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Surface modification of silica: 1. Thermodynamic aspects and effect on elastomer reinforcement

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Abstract

A thorough investigation of the interactions between silica and elastomers was conducted with the specific aim of understanding how the degree of modification with *bis*-triethoxysilylpropyltetrasulfane (TESPT) influences the surface energy of the filler and the tensile properties of technical compounds. The results of a thermodynamic study carried out by Inverse Gas Chromatography (IGC) at infinite dilution on silica modified with different amounts of TESPT indicate that from 6 to 8 wt% of grafted TESPT the surface activity of silica is considerably reduced and prevents particle fillers from interacting with each others. Tensile measurements at very low and high deformations carried out on vulcanised compounds loaded with silica, either unmodified or modified with different amounts of TESPT, confirm our thermodynamic predictions and further support the role of TESPT in promoting interactions between filler and elastomer, in achieving better dispersions and in improving mechanical properties.

Keywords: Silica modification; Inverse gas chromatography; Elastomer compounds

1. Introduction

A modern passenger car tyre has to fulfil several demands: good dry and wet grip, secure braking, reasonable service life, good treadwear and low rolling resistance. Carbon black has been widely investigated and it has been the most used for many years, as reinforcing agent [1–3]. However, at the beginning of the nineties, by using treads based on SBR-silica filled compounds remarkable improvements in terms of wet grip and rolling resistance were obtained [4–7]. In contrast to carbon black, as a result of the presence of numerous silanol groups the surface of precipitated silica is highly polar and hydrophilic. Thus, because of the strong intermolecular hydrogen bonds between hydroxyl groups, agglomerates of silica appear. Many coupling agents, such as organosilanes, have been investigated to reduce the strong filler–filler interactions and to improve the dispersion of silica in the elastomer matrices [8–12]. They are generally multifunctional molecules, which are able to establish molecular bridges between the polymer matrix and the filler surface. Among these, the *bis*-triethoxysilylpropyltetrasulfane (TESPT) is the more often used in the tyre industry because it reduces the hydrophilic character of silica surface and promotes the adhesion between silica aggregates and elastomers through the formation of sulphur bridges. In particular, by an accurate FT-IR investigation, we showed that about four of the six ethoxy groups of TESPT react with the silanol groups of silica particles [13].

Several techniques can be used to investigate the effect of the surface energy of the filler on its dispersion and then on the rubber reinforcement. Inverse Gas Chromatography (IGC) at infinite dilution is one of the most sensitive,

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reliable and convenient methods to study surface energy and filler–rubber and filler–filler interactions [14–21]. In previous works we showed that the predictions attained from IGC, by using low molecular weight analogues of the most common elastomers used in the tyre industry, are in good agreement with the results of silica dispersion analysis carried out by Transmission Electron Microscopy (TEM) and Automated Image Analysis (AIA) on technical compounds [22–24].

One of the major drawbacks in the use of TESPT, from an industrial point of view, is its high cost; thus, it appears to be a very important goal to verify which is its minimum amount necessary to optimise the silica/elastomer interactions and to guarantee the best performances of the final compounds. To this purpose a systematic investigation has been carried out within our research group to achieve a better knowledge on how the surface energy of silica changes when an increasing number of silanol groups is reacted with TESPT. In the present work the results of a thermodynamic study, carried out by IGC, aimed to correlate filler–elastomer interactions with the surface characteristics of precipitated silica modified with different amounts of TESPT, are given and discussed. The thermodynamic predictions are compared with the results obtained from tensile measurements carried out on vulcanised compounds loaded with silica, both unmodified and modified with different amounts of TESPT.

2. Experimental

2.1. Materials

Amorphous precipitated silica Zeosil 1165 MP (Rhône Poulenc), as received and modified with different amounts of *bis*-triethoxysilylpropyltetrasulfane (TESPT), was investigated by Inverse Gas Chromatography as the stationary phase. Surface modification of silica was performed by dispersing silica in a CH_2Cl_2 solution of TESPT (kindly provided by Pirelli Pneumatici S.p.A.); different amounts of TESPT were used to obtain different degrees of silylation of the silica surface. After complete evaporation of the solvent, the powder was introduced in vials under argon and thermally treated at 120 °C for 2 h. During this treatment, the silylation of silica occurs by condensation reaction between the surface hydroxyl groups and the TESPT molecules. The samples were then extracted with CH_2Cl_2 in a Soxhlet for 10 h and then dried in static vacuum at room temperature. The degree of modification was determined combining S, C and H percentages obtained by elemental analysis. The grafting degrees were 1.9, 4.9, 6.1 and 7.8 wt% of TESPT.

The probes used to characterise the silica surface were *n*-alkanes, *iso*-alkanes, 1- and 3-alkenes, dienes and alkylbenzenes, analogues of saturated (ethylene-propylene, EPR, and butyl rubber) 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 tensile measurements were kindly provided by Pirelli Pneumatici S.p.A. and prepared by the two stages mixing method: in the first step elastomers, fillers, silane supported on carbon black, aromatic oil, stearic acid and wax were mixed in a Banbury at 60 rpm, $T=120$ °C for 6 min. In the second step, to complete the reaction between silica and TESPT the mixture, cooled for 16 h, was further mixed for 6 min under the same experimental conditions previously adopted. Afterwards, sulphur, ZnO and the accelerating system (CBS, *N*-cyclohexyl-benzothiazol-sulfenamide and DPG 80, diphenylguanidine) were added in a two roll-mill at 50 °C to prevent pre-crosslinking and, finally, the compounds were cured at 170 °C for 10 min. Vulcanisates were prepared as press cured flat sheets of 1.5 mm thickness.

The formulation of s-SBR and s-SBR/BR rubber compounds filled with different amounts of silica, either untreated or modified with 8 wt% of TESPT, are reported in Tables 1 and 2, respectively. The VSL compound composition is, for instance, evaluated according to the following relation: $[126-37.5\ 100/(100+37.5)]$. In a such way is evaluated the composition of compounds in Table 2.

Moreover, the same formulation given in Table 2 was used to prepare s-SBR/BR rubber compounds filled with different amounts of silica modified with 6 and 10 wt% of TESPT.

It is important to note that the amount of sulphur was kept constant and equal to 2 phr, (phr = per hundred rubber) by reducing the addition of free sulphur on increasing the amount of TESPT.

2.2. Inverse gas chromatography (IGC)

A Varian 3700 gas chromatograph equipped with a flame ionisation detector (FID) and operating under isothermal conditions was used to measure the retention volumes. 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 $cm^3\ min^{-1}$ and methane to measure dead time. 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 silica and conditioned (carrier gas flow rate: 7 $cm^3\ min^{-1}$) before the measurements for 48 h at 250 °C for unmodified silica and at 147 °C for silicas modified with different amounts of TESPT. The probes were introduced into the column using a 1 μL syringe and injecting vapour volumes lower than 0.1 μL in order to satisfy the condition of adsorption at infinite dilution and of the gas chromatography linearity. Error analysis of measured retention times was about 1%. The measurements were carried out between 80–145 °C in order to avoid the breaking of the –S–S–S–S–

Table 1
SBR-compounds formulation (phr)

	AVSL	A20VSL	A35VSL	A50VSL	R8-20VSL	R8-35VSL	R8-50VSL
s-SBR[a]	126	126	126	126	126	126	126
SiO_2 1165MP	–	20	35	50	20	35	50
X50S[b]	–	–	–	–	3.2	5.6	8
CB N330[c]	–	5	5	5	3.4	2.2	1
Sulphur	2	2	2	2	1.64	1.37	1.10

Phr, per hundred rubber. 10 phr of aromatic oil, 2 phr of stearic acid, 3 phr of ZnO, 1.5 phr of *N*-cyclohexyl-benzothiazol-sulfenamide (CBS), 2 phr of Diphenylguanidine (DPG 80), 1.5 phr of *N*-1,3dimethylbutyl-*N*′-phenyl-*p*-phenylendiamine (6PPD) and 1 phr of wax.

[a] Copolymer styrene-butadiene with 25 wt% of styrene, 75 wt% of butadiene (vinyl content 50 wt%) added with 37.5 phr oil.

[b] Mechanical mixture of TESPT and carbon black N330, 50/50 w/w.

[c] Carbon black N330 grade.

bridge present in the coupling agent ($T=150$ °C is the equilibrium temperature of S–S– bond breaking).

2.3. Tensile properties

Tensile tests were performed by an Instron 5565 machine interfaced to a computer. The specimens, length 80 mm, width 10 mm and thickness 1.5 mm, were prepared from press cured flat sheets by a Tecnofustelle (CEAST), MF/04 type. For each composition 7–10 specimens were tested. The measurements were carried out at room temperature with an elongation rate of 450 mm/min and a distance between the clips of 40 mm. Stresses at 10 and 300% of elongation (σ_{10} and σ_{300}, respectively), strength at break (σ_b) and elongation at break (ε_b) were evaluated.

3. Results and discussion

3.1. Adsorption parameters

As widely described in previous papers [14–22], the thermodynamic parameters of probe adsorption, free energy, enthalpy and entropy (ΔG^o, ΔH^o and ΔS^o, respectively) can be calculated from the net retention volume, V_n, according to the Eqs. (1–4)

$$V_n = Dj(t_r - t_d)\left(1 - \frac{P_w}{P_a}\right)\frac{T_c}{T_f} \qquad (1)$$

where: D is the flow rate, j is the James–Martin factor for the correction of gas compressibility [25], 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 vapour pressure of pure water at the flow meter temperature (T_f), P_a is the pressure at the flow meter and T_c is the column temperature.

The adsorption free energy for one mole of solute vapour from a reference gaseous state (considered as an ideal gas), defined by the partial pressure p_o, to a reference adsorbed state, defined by the spreading pressure π_0, is given by [26]:

$$\Delta G = -RT\ln\left(\frac{p_0 V_n}{\pi_0 s g}\right) \qquad (2)$$

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, R is the gas constant.

The gas chromatographic experiments are performed at infinite dilution and then it is generally assumed that the adsorption occurs from the ideal vapour phase (at $P_o = 1.013\times10^6$ dynes/cm^2 and a given T) to an ideal adsorbed phase (phase in two-dimensions with π_o = surface pressure dyne/cm at a given T) [26]. 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: the

Table 2
SBR/BR-compounds formulation (in phr)

	A	A20	A35	A50	R8-20	R8-35	R8-50
s-SBR[a]	96	96	96	96	96	96	96
BR[b]	30	30	30	30	30	30	30
SiO_2 1165MP	–	20	35	50	20	35	50
X50S[c]	–	–	–	–	3.2	5.6	8
CB N330[d]	–	5	5	5	3.4	2.2	1
Sulphur	2	2	2	2	1.64	1.37	1.10

Phr, per hundred rubber. 10 phr of aromatic oil, 2 phr of stearic acid, 3 phr of ZnO, 1.5 phr of *N*-cyclohexyl-benzothiazol-sulfenamide (CBS), 2 phr of Diphenylguanidine (DPG 80), 1.5 phr of *N*-1,3dimethylbutyl-*N*′-phenyl-*p*-phenylendiamine (6PPD) and 1 phr of wax.

[a] Copolymer styrene-butadiene with 25 wt% of styrene, 75 wt% of butadiene (vinyl content 50 wt%) added with 37.5 phr oil.

[b] Polybutadiene 1,4 cis, 96–97% cis.

[c] Mechanical mixture of TESPT and carbon black N330, 50/50 w/w.

[d] Carbon black N330 grade.

Kemball–Rideal [27] and the deBoer [28] standard surface states.

We have chosen de Boer standard surface state, which assumes 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 $\pi_o = 0.338$ dyne/cm. Therefore, we can write the following equation:

$$\Delta G^0 = -RT\ln\left(\frac{CV_n}{Sg}\right) \tag{3}$$

where: $C = P_o/\pi_o = 2.99 \times 10^8\ \mathrm{m}^{-1}$ is the De Boer constant [28];

$$\Delta H^0 = -R\frac{\mathrm{d}(\ln V_\mathrm{n})}{\mathrm{d}(1/T)} \tag{4}$$

$$\Delta S^0 = \frac{\Delta H^0 - \Delta G^0}{T} \tag{5}$$

Silica with different surface characteristics in terms of hydroxyl groups (1.9, 4.9, 6.1, and 7.8 wt% of grafted TESPT) were characterized to determine the minimum amount of silane required to maximise the interactions between filler and polymer matrix.

According to Eqs. (3)–(5), by injecting several families of probes, the adsorption free energies, enthalpies and entropies were calculated at different temperatures. As an example, the ΔG^o of different probes, obtained at 140 °C for the stationary phase SiO_2 + 1.9 wt% grafted TESPT, as a function of the surface area of the probes is given in Fig. 1.

All the adsorption parameters increase from alkanes to alkylbenzenes, as observed in previous works [14–23]. Alkenes (independently of the position of the double bond) give rise to interactions of intermediate intensity; on the other hand, dienes are between alkenes and alkylbenzenes. Moreover, it is interesting to note that the slope of the straight line given by the alkanes is always higher than those of unsaturated hydrocarbons and alkylated benzenes. This effect might be caused by the increasing length of the hydrocarbon chains which hinders the achievement of the best spatial arrangement required to maximize the specific interactions between the groups with π-bonds (unsaturations or aromatic rings) and free-OH present onto the silica surface.

Finally, the presence of lateral methyl groups hinders the interaction with the silica surface, as shown from the lower values of the adsorption thermodynamic parameters obtained for the *iso*-alkanes and *iso*-alkenes respect to the corresponding *n*-alkanes and *n*-alkenes.

The behaviours of the free energy of adsorption at T = 140 °C of *n*-alkanes, 1-alkenes and alkylbenzenes, as a function of the surface area of the probes and for silicas modified with different amounts of TESPT, are given in Figs. 2–4.

For all the families of model compounds $-\Delta G^o$ decreases on increasing the degree of modification of the silica surface and the reduction becomes more important on increasing the probe molecular weights. Moreover, it is interesting to note that the effect of grafting degree is more pronounced for the alkylbenzenes and that $-\Delta G^o$ decreases monotonically with the increase of the grafting ratio. This last aspect differs from previous findings by Wang et al. [15] who found that adsorption free energy and enthalpy on silica modified with bis-(trimethoxysilylpropyl)tetrasulfane, TMSPT, increase at low graft ratio, and then decrease on increasing the degree of modification. In our case, a similar trend has been found only for the adsorption enthalpy and entropy of paraffines (Fig. 5(a) and (b)) with a maximum around 3–4 wt% of TESPT.

This trend was justified by Wang et al. [15] assuming that the methoxy groups present in grafted molecules would act as high-energy sites. At low degree of modification, the maximum could be due to a total number of active sites (–OH and –OC_2H_5 groups) higher than that present on unmodified silica; at high degree of grafting, the methoxy groups would be screened and then their interactions with the adsorbed probes would be hindered.

A different trend has been found in our investigation for $-\Delta H^o$ and $-\Delta S^o$ of alkenes and alkylbenzenes; their

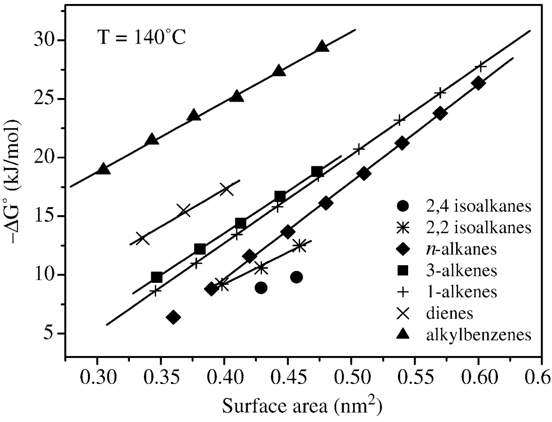

Fig. 1. Adsorption free energy, $-\Delta G^o$, as a function of surface area of hydrocarbon probes for stationary phase SiO_2 + 1.9 wt% TESPT.

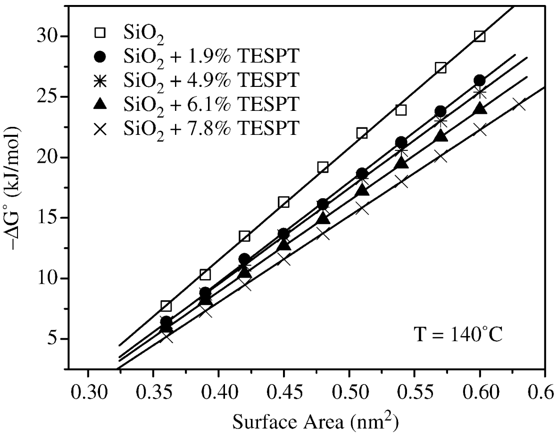

Fig. 2. Adsorption free energy, $-\Delta G^o$, versus surface area and degree of silica modification for *n*-alkanes.

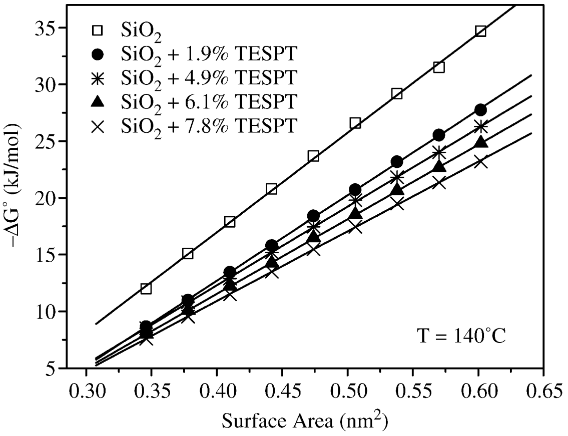

Fig. 3. Adsorption free energy, $-\Delta G^{o}$, versus surface area and degree of silica modification for 1-alkenes.

behavior as a function of chain length and degree of silica modification is shown in Fig. 6(a) and (b) and Fig. 7(a) and (b), respectively. $-\Delta H^{o}$ values of 1-alkenes (Fig. 6(a)) monotonically decrease on increasing the extent of TESPT-modification and increase with the chain length of hydrocarbons. A similar trend is observed for alkylbenzenes (Fig. 7(a)). Therefore, the decrease of adsorption enthalpies of alkenes and alkylbenzenes with modified silica must be ascribed to the substitution of silanols with ethoxy groups which changes the surface characteristics from hydrophilic to hydrophobic.

As far as the molecule mobility onto the silica surface is concerned, the adsorption induces a dramatic reduction of entropy, higher than that corresponding to the loss of one degree of freedom and increasing with the adsorbed molecule length, due to a hindered rotational isomerism, as we previously suggested [22]. The results of this work generally point out that at low grafting degrees a higher entropy loss occurs; at higher degrees of modification the decrease of $-\Delta S^{o}$ suggests higher mobility of the adsorbate.

The difference at low grafting degrees between alkanes and unsaturated or aromatic hydrocarbons might be ascribed to a rather complicated interaction mechanism due to the presence of sites with different activity and mobility on the modified silica surface with respect to the unmodified one.

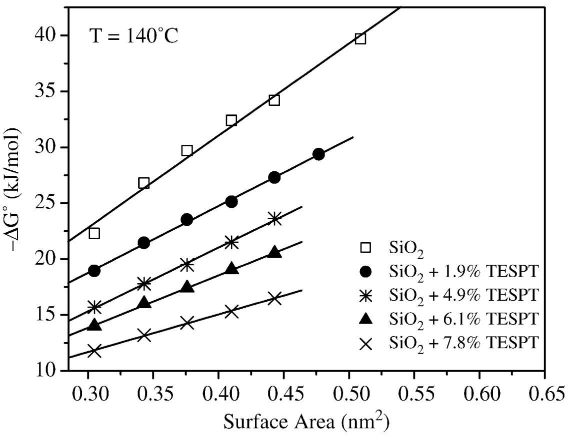

Fig. 4. Adsorption free energy, $-\Delta G^{o}$, versus surface area and degree of silica modification for alkylbenzenes.

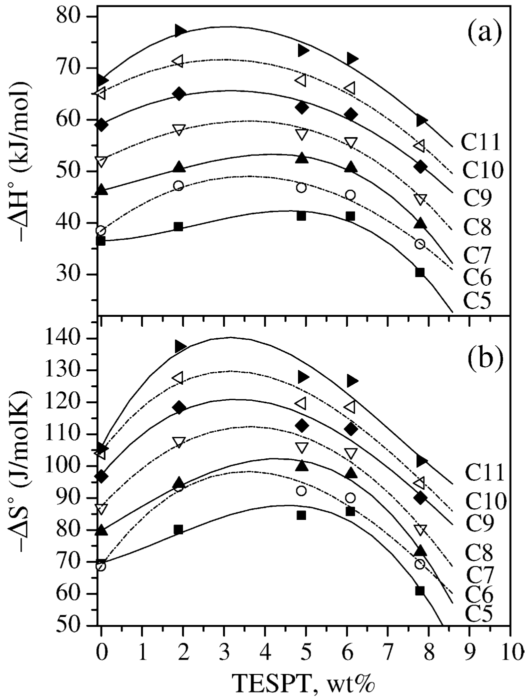

Fig. 5. Adsorption enthalpy (a) and entropy (b) of *n*-alkanes (1-pentane, C_5, up to 1-undecane, C_{11}) as a function of the degree of silica modification.

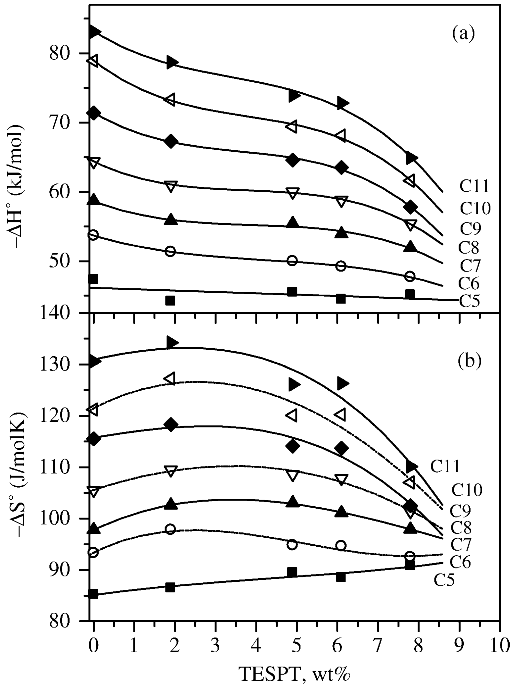

Fig. 6. Adsorption enthalpy (a) and entropy (b) of 1-alkenes (1-pentene, C_5, up to 1-undecene, C_{11}) as a function of the degree of silica modification.

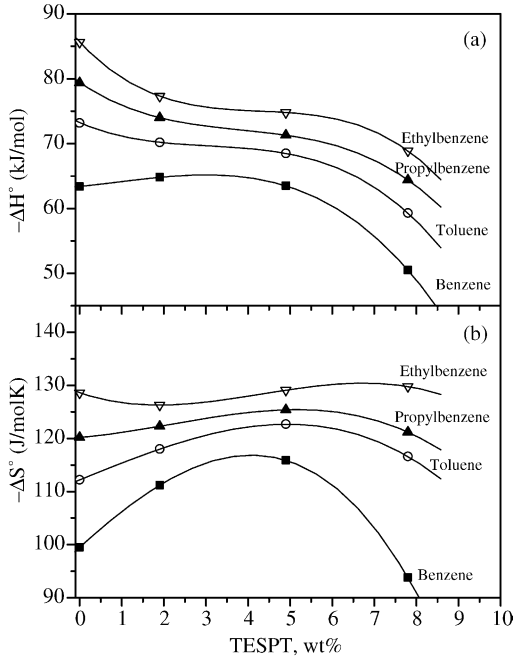

Fig. 7. Adsorption enthalpy (a) and entropy (b) of alkylbenzenes as a function of the degree of silica modification.

3.2. Surface energy of silica

The surface energy, γ_s, is generally given by the sum of the dispersive, γ_s^d, and the specific component, γ_s^{sp} [29]:

$$\gamma_s = \gamma_s^d + \gamma_s^{sp} \tag{6}$$

γ_s^d can be calculated, according to Dorris and Gray [30], from the free energy of adsorption of a CH_2 group, $\Delta G^0_{CH_2}$, on the base of the following equation:

$$\gamma_s^d = \frac{1}{4\gamma_{CH_2}}\left(\frac{\Delta G^0_{CH_2}}{aN}\right) \tag{7}$$

where: N is the Avogadro number, a is the area covered by a CH_2 group [31] and γ_{CH_2} is the surface tension of a surface constituted only by tightly packed methylene groups [32,33].

The specific component of the surface energy cannot be measured easily in a direct way; according to Wang et al. [14–16], an evaluation of its contribution can be achieved from the specific interaction parameter, I^{sp}, which relates to specific interaction established between the filler and a polar probe. I^{sp} is given by the difference in adsorption energy, $-\Delta\Delta G^0$, between a polar probe and a hypothetical or real saturated hydrocarbon with the same surface area:

$$I^{sp} = -\frac{\Delta\Delta G^0}{\sigma N} \tag{8}$$

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

Following Donnet et al. [14,34], in this work 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 interaction with silica surface via the electronic localization of the π-bond system.

The values of γ_s^d and I^{sp} as a function of the temperature were calculated through the Eqs. (7) and (8) for all the silicas. The results are reported in Figs. 8 and 9, respectively. The surface parameters decrease on increasing both the temperature and the grafting degree. In particular, the decrease of the specific interactions is more pronounced than that of the dispersive ones, as indicated by the plot of Fig. 10, where the values of γ_s^d and I^{sp} extrapolated at 20 °C vs. the grafting degree are reported.

Due to the surface modification the polarity of the filler is reduced, because the number of the free silanol groups, which favour the specific interactions with polar probes, becomes lower. Moreover, even if a grafting degree of about 6 wt% of TESPT does not neutralize all the OH groups present onto the silica surface, it seems to be enough to reduce the surface activity of silica in a significant way from the technical point of view in agreement with recent findings by Hasse et al. [35].

3.3. Tensile properties

The most commonly performed mechanical test on rubber vulcanisates is the uniaxial extension of a strip, at constant rate of strain, to its breaking point. Wolff et al. [36] demonstrated that at relatively low strain, the stress of the carbon black-filled vulcanisates is lower than for silica, but it reaches the level of silica compound at about 200% of strain. This phenomenon was explained by considering the extent of filler–filler and filler–polymer interactions, characterising the compounds at different deformation ratio [37]. In elastomer matrix silica particles tend to form agglomerates, especially at high loadings, leading to chain-like structures originating a three-dimensional filler network, generally termed secondary network. A significant amount of rubber is trapped in this secondary network, then at low

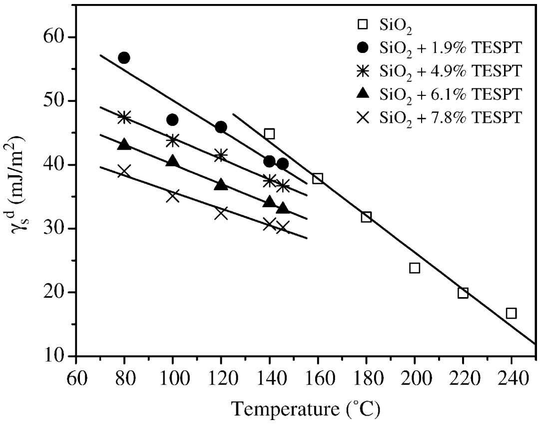

Fig. 8. Dispersive component as a function of temperature and of degree of silica modification.

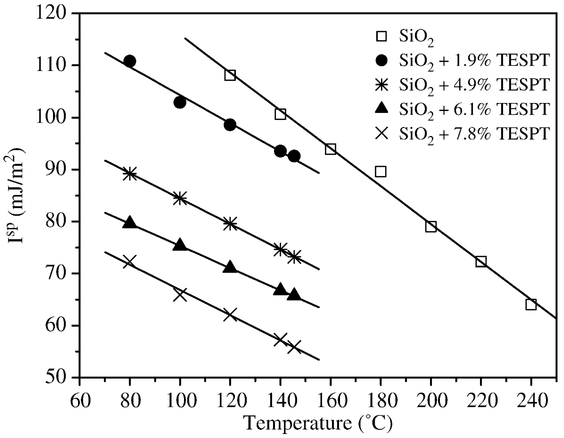

Fig. 9. Specific interaction parameter as a function of temperature and of degree of silica modification.

deformation the mechanical response is mainly ascribable to the filler network. At higher strain (200–300%), the secondary network breaks, the polymer is released and filler-elastomer interactions will become predominant. The much lower stress of the silica-vulcanisates in comparison to carbon black at high elongations can be explained by weaker filler–elastomer interactions leading to slippage between rubber molecules and the silica surface [16,22,36, 37].

According to the surface characteristics deduced from the gas chromatographic results, the silica modifications should not favour the filler–filler interactions, preventing the formation of the secondary filler network in the elastomer matrix. On the base of these results and of the previously mentioned reinforcement mechanism, one can expect that, on increasing the degree of surface modification of silica, the resulting compounds might require lower stress to achieve low elongations and higher stresses at higher elongation. To ascertain this, the tensile behaviour of vulcanised compounds was investigated, comparing the stress values at 10% (σ_{10}) and 300% (σ_{300}) of strain.

A part from the filler loadings, the σ_{10} values for SBR compounds do not show any significant differences with respect to the modification of the silica surface (Fig. 11). On the contrary for SBR/BR based compounds, the presence of TESPT leads to lower values of σ_{10} i.e. to a reduction of the filler–filler interactions (Fig. 12).

On the other hand, the values of σ_{300} are higher than those filled with untreated silica (Figs. 11 and 12). Since σ_{300} value is mainly related to the filler–elastomer interactions, the mechanical behaviour at high deformation further confirms a better dispersion of the modified filler in the elastomer matrix and an improvement of the filler–elastomer interactions.

We underline that the effect of silica modification becomes more and more significant on increasing the filler loading in the rubber compounds and, certainly, it will strongly influence the properties of technical compounds containing up to 70 phr of filler.

Finally, the influence of the nominal amount of TESPT, added during the preparation of SBR/BR-compounds, on tensile properties is shown in Fig. 13. The values of σ_{10} are always slightly lower when TESPT is present, but they are independent of TESPT content in the range 6–10 wt%; at high deformations (300%) a small effect is observed on increasing the amount of the modifier in the compound.

However, independently of the amount of filler, the increase of σ_{300} does not seem to be straightforwardly related to the nominal amount of TESPT added to the compounds. This can be ascribed to the role played by TESPT during the vulcanisation as suggested in the recent literature [35,38,39]. Indeed, TESPT has two opposite roles: (i) it subtracts free sulphur to the crosslinking reaction of the matrix, thus leading to a lower crosslink density of the neat matrix; (ii) it improves the filler–elastomer interactions by reducing the surface polarity of silica and by increasing the coupling reaction between filler and elastomer, thus promoting the dispersion of silica and consequently the improvement of mechanical performances.

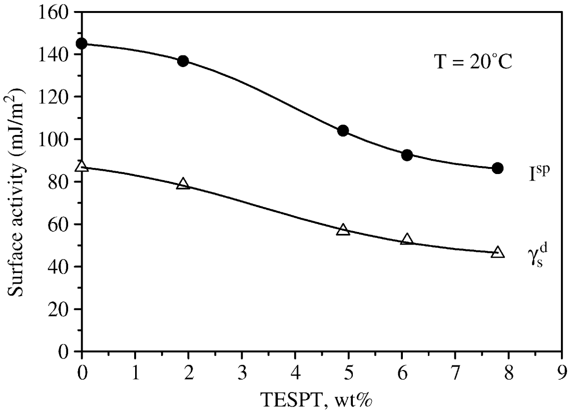

Fig. 10. Surface activity components as function of the grafting degree with TESPT at 20 °C.

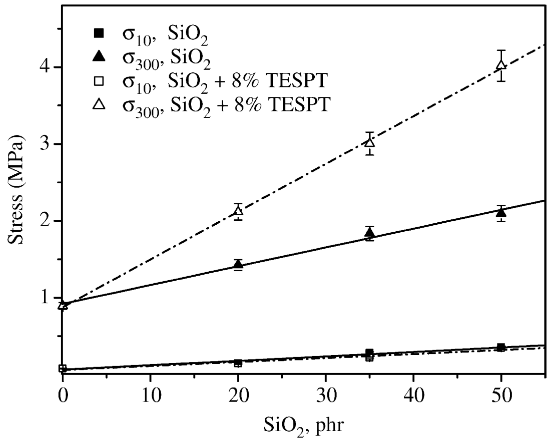

Fig. 11. Tensile behaviour of SBR compounds filled with silica and silica modified.

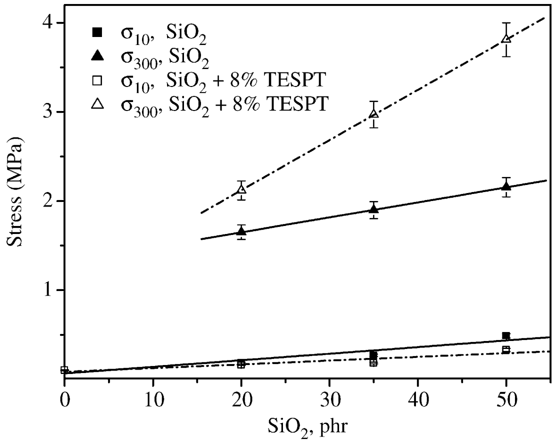

Fig. 12. Tensile behaviour of SBR/BR compounds filled with silica and silica modified.

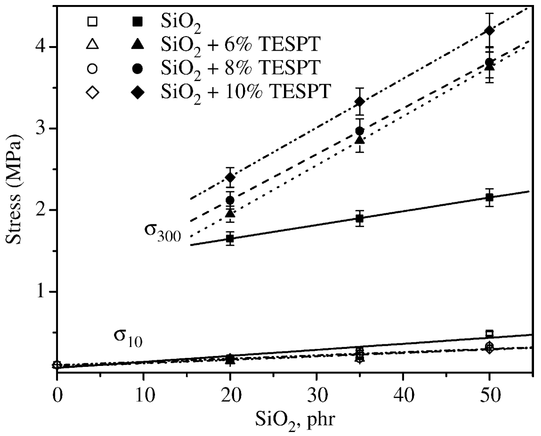

Fig. 13. Effect of the grafting ratio on tensile properties of SBR/BR compounds loaded with TESPT-modified silica.

4. Conclusive remarks

The results obtained by the thermodynamic study carried out by IGC at infinite dilution suggest that preferred interactions of silicas with elastomers containing double bonds or aromatic rings in their repeating unit (BR and SBR rubbers) are expected. However, since the interactions between the silanol groups of the filler are much stronger than those between silanol and double bond or and aromatic ring, the unmodified silica cannot be optimally dispersed in the elastomer matrix so as to respond to the technological demands. Moreover, the modified silica particles show a lower tendency to interact with themselves; thus, a higher dispersibility of the filler in an elastomer matrix is predicted. The overall results suggest that a 6 wt% of grafted TESPT seems to be enough to reduce the surface activity of silica in a significant way from the technical point of view.

The results of the tensile measurements at very low and high deformations confirm our thermodynamic predictions and further support the role of TESPT in promoting interactions between filler and elastomer, in achieving better dispersions and in improving mechanical properties. This effect is more pronounced at high filler loadings (50 phr) i.e. near to the amount of filler typically used in the production of compounds for tyre treads.

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