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Reinforcement of natural rubber: use of in situ generated silicas and nanofibres of sepiolite

Liliane Bokobza[a,*], Jean-Paul Chauvin[b]

[a]Laboratoire PCSM, E.S.P.C.I., 10 rue Vauquelin, 75231 Paris Cedex, France
[b]Institut de Biologie du Développement de Marseille, Faculté des Sciences de Luminy, case 907, Université de la Méditerranée, 13288, Marseille Cedex 09, France

Abstract

Natural rubber composites containing silica particles generated in situ by the sol–gel process are investigated. The sol–gel processing is conducted before and after the cross-linking reaction. A good dispersion of the inorganic particles is obtained when the sol–gel reaction takes place after curing. In each case, the level of reinforcement is assessed from the mechanical and orientational behaviors. The reinforcement provided by in situ silica is compared with that obtained with anisotropic particles such as nanofibers of sepiolite.

Keywords: Filler; Sol–gel; Nanofibers

1. Introduction

Reinforcement of elastomeric compounds, defined as the simultaneous enhancement of the elastic modulus and the elongation at break, by addition of particulate filler, is probably one of the most important phenomena in material science and technology.

The increase in stiffness imparted by the filler particles involves a hydrodynamic effect which depends on the filler volume fraction, but the occlusion of rubber by the aggregate and the rubber trapped within the filler agglomerates may increase the effective filler volume. On the other hand, the shape factor (anisometry) also contributes to the increase in moduli [1–3].

Nevertheless, the most important contribution to the elastic modulus arises from polymer/filler interactions which can be increased if a good dispersion of the filler is achieved. These interactions depend on the surface characteristics of the particles (active sites and surface free energy) and also on the chemical nature of the polymer. Silica particles incorporated into a hydrocarbon rubber for example, results in the formation of a strong silica–silica network caused by the low polymer–filler and high filler–filler interaction. In that case, a chemical linkage between the silica and the rubber matrix, is needed to achieve the desired reinforcement. This chemical coupling is provided by a coupling agent which is usually a bifunctional silane [4,5].

Polymer–filler interaction leads to immobilization of chain segments on the filler surface whose mobility is reduced with regard to that of the polymer matrix. It will result a rubber shell in a quasi-glassy state with a thickness depending on the polymer–filler interaction and also on the surface area of the filler. Consequently filler surface chemical characteristics and its particle size may be considered as factors influencing the effective volume of filler [6].

Recently, the sol–gel technique that can generate in situ reinforcing particles, has been widely applied for the synthesis of hybrid organic–inorganic materials [7–19]. This process, which consists of hydrolysis and condensation of an alkoxysilane such as tetraethoxysilane (TEOS) is expected to yield small and well-dispersed particles within the polymer matrix. The structure and morphology of the filler depend on the reaction conditions and essentially on the nature of the catalyst.

This in situ technique for precipitating reinforcing silica can be carried out in two different ways. In the first, the polymer is cross-linked and then swelled with TEOS which is hydrolyzed in situ. The overall reaction can be written:

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* Corresponding author. Tel.: +33 140 79 45 15; fax: +33 140 79 46 86.
E-mail address: liliane.bokobza@espci.fr (L. Bokobza).

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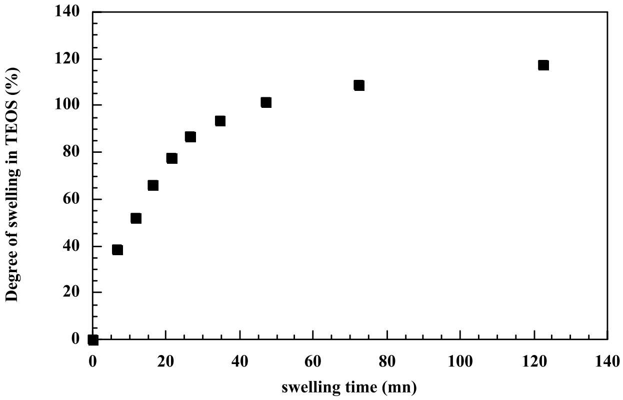

Fig. 1. Time dependence of the degree of swelling in TEOS of films of natural rubber around 500 μm thick.

$$Si(OC_2H_5)_4 + 2H_2O \rightarrow SiO_2 + 4C_2H_5OH$$

In the second way, silica particles are precipitated before the cross-linking process. In this case, the filling process can be carried out in the presence or absence a coupling agent.

In this paper, results obtained on natural rubber and on styrene–butadiene copolymers filled with in situ generated silica, will be discussed. In addition, the reinforcement provided by an other type of nanofillers (nanofibers of sepiolite) will also be presented.

2. Experimental section

2.1. Materials

The composites based on natural rubber, contain a fixed content of natural rubber (100 phr; phr = parts by weight per hundred parts of rubber) and similar amounts of sulfur (1.5 phr), cyclohexyl benzothiazole sulfenamide (1.5 phr), stearic acid (2 phr), zinc oxide (3 phr) and are thus expected to lead to a series of materials of the same chemical cross-linking density.

Styrene–butadiene rubber (Buna VSL 5025-0 from Bayer) contains 25 wt% of styrene unit and 50 wt% of vinyl configurations. It was compounded with sulfur (1.1 phr), cyclohexyl benzothiazole sulfenamide (1.3 phr), diphenyl guanidine (1.45 phr), stearic acid (1.1 phr), zinc oxide (1.82 phr).

All the mixtures were provided by Formix (Orléans, France).

Tetraethyl orthosilicate (99.999%) (TEOS) was purchased from Aldrich.

Sepiolite (Pangel B20 from Tolsa) was kindly offered by le Comptoir des Minéraux et Matières Premières (France). The pangel B20 is an organophilic sepiolite, obtained from pristine sepiolite by means of specific physico-chemical purification, micronization and chemical modification processes developed and patented by Tolsa. The micronization leads essentially to a disagglomeration of the bundles of microfibres thus favoring interactions between sepiolite particles and polymer chains. On the other hand, the hydrophilic surface of sepiolite was modified with surfactants in order to make it more compatible with low polarity polymers.

2.2. Synthesis of the elastomeric materials

2.2.1. Silica-filled materials

We have used two different approaches for the synthesis of silica-filled composites. In the first one, an unfilled film of NR is swollen with TEOS, which is then used to generate the inorganic phase by a pH-neutral catalyzed hydrolysis. In the second protocol, the sol–gel reaction is conducted before the cross-linking process.

In the in situ filling process carried out on cross-linked samples, the dried films of around 500 μm thick, were allowed to swell in TEOS (from Aldrich) in the presence of a tin catalyst, the dibutyltin diacetate, present at 3 wt%. The swelling time determines the degree of TEOS absorption and thus the filler loading. Fig. 1 displays the time dependence of the degree of swelling in TEOS at room temperature, of the cured sheets. The degree of swelling is equal to: $100[(M_s - M_d)/M_d]$, M_d and M_s being, respectively, the weight of the sample before and after swelling in TEOS. After 1 h, the degree of swelling does not increase anymore.

Both the TEOS-swollen film and a beaker containing water are 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 in order to remove any alcohol generated from the reaction and also the remaining TEOS 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. The rate of conversion of TEOS calculated from the ratio of the real filler loading against the amount of silica generated by assuming a total conversion of TEOS into silica, reaches 65% (21 phr) after 2 h.

In the second procedure, the gum (1 part) containing natural rubber and all the ingredients of formulation (zinc oxide, sulfur, stearic acid, cyclohexyl benzothiazole sulfenamide) was dissolved in toluene (5 parts) then mixed with a given amount of TEOS (calculated in order to get a filler loading of 30 phr) added with 3 wt% of dibutyltin diacetate. At this step, a silane coupling agent (the bis(3-triethoxysilylpropyl) tetrasulfide, commonly abbreviated ‘Si69’ (4 wt% relative to the weight of the polymer) was incorporated in order to increase the interaction between filler and rubber. But in order to point out the role of the silane, silica particles were also generated in the absence of Si69. A small beaker full of water was maintained on the top of the jar holding the reaction mixture. The jar is closed and the mixture is exposed for one day, under continuous magnetic stirring, to saturated water. The vulcanization

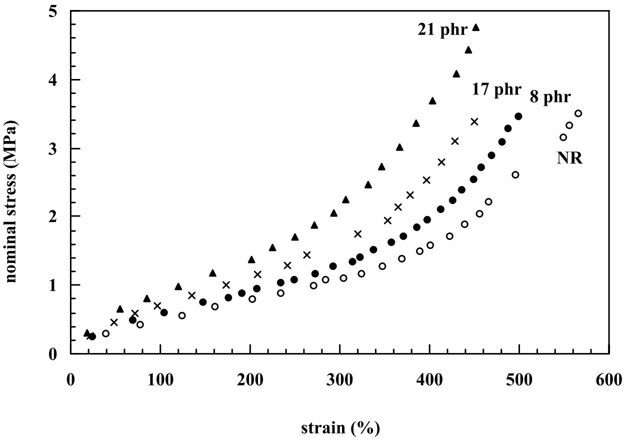

Fig. 2. Stress–strain curves for the unfilled NR and NR films filled with silica after the cross-linking process.

takes place after complete removal of toluene under vacuum at 50 °C.

2.2.2. *Sepiolite-filled materials*

Natural rubber and all the compounding reagents were dissolved in toluene then mixed for three days with 5 parts of sepiolite with vigorous stirring. The solvent in the resulting dispersion was carefully evaporated and the sample dried at 30 °C under vacuum.

The unfilled and filled samples were cured into plaques at 170 °C during 10 min under a pressure of 150 bar. The resulting films were around 500 μm thick.

2.3. *Characterization of the polymer composites*

Ultrathin sections with a thickness of approximately 120 nm were prepared at −160 °C with a cryo ultramicrotome (RMC MTX). Transmission electron microscopy (TEM) was carried out with a Leo 912 using a voltage of 100 kV for sepiolite sample and 80 kV for silica samples. Images were taken on films (Bergger MET 175) and digitalized with a scanner (AGFA Duoscan T 2500).

Stress–strain measurements reported here were carried out by simply stretching strips of $40\times10\times0.5\ \mathrm{mm}^3$ between two clamps by means of a sequence of increasing weights attached to the lower clamp. The distance between two marks is measured with a cathetometer after allowing sufficient time for equilibration.

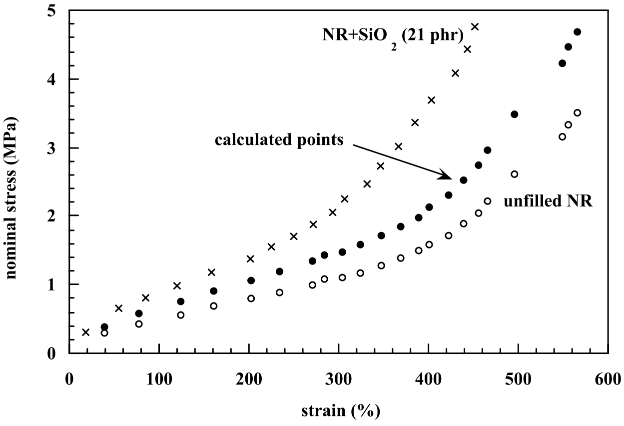

Fig. 3. Experimental and calculated stress–strain curves.

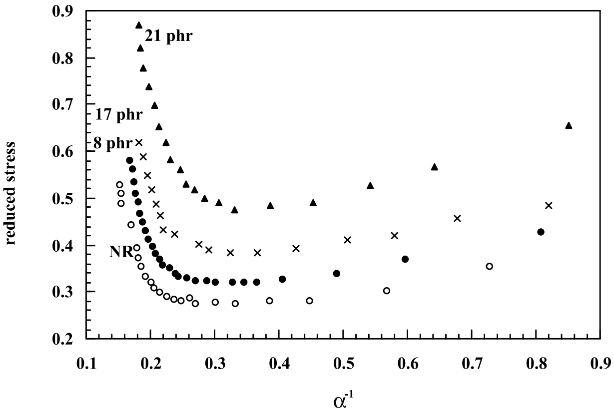

Fig. 4. Mooney–Rivlin plots for unfilled NR and in situ silica-filled NR composites.

To determine the equilibrium swelling of the vulcanizate, a sample of 20 mm×10 mm×2 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 weight swelling ratio, Q, was also determined from the lengths and the widths of the sample in the unswollen and swollen states.

Birefringence measurements were conducted as described elsewhere [20,21]. Briefly, they were obtained using an Olympus BHA polarizing microscope fitted with a Berek compensator. The thickness of each sample was determined with a micrometer comparator, with an average taken along the specimen.

3. Results and discussion

3.1. *Silica-filled materials*

Tensile stress–strain curves of the NR films submitted to the in situ silica filling process are illustrated in Fig. 2. At a given strain, the stress increases with the filler loading.

The basic processes and molecular mechanisms which contribute to the reinforcement of elastomeric materials have been widely discussed. The increase of the modulus imparted by an active filler may be regarded as the product of two terms: one involving a hydrodynamic effect arising from the inclusion of rigid particles. It is quantitatively taken into account by the Guth and Gold expression [22,23]:

$$G = G_0(1 + 2.5\phi + 14.1\phi^2) = G_0X \qquad (1)$$

where G_0 is the modulus of the unfilled matrix and ϕ is the volume fraction of filler. The second term involves an increase in the cross-linking density created by

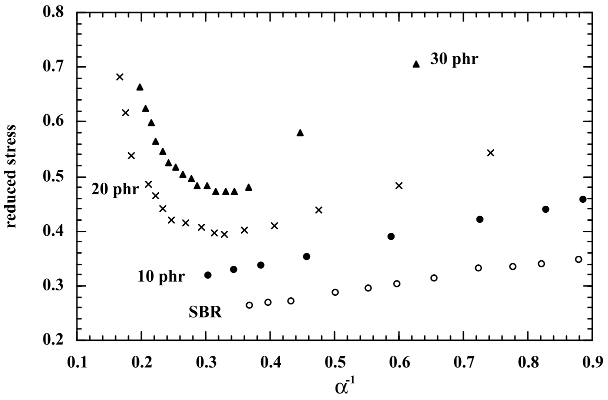

Fig. 5. Mooney–Rivlin plots for unfilled SBR and in situ silica-filled SBR composites.

polymer–filler interactions. In the absence of polymer–filler interaction as it would be expected in unpolar diene rubbers filled such as NR or SBR filled with silica without the use of a coupling agent, only hydrodynamic reinforcement is obtained.

A filler loading of 21 phr ($\phi = 0.0891$) yields a value of X equal to 1.33. By multiplying, at each given strain, the stress of the unfilled natural rubber by the X factor leads to stress values which are lower than those obtained experimentally for the filled network (Fig. 3). This result can only be explained by the presence of filler rubber interactions.

The stress–strain behavior can be presented in the Mooney–Rivlin plots (Fig. 4). The Mooney–Rivlin equation is:

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

where σ is the nominal stress (force divided by the undeformed 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. The curves of the unfilled and filled vulcanizates display, at high deformation, upturns in the modulus. Natural rubber, displays, due to its uniform microstructure, a very unique important characteristic, that is the ability to crystallize under strain, a phenomenon known as ‘strain-induced crystallization’. This phenomenon is mainly responsible of the large and abrupt increase in the reduced stress observed at high deformation corresponding in fact, to a self-toughening of the elastomer because the crystallites act as additional cross-links in the network. However, in filled samples, the elongation at which the upturn occurs, decreases with the filler loading. This result suggests the presence of some interaction between in situ silica particles and polymer chains.

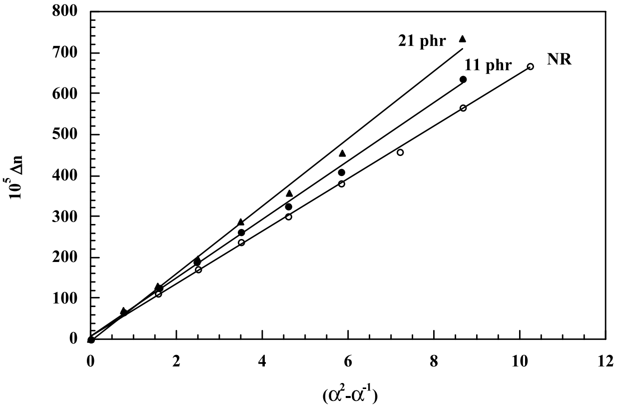

Fig. 6. Strain dependence of the birefringence for unfilled NR and NR samples filled with sol–gel silica generated after the cross-linking process.

It is worth pointing out that in the range of deformation investigated, no upturn in the modulus is evidenced for the unfilled SBR which does not exhibit any strain-induced crystallization but large increases in stress are obtained for the in situ silica-filled samples revealing once more the existence of interactions between the mineral and organic phases (Fig. 5).

In a previous paper [24] dealing with the silica-filled natural rubber composites obtained by the usual mechanical mixing, we have demonstrated that, when silica is added in the absence of any coupling agent, a decrease in the cross-linking density with regard to the unfilled formulation, is observed. This point, which was easily deduced from swelling and orientational measurements, is attributed to the fact that, in sulfur-cured systems, silica affects the cross-linking density by reacting with the chemical ingredients of formulation, thus leading to a lower overall cure state. When the in situ filling process is conducted in the NR or the SBR vulcanizates, the generated silica particles impart obviously a reinforcement effect which increases with the filler loading (Figs. 2 and 5).

Chain orientation under uniaxial extension, is only sensitive to the total cross-linking density contrary to the stress–strain measurements which contain the contribution arising from the inclusion of rigid particles. It can be evaluated either by birefringence or infrared dichroism techniques, these two techniques have been widely described elsewhere [21,25]. Only birefringence results will be reported in this paper.

In the case of an affine behavior, the birefringence is related to the strain function by the expression [26,27]:

$$\Delta n = \frac{vkTC}{V}(\alpha^2 - \alpha^{-1}) = \frac{\rho N_A kTC}{M_c}(\alpha^2 - \alpha^{-1})$$

$$= D_1(\alpha^2 - \alpha^{-1})$$

where v/V represents the number of chains per unit volume, ρ is the network density, N_A is the Avogadro’s number, M_c is the molecular weight between cross links and C is the stress-optical coefficient defined as $C = \Delta n/\sigma_t$, where σ_t is the true stress (force f divided by the deformed area).

The slope, D_1, of the strain dependences of the birefingence D_1 varies as $1/M_c$ which makes birefringence measurements suitable for an evaluation of the effective

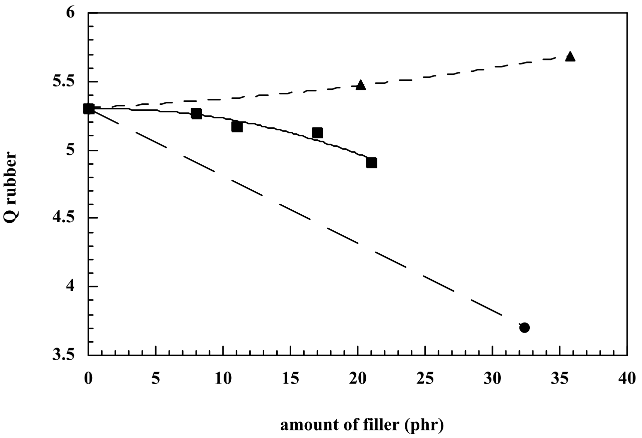

Fig. 7. Dependence of rubber swelling in toluene on the silica loading (in phr = parts per hudred parts of rubber): sol–gel process conducted after the cross-linking reaction (■); sol–gel process conducted before the cross-linking reaction with (●) and without a silane coupling agent (▲).

cross-link density arising from the chemical junctions and also from the polymer–filler interactions. The results displayed in Fig. 6 show that the filled systems exhibit, at a given extension ratio, a higher orientational level of polymer chains evidenced by a higher birefringence. This increase in orientation, observed in the case of active conventional fillers, has been associated with an increase in the cross-linking density attributed to filler–rubber interactions.

Polymer–filler interactions can also be 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 slight decrease of the equilibrium swelling ratio of NR in toluene with the silica loading shown on Fig. 7, reflects polymer–filler attachments increasing with the organic–inorganic interface. This behavior is typical of an adhering filler. Unbonded particles usually leads to equilibrium swelling ratios larger than that of the unfilled formulation indicating a dewetting of the particles and vacuole formation filled with solvent [28–30]. A slight increase in the equilibrium swelling ratio is observed when the sol–gel process is conducted before the cross-linking reaction. In our case, it is most likely due to the well known the tendency of the reactive silica particles to tie up a part of the rubber chemicals that are needed for the sulfur cross-linking reaction thus yielding a reduced state of cure [31]. The birefringence results represented as Δn against $(\alpha^2 - \alpha^{-1})$ (Fig. 8) also display, for the silica-filled natural rubber material, a lower cross-linking density than that of the unfilled formulation. This result is different from that reported by Kohjiya et al. [17] who obtained a reinforcement effect of in situ silica generated before curing. The reason has to be found in the different synthetic protocol: in our case, the in-situ filling process is carried out in a toluene solution of natural rubber containing the curing agent and

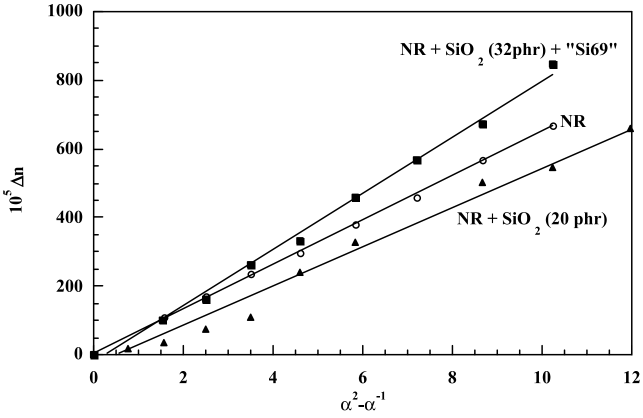

Fig. 8. Strain dependence of the birefringence for natural rubber and for composites submitted to the sol–gel process before the cross-linking reaction.

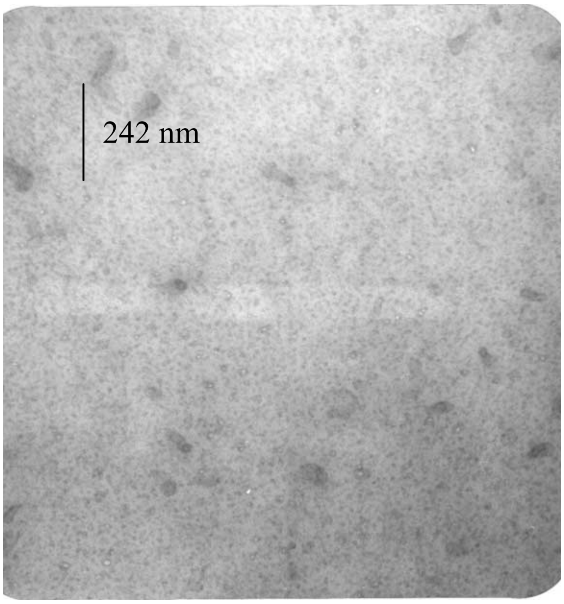

Fig. 9. Transmission electron micrograph of natural rubber containing 11 phr of silica generated after the cross-linking process.

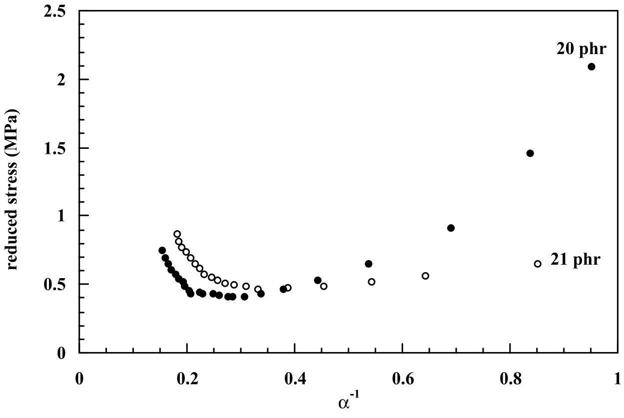

Fig. 10. Comparison in mechanical results of NR composites submitted to in situ silica filling before (●) and after (○) vulcanization.

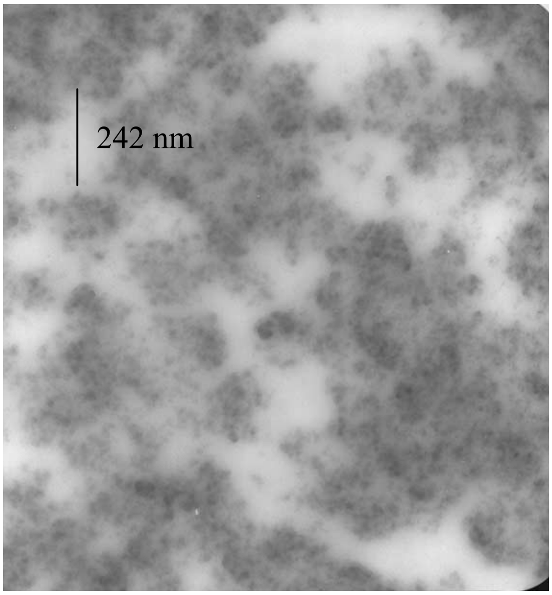

Fig. 11. Transmission electron micrograph of natural rubber containing 20 phr of silica generated before the cross-linking reaction and without the use of a silane coupling agent.

accelerator while in Kohjiya's procedure, silica particles are generated inside sheets of uncross-linked of natural rubber, the in-situ silica-filled NR and compounding reagents being subsequently mixed on a two-roll mix. That could avoid the detrimental effect of sulfur on the cross-linking reaction. Moreover, a base catalysis was used for conducting the sol-gel reaction while TEOS was added in the presence of a tin catalyst in our systems.

The mixing with the silane coupling agent (Si69) gave rise to an important decrease in Q_{rubber} indicating greater reinforcement due to an introduction of some chemical coupling between organic and inorganic components.

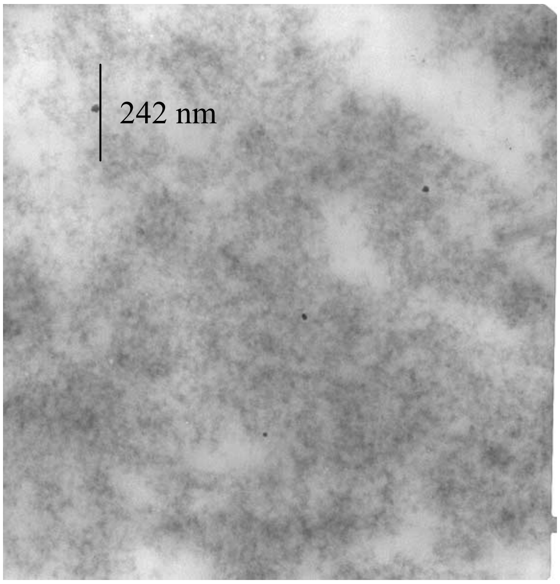

Fig. 12. Transmission electron micrograph of natural rubber containing 20 phr of silica generated before the cross-linking reaction in the presence of a silane coupling agent.

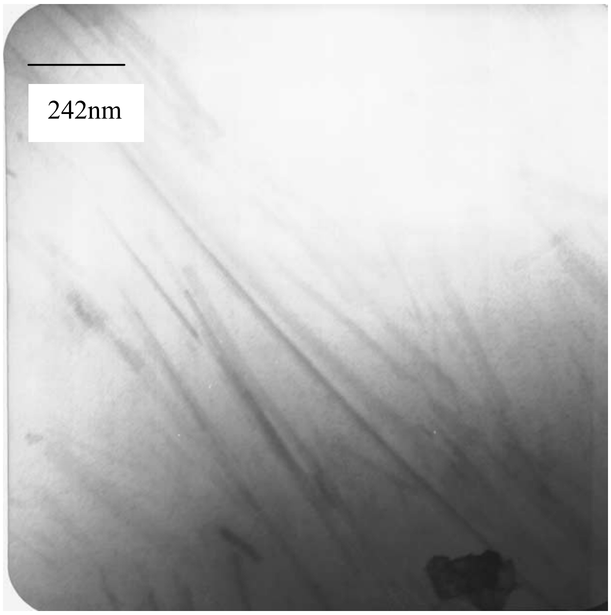

Fig. 13. Transmission electron micrograph of natural rubber containing 5 phr of sepiolite.

Our results clearly demonstrate that carrying out the sol–gel process on vulcanized rubbers even without the use of a silane coupling agent leads to a substantial reinforcement effect because, as already mentioned in the literature, the silica structures grow within the preformed organic network. TEM revealed a very fine morphology, showing a rather small size of silica domains, the good dispersion is probably due to the a steric limitation for cluster growth by the network chains (Fig. 9).

Silica particles generated before vulcanization, seem to inhibit the cross-linking reaction of NR compound by sulfur. On the other hand, the existence of a filler networking structure, due to the aggregation of silica particles, is revealed, in the Mooney–Rivlin plots at low deformations, by the large decrease in the reduced stress (Fig. 10). In fact, in the case of insufficient polymer–filler interaction, there is a tendency for silica particles to attach to each other, via the active silanols present on their surface, and form a strong silica network (Fig. 11). As it can be seen, the tendency to form a silica–silica network is eliminated when filler particles are precipitated in the rubber vulcanizate (Fig. 9). On the other hand, when the sol–gel process is conducted before the cross-linking reaction in the presence of a coupling agent, less clustering is obtained (Fig. 12) but the dispersion is more heterogeneous than that obtained in the case of a silica-filling of an already-formed network.

3.2. Sepiolite-filled material

The aspect ratio (length/width) of the particles is also expected to affect the properties of the final materials.

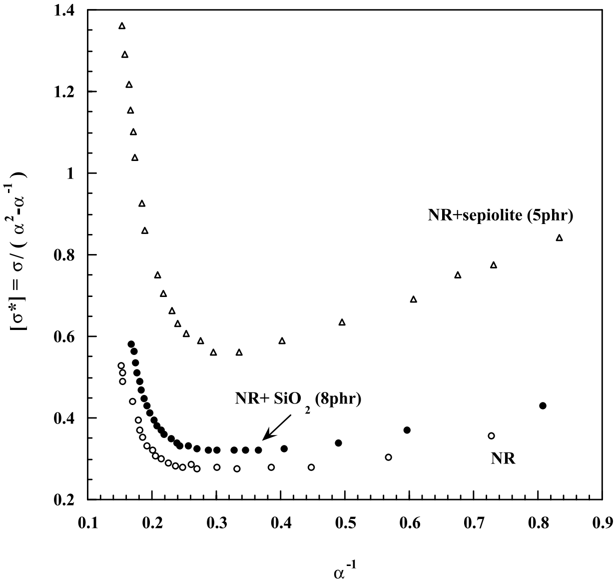

Fig. 14. Reduced stress shown as a function of reciprocal elongation for pure natural rubber and for composites.

Although isometric, i.e. spherical shaped particles such as silica or carbon blacks have been widely used for the reinforcement of polymeric materials, the reinforcement provided by anisometric fillers has received much interest in the last few years. Acicular fillers such as fibers or nanotubes, 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.

Nanocomposites based on natural rubber (NR) filled with nanofibers of micronized sepiolite (Pangel B20) have been investigated in order to evaluate the role played by the shape of the inclusion on the mechanical and orientational properties of the resulting materials. As seen in Fig. 13, a very good dispersion of the filler particles is obtained within the polymeric medium, the particles are not aggregated and exhibit their characteristic elongated shape.

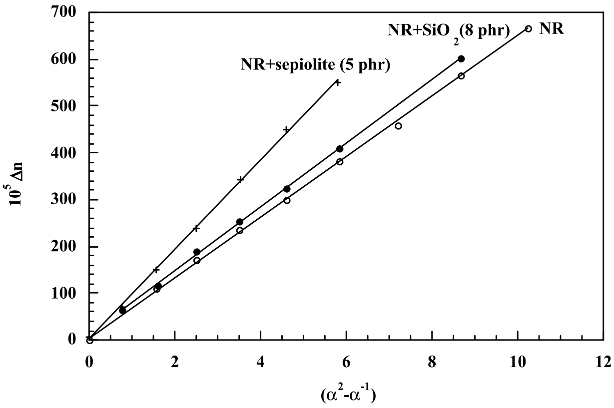

Fig. 15. Birefringence measurements measurements for natural rubber and for composites.

Plots of the reduced stress against the reciprocal of the extension ratio are displayed in Fig. 14 for the pure natural rubber and for two composites filled with in situ precipitated silica and with nanofibers of sepiolite, respectively. The data show that, at a same filler loading, the sepiolite fibers impart a higher extent of reinforcement than the spherical silica particles. Moreover, the upturn at high deformations occurs at a lower strain in the sepiolite-filled natural rubber, indicating a stronger interaction between the polymer chains and the filler particles.

The equilibrium swelling ratio of the composite, Q, is expressed in the case of an isotropic swelling by:

$$Q = (L_{\text{swollen}}/L_{\text{unswollen}})^3 = (l_{\text{swollen}}/l_{\text{unswollen}})^3,$$

where L and l refer to the length and the width of the sample.

Under the assumption that the filler does not swell, the equilibrium swelling ratio of the rubber alone is equal to:

$$Q_{\text{rubber}} = (Q - \phi)/(1 - \phi)$$

where ϕ is the volume fraction of filler.

An interesting feature with regard to the composite containing fibers of sepiolite is the anisotropic swelling. Q_{rubber} is equal to 2.91 and 4.13 when it is evaluated from the length or the thickness of the sample, respectively. But besides the anisotropic character, the higher restricted swelling with regard to silica-filled natural rubber, reflects polymer–filler attachments at the organic–inorganic interface. This behavior is typical of an adhering filler.

The analysis of the orientational properties by birefringence measurements of pure natural rubber and the corresponding composites confirm the mechanical results. As expected, Fig. 15 displays, at a given deformation, a higher level orientation for the composite containing nanofibers of sepiolite. The acicular morphology of the sepiolite particle leads to a large amount of polymer chains bound at the interface.

4. Conclusion

In addition to the conventional technique of blending silica into the elastomer prior to cross-linking, reinforcement of natural rubber can also been obtained by in situ generated filler particles. In conformity with the previous results [7–11,15,16] small and well-dispersed in situ silica particles are generated when the sol–gel reaction is conducted after curing. Under our experimental conditions, silica particles generated before vulcanization, seem to inhibit the cross-linking reaction of NR compound by sulfur and form a silica–silica network via the silanol groups present on the silica surface. But the use of a silane coupling agent leads to a substantial extent of reinforcement.

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