

# Reinforcement of poly(dimethylsiloxane) by sol-gel *in situ* generated silica and titania particles

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**Abstract.** The usual sol-gel process was applied to precipitate silica or titania particles in a preformed poly(dimethylsiloxane) (PDMS) network under the presence of dibutyltin diacetate used as a catalyst. The resulting structures of the reinforcing fillers were studied by transmission electron microscopy and small-angle neutron scattering. Stress-strain measurements in elongation and equilibrium swelling experiments revealed distinct behaviors mainly attributed to the nature and the size of the generated particles and to the formation, in the case of titania, of a filler network even at low filler loadings.

**Keywords:** nanocomposites, reinforcement, poly(dimethylsiloxane), silica, titania

## 1. Introduction

In the unfilled state, poly(dimethylsiloxane) (PDMS) elastomers have generally poor mechanical properties which can be greatly improved by incorporation of mineral particles. Uniformity of the dispersion and good interfacial adhesion between the matrix and the filler have a strong influence on the performance of the elastomeric material. PDMS is traditionally reinforced with silica and the interaction between the two phases is ensured via hydrogen bonds between the silanols on the silica surface and the oxygen atoms of the polymer chains. Although fillers can be incorporated by the usual technique of blending them into the polymer before cross-linking, a number of alternative novel techniques for incorporation of fillers have been developed. They include a sol-gel process to precipitate particles into the elastomeric matrix. This process produces a finely divided morphology of filler resulting in optically transparent materials. The formation of the inorganic component is carried out under mild synthetic conditions and involves

various alkoxides ( $[M(OR)_x]$ , where  $M = Si, Ti, Zr, Al...$  and  $R$  is an aliphatic group) that are hydrolyzed and condensed under either acidic or basic catalysis, in order to form  $M-O-M$  bridging units.

A series of previous investigations [1–7] has shown the feasibility of precipitating silica, titania or mixed silica-titania phases into PDMS networks. All these studies report significant property improvements in the hybrid composites with regard to the unfilled networks.

Although there are a number of ways to carry out the sol-gel technique to prepare hybrid organic composites, the method chosen in this paper is to synthesize the mineral phase in already crosslinked networks by using a synthetic protocol different from those previously reported in the literature. Additionally, the sol-gel approach developed for the *in situ* generation of silica into an elastomer is extended to the generation of titania by hydrolyzing a titanate instead of a silicate. PDMS networks filled with *in situ* generated reinforced particles are

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prepared and characterized through their morphological, mechanical and swelling properties in order to compare titania-filled materials with those filled with silica.

## 2. Experimental

### 2.1. Materials

PDMS having hydroxyl chain ends and a number-average molecular weight of 18 000 g·mol<sup>-1</sup> was obtained from Gelest (Morrisville, PA, USA). The catalysts: stannous-2-ethyl-hexanoate for the cross-linking reaction and dibutyltin diacetate for the sol-gel process were respectively supplied by Sigma and Aldrich. The alkoxides, tetraethoxysilane (TEOS) and titanium n-butoxide (TBO) were provided by Gelest (Morrisville, PA, USA) and Acros Organics (Geel, Belgium), respectively. All of these materials were used as received.

### 2.2. Synthetic aspects

In this study, unfilled PDMS networks are first prepared and are then swollen in the adequate alkoxide.

#### 2.2.1. Preparation of the unfilled PDMS networks

The unfilled networks are prepared from hydroxy-terminated PDMS by end-linking reactions using tetraethoxysilane (TEOS) as the cross-linking agent. In this method of network synthesis, a stoichiometric balance between ethoxy groups of the tetrafunctional alkoxysilane cross-linker and the hydroxyl chain ends of the hydroxyl-terminated PDMS precursor chains, should be required to get model networks characterized by constant junction functionality and known molecular weight between cross-links (close to the number-average molecular weight of precursor chains) [1, 2, 8–12]. Actually, networks prepared at stoichiometric conditions have an elastic modulus lower than that deduced from the molecular weight between cross-links and great soluble fraction (around 10%). This may be due to the volatility of TEOS thus reducing the amount of cross-linker required for the alkoxy-functional condensation reaction. Much greater ratios of cross-linker functions to chain ends than that required by stoichiometry have already been

used in the literature [13, 14] but a systematic study of the effect of excess of TEOS on the mechanical properties of networks synthesized from OH-terminated chains shows that a 50% excess (and not higher values as already reported) are enough to ensure correct modulus and reasonable soluble fraction. So, hydroxyl-terminated PDMS ( $M_w = 18\,000$ ) is mixed for half an hour with TEOS, in excess of 50%. A small amount of stannous-2-ethyl-hexanoate used as catalyst, is then added to the mixture under mechanical stirring just for 5 minutes to avoid cross-linking reaction during mixing. The reacting mixture is slowly cast into a Teflon mold and left for a few minutes at room temperature then at 80°C for one day for complete curing. The films are extracted with toluene for 72 hours to remove any unreacted materials. The sol fractions are between 4 and 5%.

#### 2.2.2. Preparation of the *in situ* filled PDMS networks

The next step for composite preparation involves swelling the unfilled extracted polymer network in a silicon alkoxide for silica or in a titanium alkoxide for titania generation. The inorganic precursor is TEOS for silica and titanium n-butoxide (TBO) for titania. In fact, titanium alkoxides have much higher reactivity than silicon analogues and the resistance to hydrolysis can be obtained by increasing the length of the alkyl chain [15]. Therefore, as in other studies [16, 17] titanium n-butoxide (TBO) has been chosen as the precursor of TiO<sub>2</sub> in the sol-gel process.

The two overall reactions can be summarized as shown in Equations (1) and (2):



For *in situ* precipitation of filler particles, the PDMS films are swollen in the alkoxide (TEOS or TBO) in the presence of a pH-neutral catalyst: dibutyltin diacetate (DBTDA) used at 3 weight percent. The swelling time determines the degree of alkoxide absorption and thus the filler loading. Both the swollen film and a beaker containing water are placed for 48 hours into a desiccator maintained at a constant temperature (30°C) thus exposing the swollen film to saturated water vapor.

The film is then vacuum-dried at 80°C for several days to constant weight in order to remove any alcohol generated from the reaction and also the remaining alkoxide which 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. As a result of lower viscosity, the rate of diffusion of TEOS is much faster than that of TBO in PDMS films, leading, at a given swelling time, to a much higher swelling ratio. As a typical example, a degree of swelling of 100% of the initial PDMS film requires a swelling time of about 10 min in TEOS and 1000 min in TBO.

Infrared spectroscopy has been used to follow the sol-gel process. In particular, we note a progressive reduction in intensity of absorption bands associated with the alkoxides during the hydrolysis process and a total disappearance of these bands after total reaction. On the other hand, silica formation within the preformed PDMS network can be followed in the infrared spectra of the silica-filled PDMS networks where it is seen that the bands associated with silica increase with the silica content in the composite

### 2.3. Characterization techniques

For the transmission electron microscopy (TEM), ultrathin sections were cryomicrotomed using a diamond knife at -140°C. The nominal section thickness was 100 nm. The samples were observed on a JEOL JEM 1230 Transmission Electron Microscope, operating at 80 kV.

Small-angle neutron scattering (SANS) were collected using the equipment PACE provided by the Laboratoire Léon Brillouin at Saclay (France). A wavelength between 4 and 20 Å can be used with a wavelength spread of  $\Delta\lambda/\lambda = 0.10$  and a sample-to-detector distance between 1 to 5 m. The scattering vector  $q$ , ranges between  $3 \cdot 10^{-3}$  and  $0.3 \text{ \AA}^{-1}$ .

Strips of unfilled and filled elastomers were used in the uniaxial elongation experiments carried out to obtain the stress-strain curves at equilibrium [18]. The nominal stress  $\sigma$ , was calculated from Equation (3):

$$\sigma = \frac{f}{A} \quad (3)$$

where  $f$  is the elastic force and  $A$  is the undeformed cross-sectional area and the reduced stress,  $\sigma^*$  was calculated from Equation (4):

$$\sigma^* = \frac{\sigma}{\alpha - \alpha^{-2}} \quad (4)$$

where  $\alpha$  is the extension ratio (ratio of the final length of the sample in the direction of stretch to the initial length before deformation).

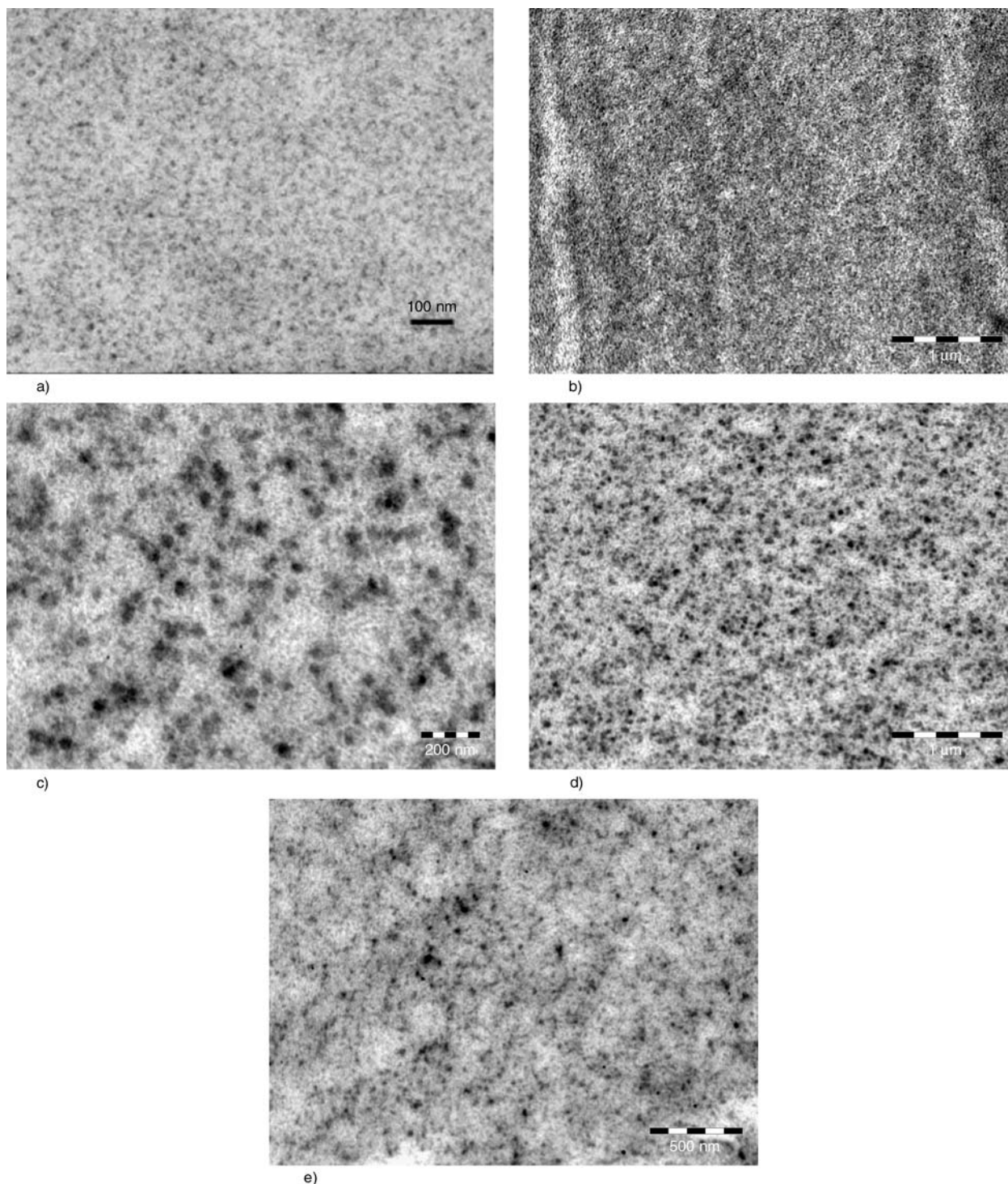
To determine the equilibrium swelling of the vulcanizate, a sample of 20 mm×10 mm×1 mm was put into toluene. After 72 h at room temperature, the sample was taken out of the liquid, the toluene removed from the surface and the weight determined. The swelling ratio,  $Q$ , was also determined from the lengths of the sample in the unswollen and swollen states.

## 3. Results and discussion

### 3.1. Filler characterization

Microscopy and scattering techniques are very useful for the characterization of generated filler structures. For filled materials formed by swelling an elastomeric network in alkoxides and subsequently polymerizing by the sol-gel technique, the generated particles are usually more finely dispersed than those prepared by a physical blending of preformed filler particles into polymers.

Figure 1 show TEM images of composites filled with SiO<sub>2</sub> (Figure 1a and 1b) or TiO<sub>2</sub> (Figure 1c –1e) particles *in situ* generated in already-formed PDMS networks. But although *in situ* precipitated filler particles seem to be uniformly dispersed in both cases, different morphologies are revealed. The diameter of the generated silica particles is seen to be much smaller than that of titanium dioxide particles. The composite containing 10 phr of SiO<sub>2</sub> (Figure 1a) shows an excellent dispersion of the mineral phase in the polymer with small silica domains around ~5 nm in diameter and rather diffuse interfaces. For the higher content, a fine morphology of the silicate structure is still obtained suggesting an interpenetrated polymer-silica structure and the sample may be regarded as microscopically phase separated but macroscopically uniform. TEM images of titania-filled PDMS composites indicate an obvious two-phase structure with particles approximately spherical in shape and



**Figure 1.** TEM images of PDMS composites filled with *in situ* generated particles: a) 10 phr of SiO<sub>2</sub>, b) 28 phr of SiO<sub>2</sub>, c) 12 phr of TiO<sub>2</sub>, d) 12 phr of TiO<sub>2</sub>, e) 25 phr of TiO<sub>2</sub>

diameters between 20 and 40 nm in size. The interface between the polymer and the particles is better defined than in the case of silica-filled systems and even at the lowest filler content (Figure 1c and 1d), the titania particles are almost connected in a branched network structure.

With the aid of concepts in fractal geometry, some aspects of the filler structure can be derived from small-angle scattering techniques. The scattering profiles of fractal objects are a power law of the type described by Equation (5):

$$I(q) = q^{-P} \tag{5}$$

where  $I$  is the scattered intensity at wave vector  $q$  and the exponent  $P$  allows to distinguish between mass and surface fractals [9, 10, 19]. A slope of  $-4$  in log-log axes, indicates that the system follows the Porod's law ( $P = D_s - 6$ ),  $D_s$  being the surface fractal dimension. The scatterers are, in this case, dense objects characterized by smooth surface fractal dimension ( $D_s = 2$ ). A value of  $P$  between  $-3$  and  $-4$ , is indicative of compact objects with fractally rough surfaces. If  $P < 3$ , scatterers are mass fractal objects with a fractal dimension  $D_f = P$ . A slope of  $-2$  suggests the presence of a polymeric structure.

As seen in Figure 2, the two types of composites yield distinctive small-angle scattering profiles. The slope of 3.3 obtained for the PDMS/TiO<sub>2</sub> composite indicated that the system is close to the Porod's law with uniformly dense objects characterized by almost rough surface fractal dimension. A correlation peak, observed at about 0.035 Å, associated with a characteristic length,  $L_{cor}$  of about 18 nm is observed for the silica-filled compound. In a previous study [7], the maximum of the correlation peak has been shown to shift to smaller  $q$  with the amount of filler. In our synthetic protocol, silica formation takes place in a swollen network, the network swelling ratio in TEOS,  $Q$ , determining the amount of filler. So the mean-squared end-to-end distance of a network chain in the swollen state,  $\langle r^2 \rangle_{sw}^{1/2}$  can be correlated to the swelling ratio  $Q$  through the Equation (6):

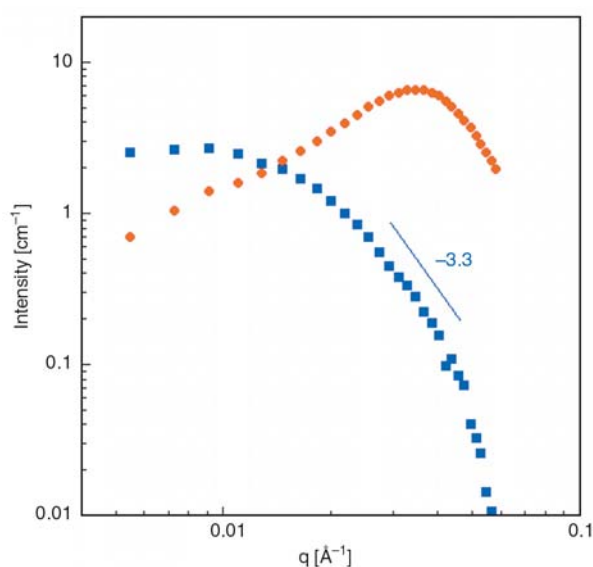
$$\langle r^2 \rangle_{sw} = Q^{2/3} \langle r^2 \rangle_0 = Q^{2/3} C_\infty n l^2 \quad (6)$$

where  $C_\infty$  is the characteristic ratio of a chain of  $n$  bonds of length  $l$  and  $\langle r^2 \rangle_0$  is the mean-squared end-to-end distance of a network chain in the unperturbed state.

A linear dependence of  $L_{cor}$  with  $\langle r^2 \rangle_{sw}^{1/2}$  has been found [7] which has led to the belief that the network itself imposes a length scale on the growth of the generated particles.

### 3.2. Stress-strain behavior

According to the different morphologies deduced from TEM and SANS, one would predict different mechanical properties for the two types of composites. As revealed in Figure 3a, a quite different tensile behavior is observed. At small strains, a higher level of reinforcement is obtained for the titania-filled sample while at higher strains, the silica-filled sample displays a sharp increase in stress. Plots of the reduced stress,  $\sigma^*$  against reciprocal elongation, are presented in Figure 3b. They show a marked decrease in stress attributed to the breakdown of the filler network upon application of the deformation and an upturn in modulus at high elongations for the PDMS/SiO<sub>2</sub> composite. The existence of a titania network even at low filler contents has been already revealed by TEM images. The upturn in the modulus observed in the silica-filled compound is attributed to non-Gaussian effects arising from the limited extensibilities of the network chains. It is somewhat the signature of a strong polymer-filler interface resulting from the interaction between the silanols present on the silica surface and the PDMS chains. On the other hand, the excellent dispersion as well as the small size of the particles offer a large interfacial area available for polymer-filler interactions. The PDMS/TiO<sub>2</sub> composite does not exhibit the upturn in the modulus which reflects less interfacial adhesion between the filler particles and the polymer chains. At large deformations, the mechanical behavior of the titania-filled composite is close to that of a thermoplastic polymer with a smaller strain dependence of the stress. This plastics-like stress-strain curve is probably related to the deformation of polymer chains confined between filler particles. These network chains, which are immobilized, behave as hard filler.



**Figure 2.** Small-angle neutron scattering of composites filled with 22 phr of generated particles: SiO<sub>2</sub> (●); TiO<sub>2</sub> (■)

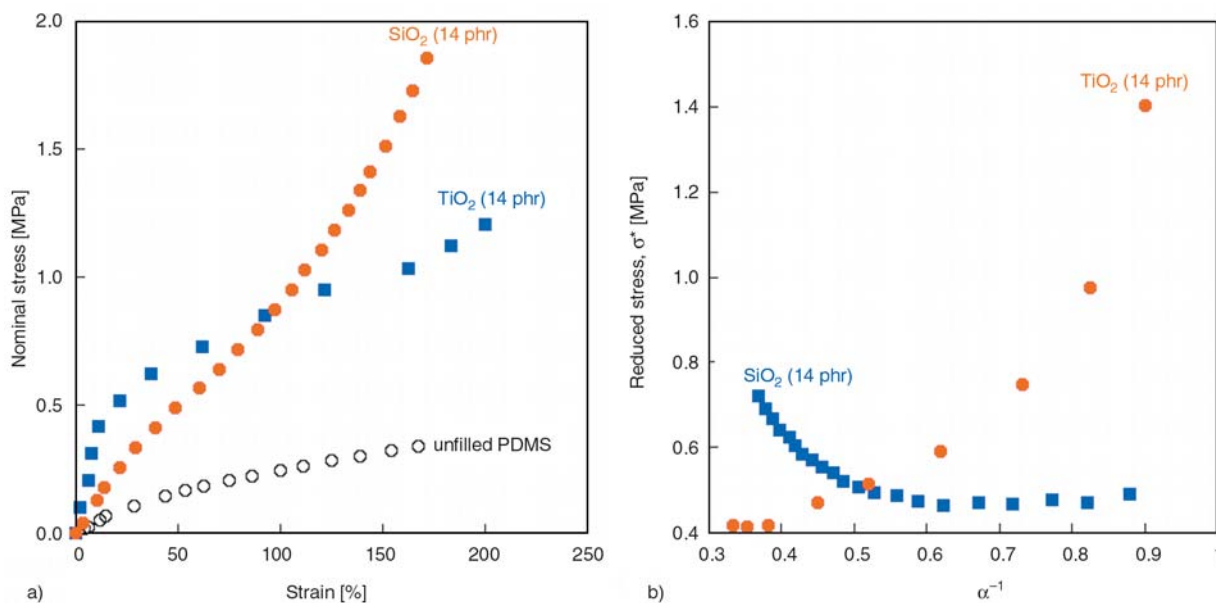


Figure 3. Comparison of the tensile behavior of PDMS composites containing a same amount of filler

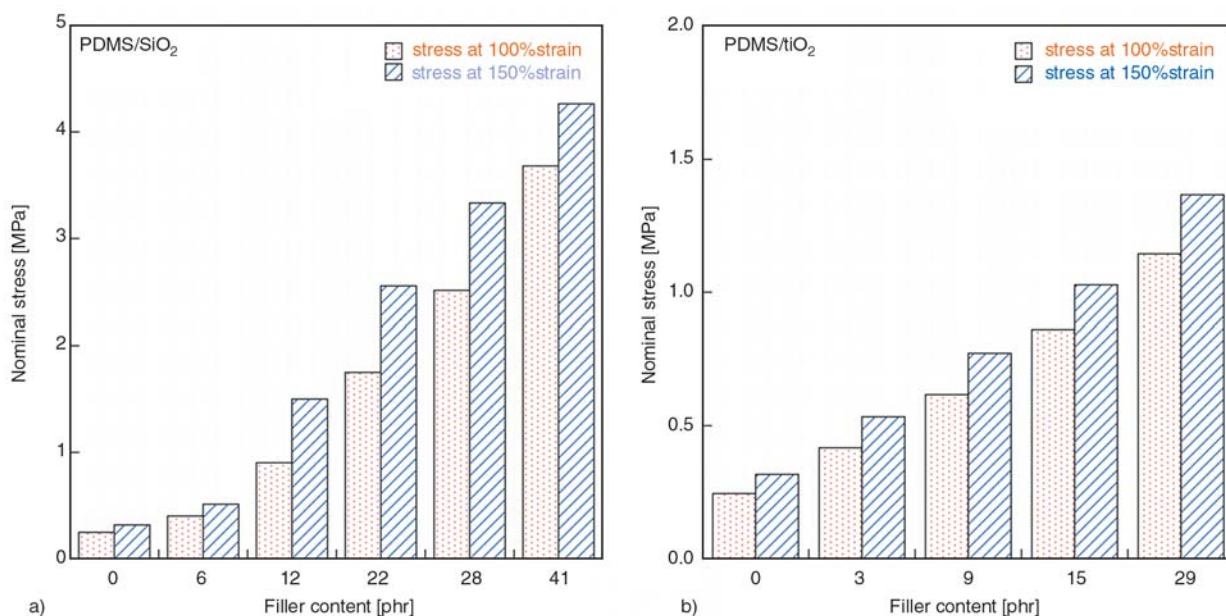


Figure 4. Tensile tests of the PDMS composites as a function of the amount of filler

Figure 4 shows the dependence of the stress at 100 and 150% strain on the amount of filler. The moduli of the composites are found to increase significantly with increase in amount of either type of filler with larger reinforcing effects at high elongations in the case of silica.

### 3.3. Swelling measurements

Besides the increase in the elastic modulus, another characteristic feature of filler reinforcement is a reduction in the ability of filled vulcanizates to swell in solvents. This restriction of swelling has

been associated with the degree of interaction between rubber and filler. More generally, the swelling procedure has been applied in filled vulcanizates to evaluate the number the total network chain density  $\nu$  ( $\nu = \nu_r + \nu_f$ , where  $\nu_r$  is the number of effective network chains in the unfilled rubber, and  $\nu_f$  is the number of additional chains produced by the bonding to the filler). This number,  $\nu_f$ , of filler-rubber attachments is expected to be strongly dependent of the surface chemistry of the reinforcing filler. The advantage of the swelling measurements over the use of stress-strain measurements for estimating additional cross-linking provided by

the presence of filler is that they are free from hydrodynamic reinforcement.

Under the assumption that the filler particles do not swell, one can calculate the equilibrium swelling ratio of the rubber phase,  $Q_r$  (see Equation (7)), from the equilibrium swelling ratio,  $Q$  of the composite ( $Q = V/V_d$ ,  $V$  being the volume of the sample plus solvent and  $V_d$  that of the dry sample) and the volume fraction of filler,  $\phi$ :

$$Q_r = \frac{Q - \phi}{1 - \phi} \tag{7}$$

According to Kraus [20, 21], the swelling for a large number of vulcanizates containing highly reinforcing fillers has been found to obey Equation (8):

$$\frac{Q_r}{Q_{r0}} = \frac{v_{r0}}{v_r} = 1 - \frac{m\phi}{1 - \phi} \tag{8}$$

where  $Q_r$  and  $Q_{r0}$  are the rubber equilibrium swelling ratios for the filled and unfilled samples, respectively,  $v_{r0}$  is the volume fraction of the unfilled rubber after swelling,  $v_r$  is the volume fraction of rubber in the gel of the filled vulcanizate after swelling and  $m$  is defined by Equation (9):

$$m = 3c(1 - v_{r0}^{1/3}) + v_{r0} - 1 \tag{9}$$

$c$  is a constant characteristic of the filler, but independent of the polymer, the solvent or the degree of vulcanization. This parameter arises from the man-

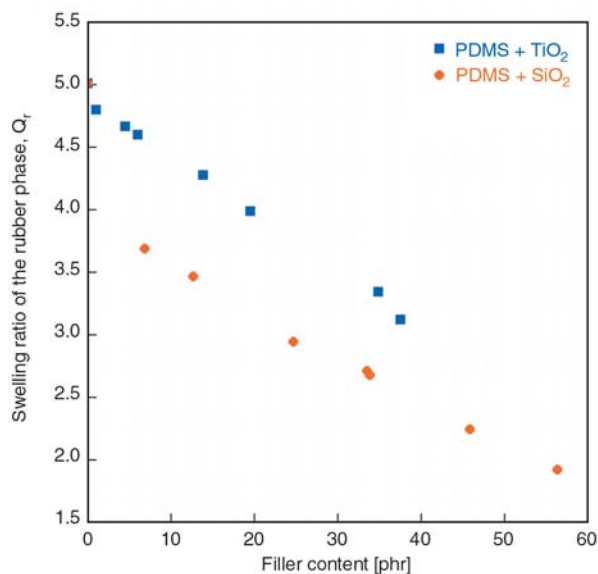


Figure 5. Dependence of rubber phase swelling on the amount of filler

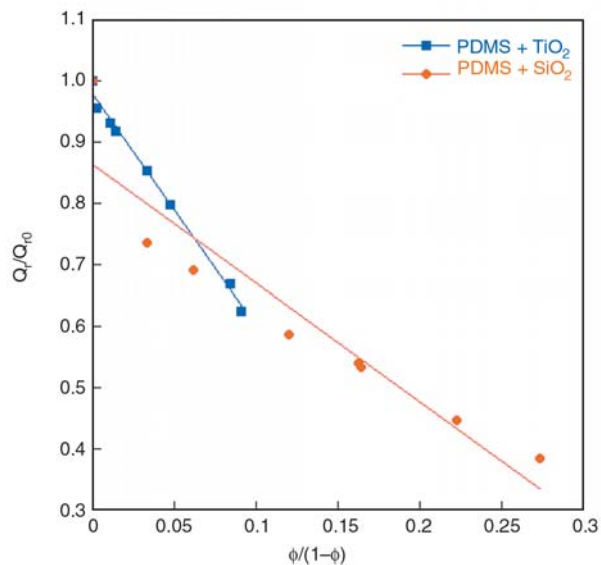


Figure 6. Plot of  $Q_r/Q_{r0}$  against filler loading expressed as volume ratio of filler to rubber

ner in which the local restriction of swelling varies with the distance from the surface.

Figure 5 displays the equilibrium swelling ratio of the rubber phase in toluene,  $Q_r$ . For each type of composite,  $Q_r$  decreases with the amount of filler, indicating a pronounced restriction in swelling in the filled samples. Nevertheless, at a given filler loading,  $Q_r$  is higher for the titania-filled samples reflecting less polymer-filler linkages. Representation of Equation (8) is reported in Figure 6 and leads to slopes equal to 1.9 and 3.8 for SiO<sub>2</sub> and TiO<sub>2</sub>, respectively. Values of the parameter  $c$  equal to 2.2 and 3.7 respectively can be extracted from the slopes according to Equation (9). The larger value obtained in samples filled with titania shows that restriction of swelling is extended to a larger distance from the particle surface with regard to silica analogs. This interpretation is consistent with the existence of confined polymer chains between titania particles as discussed in the previous section.

#### 4. Conclusions

The usual sol-gel technique for the *in situ* precipitation of reinforcing particles within an elastomer is applied for the generation of silica and titania as an extension of preliminary studies reported earlier. The two types of particles exhibit two distinct morphologies, two different polymer-filler interfaces

that influence the mechanical properties of the resulting materials.

Although all composites have mechanical properties that are very much improved compared to the unfilled network, the two types of particles impart to the resulting materials a quite different tensile behavior. The high level of stress obtained at small deformations for the titania-filled PDMS reflects the formation of a filler network at a relatively low filler content. On the other hand, the low strain dependence of the stress and the absence of upturn in modulus at large deformations lead to the belief that TiO<sub>2</sub> is less interacting with the elastomeric phase and the polymer chains are confined between filler particles.

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