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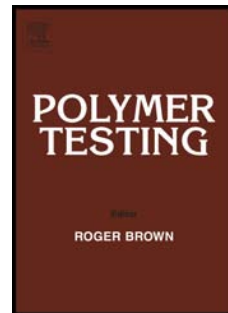
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Reinforcement of EPDM rubber with *in situ* generated silica particles in the presence of a coupling agent *via* a sol-gel route

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Material Properties

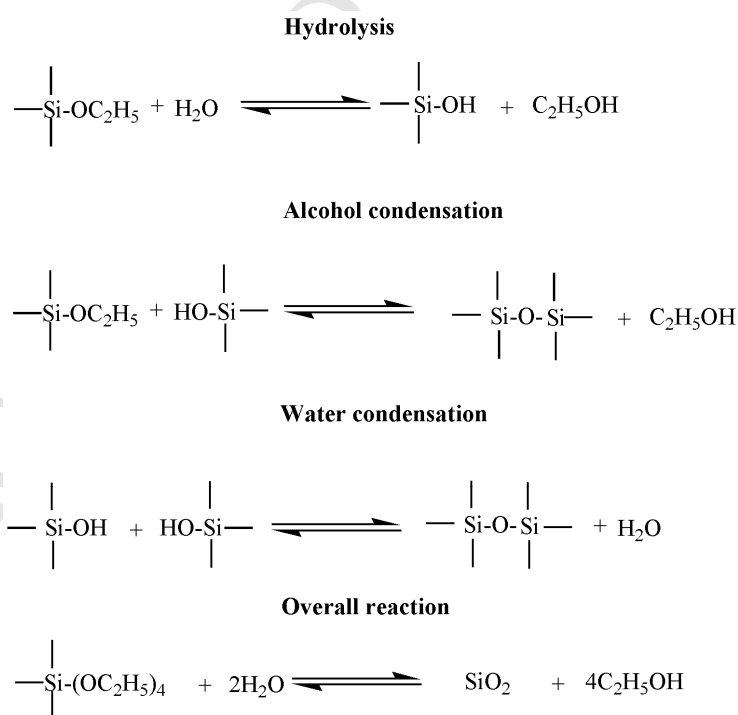
**Reinforcement of EPDM rubber with *in situ* generated silica particles in the presence of a coupling agent via a sol-gel route**T. H. Mokhothu<sup>1</sup>, A.S. Luyt<sup>1\*</sup><sup>1</sup>*Department of Chemistry, University of the Free State (QwaQwa Campus), Private Bag X13, Phuthaditjhaba, 9866, South Africa*M. Messori<sup>2</sup><sup>2</sup>*Department of Engineering 'Enzo Ferrari', University of Modena and Reggio Emilia, Via Vignolese 905/A - 41125 Modena, Italy***Abstract**

Ethylene propylene diene monomer rubber (EPDM)-silica (SiO<sub>2</sub>) composites were prepared by means of an *in situ* sol-gel process with tetraethoxysilane (TEOS) as precursor and bis-[-3-(triethoxysilyl)-propyl]-tetrasulfide (TESPT) as coupling agent. Homogenous dispersion of the silica particles was observed in all cases, as well as good adhesion between the filler and the matrix. The swelling and gel content results indicated that the number of crosslinks decreased, while the network was still extensive enough to maintain the high gel content. These results indicate that the coupling agent acted as a bridge between the hydrophilic silica and the hydrophobic rubber and enhanced the rubber-silica interactions. This enhanced interaction gave rise to increased thermal stability of the EPDM. The values of the Nielsen model parameters, which gave rise to good agreement with the experimentally determined Young's modulus values, indicate improved dispersion and reduced size of silica aggregates in the EPDM matrix. Good agreement was found between the storage modulus and Young's modulus values. The filler effectiveness (Factor C) indicated a mechanical stiffening effect and a thermal stability contribution by the filler, while the damping reduction (DR<sup>Norm</sup>) values confirmed that the EPDM interacted strongly with the well dispersed silica particles, and the polymer chain mobility was restricted.

**Keywords:** EPDM; silica; nanocomposites; coupling agent; reinforcement\* **Corresponding author** (LuytAS@qwa.ufs.ac.za)

## 1. Introduction

Growing of *in situ* sol-gel derived inorganic metal oxides (silica, titania, zirconia) is one of the promising routes for producing rubber matrices filled with uniformly dispersed particles [1-8]. However, an important disadvantage of reinforcement with inorganic fillers is their incompatibility with the rubber matrix, which ultimately gives rise to the formation of large aggregates in the matrix. An example is the very strong interaction between silica particles caused by hydrogen bonding of the silanol groups to the silica surface [1,2]. This interaction prevents the filler from uniformly dispersing in the matrix and, therefore, results in the formation of silica aggregates. This problem can be solved by the introduction of different types of silane coupling agents in the sol-gel process during the *in situ* generation, which should make it possible to modify the filler-matrix and filler-filler interactions [1,6,9,10]. The sol-gel reaction of tetraethoxysilane (TEOS) occurs in two steps, hydrolysis and condensation, and results in the formation of SiO<sub>2</sub>, as shown in Scheme 1. This application of the sol-gel process in rubber chemistry is related to the use of silane coupling agents and of moisture or silane curing, and it has already been carried out on natural rubber (NR), styrene-butadiene, ethylene propylene diene monomer rubber (EPDM) and butadiene rubber [2-5,9,11-14].



**Scheme 1 Sol-gel reaction of trioxysilane (TEOS)**



agglomeration with increasing filler content, as well as a decrease in the crosslinking density of the matrix as a result of the presence of silica particles. In this work, we focused on the preparation of *in situ* silica-EPDM rubber composites by introducing a silane coupling agent bis-[-3-(triethoxysilyl)-propyl]-tetrasulfide in the sol-gel process. The coupling agent was first pre-mixed with the EPDM matrix, followed by the addition of the precursor TEOS, after which the sol-gel reaction was initiated. This approach is expected to reduce the filler-filler interaction and give rise to improved thermal, mechanical and thermomechanical properties, as well as a better morphology and improved crosslinking.

## 2. Experimental

### 2.1 Materials

Tetraethoxysilane (TEOS), tin(II)2-ethylhexanoate, dicumyl peroxide, toluene, bis-[-3-(triethoxysilyl)-propyl]-tetrasulfide (TESPT, commonly known as Si-69) and ethanol were all supplied by Sigma-Aldrich. The materials were used as received without further purification. Ethylene propylene diene monomer rubber (EPDM), Polimeri Europa Dutral<sup>®</sup> TER 4038, density 0.91 g cm<sup>-3</sup>, was provided by ATG Italy (Castel d'Argile, BO, Italy).

### 2.2 Preparation of EPDM/SiO<sub>2</sub> nanocomposites

EPDM rubber was dissolved in toluene (3g/100ml) at room temperature, followed by addition of TESPT (4 wt% with respect to EPDM) under stirring. The EPDM/SiO<sub>2</sub> composites were prepared by the addition of TEOS, H<sub>2</sub>O, ethanol and tin(II)2-ethylhexanoate (1:4:4:0.04 mol ratio), respectively, in the EPDM-TESPT solution. The reaction mixtures were magnetically stirred and heated at 80 °C for 20 hours to activate the hydrolytic condensation of TEOS to silica (SiO<sub>2</sub>). The solutions were cooled to room temperature, followed by the addition of dicumyl peroxide (DCP) (1 wt% with respect to EPDM) under stirring. The reactions were taken to a rotating evaporator for elimination of about 80% of solvent and other by-products. The samples were obtained by casting the solution in Petri dishes and dried overnight. The cast samples of EPDM/SiO<sub>2</sub> (90/10, 80/20, 70/30 w/w) were vulcanized by compression at 160 °C for 20 min.

### 2.3 Characterization methods

The morphologies of the EPDM/SiO<sub>2</sub> nanocomposites were examined by a TESCAN VEGA3 scanning electron microscope (SEM) at a voltage of 25 kV. Cross-sections of the samples were coated with gold by an electro deposition method to impart electrical conductivity before the SEM micrographs were recorded.

ATR-FTIR spectra of the pure EPDM and its silica filled composites were obtained using a Perkin Elmer Spectrum 100 FTIR spectrometer. The samples were analyzed over a range of 600-4000 cm<sup>-1</sup> with a resolution of 4 cm<sup>-1</sup>. All the spectra were averaged over 16 scans.

The degree of crosslinking was determined through equilibrium swelling tests by immersing at least three rectangular specimens for each composition in 15 ml of toluene at room temperature for several hours, and the mean values are reported. The solvent was replaced hourly after each measurement to eliminate all uncrosslinked fractions, such as unvulcanized EPDM chains, which could lead to incorrect values of the swelling ratio. Equilibrium swelling was determined until the swollen mass ( $m_s$ ) reached a constant value, after which the samples were dried to constant mass (dried mass ( $m_d$ )) and the absolute swelling ratio ( $q$ ) was evaluated using Equation 1.

$$q = \frac{m_s}{m_d} \quad (1)$$

The absolute extractable fraction ( $f$ ), where  $m_0$  is the mass of the sample before immersion in toluene, was determined using Equation 2.

$$f = \frac{m_s - m_d}{m_0} \times 100 \quad (2)$$

The values of  $q$  and  $f$  were also normalized to the actual EPDM weight. Their values were determined using Equations 3 and 4.

$$q_{EPDM} = \frac{q}{C_{EPDM}} \quad (3)$$

$$f_{EPDM} = \frac{f}{C_{EPDM}} \quad (4)$$

where  $C_{EPDM}$  is the weight fraction of EPDM present in the composites. The gel content was determined using Equations 5 to 7, where  $m_{EPDM}$  is the mass of EPDM without silica and  $\%wt_{EPDM}$  is the weight % EPDM in the composite.

$$m_{EPDM} = m_0 \times \%wt_{EPDM} \quad (5)$$

$$\% \text{ Extraction} = \frac{m_o - m_d}{m_{EPDM}} \times 100 \quad (6)$$

$$\% \text{ Gel} = 100 - \% \text{ Extraction} \quad (7)$$

Thermogravimetric analysis (TGA) was performed with a Perkin Elmer STA6000 simultaneous thermal analyzer. The analysis was done under nitrogen at a constant flow rate of 20 ml min<sup>-1</sup>, and the samples (20-25 mg) were heated from 25 to 600 °C at a rate of 10 °C min<sup>-1</sup>.

The tensile properties of the samples were determined using a Hounsfield H5KS tensile tester at a crosshead speed of 100 mm min<sup>-1</sup> and 20 mm gauge length at ambient temperature. The samples were rectangular shaped with a width of 12 mm and thicknesses varying between 0.47 and 0.69 mm. At least five samples were tested for each composition and the mean values are reported. Young's modulus was predicted according to Nielsen's theoretical model [15-19].

The dynamic mechanical analysis (DMA) of the samples was done on a Perkin Elmer Diamond DMA dynamic mechanical analyzer. Rectangular shaped samples, with dimensions of 40 mm length, 10 mm width and thicknesses varying between 0.47 and 0.69 mm, were tested in tensile mode at a frequency of 1 Hz while heated under nitrogen flow from -100 to 100 °C at a rate of 3 °C min<sup>-1</sup>.

### 3. Results and discussion

The SEM micrographs of cross-sections of the EPDM/SiO<sub>2</sub> composites are shown in Figures 1 to 3, while the particle size distributions are shown in Figure 4. The particle size distribution was determined from an average of 40 particles per sample. The light areas in the



micrographs correspond to the silica particles and are spherically shaped. The silica particles in the EPDM/SiO<sub>2</sub> samples are homogeneously dispersed in the rubber matrix and have good particle-matrix adhesion, which confirms the effectiveness of the *in situ* filler generation process used for the preparation of the filled rubbers.

The silica filled composites show both large and small particles at higher silica contents (Figure 3), and the particle size distribution determined from the visible particles confirms the increase in particle size (Figure 4). Figure 2 shows that some particles are fully imbedded in the EPDM matrix, which indicates good particle-matrix interaction. Increased agglomeration with increasing filler content has been observed and reported by other authors for similar systems [20-22], and is the result of increased coalescence of the growing silica particles when increasing the amount of *in situ* formed dispersed phase. The silica particles may also have agglomerated in the suspension, because the hydrophilic silica particles have a tendency to associate *via* hydrogen bonding [22]. When comparing these results with those obtained during our study on the same system, but with the samples prepared in the absence of a coupling agent [14], similar particle size distributions were observed. It is, however, difficult to draw any conclusions from this observation, since SEM analysis only shows the surface morphology of the investigated samples, and not enough particles could be measured to ensure statistically sound conclusions.

The FTIR spectra of EPDM, TESPT, EPDM-TESPT and the EPDM/SiO<sub>2</sub> composite containing 30 wt.% SiO<sub>2</sub> are shown in Figure 5. The neat rubber can be identified by two strong absorption peaks at 2920 cm<sup>-1</sup> and 2850 cm<sup>-1</sup> assigned to the C-H stretching vibration. The peaks at 721, 1376 and 1464 cm<sup>-1</sup> are assigned to the CH<sub>2</sub> stretching, and CH<sub>3</sub> and CH<sub>2</sub> bending, respectively [23,24]. The modification of the neat EPDM matrix with TESPT resulted in additional bands observed at 1073 and 952 cm<sup>-1</sup>, both assigned to Si-O-CH<sub>2</sub>CH<sub>3</sub> as a result of the asymmetric stretching of the Si-O group [25]. The FTIR spectrum for TESPT shows the following additional bands: asymmetric stretching of CH<sub>3</sub> (Si-O-CH<sub>2</sub>CH<sub>3</sub>) in the region 1390 cm<sup>-1</sup>, CH<sub>2</sub>CH<sub>3</sub> rocking of Si-O-CH<sub>2</sub>CH<sub>3</sub> around 1167 cm<sup>-1</sup>, band stretching of Si-C at 780 cm<sup>-1</sup>, CH<sub>2</sub> wagging in CH<sub>2</sub>-S- at 1246 cm<sup>-1</sup>, and C-H stretching at 2373 cm<sup>-1</sup> [25].

TEOS undergoes hydrolysis by water to produce silanol groups (Si-OH) in the presence of the EPDM matrix during the sol-gel process. The silanol groups react with the ethoxysilane (Si-OCH<sub>3</sub>CH<sub>2</sub>) and produce siloxane groups. The ethoxy group (CH<sub>3</sub>CH<sub>2</sub>O) from TESPT can

also react with silanol to form a siloxane linkage. Networks of siloxane linkages will, therefore, form silica particles embedded in the rubber matrix. The siloxane linkage can be identified from the FTIR spectra of the vulcanized EPDM/SiO<sub>2</sub> composite as an asymmetric stretch (Si-O-Si) in the region 1055 cm<sup>-1</sup> (Figure 5). The vulcanized composite shows additional FTIR peaks at 803 and 944 cm<sup>-1</sup>. They are assigned to Si-OH, which shows the presence of silanol groups, and to the asymmetric stretching of Si-O-C from unreacted TEOS [26-28]. The appearance of these functional groups implies that some of the silanol and ethoxysilane/ethoxy groups from both the TEOS and the coupling agent might have grafted on the rubber chains through reacting with the dicumyl peroxide initiator during vulcanization. The sulphide from the coupling agent has probably participated in sulphur vulcanization, as observed from the absence of a sulphide peak (CH<sub>2</sub>-S-) for the EPDM/SiO<sub>2</sub> composite. The coupling agent probably formed bridges between the silica particles and the EPDM rubber, thereby leading to stronger chemical linkage between the silane coupling agent and the rubber molecule. The -OH bending vibration around 3300 cm<sup>-1</sup> is much weaker than that observed in the spectra of the samples prepared in the absence of coupling agent [14]. In the presence of coupling agent, the interaction between the EPDM rubber and the silica particles follows the reaction scheme proposed by Das *et al.* [1]. According to this scheme, the silanol groups are incorporated in the coupling agent generated crosslinks between the rubber chains. However, in the present case the silanol groups that formed part of the crosslinks obviously reacted further to form silica links, with the accompanying reduction in the number of free -OH groups.

The equilibrium swelling and gel content results of the vulcanized EPDM and the EPDM/SiO<sub>2</sub> composites are reported in Table 1. Equilibrium swelling analysis is well-known to evaluate the crosslink density obtained after vulcanization of an unfilled rubber. In the case of silica filled rubber composites, the swelling behaviour could be influenced by (1) the ability of the silica particles to act as crosslinking points and/or absorb solvent, and (2) the degree of crosslinking of the unfilled rubber matrix.

**Table 1 Swelling ratio and gel content of EPDM and EPDM/SiO<sub>2</sub> composites**

Samples (w/w)	$q$	$q_{EPDM}$	$f / \%$	$f_{EPDM} / \%$	Gel / %
EPDM	3.7 ± 0.2	3.7 ± 0.2	6.4 ± 2.5	6.4 ± 2.5	93.6 ± 2.5
90/10 EPDM/SiO <sub>2</sub>	5.9 ± 0.6	6.6 ± 0.6	1.8 ± 0.4	2.0 ± 0.4	98.2 ± 0.3

80/20 EPDM/SiO <sub>2</sub>	4.3 ± 0.6	5.0 ± 0.7	3.0 ± 1.6	3.6 ± 1.9	96.2 ± 2.0
70/30 EPDM/SiO <sub>2</sub>	4.3 ± 0.0	6.0 ± 0.0	2.5 ± 1.5	3.6 ± 2.2	96.4 ± 2.2

Swelling ratios ( $q$  and  $q_{EPDM}$ ), extractable fraction ( $f$  and  $f_{EPDM}$ ) and gel content for EPDM and EPDM/SiO<sub>2</sub> nanocomposites

The normalised swelling ratio in Table 1 shows an increase for the silica containing samples, while the gel content remained effectively constant. This indicates that the number of crosslinks decreased, while the network is still extensive enough to maintain the high gel content. Another possibility is that longer chain crosslinks have been formed between the rubber chains (as proposed by Das *et al.* [1]). In this case, an extensive network will still exist but there will be enough free volume between the chains to accommodate the toluene molecules during the swelling test, which explains the increase in swelling ratios. In our previous paper [14] where the nanocomposites were prepared in the absence of a coupling agent we also observed an increase in swelling ratio, but in that case the extractable fraction increased and the gel content decreased significantly, which clearly showed inhibition of the rubber crosslinking in the presence of silica nanoparticles. In this case, the silica particles became part of the crosslinks through the action of the coupling agent [1]. The introduction of TESPT has, therefore, an influence on the effectiveness of crosslinking and on the length of the crosslinks in the vulcanized EPDM/SiO<sub>2</sub> composites

The TGA curves of EPDM rubber and silica filled composites are shown in Figure 6. The thermal stability was characterized through temperatures taken at the onset and at 50% mass loss (Table 2). The TGA curves of the EPDM/SiO<sub>2</sub> nanocomposites clearly show two distinct mass loss steps, and an increasing amount of char with increasing silica content (Figure 6 and Table 2). The first mass loss is observed from 100 °C and is due to a loss of water and alcohol, and progresses to higher temperatures due to the presence of organic by-products such as unhydrolyzed TEOS that decompose and evaporate around 350 °C. The second mass loss around 400-470 °C is related to the main degradation of EPDM rubber chains or segments. The degradation temperatures of EPDM initially decrease for the 10% silica containing sample, but increase to temperatures higher than that of EPDM for the samples containing 20 and 30% silica (Table 2). The introduction of the coupling agent obviously improved the interaction with and dispersion of silica particles in the EPDM matrix, which gave rise to the increased thermal stability of the EPDM. The strongly bound and well dispersed silica particles reduced polymer chain mobility and retarded the diffusion of volatile products from the sample. It probably also changed the decomposition mechanism

of EPDM, similar to that reported in other thermal degradation studies [7,29-32]. Our previous results, obtained in the absence of a coupling agent, showed very little influence of the silica filler on the thermal stability of the matrix.

The actual silica content after conversion was determined through TGA analysis as the percentage residue after heating to 600 °C. The data in Table 2 show a very good correlation between the % residue and the amount of silica introduced through the sol-gel reaction. The small standard deviation values in Table 2 indicate that the silica particles were well dispersed in the rubber matrix, because samples were taken from different positions in the pressed sheets for the repeat TGA analyses.

**Table 2 Summary of TGA results for the EPDM rubber and its composites**

Samples (w/w)	T <sub>onset</sub> / °C	T <sub>50%</sub> / °C	% SiO <sub>2</sub>
EPDM	426 ± 0.1	454 ± 0.1	0
90/10 EPDM/SiO <sub>2</sub>	420 ± 2.7	452 ± 1.3	9.0 ± 0.4
80/20 EPDM/SiO <sub>2</sub>	435 ± 1.6	463 ± 3.4	19.1 ± 2.3
70/30 EPDM/SiO <sub>2</sub>	436 ± 2.8	469 ± 0.1	29.0 ± 0.7

T<sub>onset</sub> and T<sub>50%</sub> are the temperatures at the onset and at 50% mass loss

The Young's modulus as function of volume fraction of neat EPDM and its silica filled composites are shown in Figure 7, together with its prediction according to the Nielsen theoretical model [15-19]. The values for Young's modulus, stress and elongation at break, are summarized in Table 3. For composite materials consisting of spherical particles in the matrix, the Nielsen equation has the form given in Equations 8 and 9.

$$E = E_1 \left[ \frac{1 + AB\phi_2}{1 - B\phi_2} \right] \quad (8)$$

$$B = \frac{E_2/E_1 - 1}{E_2/E_1 + A} \quad (9)$$

where  $E$ ,  $E_2$  and  $E_1$  are the modulus values of the composite, filler and matrix respectively, and  $\phi_2$  is the volume fraction of the filler assuming spherical particles. The theoretical

modulus used for the silica particles was  $E_2 = 70$  GPa [33]. The factor  $\psi$  takes into account the values of  $\phi_m$  of the dispersed phase, and it is given by Equation 10.

$$\psi = 1 + \left[ \left( \frac{1 - \phi_m}{\phi_m^2} \right) \phi_m \right] \quad (10)$$

where  $\phi_m$  is the maximum packing fraction. The constant B takes into account the relative moduli of the filler and matrix phases, and its value is 1.0 for very large  $E_2/E_1$  ratios (the values for  $E_2$  and  $E_1$  are 70 GPa and 2.4 MPa, respectively, and therefore we could confidently use a value of 1.0). The constant A is related to the Einstein coefficient given by Equation 11 and is determined by the morphology of the system; for strong aggregates, the value of A can become quite large while  $\phi_m$  of the dispersed phase will decrease.

$$A = k_E - 1 \quad (11)$$

An A value of 4.5 gave the best fit of the experimental modulus values (Figure 7). It is interesting to observe that the addition of TESPT reduced the values of A and  $\phi_m$  significantly when compared to our previous study, where the same system in the absence of a coupling agent was investigated [14]. The values of A and  $\phi_m$  were then 25 and 0.37, respectively,

which indicated a large extent of silica aggregation in the EPDM matrix with increasing silica content. Furthermore, the silica aggregates were large enough to increase the value of A and

reduce the value of  $\phi_m$ . In the current study, the introduction of a coupling agent improved the

dispersion of the filler and reduced the size of the aggregates, as was also observed from the

SEM images in Figures 1 to 3. The low value of  $\phi_m$  indicates the presence of agglomerated

silica particles, but the aggregates are small enough for the value of A to be significantly reduced.

**Table 3 Summary of tensile results of EPDM and the EPDM/SiO<sub>2</sub> composites**

Samples	$\sigma_b$ / MPa	$\varepsilon_b$ / %	E / MPa
EPDM	$1.7 \pm 0.5$	$482 \pm 84$	$2.4 \pm 0.3$
90/10 w/w EPDM/SiO <sub>2</sub>	$3.1 \pm 0.4$	$763 \pm 62.9$	$5.0 \pm 0.6$
80/20 w/w EPDM/SiO <sub>2</sub>	$3.7 \pm 0.7$	$1060 \pm 20.0$	$7.4 \pm 0.3$
70/30 w/w EPDM/SiO <sub>2</sub>	$3.2 \pm 0.4$	$730 \pm 28.9$	$18.7 \pm 1.0$

$\varepsilon_b$ ,  $\sigma_b$ , and E are elongation at break, stress at break, and Young's modulus of elasticity

It is also interesting to observe that both the stress and elongation at break increase with increasing filler content for 10 and 20 wt.% silica (Table 3). This is the result of improved adhesion between the filler and the matrix because of good interfacial interaction brought about by the coupling agent, giving rise to effective stress transfer. Das *et al.* [1] also reported high stress and elongation at break values in their investigation of silica-EPDM rubber networks by an *in situ* sol-gel method. They explained this as the polysulfidic linkage from the TESPT causing a strong reinforcement between the rubber and the filler, which explains the larger stress at break values. The longer crosslink chains formed in the presence of the coupling agent explain the larger elongation at break values. A larger amount of filler led to agglomeration of the filler particles, which resulted in a decrease in the stress and elongation at break for the sample containing 30 wt.% silica. In this case, there were probably silica

particles that were not incorporated in the crosslinks through the action of the coupling agent, and that formed agglomerates acting as stress concentration points. Aggregation of the filler in the composite probably caused a dewetting or crazing effect in which the adhesion between the filler and matrix phase was destroyed, and this resulted in a decline in the mechanical properties. When comparing these results with those obtained during our study on the same system, but with the samples prepared in the absence of a coupling agent [14], it is observed that the tensile modulus values for the different nanocomposites, prepared in the absence and presence of TESPT, are similar, but that the stress and elongation at break values for the samples prepared in the presence of TESPT are significantly higher. This can also be explained by the better interaction between the rubber chains and the silica particles incorporated in the crosslinks [1], which improved the interfacial interaction and reduced the number of stress concentration points, and by the longer crosslink chains, which increased the strain-ability of the nanocomposites.

The DMA results of EPDM and its nanocomposites are shown in Figure 8. The glass transition temperature, the  $\tan \delta$  value at the glass transition peak maximum, the storage modulus at 50 °C, Factor C and the damping reduction values are summarized in Table 4. From the values of the storage modulus obtained in the glassy and rubbery regions, the filler effectiveness (Factor C) in the rubber matrix can be evaluated from Equation 12 [35].

$$\text{Factor } C = \frac{\left(\frac{E'_g}{E'_r}\right)_{\text{composites}}}{\left(\frac{E'_g}{E'_r}\right)_{\text{matrix}}} \quad (12)$$

where,  $E'_g$  and  $E'_r$  are the storage moduli determined in the glassy and rubbery regions, respectively. The state of filler dispersion in the rubber matrix was determined by calculation of the damping reduction (DR) from the normalised damping values obtained from the maxima of the  $\tan \delta$  peaks ( $\tan \delta_{\text{rubber}}$  and  $\tan \delta_{\text{composite}}$ ), and is given by Equation 13 [35].

$$\text{DR} = \frac{\tan \delta_{\text{EPDM}} - \tan \delta_{\text{composite}}}{\tan \delta_{\text{EPDM}}} \times 100\% \quad (13)$$

In the rubbery region, there is a significant increase in the storage modulus with increasing silica content in the vulcanizates (see  $E'_{T=50^\circ\text{C}}$  values in Table 4). These modulus values depend on both the degree of crosslinking of the rubber matrix and the content of the

rigid dispersed phase. Both these factors will contribute to an increase in modulus. As can be seen from Table 1, the degree of crosslinking remained fairly constant with increasing silica content (see  $q_{EPDM}$  values for filled samples). However, the content of the rigid dispersed phase increased significantly and the interaction between the rubber and filler was very good because of the presence of coupling agent during the preparation of the composites. These factors gave rise to much higher storage modulus values that correlate well with the tensile modulus values in Table 3. The modulus values, reported in Table 4, are very similar to those reported for the same samples prepared in the absence of a coupling agent [14]. This indicates that the rigidity of the fillers makes the biggest contribution to the elastic modulus of the EPDM nanocomposites.

**Table 4 Summary of DMA results of EPDM and EPDM/SiO<sub>2</sub> composites**

Samples (w/w)	$E'_{T=50^{\circ}\text{C}}$ / MPa	$\tan \delta_{\max}^{\text{Norm}}$	$T_g$ / °C	Factor C	DR / %
EPDM	3.2	0.622	-41.5	1	-
90/10 EPDM	6.0	0.603	-41.9	0.77	3.1
80/20 EPDM	12.0	0.390	-42.5	0.18	37.3
70/30 EPDM	24.5	0.363	-42.3	0.11	41.6

$E'_{T=50^{\circ}\text{C}}$ ,  $\tan \delta_{\max}^{\text{Norm}}$ ,  $T_g$ , Factor C and  $\text{DR}^{\text{Norm}}$  are the modulus at 50 °C, maximum  $\tan \delta$  (normalised to the amount of rubber in the nanocomposites), glass transition temperature, filler effectiveness and the damping reduction (calculated from  $\tan \delta_{\max}^{\text{Norm}}$ )

The filler effectiveness (Factor C) (Table 4) can be used to indicate the composite reinforcing capacity. By definition, an unfilled rubber matrix has a Factor C equal to 1, and a Factor C lower than 1 indicates a mechanical stiffening effect as well as a thermal stability contribution of the filler [35]. The values in Table 4 clearly show that the silica particles contributed to the EPDM matrix stiffness as the silica content increases.

The addition of rigid fillers to a polymer matrix is expected to restrict the mobility of the polymer chains, leading to a decrease in damping and a shift in the glass transition temperature to higher values. The normalized  $\tan \delta$  values in Table 4 clearly decrease with increasing silica content. The decrease in the damping factor is attributed to good adhesion between the filler and the matrix, which resulted in restriction in the mobility of rubber chains



in the composite. The increasing damping reduction ( $DR^{\text{Norm}}$ ) values with increasing silica content confirm that the EPDM interacts strongly with the well dispersed silica particles, which leads to a reduction in polymer chain mobility. The glass transition temperature slightly increased for the silica containing samples, which is expected because of the reduced chain mobility of EPDM in the nanocomposites.

### 3. Conclusions

Reinforcing of EPDM rubber with *in situ* generated silica particles in the presence of a coupling agent (TESPT) *via* a sol-gel route was investigated. The silica filled composites showed both large and small particles at higher silica contents in the composites, and some particles were fully imbedded in the EPDM matrix, which indicated good particle-matrix interactions. The particle size distribution increased with increasing silica content as a result of increased coalescence of the growing silica particles when increasing the amount of *in situ* formed dispersed phase. The FTIR results indicate that the TEOS and TESPT reacted to form silica containing crosslinks between the rubber chains. In the presence of the silica particles, there was a decrease in crosslink density, but the networks were still extensive enough to maintain a high gel content. The introduction of the coupling agent improved the interaction of the silica particles with, and dispersion in, the EPDM matrix, which gave rise to an increased thermal stability of the EPDM. The tensile results showed that longer crosslink chains formed in the presence of the coupling agent gave rise to larger elongation at break values, and the polysulfidic linkage from the TESPT produced strong reinforcement between the rubber and the filler, which gave rise to the larger stress at break values. However, larger amounts of filler led to agglomeration of the filler particles, which resulted in a decrease in the stress and elongation at break. A Nielsen's model fit to the Young's modulus values shows improved dispersion and reduced size of the silica aggregates in the EPDM matrix. There is good correlation between the storage modulus and Young's modulus, and these values increased significantly with increasing filler content. The increased stiffness and thermal stability are confirmed by the filler effectiveness factor values. The damping reduction values confirm that the EPDM interacted strongly with the well dispersed silica particles, which led to a reduction in the polymer chain mobility. When the results of this study are compared with those of our previous study on the same system in the absence of a coupling agent, it is clear that the introduction of the coupling agent improved the interaction and dispersion of silica particles in the EPDM matrix, and had an influence on the

effectiveness of crosslinking and on the length of the crosslinks in the vulcanized EPDM/SiO<sub>2</sub> composites. Because of this influence, the EPDM/silica nanocomposites showed much better thermal and mechanical properties.

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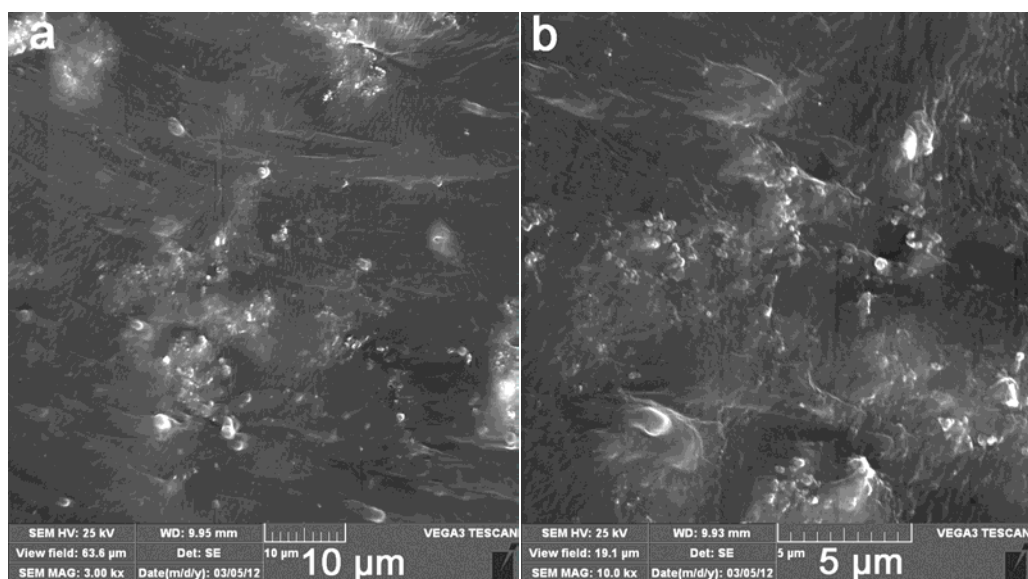


Figure 1 SEM micrographs of the 90/10 w/w EPDM/SiO<sub>2</sub> composite

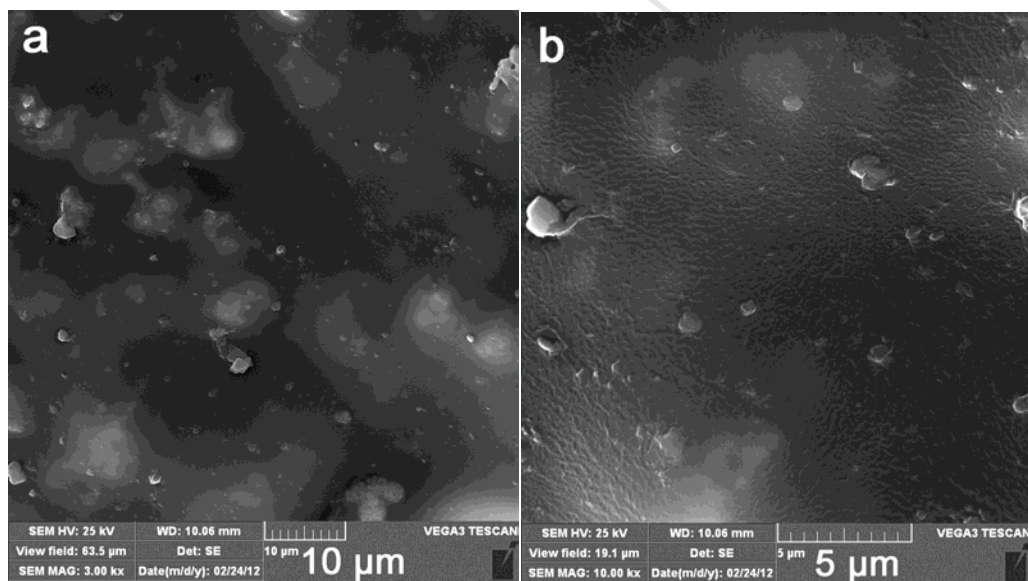


Figure 2 SEM micrographs of the 80/20 w/w EPDM/SiO<sub>2</sub> composite



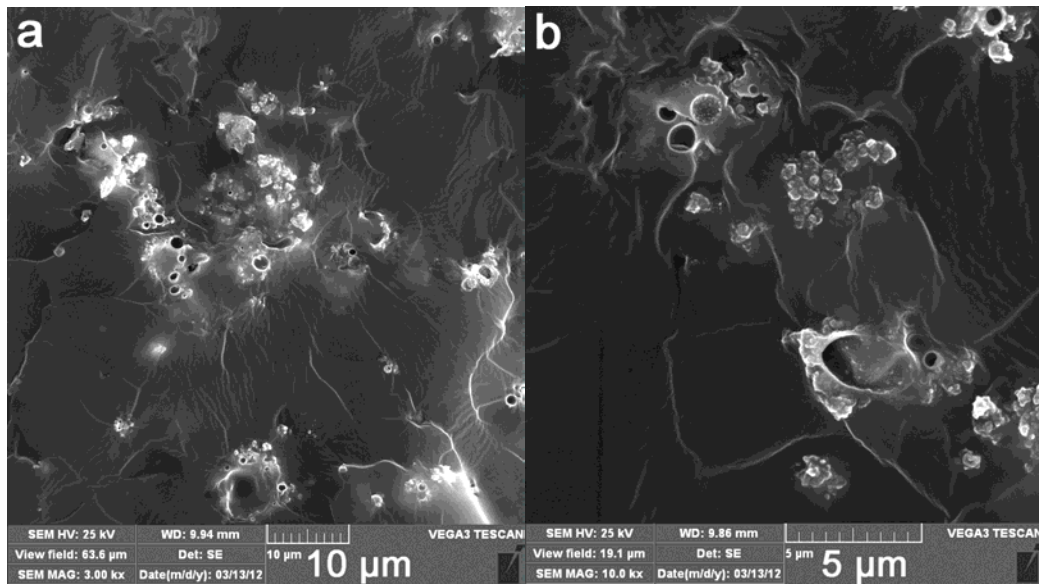


Figure 3 SEM micrographs of the 70/30 w/w EPDM/SiO<sub>2</sub> composite

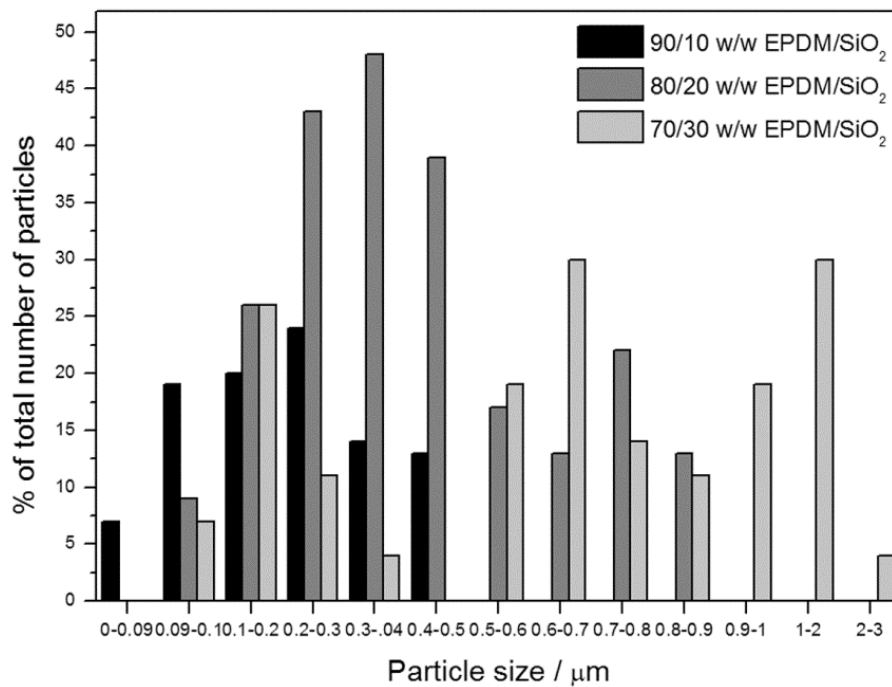
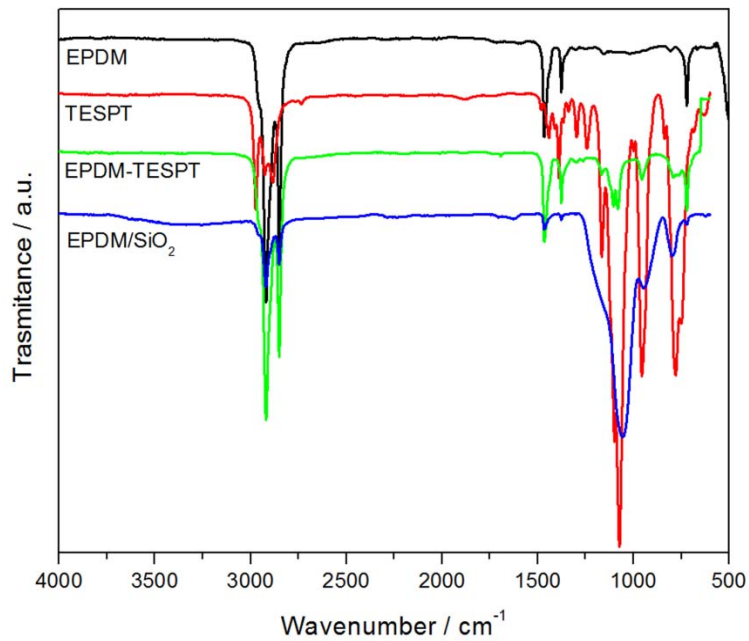
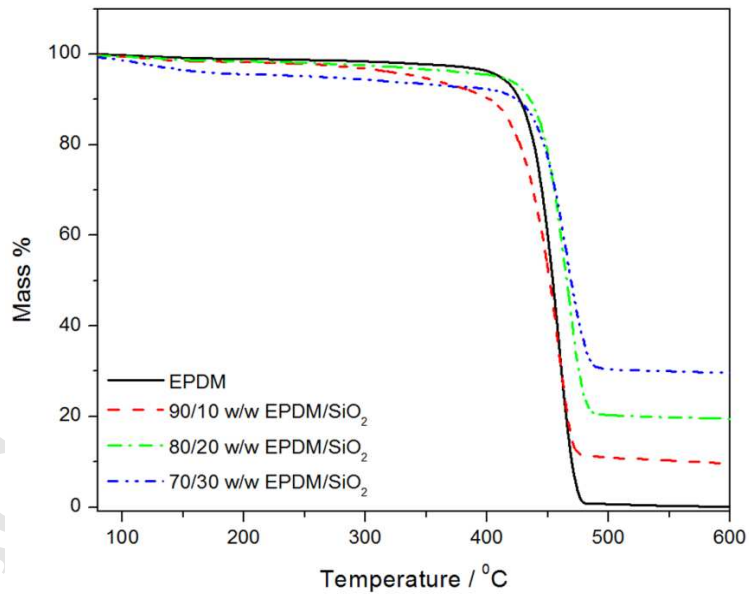


Figure 4 Particle size distribution graphs of the EPDM/SiO<sub>2</sub> composites

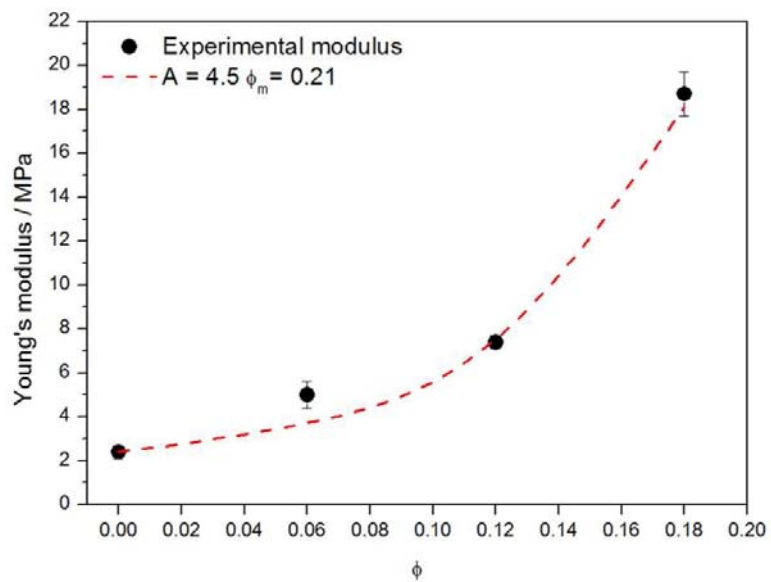




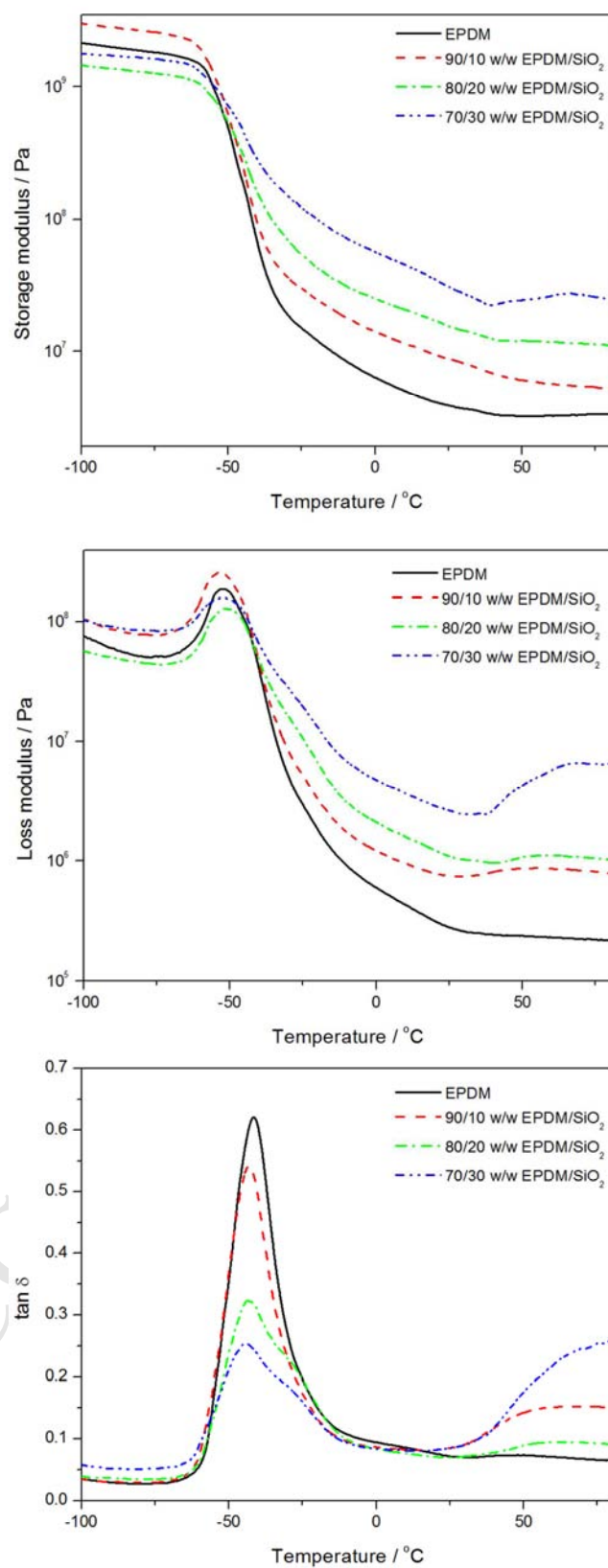
**Figure 5** FTIR spectra of EPDM, TESPT, EPDM-TESPT and the EPDM/SiO<sub>2</sub> composite containing 30 wt.% silica



**Figure 6** TGA curves of EPDM and silica filled EPDM composites



**Figure 7** Young's modulus as a function of volume fraction of SiO<sub>2</sub> in EPDM/SiO<sub>2</sub> composites: experimental modulus and Nielsen predicted modulus



**Figure 8** DMA storage modulus, loss modulus and damping factor curves of EPDM and its composites