

Preparation and Characterization of EPDM Rubber Modified with *in Situ* Generated Silica

Davide Morselli,¹ Federica Bondioli,¹ Adriaan S. Luyt,² Thabang H. Mokhothu,² Massimo Messori¹

¹Department of Engineering 'Enzo Ferrari', University of Modena and Reggio Emilia, Via Vignolese 905/A - 41125 Modena, Italy

²Department of Chemistry, University of the Free State (Qwaqwa Campus), Phuthaditjhaba 9866, South Africa

Correspondence to: M. Messori (E-mail: massimo.messori@unimore.it)

ABSTRACT: This article is concerned with the preparation of a filled elastomer by means the nonconventional bottom-up approach to polymer composites, alternatively with the conventional mechanical compounding of preformed filler particles with rubber. EPDM rubber was modified with *in situ* generated silica particles prepared by means of a sol-gel process adopting a solution process. The used synthetic procedure permitted the preparation of highly filled rubbers (up to 40 wt % of silica) with silica particle dimensions ranging from 0.2 to 2 μm . Equilibrium swelling and extraction tests indicated a hindering effect of the presence of *in situ* generated silica on the vulcanization process which reduced the cross linking degree of the rubber matrix. Both tensile tests and dynamic-mechanical analysis showed a significant improvement in the mechanical properties due to the presence of the reinforcing filler, with an enhancement more significant than that expected from a simple hydrodynamic reinforcing mechanism. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 128: 2525–2532, 2013

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INTRODUCTION

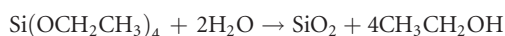
Rubbers usually require the addition of inorganic fillers to enhance their basic properties and make them useful for practical applications. In addition to carbon black, which is one of the most used reinforcing fillers for rubber materials (especially in the tyre industry), silica represents another important filler used for reinforced elastomers. Silica compounding offers several advantages with compared with carbon black, such as better combination of tear strength, abrasion resistance and ageing resistance. Furthermore, in the tyre industry, silica imparts to tyre treads a lower rolling resistance than carbon black and at the same time an equal wear resistance and wet grip.¹

One of the main disadvantages of the use of silica prepared by the conventional *ex situ* synthesis methods is the high tendency for the particles to agglomerate within the rubber matrix due to the strong particle-particle interactions, which can result in high compound viscosity and reduced processability. Furthermore, the incompatibility between silica and nonpolar elastomers, such as styrene-butadiene rubber or natural rubber, often requires the use of silane coupling agents to improve the reinforcing efficiency of silica.²

An alternative and interesting approach to the incorporation of preformed particles into the elastomer matrix by mechanical

mixing (compounding) before its vulcanization (*ex situ* process), is the *in situ* generation of inorganic oxides (silica or other) through a sol-gel process, which is the so-called bottom-up approach to obtain organic-inorganic hybrid materials.

The sol-gel process involves the generation of ceramic-type materials by the hydrolysis and condensation reactions of organometallic compounds such as metal alkoxides.³ One of the mostly used reactions is the hydrolysis and condensation of tetraethoxysilane (TEOS) to form silica according to the following reaction:



Organic-inorganic hybrid materials can be prepared with these reactions in the presence of organic molecules or macromolecules, which should preferably contain functional groups to improve their bonding to the inorganic phase. The possibility of preparing rubbers, modified with metal oxides generated *in situ* by a sol-gel process, has already been reviewed by several authors in recent publications.^{4–9}

It is generally accepted that the extent of mechanical reinforcement of elastomers is controlled by three main factors, namely: the dispersion state of the filler, the filler-matrix interactions and the filler-filler interactions.^{10–12} A major potential of the

sol-gel technique stems from the possibility to control the amount of silica generated *in situ* and its morphological characteristics by a proper selection of the reaction conditions (e.g., amount of TEOS, type and amount of catalyst, temperature and reaction time). Furthermore, it is possible to tailor filler-filler and filler-rubber interactions through the incorporation of silane coupling agents in the reaction mixture. These compounds have functional groups suitable for improving filler-matrix interactions, thus allowing for a better silica dispersion and a higher mechanical reinforcement.⁴

Messori et al. recently published several papers on the *in situ* generation of silica from TEOS into isoprene rubber,^{13–15} in particular reporting detailed studies of the interrelation between preparation conditions, structure and mechanical reinforcement. A similar approach was used in the present study on the preparation and characterization of ethylene-propylene-diene-monomer (EPDM) rubbers. Concerning EPDM-based materials modified by *in situ* generation of silica, Das et al.¹⁶ swelled triethoxysilyl-grafted EPDM in TEOS and activated the sol-gel process by adding *n*-butyl amine as a basic catalyst. After rubber vulcanization, mechanical characterization showed that *in situ* sol-gel derived fillers had superior reinforcing efficiency, compared with the externally added silica at the same concentration of these fillers in an EPDM matrix. The main limitation of the proposed synthetic method was the relative low value of the maximum concentration of *in situ* generated silica, which appeared limited by diffusion phenomena of TEOS within the unvulcanized rubber matrix during the swelling step. In order to overcome this drawback, a solution process¹⁵ was proposed in this work as described in the following:

1. dissolution of both the metal alkoxide (metal oxide precursor) and unvulcanized rubber in a common solvent;
2. addition of water, sol-gel catalysts and vulcanization ingredients and activation of the sol-gel process at a given temperature and for a given reaction time;
3. removal of solvent and by-products by evaporation;
4. vulcanization of the filled rubber.

In principle, this solution procedure ensures a highly homogeneous dispersion of the *in situ* generated filler in the rubbery matrix, also for high reinforcing metal oxide contents.

EXPERIMENTAL

Materials

EPDM rubber (Polimeri Europa Dutral[®] TER 4038, density $\rho_{\text{EPDM}} = 0.91 \text{ g cm}^{-3}$) was kindly provided by ATG Italy (Castel d'Argile, BO, Italy).

Tetraethoxysilane (TEOS), toluene, ethanol (EtOH), and dicumyl peroxide (DCP) were purchased from Sigma Aldrich (Milan, Italy). All materials were high purity reactants and were used as received without any further purification.

Preparation and Characterization of EPDM-Silica Composites

For kinetic analysis, EPDM rubber was dissolved in toluene (about 3 g in 100 mL) at room temperature. After complete dissolution, a given amount of TEOS, H₂O, EtOH (TEOS : H₂O : EtOH = 1 : 4 : 4 mol) and dibutyltin dilaurate (2 wt % relative

Table I. Composition of the Prepared Materials

Material code	SiO ₂ content ^a (wt %)	SiO ₂ content ^b (wt %)	SiO ₂ volume fraction (–)
EPDM_0	0	0.0	0.00
EPDM_05	5	5.0	0.03
EPDM_15	15	15.0	0.09
EPDM_30	30	27.8	0.17
EPDM_45	45	40.7	0.27

^aNominal value calculated by assuming the complete conversion of TEOS to silica.

^bExperimental value obtained by thermogravimetry.

to TEOS, as a catalyst for the sol process) were added. TEOS was added in different quantities in order to obtain silica contents ranging from 0 to 45 wt %. The mixture usually assumed the an emulsion state due to the presence of a significant amount of water in an organic medium. The mixture was magnetically stirred and heated at 80°C to activate the hydrolytic condensation of TEOS to silica. After a given reaction time (from 1 to 9 h), a portion of the suspension was collected and toluene and other volatile products, such as H₂O and EtOH, were eliminated with a rotary evaporator operating at a reduced pressure and room temperature to prevent any significant further progress of the sol-gel reaction.

The actual silica content in the filled rubber was determined by thermogravimetric analysis (TGA).

For the preparation of the samples for the other characterizations, the above described procedure was adopted for a fixed reaction time of 6 h. Solvents and other volatile products were partially eliminated (~50% of the total amount) and DCP was added to the suspension at a concentration of 2 phr (parts per hundred resin). The suspensions were cast into Petri dishes and the volatiles were completely eliminated by leaving the systems under an aspiration hood overnight.

The films (about 0.5 mm thick) were vulcanized by hot-pressing at 160°C for 20 min. The filled materials were coded as EPDM_*x* in which *x* represents the nominal final weight percent of silica (by assuming the complete conversion of TEOS to silica during the sol-gel reaction).

Nominal and actual silica concentrations are reported in Table I. Volume fraction values were calculated under the assumption of volume additivity after experimental determination of the density of silica obtained from TEOS (under experimental conditions similar to those used for the EPDM_*x* composites, $\rho_{\text{SiO}_2} = 1.66 \text{ g cm}^{-3}$).¹⁵

The morphological investigation was carried out with scanning electron microscopy (SEM, TESCAN VEGA3 scanning electron microscope) by the application of an accelerating voltage of 15 kV. The samples (cross section) were coated with gold (thickness 10 nm) by an electrodeposition method to impart electrical conduction before the SEM micrographs were recorded.

Swelling experiments were carried out by the immersion of punch-cut specimens (size 7 × 3 × 0.5 mm³) in 50 mL of

toluene at room temperature for several hours. Toluene was replaced hourly with fresh solvent to eliminate all uncross linked fractions, such as unvulcanized EPDM chains, which would lead to wrong values of the swelling ratio. When the swollen mass (m_s) reached a constant value, the sample was dried to a constant mass (i.e., the dried mass m_d), and the absolute swelling ratio (q) was evaluated according to the following equation:

$$q = \frac{m_s}{m_d}$$

The absolute extractable fraction (f) was determined as follows:

$$f = \frac{m_0 - m_d}{m_0} 100$$

where m_0 is the mass of the sample before its immersion in toluene.

The values of q and f were also normalized to the actual EPDM weight (i.e., the swellable phase and, in the case of incomplete vulcanization, the extractable phase), and these values were called q_{EPDM} and f_{EPDM} , respectively. Their values were calculated as follows:

$$q_{\text{EPDM}} = \frac{q}{w_{\text{EPDM}}}$$
$$f_{\text{EPDM}} = \frac{f}{w_{\text{EPDM}}}$$

where w_{EPDM} is the weight fraction of EPDM present in the composite.

Uniaxial tensile tests were performed by a Hounsfield dynamometer (model H5KS). The experiments were run at room temperature, on strips of $65 \times 12 \times 0.5 \text{ mm}^3$ in size, using a gauge length of 20 mm and a crosshead speed of 100 mm min^{-1} . Tensile test data were presented as nominal stress $\sigma_n = F/A_0$ versus elongation $\varepsilon = \Delta l/l_0$ curves, where F is the applied force and A_0 is the initial cross-sectional area of the specimen, while Δl and l_0 are the change in length and the gauge length, respectively. The initial modulus E_{in} was calculated as the slope of the initial portion of the $\sigma_n - \varepsilon$ curves. The secant modulus at a given elongation E_{sec} , ε was calculated as E_{sec} , $\varepsilon = \sigma_{n(\varepsilon)}/\varepsilon$ where $\sigma_{n(\varepsilon)}$ is the nominal stress at the elongation ε considered. All mechanical properties were determined on an average of at least five specimens.

The glass transition temperature (T_g), storage modulus (E') and loss factor ($\tan \delta$) were determined through dynamic-mechanical analysis (DMA) using a Diamond DMA (Perkin Elmer); punch-cut specimens ($40 \times 10 \times 0.5 \text{ mm}^3$) were tested in tensile mode at a constant frequency of 1 Hz, while heated from -100 to 100°C at a rate of 3°C min^{-1} under nitrogen gas.

T_g values were also determined by using differential scanning calorimetry (DSC). The DSC curves were recorded at a heating/cooling rate of 5°C min^{-1} over the range $-70/0^\circ\text{C}$ by using a TA Instruments DSC 2010 purged with nitrogen.

Thermogravimetric analysis (TGA) was carried out on a Perkin-Elmer TGA7 Thermogravimetric Analyzer under nitrogen

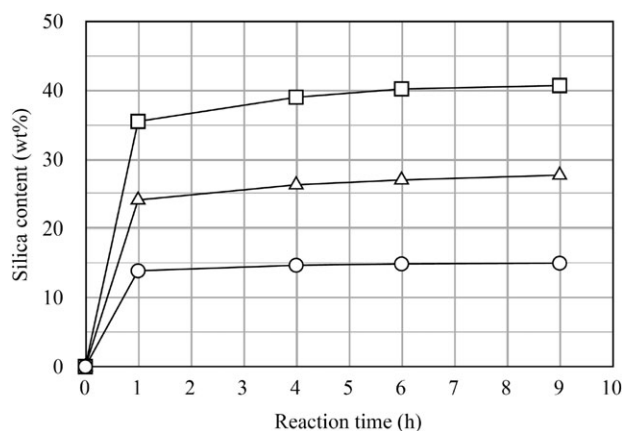


Figure 1. Silica content (determined by TGA) as a function of the reaction time for (○) EPDM_15, (△) EPDM_30 and (□) EPDM_45.

flow (20 mL min^{-1}), from 30 up to 600°C at a heating rate of $10^\circ\text{C min}^{-1}$.

Film transparency was characterized by UV-Vis spectrophotometry (Perkin-Elmer, Lambda 19) in the $400\text{--}800 \text{ nm}$ range. The reported spectra were normalized against air and with respect to the thickness of unfilled vulcanized rubber.

RESULTS AND DISCUSSION

Kinetic Analysis

The progress of the sol-gel reaction was followed by determining the actual silica content through TGA at different reaction times. The real silica content values are reported as a function of the reaction time, as shown in Figure 1, for the EPDM_ x samples.

As expected, the actual silica content, correlated with the degree of conversion of TEOS to silica, increased with the sol-gel reaction time, i.e., with the time allowed for the mixture to react before it underwent the solvent elimination step. Under the used experimental conditions (time and temperature) for the *in situ* generation of silica within the rubber matrix, the maximum silica weight percentages for EPDM_15, EPDM_30 and EPDM_45 were 15.0, 27.7 and 40.7 wt %, respectively. The data indicate a quantitative conversion of TEOS to silica for relatively low TEOS initial content (EPDM_15 sample) and a progressive reduction of TEOS conversion by increasing the amount of TEOS present at the beginning of the reaction. However, it is important to observe that generally a very high conversion value (higher than 90%) was obtained.

The data reported in Figure 1 indicate that silica content values very close to the maximum (i.e., by assuming the complete conversion of TEOS to silica) were obtained for all of the samples after a reaction time in the range 4–6 h. On the basis of these results, the subsequent characterizations were carried out on samples prepared with a reaction time fixed at 6 h.

Morphology

The specimens were broken in liquid nitrogen and the cross-sections were analyzed by scanning electron microscopy (SEM).

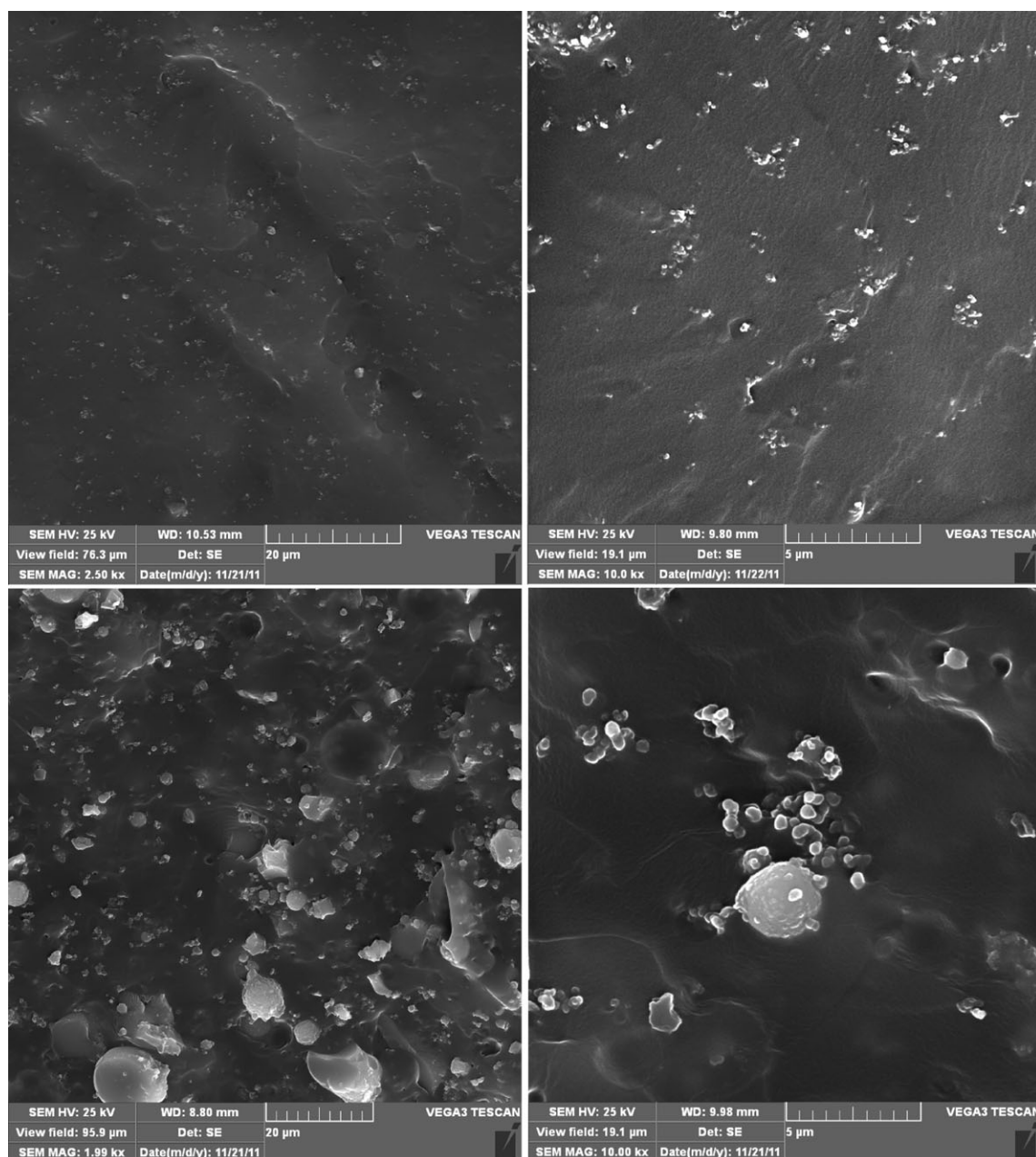


Figure 2. SEM micrographs of the cross-section of EPDM_5 (top) and EPDM_30 (bottom).

The typical SEM micrographs of vulcanized rubber with a nominal silica content of 5 and 30 wt % are reported in Figure 2.

The cross-section of the EPDM_5 sample shows the presence of a dispersed phase with a homogeneous distribution of silica particles in the rubber matrix and good particle–matrix adhesion, supporting the effectiveness of the *in situ* filler generation process adopted for the preparation of the filled rubbers. The dispersion degree was also good as indicated by the almost negligible presence of particles agglomerates. The average dimension of the spherical silica particles was below $0.2 \mu\text{m}$.

By increasing the initial TEOS content (EPDM_30 sample), the particles distribution remained good enough, though a significant increase in particle size and size distribution clearly occurred. In

particular, large particles having diameters larger than $10\text{--}15 \mu\text{m}$ were present together with smaller particles (about $1 \mu\text{m}$ in size). Particles aggregation was also present indicating a general reduction in the degree of dispersion. This behavior has already been observed and reported by other authors for similar systems,^{15,17} and can be tentatively explained by considering that an increase in the amount of *in situ* formed dispersed phase (silica from TEOS) gives rise to an increase in the coalescence of the growing silica particles, and thus an increase in both the average dimension of the dispersed particles and aggregation phenomena are expected.

Equilibrium Swelling Analysis and Extractable Fraction

The values of q , q_{EPDM} , f and f_{EPDM} in toluene are reported in Table II. For the unfilled rubber, equilibrium swelling analysis is

Table II. Swelling/Extraction Tests: Absolute Swelling Ratio (q) and Extractable Fraction (f) and Values Normalized with Respect to the EPDM Content (q_{EPDM} and f_{EPDM})

Material code	q (–)	q_{EPDM} (–)	f (%)	f_{EPDM} (%)
EPDM_0	3.0	3.0	5.3	5.3
EPDM_05	3.1	3.3	6.8	7.2
EPDM_15	3.7	4.3	7.2	8.5
EPDM_30	5.1	7.0	15.1	20.9

a well-known method to evaluate the number of effective network chains per volume unit (i.e., the crosslinking density) of an elastomer after vulcanization.

In the case of the filled vulcanized rubber, the swelling behavior depends on complex and different phenomena, such as the crosslinking degree of the rubber matrix, the solvent absorption contribution of the silica phase, the ability of the silica particles to act as crosslinking points (i.e., density of polymer–filler attachments), and so on.

Taking into account that conversion of TEOS to silica was almost quantitative for the samples of Table II, as indicated by the above discussed kinetics analysis, the extractable fraction in toluene was mainly derived from the uncrosslinked fraction of EPDM. In other words, it could be considered an indicator of the progress of the vulcanization process of EPDM.

In principle, the presence of an inorganic filler should lead to a reduction of the swelling ratio with respect to the unfilled vulcanized rubber, because of the fact that the filler does not absorb toluene during the experiment. In the present case an opposite trend was observed with both the absolute and normalized swelling ratio values q and q_{EPDM} progressively increasing with the content of silica in the vulcanized rubber. In particular, the increment of q_{EPDM} (i.e., the swelling ratios referring only to the organic rubber phase) was attributable to the decreasing crosslinking density of the rubber phase after vulcanization. This hypothesis is also supported by the observation that f_{EPDM} in toluene increased with increasing silica content (and thus the initial TEOS concentration); this clearly indicates an interfering effect of the sol–gel reaction of TEOS to silica on the vulcanization process of the rubber.

From the swelling and extraction tests, it is possible to conclude that the *in situ* generation of silica particles by means of the sol–gel process led to a hindering effect on the vulcanization process, which limited the extent of the crosslinking of the

EPDM phase, as already observed for similar materials based on isoprene rubber.¹⁴

Tensile Properties

The results obtained by mechanical characterization (tensile tests) are summarized in Table III.

Extraction tests clearly show that the materials under investigation were characterized by different cross linking densities inversely depending on the silica content. The mechanical properties of the EPDM rubber matrix would then presumably be different for the EPDM_ x series (in particular the modulus and strength were expected to decrease as a result of the decreasing cross linking density). Notwithstanding this important consideration, data shown in Table III indicate that the presence of silica as rigid filler in the elastomeric EPDM matrix led to a significant increase in stiffness (both initial and secant moduli) and of the ultimate properties such as stress at break (σ_b). Concerning the low deformation range, the initial modulus increased monotonically by increasing the silica content with an average value for EPDM_30 (4.48 MPa) 2.5 times higher than that of the unfilled vulcanized EPDM_0 (1.76 MPa). Stiffening and reinforcing effects due to the presence of silica were also observed in a large deformation range with values of secant modulus $E_{sec,\epsilon=1}$, $E_{sec,\epsilon=2}$ and $E_{sec,\epsilon=3}$ and of stress at break σ_b being systematically higher than those of the unfilled rubber. In this case, the maximum values of $E_{sec,\epsilon}$ and σ_b were observed for the intermediate silica contents (EPDM_15), suggesting that the ultimate properties in the large deformation range were the result of a complex balance between the increasing content of rigid filler and the decreasing crosslinking density of the rubber matrix.

Das et al.¹⁶ proposed a “reinforcing efficiency” (RE) parameter to evaluate the reinforcing effect due to the presence of silica with respect to the unfilled rubber. RE is defined as the quotient of the difference of the secant moduli at 100% elongation of filled and unfilled vulcanized rubber ($(E_{sec,\epsilon=1})_{filled}$ and $(E_{sec,\epsilon=1})_{unfilled}$, respectively), with reference to the amount of filler (wt %SiO₂). The reinforcing efficiency is thus defined by:

$$RE = \frac{(E_{sec,\epsilon=1})_{filled} - (E_{sec,\epsilon=1})_{unfilled}}{\text{wt \%SiO}_2}$$

RE values varied from 0.008 to 0.018, showing a maximum value for the intermediate silica content (EPDM_15, see Table III) as already discussed for secant moduli. Even if a direct comparison can be debatable, taking into account the different vulcanizing agents used and thus the different cross linking degrees, it is interesting to observe that the present RE values

Table III. Mechanical Characterization: Initial Modulus (E_{in}), Secant Modulus at an Elongation $\epsilon = 1,2,3$ ($E_{sec,\epsilon=1}$, $E_{sec,\epsilon=2}$, $E_{sec,\epsilon=3}$), Stress at Break (σ_b), Deformation at Break (ϵ_b) and Reinforcing Efficiency (RE)

Material code	E_{in} (MPa)	$E_{sec,\epsilon=1}$ (MPa)	$E_{sec,\epsilon=2}$ (MPa)	$E_{sec,\epsilon=3}$ (MPa)	σ_b (MPa)	ϵ_b (–)	RE (MPa/wt%)
EPDM_0	1.76	1.01	0.63	0.53	1.57	3.35	–
EPDM_05	2.06	1.08	0.67	0.53	2.07	4.57	0.013
EPDM_15	2.93	1.28	0.78	0.59	2.32	6.10	0.018
EPDM_30	4.48	1.24	0.69	0.49	2.09	10.14	0.008

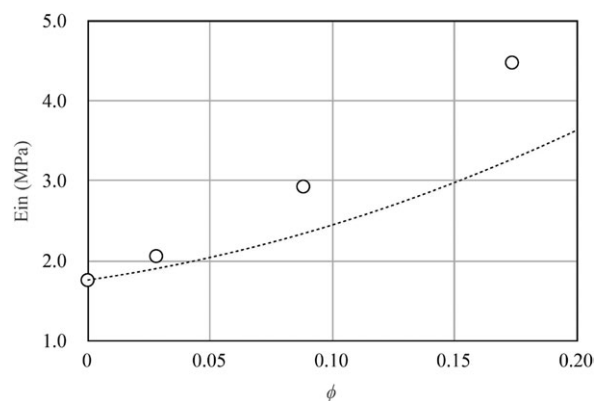


Figure 3. Initial elastic modulus as a function of filler volume fraction for EPDM_x: (dashed line) predicted values from the Smallwood-Guth-Einstein equation and (○) experimental data.

are about one order of magnitude lower than those observed by Das et al.¹⁶ (in the range 0.03–0.12). These results can be tentatively explained taking into account the absence of any coupling agent for the improvement of filler–matrix interfacial bonding for the materials reported here. The use of triethoxysilyl-grafted EPDM in the above mentioned paper presumably resulted in a better interfacial interaction between the silica particles and the rubber matrix, and thus to a higher reinforcement effect. In this respect, the present solution process could be reasonably enhanced by using a suitable coupling agent for the improvement of filler–matrix adhesion.

Concerning the initial modulus, the effect due of the inclusion of rigid filler particles is known as hydrodynamic reinforcement and can be quantitatively predicted by using the Smallwood-Guth-Einstein equation¹⁸:

$$E = E_0(1 + 2.5\phi + 14.1\phi^2)$$

in which ϕ represents the filler volume fraction. Notwithstanding the strict assumptions of this equation (the filler particles are spherical, completely wetted by the rubber and interact only pair-wise), it could be a useful preliminary evaluation of the expected hydrodynamic reinforcement due to addition of a rigid filler. The initial elastic modulus E_{in} of filled EPDM predicted by the Smallwood-Guth-Einstein equation is reported in Figure 3, together with the experimental data obtained with tensile tests. The figure clearly shows significantly higher modulus values with respect to the theoretical calculation based only on a hydrodynamic effect. Remembering once again that the investigated materials were formed by a rubber matrix having a cross linking density which decreases by increasing the silica content, it is very interesting to observe the presence of an additional reinforcement with respect to the theoretical prediction, which is attributed to structure effects (the filler aggregates into chair-like structures producing a greater stiffening) and to the introduction of additional crosslinks into the network by the filler.

Kinetic theory predicts that the equilibrium stress in an unfilled vulcanized rubber is proportional to the number of elastically

effective network chains supporting the load.¹⁹ This number depends on the primary molecular weight of the rubber, the number of crosslinks forming the network and the number of chain entanglements isolated between these crosslinks. In this respect, additional fixed points in the network generated by filler–rubber attachments could be regarded simply as additional crosslinks. In other words, the mechanical properties of the rubber are modified more than it would have been by means of a mere addition of rigid particles to a soft elastomeric matrix. An additional contribution arises from molecular interaction between the rubber and the filler which can be evaluated by equilibrium swelling tests.

Dynamic–Mechanical Analysis

Storage modulus (E') and loss factor ($\tan \delta$) as a function of temperature are reported in Figure 4 for the EPDM_x samples. The values of storage modulus measured in the rubbery region (at a temperature of 60°C, that is at about $T_g + 100^\circ\text{C}$), damping (expressed as maximum value of loss factor, $\tan \delta_{\max}$) and of the glass transition temperature (determined as the peak temperature value of the loss factor $\tan \delta$) are reported in Table IV.

The DMA results show that some dynamic–mechanical properties of the vulcanized rubber were significantly affected by the silica content. It is usually expected that in particulate filled polymers, the addition of rigid fillers to the polymer matrix restricts the movement of the polymer chains leading to a

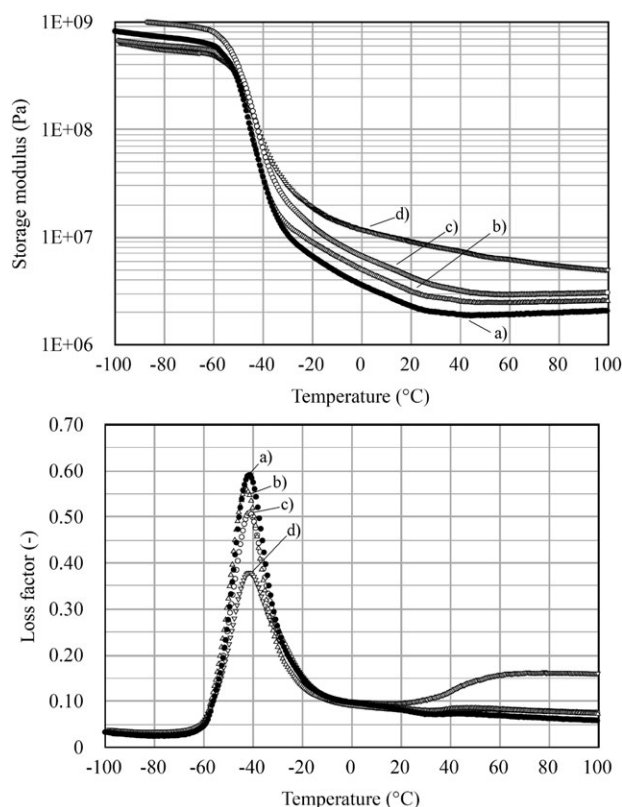


Figure 4. Dynamic–mechanical analysis: storage modulus (E') and loss factor ($\tan \delta$) as a function of temperature for (a) EPDM_0, (b) EPDM_5, (c) EPDM_15, and (d) EPDM_30.

Table IV. Storage Modulus Measured in the Rubbery Region (at a Temperature of 60°C, $E'_{T=60^\circ\text{C}}$), Damping (Maximum Value of $\tan \delta$, $\tan \delta_{\text{max}}$) and Glass Transition Temperature ($T_{g, \text{DMTA}}$ from $\tan \delta$ Peak Value, $T_{g, \text{DSC}}$ from DSC Analysis)

Material code	$E'_{T=60^\circ\text{C}}$ (MPa)	$\tan \delta_{\text{max}}$ (-)	$T_{g, \text{DMTA}}$ (°C)	$T_{g, \text{DSC}}$ (°C)
EPDM_0	1.89	0.591	-41.6	-50.3
EPDM_05	2.44	0.560	-42.9	-51.2
EPDM_15	2.94	0.509	-41.1	-50.9
EPDM_30	6.27	0.379	-41.4	-51.8

reduction in damping and a shift of T_g values to higher temperatures.²⁰

In this study, a significant reduction of damping (here evaluated as $\tan \delta_{\text{max}}$) was observed by increasing the silica content in the vulcanized rubber. On the contrary, the glass transition temperature was not affected by the presence of *in situ* generated silica with values ranging from -43 to -41°C independent on the silica content. The same results were also obtained by measuring the T_g values by means of differential scanning calorimetry (data reported in Table IV). The absence of a significant shift in T_g values to higher temperatures by increasing the filler content could be tentatively attributed to a weak filler–matrix interface or, more probably, to the decrease in the crosslinking density of the rubber matrix (as discussed above) which counterbalanced the presence of the rigid filler.

Concerning the mechanical properties in the rubbery region, a significant increase in storage modulus $E'_{T=60^\circ\text{C}}$ was observed by increasing the silica content in the vulcanizates. The $E'_{T=60^\circ\text{C}}$ values determined at $T_g + 100^\circ\text{C}$ of unfilled EPDM_0 (1.89 MPa) increased to 2.44, 2.94, and 6.27 MPa for EPDM_05, EPDM_15 and EPDM_30, respectively. The observed trend was

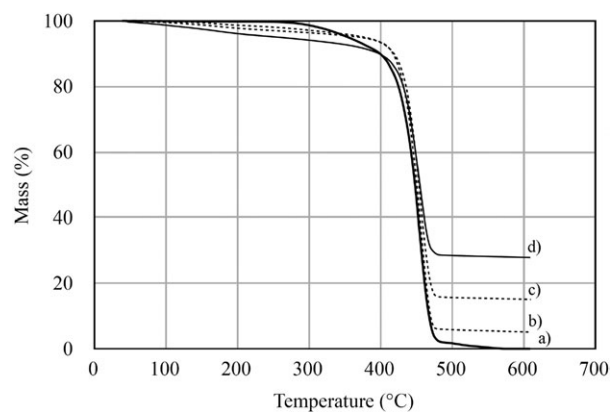


Figure 5. TGA curves of (a) EPDM_0, (b) EPDM_5, (c) EPDM_15, and (d) EPDM_30.

in perfect agreement with the tensile properties measured at low deformation (initial modulus, E_{in}) and previously discussed.

Thermal Stability

Representative TGA curves of EPDM_x are reported in Figure 5. The weight losses of the filled vulcanized rubber (Curves b, c, and d) occurred in two distinct steps. In the first step, the weight loss at around 100–350°C was probably due to the evaporation of strongly absorbed water and/or condensation by-products of the reaction of TEOS to silica. The second step, corresponding to the maximum weight loss in the range of 400–470°C, was ascribed to the thermal decomposition of the polymer chains.

The behavior of the unfilled EPDM_0 was slightly different due to the absence of silica and eventual by-products of the sol–gel reaction. The first decomposition started at about 270°C up to the main weight loss in the range of 400–470°C. It is interesting

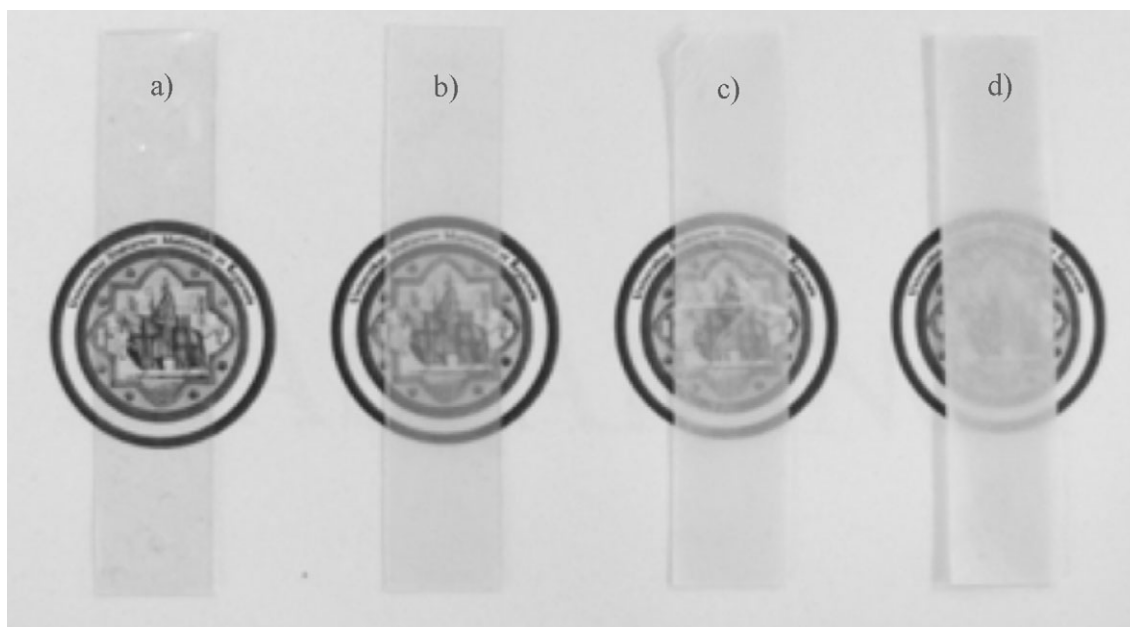


Figure 6. Photographs of (a) EPDM_0, (b) EPDM_5, (c) EPDM_15, and (d) EPDM_30 films.

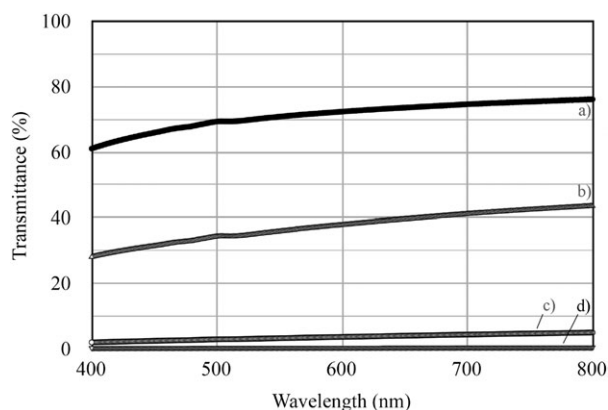


Figure 7. Visible spectra of (a) EPDM_0, (b) EPDM_5, (c) EPDM_15, and (d) EPDM_30 films.

to observe the presence of a third step with a small weight loss at around 470–550°C, presumably due to the combustion of char residues previously formed.

In general terms, the presence of *in situ* generated silica produced a very limited curve shift towards higher temperatures indicating an almost negligible enhancement of the thermal stability of the filled rubber compared with the unfilled one.

Optical Properties

The optical properties of the EPDM_x films can be deduced from the optical photographs and visible spectra reported in Figures 6 and 7, respectively.

As expected, the transparency evaluated by visual inspection (Figure 6) progressively decreased by increasing the filler content, presumably due to scattering phenomena present in the biphasic filled vulcanized rubber, and to the increasing average size of the silica particles.

The spectrophotometric analysis carried out in the visible wavelength range (400–800 nm), reported in Figure 7, shows that the unfilled EPDM_0 appeared relatively highly transparent with transmittance values ranging from 61 to 76% according to its amorphous and homogeneous character. The presence of a limited amount of silica particles influenced the transparency of the films as shown by the EPDM_5 sample with the transmittance values approximately reduced by half. The transparency was significantly inhibited by further increasing the filler content and particle sizes (EPDM_15 and EPDM_30).

CONCLUSIONS

Silica particles were *in situ* generated in an EPDM matrix by using a sol-gel process. The solution process adopted permitted the preparation of rubbers with very high filler content (greater than 40 wt %) with particle dimensions ranging from 0.2 to 2 μm. Particle diameter, size distribution, and agglomeration phenomena were found to increase by increasing the silica content due to coalescence phenomena during the growing of the particles. Optical properties (transparency) were accordingly reduced. Equilibrium swelling and extraction tests indicated a hindering effect of the presence of *in situ* generated silica on the vulcanization process which reduced the cross linking degree of

the vulcanized EPDM rubber. Notwithstanding the decrease in the cross linking degree of the matrix, both quasi-static tensile tests and dynamic-mechanical analysis showed a significant enhancement in the mechanical properties due to the presence of the reinforcing filler with improvements higher than those expected for a simple hydrodynamic reinforcing mechanism. The thermal stability of the filled rubbers was almost unchanged with respect the unfilled vulcanized rubber.

In conclusion, the use of the solution procedure, possibly coupled with the presence of suitable coupling agent for the enhancement of filler-matrix adhesion, seems to be a very promising way to produce silica reinforced vulcanized EPDM.

REFERENCES

- Mouri, H.; Akutagawa, K. *Rubber Chem. Technol.* **1999**, *72*, 960.
- ten Brinke, J. W.; Debnath, S. C.; Reuvekamp, L. A. E. M.; Noordermeer, J. W. M. *Compos. Sci. Technol.* **2003**, *63*, 1165.
- Brinker, C. J.; Scherer, G. W. *Sol-Gel Science: The Physics and Chemistry of Sol-Gel Processing*; Academic Press: Boston, **1990**.
- Messori, M. In *Recent Advances in Elastomeric Nanocomposites*; Mittal, V.; Kim, J. K.; Pal, K., Eds.; Springer: Berlin Heidelberg, **2011**.
- Bandyopadhyay, A.; Bhowmick, A. K. *Rubber-Silica Hybrid Nanocomposites*, Chapter 3; Bhowmick, A. K., Ed.; CRC Press; **2008**, pp 57.
- Bandyopadhyay, A.; Bhowmick, A. K. *J. Polym. Eng.* **2006**, *26*, 821.
- Mark, J. E. *Current Opinion in Solid State and Materials Science* **1999**, *4*, 565.
- Mark, J. E. *Acc. Chem. Res.* **2006**, *39*, 881.
- Bandyopadhyay, A.; Maiti, M.; Bhowmick, A. K. *Mater. Sci. Technol.* **2006**, *22*, 818.
- Yatsuyanagi, F.; Suzuki, N.; Ito, M.; Kaidou, H. *Polymer* **2001**, *42*, 9523.
- Berriot, J.; Martin, F.; Montes, H.; Monnerie, L.; Sotta, P. *Polymer* **2003**, *44*, 1437.
- Frohlich, J.; Niedermeier, W.; Luginsland, H. D. *Compos. Part A-Appl. Sci. Manufact.* **2005**, *36*, 449.
- Bignotti, F.; Borsacchi, S.; de Santis, R.; Geppi, M.; Messori, M.; Sudhakaran, U. P. *J. Appl. Polym. Sci.* **2012**, *125*, E398.
- Messori, M.; Fiorini, M. *J. Appl. Polym. Sci.* **2011**, *119*, 3422.
- Messori, M.; Bignotti, F.; De Santis, R.; Taurino, R. *Polym. Int.* **2009**, *58*, 880.
- Das, A.; Jurk, R.; Stockelhuber, K. W.; Heinrich, G. *J. Macromol. Sci. Part A-Pure Appl. Chem.* **2008**, *45*, 101.
- Ikeda, Y.; Kameda, Y. *J. Sol-Gel Sci. Technol.* **2004**, *31*, 137.
- Kraus, G. In *Reinforcement of Elastomers*; Kraus, G., Ed.; Wiley: New York, **1965**, Chap. 4.
- Flory, P. J. *Principles of Polymer Chemistry*; Cornell University Press: Ithaca, **1953**.
- Nielsen, L. E.; Landel, R. F. *Mechanical Properties of Polymers and Composites*; Marcel Dekker: New York, **1994**.