Macromol. Symp. ***187****, 573–584 (2002)*

Fumed Silica – Rheological Additive for Adhesives, Resins, and Paints

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Summary: Fumed silica, a synthetic silicon dioxide, is a powerful rheological additive for resins and paints to introduce thixotropy or even a yield point. The rheological effectiveness of fumed silica is based on its ability to form percolating networks which immobilize large volumes of liquid. By a combination of advanced rheological experiments, spectroscopical investigations, and quantum chemical calculations it could be demonstrated that the formation and stability of the silica network is strongly influenced by particle-resin interactions. The results can be used to develop comprehensive models, which explain the rheological performance of different grades of fumed silica in different resins.

Keywords: fumed silica/ unsaturated polyester resins/ vinyl ester resins/ intermolecular interactions/ rheology

Introduction

Fumed silica is a synthetic amorphous silicon dioxide produced by hydrothermal hydrolysis of chlorosilanes in an oxygen-hydrogen flame. In this process, as a first step, SiO_2 molecules are formed which collide and react to nano-size proto particles, which by further collision in a second step form primary particles of around 10 nm in size. The flame process itself leads to the formation of smooth particle surfaces, which provides fumed silica with a high potential for surface interactions. [1, 2] At the high temperatures of the flame primary particles are not stable but are fused together to form space-filling aggregates. Leaving the flame, at lower temperatures, the silica aggregates stick together by physico-chemical forces building up large micron-sized agglomerates and finally fluffy flocks . [3, 4]

Fumed silica is widely used in industry as an efficient thickening agent providing shear thinning and thixotropy to liquid media like adhesives, resins, paints, and inks. Various parameters control the rheological performance of fumed silica: (a) The smoothness of the primary particle surfaces which provides a maximum contact area for various types of interactions like H-bonding and Van-der-Waals interactions of dipolar and dispersive character. (b) The space-filling structure of the aggregates with a mass fractal dimension of $D_m < 2.7$, leading to a fluffy structure of agglomerates, typically with a 'density' d = 50-100 g/l (remark: density of amorphous silicon dioxide $d_{SiO2} = 2200$ g/l), and agglomerate sizes > 1 µm. (c) The high physico-chemical interaction potential of the fumed silica surface is based on its reactive surface silanol groups (surface density 1.8 SiOH/nm²), but is also due to its polar Si-O bonds containing bulk. By surface modification, most commonly surface silylation, these interactions can be controlled precisely.

Particle interactions are the driving force for agglomerate and network formation, enabling fumed silica to form percolating networks in liquid media. [5-7] Basically, two kinds of networks are possible: Firstly, a network of fumed silica particles or aggregates originating from direct particle-particle-contacts and, secondly, a network based on polymer bridging where aggregates are interacted by polymers at least on two particles. Real systems may consist of both and mixed types. At rest or very low shear rates these networks are able to immobilize large volume fractions of liquids even at low fumed silica loading (< 5 wt%), resulting in very high viscosities or a yield point, respectively. Upon applying shear forces the network structure is reversibly destroyed and the apparent viscosity of the mixture decreases with increasing shear rate. When the shearing stops the system is able to recover the network structure. Fig. 1 depicts this process schematically.

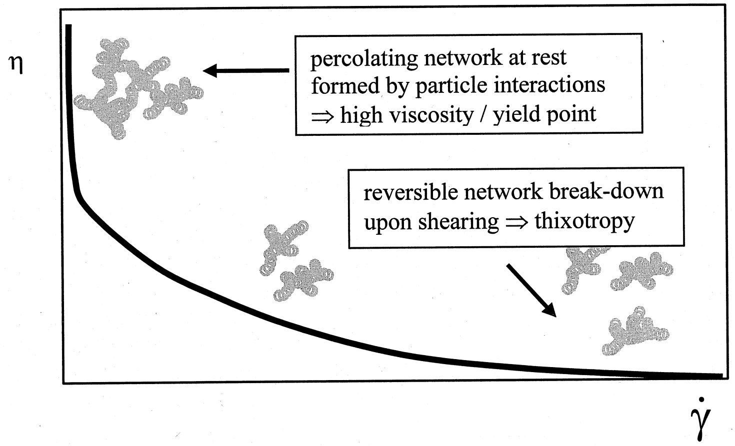

Figure 1. Dependence between shear rate, network structure, and viscosity.

Obviously, the rheological performance of fumed silica in adhesives, resins, and paints is mainly determined by the stability of the colloidal network. This raises the question which parameters influence the formation and stability of a colloidal silica network. In order to answer this question we have to understand a) the nature of interactions in silica/resin/solvent mixtures in terms of the interactions silica-silica, silica-resin, and silica-solvent, and b) how these interactions influence the rheological behavior of the mixtures. From these information we should be able to develop a comprehensive model that explains the rheological performance of different grades of fumed silica in different resin types.

Aim of this paper is to present comprehensive models of interactions comparing rheological results, analytical data from spectroscopic methods such as solid state NMR and IR, and quantum chemical calculations. Furthermore we demonstrate how these interactions influence the rheology of fumed silica in unsaturated polyester (UP) and vinyl ester (VE) resins.

Experimental

Two grades of fumed silica with a different degree of surface treatment and different polarity have been used: A non-treated, hydrophilic Wacker HDK® N20 (BET surface area 200 m^2/g, 1.8 $SiOH/nm^2$ equivalent to 100 % residual SiOH) and a fully silylated hydrophobic Wacker

HDK® H18 (carbon content 4.5 %C, 15% residual SiOH), the latter is covered by a chemically grafted PDMS layer. Both silicas are products from Wacker-Chemie GmbH, Germany. The resins used are an unsaturated polyester resin Palatal P4 (UP resin), a co-condensate of a diol, maleic acid and orthophatalic acid, and the vinylester resin Atlac 590 (VE resin), a co-condensate of glycidine, methacrylic acid and bisphenol A. Both resins have a styrene content of 35% and were provided by DSM, NL.

Rheological studies have been performed using 3 techniques: (a) Measuring the step profile of the dynamic viscosity at a controlled but constant shear rate D at 1 s^{-1}, 10 s^{-1} and 100 s^{-1}, each 120 s, respectively. (b) Recording the dynamic behavior and thixotropy using a shear rate controlled relaxation experiment at D = 0.5 s^{-1} (conditioning), 500 s^{-1} (shear thinning), and 0.5 s^{-1} (relaxation). (c) Oscillation at a frequency of 1.6 s^{-1} and a deformation sweep between 0.001 to 10. (d) Determination of the yield point from a log-log plot of deformation γ vs. shear stress τ. The yield point is defined as the stress τ where the corresponding γ - τ curve exhibits a deviation > 5% from a tangent defined by data points at low shear stresses. All samples contained 3%wt of fumed silica.

^{13}C CPMAS spectra were recorded with cross polarization (CP) times of 0.5 and 8 ms for samples with a silica content of 4%.[8]

IR spectra were obtained from liquid samples using NaCl plates on a standard FT-IR spectrometer under compensation of the solvent signal.

Quantum chemical calculations were using cluster approach methods in a software Cluster Z1 and a modified PM3 parameter set.

Results and discussion

Rheological studies

It is well known that both, hydrophilic and highly hydrophobic fumed silica are efficient rheological additives for unsaturated polyesters. In more polar systems such as vinyl esters, however, only highly hydrophobic fumed silica is suitable. This observation is illustrated by the viscosity step profile of Wacker HDK N20 and H18 in Palatal P4 (UP) and Atlac 590 (VE), respectively, depicted in Fig. 2.

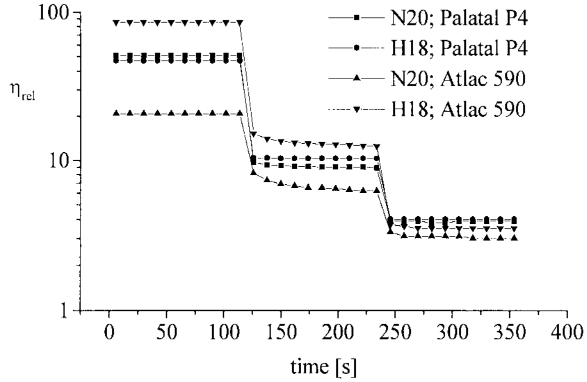

Figure 2. Relative viscosity in a shear rate step profile at D =1 s^{-1}, 10 s^{-1} and 100 s^{-1}, each 120 s, respectively, of 4 resin systems: Wacker HDK N20 and HDK H18 in Palatal P4 (UP resin) and Atlac 590 (VE resin); 35%wt styrene; 3%wt fumed silica.

The step profile reveals that N20 and H18 dispersed in Palatal P4 exhibit an almost identical rheological behavior, whereas the apparent relative viscosities of N20 and H18 dispersed in Atlac 590 at low and moderate shear rates are distinctly different. To explain this behavior it is necessary to consider the polarity, functional groups, and chain length of the resins but also the surface properties of the fumed silica. All parameters together will influence the nature and strength of the colloidal forces, which govern the rheology of the mixtures.

Firstly we investigated the rheology of Wacker HDK N20 and H18 in pure styrene. Fig. 3a shows the relaxation test experiment, 3b) the deformation sweep, and 3c) the determination of the yield point.

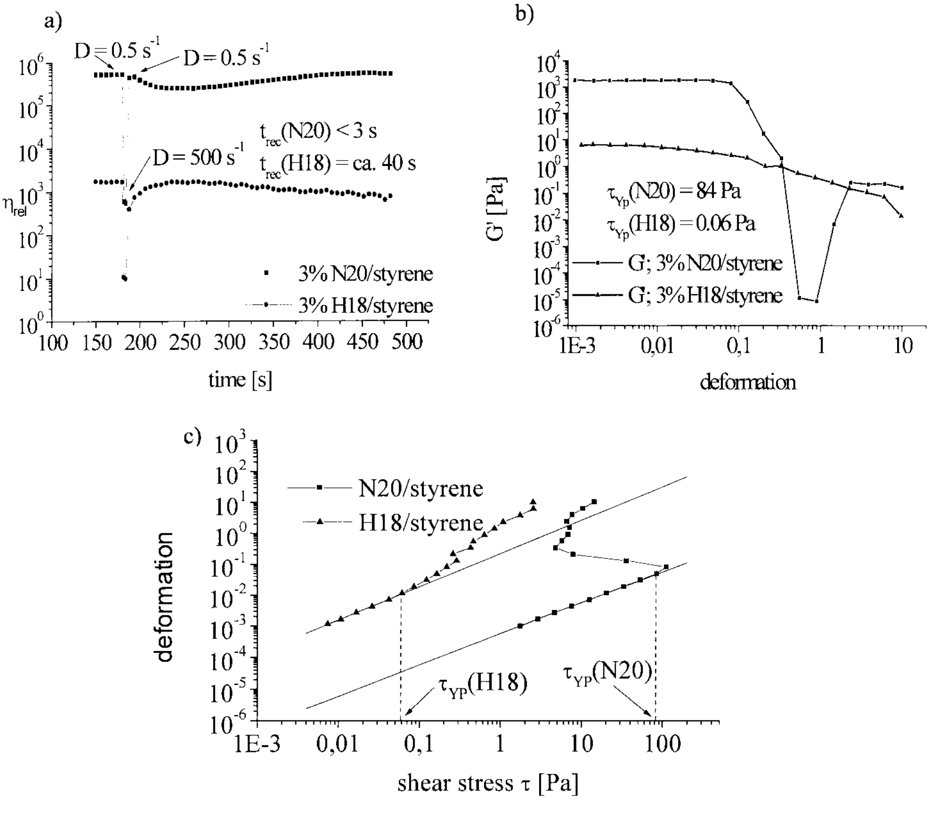

Figure 3: a) Controlled shear rate: relaxation experiment (profile D = 0.5 s^{-1}, 500 s^{-1}, and 0.5 s^{-1}) of N20 and H18 dispersed in styrene; b) oscillation: deformation sweep at a frequency of 1.6 s^{-1} and a deformation of 0.001 to 10 of N20 and H18 dispersed in styrene; c) determination of the yield point of N20 and H18 dispersed in styrene: data from deformation sweep.

Hydrophilic silica N20 forms an extremely stable and rigid network with a yield point of 84 Pa at 3%wt loading in pure styrene. Both experiments, relaxation and oscillation, reveal an instantaneous break down of the percolating structure upon exceeding the yield point, resulting in a low relative apparent viscosity η_{rel}, and a fast and complete recovering (< 3 s). However, under similar conditions, fully silylated silica exhibits a much weaker network with a yield point of around 0,06 Pa. The network is more elastic according to the deformation sweep experiment but recovers its structure after shear thinning markedly slower (ca. 40 s). The difference can be understood by H-bonding particle-particle interactions in the case of hydrophilic silica, which can recover the network structure almost instantaneously. For fully silylated silica we suggest a combination of hydrophobic interactions (interactions of hydrophobic particles in a hydrophilic environment are related to phase separation phenomena)[9] and entanglement of the grafted PDMS chains. This process of network forming can be seen as a kind of phase separation between the grafted PDMS and the styrene matrix. In this context it is important to know, that styrene is a worse-than Θ-solvent for PDMS.[10] However, phase separation between compounds of comparable polarity are inherently slow. The occurrence of a yield point for H18 in styrene is a strong indication for a combination of hydrophobic interactions and chain entanglement. Systems flocculated exclusively by hydrophobic interactions are supposed to show no yield point.[11]

In the presence of resin oligomers the situation is changed distinctly. Mixtures of UP resin Palatal P4/N20/styrene exhibit a much weaker but more flexible network than N20/styrene mixtures indicated by a yield point of about 10 Pa and a slow degradation of the network structure by increasing the deformation in the oscillation experiment (Fig. 4b).

More interestingly this structure degradation occurs in a step-wise manner which can be explained with a polymer bridging of the resin molecules between the fumed silica particles. The relaxation time of the N20 network structure after shearing is dramatically increased in the presence of Palatal P4 (Fig. 4a).

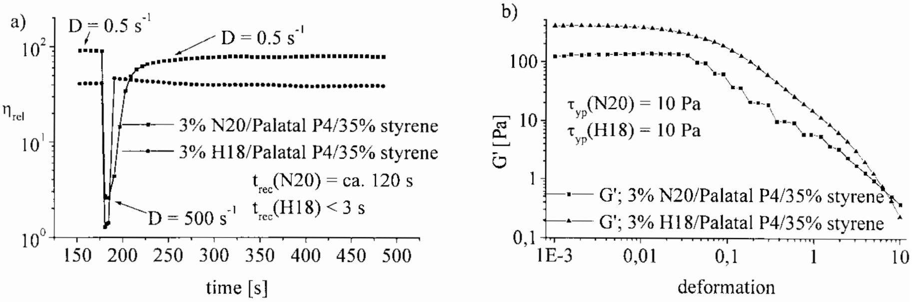

Figure 4. a) Controlled shear rate: relaxation experiment (profile D = 0.5 s^{-1}, 500 s^{-1}, and 0.5 s^{-1}) of N20 and H18 dispersed in Palatal P4/styrene; b) oscillation: deformation sweep at a frequency of 1.6 s^{-1} and a deformation of 0.001 to 10 of N20 and H18 dispersed in Palatal P4/styrene.

This effect can be explained with a reversible adsorption of resin molecules to the freshly provided surfaces of silica particles produced by shearing down the cluster structure of the N20 network. The re-formation of the network requires at least a partial desorption of the resin molecules which is a slow and time consuming process due to the multi-point interaction of the resin chains with the silica surface.[12]

For H18 we observe an increase of the network stability (yield point 10 Pa) in the oscillation experiment and a decrease of the relaxation time to less than 3 s in the presence of Palatal P4. Both effects can be put down to the fact that the polarity of the mixture is enhanced by the resin oligomers which increases the interaction energy with respect to PDMS-PDMS entanglement and the phase separation between the grafted PDMS layer and the surrounding medium occurs faster. When hydrophilic fumed silica N20 is dispersed in a vinyl ester Atlac 590/styrene mixture the oscillation experiment reveals that the fumed silica is not able to build up a percolating network indicated by the lack of a yield point (Fig. 5b). This is also supported by the observation that the relaxation time of the system N20/Atlac 590/styrene is markedly longer than the time frame of the viscosity relaxation experiment of 500 s (Fig. 5a).

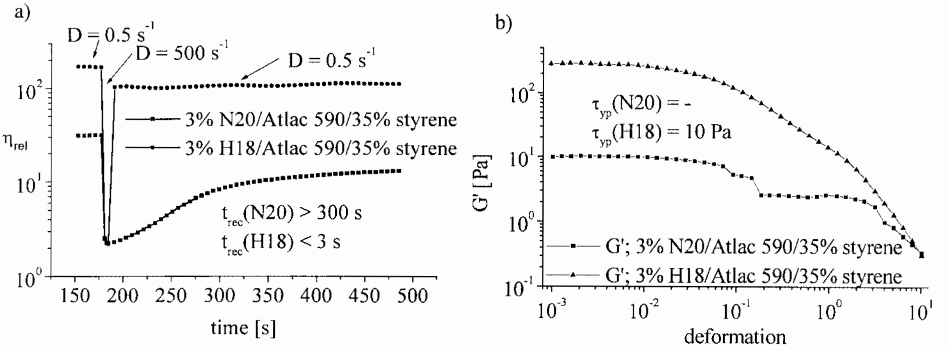

Figure 5. a) Controlled shear rate: relaxation experiment (profile D = 0.5 s^{-1}, 500 s^{-1}, and 0.5 s^{-1}) of N20 and H18 dispersed in Atlac 590/styrene; b) oscillation: deformation sweep at a frequency of 1.6 s^{-1} and a deformation of 0.001 to 10 of N20 and H18 dispersed in Atlac 590/styrene.

Vinyl esters resins are characterized by pending OH groups in the chain which are able to form strong H-bonds to the silanol groups of silica particles. Due to the strength of this interaction the adsorption of vinyl ester molecules at silica surfaces should be almost irreversible and result in a kind of steric stabilization of the silica particles. The formation of a silica network is suppressed and the achieved relative viscosities remain low.

In the case of H18/Atlac 590/styrene we observe a behavior in terms of network stability and relaxation which is comparable to the H18/Palatal P4/styrene system. This reveals that the net polarity of the medium is probably a more important driving force for the network stability of fully hydrophobic fumed silica than the specific chemical structure of the single components of the medium.

NMR and IR Spectroscopies

The results of our rheological study demonstrate that interactions between resin molecules and fumed silica particles significantly influence the network stability and its formation. In order to get a deeper understanding of the nature of such interactions a ^{13}C CPMAS study at different cross polarization times τ_{cp} from 0.5 to 8 ms has been performed. At short τ_{cp} spectra intensities are enhanced by ^{13}C resonances of the least mobile chain fragments. This study includes two different fumed silicas, hydrophilic Wacker HDK N20 and fully silylated Wacker HDK H18, with an unsaturated polyester resin Palatal P4 and a vinyl ester resin Atlac 590, respectively. Fig. 6 depicts the ^{13}C CPMAS spectra of N20 and H18, respectively, in Palatal P4/35% styrene at different cross polarization times τ_{cp}.

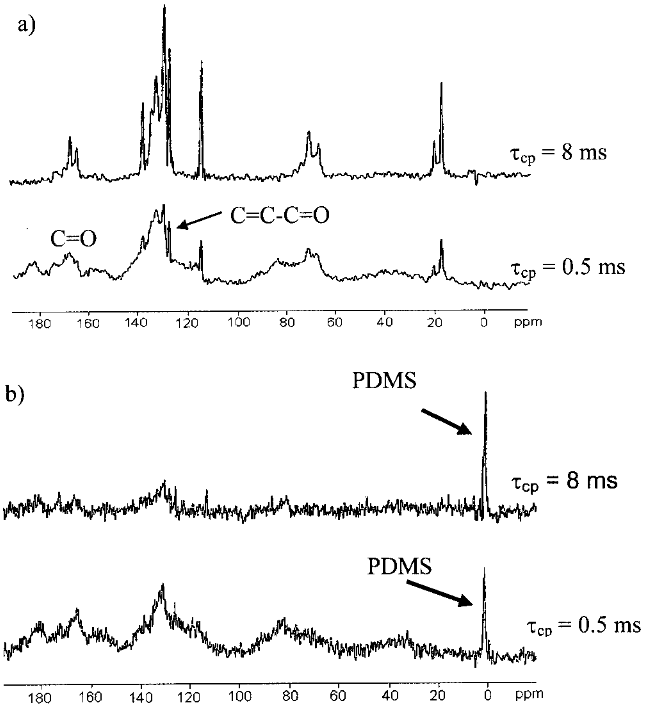

Figure 6. ^{13}C CPMAS spectra at different cross polarization times τ_{cp} of a) N20 in Palatal P4/35% styrene and b) H18 in Palatal P4/35% styrene.

The N20/Palatal P4 ^{13}C CPMAS spectra exhibit an enhanced intensity of the C=O and C=C signals at short τ_{cp} whereas Palatal P4 without added N20 shows no signals in the same experiment. This indicates that specific interactions of carbonyl and C=C-C=O groups of the resin oligomers with the fumed silica surface result in an immobilization of the resin molecules.[8, 13] This finding supports our interpretation of the rheological relaxation experiment, where we suggested that the increased relaxation times in the presence of Palatal P4 are related to the reversible adsorption of the resin oligomers at the silica surface after shear deformation.

The ^{13}C CPMAS spectra of H18 in Palatal P4/35 % styrene show an enhanced intensity of the grafted PDMS chains at short τ_{cp}. In a ^{13}C MAS experiment no signals for the PDMS chains of H18 could be detected. The fact that it was possible to detect the grafted PDMS by ^{13}C CPMAS indicates a strong immobilization of the chains, which is in agreement with our suggestion of H18 silica-silica network formation by a combination of hydrophobic interactions and chain entanglement. Both mechanisms are supposed to immobilize the PDMS chains in the grafted layer.

Further support for a specific interaction between the silanol groups of hydrophilic fumed silica and the C=O groups of resin molecules comes from IR spectroscopy, where additional to the carbonyl band of free Atlac 590 oligomers at 1724 cm^{-1} a second band at 1704 cm^{-1} appears under adsorption at the N20 surface (Fig. 7).

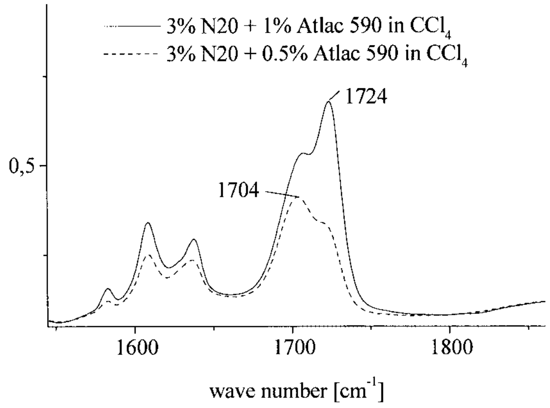

Figure 7. IR spectra of 3% N20 in CCl_4 after addition of 0.5 and 1% Atlac 590.

This indicates an interaction of the C=O function with the silica surface and particularly with the silanol groups of the silica.[14] At very low resin concentrations of less than 1.0 wt% the fraction of adsorbed oligomer is approximately 60% of the total resin, as seen from the IR intensities. Upon increasing the amount of resin the fraction of adsorbed resin oligomer remains small and does not exceed 5-8 wt% relative to the silica. The fact that only a small portion of the resin molecules is immobilized is in accordance with our model of thickening by hydrophilic fumed silica based on (a) direct particle-particle interactions, (b) polymer bridging, and (c) steric stabilization.

Quantum chemical calculations

Quantum chemical modeling is a suitable tool to elucidate the microscopic mechanisms of the adsorption processes of polymers on silica surfaces.[15] In the current study quantum chemical modeling has been used to quantitatively compare energies of interactions in the system silica and resin molecules.

For modeling of hydrophilic silica HDK N20 particles a hydroxylated silica cluster [$SiO_2$48-OH9],[15] containing 48 silicon dioxide units and 9 surface silanol groups, has been used; grafting two five-membered dimethylsiloxy (DMS) chains lop-wise (bonded at both ends) on it provided the model for the fully silylated silica HDK H18, silica cluster [$SiO_2$48-OH5-$DMS_5$2]. Two resin models have been simulated representing all typical functional groups of unsaturated polyester resins (UP) and vinyl ester resins (VE): sequence of UP model: methylether of 1,2-propanediol - maleic acid - 1,2-propanediol - orthophatalic acid - methylether of 1,2-propanediol; sequence of VE model: methacrylic acid - glycidine - bisphenol A - glycidine - methacrylic acid.

A special study has been dedicated to the nature of bonds in the system, in particular in the silica-resin system. The interaction energies of different kinds of H-bonds decrease in the order C-O-H···O(H)-Si > C=O···H-O-Si > C-(H)O···H-O-Si, which is summarized in Table 1. The oxygen atom of Si-OH bears a higher negative charge than that of C-OH, but the hydrogen of the latter is slightly more positively charged than in Si-OH; in consequence -C-OH···O(H)-Si is the strongest H-bond, but which occurs only in a VE system. Surprisingly, the carbonyl function also shows a rather high H-bond energy – linking an important interaction energy to carbonyl group immobilization as seen by ^{13}C CPMAS NMR and carbonyl band red shift as observed by IR. In summary this indicates that a VE-like resin structure shows strong adsorption affinity towards hydrophilic fumed silica.

Additionally to the superior interaction energy of -C-OH···O(H)-Si vs. -C-(H)O···HO-Si steric considerations suggest that end-of-the-chain carbinols in a resin are forming stronger H-bonds with a silica surface than in-chain carbinols; however, this suggestion has to be verified in future studies.

Fig. 8 shows fully optimized structures of adsorption complexes of VE and UP resin models with the [$SiO_2$48-OH9] and [$SiO_2$48-OH5-$DMS_5$2] silica clusters.

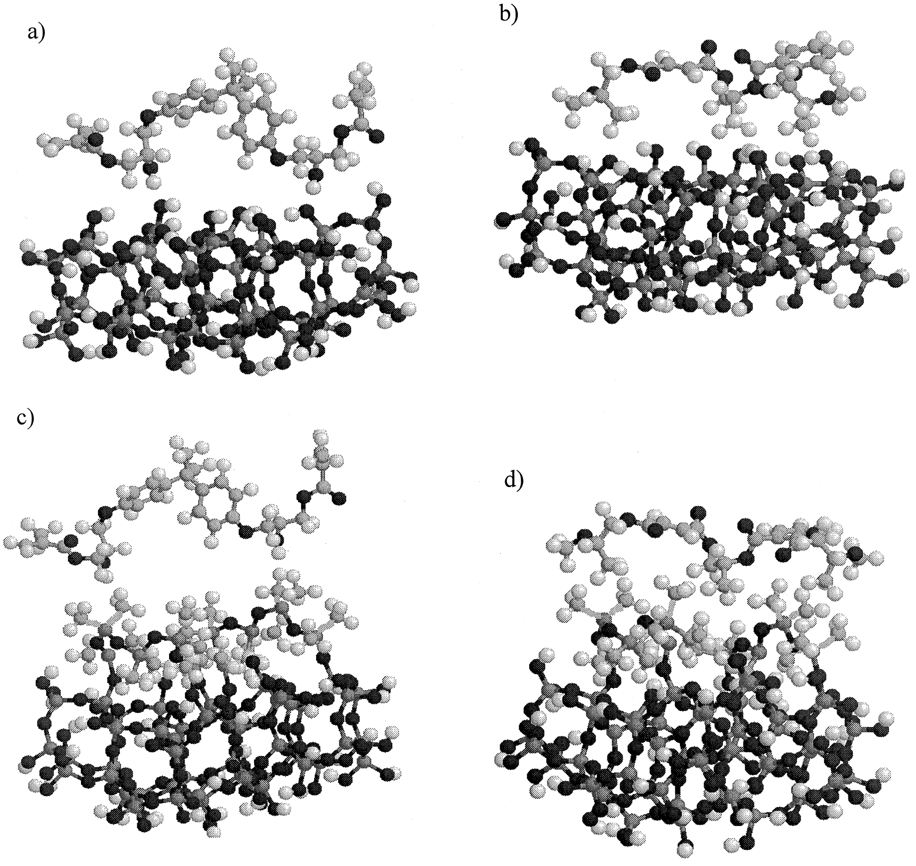

Figure 8. Fully optimized structures of the adsorption complexes of a) hydrophilic silica and vinyl ester [$SiO_2$48-OH9]/VE; b) hydrophilic silica and unsaturated polyester and [$SiO_2$48-OH9]/UP; c) hydrophobic silica and vinyl ester [$SiO_2$48-OH5-$DMS_5$2]/VE; d) hydrophobic silica and unsaturated polyester [$SiO_2$48-OH5-$DMS_5$2]/UP.

Calculated interactions energies of silica-silica, silica-resin, and resin-resin adsorption complexes are given in Fig. 9.

Table 1. Energies of specific interactions: silica model [SiO$_2$18-OH5][15] and VE model: methylether of glycidine - methacrylic acid.

System	energy of interaction [kcal/mol]	Bond distance [nm]
-C-H···O-Si(Si)	- 2.80	0.283
-C-(H)O···HO-Si	- 4.46	0.185
-C=O···HO-Si	- 5.60	0.183
-C-OH···O(H)-Si	- 9.51	0.177

VE system

Hydrophilic silica particles interact strongly with the VE molecule ([SiO$_2$48-OH9]/VE) due to H-bonds of the form -C-OH···O(H)-Si additional to H-bonds of the form C=O···H-O-Si and dispersion interactions – it is the most favorable interaction in all system combinations in terms of energy. As it is even stronger than the silica-silica interaction ([SiO$_2$48-OH9]/[SiO$_2$48-OH9]), strong adsorption is expected, leading to steric stabilization of the colloidal system by hampering direct particle-particle contacts. Rheologically, we would interpret this as low thickening efficiency – in deed, experiments show that N20 is not a stable thickener for VE resin systems. and resin molecule. The contact areas a = 0.82 nm^2 are identical (2-4 % deviation) for resin-resin and resin-silica interaction for both UP and VE, and hydrophilic and silylated silica, and therefore interaction energies are taken as directly comparable. Silica-silica contact areas are larger both by a factor of 3.2, the interaction energies are normalized therefore by the ratio of the contact areas.

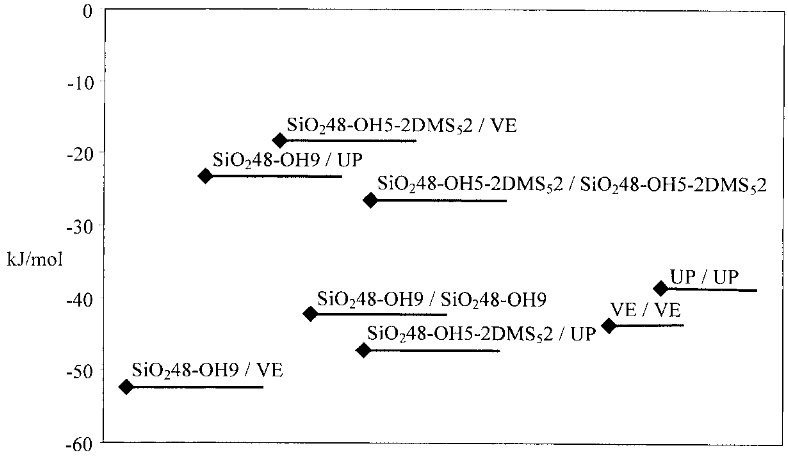

Figure 9. Calculated energies of intermolecular interactions in the system silica particles

The weakest interaction in the system is that of silylated silica with a VE molecule ([SiO$_2$48-DMS$_5$2]/VE). It is even weaker than the interaction of silylated silica with itself ([SiO$_2$48-DMS$_5$2]/[SiO$_2$48-DMS$_5$2]). The medium interaction energies of the latter surprises, as only nonspecific components are involved – however modeling makes evident a particle-to-particle entanglement of the 5-membered-DMS chains on the silica clusters: In fact, the additional immobilization of PDMS chains on H18 as seen by ^{13}C CPMAS NMR seems to be correlated with energies of interaction. The strongest complexes in the system VE and silylated silica are those of the VE resin molecules with each other. In consequence, the interface of highly silylated silica towards a VE phase is energetically less favorable: In order to optimize VE-VE contacts the silylated silica particle surfaces separate from the system by direct silylated silica-silylated silica particle contacts – a phenomenon which is well-know as 'hydrophobic interaction'.[9] However, real systems contain monostyrene, which is not or only very weakly adsorbed on a silica surface according to calculations and spectroscopic experiments. Hence, styrene is enhancing the effect of silylated silica separation from the VE-styrene phase. In fact, HDK H18 is an excellent and stable thickener and rheology control additive for all VE and epoxy resin-like systems.

UP system

The complex UP on hydrophilic silica is rather weak, but the interaction of two hydrophilic silica cluster is rather strong, even in competition to the resin-resin interaction, which are of comparable strength or weaker. Additionally, not depicted in Fig. 9, modeling shows that styrene is not adsorbed at all on hydrophilic silica. In consequence, following the interpretations given above, hydrophilic silica HDK N20 is an excellent and powerful thickener and thixotropic agent for UP resins, as strong particle-particle interactions occur. However, spectroscopic and rheological results indicate an adsorption of UP oligomers to hydrophilic silica surfaces. In accordance with our calculations this adsorption is only weak and reversible and therefore influences only the rate of gelation but not the network stability.

Surprisingly, the adsorption complex of UP molecule on the silylated silica cluster shows a distinctly higher interaction energy. Following the interpretations given above, this should result in wetting, adsorption, steric stabilization, and a weak colloidal network. However, as shown by the rheological data given above, HDK H18 is an excellent thickener for UP resins, too. It seems that in a system of real UP resins, the solvent styrene plays a key role: Being a bad or worse-than-θ-solvent for (the) PDMS (layer on silica) styrene is the driving force of hydrophobic interactions – in the case of silylated silica in UP resins the adsorption of UP molecules on the silylated silica surface seems not to hinder hydrophobic interaction: A reasonable assumption as the latter is not particle-particle contact but phase separation driven.

Conclusion

In order to develop a comprehensive model for the thickening behavior of different grades of fumed silicas advanced rheological and spectroscopic experiments as well as quantum chemical calculations have been performed. The results indicate that fundamentally different mechanism are responsible for the formation of colloidal networks of hydrophilic and fully silylated silica.

Hydrophilic silica forms a strong and rigid network by strong short-range H-bonds between silica particles. Addition of UP resin reduces the network stability but increases network flexibility and relaxation time after shearing. VE resins hamper the formation of a percolating network due to irreversible adsorption of OH end groups on the silica surface.

Fully silylated silica exhibits hydrophobic interactions between the PDMS covered surface and the solvent as well as entanglement of the PDMS layers. Addition of UP or VE resins increases the polarity of the medium. As a result, the mismatch between the matrix and the PDMS layer is increased which favors PDMS-PDMS interactions and therefore enhances the network stability and decreases the network relaxation time.

For both grades of silica the formation and strength of their percolating networks in terms of both particle-particle and particle-polymer-particle interactions is strongly influenced by the polarity of the surrounding medium and the nature of the resins. In particular, adsorption processes have been identified to play an important role for the rheological performance of hydrophilic fumed silica. From these results recommendations for the application of fumed silica in different types of resins have been derived, which are summarized in Table 2.

Table 2. Recommendations for the application of fumed silica in different resin types depending on their polarity and the potential to form strong specific interactions.

Resin oligomer	Polarity and type of interaction	Rheological additives
• Alkyd resins, • Saturated polyester resins	non-polar; no strong specific interactions	• hydrophilic fumed silica HDK N20
• unsaturated polyester resins	non-polar to medium polarity; no strong specific interactions	• hydrophilic fumed silica HDK N20 • fully silylated fumed silica HDK H18
• vinyl ester resins • melamine-polyesters	medium to highly polar; strong specific interactions	• fully silylated fumed silica HDK H18
• epoxy resins • polyurethane system • acrylate systems	polar; strong specific interactions	• fully silylated fumed silica HDK H18

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