



Reinforcement of natural rubber using a novel combination of conventional and *in situ* generated fillers

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ABSTRACT

Carbon black (CB) is the most widespread reinforcing filler found in rubber compounds. However, the need to reduce its use due to the environmental consequences of its production has led to the incorporation of other fillers such as precipitated silica (p-Si), although latter does not provide an equivalent reinforcement owing to its inherent incompatibility and difficulties during mixing. The sol-gel method stands up as a non-conventional technique to overcome these issues. This methodology enables the incorporation of fillers *in situ*. By this means, compatibility is improved, and superior reinforcement is achieved because of better dispersion and smaller particle size. In this work, natural rubber (NR) composites with conventional fillers (CB and p-Si), non-conventional (*in situ* silica, i-Si and *in situ* zirconia, i-Zi) and novel combinations among them were prepared by merging standard mechanical mixing and the sol-gel method, and systematically characterized. The compound in which CB is combined with i-Si presents the best overall performance with a higher mechanical strength at low (100%) and medium (300%) deformations, a tear resistance of (70 ± 5) kN/m and an abrasion resistance of $(156 \pm 9)\%$ (considerably higher values than the pure NR and the formulations with the separate fillers). The methodology here presented facilitates the incorporation of nanofiller precursors into a vulcanized elastomeric matrix in a post-processing stage; hence, this approach can be considered in the near future as an effective way to reinforce already discarded or recycled rubbers, including end-of-life tires.

1. Introduction

In the reinforcement of elastomers in general, and in tire manufacturing particularly, the use of carbon black (CB) as conventional filler is widespread. [1,2] However, with the objective of reducing the pollution generated during its processing, research has turned towards another material that has gained importance among the rubber world: silicon dioxide, known as silica (Si). The incorporation of this filler in an elastomeric matrix also improves characteristics such as the wet grip of the tire tread, thus increasing the attention given to the use of precipitated silica (p-Si) as reinforcing filler for tires. Nonetheless, its use has difficulties in achieving a good distribution and dispersion in the elastomeric matrix due to the formation of agglomerates, because of the strong interaction between particles and the polar nature of its surface. An additional drawback is that its reinforcing effect is inferior to that of CB. Even in the presence of coupling agents, such as bis-(triethoxysilylpropylsulfide) (TESPT), the incorporation of p-Si in a rubber matrix using conventional mechanical mixing methods does not completely solve the limitation of the poor dispersion; besides, its

incorporation requires higher energy consumption than that of CB. To overcome this issue, the scientific community has focused its efforts on the generation of silica without the need for mechanical mixing. An attractive and synthetic approach has evolved by the generation of *in situ* silica particles (i-Si) of nanometric size using the well-known sol-gel chemistry, which helps to improve the dispersion within the elastomer, achieving a reinforcement almost as effective as that generated by CB, with lower filler contents. [3,4]

The sol-gel method offers a flexible approach for preparing advanced composites, using colloidal solutions as starting materials. [5-8] It consists of immersing the elastomer in a precursor solution of the filler to be incorporated, which, in the case of silica, can be tetraethylorthosilicate (TEOS). After swelling, hydrolysis and condensation reactions take place, producing the synthesis of i-Si within the rubber network. In most rubbers, the swelling and reactions occurs at a stage prior to vulcanization or curing. [9,10]

Kohjiya and Ikeda [11] were the first to expand the generation of i-Si towards general-purpose elastomers. They used acid and basic catalysts to accelerate the hydrolysis and condensation reactions of TEOS

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after swelling of SBR. They found that both catalysts are effective in increasing the percentage of i-Si generation; however, the use of basic catalysts yielded slightly higher concentrations and a better dispersion into the elastomeric matrix, which resulted in improved mechanical reinforcement. They also found that in BR with a 15.8% i-Si content, tensile strength increased two-fold compared to samples with a 21.7% p-Si content in presence of a coupling agent. In addition, they analyzed the influence of the crosslink density on the generation of silica, concluding that, at a higher crosslink density, the content and particle size of i-Si generated are smaller, achieving greater reinforcement. Murakami et al. [12] prepared NR composites with CB, p-Si, and i-Si, and studied their mechanical properties and hysteresis. They concluded that the use of i-Si produces better results than p-Si, although they did not observe large differences in hysteresis. Since then, many researchers have studied the different process parameters to optimize the generation of i-Si in different elastomers. Ikeda et al. [13] sought to accelerate the hydrolysis and condensation reactions of TEOS to increase their yield. They used different types of amines as basic catalysts and compared the use of several aqueous solutions, concluding that a solution of n-hexylamine 0.1 M is more effective in the generation of i-Si, stabilizing the maximum i-Si content that can be generated after 22 h of reaction between the aqueous amine solution and TEOS (5:1 weight/weight ratio between water and precursor). Since then, the study of swelling in different samples has deepened. [14–18]

Another filler that has been used in a lesser extent in elastomeric composites is zirconium dioxide, commonly known as zirconia (Zi). Zirconia has excellent chemical resistance, as well as good thermal and optical properties, which are difficult to find in general purpose elastomeric materials. The use of the sol-gel method to incorporate *in situ* zirconia (i-Zi) particles into rubber matrices has been reported elsewhere. [19,20] Murugesan et al. prepared poly(dimethylsiloxane) (PDMS) films that were swollen with a zirconia alkoxide and titania. Subsequently, they employed air humidity to promote the hydrolysis of the precursors, used the typical TEOS approach for comparative purposes, and hydrolyzed by immersing the swollen films in a diethylamine aqueous solution. They concluded that PDMS networks loaded with i-Zi had better thermal properties compared to the unfilled compounds. They also observed that i-Zi had higher reinforcing capacity than titania, due to its smaller particle size. Other authors [21] incorporated i-Zi into epoxidized natural rubber (ENR). They dissolved the rubber in THF, adding different amounts of the zirconia precursor and concluded that the films of nanocomposites with i-Zi had good transparency, improved thermal stability, and lower glass transition temperature (T_g).

In this research, NR composites with conventional fillers (CB and p-Si), non-conventional (i-Si and i-Zi) and combinations among them (CB/p-Si and CB/i-Si) were prepared with the purpose of evaluating the effect of the filler type on the final properties of the elastomer. The *in-situ* generation of fillers in previously vulcanized compounds filled with CB is presented as an innovative approach, seeking to combine the excellent individual contribution of each filler to tire composites, while reducing simultaneously the consumption of CB. Moreover, the development of this methodology that facilitates the incorporation of nanofiller precursors into a vulcanized elastomeric matrix is considered as an effective way to reinforce already discarded or recycled rubbers, including end-of-life tires.

2. Experimental section

2.1. Materials

Natural rubber (NR, SIR10) supplied by *Indonesian Rubber* was used as rubber matrix. Conventional fillers such as carbon black (CB, N660) and precipitated silica (p-Si, Rubbersil RS-200) were obtained from *Negroven* and *Glassven*, respectively. Polyethyleneglycol (PEG) from *Merck-Schuchardt* was used as wetting agent to improve the incorporation of p-Si; and cyclohexyl-methyl-dimethoxy-silane (CDS) from *Catlyen* was

used as coupling agent for improving the dispersion of p-Si. The unconventional fillers incorporated into NR were *in situ* Silica (i-Si) and *in situ* Zirconia (i-Zi). To obtain them, tetraethylorthosilicate (TEOS) and zirconium n-propoxide (IV) 70 wt. % in 1-Propanol were selected as precursors, both from *Sigma-Aldrich*. An aqueous solution of n-hexylamine was used as catalyst for the hydrolysis and condensation reaction of these precursors. Sulfur (S) from *Azufrenca*, N-cyclohexyl-2-benzothiazolsulfenamide (CBS) from *Bayer*, zinc oxide (ZnO) from *Mi-nomet, C.A.* and stearic acid (SA) from *Suministros Químicos* were used as components of the vulcanization system. Table 1 summarizes the rubber compound recipes.

Before starting mixing, the p-Si was treated with the coupling agent in a sigma mixer. For this, a solution of CDS was prepared with distilled water (in a 1:9 ratio) and according to the amounts expressed in Table 1. The p-Si was added to the mixer and during the shear, the powder was sprayed with the aqueous solution. Finally, the p-Si was left to dry in an oven at 100°C for 20 h to evaporate the water. Next, the mixing of the compounds was carried out in two stages as schematically described below in Table 2. Sheets of each compound were made by compression molded at 160°C applying a pressure of 5 tons according to their curing time at 90% of the maximum torque (t_{90}).

2.2. Sol-gel method

For the generation of fillers *in situ*, test specimens of each vulcanized NR compound were placed in a glass container. The precursors were added directly to the flask, ensuring that all the specimens were completely immersed in the liquid. Next, the flask was placed in an ultrasound cuvette for 1 h, measuring the temperature every 15 min to prevent NR degradation. All compounds were left immersed in the precursors for 48 h, except F5-II that was left for 72 h. Due to the high viscosity of the i-Zi precursor, their flask was placed in an oven at 40°C for 2 h. At the end of the swelling period, the specimens were removed; their mass was measured to determine the swelling of each precursor and subsequently relocated into the flask. Then, an excess of the n-hexylamine aqueous solution was added and the samples were kept immersed for 22 h. After this period, the solution was removed, the surface was cleaned in order to eliminate the excess of solvents, and then the specimens were dried for 24 h at room temperature and for 72 h in a vacuum oven at 45°C.

2.3. Characterization of NR composites

2.3.1. Vulcanization characteristics

The vulcanization characteristics of the compounds were determined in a moving die rheometer (EKT 2000SP, *EKTRON TEK*), repeating the measurements three times. The samples were placed between polyester films in the equipment and tested with an amplitude of 1° at a temperature of 160°C for 15 min and their vulcanization curves were recorded (see Supporting Information S1).

2.3.2. Ash content

The ash content was calculated following ASTM D297 (2015) procedure to determine the filler content generated *in situ*. 1 g of each sample was cut into pieces of approximately 2 mm to ensure that they burned evenly. The sample pieces were introduced in an oven maintained initially at 400°C, and then the temperature was increased to 800°C at a heating rate of 10°C/min.

2.3.3. Crosslink density

Swelling measurements were carried out in toluene on five squared specimens of each compound. First, their mass in air was determined. Then, after immersion for 72 h, samples were extracted and weighted. Then, they were re-weighted after evaporation of the solvent. Crosslink density, ν (in moles per volume of rubber, mol/cm³) was calculated as

Table 1
NR compounds expressed in parts per hundred parts of rubber (phr).^a

Ingredient	F1	F2	F3	F4	F5-I	F5-II	F6	F7
NR	100	100	100	100	100	100	100	100
PEG	-	-	1	0.2	-	-	-	-
CDS	-	-	2	0.4	-	-	-	-
CB	-	20	-	16	-	-	16	-
p-Si	-	-	20	4	-	-	-	-
i-Si	-	-	-	-	<i>in situ</i>	<i>in situ</i>	<i>in situ</i>	-
i-Zr	-	-	-	-	-	-	-	<i>in situ</i>

^a All compounds have 5 phr of ZnO, 1 phr of SA, 1 phr of CBS and 2.5 phr of S.

Table 2
Mixing protocol.

Steps	Time (min)
Stage 1: Internal mixer. (Banbury, Farrel)	
Set rotor speed at 75 rpm	-
Add NR	0 min
Add ZnO	1 min 30 s
Add SA	2 min
Add conventional fillers and PEG	3 min
Reduce rotor speed to 25 rpm	5 min 30 s
Discharge	6 min
Stage 2: Two roll mixer. (2-roll Rubber Lab Mill, Farrel)	
Add the mixture from Stage 1	0 min
Add S	2 min
Add CBS	3 min
Make six transversal cuts	4 min
Discharge	6 min

follows:

$$v = \frac{\rho_r}{2M_c} \quad (1)$$

The Flory-Rehner equation [22,23] was used to calculate the relationship between the density of the compound (ρ_r) and the molecular weight between crosslinks (M_c), according to Eq. 2:

$$\ln(1 - V_r) + V_r + \chi V_r^2 = -\frac{\rho_r}{M_c} V_s \left(V_r^{\frac{1}{3}} - \frac{V_r}{2} \right) \quad (2)$$

where χ is the Flory-Huggins interaction parameter between the NR and toluene (0.42), V_o is the molar volume of toluene (106.20 cm³/mol) and V_R is the volume fraction of rubber in the compound that was calculated according to Eq. 3:

$$V_R = \frac{\frac{m_1}{\rho_r} - V_f}{\frac{m_1}{\rho_r} - V_f + \left(\frac{m_2 - m_3}{\rho_s} \right)} \quad (3)$$

where m_1 is the mass in air of the samples before swelling, m_2 is the mass of the swollen samples, m_3 is the mass of the dry samples after evaporation of the solvent and ρ_s is the density of toluene (0.867 g/cm³).

The results obtained from the swelling measurements were used for determining the rubber-filler interaction parameter ($\frac{Q_c}{Q_s}$), according to the Lorenz-Park relationship [24]:

$$\frac{Q_c}{Q_s} = ae^{-z} + b \quad (4)$$

where Q_c represents the grams of solvent per grams of rubber with filler, Q_s are the grams of solvent per grams of rubber without filler, z is the weight ratio between filler and rubber, and a and b are constants that are obtained from a linear adjustment. Each Q was calculated according to Eq. 5:

$$Q = \frac{m_2 - m_3}{100 \frac{m_1}{m}} \quad (5)$$

where m is the phr of the compound. And z was calculated according to Eq. 6:

$$z = \frac{m_f}{m_r} \quad (6)$$

where m_f is the mass of filler and m_r is the mass of rubber in the compound.

2.3.4. Scanning electron microscopy (SEM)

The morphology of the composites was analyzed by means of a SEM microscope (JSM 3690, JEOL). The fracture surface from tensile tests was analyzed after sputter coating with gold. The acceleration voltage was set at 25 kV. In the SEM microscope, the elemental chemical analysis of the samples was carried out by Energy-dispersive X-ray spectroscopy (EDS), which allowed obtaining the approximate percentage of the different chemical elements in the formulation with *in situ* filler across the samples. The total percentage of silicon and zirconium was assigned to the contents of i-Si and i-Zr, respectively. Three measurements were made in different zones of each area of interest and the average was reported.

2.3.5. Mechanical properties

Hardness values were determined according to ASTM D2240 (2010) procedure, using the sample stacking method to reach the minimum thickness required. Abrasion test was performed following ASTM D5963 (2015) procedure, using Method B. Samples were prepared directly by compression molding. The tear test was carried out following ASTM D624 (2012) using angular specimens (type C); and tensile tests were performed according to ASTM D412 (2013), using dumbbell specimens (type C). In both cases, the crosshead speed of the universal testing machine (EZ 20, Lloyd Instruments) was set at 500 mm/min. All measurements were taken at room temperature. The values of the stress at 100%, 300% and 500% of deformation (M_{100} , M_{300} and M_{500} respectively), tensile strength (σ_R), elongation at break (ϵ_R) and tear strength (TS) were recorded.

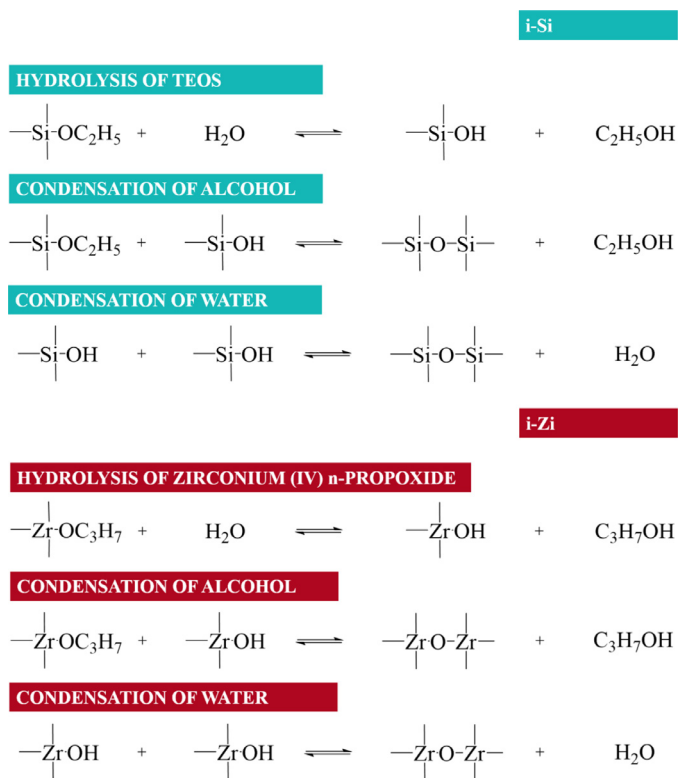
2.3.6. Viscoelastic properties

The study of the Payne Effect [25,26] was carried out using a dynamic rheometer (AR 2000 from TA Instruments) with parallel plate geometry. Cylindrical samples of 25 mm in diameter and an approximate thickness of 2 mm were employed. Strain rate sweeps between 0.001 and 100% were performed at a frequency of 1 Hz and a temperature of 23°C. To avoid the slipping of the samples, a rough bottom plate was used. The process was carried out three times per compound using fresh samples every time, to guarantee the reproducibility of the results.

3. Results and discussions

3.1. In situ generation of fillers

Filler content obtained by the sol-gel method here described was quantified experimentally by the ash content test. After heating at 800°C, ash residue consists of filler plus a negligible content of other inorganic elements (e.g. ZnO). A theoretical calculation was also performed considering a stoichiometric ratio of 1:1. Scheme 1 shows the chemical reaction associated with TEOS and zirconium (IV) n-propoxide. [27,28] The yield of the reaction was calculated as the ratio between the experimental content and the theoretical one. The maximum percentage of i-Si and i-Zr is proportional to the maximum mass



Scheme 1. Hydrolysis and condensation reactions of TEOS (i-Si) and zirconium (IV) n-propoxide (i-Zr).

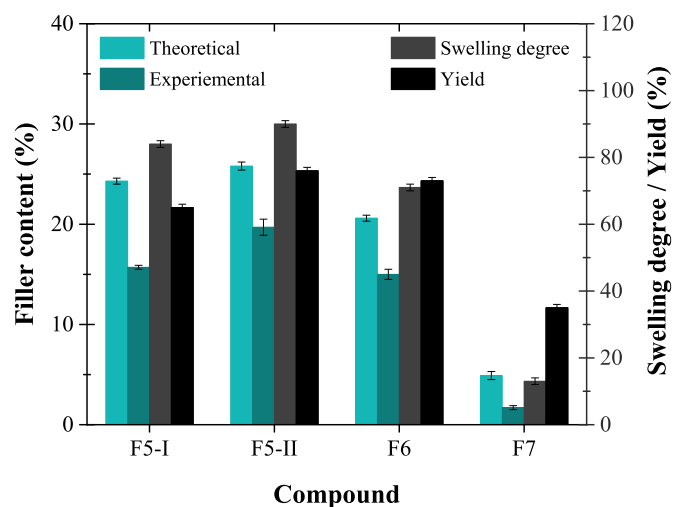


Fig. 1. Swelling degree in precursors, experimental and theoretical contents and reaction yield of fillers generated *in situ*.

of absorbed precursor, determined from the degree of swelling of the rubber, as seen in Fig. 1.

Three variables can be analyzed: swelling time (F5-I and F5-II), free volume (F5-I and F6) and solubility parameter (F5-I and F7). As shown, longer swelling times (F5-II > F5-I) result in higher precursor contents absorbed by the specimens and, thus, both experimental and theoretical percentages of i-Si contents are higher. Additionally, as free volume increases, swelling in the precursor also increases. F6 has less free volume due to the spaces occupied by CB, lowering the swelling in the precursor. Third, TEOS (16.09 MPa^{1/2}) [15,29] has a Hildebrand solubility parameter closer to that of NR (16.2 MPa^{1/2}) [15] so higher swelling values are obtained for F5-I compared to F7; zirconium (IV) n-propoxide

Table 3

Average percentage of fillers generated *in situ* in the different fracture surfaces.

Compound	Filler	Area A[%]	Area B[%]	Area C[%]
F5-I	i-	21 ± 1	20 ± 1	3.3 ± 0.1
F5-II	Si	26 ± 2	23 ± 3	7.8 ± 0.6
F6		18 ± 1	9.1 ± 0.2	6.2 ± 0.5
F7	i-Zr	1.0 ± 0.2	-	-

was mixed 70 wt. % in 1-Propanol that has a higher solubility parameter (24.9 MPa^{1/2}) [30] that hinders its diffusion into the rubber matrix. Fig. 1 also shows the yield of the hydrolysis and condensation reactions. Swelling in TEOS during 72 h (F5-II) gives the highest reaction yield, followed by F6 despite its lower free volume and lower swelling in the precursor. One possible explanation could be that CB particles act as i-Si nucleation sites, although this assumption needs further confirmation. On the other hand, F7 shows the lowest yield and the lowest filler content generated *in situ* given its lower swelling.

A systematic analysis of the morphology of the composites with *in situ* fillers was also carried out. The different photomicrographs obtained from the fracture surfaces of F5-I, F5-II, F6 and F7 are shown in Fig. 2. According to what is observed, the i-Si contents in the fracture surface edges and in the center of the specimens seem to be different, while i-Zr particles are seen agglomerated in the sample. Elemental chemical analysis by EDS in SEM was performed in the differentiated areas in each fracture surface to corroborate this fact. Table 3 reports the average percentages of i-Si and i-Zr.

The yield of the TEOS hydrolysis reaction seems to be higher at the surface (area A) and decreases as the distance to the center of the specimen decreases. This fact could be associated with the diffusion of the precursor and the aqueous solution of the amine. Some other authors report a homogeneous distribution of the *in situ* filler across the sample. [31,32]

3.2. Mechanical properties of NR composites

Fig. 3 shows hardness and abrasion resistance of all rubber composites. The results of the hardness test are perhaps the most reported within the specifications of a rubber due to its simplicity, while the abrasion test is mandatory for the selection of the ideal material in the manufacture of tires. One conclusion that can be extracted from the hardness test is based on a fair comparison between conventional and unconventional filler systems. It can be said that F5-I, F5-II, F6 and F7 composites (unconventional fillers) present higher hardness values, compared to their counterpart compounds (F2, F3 and F4) with similar content of conventional fillers. This fact can be attributed to the nature of the test, which is usually influenced by the behavior on the surface of the material. As previously demonstrated by SEM, a large portion of the filler generated *in situ* is located in the surface, increasing the hardness of the material due to their rigid nature. [15]

Looking at these groups separately, a relationship between hardness and filler content can be seen, regardless of its nature; F2, F3, and F4 (with the same filler content) have similar and higher hardness than F1 (unfilled). On the other hand, F6, which turned out to be the formulation with the maximum filler content (conventional + unconventional) and the highest crosslink density determined by its curing curve reaches the highest hardness value. This corroborates the well-known trend in which incorporating a filler and increasing its content, increases hardness. No major differences can be established between F5-I and F5-II, although the slightly higher hardness value for F5-II could be due to its higher filler content, according to ash content results. Finally, F7, despite its low filler content, shows a higher hardness value than F1, which could be attributed to the difficulties in the diffusion of zirconium n-propoxide (IV), which caused the generation of the filler mostly in the surface.

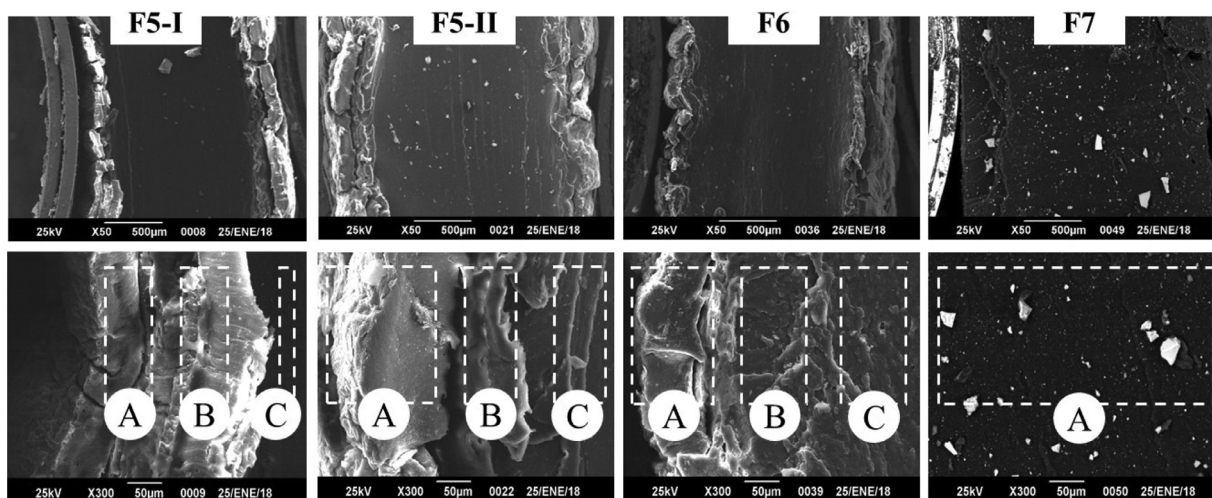


Fig. 2. Photomicrographs of fracture surfaces of NR composites with fillers generated in situ.

Table 4
Tensile properties and tear strength of the composites.

Compound	M_{100} [MPa]	M_{300} [MPa]	M_{500} [MPa]	σ_R [MPa]	ϵ_R [%]	TS [kN/m]
F1	0.98 ± 0.03	2.8 ± 0.1	7.3 ± 0.1	27 ± 1	921 ± 19	40 ± 1
F2	1.38 ± 0.05	6.5 ± 0.4	16.7 ± 0.7	33 ± 1	772 ± 20	62 ± 4
F3	1.10 ± 0.03	3.8 ± 0.1	9.8 ± 0.3	28 ± 2	886 ± 31	46 ± 3
F4	1.40 ± 0.04	6.5 ± 0.4	16.9 ± 1.2	34 ± 2	780 ± 2	56 ± 4
F5-I	1.89 ± 0.07	4.3 ± 0.4	9.2 ± 0.5	20 ± 2	675 ± 28	41 ± 2
F5-II	2.81 ± 0.17	6.4 ± 0.6	-	12 ± 1	464 ± 30	41 ± 4
F6	3.60 ± 0.22	9.8 ± 0.2	-	19 ± 3	493 ± 47	70 ± 5
F7	0.94 ± 0.03	2.8 ± 0.1	7.1 ± 0.1	25 ± 2	857 ± 40	38 ± 3

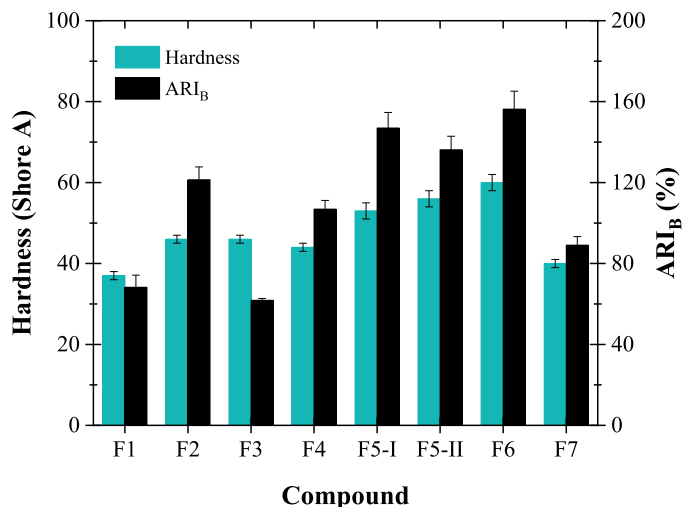


Fig. 3. Hardness and abrasion resistance of the rubber composites.

Abrasion resistance is influenced by the hardness of the compound and the surface morphology due to the superficial nature of the test. Thus, it is expected that composites in which the filler is mainly located near the surface (F5-I, F5-II and F6) have higher abrasion resistance index (ARI_B) compared to compounds filled with conventional fillers (F2, F3 y F4). Besides, F7, with lesser amount of *in-situ* filler and located near the surface, shows a higher abrasion resistance index compared to the unfilled compound.

The reinforcement effect of the filler systems is another aspect that can be ascertained from the results of mechanical tests. Table 4 summarizes all the characteristic parameters obtained from the stress-strain

(see Supporting Information S2) and tear curves of the prepared composites.

From these results, it is evident that the unfilled rubber compound (F1) shows a notorious elongation at break and the lowest moduli and tensile strength, due to the absence of reinforcement. As for F7, no major differences are observed with F1, except for a slight decrease in elongation at break, probably because the amount of zirconia generated *in situ* was not enough to cause a change in tensile properties, or because the formation of agglomerates that act as stress concentration sites. F2 and F4 show similar and the highest tensile strengths, due to the widely reported reinforcement capacity of CB [33-35], and a noticeable decrease in elongation at break ($\sim 15\%$ lower than F1). In the case of F3, the incorporation of p-Si provides an increase in the stiffness of the material, which results in higher moduli, as expected. However, the properties at the break point are comparable to those of F1. Hence, the coupling agent was not efficient in improving the interactions of the p-Si with the NR matrix.

Regarding the composites with *in situ* silica, results are varied. In all cases (F5-I, F5-II and F6) a large increase of the modulus values is observed at low strains (less than 500%), which reflects their high stiffness compared to that of the CB and p-Si filled systems. Nevertheless, it is important to note that at the break point, their stress values were higher than those of their counterpart compounds with conventional fillers at the same strain values. This can be especially beneficial in applications where very high deformation values (higher than 500%) are not required. Among these last three formulations, F5-II (with $\sim 20\%$ i-Si, and 72 h swelling time) presents the worst tensile properties, being lower than F5-I (with $\sim 16\%$ i-Si and 48 h swelling time), and much lower than its homologous formulation F3 (with 20 phr p-Si). This fact could be related to the particle size of the incorporated silica. When the filler has nanometric dimensions, lower concentrations are required to generate comparable effects, hence the best performance of F5-I. However, by incorporating higher contents by prolonged swelling in the pre-

cursor (F5-II), the opposite effect is produced because some agglomerates may form. Thus, it is likely that for improving tensile properties, it is necessary to consider decreasing the swelling time in TEOS (less than 48 h) or decreasing the reaction time for the hydrolysis, in order to continue with the optimization of the filler content generated *in situ*.

One final comparison regarding mechanical strength should be made between F2 (20 phr CB), F5-II (20% i-Si) and F6 (16 phr CB + 15% i-Si). A synergy seems to be occurring in F6 between both fillers (CB and i-Si), since modulus values up to 500% deformation are higher than those of the compounds with individual fillers in higher amounts. As previously said, a plausible explanation to this behavior could be that CB is acting as a nucleating agent of i-Si. Table 4 also shows the tear strength (TS) of all the rubber composites. As expected, CB filled compounds (F2, F4 and F6) present higher tear resistance values. F6 shows the highest value since the combination of CB and i-Si makes the crack propagation even more difficult. No significant differences were detected in the tear resistance of F3, F5-I and F7 with p-Si, i-Si and i-Zi, respectively.

Summarizing, F6 seems to be the compound with the best overall performance and balance between properties. In this system, two fillers of different nature are used; one conventional such as CB, and another considered non-conventional such as i-Si. Other authors have written about the use of combined CB/Si as reinforcing systems. Rattanasom et al. [36] report the use of CB/p-Si in NR at a constant filler content of 50 phr. According to their results, there is no significant change in the tensile strength of the vulcanizates when varying the content of p-Si. However, the values of the modulus at 100% of strain and the abrasion loss decreased with the incorporation of higher contents of p-Si. These results contrast with those obtained in this research, where a synergistic effect between the CB and i-Si was achieved in mechanical properties at strains below 500% and in the abrasion resistance index. This synergistic effect was recently reported by Sattayanurak et al. [37] in NR composites with CB/p-Si but at considerable higher filler contents (55 phr in total). This confirms one of the advantages of the sol-gel method: obtaining good properties at significant lower contents due to the decrease in the particle size of the incorporated fillers. Furthermore, the fact that silica is generated *in situ* in a post-processing stage in already vulcanized compounds filled with CB represents an important contribution to the manufacturing of rubber goods. Such experimental approach is also, with no doubt, a new way for reinforcing recycled and waste rubbers.

3.3. Understanding the interactions in combined filler systems

It is widely known that the introduction of fillers in a rubbery matrix strongly modifies its viscoelastic behavior. To understand the best mechanical performance displayed by the combined filler system (CB + i-Si), the rubber-filler and filler-filler interactions were analyzed using the Lorenz-Park relationship and the strain-dependent dynamic modulus effect (Payne effect), respectively. Both methods enable studying the compatibility between the reinforcing additives and the rubber matrix, and between filler particles themselves. According to the Lorenz-Park relationship [24], the lower the interaction parameter $\frac{Q_c}{Q_s}$, the higher the rubber-filler interaction. Fig. 4 shows the values corresponding to all the filled compounds.

The combined systems F4 (CB + p-Si) and F6 (CB + i-Si) should be analyzed comparatively. A clear trend is observed. F4 has equivalent values to F2; hence, the interactions take place mainly between the rubber matrix and CB, whereas p-Si acts as an inert filler. F6, with the same CB content as F4, presents the lowest interaction parameter, which indicates the best rubber-filler interaction when the silica is generated *in situ* and combined with CB. Such good interaction is responsible for the best mechanical performance, that is, higher modulus values up to 500% strain, although not reflected in a higher tensile strength. A plausible explanation for this phenomenon may be attributed to a competitive process between rubber-filler and filler-filler interactions, because if the latter are higher, by exceeding the percolation threshold, the me-

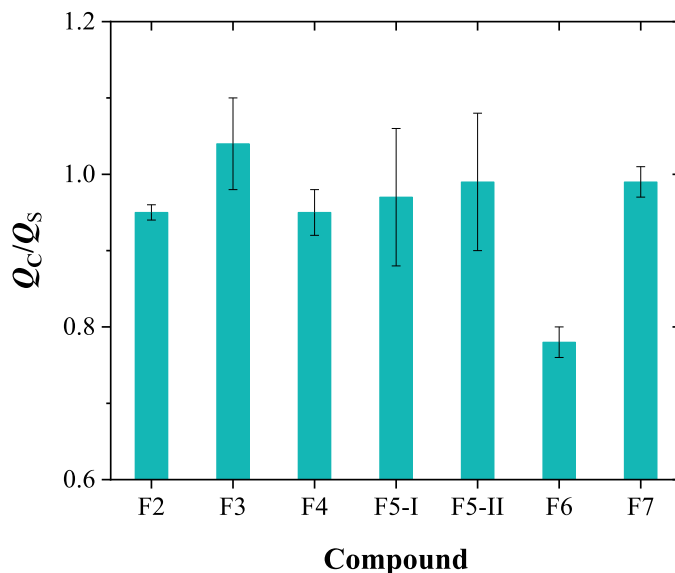


Fig. 4. Rubber-filler interaction parameter $\frac{Q_c}{Q_s}$ of the filled rubber composites.

chanical properties will tend to decrease. [36] The trend on the rubber-filler interactions in systems with only one type of filler is as expected. The compound with CB (F2) presents the lowest interaction parameter, demonstrating its higher reinforcing capacity compared to all other individually filled compounds, while those with i-Si (F5-I and F5-II) display lower values than the corresponding compound with p-Si (F3). Thus, the sol-gel method promotes the formation of smaller particles, improving the dispersion and increasing the interaction with the rubber matrix.

Next, filler-filler interactions were determined by the analysis of the viscoelastic properties and the so-called Payne Effect. According to Payne, [25,26] straining a filled rubber compound causes the storage modulus (G') to decay because of the rupture of the filler-filler interactions. Filler particles are rigid solids whose shape will not change with the imposed strains in a dynamic test. This fact has an influence on the hydrodynamic effect that contributes to the increase of the modulus. Furthermore, when rigid solids are incorporated into rubber, structures known as aggregates are formed because of attractive and repulsive Van der Waals forces, which end up building a filler network. Another factor that increases the modulus values derives from the possibility of transmitting stress through this filler network. [38] When applying a strain, the filler network breaks and portions of trapped rubber are released, thereby decreasing its modulus. [39,40] The magnitude of this decrease, i.e. Payne Effect, is given by the difference ($G'_0 - G'_\infty$) between the maximum modulus in the plateau region at low strains (G'_0) and the minimum modulus (G'_∞). Results obtained for G' as a function of strain are shown in Fig. 5.

A clear difference can be noticed among the combined filler systems in Fig. 5. F4 (with 16 phr CB and 4 phr p-Si) presents a later rupture of the filler-filler network. The fastest drop in G' at very low deformations is seen in F6 (16 phr CB and 15% i-Si), reducing the amplitude of the linear region and indicating the highest filler-filler interactions. This fact could be attributed to the high filler content, exceeding their percolation threshold. When this value is exceeded, a loss on the material properties can occur. In addition, at high content of small particle-size fillers (such as those generated by the sol-gel method) the formation of aggregates is intensified by the increase in the number of effective contact points due to the high specific surface of the particles, causing the drop in the modulus at lower strains. [41,42] On the other hand, formulations with higher individual filler contents, F2 (with 20 phr CB), F3 (with 20 phr p-Si) and F5-I and F5-II (with ~ 16% and 20% i-Si, respectively) exhibit smaller storage moduli and a later decay than F6 (16

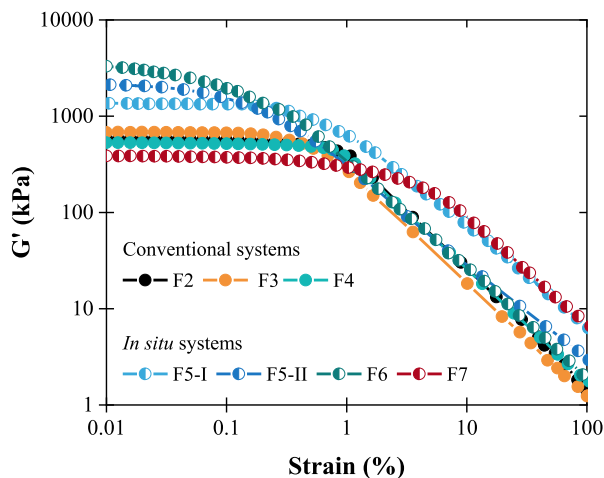


Fig. 5. Payne effect of prepared rubber compounds.

phr CB and 15% i-Si), as a consequence of lower filler-filler interactions. This fact corroborates that in F6, CB has acted as a nucleating agent of the i-Si, [6] generating new interactions between the filler particles and increasing the Payne Effect.

4. Conclusions

In this work, a novel experimental approach based on the sol-gel chemistry for the generation *in situ* of Si and Zi nanoparticles in previously reinforced NR compounds is presented. The results here obtained allow us to conclude that Si particles generated *in situ* have a reinforcement effect at low to medium strains (500%) and increase the stiffness of the rubber, due to an increase in its hardness, as well as in its abrasion resistance. Additionally, when *in situ* Si is generated where CB is already present, a synergy seems likely to occur, reinforcing NR and increasing the modulus values more than 200% at medium strain values. The good rubber-filler interactions and the increase in filler-filler interactions, as seen through the Payne Effect analysis, show that CB particles act as nucleating sites for i-Si. These results open a new path for reusing of discarded or recycled rubber materials, allowing them to have a second life with improved mechanical performance due to the incorporation of *in situ* nanofillers during a post-processing stage.

Authors contribution

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Declaration of Competing Interest

The authors declare no competing financial interest

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.jcomc.2021.100133.

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