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EFFECT OF FUNCTIONALIZATION ON SBR'S INTERACTION WITH CARBON BLACK AND SILICA

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The effect of functionalization of random styrene-butadiene copolymers (SBR) and type of functional group on the interaction with fillers like carbon black and silica was analysed. The SBR were functionalized using tin (R_3SnCl) and organosilane ($RSi(OR')_3$) compounds. The polymers, functionalized and non-functionalized, were characterized by spectroscopy (FTIR), chromatography (GPC) and differential calorimetry (DSC). Carbon black and silica were used to obtain typical tread specimens, which were characterized in terms of rheometric, mechanical and dynamic-mechanical behavior.

The rheometric results indicate that higher modulus (ML and MH) and longer curing times ($Tc90$) were obtained when silica was used.

The 100 and 300% modulus were higher when carbon black was used and the reinforcing index was improved with the presence of functional groups.

The tan delta values of functionalized polymers at 50–80°C were lower than those of non-functionalized polymers, indicating that lower rolling resistance is obtained using functionalized polymers.

Keywords: Anionic polymerization, random SBR, functionalization, polymer-filler interaction, carbon black, silica

INTRODUCTION

Anionic polymerization allows synthesis of copolymers of narrow molecular weight distribution, with controlled monomer distribution,

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microstructure, architecture and end group functionality [1–4], and thus facilitates the engineering of thermo-mechanical properties [5]. Anionically prepared random copolymers of styrene with butadiene have been widely synthesized and thoroughly studied by many researchers [6–9].

The random styrene-butadiene copolymers have been used in the tire industry in order to produce treads that comply with current environmental requirements: better wet traction and low rolling resistance [10–12]. It is known that compounds having a high $\tan \delta$ value at low temperatures (-25 to 0°C) exhibit a high wet traction, whilst a low $\tan \delta$ value at 50 – 70°C range is desired in order to obtain low rolling resistance [11].

On the other hand, some studies have shown that functionalization of polymers can improve the interaction between polymers and fillers, improving the tire's performance, mainly reducing the rolling resistance [13–15]. The interaction of functionalized polymers with fillers depends upon the kind of functional group present in the polymers and type of filler.

The functional groups present in the surface of carbon black and silica are different, therefore the interaction of these fillers with polymers are not necessarily the same. Carbon black as filler has been studied [15–21] since several years ago, due to the interesting and particular properties of this compound.

Several attempts to totally replace the carbon black with white fillers like silica have been done. However, they have not been successful due to strong filler-filler interaction and weak filler-polymer interaction of silica, producing poor cure characteristics and poor processability. Studies [22–26] about the use of silica using promoters as silane coupling agents in order to enhance filler-polymer interaction and, consequently, to obtain better tire performance have been done with good results.

In a first approach, the aim of this work is to study the global performance of a typical tread compound as a result of the interaction between anionically synthesized and functionalized polymers with specific functional groups, which could exhibit better affinity toward silica or carbon black without using a silane coupling agent.

EXPERIMENTAL

Chemicals

Dynasol Elastómeros S.A. de C.V., Mexico, supplied cyclohexane (solvent), butadiene and styrene (monomers). N,N,N',N'-tetra methyl-

ethylenediamine (TMEDA, 98%) and *n*-butyl lithium (16 % w/w, in cyclohexane) were purchased from Merck and FMC-Lithium Division, respectively. The silane reactive (γ -glycidoxy propyl trimethoxysilane, 98%) and the trioctyl tin chloride (99%) were purchased from Witco, Co.

Polymerization and Functionalization

All SBR's were prepared by anionic polymerization of butadiene and styrene in cyclohexane with *n*-butyl lithium as initiator and using TMEDA as a randomizer agent. In order to keep the living species active, the system was kept free from proton-donating substances, achieved by setting up a system that allowed monomer and solvent storage, purification, measurement, transfer, polymerization and sampling under an inert atmosphere. Ultra high purity nitrogen was used as the driving force to transfer monomer, solvent and polymer solution in and out of the reactor. Both the monomer and the solvent were purified in two columns, both packed with activated alumina, providing adequate purification. Before each polymerization, the reactor was conditioned by a procedure based on a colorimetric titration of all protonic impurities with *n*-butyl lithium in the presence of a chromophoric indicator [27].

Once the solvent was free from protonic impurities, measured amounts of styrene and butadiene were added to the reactor, and the titration procedure was again applied to eliminate monomers impurities. Then, the polymerization was initiated by addition of appropriate *n*-butyl lithium quantity. Once the monomers were consumed (complete polymerization), the required quantity of the functionalizer agents was added to the reactor and it was allowed to react during 15 minutes. At the end of the reaction, the polymers were drawn from the reactor and were deactivated with an alcoholic solution (methanol/cyclohexane, 2M) and dried for gel permeation chromatography (GPC) and infrared spectroscopy (FTIR) analysis.

The overall composition of the SBR's was 21% styrene and 79% butadiene, with average number molecular weight in the range $260,000 \pm 15,000$ g/mol.

The microstructure of the butadiene portion of the copolymers, determined by FTIR, was in the range 48%–63% of 1,2-vinyl bonds.

Formulation

Two different fillers were used to formulate the tread specimen: carbon black (IRB6) and silica (Ultrasil 7000 from Degussa). The tread

TABLE 1 Recipe used to Obtain the Tread Specimen

Compound	Content (phr)
Polymer	100
Filler	53.28
Zinc oxide	3.20
Stearic acid	1.07
Sulphur	1.86
TBBS	0.90
Total	160.31

specimens were prepared in a Brabender type mill according to the recipe shown in Table 1.

Characterization

Once the different synthesized copolymers were dyed at 60°C during 1 hour, they were characterized in terms of microstructure, molecular weight and its distribution and glass temperature (T_g). Then the tread specimens were characterized in terms of stress-strain properties, rheometric behavior, Mooney viscosity, resilience and dynamic-mechanical behavior.

The vinyl and styrene content in the copolymers were determined from infrared spectroscopy (Fourier transform, FTIR). These measurements were carried out using CS_2 solutions (1.5% w/w) and analyzed in a Magna 560 spectrophotometer (Nicolet). The spectra were taken in the range of wave numbers of 4000 to 400 cm^{-1} , especially at 910 and 698 cm^{-1} , which corresponds to 1,2-vinyl bond and styrene, respectively. In order to quantify the 1,2-vinyl content a H^1NMR characterized sample was utilized as a reference. Both samples, the H^1NMR characterized and the tested sample have the same composition.

In order to determine the molecular weight and molecular weight distribution, the polymers were analyzed by size exclusion chromatography (SEC), using an Alliance 2690 (Waters) equipment. This equipment has a differential refractometer and three columns, Shodex KF803, KF804 and KF805. The samples were prepared using tetrahydrofuran as solvent at a concentration of 1% w/w.

The stress-strain properties were evaluated by using a universal machine (Instron 5565) following the ASTM D-3182 and ASTM D-412 procedures.

The rheometric behavior was determined by an ODR2000 rheometer (1° arc) at 160°C according with ASTM D-2084 procedure.

A viscometer MV2000 (Monsanto) was used in order to determine the Mooney viscosity (M_{L1+4}) following the ASTM D-1646 procedure.

The vertical resilience at 0 and 50°C was evaluated using a vertical resiliometer SR-1 (The Shore Instrument & MFG Co.) according to ASTM D-2632 procedure.

The dynamic-mechanical behavior was determined using a universal spectrometer, UDS2000 (Paar Physica), in the temperature range of -90° to 100°C at 1 rad/s of frequency. The initial deformation was 0.1% and a heat rate of $3^{\circ}\text{C}/\text{min}$ was used with a torsion geometry.

RESULTS AND DISCUSSION

The microstructure, styrene content, glass transition temperature (T_g) and molecular weight characteristics of the different samples are shown in Table 2.

As can be noted from Table 2, the three polymers are similar in styrene content and molecular weight. However, two samples are different from the other in vinyl content, consequently in T_g values. The main expected difference about the performance of polymers, due to the different vinyl content, is on the low temperature range; i.e., the wet skid resistance will be higher for polymers with higher vinyl bonds content. It is assumed that this difference in vinyl bond content will not have an important effect on the interaction between polymer and fillers.

Rheometric Results

In order to directly compare the results, it has been decided to use the same quantity of carbon black and silica in the tread compound without a silane coupling agent. The mixing procedure was the same for all the cases, since it is known that energetic requirements and some properties can be changed and improved by modifying the formulation and mixing procedure [14,16–18]. Table 3 summarizes the

TABLE 2 Basic Characteristics of Synthesized Polymers

Polymer type	MW (gmol^{-1})	Styrene content	Vinyl %	T_g ($^{\circ}\text{C}$)
SBR non-functionalized	245,000	21%	61	– 22.3
SBR functionalized with R_3SnCl	275,000	21%	63	– 20.6
SBR functionalized with $\text{RSi}(\text{OR}')_3$	246,000	22%	48	– 32.6

TABLE 3 Rheometric Results

Filler type Property	Carbon black			Silica		
	ML (lb-in)	MH (lb-in)	Tc90 (min)	ML (lb-in)	MH (lb-in)	Tc90 (min)
SBR non-functionalized	6.28	44.35	17.2	28.73	68.0	24.9
SBR functionalized with R ₃ SnCl	7.84	42.92	19.2	32.45	72.63	24.1
SBR functionalized with RSi(OR') ₃	13.33	47.02	15.2	43.81	73.98	23.7

rheometric results obtained for the different samples with both used fillers.

From Table 3 it can be seen that energetic requirements are increased when silica was used as filler. In contrast, with carbon black, the generated modulus are 1.5–5.5 times less. This behavior is due to agglomeration, since there is a strong filler-filler interaction with silicas, which is a drawback when this filler is used [12–14]. Also, from Table 3 it can be noted that the cure time is increased with silica, independent of whether the polymer is functionalized or not, relative to those results obtained for carbon black. In order to decrease this high modulus, a silane coupling agent could be used during mixing process; however, as was mentioned, such compounds were not used in the present study, in order to establish the real effect of functional groups chemically attached at polymer chain ends.

It is interesting to note that for polymers with functional groups having affinity toward silica such as silane, the low and high modulus were increased but the curing time was slightly reduced; however, in this work no attempt to adjust cure rate was made for the purposes of this study.

In the case of carbon black containing formulations, the lower modulus obtained is an indication of weak filler-filler interaction in comparison to the case of silica. Formulating with carbon black, certain difference is noticed in the modulus depending on the functional group, for example when tin compound is used, the modulus is lower than that exhibited by the other samples, indicating a better polymer-filler interaction as has been mentioned by other authors [15].

Stress-Strain Properties

The stress-strain properties are presented in Table 4.

When silica is used in the formulation, the modulus at 100% and 300% and the tensile strength are lower than those obtained when

TABLE 4 Stress-strain Properties

	Filler type					
	Carbon black			Silica		
	SBR A	SBR B	SBR C	SBR A	SBR B	SBR C
Modulus 100% (MPa)	4.03	4.01	5.23	2.87	3.35	4.23
Modulus 300% (MPa)	15.26	17.02	18.96	6.27	7.79	11.23
Tensile strength (MPa)	17.83	17.73	22.39	9.09	11.75	17.99
Elongation at break (%)	378	346	402	440	433	457
Reinforcing index*	3.79	4.24	3.63	2.18	2.33	2.66

*300% modulus / 100% modulus ratio

SBR A = SBR non-functionalized

SBR B = SBR functionalized with R_3SnCl

SBR C = SBR functionalized with $RSi(OR')_3$

carbon black is used, as can be seen from Table 4. However, it is interesting to note that modulus values increased according to affinity to filler for the case of silica. These results show that silica is very sensitive to the presence of functional groups, especially if the groups can interact with those present at silica surface, like the silane groups do.

The ratio of 300% modulus to 100% modulus is accepted as an index of reinforcing, indicating the polymer-filler interaction degree, i.e. a higher index a higher interaction between polymer and filler. It is interesting to note that the presence of functional groups improves those parameters. Especially when silica was used. In the case of carbon black, the functionalized polymer with the tin compound exhibits a better reinforcing index; it means that this compound has a higher affinity for carbon black than the silane compound.

Resilience

The resilience is a traditional simple technique that gives a good idea about the performance of the tread specimen. A low rebound value at 0°C is associated with a better wet traction, whilst at 70°C a higher rebound value signifies a lower rolling resistance. Figure 1 shows the results obtained at 0 and 70°C.

From Figure 1 it can be seen that with this technique no influence due to functionalization is evident at 0 or 70°C, especially when carbon black is used. When silica is used at 70°C, the polymer functionalized with the silane compound exhibits a higher rebound and therefore a lower rolling resistance could be expected.

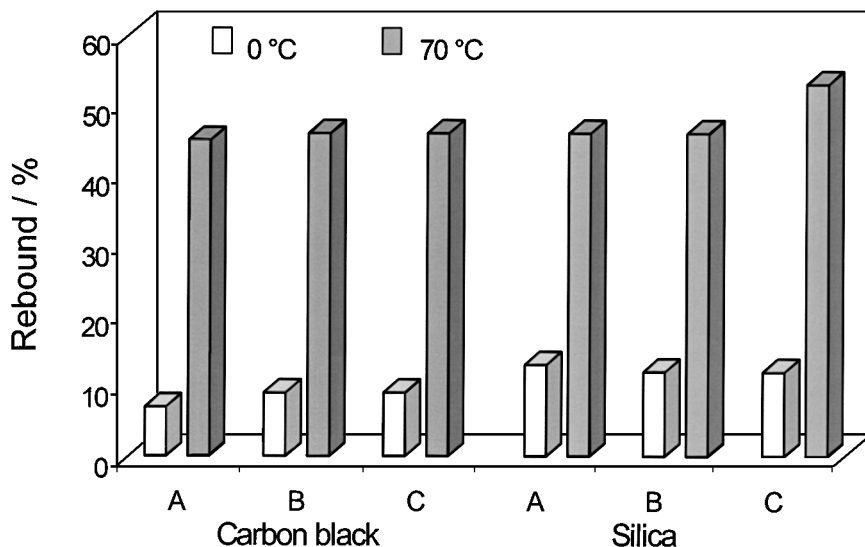


FIGURE 1 Resilience results. A-non-functionalized polymer; B-SBR functionalized with R_3SnCl , C-SBR functionalized with $RSi(OR')_3$.

Comparing the obtained values with silica and carbon black, it can be noted that higher values at 0°C are obtained when the former is used. This is a consequence of poor dispersion in the polymeric matrix. These results are in agreement with the results obtained by rheometric characterization.

Dynamic Mechanical Behavior

A high confidence technique to predict the performance of the tread specimen is the Dynamic Mechanical Analysis (DMA), since it is possible to obtain the $\tan \delta$ values at 0 and 70°C, which are related to high frequencies and low frequencies processes that occur during the brake and rolling, respectively.

Figures 2, 3 and 4 show the $\tan \delta$ behavior of the three kinds of synthesized polymers using both types of fillers.

From Figures 2, 3 and 4 it is noted that using silica, lower $\tan \delta$ values at 0°C and 70°C are obtained than with carbon black. This means that low fuel consumption can be expected, as a consequence of a low rolling resistance.

However, in all the cases a slight reduction of wet traction performance must also be expected, because lower values of $\tan \delta$ at 0°C were obtained.

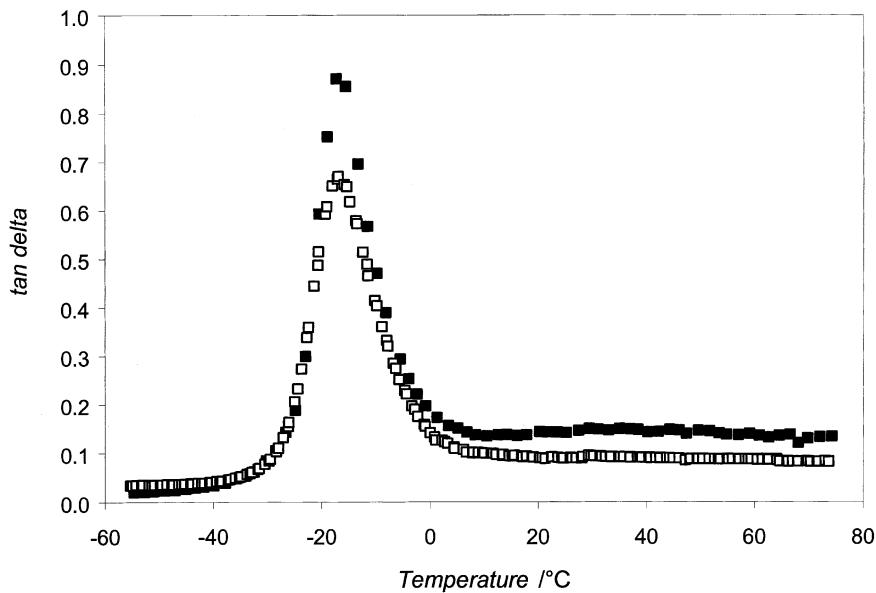


FIGURE 2 Dynamic mechanical behavior of SBR non-functionalized. ■-Carbon black, □-Silica.

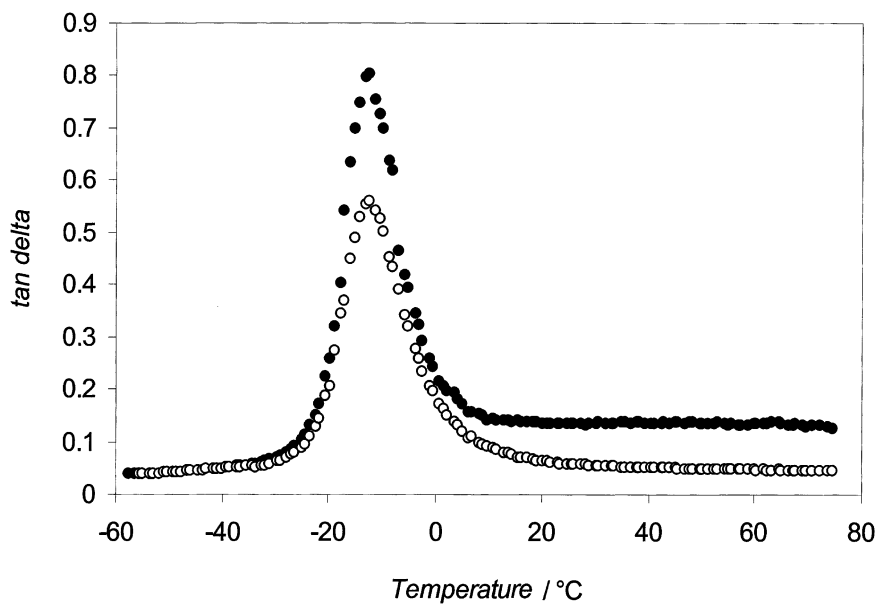


FIGURE 3 Dynamic mechanical behavior of SBR non-functionalized with R_3SnCl . ●-Carbon black, ○-Silica.

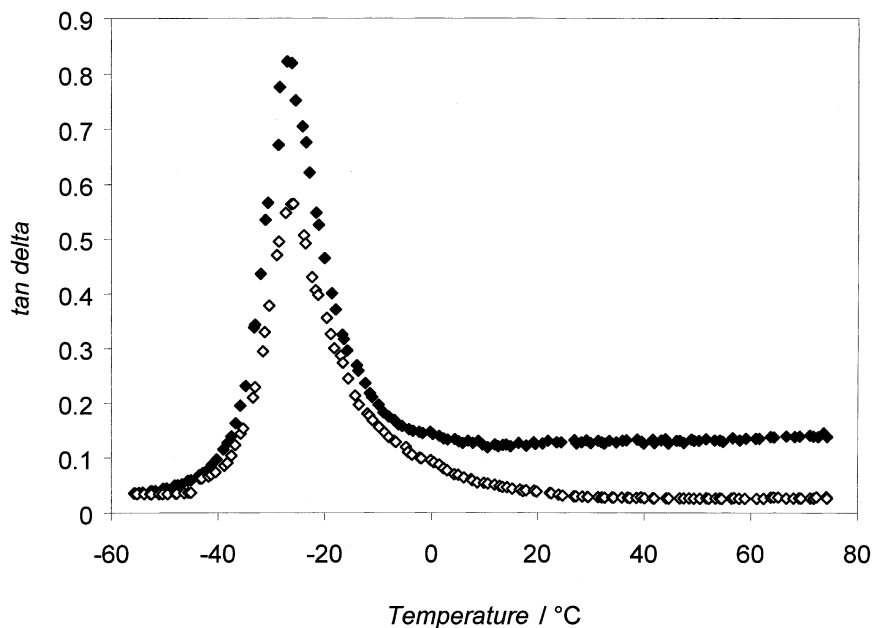


FIGURE 4 Dynamic mechanical behavior of SBR non-functionalized with RSi(OR)_3 . \blacklozenge -Carbon black, \diamond -Silica.

In the case of using carbon black, higher $\tan \delta$ values at 0°C are obtained, resulting in better wet traction performance, but also higher $\tan \delta$ values at 70°C are obtained; therefore, the samples will exhibit higher rolling resistance.

It is important to point out that the peaks observed in the three samples are lower when silica was used, in contrast with those obtained using carbon black. These differences imply that at low temperatures, 0°C and lower, the samples formulated with carbon will show better wet and ice traction since the loss modulus (G'') is high and this modulus helps to prevent the slippage of the polymeric chains during breaking. The use of silica to formulate tread compounds has been followed, mainly to reduce the rolling resistance with no detrimental behavior at 0°C .

Figure 5 shows the comparative curves of the three samples formulated with carbon black.

From Figure 5 it can be seen that functionalization has no important effect on the rolling resistance performance since at the temperature range of $50\text{--}80^\circ\text{C}$, the $\tan \delta$ value is almost the same for

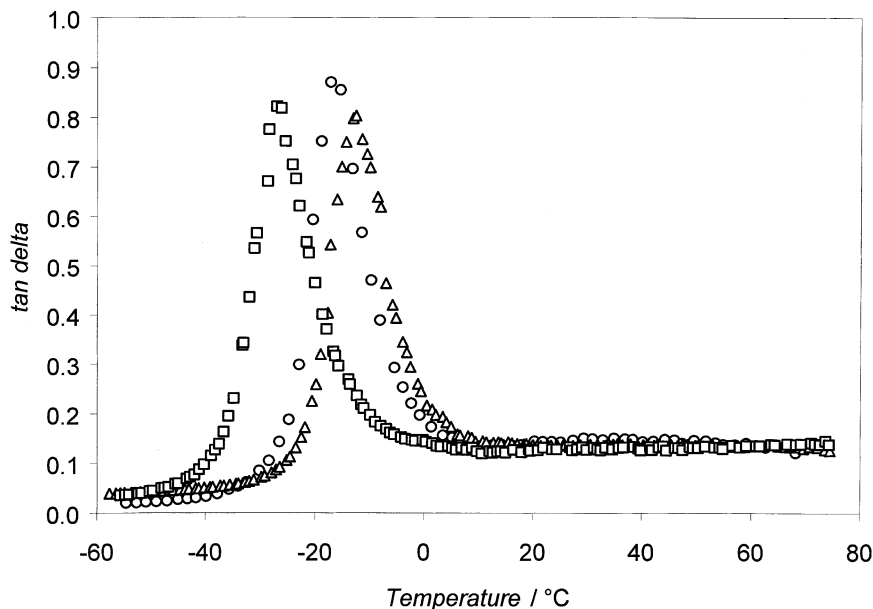


FIGURE 5 Comparative curves of dynamic-mechanical behavior of SBR formulated with carbon black, \circ -SBR non-functionalized, \triangle -SBR with R_3SnCl , \square -SBR with $RSi(OR')_3$.

the functionalized polymers and for the non-functionalized polymer. It could be an indication that polymer-filler interaction is not highly improved in the presence of functional groups or maybe that the functionalization degree achieved is not high enough to improve such interaction.

Unfortunately, it was not possible to evaluate the functionalization degree due to molecular weight of the samples, but it was assumed that quantitative reaction occurred with the remaining living chains after the polymerization ends.

On the other hand, the $\tan \delta$ peak of the functionalized polymer with the silane compound has a lower value because the vinyl content in this polymer is lower than the content of the other polymers. The polymer with the higher vinyl content has the higher $\tan \delta$ value at $0^\circ C$ and peak. It seems that difference in the low temperature range behavior obeys more the microstructure characteristics than the presence of functional groups.

The comparative curves for the polymers formulated with silica are shown in Figure 6.

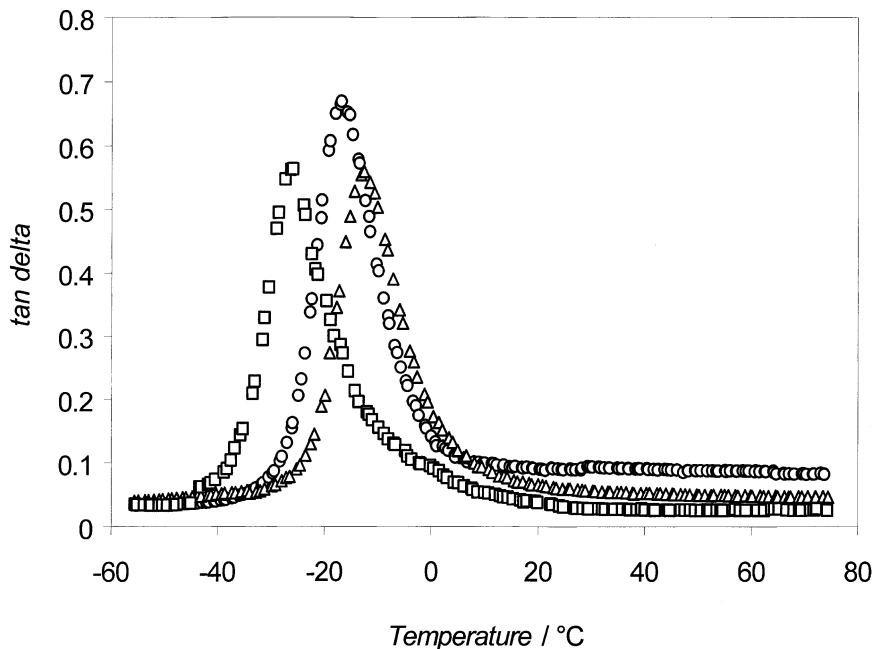


FIGURE 6 Comparative curves of dynamic-mechanical behavior of SBR formulated with silica, ○-SBR non-functionalized △-SBR with R_3SnCl , □-SBR with $RSi(OR)_3$.

From Figure 6, it can be mentioned that reduction of $\tan \delta$ at 50–80°C range depends on the kind of functional group present. With a silane compound where the methoxy groups have more affinity for the silanol and siloxanes groups of the silica's surface, an important reduction of $\tan \delta$ is obtained as can be seen. In the case of the tin compound, it also exhibits affinity toward these silica's groups and therefore there is an important reduction of $\tan \delta$ at the desired temperature range, however this reduction is lower than that obtained with the silane compound.

Figure 7 shows the most probable interaction between the functionalized polymer with silane compound and the silica by methoxy groups.

Also it is possible that functionalization takes place by reacting methoxy groups this leaving the glycidoxy termination free. This functional group can also react with silica. In the case of low molecular weight polymers, it was confirmed [28] that the functionalization reaction takes place by glycidoxy functionality. This result could be extrapolated to our case.

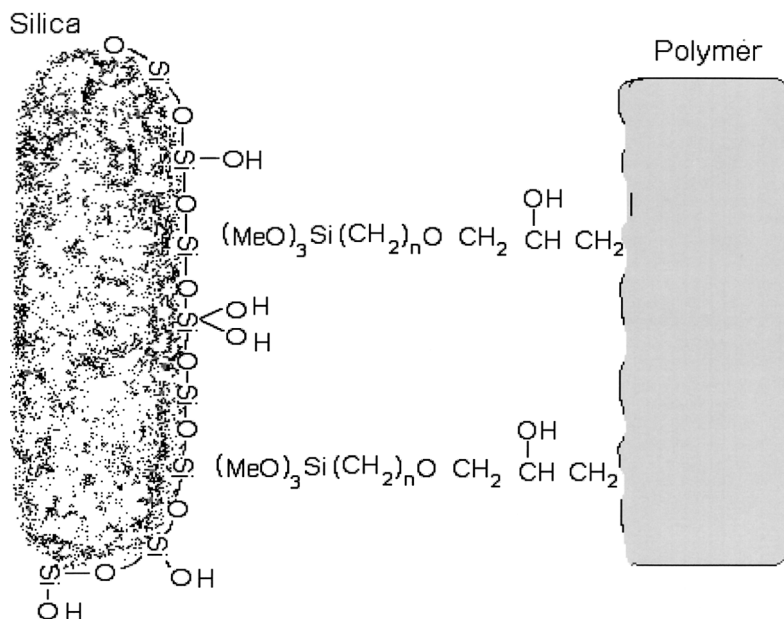


FIGURE 7 Silica-functionalized polymer interaction. A = SBR non-functionalized, B = SBR with R_3SnCl , C = SBR with $\text{RSi}(\text{OR}')_3$.

CONCLUSIONS

The effect of functionalization of anionically synthesized SBR's on global performance of a typical tread specimen using these polymers and fillers like carbon black or silica has been investigated in this paper. The concluding remarks follow:

The use of silica without silane coupling agent produces a higher energetic demand during the mixing procedure, which is a consequence of a strong filler-filler interaction, in contrast with the relative low energetic requirements when carbon black is used.

The stress-strain properties of the formulations using silica were poorer than those obtained with carbon black due to the tendency of silica to form aggregates with itself. However, the presence of functional groups, as those utilized in this study, improves the interaction of polymer-filler and consequently the reinforcing index.

The functional groups used in this study, especially the silane compounds with methoxy groups, promote the interaction with the functional groups of silica giving an important reduction of the $\tan \delta$ value at the 50–70°C range and, consequently, an excellent improvement of rolling resistance with no use of silane coupling agent.

Therefore, it is possible to improve one of the most desirable properties in today's tire, the rolling resistance, by chemical functionalization of the active ends with an appropriate reagent.

REFERENCES

- [1] Fontanille, M. *Comprehensive Polymer Science* (Pergamon, Great Britain, 1989), 1st ed., Chapt. 25.
- [2] Quirk, R. P., Kinning, D. J. and Fetters, L. J., *Comprehensive Polymer Science* (Pergamon, Great Britain, 1989), 1st ed., Chapt. 1.
- [3] Hsieh, H. L. and Quirk, R. P., *Anionic Polymerization: Principles and Practical Applications* (Marcel Dekker, Inc., New York, 1996).
- [4] Cernohous, J. J., Macosko, C. W. and Hoye, T. R. (1997). *International Symposium on Ionic Polymerisation*, Paris, 7–11/July.
- [5] Salinas, M., Manero, O., Alcántara, R. and Herrera, R. (1995). *J. App. Polym. Sci.* **57**, 1173.
- [6] Antkowiak, T. A., Obserster, A. E., Halasa, A. F. and Tate, D. P. (1972). *J. Polym. Sci., Part A-1*, **10**, 1319.
- [7] Bywater, S., Mackerron, D. H. and Worsfold, D. J. (1985). *J. Polym. Sci. Polym. Chem. Ed.*, **23**, 1997.
- [8] Hsieh, H. L. and Wofford, C. F. (1969). *J. Polym. Sci., Part A-1*, **7**, 461.
- [9] Kuntz, I. (1961). *J. Polym. Sci.*, **54**, 569.
- [10] Ogawa, M. and Ikegami, M. (1983). US Patent 4 387 756 assigned to Bridgestone Tire Co.
- [11] Nordsiek, K. H. (1985). *Kautsch. Gummi Kunst.*, **38**, 178.
- [12] Takao, H. and Imai, A. (1985). *International Rubber Conference (IRC)*, Kyoto.
- [13] Agostini, G., Bergh, J. and Materne, Th. (1994). Akron Rubber Group Meeting, October 27.
- [14] Cochet, Ph., Barriquand, L., Dejean, B. and Bomal, Y. (1996). Tyretech '96, China, October.
- [15] Ruiz-Santa Quiteria, V. et al. (1997). *Die Angew. Makromol. Chem.*, **246**, 85.
- [16] Medalia, A. I. (1978). *Rubber Chem. Technol.*, **51**, 437.
- [17] Wolf, S. and Wang, M. J. *Carbon Black: Science and Technology* (Marcel Decker, Inc. 1993) 2nd ed., Chapter 9.
- [18] Kraus, G. (1984). *J. Appl. Polym. Sci., Appl. Polym. Symp.*, **39**, 75.
- [19] Payne, A. R. (1966). *Rubber Chem. Technol.*, **39**, 365.
- [20] Ulmer, J. D., Chirico, V. E. and Scott, C. E. (1973). *Rubber Chem. Technol.*, **46**, 897.
- [21] Ayala, J. A., Hess, W. M., Dotoson, A. O. and Joyce, G. A. (1990). *Rubber Chem. Technol.*, **63**, 747.
- [22] Wang, M. J. (1998). *Rubber Chem. Technol.*, **71**, 520.
- [23] Edwards, D. C. and Sato, K. *Rubber Chem. Technol.*, **53**, 66.
- [24] Gorce, J. N. and Labauze, G. (1997). US Patent 5 665 812 assigned to Compagnie Generale des Etablissements Michelin-Michelin & Cie.
- [25] Moneypenny, H. G., Harris, J. and Laube, S. (1995). *Meeting of Rubber Division, ACS*, Cleveland, Ohio, USA, October.
- [26] Nakamura, M. and Takagishi, Y. (2000). *Meeting of Rubber Division, ACS*, Dallas, Texas, USA, April.
- [27] Guevara, G., Monroy, V. Correa, A. and Herrera, R. (1993). *Rubber Chem. Technol.*, **66**, 588.
- [28] Quirk, R. P. (2000). personal communication, November.