Influence of the Silane Modifiers on the Surface Thermodynamic Characteristics and Dispersion of the Silica into Elastomer Compounds

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A good dispersion of silica into elastomers, typically used in tire tread production, is obtained by grafting of the silica with multifunctional organosilanes. In this study, the influence of the chemical structure of a triethoxysilane (TES), octadecyltriethoxysilane (ODTES), and ODTES/bistriethoxysilylpropyltetrasulfane (TESPT) mixture was investigated by inverse gas chromatography (IGC) at infinite dilution. Thermodynamic results indicate a higher polarity of the silica surface modified with TES as compared to that of the unmodified silica due to new OH groups deriving from the hydrolysis of ethoxy groups of the silane; the long hydrocarbon substituent of the ODTES lies on the surface of silica and reduces the dispersive component of the silica surface tension. A comparison with silica modified with TESPT is discussed. An accurate morphological investigation by transmission electron microscopy (TEM) and automated image analysis (AIA) was carried out on aggregates of silica dispersed into a SBR compound loaded with 35 phr (per hundred rubber) of untreated and TESPT-treated silica. Morphological descriptors such as the projected area/perimeter ratio (A/P) and roundness ($P^2/4\pi A$) provided direct and quantitative indications about the distribution of the filler into the rubber matrix.

Introduction

Among the active fillers used in the passenger tire industry, precipitated silicas have been found to improve performances of the tread; the wet grip is increased and the rolling resistance is reduced, thus lowering the fuel consumption.[1−4] However, the tread wear is critical; in fact, due to the high surface energy, strong interactions take place between silica particles, leading to a very poor dispersion of the filler in the conventional nonpolar tire elastomers.

In order to enhance the dispersion of the filler in the elastomer matrix, the grafting of the silica surface has been suggested.[5−17] For this purpose, multifunctional organosilanes are generally used as coupling agents which can react with both filler and polymer.

Bistriethoxysilylpropyltetrasulfane (TESPT) is, at the moment, the coupling agent typically used in the tire industry. Because of its multifunctionality, it reacts both with the silanol groups present on the silica surface and, in combination with an accelerator and sulfur, with the polymer during the vulcanization. However, due to its high price, a great deal of interest is devoted to replace it partially or totally with other organosilanes that are equally effective but less expensive.

For several years, our research has been aimed to investigate the influence of the silica surface modification on the rubber reinforcement.[18−21] Recently, the characterization by inverse gas chromatography (IGC) at infinite dilution of silicas modified with different amounts of TESPT allowed us to indicate that 6−8 wt % of grafted TESPT prevents particle fillers from interacting with each others since it considerably reduces the surface polarity of SiO_2.[21] The improved tensile mechanical properties of vulcanized compounds filled with TESPT-modified silica confirmed our thermodynamic predictions and supported that TESPT promotes filler−elastomer interactions.[21]

In this work, we present the results of a thermodynamic study aimed to investigate the influence of chemical structure of some silanes on the surface characteristics of silica and then on the interactions between silica and elastomers; moreover, to deepen the knowledge and to attain a quantitative evaluation of the effect of TESPT on silica dispersion, in the present contribution, we report morphological results obtained by TEM−AIA from technical compounds based on a SBR matrix loaded with different amounts of silica either untreated and treated with TESPT.

Experimental Methods

1. Materials. Amorphous precipitated silica (Zeosil 1165 MP, Rhône Poulenc), as received and modified with triethoxysilane (TES), bistriethoxysilylpropyltetrasulfane (TESPT), and different amounts of a octadecyltriethoxysilane (ODTES) and TESPT/ODTES mixture was investigated by IGC as the stationary phase. Surface modification of silica was performed by a method previously described.[19] TES was purchased from Aldrich and TESPT and ODTES were kindly provided by Pirelli Tyre S.p.A. (Italy). The degree of modification was determined combining S, C, and H percentages obtained by elemental analysis; the grafting degrees of the silanes onto silica particles are shown in Table 1.

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TABLE 1: Modifiers and Grafting Degree of the Silica

silicas	TES wt %	TESPT wt %	ODTES wt%
SiO$_2$	—	—	—
SiO$_2$ + 6.4 TES	6.4	—	—
SiO$_2$ + 7.8 TESPT	—	7.8	—
SiO$_2$ + 4.6 ODTES	—	—	4.6
SiO$_2$ + 9.6 ODTES	—	—	9.6
SiO$_2$ + 4.6 TESPT + 4.2 ODTES	—	4.6	4.2

TABLE 2: SBR Compound Formulation (phr)[a]; Unmodified and TESPT-Modified Silica in A35VSL and in R8-35VSL Compounds, Respectively

	A35VSL	R8-35VSL
s-SBR[b]	126	126
SiO$_2$ 1165MP	35	35
X50S[c]		5.6
CB N330[d]	5	2.2
sulfur	2	1.37

[a] phr = per hundred rubber. Conditions: 10 phr of aromatic oil, 2 phr of stearic acid, 3 phr of ZnO, 1.5 phr of *N*-cyclohexylbenzothiazolsulfenamide (CBS), 2 phr of diphenylguanidine (DPG 80), 1.5 phr of *N*-1,3-dimethylbutyl-*N'*-phenyl-*p*-phenylendiamine (6PPD), and 1 phr of wax. [b] Copolymer styrene−butadiene with 25 wt % of styrene, 75 wt % of butadiene (vinyl content, 50 wt %), and 37.5 phr of oil; [126 − (37.5 × 100)/(100+37.5)] ≈ 100 phr of dry copolymer. [c] Mechanical mixture of TESPT and carbon black, N330, 50/50 w/w. [d] Carbon black, N330 grade.

The probes used to characterize the silica surface were *n*-alkanes, isoalkanes, 1- and 3-alkenes, dienes and alkylbenzenes, which are analogues of the repeating unit of saturated (ethylene−propylene, EPR, and butyl rubbers) and unsaturated rubbers (natural rubber, NR, butadiene rubber, BR, and styrene−butadiene copolymer, SBR). All chemicals were chromatographic-grade products (Fluka and Sigma−Aldrich) and were used as received without further purifications.

The rubber compounds, used to perform the morphological investigation, were prepared by Pirelli Tyre S.p.A. (Italy) following the two-stage mixing method described elsewhere.[12] SBR compounds contain a small amount of carbon black (5 wt %), used to facilitate the addition of TESPT, and were filled with 35 phr of silica Zeosil 1165MP. The SBR is the copolymer styrene−butadiene with 25 wt % of styrene, 75 wt % of butadiene (vinyl content, 50 wt %), and 37.5 phr of oil. Two samples were prepared; in the first one, silica is unmodified, A35VSL, and in the second one, it is modified with 8 wt % of TESPT, R8-35VSL, as reported in Table 2.

It is worth noting that the amount of sulfur was kept constant (2 phr) by reducing the addition of free sulfur upon increasing the amount of TESPT.

2. Inverse Gas Chromatography. Measurements of the retention times were carried out using a Varian 3700 gas chromatograph equipped with a flame ionization detector (FID) and operating under isothermal conditions. The peaks were recorded using a computer interfaced to the gas chromatograph. Helium was used as the carrier gas with a flow rate of 30 cm^3·min^{-1}; the column inlet and outlet pressure was measured using standard pressure gauges. A stainless steel column with a length of 40 cm and an internal diameter of 2.5 mm was filled with about 0.5 g of silica. Before the measurements, the column was conditioned with a carrier gas flow rate of 7 cm^3·min^{-1} for 48 h at 250 °C for silica as received, at 210 °C for silicas modified with TES or ODTES, and at 147 °C when TESPT was the modifier.

The probes were introduced into the column using a 1 μL syringe and injection vapor volumes lower than 0.1 μL in order
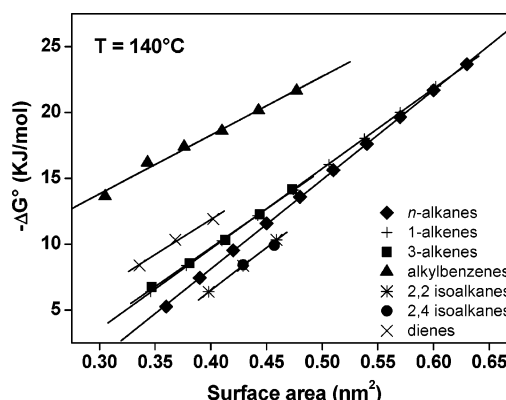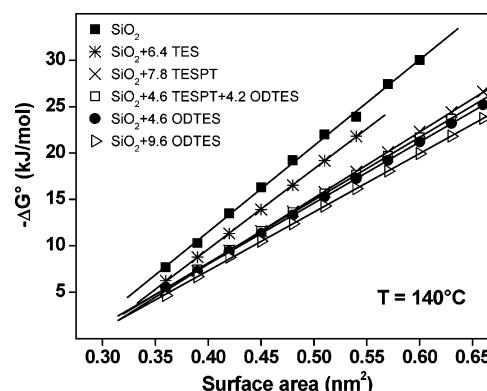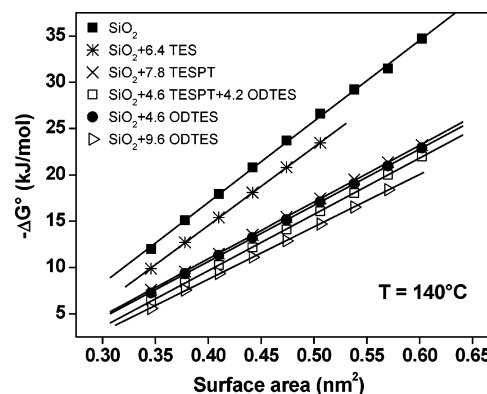

Figure 1. Adsorption free energy as a function of surface area of hydrocarbon probes; stationary phase SiO$_2$+ 4.6 TESPT + 4.2 ODTES.

Figure 2. Adsorption free energy versus surface area of *n*-alkanes for differently modified silicas.

Figure 3. Adsorption free energy versus surface area of 1-alkenes for differently modified silicas.

to satisfy the conditions of adsorption at infinite dilution and of the gas chromatography linearity. Error analysis of measured retention times was about 1%.

Silicas modified with TES or ODTES were analyzed between 120 and 210 °C; when TESPT was grafted, the measurements were carried out between 80 and 145 °C in order to avoid the breaking of the −S−S−S−S− bridge present in the molecule (*T* = 150 °C is the equilibrium temperature of S−S bond breaking).

3. Transmission Electron Microscopy. Morphological investigation on the compounds was carried out using a transmission electron microscope ZEISS EM 900, applying an accelerating voltage of 80 KeV. Ultrathin sections of about 50 nm thickness were prepared with a Leica EM FCS ultracryomicrotome equipped with a diamond knife cooled at −60 °C, keeping the sample cooled at −130 °C.
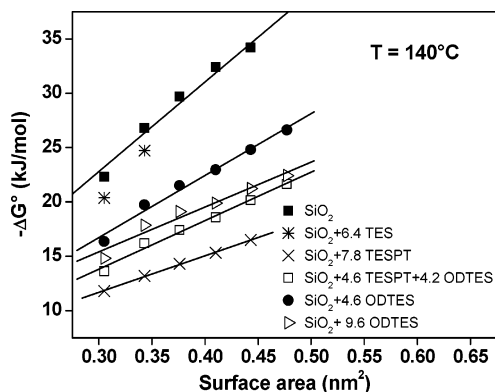
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Figure 4. Adsorption free energy versus surface area of alkylbenzenes for differently modified silicas.

4. Automated Image Analysis. For each compound, 10 representative micrographs (20000x) were selected on which AIA was carried out by Image Pro Plus software according to the procedure reported in a previous paper.[20] After the fundamental filtering procedure of the micrograph, it was possible to select the gray tone of the single particle of filler (the tone next to that was attributed to the polymer matrix) and to count and to measure all of the aggregates by application of different morphometric descriptors.[20] Among these, projected area (A), perimeter (P), the area−perimeter ratio (A/P), and the roundness ($P^2/4\pi A$) were chosen to attain a quantitative morphological characterization of the filler dispersion as a function of the surface modification of silica.

Results and Discussion

1. Adsorption Thermodynamics. As widely described in previous papers,[10,11,18,19,21,22] the thermodynamic quantities of probe adsorption, free energy ($\Delta G°$), enthalpy ($\Delta H°$), and entropy ($\Delta S°$) can be calculated, knowing the neat retention volume, V_n, from the eq 1

$$V_n = D \cdot j \cdot (t_r - t_d)\left(1 - \frac{P_w}{P_a}\right)\frac{T}{T_f} \qquad (1)$$

where D is the flow rate, j is the James−Martin factor for the correction of gas compressibility,[23] t_r and t_d are the retention and dead times measured with a specific probe and a non-adsorbing probe (such as methane), respectively, P_w is the vapor pressure of pure water at the flow meter temperature (T_f),

Figure 6. Adsorption enthalpy versus surface area of *n*-alkanes for differently modified silicas.
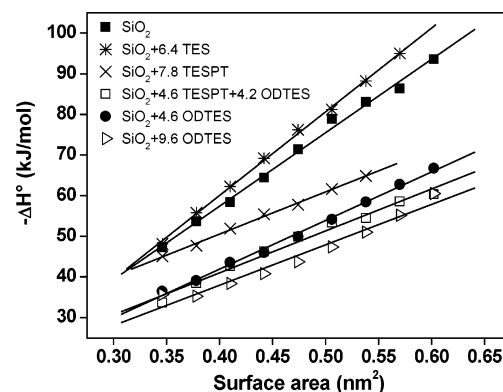
Figure 7. Adsorption enthalpy versus surface area of 1-alkenes for differently modified silicas.

P_a is the pressure at the flow meter, and T is the column temperature.

The gas chromatographic experiments are performed at infinite dilution, thus adsorbate−adsorbate interactions are considered absent, while the interactions of the adsorbed molecules with the surface are, of course, present. Then, instead of 1 atm pressure, it must be recognized that the surface state is essentially two dimensional, and a given "surface pressure", π_o, must substitute the usual gaseous pressure, as discussed in detail by N.K. Adam.[24]

In other words, the adsorption free energy for 1 mol of solute vapor from a reference gaseous state (considered as an ideal gas), defined by the partial pressure p_o (1.013×10^6 dynes/
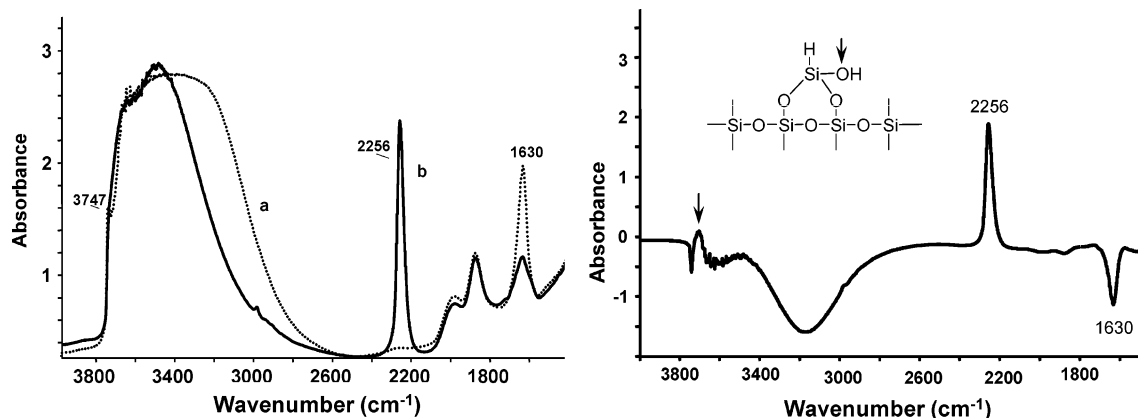

Figure 5. Left: room-temperature FT−IR spectra of silica unmodified (spectrum a) and modified with 6.4 wt % of TES (spectrum b). Right: subtraction spectrum defined as spectrum b − spectrum a.
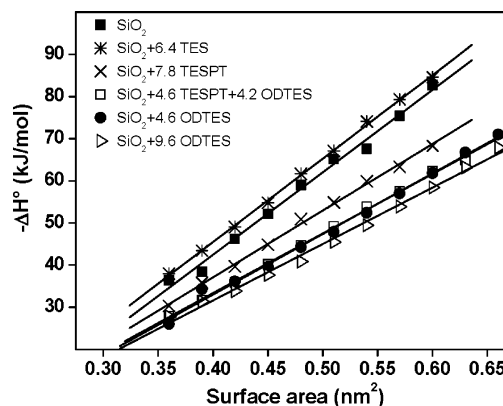
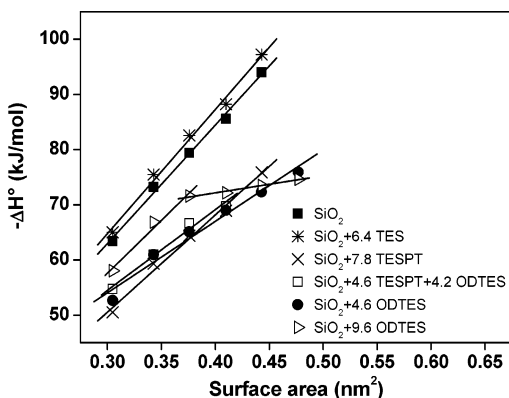**4498** *J. Phys. Chem. B, Vol. 111, No. 17, 2007*

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Figure 8. Adsorption enthalpy versus surface area of alkylbenzenes for differently modified silicas.

cm^2), to a reference adsorbed state, defined by the spreading pressure π_o, is given by

$$\Delta G° = -RT \ln\left(\frac{p_o \cdot V_n}{\pi_0 \cdot s \cdot g}\right) \quad (2)$$

where s is the specific surface area of silica, g is the mass of the filler in the column, T is the column temperature in K, and R is the gas constant.

The value of π_o depends on the chosen reference state. There are two frequently used states, which serve to illustrate the arbitrariness of choice.[25,26] According to the De Boer standard surface state, it is assumed that the adsorbed molecules are at the same distance apart as they are in the 1 atm gas state at 0 °C. In this state, $\pi_o = 0.338$ dyn/cm, and the ratio $p_o/\pi_o = 2.99 \times 10^8$ m^{-1} is the well-known De Boer constant C.[26] Therefore, we can write the equation

$$\Delta G° = -RT \ln\left(\frac{2.99 \times 10^8 \cdot V_n}{s \cdot g}\right) \quad (3)$$

For the same standard process to which $\Delta G°$ refers, the adsorption enthalpy can be calculated from the Gibbs–Helmholtz equation, given the temperature dependence of V_n

$$-\left(\frac{\delta\Delta G°/T}{\delta T}\right)_P = \frac{\Delta H°}{T^2} = R\frac{d\ln V_n}{dT} \quad (4)$$

$\Delta H°$ is usually assumed to be independent of the temperature; a plot of $\ln V_n$ versus $1/T$ yields a line whose slope is $-\Delta H°/R$.

Therefore, the adsorption entropy is given by

$$\Delta S° = \frac{\Delta H° - \Delta G°}{T} \quad (5)$$

Equation 4 indicates that $\Delta H°$ does not depends on the choice of the surface standard state, whereas eq 5 shows that $\Delta S°$ is effected by such a choice.

According to the eqs 3, 4, and 5, by injecting several families of probes, the adsorption free energies, enthalpies, and entropies were calculated at different temperatures for each kind of silica. As an example, the behaviors of $-\Delta G°$ of different hydrocarbons obtained at 140 °C for the stationary phase SiO_2 + 4.6 TESPT + 4.2 ODTES, as a function of the surface areas of the probes, are given in Figure 1.

As previously observed,[18,19,21] all of the adsorption parameters increase from alkanes to alkylbenzenes. This leads to the deduction that the filler–elastomer interactions increase according to the following scale: alkanes < alkenes < dienes <

alkylbenzenes. As a consequence, the interactions between elastomeric matrices and silica, both unmodified and modified, would be preferred with SBR rubber as compared to BR and NR.

Following the FT–IR results, widely discussed in a previous work,[27] the conclusion was drawn that two or four ethoxy groups are involved in the reaction with silanol groups for each molecule of TES or TESPT, respectively. Consequently, we can suppose that, also in the case of ODTES, each molecule reacts with two ethoxy groups.

The maximum amounts of chemically bound silanes are 6.4% for TES, 7.8% for TESPT, and 9.6% for ODTES by weight; they correspond to 12×10^{-2}, 8.4×10^{-2}, and 6.9×10^{-2} moles of ethoxy groups, respectively. Considering that only two-thirds of these groups are, on average, involved in the reaction with the hydroxyl groups at the surface of silica, one can infer that the number of silanols neutralized decreases in going from TES to TESPT to ODTES. As a consequence, the surface polarity of the filler should be the highest for ODTES and the lowest for TES. The experimental data of $-\Delta G°$ obtained with silicas modified by the three silanes are shown in Figures 2–4 for the three main families of probes.

As a general comment, we can say that the adsorption free energy for silicas variously modified, as detailed in Table 1, decreases considerably upon grafting; this effect is highly dependent on the probe, on the chemical structure of the modifier, and on the grafting degree (Figures 2–4). As expected, $-\Delta G°$ decreases upon increasing the grafting degree onto the silica surface, independent of the silane used. Furthermore, the values of $-\Delta G°$ for silicas modified with the highest amount of the silane show the following trends: *n*-alkanes and 1-alkenes: $SiO_2 > SiO_2 + 6.4$ TES $> SiO_2 + 7.8$ TESPT $> SiO_2 + 9.6$ ODTES; alkylbenzenes: $SiO_2 > SiO_2 + 6.4$ TES $> SiO_2 + 9.6$ ODTES $> SiO_2 + 7.8$ TESPT.

Contrary to what is expected on the basis of the neutralized silanols, the grafting with TES leads to the lowest effect on the adsorption free energy as compared to unmodified silica, independent of the probe. To explain this result, two main phenomena can be invoked, (i) with TES, a small group inserts onto the silica surface, thus leaving the remaining free silanols easily accessible and (ii) the unreacted ethoxy groups of the adsorbed TES can undergo a hydrolysis reaction which produces new silanol groups, as supported by our previous FT–IR spectroscopic investigation[28] and shown in Figure 5, where spectra of pure silica and silica modified with TES, both outgassed at room temperature, are compared. The sample with TES shows a much-less-intense absorption in the 3200–2600 cm^{-1} region and near 1630 cm^{-1} (stretching and scissoring modes of hydrogen-bonded water, evident also as negative bands in the subtraction spectrum; see Figure 5 right), indicating that the TES-modified sample contains much less water. The TES-free sample shows the sharp peak at 3747 cm^{-1} due to free silanols, even if not very evident, whereas the same peak is definitely not present in the spectrum of TES-containing silica. However, TES-containing silica absorbs more than pure silica in the 3730–3650 cm^{-1} region and shows a strong Si–H stretching at 2256 cm^{-1}, as is evident in the subtraction spectrum. According to our previous work,[28] the Si–H stretching at this position is indicative of the formation of adsorbed species where the Si–H group binds through two Si–O–Si bridges to the silica surface. The absorption in the 3730–3650 cm^{-1} range is due to new OH groups likely formed by hydrolysis of the residual ethoxy group of the TES molecules, as sketched in

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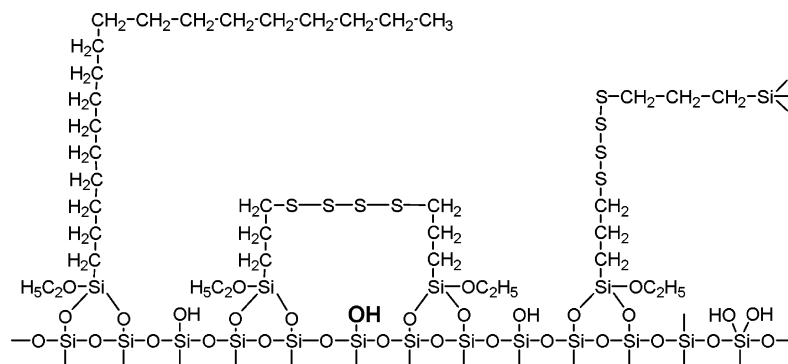*J. Phys. Chem. B, Vol. 111, No. 17, 2007* **4499**

Figure 9. Silica surface partially modified with TESPT and ODTES.

Figure 5 right. Thus, the adsorption of TES in these conditions would not substantially affect the hydrophilic character of silica surface.

In the case of ODTES, the presence of the long octadecyl chain onto the silica surface results in the greatest reduction of the free energy of adsorption for *n*-alkanes and 1-alkenes (Figures 2 and 3), in agreement with the results by Wang et al.[28] For a detailed interpretation of these results, the enthalpy and entropy data for all of the probes have been also calculated.

Trends of $-\Delta H°$ as a function of surface area of the three different families of probes (Figures 6−8) indicate that the dependence of $-\Delta H°$ on chemical nature and amount of modifier is practically the same as that of $-\Delta G°$; we only observe that the adsorption onto TES-modified silica is little more exothermic than that onto unmodified silica.

The enthalpy data related to saturated and unsaturated hydrocarbons might be explained by considering that interactions between silanol groups and hydrocarbon chains of the probes are substituted by weaker interactions between probes and the hydrocarbon tail of the modifier. In fact, it is well-known that hydrogen bondings, weaker than those with polar molecules, also occur between the silica silanol groups and nonpolar molecules such as hydrocarbons.[29,30] Furthermore, the long flexible chain of the modifier can shield the free silanol groups still present on the silica surface; therefore, the highest values of enthalpy obtained for TES-modified silica can be justified by considering the absence of the shield effect and a higher number of silanol groups able to interact with the probe.

For alkylbenzenes, the influence of ODTES is less pronounced than that of TESPT, probably due to the fact that TESPT, a multifunctional and symmetrical molecule, tends to form rigid bridges onto silica surface,[27] thus screening some silanol groups, as shown in Figure 9.

As a consequence, the interactions between the aromatic probes and some silanols are hindered and substituted by weaker interactions of the alkylbenzene with the TESPT molecule. In the case of *n*-alkanes and 1-alkenes, this screening effect seems to be less important, probably because their higher flexibility would facilitate them to find interaction sites on the silica surface and to establish more stable interactions with TESPT than with ODTES.

This explanation can also account for the results obtained for silicas modified with TESPT/ODTES mixtures, even if, in this case, the interaction mechanism seems to be more complex.

The unexpected behavior of ODTES, which linearly increases up to ethylbenzene and than tends to reach a constant value (Figure 8), can be ascribed to the increasing influence of the aliphatic tail of the probe. In other words, up to ethylbenzene,
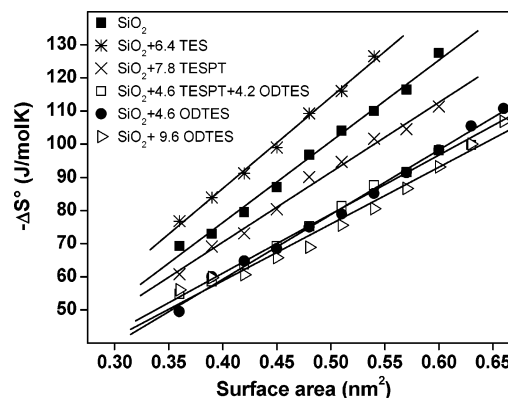

Figure 10. Adsorption entropy versus surface area of *n*-alkanes for differently modified silicas.
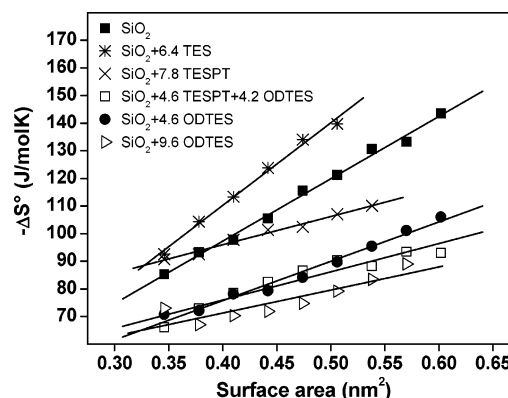

Figure 11. Adsorption entropy versus surface area of 1-alkenes for differently modified silicas.

the interactions of the aromatic ring of the probe and the polar groups at the silica surface (specific interactions) are favored and predominant; upon increasing the length of the aliphatic tail of the probe, the dispersive interactions with the long hydrocarbon chain of the modifier become more relevant.

The dependence of adsorption entropy, $-\Delta S°$, on surface area of the probe is shown in Figures 10−12. Independent of the modifier, $-\Delta S°$ monotonically raises, which is indicative of an increasing loss of molecular mobility upon increasing the surface area of the probe. As previously suggested, this can be attributed to a hindered rotational isomerism.[18,21] By changing the modifier, the trend of $-\Delta S°$ is in agreement with the enthalpic results; the probe mobility on TES−silica is lower than that on ODTES−silica, with an intermediate behavior for TESPT. In other words, the loss of freedom of the adsorbate increases upon increasing the interaction enthalpy.
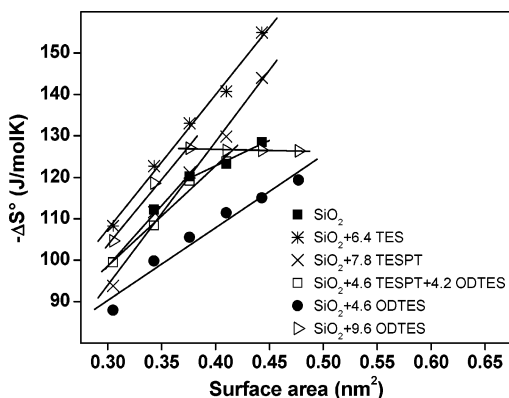
Figure 12. Adsorption entropy versus surface area of alkylbenzenes for differently modified silicas.

2. Surface Energy of Silica. Generally, the surface energy, γ_s, is assumed to be given by two contributions, the dispersive component, γ_s^d, and the specific one, γ_s^{sp}[31]

$$\gamma_s = \gamma_s^d + \gamma_s^{sp} \qquad (6)$$

Following Dorris and Gray,[32] γ_s^d can be calculated from the free energy of adsorption of a CH_2 group, $\Delta G^{\circ}_{CH_2}$, using the following equation

$$\gamma_s^d = \frac{1}{4\gamma_{CH_2}} \cdot \left(\frac{\Delta G^{\circ}_{CH_2}}{a \cdot N}\right)^2 \qquad (7)$$

where a is the area covered by a CH_2 group,[10] γ_{CH_2} is the surface tension of a surface constituted only of tightly packed methylene groups,[33,34] and N is Avogadro's number.

No easy direct way exists to measure the specific component of the surface energy. Therefore, by considering the specific interactions that can establish between the filler and a polar probe, an evaluation of the γ_s^{sp} contribution can be achieved from the specific interaction parameter, I^{sp}, as suggested by Wang et al.[10−12, 22] The I^{sp} is given by the difference in adsorption energy, $-\Delta\Delta G^{\circ}$, between a polar probe and a hypothetical or real saturated hydrocarbon with the same surface

$$I^{sp} = -\frac{\Delta\Delta G^{\circ}}{\sigma \cdot N} \qquad (8)$$

where σ is the surface area occupied by the polar probe.

In this work, as suggested by Donnet et al.,[22,35] we used benzene as the probe able to realize an electron donor−acceptor complex with the OH groups present on the silica surface. Benzene, in other words, is capable of specific interactions with the silica surface via the electronic localization of the π-bond system.

Through eqs 7 and 8, the values of γ_s^d and I^{sp} as a function of the temperature were calculated for all of the silicas. The results are reported in Figures 13 and 14, respectively.

Both γ_s^d and I^{sp} are drastically reduced by the surface modification, other than for TES, as already observed for the adsorption free energy.

The higher hydrophobicity of the modified silicas can account for the lower influence of the temperature on their surface tension with respect to unmodified silica.

Moreover, as observed for the thermodynamic parameters of adsorption, the surface activity decreases upon increasing the grafting degree of the silica surface. The reduction of the
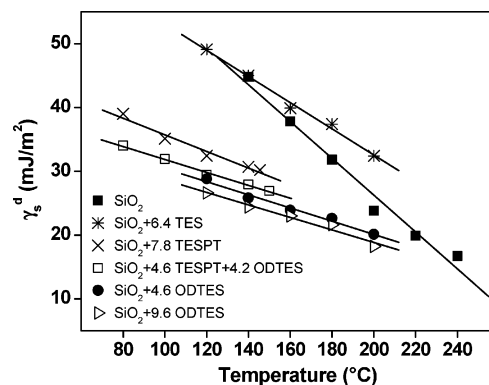

Figure 13. Dispersive component of the surface tension of silica as a function of temperature for different degrees and types of modifications.
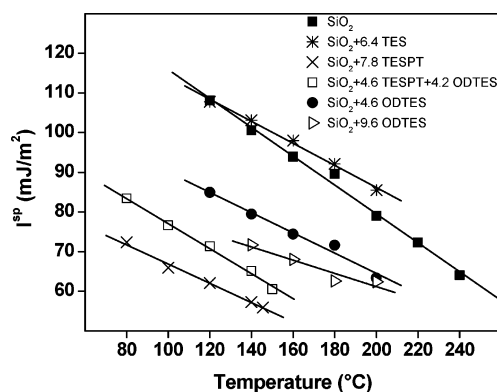

Figure 14. Specific interaction parameter of the surface tension of silica as a function of temperature for different degrees and types of modifications.
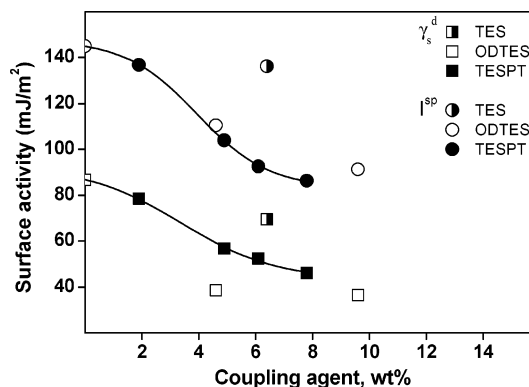

Figure 15. Surface activity components at 20 °C of silica modified with TESPT and ODTES as a function of the grafting degree. Bold points are from ref 21.

dispersive component is more pronounced with ODTES than with TESPT, as shown in Figure 15.

In fact, a grafting degree with 4.6 wt % of ODTES is enough to obtain a constant γ_s^d value at 20 °C (38.6 mJ/m²), similar to those of hexadecanol-modified silicas (34 mJ/m²)[36] and of polyethylene (24 ÷ 42 mJ/m²),[37,38] being the last considered a typical low-energy surface. The corresponding value for TESPT-modified silica is 58 mJ/m²; this suggests that the long alkyl chains of ODTES may form a layer, leading to a low-polarity surface.

On the other hand, Figure 15 indicates that, if the amount of modifier onto the silica surface is higher than 4 wt %, the grafting with TESPT leads to silicas with always lower values of the specific interaction parameter. In fact, as previously
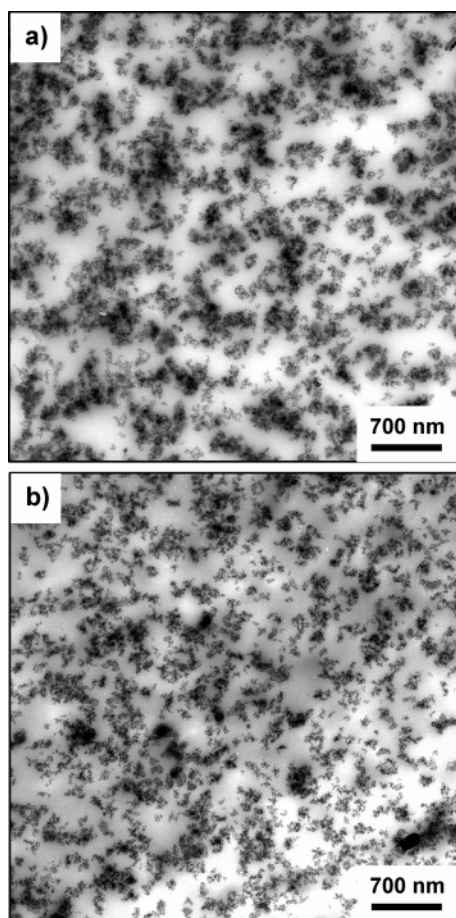
Influence of the Silane Modifiers

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Figure 16. TEM micrographs of ultrathin sections of SBR compounds loaded with 35 phr of silica (a) unmodified and (b) modified with TESPT.
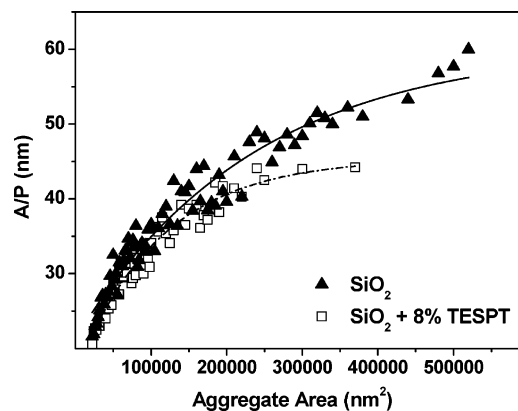

Figure 17. *A/P* ratio of aggregates in SBR compounds loaded with 35 phr of filler as a function of their area.

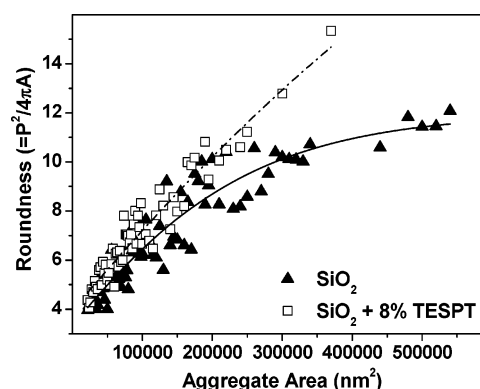**Figure 18.** Roundness of aggregates in SBR compounds loaded with 35 phr of filler as a function of their area.

emphasized, the same amount, by weight, of the modifier leaves a higher number of free silanol groups on the silica surface when ODTES is used.

When mixtures of two silanes are used, the thermodynamic characteristics of the silica surface exhibit intermediate values depending on the composition; SiO_2 + 4.6 TESPT + 4.2 ODTES shows γ_s^d = 40 mJ/m^2 and I^{sp} = 102.4 mJ/m^2, at 20 °C.

3. Dispersion of Silica into SBR Compounds. The influence of the surface characteristics of the filler on its interactions with a polymer matrix has been also investigated through a morphological study; in particular, the effect of TESPT on silica dispersion is analyzed here.

The combination of TEM and AIA makes it possible to obtain quantitative and representative information on the filler distribution into the elastomer matrix (homogeneity of the dispersion and size and shape distribution of the aggregates) and, consequently, on the filler—elastomer interactions. The simple morphological analysis, carried out on samples filled with the same amount of untreated or surface-modified silica, indicates only a qualitative difference in the distribution of the filler and between the structures of treated or untreated silica aggregates dispersed into the polymer matrix (Figure 16). Thus, image analysis on digitalized TEM micrographs was performed to attain quantitative results.

By considering the same surface area (203.3 μm^2, corresponding to 10 micrographs), the average density of particles is much higher when silica is modified, 35 particles/μm^2, than that found for untreated silica, 25 particles/μm^2. In both cases,

the aggregates with a surface area lower than 20×10^3 nm^2 are predominant and correspond to 88 and 85% for treated and untreated silica, respectively. In a first instance, these results are indicative of a better dispersion of the filler when its surface polarity is reduced. The beneficial effect of TESPT is even more clearly evidenced if bigger aggregates are considered; indeed, the maximum area measured for TESPT-modified silica aggregates, 370×10^3 nm^2, is much lower than that found in the case of unmodified SiO_2, 580×10^3 nm^2 (Figure 17).

Since aggregates with similar surface area can have completely different shapes and, consequently, very different perimeters, more accurate indications about the filler—elastomer interaction surface can be obtained by using different morphometric descriptors, such as the area-to-perimeter ratio, *A/P*, and the roundness, $P^2/4\pi A$, which is indicative of a more or less elongated shape. All of the silica particles were selected on the basis of proper ranges of area, that is, only objects with very similar surfaces (differences <10%) are included in the same group. For each range of area, the mean perimeter and, consequently, *A/P* and roundness were evaluated.

The behavior of *A/P* as a function of consecutive ranges of area is reported in Figure 17. The *A/P* ratio values of a SBR compound loaded with modified silica are generally lower than those obtained for samples filled with the same amount of unmodified silica. This indicates that, despite the similar area, aggregates of modified silica are characterized by higher perimeters, which means a higher contact surface between filler and elastomer.

Similar indications are obtained from the behavior of the roundness as a function of the aggregates area (Figure 18). This morphometric descriptor, indicative of a more or less elongated shape, is more sensitive than the *A/P* ratio and highlights the

differences between the aggregate morphology observed in the two systems.

These findings are in good agreement with the predictions obtained by the thermodynamic studies carried out by IGC at infinite dilution reported here and in previous papers.[18−20] They have to be ascribed to the reduced polarity of the silica surface and, consequently, to the reduced tendency of silica particles to form agglomerates.

Conclusions

The influence of chemical structure and the amount of different surface modifiers of silica on the interactions with hydrocarbons, model compounds of the repeating unit of SBR and BR elastomers, has been investigated by IGC.

The hydrocarbon substituent of the silane modifier plays an important role in determining the $\Delta G°$, $\Delta H°$, and $\Delta S°$ of adsorption of the hydrocarbon probes on the silica surface.

Thermodynamic results for TES indicate a higher polarity of TES−silica as compared to the unmodified silica, supporting the evidence from our previous FT−IR study on the formation of −OH groups due to the hydrolysis of the ethoxy groups of the silane.

The long hydrocarbon substituents on the silane molecule tend to lie on the surface of silica to reduce the dispersive component of the SiO_2 surface tension, γ_s^d, and to weaken the interaction with the probe.

Morphological results, obtained on SBR compounds loaded with 35 phr of modified and unmodified silica, are in good agreement with thermodynamic predictions deduced by IGC at infinite dilution; in fact, they show that the presence of a coupling agent like TESPT gives silica uniformly dispersed into the SBR compounds due to the reduced surface polarity of the silica, thus improving the compatibility between the components.

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