Investigation into the Interactions between Filler and Elastomers Used for Tyre Production

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SUMMARY: An investigation in the interactions between silica and elastomers used in the production of tyre treads was carried out. To achieve some knowledge on the interactions between reinforcing agent and elastomers, which are fundamental in determining the rubber reinforcement, inverse gas chromatography (IGC) at infinite dilution was used to evaluate surface properties of both unmodified and modified silica and to calculate the adsorption free energy and enthalpy of low molecular weight analogues of elastomers. The predictions derived from the thermodynamic study were compared with some of the results obtained by a morphological analysis of silica-filled compounds carried out by transmission electron microscopy (TEM) and automated image analysis (AIA).

Introduction

Compounds used in the tyre industry are rather complicated materials; they are made from natural and synthetic rubbers to which are added different amounts of specific products such as, for example, stabilisers, crosslinking agents, aid-processing and reinforcing agents, to enhance their performances. The basic aim is to achieve reach a significant improvement in the mechanical properties of these composite materials.[1-5] The reinforcement of elastomers by particulate fillers such as carbon black or silica depends, to a large extent, on the polymer properties, filler characteristics and processing conditions. The most important parameters related to the filler are particle size, structure and surface activity.[6-8] The maximum efficiency is attained when a continuous, structured network of the filler, homogeneously dispersed within the

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polymeric matrix, is formed.

Carbon black has been widely investigated and has been the most used for many years.[5]

In the past decade, much attention has been devoted to the use of silica. Improved performance, such as reduction of rolling resistance and improvement of wet grip, has been shown by silica-reinforced treads.[9-12] However, the reinforcing ability of silica depends on its dispersion into the elastomer matrix. High dispersion can be obtained by reducing silica-silica and improving silica-elastomer interactions. This can be achieved by modifying the silica surface, for example, by using organosilanes which promote filler-polymer interaction via physical and chemical linkages.[9,10,13-16]

In the present contribution some of the results obtained by our research group, both from a thermodynamic study carried out with Inverse Gas Chromatography on low molecular weight analogues of elastomers and from a morphological investigation performed by Transmission Electron Microscopy and automated image analysis on filled compounds, are presented. In particular, the effects of surface modification of the filler on the chemical structure of the matrix, and some of the processing conditions, have been investigated.

Experimental

Materials. Precipitated silica Zeosil 1165 MP (Rhône Poulenc) modified with bis-triethoxysilylpropyltetrasulfane (TESPT) was used as stationary phase. Surface modification of the silica was performed by first immersing it in a CH_2Cl_2 solution of TESPT. After evaporation of the solvent, the silica covered with TESPT was sealed in a vial, under Argon, and thermally treated at 120°C for two hours. During the treatment, silylation of the silica surface occurs by a condensation reaction between the surface hydroxyl groups and the hydrolyzed TESPT molecules. Thermal treatment was followed by soxhlet extraction with CH_2Cl_2 for six hours. The elemental analysis result of TESPT-grafted silica was found to be 7.9 % w/w. The stationary phase was made with silica particles ranging in size from 150-250 μm.

Alkanes, olefins and alkylated benzenes were used as low molecular weight analogues of

saturated rubbers (ethylene-propylene (EPR) and butyl rubber), unsaturated rubbers (natural (NR) and butadiene (BR) rubber) and styrene-butadiene copolymers (SBR), respectively.

Crude rubber specimens for TEM, based on different elastomeric matrices filled with silica and mixed with all typical required ingredients,[17] were kindly provided by Pirelli Pneumatici S.p.A.

Gas Chromatography. A Varian 3700 gas chromatograph equipped with a flame ionization detector (FID) and operating under isothermal conditions was used. Helium was used as the carrier gas and the column inlet and outlet pressure was measured using standard pressure gauges. The carrier gas flow rate was determined using a bubble flow meter (30 cm^3/min).

A stainless steel column with a length of 40 cm and a diameter of 2.5 mm was filled with about 0.5 g of silica. Before the measurements, the column was conditioned for 40 h in the gas chromatograph at 250°C, at a carrier gas flow rate of 6-8 cm^3/min.

The solute samples were introduced into the column using a 1μL syringe. The injected vapor volume was as small as possible, generally lower than 0.1 μL, to avoid any solute-solute interactions. The measurements were carried out between 80-250 °C.

Transmission Electron Microscopy. Morphological investigations were carried out using a transmission electron microscope ZEISS EM 900, applying an acceleration voltage of 80 kV. Ultrathin sections 50 nm thick were prepared with a Leica EM FCS ultracryomicrotome, equipped with a diamond knife cooled at –60°C, keeping the sample cooled at –130°C.

Image Analysis. Digital image analysis of micrographs was carried out by using the Image-Pro® Plus software. The computation and measurement of all the aggregates were made in terms of area, in the range 200 – 20000 nm^2.

Results and Discussion

In order to achieve some knowledge of the ability of the filler surface to interact with rubber, inverse gas chromatography (IGC) at infinite dilution was used to determine the free energies and enthalpies of adsorption as well as the dispersive component of surface free energy, γ_s^d, and the

interaction parameter, I^{sp}. [6-8, 18]

The neat retention volume (V_N) can be obtained from the retention time (t_r) on the basis of equation [1]:

$$V_N = Dj\,(t_r - t_m)\,(1 - P_w / P_0)\,T_c / T_f \qquad [1]$$

where: t_r and t_m are the retention times measured with a specific probe and with a non adsorbing probe (such as methane), respectively; D is the flow rate; P_w is the vapor pressure of pure water at the flowmeter temperature and P_0 is the pressure at the flowmeter; T_c and T_f are the column and the flowmeter temperatures and j is the James-Martin factor[19] for the correction of gas compressibility when the column inlet (P_i) and outlet (P_{ou}) pressures are different.

At infinite dilution one can calculate the adsorption free energy according to equation [2]:

$$\Delta G^0 = -RT\ln(C \cdot V_N / S \cdot g) \qquad [2]$$

where: S is the specific surface area of silica, g is the mass of the filler in the column, T is the temperature of the column in K, R is the gas constant and $C=2.99 \cdot 10^8$ m^{-1} is the De Boer constant. [20]

If the covered surface is negligible, the enthalpy of adsorption is given by the differential heat of adsorption and, according to the Gibbs-Helmotz equation, can be calculated from the temperature dependence of the retention volume as:

$$\Delta H^0 = -R\, d(\ln V_N) / d(1/T) \qquad [3]$$

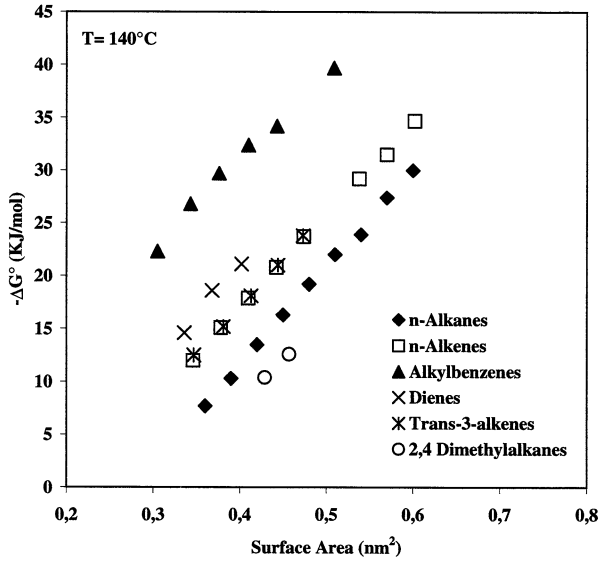
Thus, by injecting several families of probes, the related adsorption free energies and enthalpies could be calculated. Results show, as expected, that there is a decrease in the adsorption free energy, when the measurement temperature increases. On the other hand, ΔG^0 increases when the molecular weight of the model compound, e.g. its surface area, increases. This behavior is common to both surface modified and unmodified silica, as shown in Figure 1 a) and b), where the free energy of adsorption (ΔG^0), obtained at 140°C, is given for the two silicas.

Although in the case of unmodified silica the thermodynamic study was carried out up to 250°C, this comparison is made at 140°C because, in the case of silica modified with TESPT, measurements could not be performed at higher temperatures as we wished to avoid the breaking of the -S-S-S- bridge present in the coupling agent, which takes place around 150°C.

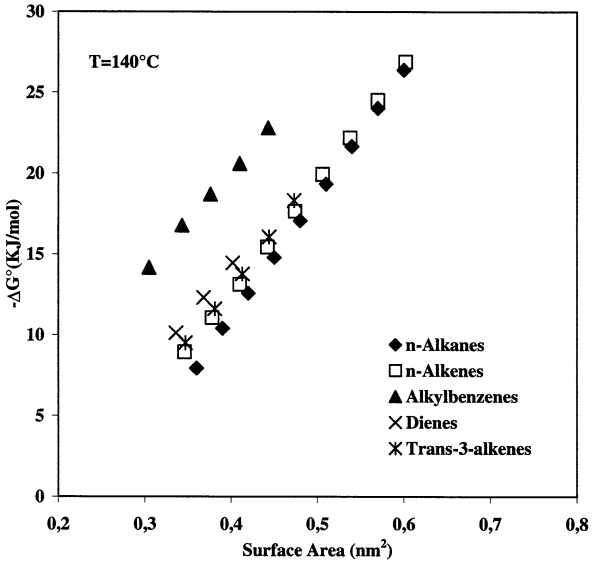
The linear relationship between the free energy (ΔG^0), and the number of carbon atoms, which holds for any kind of probe and for both surface unmodified and modified silica, indicates that in the range of molecular weight explored, each CH_2 group gives the same contribution to the variation of the free energy, which means that there are similar interactions between each methylene group and the silica-active sites. Moreover, going from n-alkanes to olefins and alkylaromatics, stronger interactions with the stationary phase are found, although the differences among the three families of probes are somehow reduced when the silane modifier is used.

Indeed, while in the case of paraffins the values of the adsorption free energy for the two silicas are almost the same, for unsaturated hydrocarbons and aromatic derivatives the ΔG^0 calculated when the stationary phase is surface modified silica are always lower. In this case the polarity of the filler surface is reduced, as the number of free silanol groups which favor the specific interactions with polar probes is lower. It is also interesting to note that the slope of the straight line given by the paraffins is always higher than that of olefins and alkylaromatics. This is even more evident when TESPT is present.

This effect might be explained by taking into account that, by increasing the length of hydrocarbon chains, the contribution to the adsorption free energy given by the specific interactions due to the double bonds (olefins) or the aromatic rings (alkylaromatics) becomes less important than that given by the dispersive ones. Furthermore, in the case of surface-modified silica, the number of silanol groups of the filler which can interact with the olefinic or aromatic π-bonds are considerably reduced because, by reacting with the ethoxy groups, they are chemically bonded with TESPT, as sketched in Figure 2.



a)



b)

Fig. 1 Adsorption free energy vs. surface area of hydrocarbon probes; stationary phase: a) SiO_2 as received; b) SiO_2 modified with TESPT.

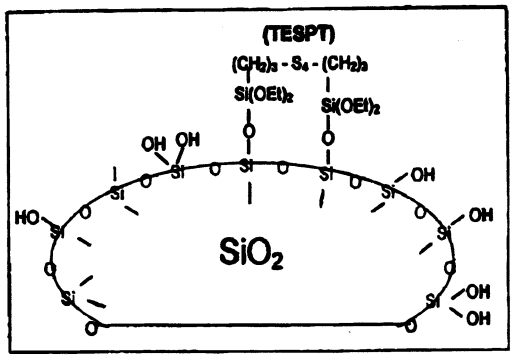


Fig. 2 Bis-triethoxysilyl propyltetrasulfane chemically bonded to vicinal silanol groups at the silica surface.

This can be verified by the evaluation of the filler surface energy after modification with TESPT. One has to remember that the surface energy, γ_s, is given by the sum of two contributions, the dispersive γ_s^d and the specific or polar component γ_s^{sp}:

$$\gamma_s = \gamma_s^d + \gamma_s^{sp} \qquad [4]$$

The dispersive component can be calculated, according to Dorris and Gray[21,22], from the free energy of adsorption of a CH_2 group (ΔG^0_{CH2}) which, in turn, can be obtained from the neat retention volume, on the base of the following equations:

$$\Delta G^0_{CH2} = - RT \ln V_{N(n)} / V_{N(n+1)} \qquad [5]$$

$$\Delta G^0_{CH2} / N \cdot a = 2 (\gamma_{CH2} \cdot \gamma_s^d)^{1/2} \qquad [6]$$

where: N is the Avogadro number, a is the area covered by a CH_2 group[23] and γ_{CH2} is the surface tension of a surface constituted only of tightly packed methylene groups.[24,25]

The specific component of the surface energy, γ_s^{sp}, cannot be evaluated directly. According to Wang et al.[6,7], an evaluation of its contribution can be achieved from the specific interaction

parameter (I^{sp}), which relates to the specific interactions 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 (eg. benzene) and a hypothetical or real saturated hydrocarbon with the same surface area, as given by the following equation:

$$I^{sp} = -\Delta\Delta G^0 / N \cdot a \qquad [7]$$

where a is the surface area occupied by benzene.

The behavior of γ_s^d and I^{sp} as a function of the temperature has been studied for silica, both as received and after treatment with the coupling agent. The results are reported in Figures 3 and 4, respectively.

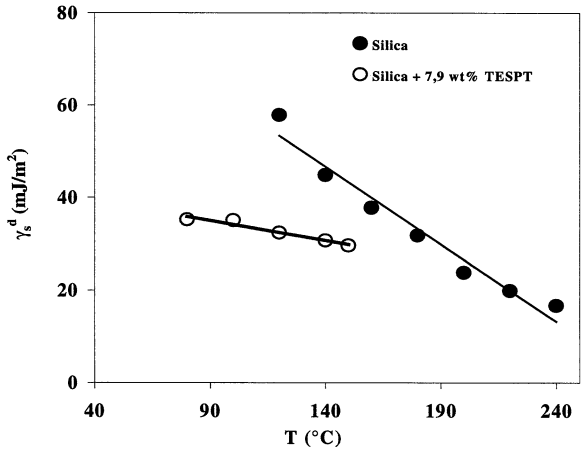


Fig. 3 Dispersive component as a function of temperature.

General features of these results are: i) the specific and dispersive components of the surface unmodified silica are always higher than those of TESPT-modified silica; ii) both γ_s^d and I^{sp} decrease with increasing temperature.

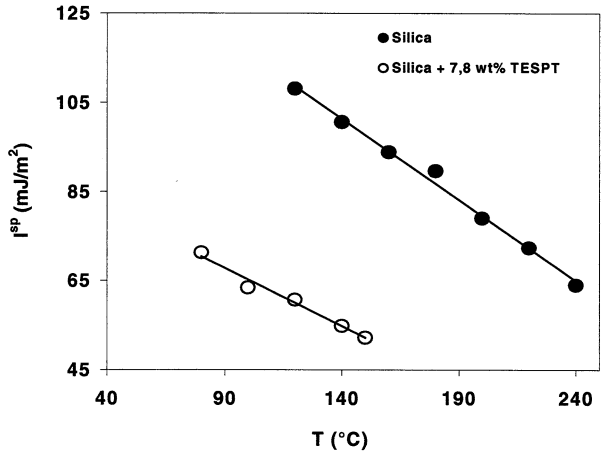


Fig. 4 Specific interaction parameter as a function of temperature.

The decrease in the specific contribution is more relevant than that of the dispersive component, meaning that the filler-filler interactions will be less favored when the silanol groups on the silica surface are substituted by TESPT molecules, as clearly evidenced in Figure 2.

The thermodynamic predictions obtained in this study lead to the conclusions that preferred interactions of the filler will occur with elastomers containing double bonds or aromatic rings in their repeating unit.

To ascertain the reliability of these predictions and to study the influence of some processing parameters on the filler distribution within the polymer matrix, a morphological characterization was performed on compounds containing different amounts of silica (20 and 35 phr), with or without TESPT, and prepared at different mixing times (t_{mix} = 15 and 30 min).

Morphological analysis performed on compounds based on different elastomeric matrices (natural rubber, butadiene rubber, styrene-butadiene rubber) filled with unmodified silica has shown a very good agreement with the thermodynamic prediction obtained from IGC.[17] The preliminary results reported here, obtained through the elaboration of the TEM micrographs by digitalized image analysis on crude samples containing silica modified with TESPT, suggest a similar interaction scale as that found for unmodified silica.

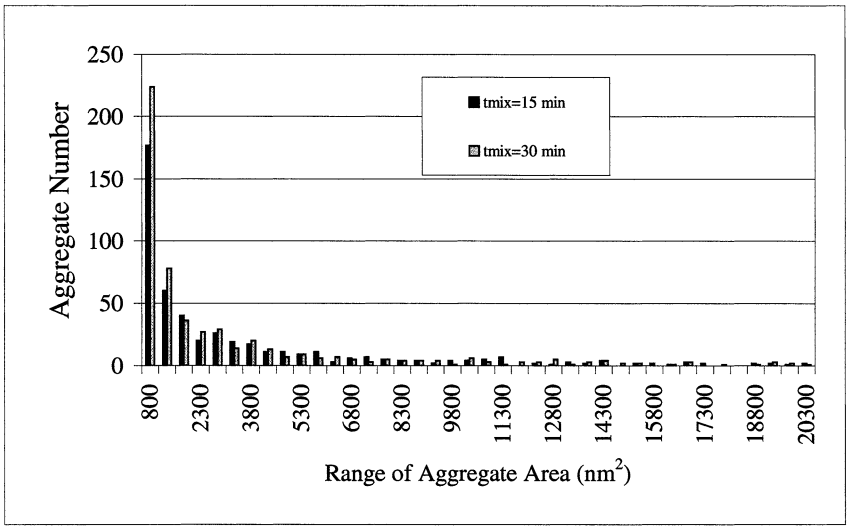


Fig. 5 Aggregate number as a function of the aggregate area for SBR filled with 35 phr unmodified silica (the number on the axis refers to the upper limit of the range).

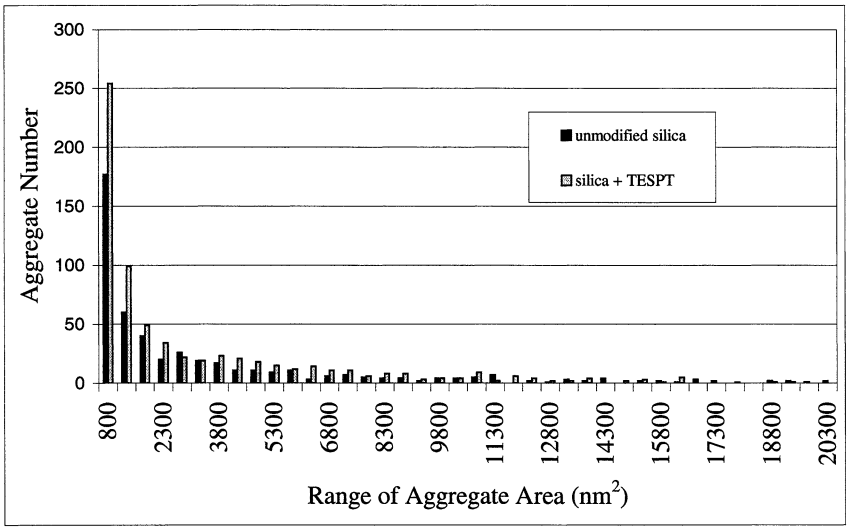


Fig. 6 Aggregate number as a function of the aggregate area for SBR with 35 phr of filler; t_{mix} = 15 min. (the number on the axis refers to the upper limit of the range).

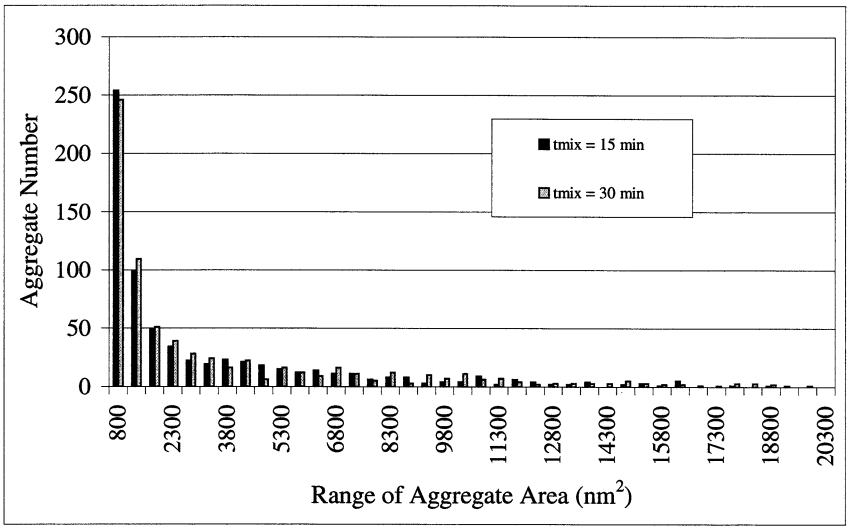


Fig. 7 Aggregate number as a function of the aggregate area for SBR filled with 35 phr modified silica (the number on the axis refers to the upper limit of the range).

As far as the loading amount and mixing time are concerned, our findings show that at low loading (20 phr) the mixing time does not lead to any significant difference in the filler distribution. When 35 phr of silica are added, a more homogeneous distribution is attained after a longer time (30 min) for all the matrices. In Figure 5 results concerning SBR/Silica compounds are reported and show that the number of small aggregates is always higher for t_{mix}=30 min.

Improved dispersions are achieved when the silane is added, independently of the matrix and even at lower mixing times, as indicated by the histograms reported in Figure 6, where it can be seen that the number of small aggregates in SBR filled with 35 phr of modified silica, mixed for 15 min, is comparable to that of compounds containing the same amount of unmodified silica and mixed for 30 min (Figure 5). The positive influence of TESPT on the filler dispersion is confirmed by the results shown in Figure 7, which does not show any improvement of dispersion by increasing the mixing time from 15 to 30 min. This can be ascribed to the reduced filler-filler interactions, which favor the formation of small-size aggregates.

Conclusions

The thermodynamic predictions obtained by IGC suggest that preferred interactions of unmodified as well as TESPT-modified fillers with the elastomers are on the following scale: *poly(isoprene) < poly(butadiene) < styrene-butadiene copolymers.*

These predictions are partially confirmed by morphological analysis carried out on technical compounds.

The modification of silica by TESPT favors the dispersion of silica in all kinds of elastomers used and reduces the mixing time necessary to achieve the best distribution of the filler.

Acknowledgements

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[1] S. Wolff, M.-J. Wang, in "*Carbon Black*", J.-B Donnet, R. C. Bansal and M.-J. Wang Eds., Marcel Dekker, New York 1993, chapter 9.
[2] S. Wolff, *Rubber Chem. Technol.* **1996**, *69*, 325.
[3] M.-J. Wang, *Rubber Chem. Technol.* **1998**, *71*, 520.
[4] M.-J. Wang, *Rubber Chem. Technol.* **1999**,*72*, 430.
[5] K. A. Grosch, *Rubber Chem. Technol.* **1996**,*69*, 495.
[6] M.-J. Wang, S. Wolff, J.-B. Donnet, *Rubber Chem. Techn.*, **1991**, *64*, 559.
[7] S. Wolff, M.-J. Wang, E.H. Tan, *Kautsch. Gummi Kunstst.*, **1994**, *47,* 780.
[8] S. Wolff, M.-J. Wang, E.H. Tan, *Kautsch. Gummi Kunstst.*, **1994**, *47,* 873.
[9] M. Gerspacher, C.P. O'Farrell, *Kautsch. Gummi Kunstst.*, **1998**, *51,* 488.
[10] L.R. Evans, W. H. Waddell, *Kautsch. Gummi Kunstst.*, **1995**, *48,* 718.
[11] U.S. Patent 5227,425 (1993), Compagnie Generale des Etablissement Michelin-Michelin & Cie, inv.: R. Rauline.
[12] T. C. Gruber, T. W. Zerda, M. Gespacher, *Rubber Chem. Technol.* **1994**, *67*, 280.
[13] A. Hunsche, U. Görl, A. Müller, M. Knaack, Th. Göbel, *Kautsch. Gummi Kunstst.*, **1997**, *50,* 881.
[14] A. Hunsche, U. Görl, H.G. Koban, Th. Lehmann, *Kautsch. Gummi Kunstst.*, **1998**, *51,* 525
[15] U. Görl, A. Parkhouse, *Kautsch. Gummi Kunstst.*, **1999**, *52,* 493.
[16] U. Görl, J. Münzenberg, D. Luginsland, A.Müller, *Kautsch. Gummi Kunstst.*, **1999**, *52,* 588.
[17] M. Castellano, L. Falqui, G. Costa, A. Turturro, B. Valenti, G. Castello, *J. Macromol. Sci.-Phys.*, **2002**, *41*, 451.
[18] S. Wolff, M.-J. Wang, in "*Carbon Black*", J.-B. Donnet , R.C. Bansal and M.-J. Wang, Eds., Marcel Dekker, New York 1993, Chapter 6.
[19] A.T. James, A.J.P. Martin, *Biochem. J.*, **1952**, *50,* 679.
[20] J.-H de.Boer, "*The dynamical character of adsorption*", Oxford University Press, London 1953.

[21] G.M. Dorris, D.G. Gray, *J. Colloid Interface Sci.,* **1979**, *71,* 93.
[22] G.M. Dorris, D.G. Gray, *J. Colloid Interface Sci.,* **1980**, *77,* 353.
[23] P.H. Emmet, S. Brunauer, *J. Am. Chem. Soc.,* **1937**, *59,* 1553.
[24] R.J. Aveyard, *J. Colloid Interface Sci.,* **1975**, *52* ,621.
[25] G.L. Gaines *Polymer Eng. Sci.,* **1972**, *12*, 1.