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Reinforcing of Elastomers with Mesoporous Silica

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Abstract: Mesoporous silica is used as filler for styrene–butadiene rubber (SBR); filler–polymer interactions are compared with those exhibited when commercial ultrasil silica (VN3) is used. A silane coupling agent is added to improve the filler dispersion and its influence on the bound rubber formation is also investigated before vulcanization. The bound rubber content is higher for the mesoporous silica and increases further for the sample containing alquil silanes improving the mechanical properties. For vulcanized samples, the reinforcing is measured by the vulcanization degree and the mechanical properties. The swelling degree, elastic modulus and glass transition temperature (T_g) are higher for samples containing mesoporous silica and increased by the use of organosilane (bis- trietoxisililpropil tetrasulfano (TESPT) or bis-trietoxisililpropil disulfano (TESPD) during vulcanization. The vulcanization kinetics of the SBR is evaluated by rheometry and differential scanning calorimetry. The vulcanization rate is higher for the rubber filled with mesoporous silica indicating its autocatalytic effect. This can be explained by chemical interactions between the filler and rubber and the penetration of the rubber chains into the mesopore.

Keywords: composite; mechanical and thermal properties; mesoporous silica; styrene butadiene rubber

Introduction

The rubber materials are reinforced with fillers to improve the mechanical properties. The most common fillers are carbon black and amorphous silica, which are used as powders where the surface area, the particle size, their degree of dispersion and degree of the interactions between the filler and rubber chains are important characteristics in the rubber reinforcement.[1,2] Reinforcement is readily obtained with particle sizes smaller than 100 nm and semi reinforcement with particle sizes smaller than 1000 nm. Particle larger than 10^3 nm do not have reinforcing capabilities or have detrimental action,[3] The use of silica as a reinforcement agent offers a number of advantages in the tear strength, abrasion, heat resistance, hardness, high modulus, high resilience, improved rolling resistance and reduction in heat build-up. However, silica does not provide the same level of reinforcement when compared to carbon black of the same particle size since the silica-silica interactions promotes the aggregates formation because the intermolecular hydrogen bonds between hydroxyl groups on the surface of silica are very strong, the silica can aggregate tightly exhibiting a complex geometry which not only will increase the viscosity of the rubber but also will decrease the exposed surface area and therefore the interactions with the rubber even more the silica presents poor chemical affinity for the non-polar elastomer like styrene–butadiene (SBR). In order to enhance filler dispersion and the compatibility between the SBR rubber and silica, it is necessary to modify the silica surface by the addition of a silane coupling

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agent, which reacts with silanol groups to form siloxane bonds. The silane molecules bonded to the silica surface provide better interaction with the SBR rubber because they have a higher chemical compatibility and also the silylation weakens the silica inter-particle interaction and improves the filler dispersion.[4]

Since the total specific surface area of the particles and the pores of a filler give important contribution to the filler reinforcement properties, it is expected that the development of new mesoporous silicas with different properties, compared to precipitated silicas, such as high BET surface areas and their organized pore structures with pore sizes 1.5–10 nm, could increase the reinforcement because they present more sites to interact with the rubber matrix. Moreover, the rubber chains can penetrate the pores increasing the interaction. This effect of filler–rubber interactions is related to the occlusion or trapping of rubber in the pores or between or within aggregates, producing bound rubber. The mesoporous silicas are prepared by a mechanism in which a surfactant participates as pore formation template.[5]

The most adequate and economical silylation agents are the sulfur containing silanes because lead to the formation of silica-rubber bonds and can also act as sulfur donors during the vulcanization.[6]

The aim of this work is to study the real origin and the strength of the interaction rubber/mesoporous silica before and after silylation, before and after vulcanization and establish a difference in behavior with those exhibited for the commercial precipitated Ultrasil silica.

Before vulcanization process this interaction is study based in the measurement of the amount of bound rubber, defined as the insoluble rubber after extraction with a good solvent. The samples and their toluene extracted residues are study by infrared (FTIR), thermogravimetry (TGA), differential scanning calorimetry (DSC). After vulcanization the degree of reinforcement is measured by degree of swelling, the state of cure, the energy consumed during this process and the mechanical properties of the blends.

The swelling ratio is a direct measurement of the degree of cross linking. The smaller the ratio, the degree of cross linking is higher.[7] The swelling ratio is defined as $R = \frac{m_1 - m_0}{m_0}$ where m_o is the weight of the test piece before swelling and m_1 is the weight of the swollen test piece after t time of immersion.

To determine the extent of vulcanization reaction, the torque rheometry and differential scanning calorimetry (DSC) are the most popular due to their simple operation and reliable results. While the torque rheometry measures the change in the stiffness of a rubber compound, the DSC measures the change in the heat flow upon cross linking.

The degree of curing (α) is defined in the following ways depending on the method to determinate under isothermal conditions[8,9]:

$$\text{for cure meter}\, \alpha = \frac{M_t - M_0}{M_h - M_0},$$

$$\text{for DSC}\, \alpha = \frac{\Delta \mathrm{H_t}}{\Delta \mathrm{H}\infty}$$

Where, M_0, M_t and M_h are the torque values at the time zero time, at a given time of curing and at the end of cross linking respectively, ΔH_t is the accumulated heat evolved at the time t and ΔH_∞ is the total heat evolved during vulcanization.

Experimental

Preparation of the Mesoporous Silica

Reactants: Sodium silicate solution (technical grade, weight % SiO_2: 27, Na_2O: 11.9). Non-ionic surfactant (Triton ×100, Polyethyleneglycol 4-teroctyl-phenylether from Aldrich), Sodium hydroxide (Aldrich, analytical grade). The silica samples are denominated as Mesosil B. Commercial SBR 1502 rubber (17 of styrene/100 of butadiene: from the 100 butadiene: 85 butadiene 1-4 and 15 butadiene 1–2) Monsanto is used.

Synthesis Procedure

The samples were prepared according to the procedure reported before[10] with the following molar composition: 1 SiO_2, n(1.20 Na_2O), 0.26 Triton, 220 H_2O. The polymerization pH varied from 6.5 to 8.5. The synthesis gel is left under stirring at room temperature 24 hours. The solid is recovered by filtration, washed with water and dried 24 hours at 75 °C, then there are slightly crushed and passed through a Taylor #400 sieve in order to eliminate agglomerates larger than 40 μm and then calcinated under air to remove the surfactant. The calcinations consisted of heating at the rate of 1.5 K/min up to 480 °C and holding at this temperature for 3 hours.

Incorporation of the Mesoporous Silica into the SBR-type Elastomer

In order to analyze interactions between the rubber and the silica, different mixtures are prepared without the additives normally used during vulcanization.

The mixtures of SBR/silica without silylation and vulcanization are prepared with 60 parts of silica per 100 parts of rubber. The silica and rubber were first milled and mixed at room temperature (mixtures at 25 °C) and then processed in controlled temperature heater plates at 150 °C. A mixture of SBR and silica Ultrasil-VN3, commonly used as reinforcement load for rubber, is prepared in the same way and used as reference for comparison with the results obtained with the mesoporous silicas.

Silylation

Silica samples are activated under vacuum at 200 °C. The samples are mixed with 5% dimethyldichlorosilane in toluene at 65 °C during three hours and finally washed several times with toluene and then with methanol to extract the excess of silane reagent and toluene. The samples are dried at 80 °C for 4 hours. The amount of dimethyldichlorosilane needed for the reaction was calculated assuming that there are three silanol groups (SiOH)/nm^2, hence

$$
\begin{aligned}
M_{DMDCS} &= \frac{1000\,m^2}{1\,g\ \text{silica}} \times \frac{3\,SiOH}{1\,nm^2} \times \frac{10^{18}\,nm^2}{1\,m^2} \\
&\quad \times \frac{1\ \text{molecule of DMDCS}}{2\,SiOH} \\
&\quad \times \frac{128.99\ \text{g of DMDCS}}{6.023 \times 10^{23}\ \text{molecules of DMDCS}}
\end{aligned}
$$

Determination of the Bound Rubber

The extraction of the silica-rubber mixtures with toluene is done in the following way: the materials are cut in small squares of 3–5 mm length and put over a stainless steel sieve (40 μm meshes) which is immersed in toluene. The toluene is changed with fresh toluene three times during 4 days. To eliminate the toluene the solids were extracted three times, by periods of one day, with acetone and finally dried at 85 °C during 48 hours.

Preparation of Vulcanized Rubber Silica Mixtures

Mixture rubber samples are prepared in an open two-roll mill. All samples contain the same amount of vulcanization additives that are added after the incorporation of the silica. All the mixtures contain 60 phr of silica, 5 phr of ZnO as activator of S_8, 2 phr of stearic acid as surfactant to avoid that the ZnO be chemisorbed, 1 phr of zinc diethyl ditiocarbamate as accelerating agent, 3 phr Strukol WB16 to improve the fluency, 4,8 phr of organosilane (bis- trietoxisililpropil tetrasulfano (TESPT) or bis-trietoxisililpropil disulfano (TESPD) and 1 phr of sulfur when silane is not used, 0.5 phr when TESPT or 0.7 when TESPD are used.

Swelling Ratio Measurement

A 1 g rubber sample cut in small pieces is immersed in pure toluene at room temperature for 17 hours to allow the swelling to reach diffusion equilibrium. At the end of this period, the sample was taken out and the adhered liquid was rapidly removed, the swollen weight was immediately measured. The samples are dried in vacuum to constant weight and the desorbed weight is taken.

Characterization of the Materials

The mesoporous silica samples are characterized before the preparation of the rubber/mesoporous silica mixtures by:

Nitrogen Adsorption/Desorption: The isotherms are measured with an ASAP2010 (Micromeretics) on calcinated samples after activation at 300 °C under vacuum for 6 hours. The calculation of the specific surfaces (BET), porous volumes and pore size distribution (BJH method) are performed with the software of the apparatus.

Microscopy: all samples are examined with an optical microscope (Axioskop Zeiss) equipped with a camera (IVC 800 12S) in order to determine the particle morphology, size and aggregation.

NMR Spectrometry: ^{29}Si MAS NMR spectra are recorded using a Win Bruker 300 spectrometer, MAS with decoupling at 56 kHz; the pulse length was 2 μs corresponding to the flip angle of 45°; recycling time 1 s.; number of scans 8152; spun frequency 7 kHz; chemical shift reference: TMS.

The Rubber/Silica Mixtures were Characterized by:

Thermal analyses (TGA) The thermographs of the mixtures rubber/silica are performed in air from 25° to 800 °C, with a heating rate of 10 °C/min in a TA instrument TGA 2910 apparatus.

Differential Scanning Calorimetry (DSC): The samples are analyzed in a TA Instruments model 2920 equipped with the refrigerated cooling system, using a heating and cooling rate of 10 °C/min, under nitrogen atmosphere at a flow of 40 ml/min. Heating from 25 to 120 °C, cooling to −75 °C, again heating from −75 °C. to 150 °C. The last run is analyzed.

Dynamical Thermal analysis (DMTA): The samples of 1.5 cm length, 0.7 cm wide and 0.7 cm thin are analyzed from −100 °C to 20 °C in a Polymer Lab, model MKIII, using a strain value of ±32 μm and a frequency of 5 Hz. The tests are performed at least three times to ensure the repetitiveness of the results.

NMR Spectrometry: ^{13}C CP/MAS NMR spectra are made in Win Bruker spectrometer in order to determine the degree of the interaction between the silica and the rubber: using: $\pi/2$ pulses of 4.5 μs; rotation frequency: 7.5 kHz and recycling time: 1 s (10,11).

Infrared Spectrometry: The silica/rubber mixtures that are too opaque or too thick were analyzed by the attenuated total reflectance (ATR) FTIR technique. KBr pellets are prepared for the toluene extracted rubber + silica samples and analyzed by transmittance on a Perkin Elmer spectrophotometer, model Spectrum One.

Results and Discussion

Table 1 shows the results from the characterization of the mesoporous silicas by nitrogen adsorption/desorption. The particle sizes are between 0.5 to 2 μm. The sílicas prepared with higher sodium content are more disorganized. The sílicas prepared at higher pH show lower particle sizes and are more dispersed.

The mesoporous characteristics exhibited by samples are in agreement with the value expected for a mesoporous silica prepared with the surfactant Triton ×100 at a pH around 8.[12]

Silylated silicas are analyzed by IR and ^{29}Si MAS NMR in order to determine the efficiency of the silylation reaction. Figure 1 shows the ^{29}Si MAS NMR spectrum of B10A using TMS as a chemical reference. It

Table 1.
Characteristics of the calcinated mesoporous silicas determined by N_2 adsorption/desorption and sodium content.

Sample	pH	%Na	Porosity Properties		
			S m^2/g	V cm^3/g	Ø nm
VN3	7.0	8.6	170	0.20	16
B10	8.5	23.2	575	0.69	35
B10A	8.5	7.8	629	0.59	32

S:Superficial area, V:Poro volumen Ø: Poro diameter.

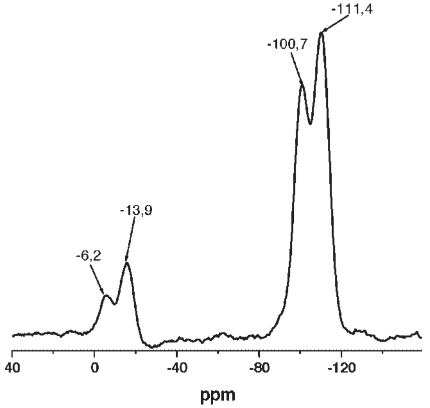

Figure 1.
^{29}Si MAS NMR spectrum of silylated B10A Mesoporous silica.

presents the typical resonance of $SiO(CH_3)_2$-OH at −6.2 ppm and –(OSi $(CH_3)_2$-O)- at −13.9 ppm, thus indicating that the sample is silylated. There is also at −100.7 ppm a signal of $Si(OSi)_3OH$ and at 111.4 ppm a signal of $Si(OSi)_4$.

The FTIR transmittance spectra of silylated silicas (Figure 2) show the C–H stretching and bending vibration bands of the dimethyl groups of the silane reagent that is attached to the silica.

The silicas without silylation treatment show agglomeration, but after the silylation the particles are dispersed, as shown in Figure 3.

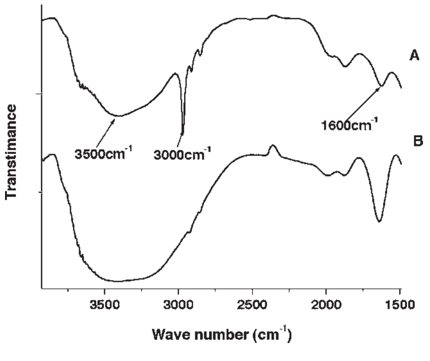

Figure 2.
Infrared of mesopores silicas (a) sílica B10A silylated (b) sílica B10A no silylated.

Determination of the Bound Polymer Content (BPC) in the Reinforcement Samples before Vulcanization

The BPC is calculated from the weight of the residue after extraction (b), the weight of the initial mixture (m), and the amount of silica present in the initial mixture (a), determined by calcination at 600 °C

The BPC is calculated related to the amount of silica in the mixture rubber/silica before the extraction, with the following expression:

% BPC (vs. sílica) = (b-a)/a)*100.

From the results shown in Table 2 it can be concluded that the mixture SBR/silica prepared with mesoporous silicas, with adequate particle sizes present the largest percentage of bound rubber compared with the mixture prepared with Ultrasil-VN3, commonly used as a rubber reinforcing filler, both having the same amount of silica. These results reveal that it is possible to obtain better SBR/silica interactions with a mesoporous silica prepared under certain specific conditions than with the conventional Ultrasil-VN3. This means that the bound rubber is favored by largest superficial area and also by the porous that let the occlusion of the chains inside the silica.

The silylated mesoporous silica with dimethyl diclorosilane (DMDCS) shows the BPC higher than the non silylated silica. The modification with DMDCS, replace the hydroxyl groups by methyl groups decreasing the polarity and let the physisorption and chemisorption of the rubber chains.

To study the interactions between the rubber and mesoporous silica, we chose the mesoporous silica B10A that presents the slower particle size, higher superficial area and higher BPC.

Differential Scanning Calorimetry (DSC)

Figure 4 shows the thermographs of the SBR rubber without reinforcement, reinforced with silica VN3 and mesoporous silica B10A. The thermographs b and c presents an endothermic reversible peak that corresponds to a melting of the SBR polymer chains at 31 °C and SBR/silica VN3 at 20.72 °C but the sample reinforced

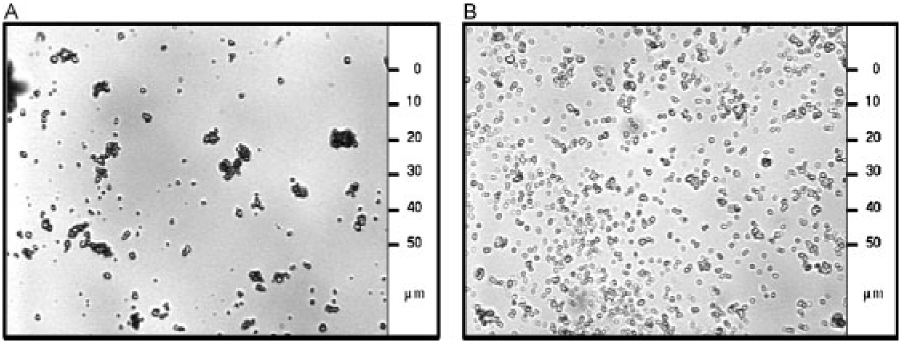

Figure 3.
Micrographs of silica samples: A) Silica B10A without silylation. B) Silica B10A silylated.

with mesoporous silica B10A does not present this peak, the possible reason is the higher chain immobilization than can organized during cooling because they are occluded inside the porous.

In the thermographs the first T_g correspond to the SBR copolymer that do not change appreciably as a result of the interactions with the silica however it is a little higher for the mesoporous silica B10A. This can be due to the high mobility of the chains and the low content of the silica in relation to the rubber. The other T_g corresponds to the bound polymer, which could present different interaction degree: the rubber that is attached closest to the silica is much stiffer than the rubber molecules that are further away. The sample SBR/B10A shows two T_g, one is due to the physorbed chains and the other to the occluded chains, the sample SBR/VN3 presents one T_g due only to the physorbed rubber.

The thermographs of the extracted mixtures prepared with B10A show two Tg due to the bound rubber, the higher T_g could be due to more constrained or chemically bound that are not seen for the VN3 mixture. The silylated extracted mixtures the T_g change to higher temperatures.

Table 2.
% SiO_2 and % BPC in the mixtures SBR/silica.

Samples	% PL vs SBR	%PL vs silica
SBR VN3	33.16	66.41
SBR VN3 S	40.8	83.5
SBR B10	30.07	60.23
SBR B10 S	43.27	86.68
SBR B10A	48.09	96.33
SBR B10A S	78.12	156.47

Infrared Analysis

The Figure 6 shows the attenuated total reflectance (ATR) FTIR spectra of SBR/silica samples. The spectra showed the characteristic bands of this type of samples (10). It is important to remark that in UVN3 silica/rubber samples shows a moderate absorption due to C=O stretching, around 1685–1720 cm^{-1}. The C=O groups can be formed by oxidation of the C=C bond of the 1–4 butadiene, especially during the milling and heating of the silica/rubber mixtures. This oxidation seems to be catalyzed by the presence of sodium, since

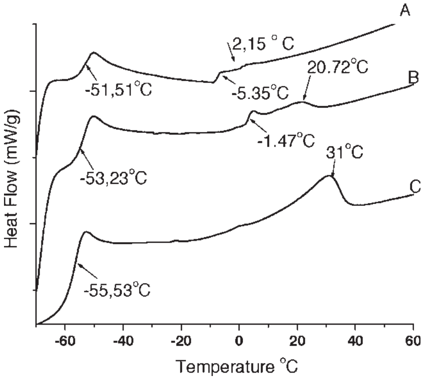

Figure 4.
DSC of non extracted, non vulcanized mixtures: A. SBR-silica B10A, B) SBR-silica VN3, C) SBR.

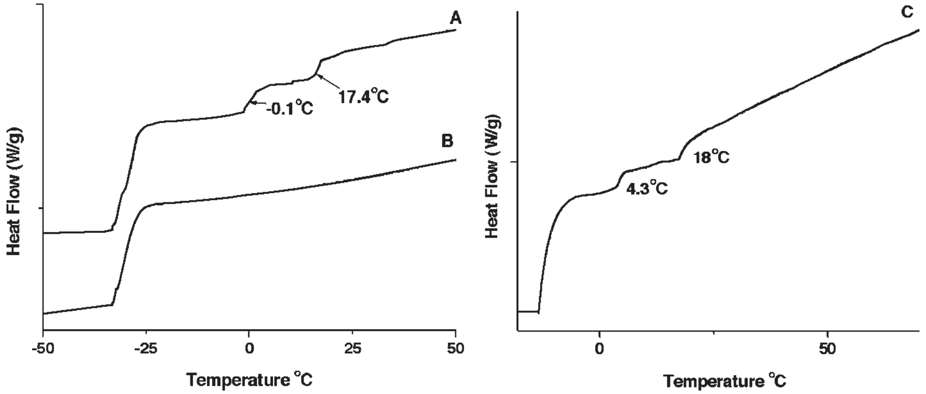

Figure 5.
DSC Thermograms of the extracted SBR + silica mixtures: A) SBR-B10A, B) SBR-VN3 C) SBR B10A silylated.

for the sample containing the largest amount of sodium, the intensity of this band is high. The band around 1685–1703 cm^{-1} does not appear in the mixtures prepared with mesoporous silica. The reason could be that the polymer-oxidized chains are deeply occluded inside of the mesoporous avoiding its observation by the ATR, since it is a superficial technique.

The band at 1062 cm^{-1} due to Si–O stretching vibration is broader for the mesoporous silica than for the VN3 silica. This could suggest the possibility of chemical interaction between the C–O group rubber chains and Si-O groups of the silica. This possibility is higher for the mesoporous silica because some of the rubber chains can be inside of the mesopores.

The spectra of the mixtures prepared with silylated silica show even broader band at 1062 cm^{-1} indicating higher interaction.

When the mixtures are extracted with toluene, the transmission infrared spectrum is run as KBr pellets. The presence of water in these samples is due to the hydrophilic character of the silica. The spectra show also differences in the absorption due to SiO_2 stretching vibrations in the region 1250–1000 cm^{-1} (Figure 7).

The spectra of extracted samples show a combination of the rubber plus silica absorptions with the following features

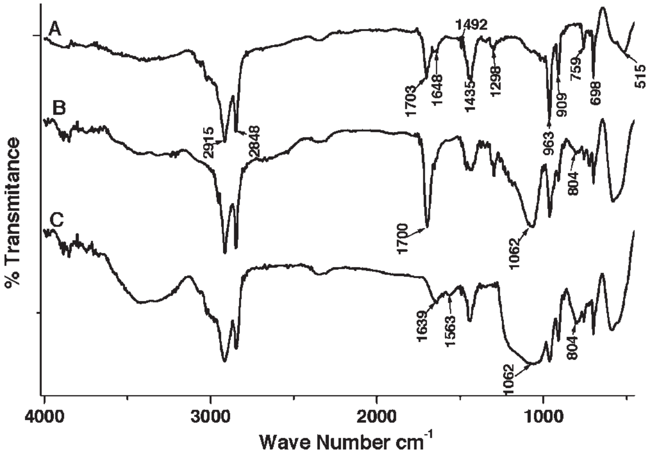

Figure 6.
IR spectra for non vulcanized rubber/silica samples A). SBR no reforzado, B) SBR VN3, C) SBR-B10A.

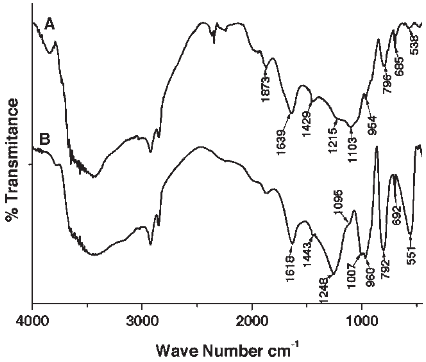

Figure 7.
Infrared spectra A) SBR-VN3, extracted sample B) SBR-B10A extracted sample.

found for the mixture prepared with the mesoporous silica when compared with the VN3 silica sample: the 963 cm^{-1} band gets more intense, the shoulder around 1248–1160 cm^{-1} is well resolved, and the band of Si-O at 1100 cm^{-1} is shifted to lower wave number (1087 cm^{-1} for VN3 and 1060 cm^{-1} for B10A). This is due to the higher BRC, indicating that the interaction of the mesoporous silica with the SBR is strong.

Kralevich et al (13) concluded that the shifting and broadening of the absorptions in this region can be mainly attributed to physical interactions from electrostatic or dipole-induced forces but the presence of a new band at 1248 cm^{-1} could indicates chemical interactions.

^{13}C CP/MAS NMR Analysis of the Extracted Samples

Figure 8 shows the spectra of the extracted samples. The characteristic peaks of SBR emulsion or solution appear at 27.6 for C of cis butadiene, 32.9 for C of trans butadiene, 114.5 for vinyl CH and 145.5 for the phenyl ring of styrene (14). Because of the high glass temperature of SBR, spectra at room temperature exhibit broad bandwidths. Hence, it is not possible to distinguish the cis and trans carbon signals of butadiene, which are at 33.3 ppm; nor is it possible to distinguish the vinyl and phenyl carbons, which are at 130.3 ppm. However, the SBR + B10A mixture shows also a different signal at 29.7 ppm; it can be assigned to aliphatic carbons in interaction with the silica particles. This implies that the chemical environment of the butadiene chains interacting with mesoporous silica is different and we can observe them at different chemical shifts. This is another indication that the interaction is stronger for the

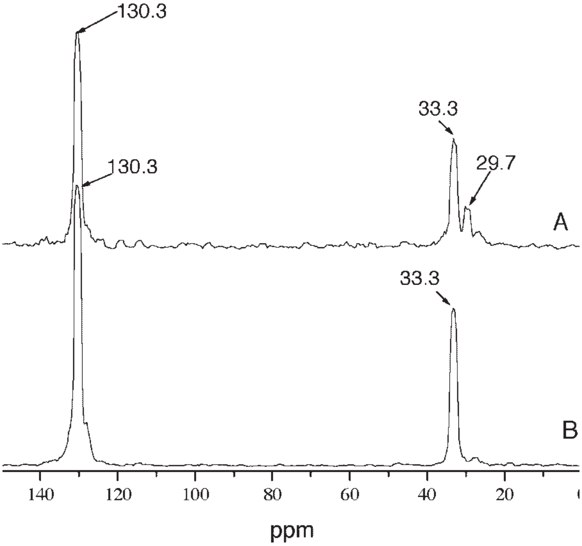

Figure 8.
^{13}C CP/MAS NMR of the extracted mixtures: A) SBR-B10A, B) SBR-VN3.

rubber + mesoporous silica mixture than for the rubber + VN3 silica system.

DMTA Results

Generally, the main relaxation temperature of the rubber T_g shifts to higher temperatures by physical mixing of the filler into the rubber matrix. However, the differences in T_g of the various samples are only about 3 °C. This transition could correspond to the noninteracting rubber chains.

The mixtures prepared with the mesoporous silica B10A that showed the higher BRC (Figure 9), the elastic storage modulus G′ is higher at low temperatures ($T = -100\,°C$) and even at room temperature ($T = 25\,°C$). This implies that the chain entanglements and filler-filler interactions are stronger in this case and the bound rubber affects the mechanical properties of the compounds.

The silylated silica rubber mixtures exhibit lower modulus compared with the non-silylated mixtures (non shown); the silica–silica interaction, which is the primary mechanism of reinforcement especially at high filler loads, becomes weaker.

TGA of the Extracted Samples

Figure 10 shows the derivative TGA curves (DTGA) for the extracted SBR/B10A and SBR/UVN3. The calculated relative weight loss % above 360 °C increases and exhibits its maximum at higher temperature for the SBR/B10A mixture. These values are 68% and 475 °C SBR/B10A and 47% and 428 °C for the SBR/VN3 mixture. This result suggests that the mesoporous silica interacts stronger with the rubber than the VN3 silica.

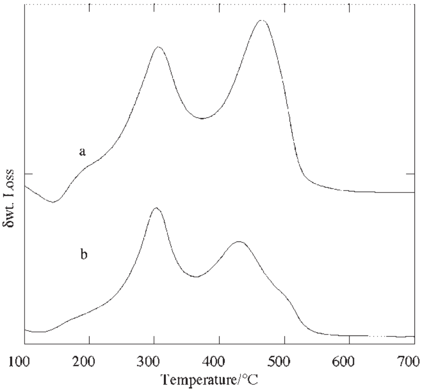

Figure 10.
DTGA graphs for the extracted silica/SBR mixtures (a) SBR/B4M (b) SBR/VN3.

Characterization of Vulcanized Samples

Vulcanization Rheometry: The Figure 11a and 11b shows the rheographs of the cure samples for the rubber mixtures filled with mesoporous silica and the commercial VN3 silica without and with coupling agents respectively.

The sample filled with mesoporous silica presents a shorter scorch time (t2) and a

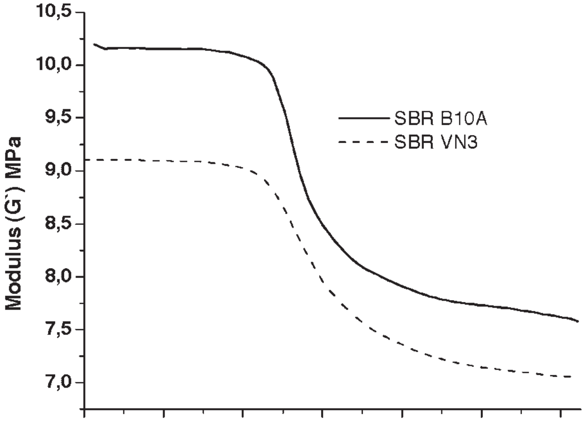

Figure 9.
Storage modulus G′ vs. temperature: SBR + B10A and SBR + VN3 mixtures.

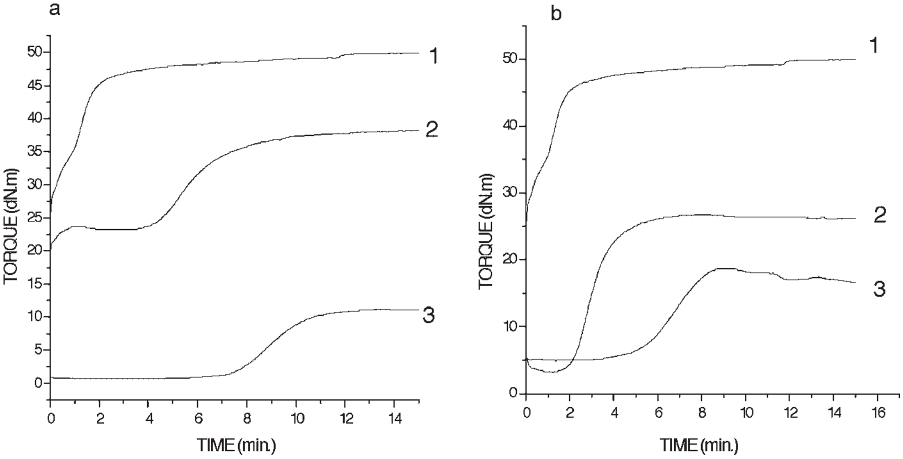

Figure 11.
Rheograph of the cure samples a) 1. SBR/B10A 2. SBR/VN3 3. SBR b) 1. SBR/B10A 2. SBR/B10A TESPT 3. SBR/B10A TESPD.

shorter cure time (t90). The higher vulcanization rate could be explained because of the interaction between the rubber and the mesoporous silica is higher due to the higher superficial area and also the mesoporous silica can occlude the rubber chains inside of the porous causing immobilization and therefore higher reaction rate. This is an advantage since it is well known that during the vulcanization of SBR,[7] the crosslink formation is relatively slow and therefore requires high amounts of accelerator. This is attributed mainly to the low number of double bonds that are responsible for cross linking and also to the non-linear molecular structure in SBR that presents fewer cross linking opportunities. The decrease in cure time is extremely beneficial because it increases the production rate. The SBR-B10A sample also present larger torque values, normally the maximum torque in the rheograph can be taken as the maximum viscosity of the rubber compound, as a measure of the stiffness of the compound and therefore it is roughly a measure of the crosslink density in this sample. As explained before this effect is due to the larger immobility of rubber chains in this sample which is related with the high bonded rubber exhibited by this sample before vulcanization.

When the coupling agents are used the scorch (t_2) and vulcanization times (t_{90}) are larger (Figure 1b). The increasing of the kinetic parameters can be due to a hysteric hindrance to the vulcanization of the polymer chains occasioned by the silane molecules attached to the sílicas.

The differences observed between the two silane coupling agents during the vulcanization process at $T = 150\,^{\circ}C$ can be ex plained based in the stability of these reagents. The tetrasulfur bond of the TESPT is more unstable than the disulfur bond of the TESPD and therefore the TESPT reacts faster with the elastomeric matrix, requiring less vulcanization time, the silane adhered to the silica surface reacts with the rubber mat rix, acting also as a sulfur donor (15).

The swelling ratio (R) of the vulcanized samples filled with mesoporous silica is higher indicating higher extent of cross linking (Table 3). This table contains also the glass transition temperature measured by DSC for the vulcanized samples The first glass transition around $-50\,^{\circ}C$ does not change appreciably with the silica type since corresponds to the non bonded rubber. It can be observed in Figure 12 that the rubber reinforced with mesoporous silica B10A which presented larger bonded rubber content exhibits the higher glass transition temperature.

Table 3.
Results of Tg by DSC and swelling data.

Sample	Tg_1	Tg_2	M_0/g	M_1/g	R
SBR	−48.4				
SBR/B10A	−51.1	43.0	1.07	3.26	2.0
SBR/B10A TESPD	−52.1	55.2			
SBR/B10A TESPT	−54.0	48.9			
SBR VN3	−50.4	26.6	2.07	7.98	2.9
SBR VN3 TESPD	−48.7	59.1			
SBR VN3 TESPT	−51.6	52.4			

Table 4.
DSC vulcanization results.

Samples	β/°C/min	T_{max}	Ea/KJ/mol	
			Ozawa	Kissinger
SBR-VN3	20	173.5	7.035	4.506
	15	162.1		
	10	149.7		
	5	135.0		
SBRB10A	20	158.2	2.978	0.977
	15	146		
	10	119.7		

The second transition observed for the vulcanized rubbers (Tg_2 in Table 3) corresponds to a change in the mobility of the elastomeric chains which are in strong interaction with the filler.

The Tg_2 for the mixtures prepared in the presence of silane coupling increases due to the better chemical interaction between the silica surface and the rubber chains. For the mixtures prepared with TESPD, the Tg_2 is higher than those prepared with TESPT since its reactivity of the TESPD is higher (16).

Analysis of the Curing Kinetics by DSC

The thermographs for the rubber reinforced with mesoporous silica and with VN3 silica are shown in figure 13. We can observe a prevulcanization peak and lower temperature to get the maximum curing (T_{max}) for the sample filled with mesoporous silica at all the heating rates, figure 13b. This effect is also produced by the polymer chains insertion inside of the mesopores which in terms of process ability means smaller energy consummation.

Table 4 shows the kinetic parameters. The activation energies are calculated by using both the Kissinger (16) and Ozawa (17) methods.

$$\beta = -R\frac{d(\ln\beta/T_{\max}^2)}{d(1/T_{\max})} \quad \beta = -\mathrm{R}\frac{d\ln\beta}{\mathrm{d}(1/\mathrm{T}_{\max})}$$

$$\beta = \mathrm{dT/dt}$$

Therefore, a plot of ln $\beta/\mathrm{T}_{\max}^2$ vs $1/\mathrm{T}_{\max}$ (Kissinger plot) or lnβ vs. $1/\mathrm{T}_{\max}$ (Ozawa plot) gives the activation energy. The rubber samples prepared with mesoporous silica

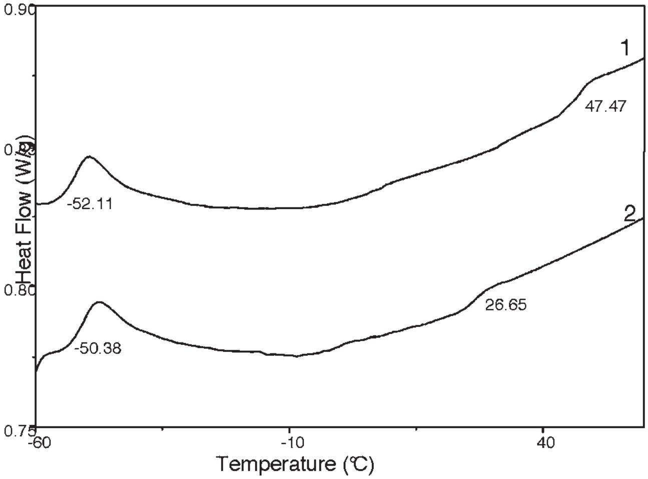

Figure 12.
DSC Thermographs of the vulcanized samples: 1. SBR-B10A 2. SBR-VN3.

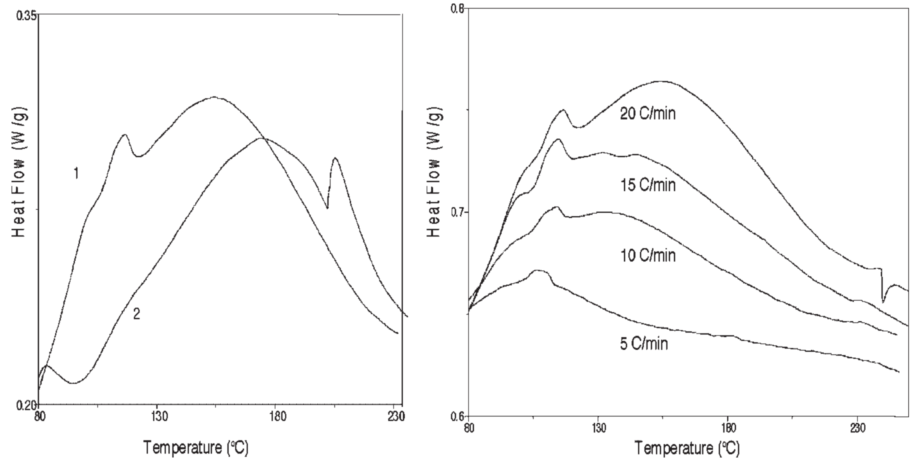

Figure 13.
DSC thermographs of the vulcanized samples a) 1. SBR/B10A. 2.SBR/VN3. b) SBR/B10A at different heating rates.

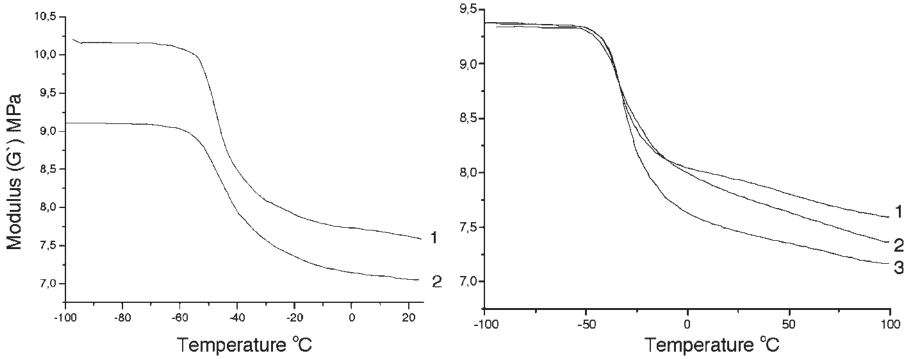

Figure 14.
DMTA of the vulcanized samples. A) 1.SBR/B10A 2. SBR/VN3 B) 1.SBR/B10A 2. SBR/B10 TESPD 3. SBR/B10A TESPT.

present lower activation energy indicating easier cross linking process. This catalytic effect can be attributed again to the greater immobilization of the rubber chains.

Analysis of the DMTA results

The Figure 14 shows the DMTA results for the vulcanized rubber silica mixtures without and with coupling agents. For the mixtures prepared with mesoporous silica, the glass transition temperature and the elastic modulus are higher. These characteristics indicate better reinforcement with this type of silica and agree with the DSC results. The elastic modulus at high temperatures is higher for the mixtures without coupling agents. Probably the silylating chains decrease the crosslinking and therefore the rigidity of the polymer.

The viscoelastic properties of polymers are markedly dependent on the type of crosslink and the degree of crosslinking. Crosslinking raises the glass transition temperature (T_g) of a polymer by introducing restrictions on the molecular motions of the chain and increases the elastic modulus. This result is in agreement with the vulcanization results for the mixtures prepared with coupling agents, which decrease the vulcanization rate (18).

Conclusions

The analysis DSC and FTIR of uncured filled with mesoporous silica indicate the possible penetration of the rubber chains into the mesoporous increasing the interaction. The bound rubber is a good measure of the interaction for non vulcanized samples and the chemical crosslink density measured by swelling ratio and curing measured by DSC and Rheometry are useful for vulcanized samples and they are in good agreement.

Based on the studies on cure characteristics, physical and dynamic mechanical properties of vulcanized SBR it has been found that the retardation in curing of the SBR could be overcome by use of mesoporous silica increasing production efficiency, in turn improves the mechanical properties of finished rubber goods.

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