flatness induced by the binding process ($R_S < \sqrt{\sigma_f}$); this chain segment is not necessarily an end side of a chain.

Variation of the initial ratio Q_i

The foregoing proposed analysis was reinforced by changing the ratio Q_i (polymer/silica) in the initial mixture from $Q_i = 10$ to $Q_i = 5$. The purpose of this variation was to prove that the binding mechanism does not depend upon the silica concentration in the mixture as long as this concentration is not too high. Residual polymer ratios obtained from the mixture characterized by the initial ratio $Q_i = 5$ are in fair agreement with measurements performed on the mixture characterized by the initial ratio $Q_i = 10$. Accordingly, it is suggested to consider that the binding of silicon onto the silica surface is an intrinsic phenomenon.

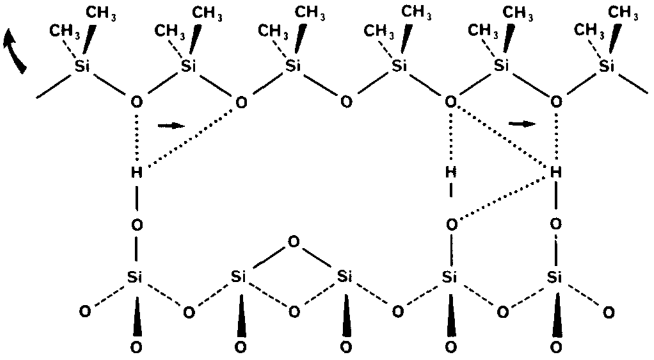

Figure 3 Illustration of the multiple-link structure of the chain binding site

CONCLUSION

Coherent data obtained from solvent extraction experiments performed at room temperature on systems prepared from a mechanical mixing, yielded information relative to the silicone–silica interface. The simplicity of the experimental law of variation of the residual polymer to filler ratio *versus* chain length has been straightforward interpreted on the basis of a spread chain adsorption site model for the fixed molecules (*Figure 2*). The interaction between any macromolecule and silica is supposed to take place through a multiple-link structure; the area of this chain binding site is ~5400 Å^2, corresponding to about 100 silanol groups which are supposed to form hydrogen-bonds with oxygen atoms of the polymer skeleton. Consequently, the chain binding site must not be pictured as a rigid lattice but rather as a dynamic system consisting of bonds which form and dissociate, permanently; although hydrogen-bonds are not considered as tight links, their large number makes the fixation of the chain quite strong (*Figure 3*).

Finally, it is worth emphasizing that this study dealt with chain adsorption from bulk polymer in which silica has been dispersed by mechanical mixing; this type of mixture has not been extensively studied to our knowledge, while polymer adsorption from a solution has been widely characterized in order to establish firmly experimental laws[1,2]. These two phenomena should be distinguished from each other on the basis of time scales and topological constraints; but at last the space organization of the polymer phase bound to the mineral surface might be represented by the same model: this could result from further comparison between the two adsorbed systems. Furthermore, silanol groups may also be involved in a complex way through binding of polystyrene chains on silica; corresponding study has been recently reported about this adsorption process taking place from a polymer solution[3].

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