Sepiolite as reinforcing Filler for Rubber Composites: From the chemical Compatibilization to the commercial Exploitation

Elastomeric composites · sepiolite · chemical modification · silanes · TEOS · natural Rubber

Chemically modified sepiolite was used as filler in silica based elastomeric composites. The sepiolite was modified through the reaction with silica (nano) particles from silanes such as TEOS and TESPD. Characterization of silica (nano) particles and sepiolite was performed by means of dynamic light scattering, thermogravimetric, elemental analysis, infrared spectroscopy and field emission scanning electron microscopy. Prepared sulphur crosslinked rubber composites were characterized for vulcanization behavior and dynamic mechanical properties. Recently, it has been announced the commercial development of rubber compounds with sepiolite, whose chemical modification allowed the compatibilization, lower rolling resistance and better wet grip.

Sepiolith als verstärkender Füllstoff für Kautschukkomposite: Von der chemischen Kompatibilisierung zur kommerziellen Nutzung

Elastomerkomposite · Sepiolith · chemische Modifizierung · Silane, TEOS · Nautrkautschuk

Chemisch modifiziertes Sepiolith wurde als Füllstoff in Kieselsäure-basierenden Elastomerkompositen eingesetzt. Das Sepiolith wurde durch die Reaktion mit Kieselsäure-Nanopartikeln aus Silanen wie TEOS und TESPD modifziert. Die Charakterisierung der Kieselsäurenanopartkiel und des Sepiolith erfolgten durch dynamische Lichtstreuung, Thermogravimetrie, Elementanalyse, Infrarotspektroskopie und Feldemissionsrasterelektronenmikroskopie. Hergestellte mit Schwefel vernetzte Kautschukkomposite wurden hinischtlich des Vulkanisationsverhaltens und der dynamisch-mechanischen Eigenschaften charakterisiert. Als neu ist die kommerzielle Entwicklung von Kautschukmischungen anzukündigen, deren chemische Modifzierung die Kompatibilisierung, niedrigen Rollwiderstand und verbesserten Naßgriff erlaubt.

Figures and Tables:
By a kind approval of the authors.

INTRODUCTION

Reinforcing fillers are indispensable ingredients of rubber composites [1-2] and, among them, inorganic oxides/hydroxides play a fundamental role. Indeed, since the end of the last century, silica in the precipitated form, with appropriate coupling agents [3-4], is the best filler for tyre compounds with low dissipation of energy and fuel consumption [1-2, 5-7]. Clays have been demonstrated and applied as efficient fillers in rubber composites, also in hybrid filler systems [8-12].

The size of a filler plays a fundamental role for the mechanical reinforcement of rubber composites: a nanosize means large surface area and, in turns, large polymer-filler interfacial area [30]. Fillers are classified as nanometric or nanostructured [1-2]. The ISO definition [13] says that the nanoscale range is approximately from 1 nm to 100 nm and a nanomaterial is a material with any external dimension in the nanoscale or having internal structure in the nanoscale. Silica is known as a nanostructured filler: its primary particles have at least one dimension below hundred nanometers and are joined together to give aggregates with a size of at least 200 nm. Clays are nanometric fillers and have a high aspect ratio, that means a high ratio between their largest and lowest dimension. Hence, clays have very large area/volume ratio and are ideal candidates to promote large mechanical reinforcement. However, such considerations hold in case nanofillers, such as clays, are able to give rise to a stable interaction with the polymer matrix.

In this work, sepiolite was selected as the reinforcing filler of elastomer composites. Sepiolite is a naturally occurring clay, easily available, not expensive, with high thermal and mechanical stability, belonging to the sepiolite and palygorskite group [14-16]. Indeed, it has the typical TOT (tetrahedral-octahedral-tetrahedral) layer-fibrous structure, with magnesium atoms, octahedrally coordinated, joining together two-dimensional layers of tetrahedral SiO4 units, which have unshared oxygen atoms facing each other. The octahedral sheet is discontinuous, whereas the tetrahedral sheet is continuous. In the direction perpendicular to the layers, connections are based on covalent bonds. This has an important consequence: sepiolite cannot swell or exfoliate. Hence, intercalation of polymer chains in the interlayer space, assumed [8] or disputed [17-20] in the literature on clay-polymer nanocomposites, cannot be hypothesized.

Sepiolite is nanosized and has high aspect ratio, hence it could be a very interesting reinforcing filler for elastomer composites, provided that stable interaction with the polymer chains is established. Indeed, published data [21-23] demonstrate that sepiolite, either pristine or modified with an organophilic cation, when used in place of silica, leads to larger mechanical reinforcement. However, also larger hysteresis is obtained, as it is not possible to establish a chemical link of sepiolite with the elastomer chains. This prevents the use of sepiolite on a large scale, for dynamic mechanical applications of rubber materials such as the one in tyre compounds.

To favor at least the dispersion of sepiolite in polymer matrices, the surface modification in water with methoxysila-

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nes was performed [24]. The chemical reactivity of sepiolite has been improved by extracting magnesium atoms with an acidic treatment [21, 25]. However, self assembly of sepiolite was observed [25] and this appears as an indication of an insufficient interaction with the polymer chains.

Objective of the work here reported was the chemical modification of sepiolite, in order to promote its chemical reactivity with an elastomeric matrix, with the aim to obtain rubber composites, based on the chemically modified sepiolite, with larger mechanical reinforcement and equal or even lower hysteresis.

Sepiolite was modified with silica particles, through the following methods:

(i) condensation on the sepiolite surface, in situ, of the following silanes: tetraethyl orthosilicate (TEOS), bis(3-triethoxysylilpropyl) disulfide (TESPD) and a TEOS/TESPD mixture (1:1 as molar ratio).

(ii) condensation of TEOS, TESPD, TEOS/TESPD (1:1 molar ratio) ex ante and successive sorption of the particles on the sepiolite surface.

Condensation reactions were promoted by ammonia, as described in the so called Stöber method [26]. The condensation products are indicated in the text below as (nano)particles, because their size was either below or above 100 nm.

Working hypothesis was that, upon successfully applying procedures (i) and (ii), a sulphur containing silane, such as (bis(3-triethoxysylilpropyl) tetrasulfide, TESPT), added to the composite, could behave as coupling agent between chemically modified sepiolite and an unsaturated rubber. Moreover, sulphur based silica particles, obtained from TESPD, present on sepiolite surface, could per se promote the filler-rubber linkage. The experimental procedures adopted for approaches (i) – (ii) are presented.

Characterization of particles from silane condensation was performed by means of dynamic light scattering. Characterization of pristine and chemically modified sepiolite was carried out as follows. The extent of sepiolite chemical modification was evaluated by using thermogravimetric analysis (TGA) and elemental analysis, in particular for determining the amount of carbon and sulphur. The qualitative inspection of functional groups was made through Fourier Transformed Infrared spectroscopy in the attenuated total reflection mode (ATR-IR). Field emission scanning electron microscopy (FESEM) was used to analyze the shape of sepiolite, before and after chemical modification.

Composites were prepared via melt blending and were based on a diene rubber such as poly(1,4-cis-isoprene) from Hevea Brasiliensis (natural rubber, NR). Silica was the main filler. A minor amount of silica was replaced with sepiolite (Sp), either pristine or chemically modified (through the (i) – (ii) procedures explained above). Dynamic mechanical properties were investigated by applying sinusoidal stresses in the shear mode at 50 °C, determining G’, G” and Tan delta as a function of the strain sweep, and in the axial mode, determining E’, E” and tan delta at 10 °C, 23 °C and 70 °C). Tensile properties were studied with quasi static measurements, at room temperature. First preliminary results of this research have been presented elsewhere [27]. Recently, it has been announced the commercial exploitation of chemically modified sepiolite for compounds for bike tyres [28, 29].

EXPERIMENTAL SECTION

Materials

All reagents and solvents were commercially available and were used without further purification.

Sepiolite Pangel S9 (SepS9) was from Tolsa and was extracted from the landfill of Vallecas (Spain).

Chemicals for the modification of sepiolite. Tetraethyl orthosilicate (molar mass = 208,33 g/mol) (98%), ammonia water solution (30 % vol/vol) and ethanol were from Aldrich. Bis[3-(triethoxysilyl) propyl]disulphide (TESPD) (molar mass = 474 g/mol) (Si266®) was from Evonik.

Ingredients for rubber composites. Rubbers. Poly(1,4-cis-isoprene) from Hevea Brasiliensis (natural rubber, NR) was SMR GP, with 65 Mooney Units as Mooney viscosity (ML(1+4)100°C), from Lee Rubber. Chemicals. bis[3-(triethoxysilyl) propyl]tetrasulfide [TESPT] (Si69®), ZnO (Zincol Ossidi), stearic acid (Sogis), N-(1,3-dimethylbuthyl)-N-phenyl-p-phenylenediamine (6-PPD) (Crompton), sulphur (Solfotecnica), N-ter-butyl-2-benzothiazyl sulfenamide (TBBS) (Flexyis).

Chemical modification of sepiolite with silica particles via in situ condensation of silanes

Chemical modification of sepiolite was performed with TEOS, TESPD and a TEOS/TESPD 1:1 mixture. The same experimental procedure was adopted to promote the silane condensation. The reaction with TEOS is reported as example. Amounts used for the other silanes are indicated.

Chemical modification of sepiolite with TEOS

In 250 mL two-neck round bottom flask equipped with a magnetic stirrer were poured in sequence: sepiolite (5.00 g), ethanol (50 mL), ammonia water solution (2 mL at 30% vol/vol in water) and deionized water (0.7 mL). The system was sonicated for 1 hours. Afterwards, the mixture was placed in the oil bath set at the temperature of 60 °C. TEOS (3.22 g, 0.0154 mol) was poured into the system drop by drop. The mixture was stirred for 5 hours at 500 rpm. At the end of the reaction, the system was cooled at room temperature and filtered using a Buchner funnel. The filtered powder was washed several times with ethanol and dried in the oven at 90 °C for 10 hours.

Chemical modification with TESPD or with TEOS/TESPD 1:1 molar mixture

4.891 g (0.0103 mol) of TESPD or 2.58 g of TEOS (0.0124 mol) and 0.98g (0.0021 mol) of TESPD were used.

Chemical modification of sepiolite with silica particles via ex ante condensation of silanes

Condensation of silanes and characterization of condensation products

The same experimental procedure was adopted to promote the condensation of TEOS, TESPD and a TEOS/TESPD mixture (1:1 molar ratio). The reaction with TEOS is reported as example. Amounts used for the other silanes are indicated.

Condensation of TEOS

A mixture of tetraethoxysilane (15 g; 0.0720 mol), deionized water (2.75 mL, 0.153 mol) and ethanol (32.25 mL, 0.554 mol) was poured in a 250 mL round bottom flask with two necks equipped with a magnetic stirrer. The mixture was then stirred at 500 rpm for 15 minutes at room temperature. Meanwhile, another mixture containing ammonia solution (0.51 mL of 30% vol/vol water solution; 0.0079 mol) and ethanol (32.25 mL, 0.554 mol) was poured in a round bottom flask and mixed for 15 minutes at 500 rpm at room temperature. The second mixture was then added in a dropwise fashion into the first mixture. The system was then stirred for 5 days at 500 rpm at room temperature.

The same procedure was adopted for the condensation of TESPD and the condensation of the TEOS/TESPD mixture. In the former case was used 22.79 g (0.0480 mol) of TESPD in substitution of TEOS; in the latter case a mixture formed by tetraethoxysilane (12 g, 0.0576 mol) and TESPD (4.55 g, 0.0096 mol) was used.

All the products were analyzed by Dynamic Light Scattering (DLS) in order to confirm the formation of silica nanoparticles.

Characterization of condensation products

Dynamic light scattering (DLS)

The nanoparticle size was analyzed with a Zetasizer Dynamic Light Scattering system (Malvern Instrument Ltd.) at room temperature using a 632.8 nm He–Ne laser. Each dispersion was prepared with a concentration of 1mg/mL: 3 mL of solution were placed using a pipette Pasteur, in a quartz cuvettes of 1 cm optical path and analyzed immediately after centrifugation and after 10, 60 and 100 minutes of storage.

Functionalization of Sepiolite with silica particles prepared ex-ante

The same experimental procedure was adopted. The functionalization with silica particles from TEOS is reported as example

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Functionalization with silica particles prepared ex-ante from TEOS.

In 250 mL two-neck round bottomed flask equipped with magnetic stirrer were poured in sequence: sepiolite (5.00 g) and ethanol (50 mL). The mixture was then sonicated for 30 minutes and subsequently placed into an oil bath set at temperature of 60 °C. A dispersion of silica nanoparticles in ethanol (41.86 mL), previously prepared (see above), was added into the mixture under stirring (500 rpm).

An additional amount of ammonia solution (2 mL of 30 % vol/vol solution in water) was added drop by drop. The mixture was then agitated for 5 hours at 500 rpm at the temperature of 60 °C. Afterwards, the solid part was filtered using a Buchner funnel and was washed several times with ethanol. The mass of the product was then measured after drying for 10 h at 90 °C.

Characterization of sepiolite and chemically modified sepiolite

Thermogravimetric analysis (TGA)

TGA was performed with a Mettler Toledo TGA/DSC Star-e System, in a temperature range from 150°C to 800 °C. The measurements were carried out by using the following temperature program: (i) from 30°C to 850°C, 10°C/min, in N2 flow 60 mL min−1 (ii) at 850°C isotherm for10 min, in air, flow 60 mL min−1

Attenuated total reflectance infrared spectroscopy (ATR-IR)

The analyses were carried out with a Perkin Elmer Spectrum 100 (1 cm-1 resolution, range of 650-4000 cm-1, 16 scans).

Field emission scanning electron microscopy (FESEM)

It was performed by using a FESEM Ultra Plus Zeiss microscope, Gemini column, in Inlens mode, with excitation of the electron beam from 3.0 to 5.0 KV and working distance from 2.7 to 4.3 mm.

Samples to be analyzed were attached to a metal target with adhesive tape and sputtered with gold, to improve electron conductivity. Samples were prepared as follows. 0.005 g of fibers were dispersed in 50 mL of a solution made by water and ethanol, in a mass ratio 8:2, in the presence of 200 ppm of the surfactant Nonidet P40. Treatment with ultrasound in immersion was carried out for 15 minutes. Fibers were separated by centrifugation at 1000 g/m for 20 minutes and dried in stove at 100°C for 3 hours.

Preparation and characterization of rubber composites

Preparation of rubber composites

All the quantities of the ingredients are expressed in phr = parts per hundred rubber.

All the ingredients for the non-productive mixing were mixed in an internal mixer for about 5 minutes. As soon as the temperature reached 145 °C ± 5 °C, the composite was discharged. The composite was then introduced into the mixing chamber, sulphur and TBBS were then added, maintaining the temperature below 60°C.

Dynamic-mechanical characterization in the shear mode

Dynamic-mechanical measurements in the shear mode were carried out with a Monsanto R.P.A. 2000 rheometer. To cancel the thermo-mechanical history, a first strain sweep (0.1–25% strain amplitude) was performed at 50°C on uncross-linked samples. To achieve fully equilibrated conditions, the samples were then kept in the instrument at the minimum strain amplitude (0.1%) for 10 min. A strain sweep (0.1–25% strain amplitude) was then performed with a frequency of 1 Hz. Curing was carried out at 150°C with a frequency of 1.67 Hz and an angle of 6.98%. Curing time was 30 min. On cross-linked samples, a first strain sweep (0.1–25% strain amplitude) was performed at 50°C, then the sample was kept in the instrument at the minimum strain amplitude (0.1%) for 10 min, to achieve fully equilibrated conditions. Finally, a strain sweep (0.1–25% strain amplitude) was performed with a frequency of 1 Hz.

Dynamic-mechanical characterization in the axial mode

Dynamic-mechanical properties were measured using an Instron dynamic device in the traction-compression mode according to the following methods. A test piece of the crosslinked elastomeric composition having a cylindrical form (length = 25 mm; diameter = 12 mm) and kept at the prefixed temperature (10, 23 and 70 °C) for the whole duration of the test, was compression-preloaded up to a 25 % longitudinal deformation with respect to the initial length and then submitted to a dynamic sinusoidal strain having an amplitude of ±3.5 % with respect to the length under pre-load, with a 100 Hz frequency. The dynamic-mechanical properties are expressed in terms of dynamic storage modulus (E’) and loss factor (Tan Delta) values. The Tan Delta value is calculated as a ratio between loss (E”) and storage modulus (E’).

Tensile tests

Tensile measurements were determined on samples of the elastomeric compositions vulcanized at 150°C for 30 minutes. Stresses at 10, 50, 100 and 300% of elongation (σ10, σ50, σ100 and σ300 respectively), stress at break (σb) and elongation at break (εB) were measured according to Standard ISO 37:2005.

RESULTS AND DISCUSSION SECTION

Chemical modification of sepiolite with silica particles prepared in situ from the condensation of TEOS, TESPD, TEOS/TESPD

Aim of the activity here described was the chemical modification of sepiolite with silica nanoparticles formed in situ, on sepiolite surface, from the condensation of silanes such as TEOS, TESPD and a TEOS/TESPD mixture (1:1 as molar ratio). The use of TESPD and of the TEOS/TESPD mixture was aimed at having a sulphur based compound, reactive in vulcanization, chemically bound to sepiolite.

The preparation of nanosilica from TEOS, with the help of either basic or acid catalysts, is well documented in the literature [30]. As mentioned in the introduction, in the present work was applied the so called Stöber method, a sol gel process [28] which allows to obtain silica particles of controlled and uniform size [31-34]. Tetraethyl orthosilicate, the silica precursor, is hydrolyzed in alcohol with ammonia as the catalyst: a mixture of ethoxysilanols and ethanol are produced. Silanols can then condense with either other silanols or TEOS, forming silica. In the literature [35], it was reported a kaolinite covered with silane-grafted silica, used as filler for styrene-butadiene rubber. However, documents on fibrillary silicates modified with sol-gel silica are not available.

Treatment of sepiolite with the selected silanes was performed with the procedure indicated in Figure 1.

Details are in the experimental section. In brief, sepiolite, ethanol, ammonia and water were mixed, then the silane was added to this mixture. After 5 hours at 60°C, the final solid product was filtered on a Buchner and washed with ethanol. The resulting modified sepiolite was then characterized by means of elemental analysis, TGA, IR, FESEM analyses.

Data of C and S content in Sp/TEOS/TESPD and Sp/TESPD samples are in Table I.

Carbon and Sulphur are present in all the samples and the amount of Carbon is higher than the amount of Sulphur. Larger amount of C and S was found in the case of the Sp/TESPD sample, as expected on the basis of the chemical composition of the silanes.

Values of mass losses determined from TGA analysis are in Table II.

The TGA graph of pristine sepiolite revealed mass losses which can be interpreted with reference to the published studies [36, 37]. Absorbed and coordinated water can account for the mass losses at T < 150°C and in the T range from 150°C to 400°C, respectively. Water trapped in the channels is lost in the T range from 400°C to 700°C. The de-hydroxylation of Mg-OH groups accounts for the mass loss in the T range from 700°C to 850°C.

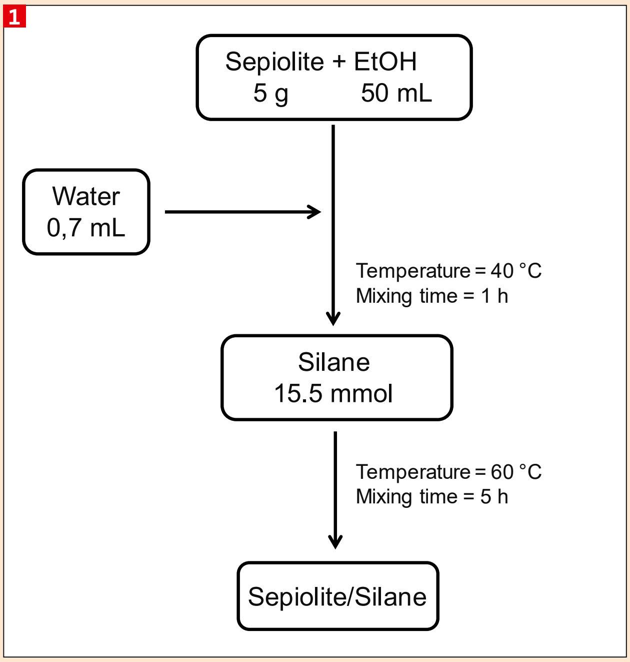

Figure 1. Experimental procedure for the chemical modification of sepiolite with silica particles prepared in situ from the condensation of TEOS, TESPD, TEOS/TESPD. TEOS/TESPD mixture: 1/1 as molar ratio.

1 Carbon and sulphur content (mass%) from elemental analysis in samples of sepiolite chemically modified with silanes condensed in situ[a]

Silane(s)	Sp/Silica (nano) particles in situ[c]		Sp/Silica (nano) particles ex ante[d]	
	C	S	C	S
TEOS/TESPD	3.39	0.56	3.13	1.27
TESPD	5.45	2.89	2.89	0.87

[a] silanes were sorbed on the sepiolite surface. [b] silane nanoparticles were sorbed on the sepiolite surface.
[c] see procedure in Fig. 1 [d] see procedure in Fig. 4

2 Mass losses for pristine Sepiolite and Sepiolite treated with a silane[a,b]

Samples	Mass losses in different T (°C) ranges				Residue
	T < 150	150 < T < 450	450 < T < 750	750< T< 900	T > 900
Sp	8.1	3.3	2.7	2.0	83.6
Sp/TEOS	6.1	5.6	2.8	2.1	83.4
Sp/TESPD	5.6	8.2	4.4	2.3	79.5
Sp/TEOS/TESPD	6.2	6.2	3.3	2.1	82.2

The sepiolite/silane samples reveal lower mass loss in the range 150°C < T < 400°C and larger mass loss in the range between 150°C and 750°C. These differences allow to hypothesize the presence of organic substance(s) in the sepiolite/silane composite. Indeed, the mass loss in such a range of temperatures is typical of a silane grafted on silica [38].

ATR-IR was performed on pristine sepiolite and on sepiolite/silane samples. The spectra are in Figure 2.

In the spectra in Figure 2, peaks indicated with dotted line are at the following wavelengths: about 3353 and 3249 cm-1 and about 2984 and 2896 cm-1. In the spectrum of pristine sepiolite (Fig. 2a), the peaks at 3353 cm-1 and 3249 cm-1 are due to H2O coordinated to the octahedral layers of sepiolite, Reduction of the intensity of these peaks can be observed in the spectra of sepio-

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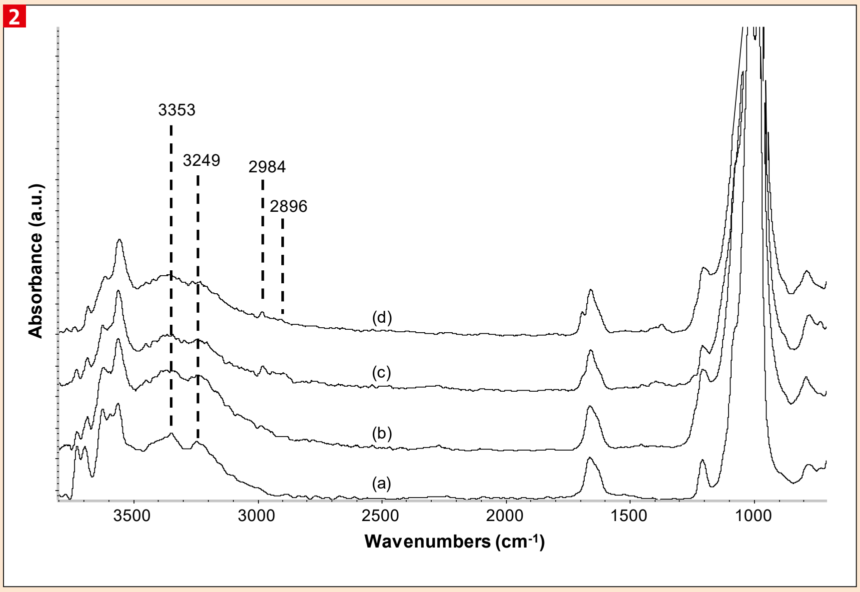

Figure 2. ATR-IR spectra of (a) pristine sepiolite, (b) sepiolite/TEOS, (c) sepiolite/TESPD (d) sepiolite/TEOS/TESPD.

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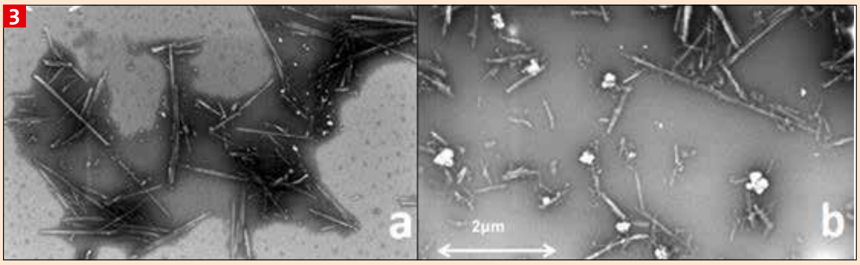

Figure 3. FESEM micrograph of: pristine sepiolite (a) and sepiolite/TEOS (b)

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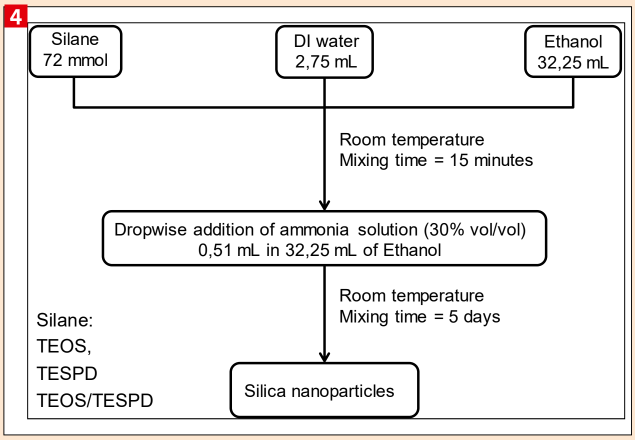

Figure 4. Experimental procedure for the preparation of silica (nano)particles from the condensation of silanes.

lite/silane (Fig. 2b, c, d), whatever the silane is. In these latter spectra, peaks at about 2984 cm-1 and 2906 cm-1 can be attributed to the stretching of -CH2 coming from TEOS.

Micrographs taken with FESEM on pristine sepiolite and on sepiolite/TEOS are Figure 3, Fig. 3a and Fig. 3b, respectively.

The typical fibrillary shape of pristine sepiolite can be observed in Fig. 3a. As it can be seen in Fig. 3b, silica particles from TEOS are prevailingly located on sepiolite fibrils. Their size appears to be larger than 100 nm. The condensation products visible in Figure 3 are indeed nanoparticles. It is indeed worth commenting that the structure of sepiolite is not appreciably affected by the treatment with TEOS.

Chemical modification of sepiolite with silica (nano)particles prepared ex ante from the condensation of TEOS, TESPD, TEOS/TESPD

The aim of the activity described in this paragraph was the chemical modification of sepiolite with silica (nano)particles prepared ex ante from the condensation of the following silanes: TEOS, TESPD and a TEOS/TESPD mixture (1:1 as molar ratio). Silica nanoparticles are available on a commercial scale and are suitable not only for reinforcing rubber composites [39-40] but also for reducing the calcium leaching rate of cement paste [41] and for removing sulphur mustard from solutions [42].

Preparation of silica (nano)particles

The experimental procedure for the preparation of silica nanoparticles, described in detail in the Experimental Section and shown in Figure 4, was inspired to what reported in the scientific literature [28, 43]. Experimental conditions were tuned in order to have silica nanoparticles, with size lower than 100 nm.

Dynamic light scattering analysis was performed on all the samples. Values of average diameter and polydispersity index (PDI) (an estimate of the distribution width) are in Table 3.

The average diameter was much lower than 100 nm for the nanoparticles from TEOS and TEOS/TESPD whereas it was significantly larger for the condensation product of TESPD. In this latter case, it was not possible to have a reliable measurement of the size.

The chemical modification of sepiolite with nanoparticles was performed as described in detail in the experimental part and shown in Figure 5.

In brief, the silica (nano)particles (without or with sulphur) were allowed to react with the clay at 60°C for 5 hours. After washing with ethanol, adducts of sepiolite with silica nanoparticles were obtained. As mentioned above, the condensation product of TESPD did not have nanometric size. However, to avoid confusion with the reaction products of sepiolite with silica particles prepared in situ, discussed in the previous paragraph, all the condensation products are named as nanoparticles and are indicated with "Nps" suffix. The adducts were characterized through elemental analysis, TGA, ATR-IR and FESEM.

Results from elemental analysis of the adducts with silica (nano)particles from

TESPD and TEOS/TESPD are in Table 1. Results from TGA analysis are in Table 4.

Results from elemental and thermogravimetric analysis indicate that the treatment of sepiolite with the silica particles prepared ex ante led to a lower amount of organic modifier in the final adduct with respect to the treatment of sepiolite with silica particles prepared in situ, in particular with TESPD as the silane. It is indeed worth observing the low amount of C and S in the Sp/TESPD Nps adduct. It seems that larger amount of sulphur is grafted on the sepiolite surface by using the hybrid TEOS/TESPD system.

FESEM analysis was performed on adducts of sepiolite with nanoparticles from TEOS/TESPD and from TESPD. Pictures are in Figure 6, Fig. 6a and 6b, respectively.

In the case of TEOS/TESPD as the silane, nanoparticles appear preferentially but not exclusively close to sepiolite fibers. In the case of TESPD, it is worth observing the larger size of the particles, already indicated by DLS analysis.

Rubber composites based on diene rubber and chemically modified sepiolite

Rubber composites were prepared, based on NR as the diene rubber and silica as the main filler. Formulations of the composites are in Table 5. Sepiolite, either pristine or chemically modified, was used to replace a minor amount of silica. The same mass content was used. As sepiolite has higher density than silica (2.3 g/mL with respect to 2.1 g/mL), a lower volume fraction of sepiolite, with respect to silica, was used. As described above, chemical modification of sepiolite was performed with silica (nano)particles prepared from silanes condensation either in situ on sepiolite surface or ex ante. The same content of sepiolite based filler was used in all the composites. The amount of sulphur was pretty low in the samples of modified sepiolite, from 0.6 to 2.9 as mass% (see Table 1), and thus it was very low in the composites. Hence, such amount was neglected for the preparation of the formulations and the same phrs of orthorombic sulphur and accelerators were used in all the composites.

Sulphur based crosslinking

Sulphur based crosslinking was carried out at 170 °C for 10 min. Data from the rheometer curves are in Table 6.

With respect to the composites with silica as the only filler, the composite with pristine sepiolite show lower ML and MH values. The lower value of ML is a clear indication of a lower composite viscosity and suggests that, in the presence of sepiolite, the filler network was formed to a lower extent. This finding could be expected, taking into consideration the lower volume fraction of sepiolite with respect to silica and the lower amount and reactivity of polar groups (silanols) on the pristine sepiolite surface. The lower amount of filler network can also account, at least partially, for the lower MH values. Indeed, the extent of strain amplitude explored during the crosslinking experiment is not enough for the complete disruption of the filler network. Hence, lower filler network means lower M modulus values in the whole vulcanization curve.

Composites with chemically modified sepiolite show (in most cases) ML values similar (slightly higher) to those of composites based on pristine sepiolite and lower than ML values of composites with silica as the only filler. Besides the lower volume fraction of chemically

3 **Average diameter of silica (nano)particles from TEOS, TESPD and TEOS/TESPD**

Nanoparticles from	Average diameter [nm]	PdI
TEOS	25.50	0.280
TEOS/TESPD	37.80	0.262
TESPD	n.d.	n.d.

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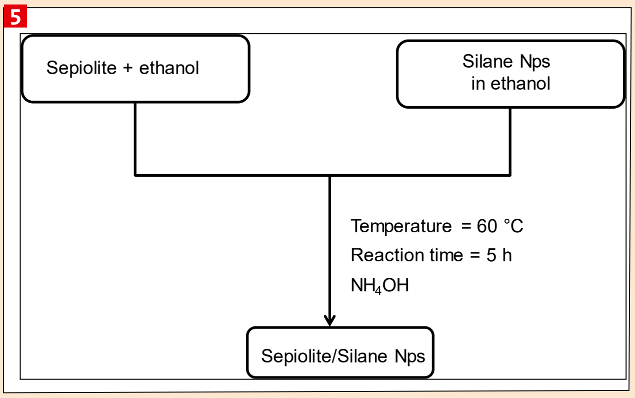

Figure 5. Experimental procedure for the chemical modification of sepiolite with silica particles prepared ex ante from the condensation of TEOS, TESPD, TEOS/TESPD. TEOS/TESPD mixture: 1/1 as molar ratio.

4 **Mass losses for pristine sepiolite and adducts of sepiolite with silica (nano)particles**[a]

Samples	Mass losses in different T (°C) ranges				Residue
	T < 150	150 < T < 450	450 < T < 750	750 < T < 900	T > 900
Sp	8.1	3.3	3.0	2.0	83.6
Sp/TEOS Np	6.8	3.4	3.2	1.6	85.0
Sp/TESPD Np	6.5	8.7	2.9	2.5	79.4
Sp/TEOS/ TESPD Np	6.6	6.5	3.1	2.5	81.3

[a] from TGA analysis

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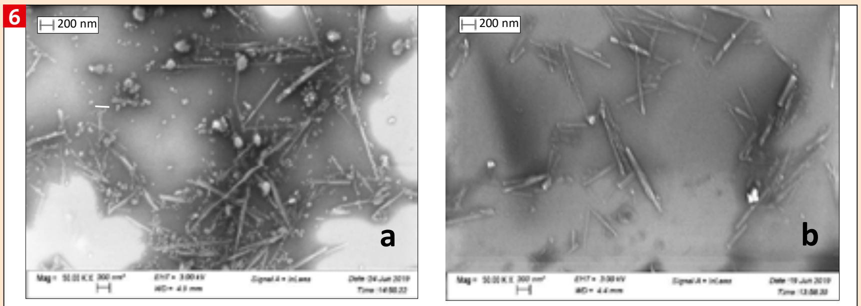

Figure 6. FESEM micrographs of adducts between sepiolite and nanoparticles from: (a) TEOS/TESPD, (b) TESPD.

5 **Formulations of NR based composites with silica and sepiolitea as the reinforcing fillers[b,c]**

Ingredient	**Filler in the composite**				
	Silica	Silica + Sp	Silica + Sp/TEOS	Silica + Sp/TEOSPD	Silica + Sp/TEOS/ TESPD
NR	100	100	100	100	100
ZEOSIL 1165	46.6	35	35	35	35
Sp	0	11.6	0	0	0
Sp/TEOS	0	0	11.6	0	0
Sp/TESPD	0	0	0	11.6	0
Sp/TEOS/ TESPD	0	0	0	0	11.6
TESPT	3.7	3.7	3.7	3.7	3.7

[a] sepiolite: either pristine or chemically modified with silica (nano)particles formed either in situ or ex ante[b] The amount of the ingredients is expressed in phr = parts per hundred rubber.

[c] Other ingredients: stearic acid (2) ZnO (3,6) 6PPD (2) sulphur (2) TBBS (1,8)

6 **Data from sulphur based crosslinking of composites of Table 5**

Property	**Filler in the composite**							
	Silica	Silica + Sp	Silica + Sp/TEOS		Silica + Sp/TESPD		Silica + Sp/TEOS/TESPD	
			in situ	ex ante	in situ	ex ante	in situ	ex ante
M_H	15.4	13.4	13.0	14.0	14.5	15.6	15.4	14.1
M_L	1.3	0.8	0.8	1.4	1.1	0.9	1.1	1.0
t_{S1}	2.3	1.8	1.8	2.4	2.1	1.9	2.1	2.0
t_{90}	4.5	4.5	4.0	4.1	4.6	4.5	4.0	4.7

modified sepiolite with respect to silica, the surface hydrophobization brought about by silica (nano)particles which contain organic moieties could contribute to the viscosity reduction. Indeed, the highest ML value in Table 1, even higher than ML of the composite with only silica as the filler, is for the composite with silica (nano)particles from TEOS prepared ex ante. In Table 4 it was shown that these (nano)particles have lower mass loss in the range from 150°C to 400°C and this could be an indication of a lower amount of organic substances on the sepiolite surface which leads to a lower hydrophobization. Such result seems to indicate that (nano)particles from TEOS prepared ex ante are able to increase the reactivity of sepiolite essentially with other filler particles.

Among the composites containing sepiolite, the higher MH values can be observed for the composites with sulphur based sepiolite. It could be assumed that the sulphur anchored on sepiolite surface, though not in large amount, has an effect on the crosslinking network.

Composites with sepiolite also reveal (in most cases) a lower induction vulcanization time (ts1 values) and similar or lower optimum vulcanization times (t90 values), with respect to composites with only silica. Lower induction vulcanization times are not correlated with the presence of sulphur on the sepiolite surface. Indeed, composites with sepiolite modified with sulphur containing silica (nano) particles show lower induction vulcanization time only in the case of particles formed ex ante. Hence, to explain the lower ts1 values, one could hypothesize the lower acidity of sepiolite surface as well as the lower absorption of vulcanization ingredients which could be thus more reactive. Moreover, one could take into consideration that, in the crosslinking experiments, the increase of Modulus is taken as the indication of crosslinking network formation. It could be thus commented that a high aspect ratio filler such as sepiolite gives rise to a faster network formation.

In conclusion, the use of sepiolite, pristine ore chemically modified, appears to have positive effects on the composite viscosity and does not substantially alter the vulcanization kinetics. In particular, appreciable differences cannot be observed among results obtained by using sepiolite modified with sulphur based silica (nano)particles formed in situ or ex ante.

Dynamic mechanical properties

Dynamic mechanical properties were investigated by applying sinusoidal stresses in the shear mode. Strain sweep tests were performed on composites of Table 5. In Table 7, are reported values of: shear modulus at minimum strain: $G'_{(0,4\%)}$, difference of G' values measured at minimum and maximum strain: $\Delta G'_{(0.4\% - 25\%)}$, normalized with respect to G' value at minimum strain: $\Delta G'_{(0,4\% - 25\%)} / G'_{(0,4\%)}$, the maximum value of the ratio between the loss G" modulus and the shear G' modulus: Tan delta max.

The reduction of modulus as the strain amplitude increases (ΔG') indicates the non linearity of the storage modulus. This phenomenon is known as Payne effect [44] and is explained with reference to various mechanisms [45]: the reversible de-agglomeration of filler aggregates [44, 46-48], the desorption of polymer chains from the filler surface [49-50], the reduction of the layer of polymer immobilized on filler particles [47], the increase of distance among filler particles [48].

The replacement of silica with pristine sepiolite led to a subtle reduction of Payne effect (from 0.46 to 0.43 as normalized ΔG'), but to appreciable increase of

7 **$G'_{\gamma min}$, ΔG'/G', Tan delta max for composites of Table 5**

Property	**Filler in the composite**							
	Silica	Silica + Sp	Silica + Sp/TEOS		Silica + Sp/TEOSPD		Silica + Sp/TEOS/TESPD	
			in situ	ex ante	in situ	ex ante	in situ	ex ante
$G'_{(0,4\%)a}$	1.58	1.35	1.13	1.58	1.5	1.57	1.39	1.4
$\Delta G'_{(0,4\% - 25\%)} / G'(0,4\%)$	0.46	0.43	0.38	0.49	0.44	0.44	0.40	0.41
Tan Delta max	0.162	0.177	0.153	0.197	0.157	0.162	0.155	0.159

[a] in MPa

Tan delta, in spite of the lower volume fraction of pristine sepiolite. This finding confirms what already reported [21-23] and commented in the introduction: pristine sepiolite brings about the increase of composite hysteresis.

The composite with silica (nano)particles from TEOS prepared ex ante shows Payne effect and hysteresis even larger than those of composite with pristine sepiolite. Also these results from strain sweep experiments seem to suggest that, in the composite based on ex ante silica (nano)particles from TEOS, sepiolite increases its reactivity prevailingly with other filler particles rather than with the elastomer chains. As commented above, to account for the higher ML value of the composite, such chemically modified sepiolite revealed (see Table 4) lower mass loss in the range from 150 °C to 450 °C and could be thus characterized by a lower hydrophobization of its surface.

All the other composites with chemically modified sepiolite show lower Payne effect and Tan Delta. In particular, better results were obtained with the in situ procedure.

In conclusion, strain sweep tests indicate that the chemical modification of sepiolite with silica (nano)particles, carried out through the appropriate procedure, leads to the reduction of hysteresis of the composite based on silica/sepiolite as the reinforcing filler system.

Dynamic-mechanical properties were also determined by applying sinusoidal stresses in the axial mode. Values of E' and Tan Delta at 10 °C, 23°C and 70 °C are in Table 8.

Tan delta values, shown in Table 8, were plotted as a function of temperature in the graphs shown in Figure 7, in Fig. 7a and in Fig. 7b for silica (nano)particles prepared in situ or ex ante, respectively. For the sake of clarity the lines referring to silica and pristine sepiolite based composites are reported

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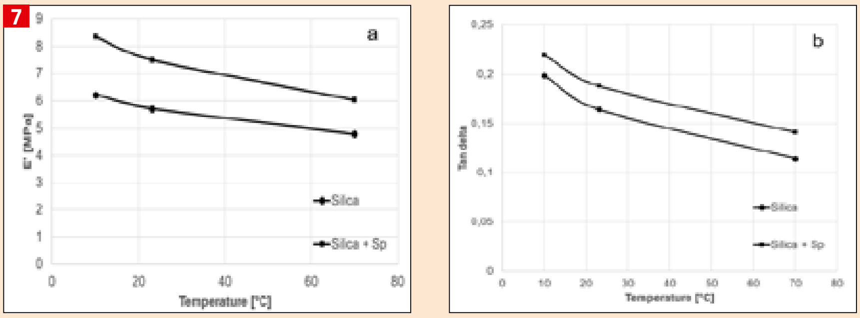

Figure 7. Tan Delta as a function of temperature for composites with silica and silica + pristine sepiolite. Data are in Table 8.

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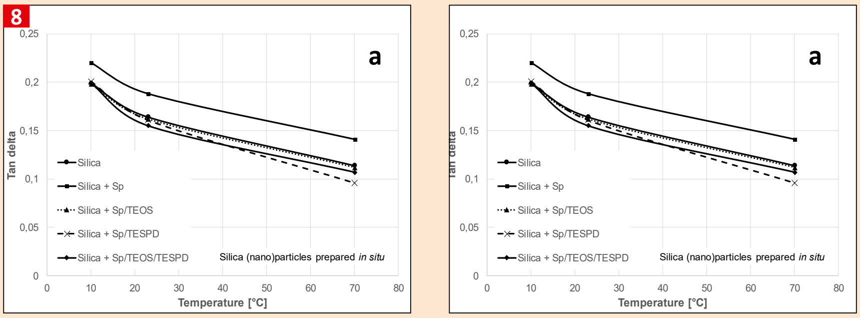

Figure 8. Tan Delta as a function of temperature for composites of Table 5, with silica (nano) particles prepared in situ (a) or ex ante (b). Data are in Table 8.

8 E', E", TAN DELTA FOR IR/BR BASED COMPOSITES OF TABLE XIII AND TABLE XIV

Property	Filler in the composite							
	Silica	Silica + Sp	Silica + Sp/TEOS		Silica + Sp/TEOSPD		Silica + Sp/TEOS/TESPD	
			in situ	ex ante	in situ	ex ante	in situ	ex ante
E' @ 10 °C	6.22	8.35	6.64	8.03	8.51	8.98	7.76	7.95
Tan δ @ 10 °C	0.199	0.220	0.198	0.213	0.201	0.206	0.202	0.210
E' @ 23 °C	5.72	7.51	6.05	7.29	7.71	8.21	7.01	7.20
Tan δ @ 23 °C	0.164	0.188	0.162	0.177	0.161	0.167	0.157	0.176
E' @ 70 °C	4.79	6.03	5.07	5.95	6.27	6.69	6.03	5.83
Tanδ @ 70 °C	0.114	0.141	0.112	0.142	0.0961	0.114	0.108	0.128
ΔE' (70°C – 10°C)	1.43	2.32	1.57	2.08	2.24	2.29	1.73	2.12

The partial replacement of silica with pristine sepiolite led to larger rigidity (higher E' values), at every temperature (Figure 7). This finding confirms that a high aspect ratio nanofiber such as sepiolite is suitable to promote larger mechanical reinforcement of elastomer composites. However, pristine sepiolite brought also about higher values of ΔE'(70°C – 10°C) and a remarkable increase of Tan delta, at all temperatures and in particular at 70°C. Graphs in Figure 8 clearly show that the line which refers to the Tan Delta points of composites with pristine sepiolite lies well above the lines due to all the other composites. The larger reduction of E' with the increase of temperature and the increase of hysteresis, particularly at high temperature, are negative aspects of elastomeric composites for dynamic mechanical applications such as the one in tyre compounds and prevent the scale up of pristine sepiolite as reinforcing filler.

Pretty similar dynamic-mechanical properties can be observed in Table 8 for the composites with sepiolite modified with silica (nano)particles from TEOS prepared ex ante. As already commented above, these nanoparticles do not appear to promote the reactivity of sepiolite with the elastomer chains.

Silica (nano)particles from TEOS prepared in situ promote composite properties pretty similar to those of the composites with only silica as the filler. It seems that the chemical modification of sepio-

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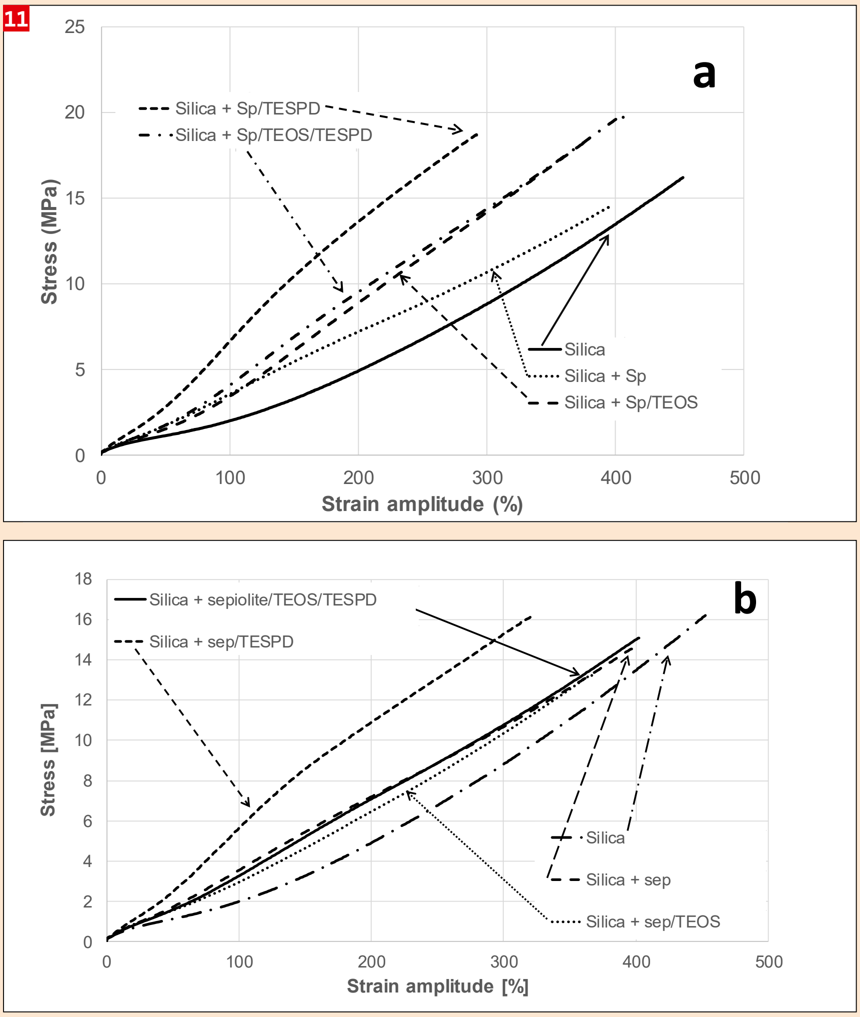

Figure 11. Stress-strain curves for composites of Table 5: silica (nano)particles prepared in situ (a) or ex ante (b)

lite with TEOS is not enough to establish chemical links with the polymer chains.

Sepiolite modified with sulphur based (nano)particles led to substantial increase of E’, at every temperature. Particularly interesting results were obtained with (nano)particles prepared with the in situ procedure: the dynamic rigidity was appreciably larger than the one of silica based composite and the hysteresis was similar at 10 °C and lower at 23 °C and 70 °C. Sulphur based (nano) particles appear to promote the chemical linkage of sepiolite with the elastomer chains. Indeed, the theory of reinforcement [1, 2] teaches that this is the typical behavior of a filler chemically bound to polymer chains. Results in Table 8 allow also to hypothesize that an appropriate tuning of the sulphur content of sepiolite could lead to the beast balance of rigidity as a function of temperature and hysteresis.

Tensile properties

Tensile properties were determined with quasi-static measurements. The dependence of stress on strain is shown in Figure 11, Fig. 11a and Fig. 11b for in situ and ex ante silica (nano)particles, respectively.

The partial replacement of silica with pristine sepiolite led to the enhancement of the stresses at every elongation and to lower stress and elongation at break. These findings are in line with the results of dynamic mechanical tests. Remarkable enhancement of the static reinforcement was obtained by performing the chemical modification of sepiolite with the in situ procedure and the largest reinforcement was achieved with sepiolite modified with particles from TESPD condensation.

The comparative analysis of results from axial dynamic mechanical and from tensile tests allows to comment that the in situ modification of sepiolite with Sulphur based silanes leads to substantial enhancement of the mechanical reinforcement and to similar or lower hysteresis.

CONCLUSIONS

This work demonstrates that sepiolite is an efficient reinforcing filler for rubber composites based on a diene rubber and silica as the main filler, as it is able to promote lower composite viscosity, larger dynamic-mechanical reinforcement and lower dissipation of energy, provided that the chemical reactivity of sepiolite with the rubber matrix is established. This work demonstrates that such reactivity can be achieved through the chemical modification of sepiolite with silica(nano)particles prepared via silanes condensation, either in situ on the sepiolite surface or ex ante, preserving its fibrillary structure. This work confirms that pristine sepiolite does enhance the mechanical reinforcement of a rubber composite but leads as well to a remarkable increase of the composite hysteresis. It is shown that, to achieve the best composites’ properties, silanes containing sulphur atoms bridges should be used and that the ideal procedure is the formation of silica nanoparticles in situ.

The commercial development of rubber compounds based on chemically modified sepiolite has been recently announced [28, 29]. Mechanical reinforcement, lower rolling resistance and better wet grip were obtained. The research on the chemical modification of sepiolite and this first commercial success pave the way for the large use of a naturally occurring nanofiller.

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