

Effect of a Fatty Amine on Processing and Physical Properties of SBR Compounds Filled With Silane–Silica Particles

J. L. Valentín, P. Posadas, A. Marcos-Fernández, L. Ibarra, A. Rodríguez

Instituto de Ciencia y Tecnología de Polímeros, Juan de la Cierva, 3, 28006 Madrid, Spain

Received 4 May 2005; accepted 14 August 2005

DOI 10.1002/app.22951

Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: The use of fatty amines, obtained from natural fatty acids, in rubber compounds to improve silica dispersion was evaluated. Fatty amines can interact with the free silanol groups of the bis(3-triethoxysilyl-propyl) tetrasulfide (TESPT) silane-modified silica forming an amine-modified silica complex, which reduces the hydrophilic nature of the silica surface, minimizing the silica–silica interactions, and reducing the formation of secondary structures of silica. The effect of the addition of different amines

and/or polyethyleneglycol to SBR compounds loaded with silane-modified silica was evaluated. Finally, incorporation of fatty amines improved the processability and traction properties of rubber compounds loaded with modified silica. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 99: 3222–3229, 2006

Key words: TESPT; Payne effect; rheological properties; physical properties

INTRODUCTION

Precipitated silica is one of the most important fillers for rubber reinforcement. Silica has been used as filler in nonblack rubber compounds as well as in combination with carbon black to reinforce rubber vulcanizates and hence increase the strength as well as some other mechanical properties.^{1,2} It is well known that the combination of silica with coupling agents in tread compounds based on SBR and NR blends, in so-called “Green Tires,”³ improves tire properties, i.e. rolling resistance and wet traction, meaning lower energy consumption and security advantages, respectively.^{4,5}

The significant reinforcing effect showed by silica contrasts with the difficulty on the processability of the silica-filled rubber compounds because of the poor dispersity of silica particles in the rubber matrix. Silica particles show strong filler–filler interactions and adsorption of polar compounds by hydrogen bonds caused by the nanometric size of silica particles and the high number of silanol groups present on its surface.⁶ Strong interactions among particles, which are produced between silanol groups of the silica surface, lead to the formation of secondary structures (aggregates and agglomerates) that cannot be easily broken.^{1,7} This fact reduces the dispersion of the silica

particles into the rubber matrix and the filler–rubber interactions, causing a weak reinforcing effect.⁸ Moreover, the adsorption of polar curing agents on the silica surface modifies the vulcanization process, changing significantly scorch time and curing time as well as decreasing the crosslink density of the vulcanizates.

It is well known that the surface modification of silica during processing and vulcanization processes, using bifunctional coupling agents, enhances the compatibility between hydrocarbon rubber and the silica, which leads to remarkable improvement on the physical properties of rubber compounds.^{9,10}

In recent years, new highly dispersible silica has been developed, reducing the time of mixing for an optimum dispersion of the filler and improving the reaction between the silanol groups of the silica and the coupling agents.^{11,12} In the same way, new silanes, such as the bis(3-triethoxysilyl-propyl) tetrasulfide (TESPT), have been developed obtaining a significant improvement in the dispersion of silica particles in NR and SBR matrices.^{13,14}

The silanization reaction between the silanol groups of the silica and the ethoxy groups of TESPT takes place via condensation with loss of ethanol, reducing the formation of aggregates and agglomerates and improving the dispersion of silica particles into the rubber matrix. However, if there are still some free silanol groups left on the silica surface, they can interact. Therefore, the addition of polar compounds, such as poly ethylene glycol or triethanolamine, to modified-silica-filled rubber compounds, by interacting

Correspondence to: J. L. Valentín (jlvalentin@ictp.csic.es).

Contract grant sponsor: CICYT; contract grant number: MAT 2001/1634.

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	Iquesil, Spain
TESPT	Si-69, sg	Degussa-Hüls, Germany
ZnO	sg	Bayer, Germany
Stearic acid	sg	Undesa, Spain
Sulphur	sg	Repsol, Spain
6PPD ^c	Vulkanox 4020, sg	Bayer, Germany
PPG ^d	Perkacit IWO, sg	Flexsys, Belgium
CBS ^e	Santocure CBS, sg	Flexsys, Belgium
PEG ^f	PEG 40,000, sg	Ineos oxide, UK
Amines	SK FLOT, sg	Kao Corporation SA, Spain

^a Conventional silica

^b Standard grade

^c *N*-(1,3 dimethyl-butyl)-*N*-phcnyl-*p*-phenylene diamine.

^d *N,N'*-diphenyl guanidine.

^e *N*-cyclohexyl-2-benzothiazol sulfonamide.

^f Poly ethylene glycol

with the free silanol groups, reduces the hydrophilic nature of the silica surface.

In this way, several authors^{15–19} studied the use of fatty cationic surfactants in rubber compounds to improve silica dispersion. It was demonstrated that amines derived from the cationic surfactants of fatty acids can interact with the free hydroxyl groups of silane-modified silica during the processing and vulcanization, forming an amine-modified silica complex, improving significantly the dispersion of the filler and the vulcanization process of NR/SBR compounds.

In this work, the use of fatty amines, obtained from natural fatty acids, as a modifier of silane-silica particles, was evaluated. These amines reduce the amount of free silanol groups of modified silica, so the silica-silica interactions are minimized, improving the incorporation and the dispersion of silane-modified silica into SBR compounds. This effect was characterized by the decrease in the elastic modulus of both vulcanized and unvulcanized samples in the dynamic test, commonly referred as Payne effect.²⁰

The influence of the amine nature in the rheological and physical properties of the samples as well as in the vulcanization process was evaluated. Therefore, two commercial fatty amines, which were obtained from

coconut oil and oleic acid, were evaluated, whereas poly ethylene glycol 4000, which is usually used in silica-SBR compounds, was used as reference.

EXPERIMENTAL

Materials and samples preparation

The trade name and manufacturer of the different ingredients used in this work are given in Table I. Tables II and III show the characteristics of the amines and the rubber recipes, respectively. In both cases, FA1 and FA2 are primary amines with hydrocarbon chains of different length, derived from coconut and oleic acid, respectively.

The compounds were prepared in two stages in a thermostated open two-roll mill. In the first stage, rubber, silica, and silane were mixed at 80°C. Then the temperature was increased to 140°C and the mixture was worked out for 8 min to increase the silanization

TABLE II
Fatty Amines Characteristic

Sample	FA1	FA2
Coconut amine	Yes	—
Oley amine	—	Yes
Molecular weight (mol/g)	210	273
Total amine value (mg KOH/g)	260	210
Typical carbon chain composition (%) (<C12:C14:C16:C18)	58:20:10:12	--:2:10:88

TABLE III
Formulation (phr) of Rubber Compounds

Compounds ingredients	C-1	C-2	C-3	C-4
E-SBR	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
Sulfur	1.5	1.5	1.5	1.5
TESPT	4.0	4.0	4.0	4.0
PEG	—	2.0	—	—
FA1	—	2.0	—	—
FA2	—	—	—	2.0

reaction between the TESPT and the silica. After resting for 24 h at room temperature, the other ingredients were added at 80°C in the second stage.

Measurements

The silica–silica interactions were evaluated using a Rubber Process Analyser, RPA 2000 from Alpha Technologies (Wilshire, UK). The tests were carried out at different dynamic deformations, with a frequency of 1 Hz. The test temperatures of the vulcanized and unvulcanized samples were 80 and 100°C, respectively.

Rheological measurements were performed with a Rheograph 2003 capillary rheometer from Göttert-Werkstoff-Promaschinen (Karlsruhe, Germany) at 100°C, with a shear rate range between 1 and 10^3 s^{-1} . The die used in these tests had a 30/2 L/D ratio and an entrance angle of 180°. The die swell was measured with a "Beta LaserMike 101 in. unit located under the capillary exit in a dynamic way for each one of the shear rates. Mooney viscosities (ML_{1+4}) were determined at 100°C, using a viscosimeter model MV-2000E from Alpha Technologies (Swindon, UK).

Measurements of cure degree were conducted by using 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 physical properties were determined on the specimens cured at 150°C at their respective optimum curing times (t_{90} of the rheometer curve) in a thermofluid 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 53,516 part 2, at the same deformation rate used for the tensile test. Five specimens were tested for each sample.

DIN 53,516 standard was used to determine the abrasion resistance, in a cylindrical abrasimeter.

Specimens with dimensions $20 \times 4 \times 2 \text{ mm}^3$ 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

Payne effect is commonly used to quantify the filler–filler interactions in rubber compounds loaded with reinforcing fillers, because those interactions are directly related to the increase in the shear modulus. It is well known that the shear modulus G^* is dependent

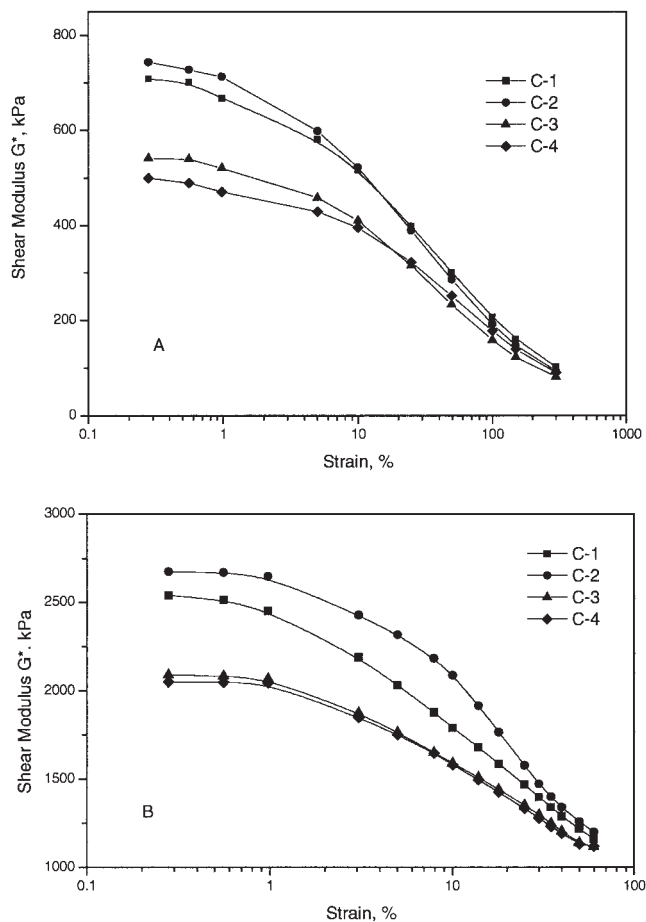


Figure 1 Payne effect in unvulcanized (A) and vulcanized (B) compounds. C-1: TESPT; C-2: TESPT/poly ethylene glycol; C-3: TESPT/amine FA1; C-4: TESPT/amine FA2.

on (i) the crosslinking density of the rubber matrix, (ii) the hydrodynamic effect caused by the filler, (iii) the filler–rubber interactions, and (iv) the filler–filler interactions.^{20,21} Filler–filler interactions are dependent of the deformation degree at lower deformations, whereas the other parameters remain constant; thus, when the deformation is increased, the filler network is eliminated, reducing the shear modulus. Therefore, the variation of shear modulus ($G_0^* - G_\infty^*$) can be understood as a measurement of the filler–filler interaction in rubber compounds.²²

In this work, the Payne effect is used to evaluate the influence of the fatty amines in the interactions between silica particles modified with TESPT in SBR compounds. Figure 1 shows the evolution of the shear modulus G^* with the deformation in the unvulcanized (A) and vulcanized (B) compounds. Obviously, the unvulcanized samples show lower shear modulus than the vulcanized samples. In both cases, the addition of fatty amines reduces the G^* value at lower deformations. It can be seen that shear modulus is reduced when the deformation is increased; until at

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

Compound	Cured compounds				Uncured compounds				$G_0^*(c)^a$	$G_\infty^*(c)$
	G_0^*	G_∞^*	$G_0^* - G_\infty^*$	(%)	G_0^*	G_∞^*	$G_0^* - G_\infty^*$	(%)	$G_0^*(uc)^b$	$G_\infty^*(uc)$
C-1	2540	1160	1400	(100)	708	103	605	(100)	1832	1057
C-2	2675	1200	1474	(105)	744	94	650	(107)	1931	1106
C-3	2090	1115	975	(69)	541	88	453	(70)	1549	1027
C-4	2050	1120	930	(66)	499	90	409	(67)	1551	1030

higher deformations, all the compounds show similar modulus.

The modulus values at lower and higher deformations, G_0^* and G_∞^* , respectively, are summarized in Table IV. The variation of the modulus in silica when the fatty amines are added (C-3 and C-4) is lower than in rubber compounds filled with TESPT-modified silica. Therefore, if the decline of G^* can be considered as a silica-silica interaction measurement, it can be concluded that the relative interaction between silica particles, when the fatty amines are added, is reduced around 70% respect to the TESPT-silica rubber compounds, whereas, the addition of poly ethylene glycol (C-2) increases the filler-filler interactions, independently of the plasticizer effect of these molecules.

The reaction of the silica particles with the TESPT molecules minimized the silica-silica interactions, reducing the Payne effect respect to the compounds filled with unmodified silica. This effect is increased with the proportion of TESPT.^{23,24} The effect of the silanization is improved with the addition of fatty amines, showing that these compounds lower Payne effect and a higher decrease in the filler-filler interactions. This fact can be explained by the reduction of the hydrophilic nature of the silica surface. The hydroxyl groups on the silica surface or on silsesquioxane layer on modified-silica surface can interact with the amine groups of the fatty amines forming a TESPT-modified silica/amine complex through hydrogen bonds. Figure 2 shows a scheme of the possible

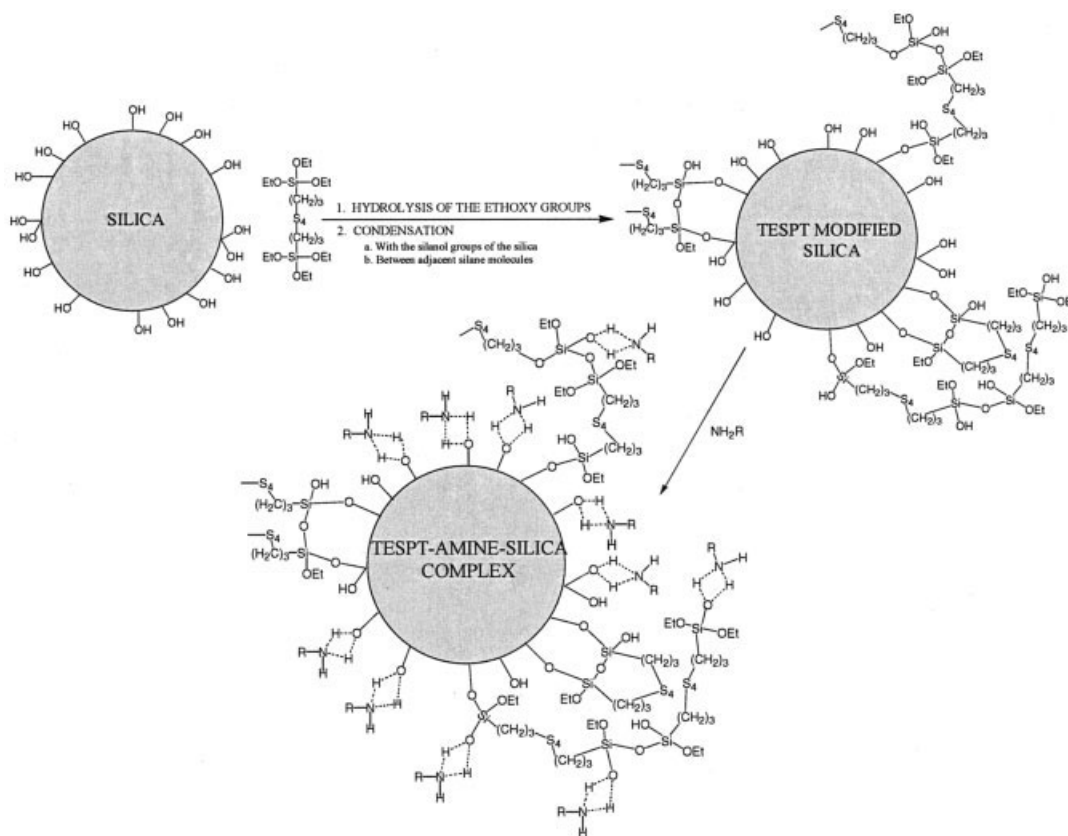


Figure 2 Scheme of the interactions between silica, TESPT, and fatty amines.

interactions between the silica particles, the TESPT molecules, and the fatty amines. In addition, fatty amines act as an internal plasticizer in rubber compounds.

The G^* modulus can be correlated with the processability of the compounds in shear conditions, i.e. injection or extrusion.²⁵ The incorporation of fatty amines to silica-loaded rubber compounds reduces the G^* value because the filler interactions are minimized. These conditions are favorable to improve 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 IV. It is shown that variation of the modulus of the different compounds is 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 amines. However, the increment of the modulus at lower deformations not only depends on the rubber matrix, but also is dependent of the filler-filler interactions.

Figure 3 shows the variation of $\tan \delta$ with the deformation. This parameter is correlated with the energy consumed when the interactions between filler particles are broken and reformed again. When the maximum of hysteresis of the C-1, C-3, and C-4 compounds are analyzed, it can be concluded that the silica aggregates are broken in the same range of deformation. However, the aggregates in the compound with poly ethylene glycol are broken at higher deformation with an increment in the energy consumption. Therefore, the addition of fatty amines facilitate the

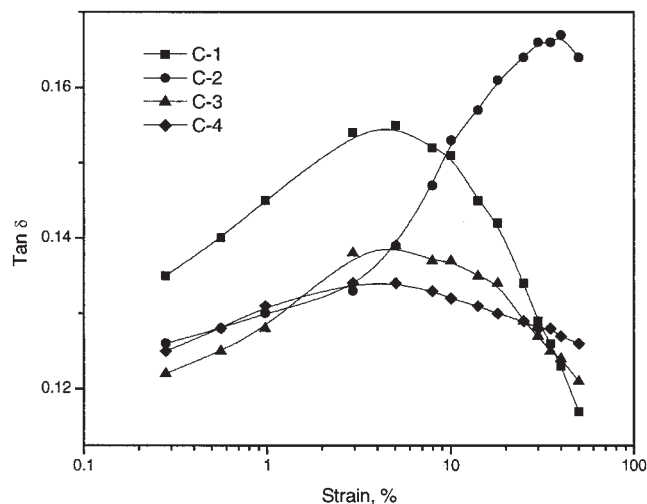


Figure 3 $\tan \delta$ dependence of shear strain on vulcanized compounds.

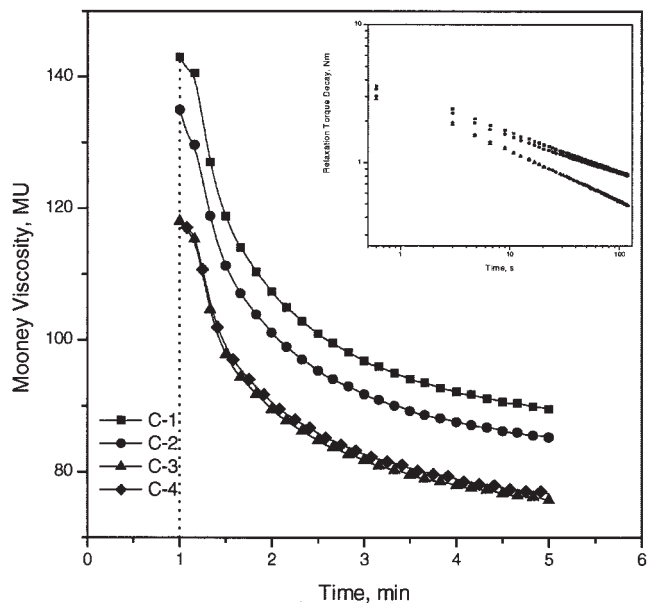


Figure 4 Mooney viscosity curves and Mooney stress relaxation (insert) of the compounds.

rupture of the silica aggregates; thus reducing the energy of the process. In the same way, it is well known²⁶ that the lower value of $\tan \delta$ in a deformation range from 1 to 10% is associated with the improvement of the rolling resistance of tires.

Therefore, it can be concluded that the interaction of the fatty amines with the unreacted silanol groups on the silica surface caused the 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 fatty amine on the rheological characteristics of the compounds: Mooney viscosity and relaxation measurements and flow behavior in capillary rheometer.

The Mooney viscosimeter not only provides the viscosity measurements but also allows, stopping the rotor (inertia < 1 s) instantaneously and measuring the relaxation torque on a certain time, to provide stress relaxation.

Figure 4 shows the Mooney viscosity and relaxation curves. The viscosity curves show a typical exponential decay behavior with the time. It can be seen that the addition of poly ethylene glycol (C-2 sample) to TESPT-modified silica compounds (C-1 sample) reduces the viscosity caused by its plasticizing effect. However, both fatty amines compounds, C-3 and C-4 samples, show lower viscosity values. It can be explained by the fact that fatty amines, in addition to

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

	C-1	C-2	C-3	C-4
<i>Rotational parameters</i>				
Mooney viscosity (ML)	89.5	85.2	75.5	76.6
Relaxation rate (α)	0.287	0.272	0.354	0.365
Constant (k , N m)	3.21	2.90	2.70	2.80
Correlation coefficient (R^2)	0.997	0.994	0.998	0.999
<i>Capillary flow parameters</i>				
Flow index (n)	0.257	0.215	0.301	0.330
Consistency index (k , 10^{-4} Pa)	15.3	17.9	9.9	7.7
Correlation coefficient (R^2)	0.999	0.999	0.991	0.999

their plasticizing effect due to their paraffinic nature, can cause a decrease in the number and size of silica aggregates, improving silica dispersion and silica-rubber interactions.

Stress relaxation decay rates curves can be fitted according to a power decay law. The log-log plot of these curves are straight lines, where the slope (α) can be correlated with the elasticity of the compounds, so the higher relaxation rate is the higher viscous component of the sample.²⁷ The values of the rheological parameters obtained with the Mooney viscosimeter are summarized in Table V. The fatty amine compounds show the highest viscous component (higher α) and the lowest Mooney viscosity. However, The C-4 compound shows a slight increment of relaxation rate with respect to the C-3 compound. It can be due to fact that oleyl amine is composed mainly by paraffinic amines (C18), whereas the main components of the coconut amine are shorter amines with less than 12 carbons in their backbone.

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°.

Figure 5 shows the log-log plots of apparent viscosity versus shear rate of the studied compounds. The flow behavior is typical for pseudoplastic materials, so the viscosity decreases with the shear rate. It can be seen that the incorporation of fatty amines to the compounds causes the reduction of the viscosity. These differences are more evident at lower shear rates but they stand up to high rates.

Table V shows the flow index and consistency values obtained by the application of the power law. The C-3 and C-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 fatty amines decreases the interactions between silica particles in the mixing stage, improving the flow behavior and the processability of the modified-silica-loaded rubber compounds.

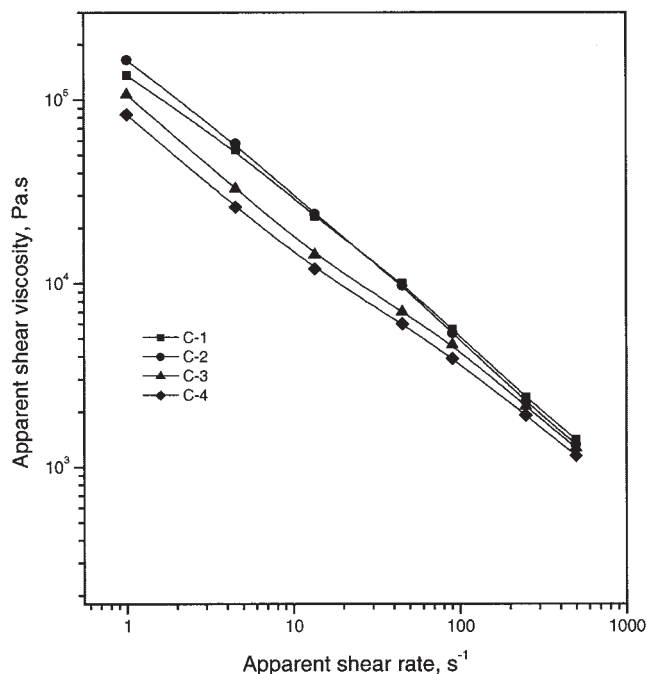


Figure 5 Variation of apparent viscosity with shear rate of the compounds.

It is known that the extruded swelling during flow capillary is related to the elasticity of viscoelastic materials. It is usually expressed as the die-swell ratio D_w/D_c , where D_w and D_c are extruded and capillary diameters, respectively. Figure 6 shows the variation of die-swell with the shear rates. The swelling increases with the shear rate due to the viscoelastic character of the samples. The fatty amine compounds show the higher swelling at every shear rate. This fact

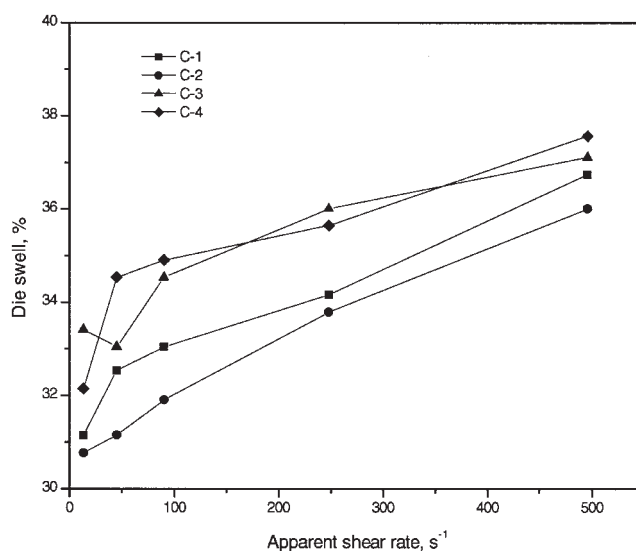


Figure 6 Variation of die-swell with shear rate of the compounds.

TABLE VI
Vulcanizates and Physical Properties of Compounds

	Compounds			
	C-1	C-2	C-3	C-4
<i>Curing parameters at 150°C</i>				
T_{\max} (dN m)	28.1	28.3	21.4	20.2
T_{\min} (dN m)	3.1	3.6	3.0	2.7
ΔT	25.0	24.7	18.4	17.6
$t_{\Delta 2}$ (Mmin)	6.1	5.6	2.6	2.1
T_{90} (min)	18.7	16.0	16.5	19.2
<i>Physical properties of cured compounds</i>				
Tensile strength (MPa)	26.6	27.5	31.2	29.4
100% modulus (MPa)	2.5	3.2	2.2	2.0
300% modulus (MPa)	14.8	16.4	11.0	11.6
Elongation at break (%)	493	466	592	560
Hardness (Shore A)	65	67	62	62
Tear (deift die) (N)	51.5	51.0	64.5	62.9
Resilience (%)	49.0	45.0	49.0	48.5
Abrasion loss (mm ³)	82	87	84	87
T_g (°C)	-375	-38.3	-35.7	-34.9

can be explained by the plasticizing effect of these amines. The swelling differences between the compounds decrease with the increment of shear rate.

Physical properties

Table VI shows the parameters of the vulcanization curves at 150°C. The maximum torque values of the fatty amines samples are smaller than that of TESPT and poly ethylene glycol samples. Increment in torque value in compounds without fatty amine could be attributed to the existence of more silica-silica interactions and ultimately the formation of silica aggregates. The vulcanization curves were obtained with an oscillation arc of 0.5° that corresponds to a 7% deformation. This deformation is not high enough to break all existing silica aggregates and therefore torque value reflects the unbroken aggregates. This fact is in agreement with the results in Figure 1. It shows that the stiffness modulus values at 7% deformation of C-1 and C-2 compounds are higher than values of fatty amine compounds. The shorter scorch time ($t_{\Delta 2}$) of C-3 and C-4 compounds is caused by the catalytic effect of the basic nature of the fatty amines; however, the optimum cure time (t_{90}) is similar in all compounds.

The best silica dispersion caused by the addition of fatty amines, not only improves the mixes processability but also has an outstanding influence on the physical properties of the vulcanizates, as can be seen in Table VI. 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 fatty amines. 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 $\tan \delta$ with the temperature is showed in Figure 7. It can be observed that the maximum of $\tan \delta$ is shifted to higher temperatures when fatty amines are added to silane-silica compounds. The increment in the glass transition tem-

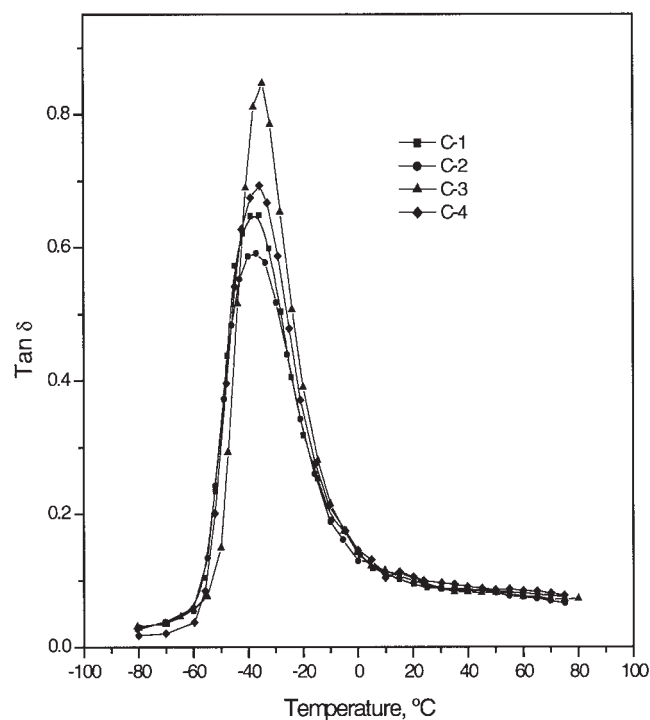


Figure 7 Variation of $\tan \delta$ with temperature of the vulcanized compounds.

perature shows that the molecular mobility of the polymer is reduced.^{28,29} This fact could be caused by the increment of filler–polymer interactions.

On the other hand, an important increase in the intensity of the $\tan \delta$ peak was observed when fatty amine is added. It is well known that filled-rubber compounds show lower intensity than 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. These segments lose the rubbery behavior increasing the effective volume of the filler and reducing the viscous component of the compound.³⁰

The addition of fatty amine reduces the hydrophilic nature of silica surface provoking a slight increase in the rubber–filler interaction, but TESPT is the main responsible of this interaction. However, the interaction of amines with the silanol groups of the modified-silica reduces the formation of secondary structure of the silica, so it decreases the proportion of rubber trapped within the secondary filler increasing the viscous component of the compound and then, the intensity of the $\tan \delta$ peak. This fact is in agreement with the results described in the rheological studies.

The dynamic properties were used to study the rolling and wet grip resistance of the compounds. Some authors^{31,32} have showed that wet skid and rolling are correlated with the $\tan \delta$ values at -20°C and 60°C , respectively. Figure 7 shows that the $\tan \delta$ values at low temperatures are higher for the C-3 and C-4 samples, whereas changes in the values at temperatures around 60°C are not observed. These results confirm that fatty amines compounds could show an increment in wet grip resistance without damaging the rolling resistance of tires.

CONCLUSIONS

Addition of fatty amines to rubber compounds filled with silica reduces the Payne effect improving the silica dispersion into the rubber matrix and so improving the processability.

Rheological measurements confirm the processing improvement provided by fatty amine addition. Associated to it there is an increase in die-swell, attributed to a more developed interaction between SBR and silica particles.

Improved SBR–silica interaction and reduced filler–filler interaction translate in improvements in some physical properties. Fatty amines loaded compounds are softer, and traction values and tear strength are

better, with other properties such as resilience and abrasion losses remaining virtually unchanged.

References

1. Wolff, S.; Wang, M. J. *Rubber Chem Technol* 1992, 65, 229.
2. Boonstra, B. B.; Cochrane, H.; Dannerberg, E. M. *Rubber Chem Technol* 1975, 48, 558.
3. Rauline, R. Eur. Pat. EP 0501227A1. Assigned to Compagnie Generale Des Etablissements Michelin-Michelin & Cie (1992).
4. Waddell, W. H.; Beanregard, P. A.; Evans, I. R. *Tire Technol Int* 1995, 24.
5. Patker, S. D.; Bice, J. A. E.; Oket, T. A. Presented at 151st Meeting Rubber Division, American Chem Society, California, USA, May 1997.
6. Ou, Y. C.; Yu, Z. Z.; Vidal, A.; Donnet, J. B. *Rubber Chem Technol* 1994, 67, 834.
7. Li, Y.; Wang, M. J.; Zhang, T.; Zhang, F.; Fu, X. *Rubber Chem Technol* 1994, 67, 693.
8. Suzuki, N.; Ito, M.; Ono, S. *J Appl Polym Sci* 2005, 95, 74.
9. Guy, L.; Bomal, Y.; Ladouce-Stelandre, L. *Kautsch Gummi Kunstst* 2005, 58, 43.
10. Yan, H.; Tian, G.; Sun, K.; Zhang, Y.; Zhang, Y. *J Polym Sci Part B: Polym Phys* 2005, 43, 573.
11. Rodríguez, A.; González, L.; Ibarra, L.; Ramos, J. Presented at the VIII Simposio Latinoamericano de Polimeros, Acapulco, México 2002, PP-CT-6.
12. Reuvekamp, L. A. E. M. Ph.D. Thesis, University of Twente, Enschede, The Netherlands, 2003.
13. Wang, M. J.; Thang, P.; Mahmud, K. *Rubber Chem Technol* 2001, 74, 124.
14. Görl, U.; Hunsche, A. Presented at the 150st Meeting Rubber División, American Chemical Society, Kentucky, USA, October 1996.
15. Hepburn, C.; Halim, H. M. In *International Rubber Conference*, Sidney, Australia, October 1988: p 247.
16. Ismail, H.; Freakley, P. K. *Eur Polym J* 1995, 31, 1109.
17. Ismail, H.; Freakley, P. K. *Eur Polym J* 1996, 32, 411.
18. Ismail, H.; Freakley, P. K. *Eur Polym J* 1997, 33, 1.
19. Ismail, H.; Freakley, P. K. *Eur Polym J* 1998, 34, 1857.
20. Payne, A. R.; Whittaker, R. E. *Rubber Chem Technol* 1971, 44, 440.
21. Wang, M. J.; Wolff, S.; Tan, E. H. *Rubber Chem Technol* 1993, 66, 178.
22. Fröhlich, J.; Niedermeier, W.; Luginsland, H.-D. *Composites Part A* 2005, 36, 449.
23. Ladouce, L.; Bomal, Y.; Flandin, L.; Labarre, D. Presented at the 157th Meeting of Rubber Division, American Chemical Society, Dallas TX, USA, April 2000.
24. Fröhlich, J.; Luginsland, H. D. *Rubber Chem Technol* 2001, 4, 28.
25. Dick, J. S. *Rubber World* 1994, 1, 19.
26. Roch, P. *Kautsch Gummi Kunstst* 1995, 48, 430.
27. Burhin, H.; Spreutels, W.; Senza, J. A. Presented at the 136th Meeting of Rubber Division, American Chemical Society, Detroit, USA, October 1989.
28. González, L.; Rodríguez, A.; de Benito, J. L.; Marcos, A. *Rubber Chem Technol* 1996, 69, 266.
29. Ayala, J. A.; Hess, W. M.; Dotson, A. O.; Joyce, G. K. *Rubber Chem Technol* 1990, 63, 747.
30. Wang, M. J. *Rubber Chem Technol* 1998, 71, 520.
31. Saito, Y. *Kautsch Gummi Kunstst* 1986, 39, 30.
32. Fujimaki, J.; Ogawa, M.; Yamaguchi, S.; Tomitsu, S.; Okuyama, M. In *International Rubber Conference*, Kyoto, Japan, October 1985: p 184.