Interactions of Stöber Silica with Natural Rubber under the Influence of Coupling Agents, Studied by ^{1}H NMR T_2 Relaxation Analysis

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ABSTRACT: ^{1}H NMR T_2 relaxation has proved to be a successful technique for the study of rubber−filler interactions in carbon black filled rubbers. For the present study, the interactions between NR and pure silica as well as silicas grafted with various coupling agents were investigated using ^{1}H NMR T_2 relaxation. Monodisperse spherical silica particles were used, prepared according to a method by Stöber, and afterward treated with the coupling agents prior to mixing into NR. Depending on the type of coupling agent and the degree of condensation, grafting densities of coupling agent on the silica range from a minimum of 62% to 100%. NMR shows that the highest amount of immobilized rubber chains on the silica surface occurs for pure silica: about 15%. Grafting of the silica leads to a decrease of the fraction of immobilized rubber chains, dependent on the chemical structure of the coupling agent and its ability to physically or chemically interact with NR: 13% immobilized rubber for a mercapto-functional coupling agent, which is expected to react with the NR unsaturation, to about 1% for a coupling agent with only a propyl group extending into the rubber matrix, unable to react. The immobilization of rubber chains to the silica surface corresponds to the formation of a physical network, which is strong enough to remain intact at 100 °C, even when swollen in a good solvent.

Introduction

The use of silica for reinforcing rubbers is attracting increasing attention on account of specific properties exhibited by such composites, especially for use in tires. In comparison with carbon black, silica reduces the rolling resistance of tires, thus leading to lower fuel consumption. In combination with this lower rolling resistance, silica provides greater wear resistance and superior wet traction.[1,2]

In the case of silica, hydrogen bond interactions between surface silanol groups in agglomerates are very strong in comparison with the interactions between the polar siloxane groups or silanol groups of the silica and the commonly nonpolar olefinic hydrocarbon rubbers. This causes great difficulty when mixing silica with rubber.[3,4] Since an optimal reinforcing power can be achieved only if the filler is well-dispersed in the rubber matrix, improving the mixing quality is of major importance. Another factor important to the reinforcing effect of the filler is the chemical or physical interaction between the filler and the rubber. Chemical modification of the silica surface using bifunctional organosilanes enhances the compatibility between hydrocarbon rubber and the silica and leads to remarkable improvements in the mechanical properties of silica-reinforced rubber vulcanizates. Despite numerous studies devoted to these materials,[5−9] the reinforcement mechanism of the silica-filled rubbers has not been clarified to such an extent as that of carbon black filled rubbers.

Low resolution proton (^{1}H) NMR is one of the few techniques successfully used in the study of rubber−filler interactions in carbon black filled and silica-filled rubbers.[10−16] In all these studies, physical adsorption of rubber chains onto the surface of the filler is observed, causing significant immobilization of the rubber chains in the vicinity of the filler surface. This immobilization is in most cases interpreted as bound rubber resulting from interactions between the filler and the rubber. This immobilized bound rubber consists of two microregions with strongly differing local chain mobilities: a tightly bound, low-mobility, almost rigid phase, which directly covers the filler surface, and a loosely bound, highly mobile rubber phase remote from this interface. A physical network exists due to absorption of rubber chains to the silica surface. Grafting of silica in particular with methanol or hexadecanol was shown to decrease the ability of the filler to exchange strong interactions with the surrounding rubber.[14] Modification of the surface activity by grafting was associated with a change in the proportion of tightly to losely bound rubber. Less active sites remaining after the grafting with either alcohol resulted in a smaller tightly bound rubber component. If the filler, with or without grafting with coupling agent, is compounded into the rubber matrix, a third phase comes into play with an even higher mobility than the other two.

In previous studies, as mentioned above, generally silica and/or carbon black were modified with alcohols. Each alcohol molecule can react with only one silanol group in the silica. In the case of silica-reinforced compounds, silanes containing three alkoxy groups per silicon atom are commonly used as grafting agents, allowing for a maximum of three reactions with silanols on the silica. With the aim of achieving a better understanding of the typical silica performance in tire applications, ^{1}H NMR T_2 relaxation experiments are used in the present study to investigate the modification of the silica surface with various silane coupling agents and the consequent effect of this on natural rubber (NR)−silica interactions. Silica-reinforced passenger car

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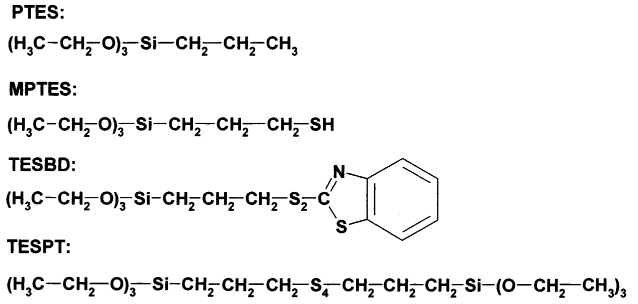

Figure 1. Chemical structures of the silane coupling agents.

tire treads normally consist of a solution styrenebutadiene rubber/butadiene rubber (S-SBR/BR) blend.[17] Truck tires are commonly composed of NR. NR was chosen for this study, because the relaxation of the styrene moieties in S-SBR tends to interfere with the relaxation of the interface between the rubber and the silica filler. Further, monodisperse spherical silica particles were used for this study in order to avoid the effect of irregularities in the surface roughness of the silica, which could result from peculiarities of the various production processes employed for the synthesis of silica.[1] Using these monodisperse silica particles, complication of data as a result of surface roughness could be avoided.

Experimental Section

Materials. Ethanol (Lamers & Pleuger, technical grade) and tetraethoxysilane (TES) (Fluka, purity ≥98%) were freshly distilled. Ammonium hydroxide (Merck, 25%) was of analytical reagent quality and contained 15.6 mol/L ammonia (NH_3) as indicated by titration. Monodisperse silica particles were synthesized in accordance with the method described by Stöber.[18] The reaction temperature was set at 20 °C. Spherical particles (average diameter 40 nm) were prepared in a mixture of ethanol and ammonia (25%) by the polymerization of silicic acid, formed by the hydrolysis of TES. The final particle size can be predetermined by the initial concentration of the reactants.[18] Concentrations of the reactants were set at 0.17 M TES and 0.65 M NH_3. The preparation and properties of nonaqueous model dispersions of chemically modified, charged silica spheres has further been described in detail by Philipse and Vrij.[19]

Surface silanol groups on these silica particles are claimed to react readily with silane coupling agents.[19] The silica particles were grafted with, respectively, propyltriethoxysilane (PTES) [Gelest Inc., ABCR GmbH & Co.], 3-mercaptopropyltriethoxysilane (MPTES) [Gelest Inc., ABCR GmbH & Co.], bis(triethoxysilylpropyl) tetrasulfide (TESPT) [OSi Specialties, Crompton Corporation, Silquest A-1289 silane] and 2-benzothiazyl-(3-triethoxysilyl)propyl disulfide (TESBD) [CAS Registry No. 173176-00-6] by hydrolysis and subsequent silanization under reflux conditions in the silica/ethanol dispersion. Structures of the coupling agents are listed in Figure 1.

TESBD was synthesized from MPTES and dibenzothiazole disulfide (MBTS) [Merck, >98%].[20] MBTS (16.63 g) was dissolved in 210 mL of toluene by heating at reflux temperature. Then, 11.92 g 3-mercaptopropyltriethoxysilane was added dropwise to the clear yellow solution. After 2 h, 90.6 mol % of the product and 9.4 mol % of tetraethoxysilylpropyl disulfide (TESPD) was formed. Impurities in the product were removed by washing with diethyl ether. The TESPD byproduct could not be removed by washing with diethyl ether and remained in the TESBD as an impurity. ^{1}H NMR spectra recorded at 300 MHz in deuterated chloroform, $CDCl_3$, were used to confirm the structure of the product: δ 0.78 (t, 2H); δ 1.22 (m, 9H); δ 1.96 (m, 2H); δ 2.72 (t, 2H), due to impurity of TESPD; δ 3.02 (t, 2H); δ 3.84 (q, 6H); δ 7.18−7.58 (m, 2H); δ 7.80−7.96 (m, 2H).

Natural rubber [SIR 20] was purified by dissolving in 1,1,2,2-tetrachloroethane [Aldrich, 98%] and filtering over a glass filter. Samples were dried in a vacuum oven at 60 °C.

Sample Preparation for the NMR Experiments. To obtain a quantitative measure of the influence of network junctions—of a chemical and/or physical nature—on the T_2 relaxation, a vulcanized gum stock of 100 phr pure NR was studied. For this purpose, pure NR was mixed on a two-roll mill with 3.05 phr CBS, 1.75 phr S, 5 phr ZnO, and 2.5 phr stearic acid and subsequently vulcanized in a hydraulic press at 145 °C for a duration corresponding to $t_c(90)$, determined by cure meter testing.

To prepare NR−silica mixes containing approximately 160 phr silica, NR dissolved in 1,1,2,2-tetrachloroethane was mixed with the various silica samples dispersed in ethanol. The ethanol and 1,1,2,2-tetrachloroethane were evaporated, while the mixes were continuously stirred to improve dispersion of silica. The samples were subsequently dried in a vacuum oven under N_2 flow at 100 °C for 72 h. Approximately 0.2 g of the pure NR and of the mixtures of NR with silicas was introduced into a 9 mm diameter NMR tube of 180 mm length. The sample mass was about the same for all the samples: 0.2022 ± 0.0033 g. For purposes of comparison, experiments were also performed on pure silica samples. The quantity of silica taken for these experiments was equal to the quantity of silica present in the silica-filled NR. This allowed determination of the contribution of the silica protons to the transverse magnetization of silica-filled NR.

Solid State NMR Experiments and Data Analysis

Equipment. ^{29}Si MAS and CP/MAS NMR spectra were recorded on a Varian Unity - 200 MHz wide-bore NMR spectrometer operating at an ^{29}Si frequency of 38.73 MHz. The experiments were performed using a 7 mm CP/MAS probe. The ^{29}Si 90° pulse width was approximately 6.5 μs.

Proton NMR T_2 relaxation experiments were performed on a Bruker Minispec NMS-120 spectrometer. This spectrometer operates at a proton resonance frequency of 20 MHz. The length of the 90° pulse and the dead time were 2.8 μs and 7 μs, respectively. A BVT-3000 temperature controller was used for temperature regulation. The temperature gradient and stability were better than 1 °C.

^{29}Si NMR Experiments. ^{29}Si NMR experiments were performed on pure and grafted silicas, as well as on the original coupling agents, in order to characterize the grafted silicas. The experiments were carried out with magic angle spinning (MAS), using high-power proton decoupling and a spinning frequency of 2.2 kHz and 6 kHz for the coupling agent and silicas, respectively. The cubic octamer silicic acid trimethylsilyl ester (Q_8M_8)[21] was used to optimize the Hartmann−Hahn condition for the ^{29}Si cross-polarization CP/MAS experiments. ^{29}Si spectra were referred to the methyl resonance of Q_8M_8 at 11.7 ppm relative to the internal standard tetramethylsilane (TMS). ^{29}Si CP/MAS spectra were recorded with a cross-polarization time of 8 ms. Recycle times of 1.5 and 30 s was used for the CP/MAS and single-pulse excitation MAS experiments, respectively. The number of scans was 200 for the MAS and 150000−200000 for the CP/MAS experiments.

^{1}H NMR T_2 Relaxation Experiments. Two different pulse sequences were used to record the decay of the transverse magnetization (T_2 decay) for both the almost rigid (1) and the mobile (2) fractions of the samples described previously.[12] (1) A solid−echo pulse sequence (SEPS), $90°_x - t_{se} - 90°_y - t_{se} -$ [acquisition of the amplitude of the transverse magnetization $A(t)$], with $t_{se} = 9\ \mu$s was used to measure the T_2 free induction decay. The point in time after the first pulse $t = 2t_{se} - t_{90}/2$ was taken as zero, where $t_{90}/2$ is the half time of the 90° pulse. (2) A Hahn−echo pulse sequence (HEPS), $90°_x - t_{He} - 180°_x - t_{He} -$ [acquisition $A(t)$ of the amplitude of an echo maximum], was used to record the slow part of the T_2 relaxation decay for the mobile fraction of the samples, where t_{He} was varied between 35 μs and 400 ms. The second pulse in the HEPS

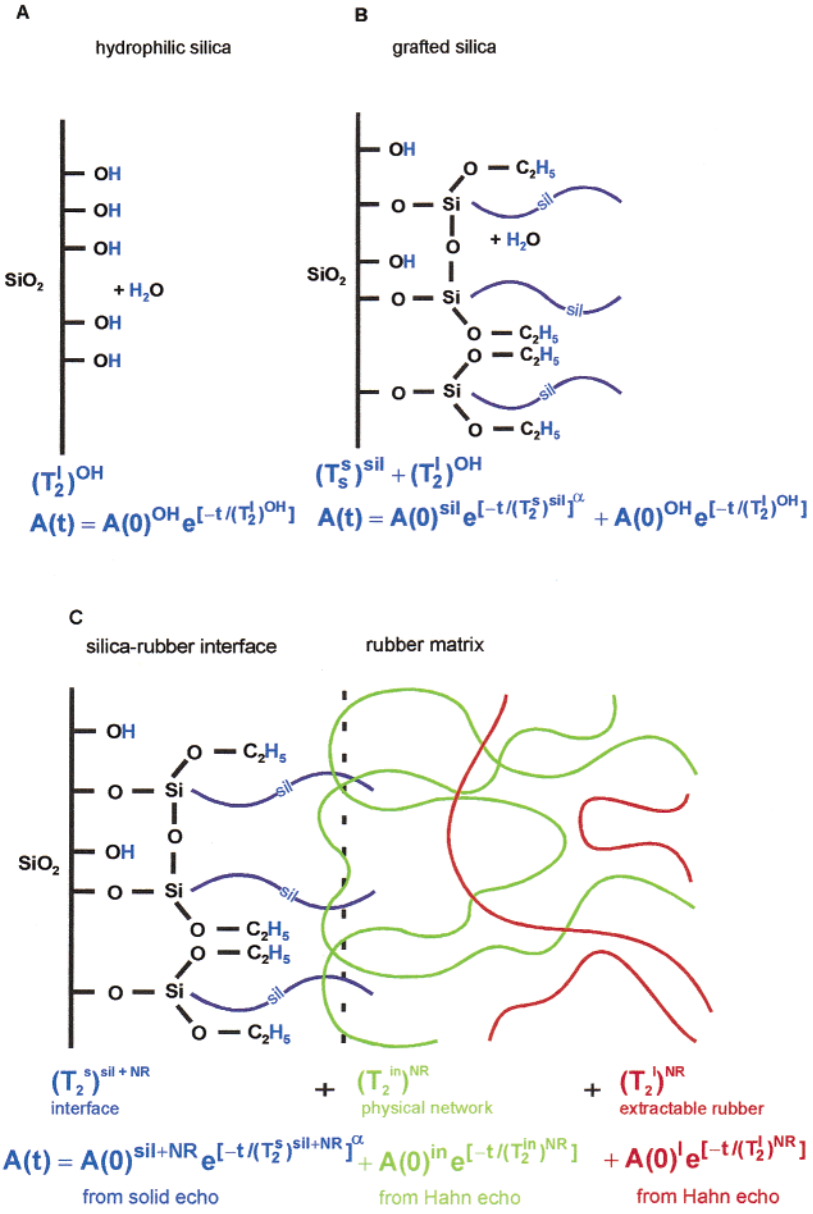

Figure 2. Molecular origin of the different relaxation components for hydrophilic silica (A), grafted silicas (B), and silica-filled NR in the swollen state (C) and the fitting functions used.

inverts nuclear spins of mobile molecules only, and an echo signal is formed with a maximum at time $t = 2t_{\mathrm{He}} - t_{180}/2$ after the first pulse, where $t_{180}/2$ is the half time of the 180° pulse. If the pulse spacing in the HEPS is varied, the amplitude of the transverse magnetization $A(t)$ can be measured as a function of time t. HEPS makes it possible to eliminate the magnetic field and chemical shift inhomogeneities and to measure the T_2 relaxation time for mobile materials accurately.

Measurements on samples swollen in 1,1,2,2-deuterated tetrachloroethane ($C_2D_2Cl_4$) were performed in order to gain insight into the strength of interactions between (grafted) silica and NR and the heterogeneity of the NR-silica physical network.

The time constants (T_2 relaxation time) characteristic of different rates of the magnetization decay curve were obtained by performing a least-squares fit of the data with the Weibull function, or a linear combination of the Weibull function and exponential functions. Depending on the system studied, one, two, or three components were used for the fit. It was not statistically significant to use a series of more than three components fit for these purposes. The different fitting functions used will be detailed in the relevant paragraphs with the results.

The relaxation component and its relative amplitude, originating from almost rigid material on the silica surface and from tightly bound rubber in the mixtures was determined by fitting SEPS data for pure as well as grafted silica-filled NR. Only the initial part of the decay ($t < 400$ μs) was fitted. In this fit, the baseline was fixed to the value that was measured under the same conditions after the sample was removed from the NMR probe. The relaxation component arising from the relaxation of loosely bound rubber and free, extractable rubber, $(T_2^{\mathrm{in}})^{\mathrm{NR}}$ and $(T_2^{\mathrm{l}})^{\mathrm{NR}}$, respectively, and their respective fractional amplitudes, $A(0)^{\mathrm{in}}$ and $A(0)^{\mathrm{l}}$, were determined from the fit of the HEPS data. The HEPS was also used for the measurement of the T_2 decay for nonvulcanized and vulcanized NR nonreinforced gum stock. Details of the fitting functions and the corresponding symbols for the various systems investigated are shown in Figure 2a−c and Table 1. It is anticipated that the analysis of the shape of the T_2 relaxation function is far from straightforward. The Gaussian decay shape is typical for rigid amorphous materials. A single-exponential decay is observed for low molecular mass liquids. In the case of low molecular mass liquids that are adsorbed on the surface of solids, a linear combination of exponential functions is observed that corresponds to free and adsorbed molecules, if the

Table 1. Fitting Functions Used for the Least-Squares Fit of the Data for the Various Systems Studied, Designation of Relaxation Components, α-Parameter in the Fitting Functions,[a] and Pulse Sequences Used

sample	T_2^{short}	$T_2^{\text{intermediate}}$	T_2^{long}
silica			$(T_2^{l})^{OH}$/SEPS
silica + $C_2D_2Cl_4$			$(T_2^{l})^{OH}$/SEPS
grafted silica	$(T_2^{s})^{sil}$/SEPS/$\alpha = 1.34$		$(T_2^{l})^{OH}$/SEPS
grafted silica + $C_2D_2Cl_4$	$(T_2^{s})^{sil}$/SEPS/$\alpha = 1.34$		$(T_2^{l})^{OH}$/SEPS
NR			$(T_2^{l})^{NR}$/HEPS
NR + $C_2D_2Cl_4$			$(T_2^{l})^{NR}$/HEPS
NR + silica	$(T_2^{s})^{sil+NR}$/SEPS/$\alpha = 1.34$	$(T_2^{in})^{NR}$/HEPS	$(T_2^{l})^{NR}$/HEPS
NR + silica + $C_2D_2Cl_4$	$(T_2^{s})^{sil+NR}$/SEPS/$\alpha = 1.34$	$(T_2^{in})^{NR}$/HEPS	$(T_2^{l})^{NR}$/HEPS

[a] Fitting function for hydrophilic silica: $A(t) = A(0)^{OH}e^{[-t/(T_2^{l})^{OH}]^{\alpha}}$. Fitting function for grafted silicas: $A(t) = A(0)^{sil}e^{[-t/(\tau_2^{s})^{sil}]^{\alpha}} + A(0)^{OH}e^{[-t/(\tau_2^{l})^{OH}]}$. Fitting function for NR filled with (grafted) silica: $\boldsymbol{A}(t) = A(0)^{sil+NR}e^{[-t/(\tau_2^{s})^{sil+NR}]^{\alpha}} + A(0)^{in}e^{[-t/(\tau_2^{in})^{NR}]} + A(0)^{l}e^{[-t/(\tau_2^{l})^{NR}]}$.

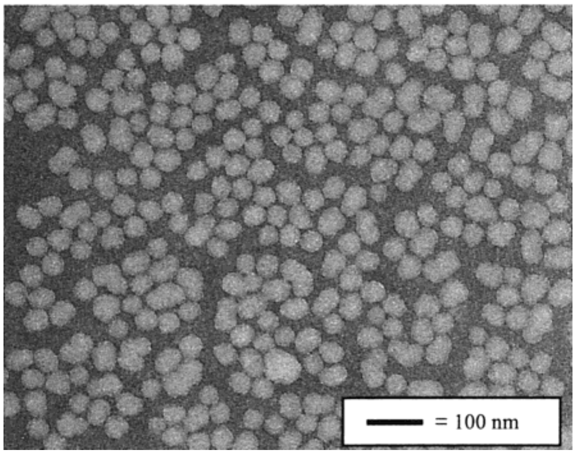

Figure 3. Transmission electron micrograph of the hydrophilic Stöber silica particles.

exchange rate between free and adsorbed (“bound”) states is slow compared to the time scale of the relaxation experiment. It should be noted that the quantitative analysis of the shape of the T_2 relaxation for adsorbed small molecules is complicated due to physical/chemical exchange between free and adsorbed molecules and the cross-relaxation effects at the surface of solids.[22,23] An apparent exponential relaxation is recorded in the case of the fast exchange rate. In the case of adsorbed polymer chains, the physical exchange is usually slow at the time scale of the T_2 relaxation process. Chain portions at the silica surface are largely immobilized because of physical adsorption. Molecular mobility of the coupling agents is also largely constrained. It is well established that polymeric chains with strongly hindered mobility reveal T_2 relaxation, which can be described with the Weibull function with the exponential parameter between 1 and 2.[24−26] In our case, the statistically relevant fit of T_2 decays was obtained with $\alpha = 1.34$ for all samples, which indicates, in addition to short T_2 values, strong immobilization of adsorbed chain portions and grafted molecules.

Results and Discussion

Characterization of the Silica Samples. The particle diameter of the silica particles obtained from the Stöber synthesis, as determined using transmission electron microscopy, was 44 ± 6 nm (Figure 3). The water content of the pure and silane-grafted silica samples was determined using the Karl-Fisher method (200 °C) and is listed in Table 2. The water content is slightly lower for the grafted silicas, as might be expected on account of the decrease in the silanol group content, these being the sites of water adsorption.

^{29}Si and ^{13}C NMR spectroscopy has been used in the past to study grafting of coupling agents to silica surfaces. It was shown by Caravajal et al.,[27] Pursh et al.,[28] Derouet et al.,[29] Simonutti et al.,[30] and Hunsche et al.[31] that the method provides quantitative information about the reactivity of different types of silanol groups on the silica surface facing the coupling agent, as well as on the fraction of various grafted structures formed at the silica surface. ^{29}Si CP/MAS spectra for the pure SiO_2 and MPTES-grafted SiO_2 are shown in Figure 4 as examples. The spectra reveal a broad signal with overlapping peaks at −91, −100, and −109 ppm that originate from, respectively, $SiO(OH)_2$ (Q^2), $SiO_{3/2}(OH)$ (Q^3), and SiO_2 (Q^4) atoms of the silica.[21] A second group of very small peaks in the range from −48 to −66 ppm results from resonances of the reaction products of alkenyltriethoxysilanes with silanol groups on the silica surface. A resonance for pure, unreacted coupling agents is observed at approximately 46.5 ppm. The silicon atoms of mono-, bi-, and trisubstituted alkenyltriethoxysilanes have chemical shifts of approximately −49, −58, and −66 ppm, respectively. It must be noted that these resonances may originate not only from silane-grafted SiO_2 material but also from hydrolyzed alkenyltriethoxysilanes and condensation products of the coupling agents.[32] The presence of resonances in the range from −48 to −66 ppm for MPTES-, TESPT-, and TESBD-grafted silica proves that the silica surface is modified by the chemical reaction of the coupling agents and/or by physical adsorption of alkenyltriethoxysilanes and their condensation products. Because of the low intensity of these resonances, no accurate information can be obtained about the fraction of mono-, bi-, and trisubstituted silicon atoms. For the PTES-grafted silica no resonance was measured in the range from −48 to −66 ppm. The coupling agent content on the silica surface seems to be below the detection limit of the recorded NMR spectrum.

Additional information about the grafting density could be obtained from the ^{29}Si resonances at −91 to −109 ppm. It has been established by Sindorf and Maciel[33] that the fraction of Q^2, Q^3, and Q^4 silicon atoms can be determined at a cross-polarization time (τ_{cp}) of approximately 10 ms, which is similar to the 8 ms employed in the present study. The high intensities of the resonances at −91 and −100 ppm indicate the presence of significant quantities of unreacted hydroxyl groups on the surface and in the pores of the silica particles, which have not reacted with a coupling agent. However, as stated before, NMR is not able to provide quantitative information about the grafting density of coupling agents on the silica, owing to the presence of condensation products of the coupling agents.

Elemental analysis was therefore used to obtain additional information about this surface coverage. Results are also listed in Table 2. It is important to note that elemental analysis also does not fully answer the

Table 2. Results of Elemental Analysis (Percentages by Weight) of Hydrophilic and Grafted Silica Particles[a] and the Minimum Possible Grafting Density Estimated in % of Reacted Silanol Groups

sample	C (%)	H (%)	N (%)	S (%)	H_2O (%)	minimum grafting density (%)
SiO_2	0.59 ± 0.06	1.16 ± 0.08			4.88 ± 0.02	
SiO_2−PTES	4.35 ± 0.04	1.75 ± 0.05			4.56 ± 0.02	91.6
SiO_2−MPTES	5.13 ± 0.02	1.75 ± 0.07		0.57 ± 0.04	4.64 ± 0.07	90.7
SiO_2−TESBD	6.50 ± 0.01	1.89 ± 0.07	0.18 ± 0.02	1.03 ± 0.09	4.06 ± 0.10	75.0
SiO_2−TESPT	5.69 ± 0.03	1.81 ± 0.14		1.15 ± 0.04	4.65 ± 0.08	62.2

[a] Errors correspond to differences in duplicate results.

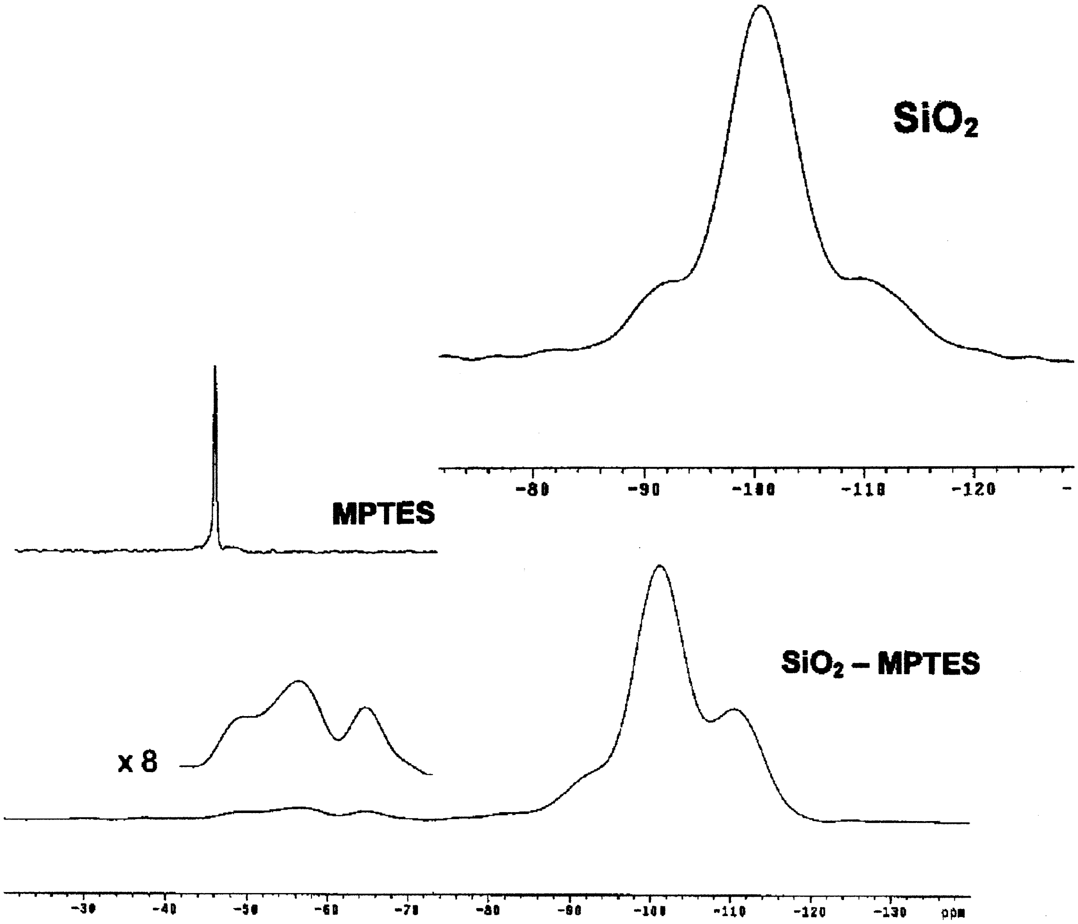

Figure 4. ^{29}Si CPMAS spectra for hydrophilic silica and silica−MPTES. The ^{29}Si MAS spectrum for liquid MPTES is shown on the insert and plotted on the same scale as silica−MPTES.

question about grafting density: it does not discriminate between a chemically grafted coupling agent and a physically adsorbed material; it depends on the way the coupling agent is condensed on the silica surface. For sake of clarity, the word "grafting density" will be used throughout the text, with the understanding that not only chemical but also physical surface coverage is included. The carbon content found for the grafted silicas is greater than for the corresponding nongrafted silica particles, confirming the presence of silane grafted to the silica surface. The carbon content of the pure, nongrafted silica must be due to C_2H_5 groups, since no other organic groups are involved in their synthesis. A range of possible grafting densities can now be derived from these elemental analyses as shown below for SiO_2−PTES, as an example. For that purpose, one has to realize that the calculated surface coverage depends on the degree of condensation. Zhuravlev and other authors[34−36] (and references in the publications of these authors) measured the OH group concentration of 100 different amorphous precipitated silicas and concluded that irrespective of their preparation method and their structural characteristics the number of silanols per unit surface area is a physicochemical constant equal to approximately 5 groups/nm^2 of SiO_2. Assuming that only one ethoxy group of PTES has reacted with one silanol group on the silica surface and that no mutual condensation of the other two ethoxysilane groups has taken place, a grafting density of 91.6% of the silanol groups on the silica surface can be derived from the carbon content. This value corresponds to the minimum grafting density, since the grafting density becomes even higher (up to >100%) if more than one ethoxy group of PTES has reacted either with silanol groups on the silica surface or by condensation between adjacent grafted silanes. Although peaks in the range −48 to −66 ppm in the ^{29}Si NMR spectra indicated the presence of such condensation products and of grafting, they were insufficiently quantitative to determine the relative contribution of either way of condensation. It can merely be concluded that the grafting density is at least 91.6%. In a similar manner, minimum grafting densities for

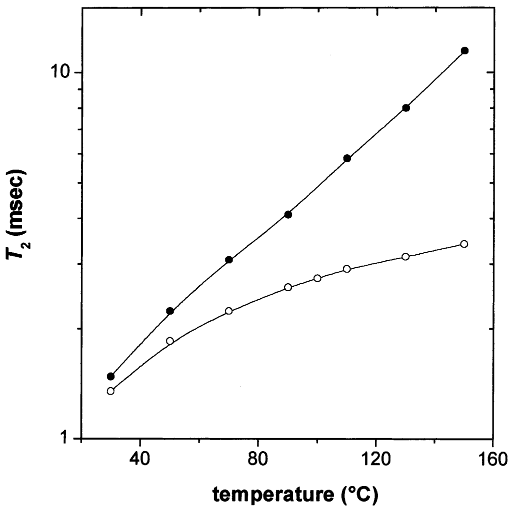

Figure 5. Temperature dependence of the T_2 relaxation time for nonvulcanized (●) and vulcanized NR (○).

MPTES, TESBD, and TESPT of 90.7%, 75.0%, and 62.2% are estimated, respectively. One reason for the grafting density being lower than 100% may, as been noted before by Chung, Kinney, and Maciel,[37] be that some of the silanol groups on the porous silica surface, presumably those occluded in the porous particle, are barely accessible for silylation.

It further appears from the ^{29}Si NMR data that the number of ethoxysilane groups that remain unreacted is greatest for the silica−TESPT sample, compared to the other silane-grafted silica samples. This may be due to a lower grafting density, but may also be because TESPT has double the quantity of ethoxy groups compared with the other silanes, leading to a greater quantity of possibly unreacted ethoxy groups. Another explanation can be the larger sterical hindrances involved with TESPT.

Identification of a Temperature to Analyze Network Density. To reveal the influence of network junctions on the relaxation behavior of NR, the temperature dependence of ^1H NMR T_2 relaxation was measured for nonvulcanized and vulcanized NR nonreinforced gum stock (Figure 5). The T_2 relaxation time for nonvulcanized NR increases continuously with rising temperature in the range studied. This behavior is commonly attributed to an increase in the amplitude and the frequency of large spatial-scale chain motions. In contrast with the nonvulcanized sample, the vulcanizate exhibits only a moderate increase in T_2 when the temperature increases. The difference in T_2 values for the samples is therefore related to the effect of cross-linking. It must be noted, however, that the temperature dependence of the T_2 relaxation for the present NR vulcanizate does not show a well-defined high temperature "rubber plateau", unlike well-cured rubbers.[38−40] This suggests that the vulcanizate still contains a significant fraction of network defects, such as chain loops, dangling chain ends, loosely cross-linked moieties, and residues of nonvulcanized material. It appears from the results in Figure 5 that a difference in T_2 values above 80 °C between nonvulcanized and vulcanized NR can be used as a quantitative measure of the density of network chains.

Immobilization of Rubber Chains at the Silica Surface and the Nature of the Physical Rubber—Filler Network for Nonvulcanized Samples. T_2 relaxation experiments for all unmodified and grafted silicas and silica-filled NR compounds were performed at 100 °C. At this temperature, the results can to a greater or lesser extent be related quantitatively to the volume-average density of physical junctions in the silica-filled NR. The amount of silica taken for the experiment was equal to that in the silica-filled NR compounds. Since the experimental setup used for the experiments with the silicas and silica-filled NR compounds was the same, this enables the contribution made by the silica protons to the relaxation of the silica-filled NR to be determined.

Molecular Mobility at the Surface of Hydrophilic and Grafted Silicas. The decay of the transverse magnetization, the T_2 decay, for pure silica can be described with a single-exponential function with the characteristic decay time $(T_2^{l})^{OH}$ of 0.1 ms (Figure 2a, Figure 6a, and Table 3). Hydrogen atoms of adsorbed water, silanol hydrogen on the silica surface, and protons of residual ethanol apparently cause this relaxation.

The T_2 decay for the noncompounded grafted silicas can be fitted by two distinct components, which are characterized by a $(T_2^{s})^{sil}$ of approximately 0.03 ms and a $(T_2^{l})^{OH}$ of 0.16−0.19 ms (Figure 2b, Figure 6b−e, and Table 3). The relative fractions of these components are represented by $A(0)^{sil}$ and $A(0)^{OH}$, respectively. These fractions are proportional to the hydrogen content of the material responsible for this relaxation. The short relaxation time $(T_2^{s})^{sil}$ in grafted silicas is most probably caused by relaxation of the grafted chains. This relaxation time is only slightly longer than that for glassy materials (≈0.01−0.02 ms), suggesting a strong immobilization of the grafted chains on the silica surface. The long relaxation time $(T_2^{l})^{OH}$ for grafted silicas is most probably caused by adsorbed water and possibly also by mobile free chain ends of the grafted and/or adsorbed material. The amplitude of this component, $A(0)^{OH}$, represents 20−32% compared to that observed for pure silica. This indicates that grafting of coupling agents is accompanied by a decrease in the amount of adsorbed water on the silica surface. A small decrease in the amount of adsorbed water had already been found previously (part 3.1) by the Karl-Fisher determination.

Rubber—Filler Interface in Nonswollen Silica-Filled NR. The situation for rubber filled with grafted silica is represented in Figure 2c. Two main microregions can be distinguished, the rubber−silica interface, which is almost glassy (blue, measured with SEPS) and the rubber matrix (green + red, measured with HEPS). The network region in the rubber matrix gives rise to two different relaxation times, one originating from rubber loosely bound to the silica (green), which forms a physical network, and one arising from free, extractable rubber (red). No statistically relevant data can be obtained by fitting of the relaxation of almost rigid material with two components. In consequence, the relaxation of the −OH, the grafted silanes and immobilized NR is represented by one relaxation time.

The normalized amplitude of the relaxation component with the short decay time, $A(0)^{sil+NR}$, is larger by about a few percent than that of the pure initial silicas, $A(0)^{OH} + A(0)^{sil}$ (Figure 7). This indicates that a small fraction of chain units of NR is strongly immobilized by interactions with the silica surface. Since direct chemical attachment of rubber chains to the silica

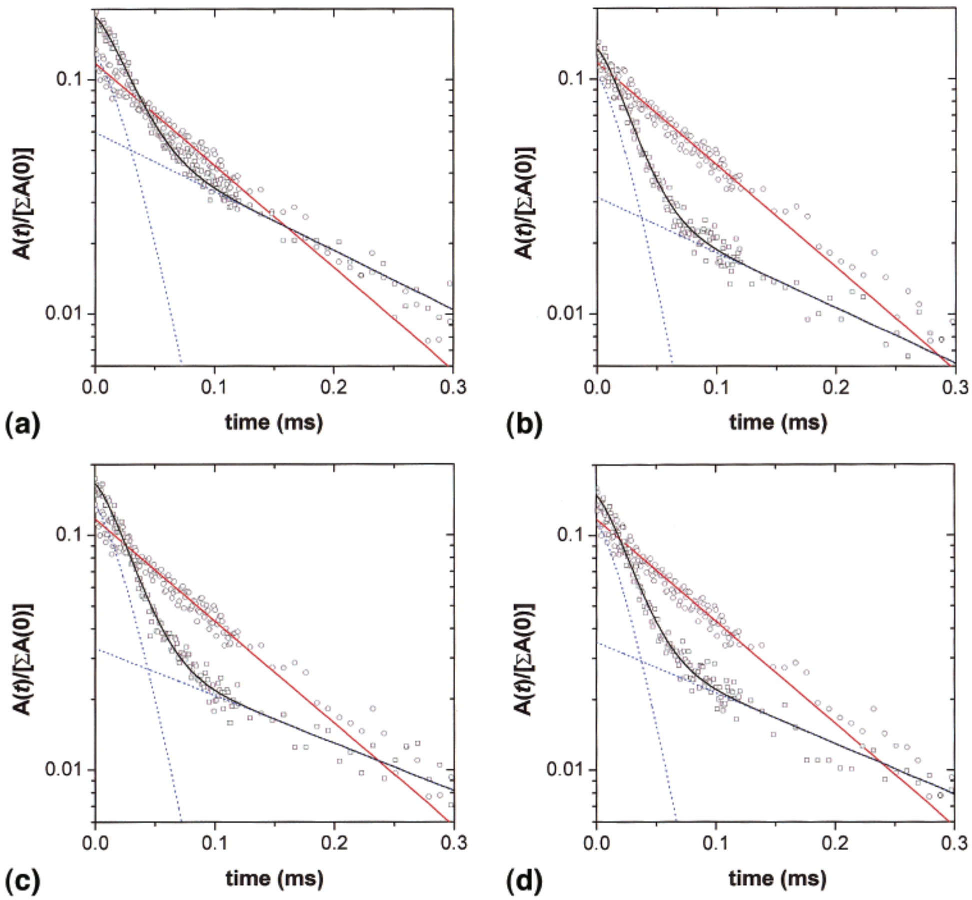

Figure 6. Decay of the transverse magnetization at 100 °C for hydrophilic silica (○ and red line, a−d) and for silica grafted with (a) PTES (□), (b) MPTES, (c) TESBD, and (d) TESPT. The decays are measured with the SEPS and normalized to the total amplitude of the transverse magnetization [$\Sigma A(0)$] measured for silica-filled NR containing the same amount of silica. Solid lines represent the result of a least-squares fit of the decay. For the grafted silica the separate components are represented by blue, dotted lines. Fitting functions and the relaxation parameters are given in Tables 2 and 3, respectively.

Table 3. ^{1}H NMR T_2 Relaxation Times and the Fractional Amplitude of the Relaxation Components, As Measured at 100 °C for Silica Samples

sample	$(T_2^s)^{sil}$ (ms)	$(T_2^l)^{OH}$ (ms)	$A(0)^{sil}$	$A(0)^{OH}$
SiO_2		0.100 ± 0.002		100
SiO_2−PTES	0.032 ± 0.001	0.17 ± 0.02	68 ± 3	32 ± 7
SiO_2−MPTES	0.029 ± 0.001	0.18 ± 0.03	77 ± 3	23 ± 9
SiO_2−TESBD	0.031 ± 0.001	0.21 ± 0.03	80 ± 2	20 ± 8
SiO_2−TESPT	0.030 ± 0.001	0.20 ± 0.03	76 ± 3	24 ± 9

surface is improbable, the immobilization must be caused by physical adsorption of NR on the silica surface. An exception is the MPTES-grafted silica, for which there is evidence that the −SH− group of the MPTES is highly reactive toward rubber.[41,42] The value of $(T_2^s)^{sil+NR}$ is comparable to that of pure NR in the glassy state: 0.0101 ± 0.0001 ms. Apparently, a shell of glasslike adsorbed NR is formed on the silica surface.

The relaxation component with the longer decay time has a rather complex shape. This component originates from the relaxation of the rubber matrix outside the interfacial layer (Figure 2c). A single exponential does not suffice in this case. The significant deviation from a single-exponential relaxation is due to the complex origin of the relaxation itself[26] and an apparent heterogeneity of the samples studied. Because of filler aggregation, which results in a heterogeneous distribution of physical rubber−filler junctions, analysis of the heterogeneous distribution of adsorption network junctions in the compounds is made more difficult by the effect of chain entanglements. Because of these reasons quantitative analysis of the relaxation components with respect to network structure in samples as a whole is complicated. On the time scale of the NMR experiment—on the order of milliseconds—the chain entanglements restrict the long spatial-scale chain dynamics in the same way as do chemical or physical adsorption junctions.[40] It has been demonstrated that valuable information concerning the structure of heterogeneous networks can be obtained by means of ^{1}H NMR T_2 relaxation experiments for swollen rubbers.[12]

Rubber—Filler Interactions and the Structure of Physical Networks in Swollen Samples. The T_2 for swollen silica-filled NR consists of three components with short, $(T_2^s)^{sil+NR}$, intermediate, $(T_2^{in})^{NR}$, and long, $(T_2^l)^{NR}$, decay times (Table 4 and Figures 2c and 7). Again the normalized amplitude, $A(0)^{sil+NR}$, is a few percent larger than that of pure initial silicas, $A(0)^{sil}$ (Table 5). The values of $(T_2^s)^{sil+NR}$ and $A(0)^{sil+NR}$ are barely affected by swelling, suggesting rubber−filler interactions so strong that they remain even in the presence of a good solvent at 100 °C. Table 6 gives estimated fractions of NR immobilized on the silica surface. For swollen samples a significant distinction can now be made in relaxation times of loosely bound and free rubber in the rubber matrix. $(T_2^{in})^{NR}$ is in a range that is typical of network chains. This relaxation

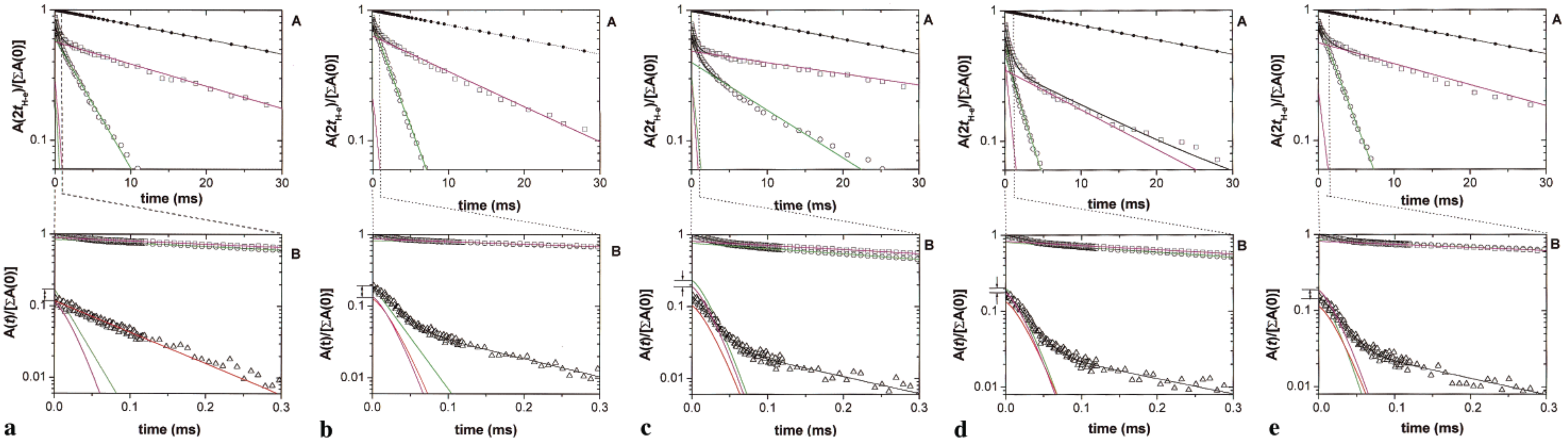

Figure 7. (A) Decay of the transverse magnetization at 100 °C for unswollen (○) and swollen (□) NR filled with hydrophilic and grafted silicas. The decay for swollen pure NR is shown by (●). The volume fraction of 1,1,2,2-$C_2D_2Cl_4$ was 40%, relative to the rubber phase. The decay is measured with HEPS and normalized to the total amplitude of the transverse magnetization [ΣA(0)]. (B) Initial part of the decay as measured with the SEPS for hydrophilic (△) (part a) and grafted silica (△) (parts b−e) and unswollen (○) and swollen (□) NR filled with the same silica. Solid, black lines represent the result of a least-squares fit of the decay. The separate components for filled NR are shown by green lines for the nonswollen and purple lines for the swollen sample. $(T_2^s)^{sil}$ relaxation components for hydrophilic and grafted silicas are shown with red and bleu lines, respectively. Fitting functions are given in Table 2. Parts a−e represent the results for hydrophilic silica and PTES-, MPTES-, TESBD-, and TESPT-grafted silicas and NR filled with the same silica, respectively. The increase in the amplitude of the relaxation component with short decay time $(T_2^s)^{sil+NR}$ is highlighted by arrows.

Table 4. ^{1}H NMR T_2 Relaxation Times and the Fractional Amplitude of the Relaxation Components of Pure NR and Silica-Filled NR Swollen in 40 vol % 1,1,2,2-$C_2D_2Cl_4$, As Measured at 100 °C^a

sample	$(T_2^s)^{sil+NR}$ (ms)	$(T_2^{in})^{NR}$ (ms)	$(T_2^l)^{NR}$ (ms)	$A(0)^{sil+NR}$	$A(0)^{in}$	$A(0)^l$
NR			39.3 ± 0.2			100
NR + SiO_2	0.027 ± 0.003	0.57 ± 0.02	25.6 ± 0.5	11 ± 6	32 ± 2	57 ± 1
NR + SiO_2−PTES	0.029 ± 0.002	0.73 ± 0.06	16.0 ± 0.4	13 ± 4	23 ± 4	64 ± 2
NR + SiO_2−MPTES	0.027 ± 0.002	0.55 ± 0.03	50.2 ± 0.9	19 ± 3	31 ± 2	50 ± 1
NR + SiO_2−TESBD	0.028 ± 0.002	0.83 ± 0.05	17.8 ± 0.9	17 ± 3	46 ± 2	36 ± 3
NR + SiO_2−TESPT	0.028 ± 0.002	0.90 ± 0.07	27.0 ± 0.7	18 ± 3	25 ± 3	57 ± 2

[a] The volume fraction of the solvent for silica-filled NR corresponds to the solvent content in the rubber matrix.

Table 5. Fractional Amplitude $A(0)$ of the Relaxation Component $(T_2^s)^{sil}$ for Silicas, and $(T_2^s)^{sil+NR}$ for Swollen Silica-Filled NR Containing 40 vol % 1,1,2,2-$C_2D_2Cl_4$ in the Rubber Matrix[a]

sample	$A(0)^{sil}$	$A(0)^{sil+NR}$
SiO_2	0	0.147 ± 0.003
SiO_2−PTES	0.125 ± 0.004	0.138 ± 0.002
SiO_2−MPTES	0.103 ± 0.003	0.230 ± 0.002
SiO_2−TESBD	0.132 ± 0.003	0.197 ± 0.003
SiO_2−TESPT	0.113 ± 0.003	0.155 ± 0.002

[a] The amplitudes $A(0)^{sil}$ and $A(0)^{sil+NR}$ are normalized to the total amplitude of the decay of the transverse magnetization, $\sum A(0)^i$, as measured with the SEPS for silica-filled NR at 100 °C.

Table 6. Mean Molar Mass $\langle M_{ad}\rangle_w$ (g/mol) and the Number of Monomer Units $\langle N_{ad}\rangle$ between Adjacent Adsorption Junctions along a Chain, the Estimated Mean Number of the Main Chain Carbon Bonds That Form a Single Adsorption Junction, $N_{C-C\ bonds\ adsorbed}$, and the Fraction of Immobilized NR (% $NR_{Immobilized}$)

sample	$\langle M_{ad}\rangle_w$	N_{ad}	$N_{C-C\ bonds\ adsorbed}$	% $NR_{immobilized}$
NR + SiO_2	710	11	8	14.7
NR + SiO_2-PTES	910	13	1	1.3
NR + SiO_2-MPTES	690	10	6	12.7
NR + SiO_2-TESBD	1040	15	4	6.5
NR + SiO_2-TESPT	1120	17	3	4.2

component has been assigned to a bound fraction of NR, similar to that in carbon black filled EPDM.[12] The longest decay time $(T_2^l)^{NR}$ of 16−50 ms is comparable to that of swollen nonvulcanized NR (39 ms). This component must therefore be assigned to the relaxation of free rubber chains, which have hardly any attachment to the silica surface.

Figure 8 shows the effect of variation in the solvent content on T_2 in the rubber phase for pure NR, and NR filled with MPTES. At volume solvent contents, V_s, of below 20%, both $(T_2^{in})^{NR}$ and $(T_2^l)^{NR}$ increase slightly with increasing solvent content (Figure 8). This is mainly the result of chain disentanglement.[12,40] At V_s > 20%, $(T_2^{in})^{NR}$ (a) and $A(0)^{in}$ (b) are hardly affected any more by the degree of swelling, whereas $(T_2^l)^{NR}$ increases continuously upon swelling, similar to that for unfilled NR (Figure 8a). This is again an indication that the $(T_2^l)^{NR}$ component is related to the relaxation of free rubber chains, which are hardly attached to the silica surface.

The Mean Molar Mass between Physical Junctions. The entire collection of data indicates that a quasi-permanent rubber−silica network is formed in the samples owing to physical adsorption of chain units at the silica surface: a value of % $NR_{immobilized}$ (Table 6) represents the fraction of NR bound so tightly that even in swollen samples it behaves in an almost rigid, glassy manner. The $A(0)^{in}$ represents the fraction of the network material known as bound rubber. Similar behavior has been observed for the bound fraction of both carbon black and silica-filled rubbers[11,13−16,40] of different nature.

The distinguishing feature of the T_2 relaxation for viscoelastic networks is the plateau observed at temperatures that are well above T_g. The temperature-independence of T_2 in that plateau (T_2^{pl}) is attributed to constraints, which limit the number of possible conformations of a network chain relative to those of a free chain. For Gaussian chains the theory of transverse relaxation in elastomeric networks relates T_2^{pl} to the number of statistical segments in the network chains, Z, between chemical and physical network junctions[38,39]

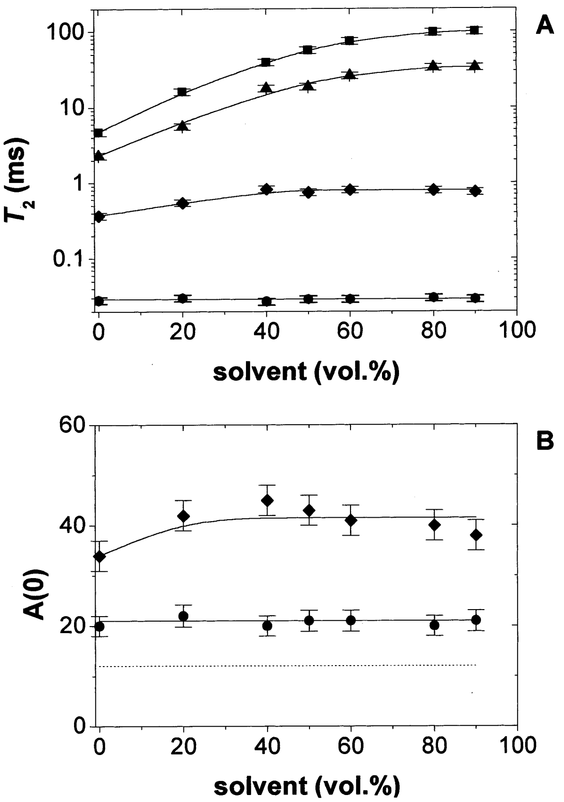

Figure 8. (A) Influence of the solvent content (vol %), relative to the rubber phase, on the T_2 relaxation time of pure NR (■), and relaxation times (●) $(T_2^s)^{sil+NR}$, (◆) $(T_2^{in})^{NR}$, and (▲) $(T_2^l)^{NR}$ of NR filled with MPTES-coated silica. (B) Influence of the solvent concentration, relative to the rubber phase, on the fraction of $A(0)^{sil+NR}$ (●) and $A(0)^{in}$ (◆). The dotted horizontal line represents the initial amplitude of the T_2 decay for silica coated with MPTES, with the amount of the silica used equal to that in the silica-filled NR.

$$Z = (T_2^{pl})/[a(T_2^{rl})] \qquad (1)$$

where a is a theoretical coefficient which depends on the angle between the segment axis and the internuclear vector for the nearest nuclear spins at the main chains. For polymers containing aliphatic protons in the main chain, this coefficient a is close to 6.2 ± 0.7.[38] T_2^{rl} is the relaxation time measured below T_g for the polymer swollen in a deuterated solvent. T_2^{rl} for NR as measured at −160 °C is 0.0101 ± 0.0001 ms. Using the number of backbone bonds in one statistical segment, designated as C_∞, the weight-average molar mass of chains between adsorption junctions and trapped chain entanglements, $\langle M_{ad+en}\rangle$, can be calculated from $(T_2^{in})^{NR}$

$$\langle M_{ad+en}\rangle = ZC_\infty M_u/n \qquad (2)$$

where M_u is the molar mass of one monomer unit of NR and n is the number of backbone bonds per monomer unit. A C_∞ of approximately 4.6 ± 0.8 rotatable bonds of the backbone of NR[43−46] was used for the calculations. The results are listed in Table 6. Since no chemical cross-links are present in the samples studied the $\langle M_{ad+en}\rangle$ value for swollen samples is determined by the density of physical junctions such as trapped chain entanglements and adsorption junctions at the filler surface.[12,40] It will be shown below that adsorption junctions make the greatest contribution to the $\langle M_{\mathrm{ad+en}}\rangle$ value. The mean molar mass of NR chains between adjacent adsorption junctions along a chain can now be calculated from $(T_2^{\mathrm{in}})^{\mathrm{NR}}$ at $V_s = 40\%$. At this solvent content temporary chain entanglements barely contribute to the $\langle M_{\mathrm{ad+en}}\rangle$ value.[12,40] Values obtained are given in Table 6. According to different authors, the molar mass between apparent chain entanglements in unfilled and unvulcanized NR ($\langle M_{\mathrm{en}}\rangle$), as derived from equilibrium moduli in rheological measurements, equals 4700 ± 800 g/mol.[43−46] The $\langle M_{\mathrm{ad+en}}\rangle$ values calculated for the present silica-reinforced samples are all lower than $\langle M_{\mathrm{en}}\rangle$ by a factor of approximately 5. This much lower $\langle M_{\mathrm{ad+en}}\rangle$ is not surprising, because it is an indication of a significant proportion of physical junctions formed by immobilized chain units at the filler surface. The stronger the interaction between the rubber and the silica, the more pronounced the quantity of immobilized NR. The samples with the largest quantity of immobilized NR of about 12−15% of the total rubber—Table 6, the hydrophilic silica-filled NR and the MPTES-grafted silica-filled NR—show the lowest $\langle M_{\mathrm{ad+en}}\rangle$, of 710 and 690 g/mol, respectively.

The Effect of Coupling Agents on the Silica—NR Interface. The mean number of carbon−carbon bonds per adsorption junction, $N_{\mathrm{C-C\ bonds\ adsorbed}}$, can be estimated from

$$\%\ \mathrm{NR}_{\mathrm{immobilized}} = N_{\mathrm{C-C\ bonds\ adsorbed}}/(N_{\mathrm{C-C\ bonds\ adsorbed}} + N_{\mathrm{phys}}) \quad (3)$$

The fraction of immobilized rubber and the length of the adsorbed chain at a single junction is largest for NR filled with pure silica and NR filled with MPTES-grafted silica, compared to the other samples (see Table 6). For pure silica as well as for the MPTES-grafted silica, the fraction of adsorbed NR chains is between 10 and 15%: Table 6. This is 2−10 times higher than with the other grafted silicas.

Several reasons can cause the differences in the fraction of immobilized NR, the number of C−C bonds per single adsorption junction and consequently, on the structure of the physical, rubber−silica network: i.e., (1) the chemical affinity, or the physical compatibility, of the silica surface with NR; (2) the grafting density of the coupling agent at the silica surface, which can be different for the silica samples; (3) the bulkiness of the grafted chains, which causes steric hindrance for the chain adsorption; (4) dispersion of silica particles in the rubber matrix.

The fraction of immobilized NR chain units decreases upon treatment of the silica with a coupling agent. In the case of pure silica, the large amount of immobilized rubber on the silica surface is somewhat surprising. However, Legrand et al.[14] also found that surface grafting of silica was associated with a decrease in the strength of adsorption of polybutatiene, similar conclusions follow from the results of the present study of silica-filled NR. Bound rubber experiments of hydrophilic and surface grafted silicas in SBR/BR blends similarly showed a relatively high percentage of bound rubber on the sample without silane grafting.[47]

Results described above imply that there is no major difference in the grafting density or loosely grafted areas on the silica surface exist. On the other hand, grafting of the silica is expected to enhance dispersion of the silica particles. At low grafting density, more aggregation of the silica remains, resulting in a smaller surface area accessible for rubber chains and hence a smaller fraction of immobilized material. However, this is in disagreement with the results found for the mixture of NR with hydrophilic silica, which showed a relatively high proportion of immobilized NR for this sample. It is therefore suggested that Si−OH groups are the active sites for chain adsorption. Surface roughness of aggregates can also increase the strength of the adsorption.[48,49]

Within the range of grafted silicas a more or less logical order is obtained for the proportion of immobilized NR. For the MPTES-grafted silica, the high fraction of immobilized rubber can be explained by the high affinity of the −SH− group of the silane for the rubber and the possibility of the formation of a chemical bond between the silane and the NR. The affinity of the −SH− group toward 1,2-vinyl, 1,4-cis, and 1,4-trans double bonds in polybutadiene, for example, was shown by Klemm and Gorski.[41,42] The 1,2-vinyl group turned out to have a very high reactivity toward the −SH− group, followed by the 1,4-cis double bond. A complex structure between the −SH− group and the 1,4-cis double bond is proposed to explain the reactivity of the 1,4-cis double bond. As before, comparison of the *cis*-polybutadiene and the *cis*-polyisoprene (NR) appears to be a logical step. The other extreme, PTES-grafted silica, shows hardly any adsorbed NR chains. In view of the aforegoing, this is to be expected because PTES has no rubber-reactive group, as well as because the strength of the physical adsorption is weak.

Conclusions

^{1}H NMR T_2 relaxation is a technique which is very useful to get information about interactions and network structure. By measurement of relaxation times of silica-filled, nonvulcanized NR samples, three separate regions with a strongly different mobility were detected.

The region with the lowest mobility originates from a layer of rubber chains and coupling agent molecules, tightly bound to the silica surface. The fraction of immobilized chains depends on the nature of the silica surface and is the largest for NR mixtures with hydrophilic silica without coupling agent. Grafting of the silica surface by coupling agent leads to a decrease in the amount of immobilized chains. This corresponds to earlier similar observations for silica−polybutadiene combinations. The immobilization of chains seems to be due to very strong physical adsorption, since the fraction of immobilized chains is not affected by the presence of a good solvent or by a high temperature of 100 °C. In the case of grafted silicas, the chemical structure of the coupling agent seems to have an influence on the fraction of immobilized rubber chains. NR filled with MPTES-grafted silica shows the highest proportion of immobilized chains. This can be explained by the great affinity of the −SH group of MPTES for the C═C-bond in NR. PTES on the other hand, cannot react with NR and only shields the silica surface, thereby making it inaccessible to physical adsorption with the NR, leading to the lowest fraction of immobilized chains.

A region with intermediate mobility can be related to network chains, with physically adsorbed chain portions acting as network junctions. In the case of MPTES-grafted silica some chemical bonds between NR and the silica by means of the coupling agent may be involved as well. The presence of a good solvent influences the mobility of these network chains to some extent mainly due to chain disentanglements.

The region with a high mobility originates from free, extractable rubber chains and is strongly influenced by the presence of a good solvent. The mobility of this rubber portion changes nearly as much as the mobility of pure NR in the presence of a good solvent.

In terms of physical interactions and the structure of the physical network, there is a marked similarity between NR filled with carbon black and NR filled with silicas. The concept of rubber chains immobilized on a carbon black surface, as represented by several authors, also appears to be applicable to silica-filled NR.

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List of Symbols and Abbreviations

^{1}H NMR	proton nuclear magnetic resonance
T_2	spin−spin (transverse) relaxation time
δ	chemical shift
m	multiplet
q	quartet
t	triplet
$t_c(90)$	curing time
$(T_2^{\mathrm{l}})^{\mathrm{OH}}$	T_2 relaxation time of silanol groups and water molecules on the surface of hydrophilic silica
$(T_2^{\mathrm{s}})^{\mathrm{sil}}$	T_2 relaxation time of the grafted chains
$(T_2^{\mathrm{in}})^{\mathrm{NR}}$	T_2 relaxation time of NR network chains
$(T_2^{\mathrm{l}})^{\mathrm{NR}}$	T_2 relaxation time of free NR
$(T_2^{\mathrm{s}})^{\mathrm{sil+NR}}$	T_2 relaxation time of silica-NR interface
(T_2^{pl})	T_2 relaxation time in the rubber plateau
(T_2^{rl})	T_2 relaxation time below the glass transition temperature
$A(0)^{\mathrm{OH}}$	relative amplitude of $(T_2^{\mathrm{l}})^{\mathrm{OH}}$ relaxation component
$A(0)^{\mathrm{sil}}$	relative amplitude of $(T_2^{\mathrm{s}})^{\mathrm{sil}}$ relaxation component
$A(0)^{\mathrm{in}}$	relative amplitude of $(T_2^{\mathrm{in}})^{\mathrm{NR}}$ relaxation component
$A(0)^{\mathrm{l}}$	relative amplitude of $(T_2^{\mathrm{l}})^{\mathrm{NR}}$ relaxation component
$A(0)^{\mathrm{sil+NR}}$	relative amplitude of $(T_2^{\mathrm{s}})^{\mathrm{sil+NR}}$ relaxation component
τ_{cp}	cross-polarization time
Z	number of statistical segments in the network chains
a	a theoretical coefficient
C_∞	number of backbone bonds in one statistical segment
$\langle M_{\mathrm{ad+en}}\rangle$	weight-average molar mass of chains between adsorption junctions and entanglements
$\langle M_{\mathrm{en}}\rangle$	weight-average molar mass of chains between entanglements
M_{u}	molar mass of one monomer unit of NR
n	number of backbone bonds per monomer unit
$N_{\mathrm{C-C\ bonds\ adsorbed}}$	number of carbon−carbon bonds per adsorption junction
% $\mathrm{NR}_{\mathrm{immobilized}}$	fraction of immobilized rubber
N_{en}	mean number of monomer units between adjacent adsorption junctions along the chain
TES	tetraethoxysilane
PTES	propyltriethoxysilane
MPTES	(3-mercaptopropyl)triethoxysilane
TESPT	bis(triethoxysilylpropyl) tetrasulfide
TESBD	2-benzothiazyl-(3-triethoxysilyl)propyl disulfide
MBTS	dibenzothiazole disulfide
TESPD	tetraethoxysilylpropyl disulfide
$\mathrm{CDCl_3}$	deuterated chloroform
S-SBR	solution SBR
BR	butadiene rubber
NR	natural rubber
MAS	magic angle spinning
CP	cross-polarization
TMS	tetramethylsilane
SEPS	solid−echo pulse sequence
HEPS	Hahn−echo pulse sequence
$\mathrm{C_2D_2Cl_4}$	1,1,2,2-deuterated tetrachloroethane
CBS	*N*-cyclohexyl-2-benzothiazolesulfenamide
S	sulfur
phr	parts per hundred rubber
ppm	parts per million
V_{s}	solvent content as vol %

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