

Elastomeric Composites. I. Silicone Composites

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ABSTRACT: The reinforcement of poly(dimethylsiloxane) (silicone rubber) imparted by different types of fillers was investigated. Three different techniques of incorporation of silica were compared: the usual blending process, *in situ* filling process, and introduction of spherical colloidal silicas (Stöber silicas). In addition, results obtained with other types of fillers—layered silicates and fibrous clays—were dis-

cussed. The role of filler is assessed essentially through the mechanical properties of the silicone composites. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 93: 2095–2104, 2004

Key words: reinforcement; elastomers; silicone rubbers; silicas; sepiolite

INTRODUCTION

Elastomeric materials are often compounded with reinforcing fillers to improve their mechanical properties. The effectiveness of a filler depends on filler characteristics such as size and shape of the particles and, more significantly, on the strength of polymer–filler interactions.^{1–3} These interactions increase the effective degree of crosslinking and such an effect is particularly strong if the particles have some reactive surface groups.

The extent of reinforcement increases as the particle size decreases, providing a higher polymer–filler interface and thus a more efficient interfacial bond, provided that a certain degree of bonding exists between the two phases. Reinforcing fillers usually have particle diameters in the range of 10 to 100 nm.

The shape of the inclusions can also play an important role with respect to the properties of the composites.^{4–6} The effect can be pronounced for highly anisotropic particles, such as needles, where a preferred orientation could modify the deformation behavior.

The state of dispersion is considered to be of crucial importance for the mechanical properties of the polymer composites. Filler aggregates tend to associate to form agglomerates, especially at high filler loadings. A question that often arises is whether the extent of reinforcement increases with unstructured fillers. This point will lead to further insight into the Payne effect,^{7–9} generally demonstrated through the analysis of the low strain dynamic mechanical properties and

characterized by a strong decrease of the storage modulus with strain amplitude. Indeed, the most commonly accepted representation to explain this effect is the destruction of filler networking upon application of the oscillatory shear.

The goal of this article is to review the reinforcement of poly(dimethylsiloxane) (PDMS; or silicone rubber) provided by different types of fillers: spherical particles, layered clays, and fibrous clays. In addition, the behavior of the organic–inorganic hybrid materials, prepared by an *in situ* sol–gel process and by the use of Stöber silicas, will be compared with that of composites filled by the usual technique of blending them.

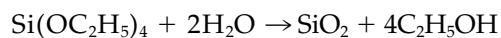
SILICA REINFORCEMENT OF SILICONE RUBBERS

In the unfilled state, PDMS elastomers generally have poor mechanical properties, which can be greatly improved by incorporation of mineral particles. PDMS is traditionally reinforced with silica and the interactions between the two phases is ensured by hydrogen bonds between the silanols on the silica surface and the oxygen atoms of the polymer chains. To meet application requirements, it is possible to monitor the interactions between the silica filler and the PDMS network by a surface treatment of the mineral. Two approaches of changing surface characteristics are frequently applied in the rubber industry: surface modification by physical adsorption of some chemicals on the filler surface and permanent surface modification by passivating part of the silanol groups present on the surface of the particle. With chemical modification, the polymer–filler interface can be tailored to a given application.

Because the usual technique of blending the filler particles into the polymer before crosslinking often

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leads to inhomogeneous systems because of the agglomeration of aggregates, a number of alternative novel techniques for incorporation of fillers have been developed. They include a sol-gel process to precipitate particles such as silica into the elastomeric matrix.¹⁰⁻¹⁹ This *in situ* technique for precipitating reinforcing silica can be carried out in three ways. In the first, the polymer is crosslinked and then swelled with tetraethyl orthosilicate (TEOS) which is hydrolyzed *in situ*. The overall reaction can be written as

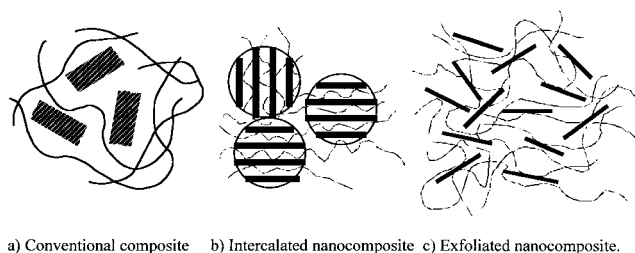


In the second way, the curing and filling processes take place simultaneously by blending hydroxyl-terminated PDMS chains with enough TEOS to end-link them and to generate the *in situ* filler. In the third way, silica particles are precipitated before the crosslinking process. In this case, the polymer end groups (vinyl groups, for example) do not react under the hydrolysis of TEOS.

The construction of inorganic/organic nanocomposites can also be achieved by the use of colloidal silicas to generate spherical nanoparticles with specific particle diameters and narrow particle size distribution. These particles are prepared by the hydrolysis and condensation of tetraalkoxysilanes in an alcoholic solution of water and ammonia using the Stöber process.²⁰ Spherical colloidal particles of silica with varying levels of vinyl functionality have been successfully dispersed into silicone polymers.²¹ The authors have demonstrated that, at sufficient loading levels, they provide mechanical reinforcement comparable to that of traditional fillers.

LAYERED SILICATE REINFORCEMENT OF SILICONE RUBBERS

In polymer-layered silicate nanocomposites based on smectite clays, the filler is present in the form of platelets of one to a few nanometers thick to hundreds to thousands nanometers long. Depending on the polymer-layered silicate interactions, three main types of composites may be obtained when a layered clay is dispersed in a polymeric medium (Scheme 1): (1) microcomposite or phase-separated composite, where the layered silicate acts as a conventional filler; (2) intercalated nanocomposite, in which one or several polymer chains are inserted between the silicate layers leading to a regular multilayer morphology; or (3) exfoliated or delaminated nanocomposite. The dispersion in the polymer matrix of 1 nm thick layers constitute the reinforcing phase of the exfoliated structure. This structure is of particular interest because it leads to a large polymer-filler interface and thus to the



Scheme 1 Schematic representation of the three types of polymer-layered silicate composites.

most dramatic changes in various properties of the resulting material.²²⁻²⁴

The clays are usually rendered organophilic through ionic exchange of the sodium interlayer cation with an organic cation, most often a bulky alkylammonium, which plays the role of a surface modifier. By increasing the interlayer spacing and making the clay more compatible with organic polymers, these alkylammonium ions allow molecules or polymer chains to diffuse between the layers. The nature of the organic cation has a significant effect on the resulting morphology of the nanocomposite.

Various polymers and different techniques to achieve matrix-filler compatibilization have been successfully used in the synthesis of polymer-layered nanocomposites. Such nanocomposites display substantial improvements in mechanical and physical properties including increased moduli, strength, and heat resistance and decreased gas permeability and flammability.

The generic term "layered silicates" refers to natural clays such as montmorillonite but also to synthesized layered silicates such as magadiite, mica, laponite, and fluorohectorite. Both types of clays have been used in the synthesis of silicone composites.²⁵⁻²⁸ The use of clays in PDMS has been reported by Burnside and Giannelis^{25,27} and by Wang et al.²⁶ In the work of Burnside and Giannelis, the nanocomposites were synthesized by sonicating a silanol-terminated PDMS ($M_w = 18,000-19,000$) with an organically modified montmorillonite. The crosslinking reaction was carried out at room temperature by adding tetraethyl orthosilicate (TEOS) as the crosslinking agent and tin 2-ethylhexanoate as catalyst. Mixing under sonication and addition of water were used to facilitate dispersion and obtain exfoliated nanocomposites. No mention has been made about the improvement in mechanical properties brought about by the addition of clay. Wang et al.²⁶ prepared intercalated nanocomposites by mechanically dispersing a hexadecylammonium-exchanged montmorillonite in a hydroxyl-terminated PDMS ($M_w = 68,000$). The mixture was heated for 8 h at 90°C, then cooled to room temperature, and TEOS and dibutyltin laurate were added. The intercalated

structure was verified by the increase in the interlayer spacing and the composites exhibit substantial improvement in tensile strength compared to that of the unfilled elastomer.

This article reports new insights into the clay reinforcement of silicone rubbers based on a different formulation than that already reported. Our samples were obtained by the hydrosilylation reaction (i.e., the addition of a silyl function $-\text{SiH}$ to an unsaturated $\text{C}=\text{C}$ bond). End-linking processes using α,ω -bifunctional polymers of known molecular weight reacting with adequate multifunctional reagent are widely used to obtain elastomeric networks with structures expected to be as close as possible to ideal. Nevertheless the reaction between hydroxyl-terminated PDMS with TEOS is difficult to control and, to be efficient, requires a larger amount of TEOS than the stoichiometric equivalent. On the other hand, the presence of clay somewhat depressed the cure kinetics and the extent of cure.

FIBER REINFORCEMENT OF SILICONE RUBBERS

As already mentioned, the aspect ratio (length/width) of the particles is also expected to affect the properties of the final materials. Acicular fillers such as fibers or nanotubes,^{29–31} characterized by two dimensions in the nanometer range, yield materials with exceptional mechanical properties only in the direction of the fiber as a result of the high anisotropy and high orienting capability of this type of particle.

In this work, nanocomposites based on PDMS and micronized sepiolite (Pangel S9) are investigated. The acicular morphology of the sepiolite particles, combined with a high density of silanol groups along the particle, is expected to favor the interaction of this type of filler with the oxygen atom of the PDMS chains.

MECHANISMS OF FILLER REINFORCEMENT

The increase in stiffness imparted by an active filler to an elastomer involves first a hydrodynamic effect arising from the inclusion of rigid particles and an increase in the crosslinking density created by polymer–filler bonding. In the absence of polymer–filler interaction as in the case of systems with inactive filler (silica-filled hydrocarbon rubber, for example) only hydrodynamic reinforcement is expected. In that case, a coupling agent is often incorporated to enhance the degree of interaction between the filler and the polymer chains.

The inclusion of rigid filler particles is quantitatively taken into account by the Guth–Gold equation³² given by the following expression:

$$G = G_0(1 + 2.5\varphi + 14.1\varphi^2) = G_0X \quad (1)$$

where G_0 is the modulus of the matrix and φ is the volume fraction of filler.

This equation is based on Einstein's equation³³ for the viscosity of a suspension of spherical rigid particles:

$$\eta = \eta_0(1 + 2.5\varphi) \quad (2)$$

where η and η_0 are the viscosities of the suspension and the matrix, respectively.

Guth and Gold generalized the Einstein concept by adding the quadratic term to account for interaction between particles. Guth³⁴ showed that for asymmetric rodlike particles eq. (1) may be replaced with

$$G = G_0(1 + 0.67f\varphi + 1.62f^2\varphi^2) \quad (3)$$

where f is the shape factor of the rod defined as the ratio of particle length to width. This equation must be regarded as largely empirical, using variable constants to fit the theoretical curve to experimental data.

Because the anisotropic character is important in some fillers such as fibers or layered silicates, a shape factor has to be taken into account in predicting nanocomposite modulus, with an effective volume fraction larger than the theoretical one.

The mechanical properties of the elastomer are modified more than by means of a mere addition of hard particles to a soft matrix. An additional contribution to the reinforcement effect arises from molecular interactions between the polymer and the filler. This interaction leads to an increase in the effective degree of crosslinking and can be evaluated by equilibrium swelling and by measurements of chain orientation (from birefringence or infrared dichroism). In fact, at intermediate strains, the increase of the modulus imparted by an active filler may be regarded as attributed to the product of two factors:

$$G = G_0XY \quad (4)$$

where X involves from the inclusion of rigid particles in a nonrigid matrix accounted for by the Guth–Gold expression [eq. (1)] and Y arises from filler–matrix linkages.

The equilibrium swelling analysis of elastomer vulcanizates is well known to provide access to the number of effective network chains per unit volume of rubber. For a filled vulcanizate, it should reflect not only the effects of chemical junctions but also the density of polymer–filler attachments. In the case of a good adhesion between particle and elastomer, the equilibrium swelling ratio of the rubber phase in the filled material (Q_{rubber}) decreases with the amount of

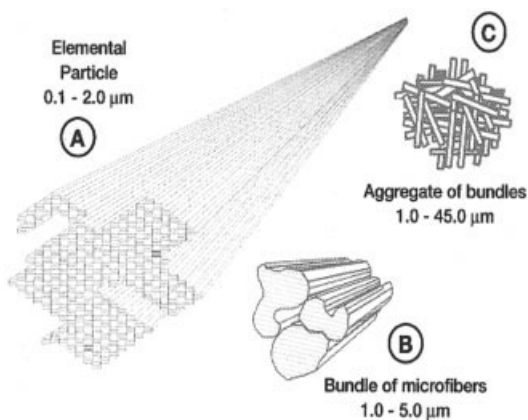


Figure 1 Sepiolite morphology (from Grupo Tolsa, Madrid, Spain).

filler. Because the filler does not swell, the equilibrium swelling ratio of the rubber alone is expressed by the following quantity:

$$Q_{\text{rubber}} = \frac{Q - \varphi}{1 - \varphi} \quad (5)$$

The advantage of the swelling measurements over the use of stress–strain measurements for estimating additional crosslinking provided by the presence of filler is that they are free from hydrodynamic reinforcement.

EXPERIMENTAL

Materials

For the standard process of blending the filler particles into the polymer before the crosslinking reaction, we used a pyrogenic untreated silica (specific surface area of $300 \text{ m}^2 \text{ g}^{-1}$ from Degussa AG, Frankfurt, Germany) and a treated one [surface treatment performed by Rhodia Silicones (Lyon, France)], to improve its dispersion in the PDMS matrix. In the rubber, silica is actually composed of stable structures of approximately 50 nm , which cannot be broken. These structures, called aggregates, may stick together to form loosely bonded agglomerates in the case of a poor dispersion.

Before incorporating the Stöber silicas into silicone elastomers, it is necessary to transfer the dispersion to a solvent compatible with the polymer. The solvent used in this study was 4-methyl-2-pentanone. After removing ammonia and residual water by distillation, the 4-methyl-2-pentanone was added to the ethanol phase. In the final step, the ethanol was removed by distillation. The mean particle diameter was 85 nm , determined by dynamic light scattering and by AFM.

The clays used in this work [sodium–montmorillonite (Na–Mt) and organically modified versions (Cloisite 30B and Claytone 34)] were kindly supplied by Southern Clay Products (Gonzales, TX). Cloisite 30B is a bis(2-hydroxyethyl) methyl tallow ammonium montmorillonite (the tallow contains 65, 30, and 5% of C18, C16, and C14) and Claytone 34 is a dimethylditalow ammonium montmorillonite in which the tallow contains 70, 25, 4, and 1% of C18, C16, C14, and C12, respectively. The clays were heated for 12 h, at 80°C under vacuum before use, to remove residual water.

Sepiolite, which belongs to the structural family known as the phyllosilicates, is a hydrous magnesium silicate, with a crystal structure formed by two sheets of tetrahedral silica units bonded to a central sheet of magnesium atoms. Sepiolite particles, which exhibit a microfibrinous nature, stick together to form a bundle of fibers that can themselves form agglomerated structures (Fig. 1). Industrial processes, such as micronization and chemical modification processes developed by Grupo Tolsa (Madrid, Spain), disagglomerate the microfibrils, thus favoring interactions between sepiolite particles and polymer chains. Two different industrial processes can be applied to obtain micronized sepiolite: a dry or a wet one (Fig. 2). The Pangel S9 results from a wet process, which tends to separate the bundles of microfibrils (Fig. 2).

Synthesis of the elastomeric materials

The synthesis of the unfilled PDMS was carried out by mixing, for 15 min at room temperature, stoichiometric mixtures of precursor chains of hydride-terminated PDMS ($M_w = 17,200$) from Gelest (Morristown, PA) with 1,3,5,7-tetravinyl-1,3,5,7-tetramethylcyclotetrasiloxane used as the tetrafunctional crosslinking agent. The syntheses were performed in the bulk in the presence of platinum–divinyltetramethylsiloxane used as a catalyst. The reacting mixture was slowly cast into a

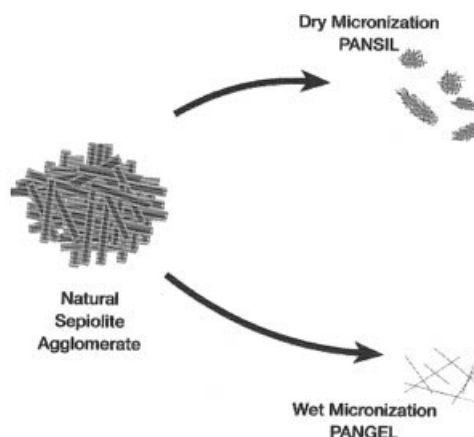


Figure 2 Industrial processes for sepiolite micronization (from Tolsa).

Teflon mold and cured at 80°C for 12 h. The films were extracted with toluene for 3 days to remove any unreacted materials. The sol fractions were between 3 and 5%.

In the *in situ* filling process, the dried PDMS films were allowed to swell in TEOS (Aldrich, Milwaukee, WI) in the presence of a tin catalyst, dibutyltin diacetate, present at 3 wt %. The swelling time determines the degree of TEOS absorption and thus the filler loading. Both the TEOS-swollen film and a beaker containing water were placed for 24 h into a desiccator maintained at a constant temperature (30°C), thus exposing the swollen film to saturated water vapor. The film was then vacuum-dried at 80°C for several days to constant weight to remove any alcohol generated from the reaction and also the remaining TEOS that has not been hydrolyzed. The amount of filler incorporated into the network was calculated from the weights of the films before and after the generation of the filler.

For the synthesis of films containing the colloidal silicas, a dispersion of 40 wt % particles in 4-methyl-2-pentanone was added to a mixture of precursor chains of PDMS and the crosslinking agent. After the mixture was stirred for 0.5 h at room temperature, the catalyst was added. The resulting mixture was cast into a mold and the solvent was allowed to evaporate overnight at room temperature. The crosslinking reaction was carried out at 80°C, as described above, then the film was placed under vacuum to ensure complete removal of the solvent.

The strategy used to prepare the PDMS samples filled with clay (organophilic montmorillonite or sepiolite) is the following. The ground clay was mixed with a small amount of hydride-terminated PDMS ($M_w = 17,200$) from Gelest, at room temperature under vigorous stirring at 300 rpm. The remaining amount of PDMS was progressively added and after the total addition of the polymer, which took about 1 h, an

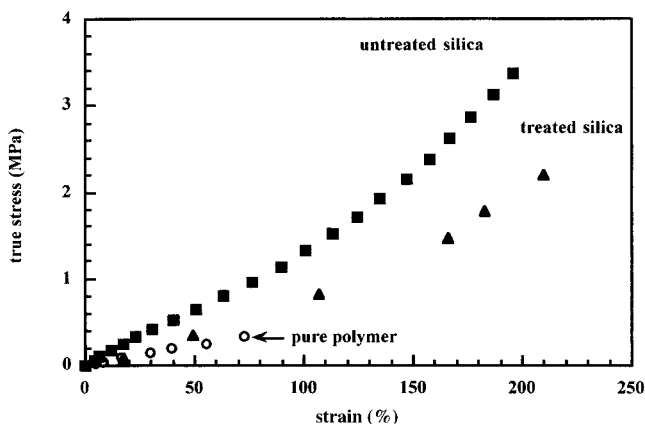


Figure 3 Stress-strain curves for pure PDMS and for blended silica-PDMS samples (filler content: 10 phr).

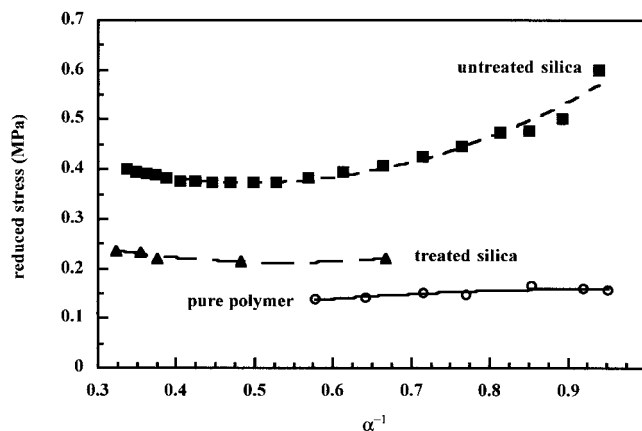


Figure 4 Reduced strain shown as a function of reciprocal elongation for pure PDMS and blended silica-PDMS composites.

adequate amount of 1,3,5,7-tetravinyl-1,3,5,7-tetramethylcyclotetrasiloxane, used as the tetrafunctional crosslinking agent, was incorporated into the system and mixed for 15 min. Then, platinum-divinyltetramethylsiloxane complex used as a catalyst was added. The resulting sample was slowly cast into a Teflon mold and cured at 80°C for 12 h. Solvent was also used to synthesize the clay-filled polymer. More precisely, the mineral phase was dispersed in toluene, which is also a good solvent for PDMS. Once the clay particles were swollen in the solvent, the polymer was added to the same solvent under stirring followed by addition of the crosslinking agent then the catalyst. After casting the film, the toluene was removed under vacuum at 80°C. Because no significant improvement in the physical properties was observed by the use of a solvent, the clay was commonly incorporated into polymer melts using high shear mixing and no solvent.

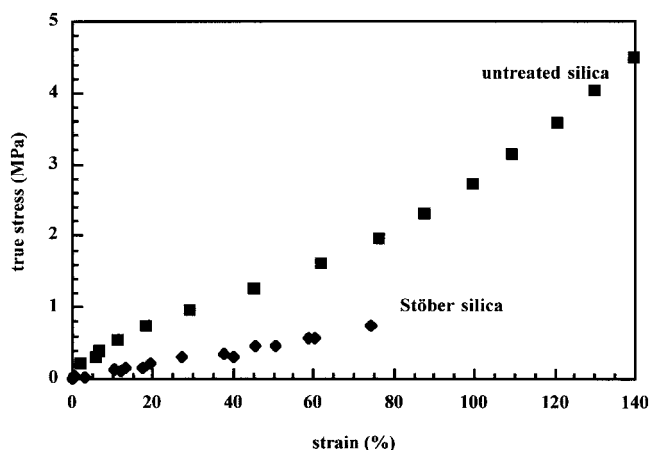


Figure 5 Stress-strain curves of PDMS composites having a filler content of 20 phr (untreated pyrogenic silica or Stöber silica).

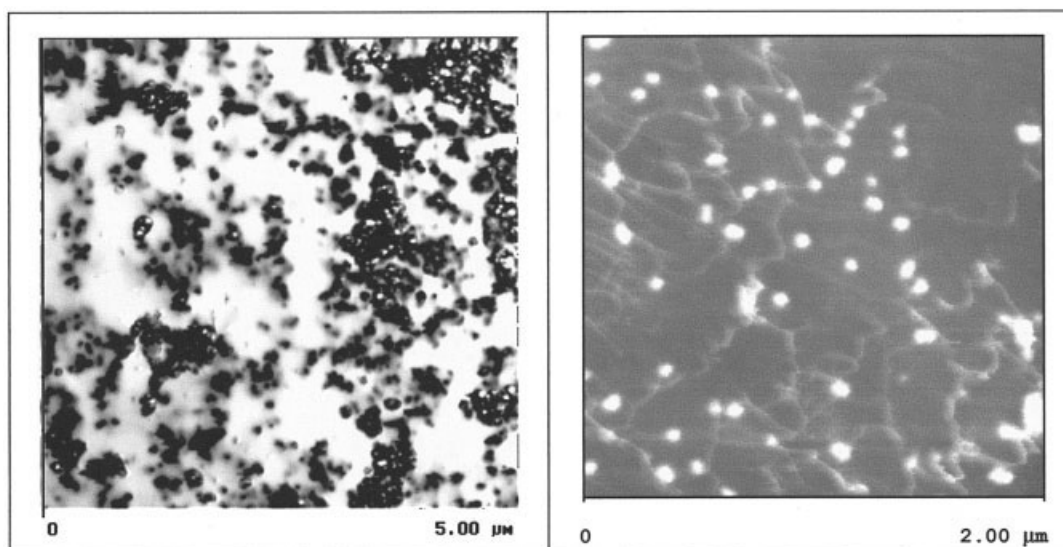


Figure 6 AFM phase image of PDMS networks filled with: (a) 20 phr of untreated fumed silica [Reproduced with permission from Polymer 2001, 42, 6259]; (b) 20 phr of Stöber silica.

Characterization

Measurements of mechanical properties and equilibrium swelling were carried out in the usual manner.

Stress–strain measurements reported here were carried out by simply stretching strips ($40 \times 10 \times 0.5$ mm³) between two clamps by means of a sequence of increasing weights attached to the lower clamp. The distance between two marks was measured with a cathetometer after allowing sufficient time for equilibration.

To determine the equilibrium swelling of the vulcanizate, a sample ($20 \times 10 \times 2$ mm) was placed in toluene. After 72 h at room temperature, the sample was removed from the liquid, the toluene was removed from the surface, and the weight was determined. The swelling ratio Q was also determined from the lengths of the sample in the unswollen and swollen states.

X-ray diffraction (XRD) was used to study the nature and extent of the dispersions samples filled with organophilic montmorillonites. The XRD patterns were obtained using an X'Pert Pro diffractometer (Philips, The Netherlands) at the Cu- K_{α} wavelength ($\lambda = 1.54$ Å).

Infrared spectra were recorded with a Magna 560 FTIR spectrometer (Nicolet Analytical Instruments, Madison, WI) with a resolution of 4 cm⁻¹ and an accumulation of 32 scans.

RESULTS AND DISCUSSION

Silica-filled PDMS composites

Tensile stress–strain curves were plotted of the unfilled network as well as of the samples filled with 10

phr (parts per hundred parts of rubber) of treated and untreated silica. The filled samples were prepared by the usual blending process. The data displayed in Figure 3 show that the incorporation of silica in PDMS leads to increases in modulus and extensibility. For the same filler loading, the increase in the modulus is much greater with the untreated silica, which exhibits a higher content of reactive groups than that of the treated one, thus pointing out the importance of bonding at rubber–filler interface and also of filler–filler interaction. In the case of the higher polar filler such as silica, in the absence of surface modification, even at low loadings, some degree of filler clustering may be obtained as a result of poor mechanical mixing. The rubber trapped within the clusters may increase the effective filler volume fraction, thus leading to higher moduli.

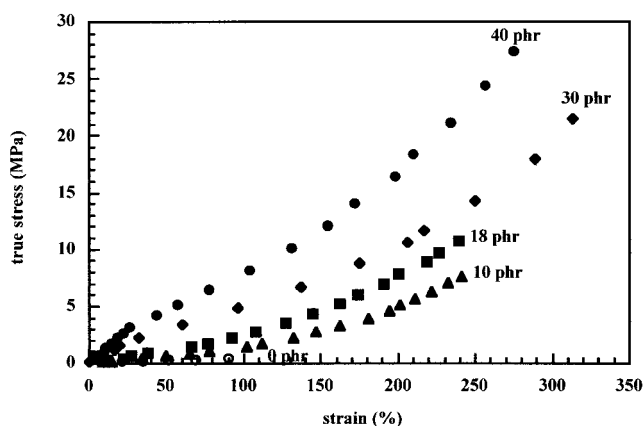


Figure 7 Stress–strain curves at room temperature for PDMS filled with *in situ* precipitated silica.

TABLE 1
Tensile Properties of the PDMS Networks Filled with *In Situ*-Generated Silica

Compound	Stress at 100% strain (MPa)	Stress at 200% strain (MPa)	Tensile strength (MPa)	Elongation at break (%)
Unfilled sample	—	—	0.43	91
10 phr SiO ₂	1.44	4.98	7.64	242
18 phr SiO ₂	2.49	7.86	10.70	240
30 phr SiO ₂	5.19	10.35	21.54	313
40 phr SiO ₂	7.99	16.38	27.34	275

Tensile results are displayed in the form of Mooney–Rivlin plot in Figure 4. The plot is based on the so-called Mooney–Rivlin equation:

$$[\sigma^*] = \sigma/(\alpha^2 - \alpha^{-1}) = 2C_1 + 2C_2\alpha^{-1}$$

where σ is the true stress (force divided by the deformed area of the sample), α is the extension ratio (ratio of the final length in the direction of stretch to the initial length before deformation), and $2C_1$ and $2C_2$ are constants independent of α . Whereas the reduced stress of the pure polymer exhibits an almost constant value, the reinforced composites show upturns in the reduced stress attributed to the limited extensibility of the short chains connecting filler particles. The sample filled with untreated silica displays a more pronounced upturn and additionally exhibits, at low strains, a strong decrease in the modulus attributed to the Payne effect, which will be confirmed later through the analysis of the low strain dynamic properties. The different behavior observed, at the same filler loading, results from a higher agglomeration of the untreated silica aggregates. The strong filler–filler interactions attributed to strong hydrogen bonding between silanol groups allow formation of strong agglomerated structures or clusters. In fact, the two additional effects, observed at low and high strains, are, to a certain extent, linked to shorter interaggregate distances in the untreated silica-filled PDMS network.

At a same filler loading (20 phr), the stress required for a given deformation is smaller for the colloidal-filled system than that for the polymer filled with a structured silica such as an untreated silica with a specific area of 300 m² g⁻¹ (Fig. 5). This different behavior can be partly ascribed to a lower polymer–filler interface in the PDMS network filled with the 85-nm particles. Most likely, however, the reason arises from the fact that, at the filler concentration used in this study, the Stöber silicas are homogeneously dispersed, in contrast to the case of the PDMS filled with untreated fumed particles where large agglomerates have been reported (Fig. 6). This phenomenon explains that the enhancement of the mechanical properties, which is attributed to the inclusion of hard particles, arises not only from the hydrodynamic effect

and polymer–filler interactions but also from the presence of filler–filler association resulting in a higher modulus. It is worth mentioning that the study by Kwan et al.,²¹ related to the use of colloidal silica for reinforcement in silicone elastomers, reported for 13 and 20 nm trimethylsilane-treated colloidal silicas, a viscosity of the filled systems remained similar to that of the neat polymer, even up to loading levels greater than 35% volume before increasing rapidly. Above this filler volume fraction, the viscosity reasonably follows that predicted by the Guth–Gold equation. The deviation from the ideal behavior increases as the size of the particles decreases. The authors explain their results by the fact that a smaller particle has a much greater specific area that can increase the probability of polymer–filler interactions, filler–filler association, and a bound rubber layer.

Stress–strain curves of the *in situ*-filled PDMS systems are shown in Figure 7. The large increases in modulus over the 0% silica sample reflect the high efficiency of the *in situ* precipitation of silica particles through the catalyzed sol–gel hydrolysis and condensation of tetraethoxysilane. Such a process is expected to provide silica with greatly improved reinforcing properties as a result of the small size of the particles and of the hydrophilic character of the filler surface, thus allowing strong interactions with the polymer

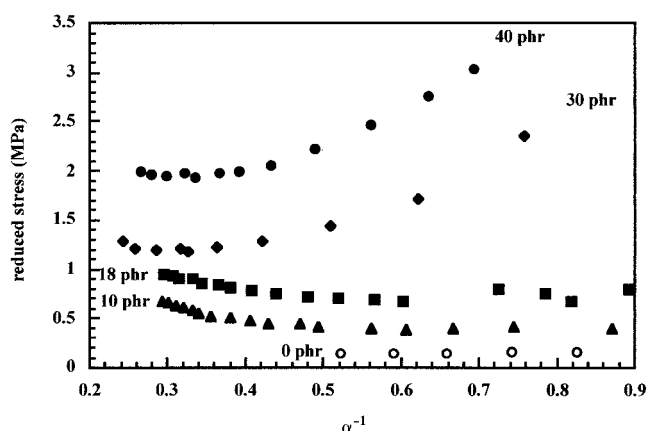


Figure 8 Mooney–Rivlin plots for the *in situ* silica-filled PDMS networks.

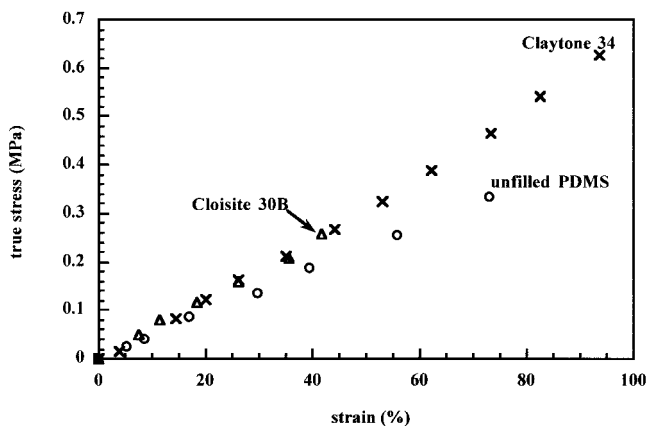


Figure 9 Stress-strain curves for PDMS filled with 10 wt % of Cloisite 30B and Claytone 34.

chains. However, these *in situ*-precipitated silica-filled networks offer not only high modulus but also good ultimate properties such as stress at rupture and maximum extensibility.

The tensile properties of the *in situ* silica-filled samples are shown in Table I. The stress at a given strain increases substantially above approximately 20 phr, which most likely corresponds to a point at which the silica network percolation begins.

As with conventional silica, the Mooney-Rivlin plots of the same composites (Fig. 8) display, above a filler loading around 20 phr, an initial decrease in the modulus followed, at high deformations, by an upturn in the modulus. Contrary to what was previously observed, however, the upturn at high deformations occurs at a higher strain above the percolation threshold. Most probably, above a certain amount of filler, the organic and mineral phases form interpenetrating networks with specific mechanical properties. This point is under investigation and will be the subject of a forthcoming report where the morphology of the reinforcing particles studied by small-angle X-ray scattering will complement the mechanical results.

PDMS-layered silicate composites

Stress-strain curves for the unfilled PDMS and the composites containing 10 wt % of modified clay (Cloisite 30B and Claytone 34) are shown in Figure 9. The two different clays lead to similar results, showing that the nature of the alkylammonium ion has no significant effect on the macroscopic properties of the final products. The extent of reinforcement provided by these clay particles is of the same order of magnitude as that obtained with 10 wt % of treated silica. Another important difference between silica and clay effects concerns the values obtained for the elongation at break of the final materials. Although the use of silica yields a large increase of the elongation at break, clays improve this property only very slightly with respect to the unfilled polymer. The rupture properties of filled elastomers have been associated with the phenomenon of "stress-softening," observed at high extensions, and characterized by a pronounced lowering in the stress when the vulcanizate is extended a second time.³⁵ This stress-softening process can be considered as a hysteretic mechanism related to an energy dissipated by the material during deformation.^{36,37} The extent of softening depends on filler-rubber bonding, which is very low in the case of a poor polymer-filler interaction. The weak improvement in the ultimate properties (stress and elongation at break) imparted by the incorporation of clay can be explained by the lack of interfacial adhesion between PDMS and the silicate particles.

X-ray diffraction (XRD) can be used to evaluate the spacing between the silicate layers. Intercalation of polymer chains, by maintaining the multilayer structure, allows the determination of the interlayer spacing, usually enlarged with respect to the pure organo-modified clay. The lack of diffraction peaks in the XRD diffractograms can suggest an exfoliated structure, although such a structure has to be confirmed by transmission electron microscopy analysis. Whereas the pure organophilic clays (Cloisite 30B and Claytone 34)

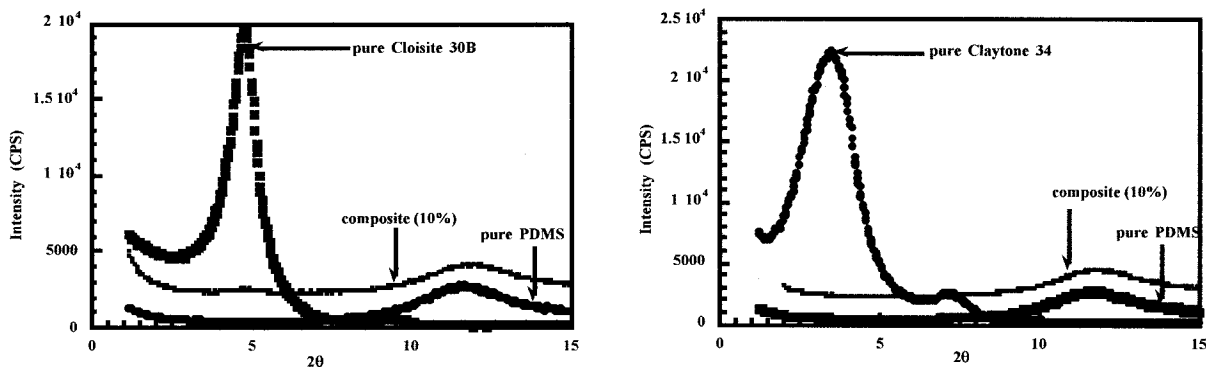


Figure 10 X-ray diffraction patterns for pure polymer, pure organomodified clays, and polymer composites.

are characterized by a strong peak located at $2\theta = 4.88$ and 3.53° , respectively, leading to layer spacing values of 1.83 and 2.50 nm, no diffraction peak appears in the XRD pattern of the composites (Fig. 10). The lack of an X-ray diffraction pattern led Burnside et al.²⁷ to conclude that the silicate layers are uniformly dispersed in the matrix, thus giving rise to an exfoliated or delaminated structure. In fact, the limits of the XRD equipment, essentially at very low angles, can yield misleading conclusions about the composite structure. On the other hand, the composites contain a small amount of clay and the XRD analysis is not sensitive enough to reveal the crystalline structure of the layered silicate.

Sepiolite-filled PDMS composites

The presence of silanol groups along the sepiolite particles as well as water molecules is evidenced by infrared spectroscopy. The infrared spectrum of sepiolite in the $3000\text{--}4000\text{ cm}^{-1}$ region exhibits absorption located, respectively, at 3689, 3620, and 3568 cm^{-1} associated with silanol stretching vibrations, where the lower wavenumbers indicate H-bonded species. The bands around 3420 and 3250 cm^{-1} are ascribed to water absorptions (Fig. 11).

The band located at 3568 cm^{-1} in the pure sepiolite spectrum is shifted to 3560 cm^{-1} when the clay particles are incorporated into the PDMS network, indicating an interaction between the OH groups and the PDMS chains.

Thanks to a routine available on the spectrophotometer, the infrared spectrum of the pure polymer can be subtracted from that of the composite, thus leading to the spectrum of the sepiolite in the polymer matrix. Besides the wavenumber shifts of the silanol groups, the wavenumbers associated with the water molecules are also modified (Fig. 12).

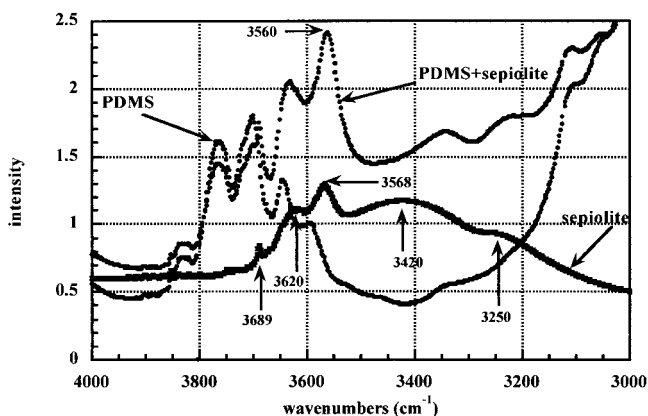


Figure 11 Comparison of infrared spectra of the $3000\text{--}4000\text{ cm}^{-1}$ region for sepiolite, PDMS, and sepiolite (5 wt %)-filled PDMS.

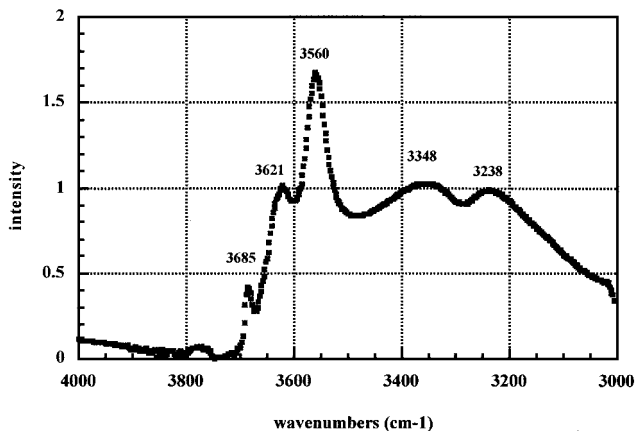


Figure 12 Difference spectrum between the composite and the pure polymer spectra.

Tensile stress–strain curves of PDMS and PDMS filled with sepiolite are shown in Figure 13. The data exhibit a progressive increase in the modulus and in elongation and stress at break with the filler loading.

Polymer–filler interactions are also evidenced through the equilibrium swelling behavior of the polymer composites. In the case of a good adhesion between particle and elastomer, the equilibrium swelling ratio of the rubber phase in the filled material (Q_{rubber}) decreases with the amount of filler. The decrease of the equilibrium swelling ratio of PDMS in toluene with the sepiolite loading, shown in Figure 14, reflects polymer–filler attachments increasing with the organic–inorganic interface. This behavior is typical of an adhering filler. Unbonded particles usually lead to equilibrium swelling ratios larger than that of the unfilled formulation indicating a dewetting of the particles and vacuole formation filled with solvent.^{38–40} Thus the reinforcement provided by sepiolite fibers arises mainly from polymer–filler interactions rather than from the shape of the particles.

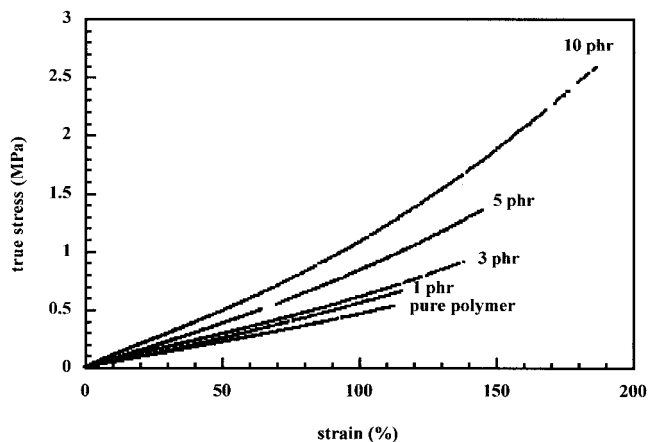


Figure 13 Stress–strain curves for pure PDMS and sepiolite composites.

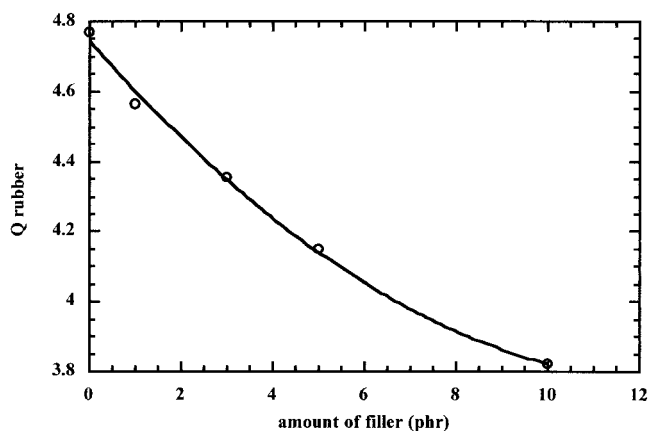


Figure 14 Dependency of rubber swelling in toluene on the sepiolite loading (in phr = parts per hundred parts of rubber).

CONCLUSIONS

Among the three types of reinforcement of silicone rubber imparted by silica particles, the *in situ* filling process (where the mineral phase is generated by the sol-gel process) is by far the most efficient. The modulus, ultimate stress, and extensibility increase with increasing filler loading. Moreover, larger increases are observed over the percolation threshold. Despite the presence of agglomeration that could result from insufficient mixing, improvement in mechanical properties is also achieved in conventional composites obtained by blending filler particles with polymer before the crosslinking process. As already demonstrated,³⁵ formation of aggregates and agglomerates is beneficial with regard to the energy dissipation and stress-softening effect. These effects have been shown to depend on strain amplification factors arising from the nondeformable character of the hard filler particles. A close relation has been established between the hysteretic phenomenon and the ultimate properties of the composite. That could explain why the ideal dispersion provided by the discrete, spherical particles yields to weak mechanical properties.

Another factor of great importance in the reinforcement of elastomers is the interaction between the polymer and the filler. The slight reinforcement obtained by the incorporation of layered silicates originates from the lack of interfacial adhesion between PDMS and clay particles. On the contrary, the interactions between the OH groups present along the sepiolite and the PDMS chains are responsible, more than the anisotropy of the particles, for the extent of reinforcement imparted by these nanofibers.

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