Effect of Oleyl Amine on SBR Compounds Filled with Silane Modified Silica

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ABSTRACT: The effect of oleyl amine on processing and physical properties of SBR compounds filled with silane–silica particles has been evaluated. Two different types of silane molecules have been used as coupling agents to minimize the silica–silica interactions and reduce the formation of secondary structures of silica, in addition with an increment in the filler–rubber interactions. Significant differences between those compounds have been found according with the silane structure. However, in both cases, the dynamic, rheological, and mechanical properties of the filled rubber compounds were improved after the incorporation of oleyl amine molecules. This fact could be related with the capacity of the amine molecules to interact with the free silanol groups of silane-modified silica forming an amine-modified silica complex, which reduces the hydrophilic nature of the silica surface. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 103: 1806–1814, 2007

Key words: silica; rubber; oleyl amine; processing; physical properties

INTRODUCTION

The reinforcing effect of fillers depends on the nature and proportion of filler–rubber interactions as well as filler dispersion in the elastomeric matrix. Therefore, both processes are linked and governed by the primary particle size and its distribution, the shape and shape distribution (structure) and the site energy distribution and functional groups on the filler surface.[1,2] Therefore, difficulties in the use of silica-like filler in rubber compounds could be related with the nanometric size of the silica particles and with the formation of filler–filler interactions via hydrogen bonds caused by the high number of silanol groups present on its surface.[3] These interactions lead to the formation of secondary structures (aggregates and agglomerates) that cannot be easily broken.[4,5] As it is well known, this fact reduces not only the dispersion of the silica particles into rubber matrix, but also the interactions created between the filler particles and the rubber matrix, causing a wear reinforcing effect.[6]

Several studies have shown that the surface modification of silica during processing and vulcanization processes using bifunctional coupling agents improves the silica dispersion and therefore increases the physical properties of rubber compounds filled with modified silica.[7–10] In this way, bifunctional organosilanes are one of the most important coupling agents used in rubber science and technology. In the last years, new silanes such as the bis(triethoxysilylpropyl) tetrasulfide (TESPT) and 3-octanoylthio-1-propyltriethoxysilane (NXT[TM]) have been developed to obtain significant improvements in the dispersion of the silica particles in NR and SBR matrix.[11–13]

The reaction between the silanol groups of the silica particles and the ethoxy groups of silane molecules takes place via condensation with loss of ethanol. This reaction causes, first, a change in the nature of the silica surface energy, the hydrophilic nature at the silica is transformed into hydrophobic particles with reactive groups on their surface that are able to interact with the rubber molecules. Second, the number of free silanol groups present on silica surface is reduced. Both facts minimize the formation of aggregates and agglomerates improving the dispersion of silica particles into the rubber matrix. However, it is quite complicated to obtain a complete modification of the silica surface. Consequently, the free silanol groups that remain on the silica surface could interact, reducing the effect of the silanization process. This problem is usually minimized by the addition of polar compounds, such as polyethylene glycol or triethanolamine, to the modified silica particles, because these molecules interact with the free silanol groups remaining on the silica surface, reducing their undesirable effect.

In this way, another polar compounds, such as the fatty cationic surfactants, have been used in rubber

TABLE I
Raw Materials

Material	Trade name and characteristics	Manufacturer
E-SBR	Intol 1500, 23.5% styrene	Polimeri Europe, Italy
Silica	Ebrosil PD[a], sg[b]	Iqesil, Spain
TESPT	Si-69, sg	Degussa-Hüls, Germany
Silane–NXT	NXT, sg	Crompton.Osi Spc., USA
ZnO	sg	Bayer, Germany
Stearic acid	sg	Undesa, Spain
Sulphur	sg	Repsol, Spain
6PPD[c]	Vulkanox 4020, sg	Bayer, Germany
DPG[d]	Perkacit DPG, sg	Flexsys, Belgium
CBS[e]	Santocure CBS, sg	Flexsys, Belgium
Oleyl amine	SK FLOT, sg	Kao Corporation SA, Spain

[a] Conventional silica.
[b] Standard grade.
[c] N-(1,3 dimethyl-butyl)-N'-phenyl-p-phenylene diamine.
[d] N,N'-diphenyl guanidine.
[e] N-cyclohexyl-2-benzothiazol sulfenamide.

compound to improve silica dispersion.[14–18] The amine group of the cationic surfactants interacts with the free hydroxyl group of silica during the mixing process, forming an amine–silica complex, enhancing the effect of silica on rubber compounds.

In the previous work,[19] our research group has studied the effect of two different fatty amines in the properties of SBR compounds loaded with silica particles modified with TESPT. The present study pretends to be a continuation of this topic. Addition of fatty amines causes important improvements not only in the silica dispersion, but also in silica–SBR interactions as it was demonstrated by rheology, mechano-dynamic, and physical measurements. The current work follows the same fundamental of the previous one, but in this case, the silica particles has been modified not only with TESPT, but also with NXT. The effect of a natural oleic amine in the dispersion of the modified silica in the SBR matrix will be evaluated by the measurement of the elastic modulus under dynamic conditions (Payne effect), rheologic behavior, scanning electron microscopy (SEM), and physical properties of the vulcanized compounds.

EXPERIMENTAL

Materials and samples preparation

The trade name and manufacturer of the different ingredients used in this work are shown in Table I. Table II shows the rubber recipes. Conventional silica with 175 m^2/g of BET area and a DBP absorption of 225 mL/100 g were used. The oleyl amine has 18 carbons in its backbone and it is characterized by a molecular weight of 273 mol/g, an amine content of 210 mg KOH/g and 88%. The structure of

the silanes TESPT and NXT are shown in Figure 1. The content of both added silanes is different to introduce the equivalent proportion of alkoxy groups that are able to react with the silane surface.

All compounds were prepared in two stages in a thermostatized open two-roll mill. In the first stage, rubber, silica, and silanes were mixed at 80°C. Then, the temperature was increased to 140°C and the mixture was worked out during 8 min to increase the silanization reaction between the silane molecules and the silica surface. After resting 24 h at room temperature, the other ingredients were added in the second stage, at 80°C.

Measurements

The silica–silica interactions were evaluated using a Rubber Process Analyzer, RPA 2000 from Alpha Technologies (Wilshire, UK). The equipment allows deformations and frequency scans. The tests were

TABLE II
Formulation of Rubber Compounds (phr)

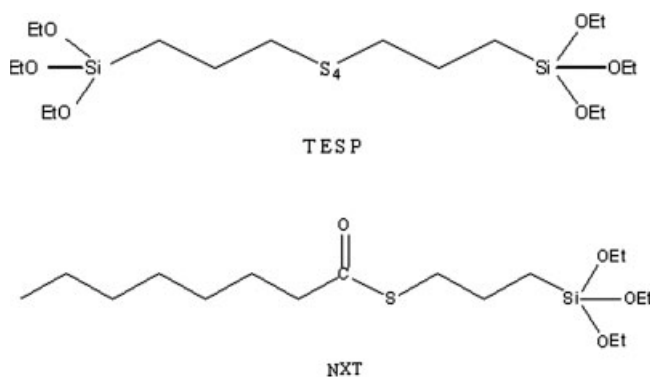| Compounds ingredients	S-1	S-2	S-3	S-4
E-SBR-1500	100	100	100	100
Silica	50	50	50	50
Stearic acid	2	2	2	2
ZnO	3	3	3	3
6PPD	1.5	1.5	1.5	1.5
DPG	1.3	1.3	1.3	1.3
CBS	2.0	2.0	2.0	2.0
Sulphur	1.5	1.5	1.5	1.5
TESPT–silane	4.0	4.0	–	–
NXT–silane	–	–	5.0	5.0
Oleyl amine	–	2.0	–	2.0

phr: Parts per hundred of rubber.

Figure 1 Chemical structures of TESPT and NXT.

carried out at different dynamic deformations with a frequency of 1 Hz. For each deformation used, the RPA supplies the value of the rigid modulus, G^*, and out-of-phase angle between the deformation applied and the obtained value for G^*. The test temperatures with the vulcanized and unvulcanized samples were 80°C and 100°C, respectively.

Rheological measurements were performed with a Rheograph 2003 capillary rheometer from Götfert-Werkstoff-Promaschinen (Karlsruhe, Germany) at 100°C with a shear rate range between 1 and 10^3 s^{-1}. The used die had a 30/2 length/diameter ratio and an entrance angle of 180°. Mooney viscosities (ML_{1+4}) were determined at 100°C using a viscosimeter model MV-2000E from Alpha Technologies (Sweden, UK).

Measurements of cure degree were carried out in a Moving Die Rheometer, model MDR 2000E, from Alpha Technologies at 150°C, with an angular deformation of 0.5° and a frequency of 1.66 Hz.

The degree of filler dispersion was examined by scanning electron microscopy ESEM Philips XL30, operating at high vacuum mode and 30 kV. The scanning electron micrographs were taken from the newly exposed surface of the rubber specimens fractured immediately after embrittling in liquid nitrogen. The specimens were coated with Au–Pd to prevent charging on the surface.

The physical properties of the specimens cured at 150°C at their respective optimum curing times (t_{90} of the rheometer curve) were determined in a thermo fluid laboratory press. Tensile tests were performed with an Instron model 4310 dynamometer (Buckinghamshire, UK), at a deformation rate of 500 mm/min on type 2 dumbbell test specimens according to ISO 37. Tearing tests were carried out on Delf-type samples according to national standard UNE 53516 Part 2 at the same deformation rate used for the tensile test. Five specimens were tested for each sample. DIN 53516 standard was used to determine the abrasion resistance in a cylindrical abrasimeter.

Specimens with dimensions 20 × 4 × 2 mm^3 were cut to measure dynamic properties (DMA) in tension-compression conditions at a frequency of 5 Hz. The temperature range spanned from −80 to 130°C. These tests were carried out in a Metravib Viscoanalyseur Mod 815 (Limonest, France).

RESULTS AND DISCUSSION

Filler–filler interaction

The analysis of the low-strain dynamic–mechanical properties, which describe the viscoelastic response of the rubbery materials to periodic deformation, is known as Payne effect.[20,21] This effect is defined as the decrease in shear modulus with the deformation. Several works have been reported on the interpretation of this effect.[22–24] The mechanism responsible for the Payne effect is still controversial, but the most commonly accepted explication is the destruction of filler networking upon application of oscillatory shear. This dynamic behavior is of great practical importance and essential in the wear tire where it affects the performance characteristics of tread compounds, such as skid and rolling resistance.

In filled elastomers, the shear modulus, G^*, is dependent on the crosslinking of rubber matrix, the hydrodynamic effect of the filler, and the filler–rubber and filler–filler interactions. The three first contributions remain constant with the deformation, in contrast with the filler–filler interactions that show an important dependence. Therefore, difference between the initial value of the modulus (G_0^*) and the modulus at higher deformations (G_∞^*), could be related with the Payne effect, which depends on several parameters. For example, it is well-known that the Payne effect increases with the filler content and filler structure, while it decreases improving the filler dispersion.

Figures 2 and 3 show the shear moduli of the unvulcanized and vulcanized compounds respectively. Obviously, the modulus are increased after the vulcanization process caused by the formation of the elastomeric network.

In both unvulcanized and vulcanized compounds, the presence of amine causes the reduction of the shear modulus. This fact could be explained by the sum of two different contributions. First, the amine molecules act as internal plasticizers in rubber compounds, although some works report that the Payne effect is not affected by the addition of plasticizers in the recipe.[25] On the other hand, the addition of oleyl amine in SBR-silica-silane compounds reduce the number of free silanol groups on the silica surface, preventing the filler–filler interactions, and therefore reducing not only the initial value of the shear
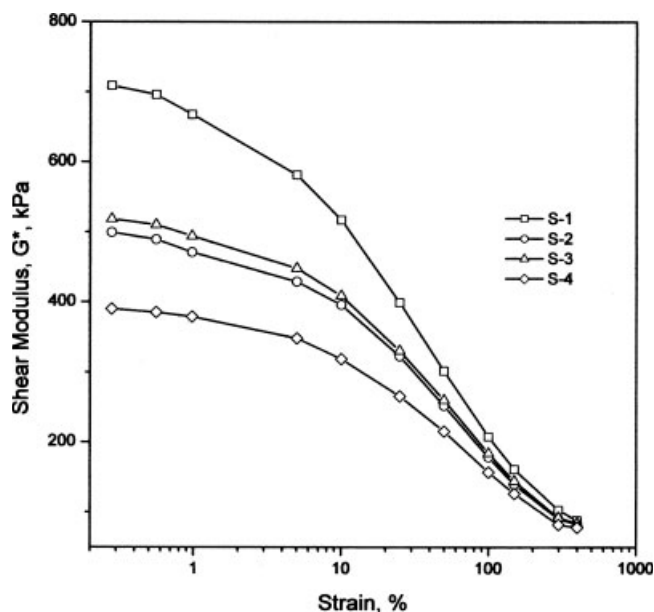
Figure 2 Payne effect in unvulcanized samples. S-1: TESPT, S-2: TESPT–oleyl amine, S-3: NXT, and S-4: NXT–oleyl amine.

modulus, but also the drop of the modulus with the deformation.

As it can be seen in Table III, differences in the shear modulus between the compounds, with and without amine, decreased with the deformation. These results are due to the fact that, under those conditions, it is possible to consider that filler–filler interactions in all the compounds are broken; consequently, the shear modulus would be only dependent of the crosslink network, hydrodynamic effect, and filler–rubber interactions.

It is well-known that the reaction of the silica particles with silane molecules minimized silica–silica interactions, reducing the Payne effect respect to the compounds filled with unmodified silica. This effect is changed with the proportion and type of silane.[13,26,27] At this form, analyzing the effect of the silane molecules, it can be deduced that addition of NXT silane not only reduces the G^* value, but also the Payne effect with respect to the compounds that contain TESPT. The addition of NXT, which are molecules with lower volume, molecular weight, and polarity than silane TESPT, facilitates the silanization reaction between the silanol groups of the silica and the alkoxy groups present in the silane molecules. The enhancement of the surface modification of silica particles reduces their capacity of aggregation, increasing the compatibility of these particles with the rubber matrix. This fact could explain the reduction in the number of broken silica–silica interactions in the rubber compounds that contains NXT as coupling agent in comparison with the compound filled with silica particles modified with TESPT.

According to $G_0^* - G_\infty^*$ values, this difference is around 30% both in vulcanized and unvulcanized samples as it is shown in Table III.

The effect of the silanization is improved with the addition of fatty amine, showing these compounds lower Payne effect caused by the reduction of the filler–filler interactions. This fact can be explained by the reduction of the hydrophilic nature of the silica surface. The hydroxyl groups, which have not reacted with the silane molecules, can interact with the amine group of the oleyl amine forming a silane-modified silica/amine complex through hydrogen bonds. Figure 4 shows a scheme of the possible reactions between the silica particles, the silane molecules, and the oleyl amine. The lowest ΔG^* ($G_0^* - G_\infty^*$) value, which is related with the Payne effect, is obtained after the addition of oleyl amine to rubber compounds filled with silica particles modified with NXT (S-4). However, the addition of fatty amine to rubber compound that contain TESPT as coupling agent (S-2) reduces the Payne effect with respect to its reference compound (S-1) in a higher proportion than the ΔG^* value is reduced in the case of S-4 compound with respect to its reference compound (S-3). This fact seems to indicate that the surface modification carried out with NXT is more effective, and therefore, the addition of amine molecules caused a slighter improvement, as shown in rubber compound S-4, which has the best results in terms of Payne effect.

The G^* modulus can be correlated with the processability of the compounds in shear conditions, i.e., injection or extrusion.[28] The incorporation of oleyl amine to silica loaded rubber compounds reduces the G^* value because the filler interactions are minimized. These conditions are favorable to improve
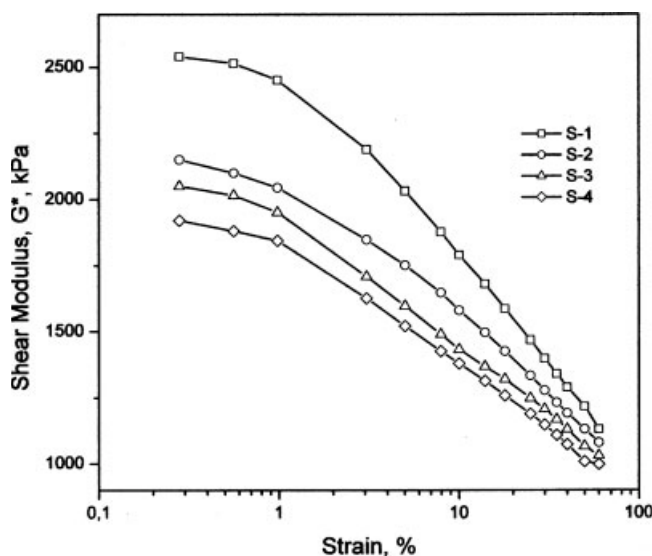

Figure 3 Payne effect in vulcanized samples.

TABLE III
Values of Shear Moduli (kPa) of Rubber Compound

Compound	Cured Compounds			Uncured Compounds			$G_0^*(c) -$ $G_0^*(uc)$	$G_\infty^*(c) -$ $G_\infty^*(uc)$
	G_0^*	G_∞^*	$G_0^* - G_\infty^*$	G_0^*	G_∞^*	$G_0^* - G_\infty^*$		
S-1	2,540	1,130	1,410 (100)	708	88	620 (100)	1,832	1,042
S-2	2,150	1,080	1,070 (75)	499	83	416 (67)	1,551	997
S-3	2,050	1,030	1,020 (72)	518	84	434 (70)	1,532	946
S-4	1,920	1,005	915 (89)[a]	390	78	312 (72)[a]	1,530	927

Values inside parentheses indicate percentage values.
[a] Relative value to S-3.

the silica dispersion into the rubber matrix and obtain significant advantages in the processability of those compounds.

The increment of the G^* modulus of the cured and uncured compounds ($G_\infty^*(c) - G_\infty^*(uc)$) were summarized in the Table III. It is shown that the variations of the modulus of the different compounds are similar in both cases. The filler network created by the silica–silica interactions is destroyed at higher deformations, so the modulus is dependent on the crosslink network of the rubber, which remains constant with the incorporation of the fatty amine. However, the increment of the modulus at lower deformations not only depends on the rubber matrix, but also on the filler–filler interactions.

Figure 5 shows the variation of tan δ with the deformation. This parameter is correlated with the energy consumed when the interactions between filler particles are broken and reformed again. It can be seen that the maximal of hysteresis of the S-1, S-3 compounds take place at higher deformations than the maximal of S-3 and S-4 compounds. This behavior seems to indicate that silica–TESPT aggregates are broken in a higher range of deformation than that of silica–NXT aggregates; this fact could be re-

lated with an increment in the energy consumption. Therefore, the addition of fatty amine seems to facilitate the rupture of the silica aggregates, reducing the energy of the process. In the same way, it is well-known[29] that lower values of tan δ in a deformation range from 1 to 10% is associated with the improvement of the rolling resistance of tires.

According to the experimental results previously described, it can be concluded that the interaction of the fatty amine with the unreacted silanol groups on the silica surface caused a decrease in the hydrophilic nature of the filler, reducing the formation of aggregates between silica particles and improving not only the dispersion of the filler into the SBR matrix, but also the processability of these compounds.

Rheological properties

Two tests have been used to evaluate the influence of oleyl amine on the rheological characteristics of the compounds: Mooney viscosity and flow behavior in capillary rheometer.
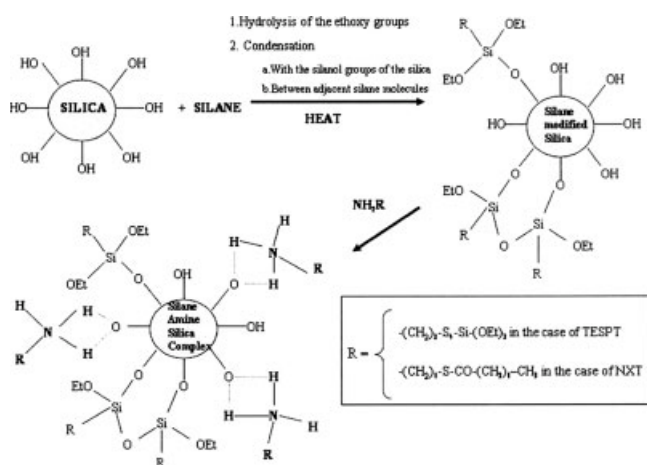

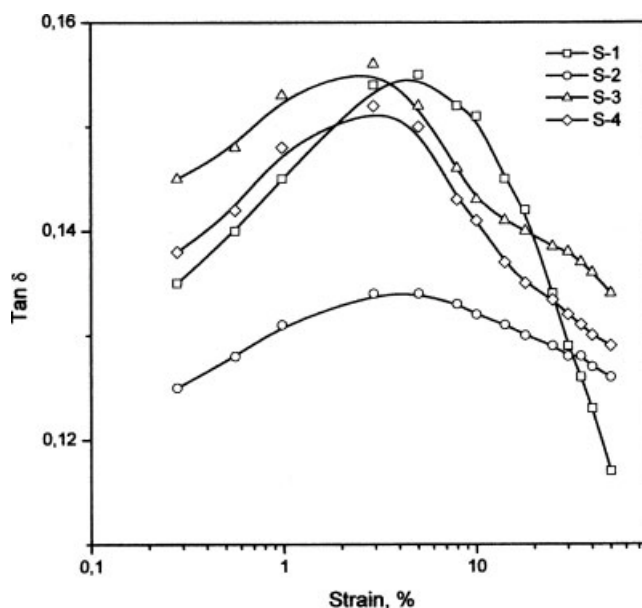**Figure 4** Scheme of the interaction between silica-TESPT-oleyl amine and silica-NXT-oleyl amine.

Figure 5 Tan δ versus shear strain on vulcanized samples.

TABLE IV
The Rotational and Capillary Flow Rheological Parameters of the Compounds

	S-1	S-2	S-3	S-4
Rotational mode				
Mooney peak, MU	141.6	117.0	117.2	104.0
Mooney viscosity, MU	89.5	76.6	73.5	65.4
8 Viscosity, MU	52.1	40.4	43.2	38.6
Capillary flow mode				
Flow index (n)	0.257	0.330	0.248	0.265
Consistency index, k (10^{-4} Pa)	15.3	7.7	14.7	11.8
Correlation coefficient, R^2	0.997	0.999	0.993	0.999

Both, the maximum value of viscosity and the Mooney viscosity are reduced by the addition of fatty amine, as it is shown in Table IV. Similar results have been found when NXT is added in opposition with TESPT. These experimental evidences could be related to the sum of two different contributions: first, the plasticizing effect of the amine and NXT silane, due to the paraffinic nature of the amine and the presence of the octanothiol group in the NXT molecule, respectively, and second, the decrease in the number and size of silica aggregates that improves silica dispersion and silica–rubber interactions.

The decrease in the viscosity (variation between the initial and final values of the viscosity) is reduced in S-2, S-3, and S-4 samples with respect to the S-1 compound. Taking into account that the shear stress caused by the shear deformation under the experimental conditions is able to break the silica aggregates and agglomerates, it could be concluded that it is the main factor that determine the variation in the viscosity with time. Therefore, the viscosity values seem to indicate that S-1 is the compound with a higher content of filler aggregates and agglomerates. In the same way, the analysis of the viscosity variation with time seems to indicate that the addition of amine molecules reduces the capacity of agglomeration of the modified silica particles because of the formation of a silica-silane-amine complex.

The melt-flow behavior was studied by the use of a capillary rheometer. The Bagley correction was not considered in the pressure effect at the capillary entrance, although the entrance angle between the barrel and the die is 180°. The apparent shear rates stress (τ_{app}) and shear rate ($\dot{\gamma}_{app}$) were calculated by the following equations:

$$\tau_{app} = \frac{\Delta P D}{4L} \qquad (1)$$

$$\dot{\gamma}_{app} = \frac{32Q}{\pi D^3} \qquad (2)$$

$$\eta_{app} = \frac{\tau_{app}}{\dot{\gamma}_{app}} \qquad (3)$$

where ΔP is the pressure drop across the length of the capillary, L and D are the length and diameter of capillary, Q is the volumetric flow rate of material, and η_{app} is the apparent viscosity. The flow behavior of a pseudoplastic material obeys the power law model:

$$\tau_{app} = K\dot{\gamma}_{app}^n \qquad (4)$$

or

$$\eta_{app} = K\dot{\gamma}_{app}^{n-1} \qquad (5)$$

where n is the flow index for non-Newtonian rheological materials and k is the consistency parameter. They were calculated by using a linear regression analysis.

Figure 6 shows the log–log plots of apparent viscosity versus shear rate of the studied compounds. The flow behavior is the typical for pseudoplastic materials, so the viscosity decreases with the shear rate. It can be seen that the incorporation of the fatty
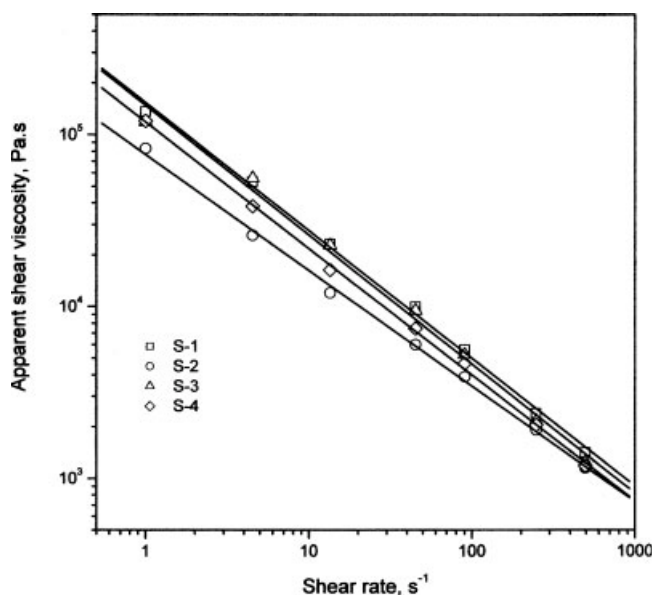

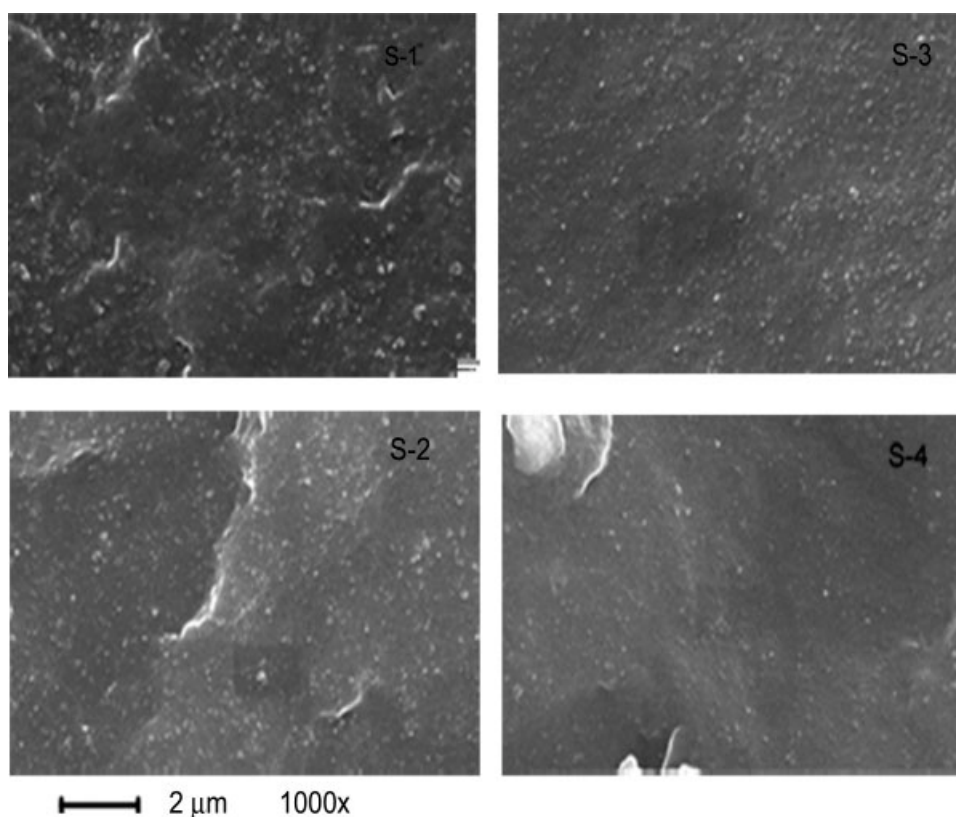**Figure 6** Variation of apparent viscosity with shear rate.

Figure 7 Scanning electron micrographs of the cured samples.

amine into the compounds causes the reduction of the viscosity. This behavior is more noticeable in the samples that contain TESPT. These differences are more evident at lower shear rates; however, they stand up to high rates.

Table IV shows the flow index and consistence values obtained by the application of the power law. The S-2 and S-4 samples show the highest values of n and the lowest values of k. Therefore, the flow energy required to be processed is lower. These results confirm that the presence of the oleyl amine decreases the interactions between silica particles in the mixing stage, together with the plasticizing effect, improving the flow behavior and the processability of the modified silica-loaded rubber compounds.

SEM analysis

Figure 7 shows the scanning electron micrographs of the fracture morphology of vulcanized samples. The compound filled with silica modified with NXT (micrograph S-3) shows a more homogeneous dispersion of silica with a lower particle size in comparison with the sample loaded with TESPT–silica (micrograph S-1). This fact is enhanced by the presence of oleyl amine in the recipes, as can be observed in S-2 and S-4 microphotographs S-2 and S-4.

These micrographs are in good agreement with the results obtained by dynamic rheological measurements, standing out that the addition of amine molecules improves silica dispersion in the SBR matrix. This fact is the main factor that determines the advantages of the processability, shown by the compounds containing fatty amine.

Physical properties

Table V shows the parameters of the vulcanization curves at 150°C. The maximum torque value of the samples with silica–TESPT is higher than values found for the silica–NXT and the fatty amine samples. Increment in torque value in compounds without oleyl amine could be attributed to the existence of more silica–silica interactions, leading to the formation of silica aggregates. The vulcanization curves were obtained with an oscillation arc of 0.5°, which corresponds to a 7% of deformation. This deformation is not enough to break the silica aggregates, therefore, the torque values could be understood as a function of not only crosslink density, but also the filler–filler and filler–rubber interactions. This fact is in agreement with the results in Figure 2. It shows that the stiffness modulus value of S-1 compound measured at 7% deformation is higher than values of compounds that contain fatty amine. The shorter

TABLE V
Vulcanizates and Physical Properties of the Compounds

Compounds	S-1	S-2	S-3	S-4
Curing parameters at 150°C				
T_{max} (dNm)	28.1	20.2	22.7	17.1
T_{min} (dNm)	3.1	2.6	2.5	2.1
ΔT	25.0	17.6	20.2	15.0
$t_{\Delta 2}$ (min)	6.1	2.0	9.5	1.8
t_{90} (min)	18.7	19.2	19.1	17.7
Physical properties of cured compounds				
Hardness (Shore A)	65	62	61	59
Tensile strengh (MPa)	26.6	29.4	28.8	28.7
100% Modulus (Mpa)	2.5	2.0	1.9	1.7
300% Modulus (Mpa)	14.8	11.6	8.8	7.8
Elongation at break (%)	493	560	593	637
Tear (delft die) (N)	51.5	62.9	66.0	59.8
Resilience (%)	49.0	48.5	50	48.5
Abrasion loss (mm³)	82	87	88	82
T_g (°C)	−38.0	−35.6	−38.5	−36.7

scorch time of S-2 and S-4 compounds is caused by the catalytic effect of the basic nature of the oleyl amine. Moreover, the optimum cure time (t_{90}) is similar for all compounds.

The better dispersion of silica particles obtained by the addition of fatty amine not only improves mixes processability, but also has an outstanding influence on the physical properties of the vulcanizates, as it can be seen in Table V. Shore A hardness is decreased, whereas the ultimate properties, such as tensile strength, elongation at break, and tear strength, are increased by the addition of the oleyl amine. The samples containing NXT in their recipes (S-3 and S-4) show lower modulus, because the silane only contains one sulfur in its structure, reducing its capacity to generate strong interactions with the rubber matrix. On the other hand, other important properties such as hysteresis and abrasion loss remain similar in all samples.

Although formulations used in this work are not specific for tread tire, they can be used to evaluate the influence of the ingredients on properties, with regard to the tread behavior. The variation of tan δ with temperature is shown in Figure 8. It can be observed that the maximum of tan δ is shifted to higher temperatures when fatty amines are added to silane–silica compounds. The increment in the glass transition temperature is due to a reduction in the molecular mobility of the polymer.[30,31] This fact could be caused by the increment of filler–polymer interactions.

On the other hand, an important increase in the intensity of the tan δ peak was observed when fatty amine is added. It is well-known that filled rubber compounds show lower intensity than that of unfilled rubber compounds, because the viscous component of the compound decreases. Polymer–filler interaction

and formation of filler aggregates or agglomerates lead to an effective immobilization of the elastomer segments. This segments lose their rubbery behavior, increasing the effective volume of the filler and reducing the viscous component of the compound.[32]

The addition of oleyl amine reduces the hydrophilic nature of silica surface, leading to a slight increase in the rubber–filler interaction, but silanes
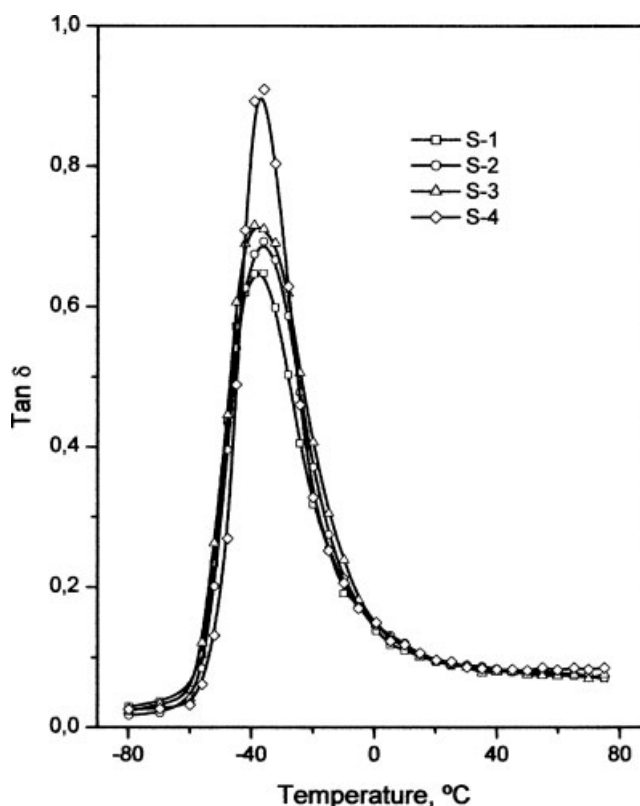

Figure 8 Tan δ versus temperature of the vulcanizates compounds.

are the main responsible of this interaction. However, the interaction of the amine with silanol groups of the silica reduces the formation of the secondary structure of the silica, decreasing the proportion of rubber trapped within the filler aggregates and agglomerates. As a result of this, the viscous component of the compound increase, and so does the intensity of the tan δ peak. This fact is in agreement with the results described in the rheological study.

The dynamic properties were used to study the rolling and wet grip resistance of the compounds. Some authors[33,34] have showed that wet skid and rolling are correlated with the tan δ values at $-20°C$ and $60°C$, respectively. Figure 8 shows that the tan δ values at low temperatures are higher in the S-2 and S-4 samples, whereas changes in the values at temperatures around $60°C$ are not observed. These results seem to indicate that the incorporation of oleyl amine to rubber compounds could improve the wet grip resistance without damaging the rolling resistance of tires.

CONCLUSIONS

Modification of silica surface with bifunctional silanes improves not only the processability, but also the physical properties of the silica-filled rubber compounds. However, these improvements seem to depend on the silane molecule used as coupling agent. When TESPT and NXT silanes are compared, it has been found that the reaction between silica surface and NXT silane, which has lower volume, molecular weight, and polarity, is enhanced in comparison with the silica–TESPT reaction. In consequence, silica particles modified with NXT have a lower capacity to form aggregates and agglomerates, improving the processability of these compounds. However, the existence of only one sulfur atom in its structure makes NXT molecules grafted on the silica surface, which are not able to form strong interactions with the rubber molecules, reducing the mechanical properties of these compounds in relation with the samples that contain TESPT.

In all cases, the processability and physical properties of rubber compounds filled with silane-modified silica particles are enhanced by the addition of oleyl amine. These polar molecules not only act as internal plasticizer, but also are able to react with free silanol groups present on the silane-modified silica surface, reducing its hydrophilic nature. These interactions minimize the silica–silica interactions and reduce the formation of secondary structures of silica, improving the dispersion of silica particles in the rubber matrix.

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