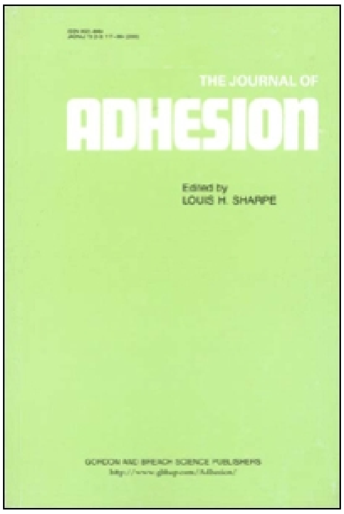

The Journal of Adhesion
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713453635

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To cite this Article Zumbrum, M. A.(1994) 'Acid/Base Properties of Fumed Silica Fillers Used in Silicone Elastomers', The Journal of Adhesion, 46: 1, 181 — 196
To link to this Article: DOI: 10.1080/00218469408026659
URL: http://dx.doi.org/10.1080/00218469408026659

J. Adhesion, 1994, Vol. 46, pp. 181–196
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Printed in the United States of America

Acid/Base Properties of Fumed Silica Fillers Used in Silicone Elastomers*

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(Received December 8, 1992; in final form April 16, 1993)

Inverse gas chromatography (IGC) and photoacoustic infrared spectroscopy (PAS) were used to investigate the effects of thermal history and silane treatment on the surface energetics of various fumed silica fillers. The specific interaction parameter, I_{sp}, was a factor of 2.3 (THF probe) lower for a silane treated fumed silica (Degussa R972) relative to an untreated filler (Degussa A200), thus confirming the deactivating effects of silane treatment. Heat treatment of raw fumed silica (Cabot HS-5) at 150°C and 650°C decreased I_{sp} (THF probe) from 15.3 kJ/mol to 10.5 kJ/mol. This decrease was attributed to the loss of bound water and surface silanols. The dispersive interactions increased with heat treatment as a result of the formation of higher electron density sites such as strained Si—O—Si bonds. Silazane-treated fillers were prepared using heat treated and hydrated feedstocks. I_{sp} values were a factor of 2–30 lower, depending upon the probe, for silazane-treated fillers made from heat treated feedstock. The dispersive interactions increased from 27.2 mJ/m^2 to 57.8 mJ/m^2 as a result of using heat treated feedstock, thus suggesting some of the strained Si—O—Si bonds formed upon drying remained intact even after silazane treatment.

KEY WORDS fillers; fumed silica; surface energetics; surface treatment; silylation; dehydration; heat treatment; polymer-filler interactions; interphase; inverse gas chromatography; infrared spectroscopy.

1 INTRODUCTION

The properties of filler-reinforced materials are generally determined by the characteristics of the interphase between the filler and the surrounding matrix. Synthetic and natural elastomers are an important class of reinforced materials, having been studied with great interest over the past 50 years, particularly since the development of high surface area fillers such as carbon blacks, precipitated silicas, and fumed silicas.[1–6] In general, efforts have focused on understanding the effects of the following factors on the properties of the polymer-filler interphase: (1) filler morphology, (2) filler surface energetics, and (3) matrix chemistry. Firstly, the morphological properties of reinforcing fillers are the subject of numerous review articles describing the geometric features of fillers.[7–10] These features result from the processes of nucleation, growth, and aggregation during production.[11] Primary parti-

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*Presented at the International Symposium on "The Interphase" at the Sixteenth Annual Meeting of The Adhesion Society, Inc., Williamsburg, Virginia, U.S.A., February 21–26, 1993.

cles, which control surface area, are formed early in the process and fuse together as time progresses to form branched structures of varying degree, called aggregates. Aggregate structure is important because it determines the effective volume fraction of filler in a matrix.[12] The topics of filler morphology and matrix chemistry[13,14] have been documented extensively in the literature; however, understanding the effects of filler surface energetics on the properties of the polymer-filler interphase has only recently been studied[15-18] and is the topic of this work.

This paper focuses on characterizing the surface chemistry attributes of various fumed silica fillers used to reinforce silicone elastomers. Specifically, Inverse Gas Chromatography (IGC) and Photoacoustic Infrared Spectroscopy (PAS) were used to investigate systematically the effects of (1) thermal history and (2) silane treatment on the surface chemistry of fumed silica fillers. IGC describes the thermodynamics of interaction between a given surface and compounds of specific functionality that are acidic, basic, or neutral, as described by the acid/base theory of Fowkes.[19,20] PAS provides molecular-level information about the type of species on the filler surface. Thus, the combination of IGC and PAS data allows one to determine the net effect of surface composition (*i.e.* silyl, silanol, and water) on surface energetics.

Silicone elastomers are reinforced typically with high surface area fumed silica to provide increased strength and toughness without sacrificing the unique thermal characteristics of silicones. The polymer-filler interphase in filled silicones is modified often on a commercial scale by surface treating the filler with various silylating compounds such as dimethyldichlorosilane, octamethylcyclotetrasiloxane, and hexamethyldisilazane.[21-25] These deactivated silicas are used to produce low viscosity silicone suspensions of controlled thixotropy. The degree of hydration of the silica is another important variable in the surface chemistry of silicas. Fumed silica is produced by the combustion of chlorosilanes in a hydrogen-oxygen flame resulting in a hydrophilic surface populated by several types of hydroxyl groups including isolated silanols, adjacent silanols, and bound water. The effects of thermal history on hydroxyl content can be observed in the infrared spectrum for each of the following species: isolated silanols (3745–3750 cm^{-1}), adjacent or hydrogen bonded silanols (3540–3660 cm^{-1}), and bound water (3400–3500 cm^{-1}).[26-29]

IGC is a rapid, sensitive technique for characterizing the surface energetics of numerous materials including polymers,[30,31] metals,[32] fibers,[33-35] and inorganic fillers[36,37] and is the topic of reviews[38] and symposia.[39] IGC examines the response of the stationary phase (*i.e.* fumed silica) to various pure compounds or probes of specific functionality in the vapor phase. A homologous series of alkanes is used to assess the non-polar or dispersive interactions with the stationary phase. Polar probes, both acidic and basic, are used to monitor the dipolar or specific interactions. Lewis originally defined acids as electron acceptors and bases as electron donors.[40] The theoretical concepts of acid/base interactions have been developed in much detail by Drago[41] and Gutmann.[42] Thus, the acidic surface of fumed silica interacts with basic probes such as diethyl ether and tetrahydrofuran. Papirer *et al.* have published on the use of IGC to characterize the effects of grafting alkyl groups onto the surfaces of fumed and precipitated silicas.[43-50] They reported that increasing the length of the alkyl graft decreased both the specific and dispersive components of the surface free energy. The dispersive component of the surface free energy was somewhat higher for fumed silicas as compared with precipitated silicas. The specific interactions were much greater for precipitated silicas, suggesting higher surface silanol concentrations. Precipitated silicas are known to have higher silanol concentrations relative to fumed silicas due to their aqueous processing conditions.[26] The treatment of silicas with $\alpha-\omega$ diols having between 4 and 16 carbon atoms was also investigated by IGC. The dispersive interactions were governed mainly by surface coverage and the specific interactions were found to be greater for grafts having an odd number of carbon atoms. These results were attributed to the conformational characteristics of the grafts. Papirer *et al.* also used IGC to investigate heat treated silicas.[51,52] The specific interaction for chloroform decreased from 7 kJ/mol to 4.5 kJ/mol upon heat treatment at 700°C; however, the dispersive interaction increased from 75 mJ/m^2 for treatment at 150°C to 100 mJ/m^2 at 550°C and finally decreased to 90 mJ/m^2 at 700°C. Even after heat treatment at 700°C, they observed different specific interactions between the fumed and precipitated silicas, indicating that the surface chemical states were not equivalent.

Wolf *et al.* published a series of papers on the use of IGC to determine the surface energetics of various silicas and carbon blacks.[15-18] In particular, the energies of interaction between fillers and elastomers were estimated from the adsorption of low molecular weight elastomer analogs on various filler surfaces. The free energy of interaction decreased in the order of nitrile>phenyl>vinyl>alkyl, indicating that polymer-filler interactions depend not only on filler surface energies but also on the chemistry of the elastomers. They noted also that the dispersive interactions of fumed silicas were greater than those for precipitated silicas but that the specific interactions were much higher for the precipitated silicas. This was attributed to the higher silanol concentrations in precipitated silicas.

2 EXPERIMENTAL

2.1 Materials

The Degussa Corp. provided an untreated 193 m^2/gm fumed silica (Aerosil® 200) and a dimethyldichlorosilane-treated 117 m^2/gm fumed silica (R972). The Cabot Corp. provided a 320 m^2/gm untreated fumed silica (HS-5). Two hydrophobic fumed silicas were prepared having significantly different concentrations of bound water. Hexamethyldisilazane (HMDZ) (Aldrich Chemical Co.) was used to silylate both a heat treated and an "as-received" HS-5 sample at room temperature. A sample of HS-5 was heat treated in a quartz flask at 800°C in a nitrogen atmosphere to produce a dehydrated feedstock. The samples of fumed silica (approximately 40 gm) were placed under vacuum in a glass desiccator containing 25 gm of HMDZ in a Petri dish at the bottom of the vessel. Once vacuum was achieved, the desiccator was sealed to allow the HMDZ vapors to react with the silica overnight. After treatment, the samples were removed from the desiccator and placed under vacuum at 110°C to remove residual ammonia and unfunctionalized silicone. The samples were treated a second time and dried. BET nitrogen adsorption measurements were made using an Omnisorp® 100 with nitrogen as the adsorbate.

2.2 Inverse Gas Chromatography

IGC measurements were made using a Perkin-Elmer Auto GC system equipped with an autosampler, a flame ionization detector, and a computer data acquisition system (Model 1020). Testing was conducted with the column and injection ports maintained at 110°C and the detector at 150°C. A 5 μl syringe was used for injections with 3 pre-injection pumps, 2 pumps for sampling, and 3 post-injection pumps to purge the syringe. An injection volume of 3 μl of vapor was used from 2 ml sealed vials initially containing 0.1 to 30 μl of liquid depending upon the vapor pressure of the probe. Vapor pressures at 110°C were calculated using the Clausius-Clapeyron equation and data from the literature.[53,54]

IGC columns were prepared by agglomerating the fumed silicas. Samples of fumed silica (~2 g) were dispersed in hexane (~75 ml) and allowed to dry in open Petri dishes in a nitrogen blanketed glove bag. The cake-like materials were sieved through wire meshes to obtain particles ranging from 500 to 1000 μm in diameter. The agglomerated filler enabled sufficient carrier gas to pass through the column with negligible pressure drop across the column; unagglomerated silica prevented passage of carrier gas through the column. A flow rate of 15 ml/min was used for all analyses. Prior to analysis, packed columns were conditioned at 150°C for 12 hours using helium (research grade) as the carrier gas. Silane-treated glass columns, 150 mm long × 3.9 mm ID (Supelco® 2-1171), were used to contain 200 mg of Degussa R972 and 225 mg of Degussa A200. A quartz tube containing 142 mg of Cabot HS-5 was used to study the effects of heat treatment on surface energetics. Nichrome wire was used to heat the column resistively to a given temperature, as measured by a thermocouple between the wire and the column, for a total of 20 min with a carrier gas flow of 15 ml/min. The two HMDZ-treated HS-5 samples were placed in glass columns (Supelco® 2-1171) containing 193 mg of the hydrated filler and 255 mg of the heat treated filler.

2.3 Photoacoustic Fourier Transform Infrared Spectroscopy

Photoacoustic FTIR data were collected using a Nicolet® 800 FTIR equipped with an MTEC® photoacoustic detector (Model 200). The spectrometer was operated at 8 cm^{-1} resolution using 32 co-added scans. A mirror velocity of 0.05 cm/sec was used. All spectra were ratioed to a carbon black background. A 100 ml/min nitrogen purge through the sample and microphone compartments was used to remove water vapor out of the path of the IR beam. Water vapor peaks were observed in most spectra between 3750 and 4000 cm^{-1}. The heat treated samples were loaded into the photoacoustic detector from within a nitrogen blanketed glove bag.

3 RESULTS AND DISCUSSION

3.1 Chromatographic Calculations

The thermodynamics of adsorption at infinite dilution, *i.e.* Henry's Law region, relate the net retention volume, V_n, to the free energy of adsorption of one mole of probe molecules onto a surface under standard conditions:

$$\Delta G_{ads} = -\Delta G_{des} = -R\ T\ \ln[V_n \cdot P_o / S \cdot g \cdot \Pi_o] \tag{1}$$

where P_o (1.013×10^5 Pa) is the partial pressure of the probe and Π_o (3.38×10^{-4} N/m) is the bidimensional spreading pressure of an adsorbed film for the reference state described by DeBoer.[55] S is the BET surface area (m^2/gm), g is the sample mass (g), R is the ideal gas constant (8.314 J/mol·K), and T is the absolute temperature of the column. The net retention volume for a given probe was calculated from the retention times of the probe, t_p, and the methane marker, t_m, correcting for the pressure drop across the column, J, the temperature difference between the flowmeter and the column, F, and the vapor pressure of water in the soap bubble flow meter, C:

$$V_n = (t_p - t_m)\ J \cdot C \cdot F \tag{2}$$

$$C = 1 - (P_{H_2O}/P_o) \tag{3}$$

$$J = 1.5\ \{[(P_i/P_o)^2 - 1]/[(P_i/P_o)^3 - 1]\} \tag{4}$$

$$F = F_o\ (T_{col}/T_{meter}) \tag{5}$$

The standard free energy of adsorption was considered to be a sum of the dispersive and specific components:

$$\Delta G^o_{ads} = \Delta G^o_d + \Delta G^o_{sp} \tag{6}$$

In the case of dispersive interactions, retention times of the alkane probes are determined solely by the London forces established between the probes and the solid surface. According to Fowkes[56] ΔG^o_d is related to the work of adhesion, W_a, between the solute and the solid surface by:

$$\Delta G^o_d = a \cdot N \cdot W_a \tag{7}$$

where a is the area of an adsorbed probe and N is Avogadro's number. Furthermore, the work of adhesion is given by the geometric mean of the surface energies of the probes, γ^D_L, and the solid, γ^D_S:

$$W_a = 2(\gamma^D_S \cdot \gamma^D_L)^{1/2} \tag{8}$$

Thus, by combining equations 7 and 8, the dispersive component of the surface free energy of a solid can be obtained from the slope of a plot of ΔG^o_{ads} *vs.* $aN(\gamma^D_L)^{1/2}$; however, this approach requires assigning a value to the area of an adsorbed probe at a given temperature. Nardin and Papirer described an alternative approach to obtain γ_S^D, relying on the use of vapor pressures instead of areas of the probes.[57] Experimentally, ΔG^o_{ads} is a function of probe vapor pressure according to:

$$\Delta G^o_{ads} = -K \cdot \ln(P_o) + \nu \tag{9}$$

where the slope, K, provides γ_S^D:

$$K = 3 \cdot R \cdot T\,(\gamma_S^D)^{1/2} / \chi(\gamma_o)^{1/2} \tag{10}$$

and

$$\nu = K\{\chi/3\mu + c - 1\} \tag{11}$$

The parameter χ describes the number of atoms located around a probe that can exchange electron density. A χ value of 3.3 was used for hydrocarbon probes. The surface energy, γ_o, of a non-polar solid (*i.e.* polyethylene) was taken as 31.1 mJ/m^2 at 110°C. The packing density, μ, of adsorbed hydrocarbons and the empirical constant, c, describe the intercept ν.

The specific free energy of interaction was estimated from the difference between the free energy of adsorption for the polar probes and the dispersive free energy of adsorption for the alkanes:

$$I_{sp} = RT \ln(V_n/V_n^{ref}) \tag{11}$$

where V_n^{ref} is the net retention volume of a hypothetical alkane of the same vapor pressure as the polar probe appearing at retention volume V_n.

3.2 Surface Energetics of Untreated *vs.* Silane Treated Fumed Silicas

Probe retention times ranged from seconds to several hours depending upon the nature of the silica surface and the type of probe. The retention diagrams for the untreated fumed silica (A200) and the dimethyldichlorosilane-treated fumed silica (R972), are shown in Figures 1 and 2, respectively. Overall, both samples exhibited

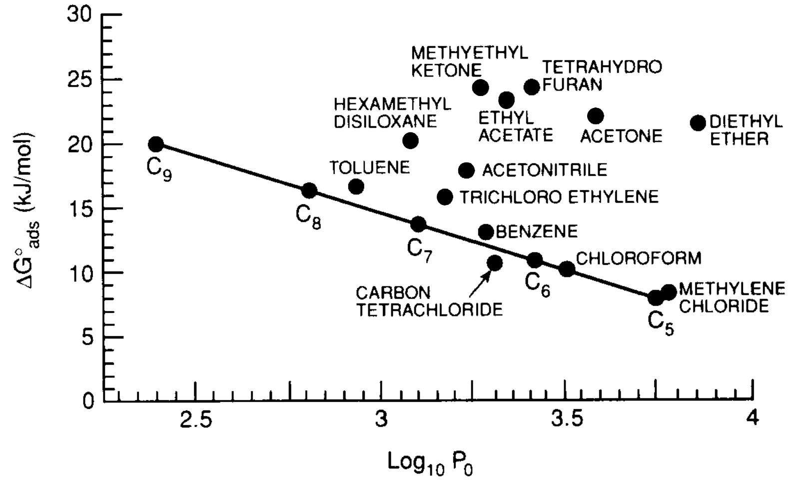

FIGURE 1 Retention diagram for hydrophilic, untreated fumed silica (Degussa A200) at 110°C.

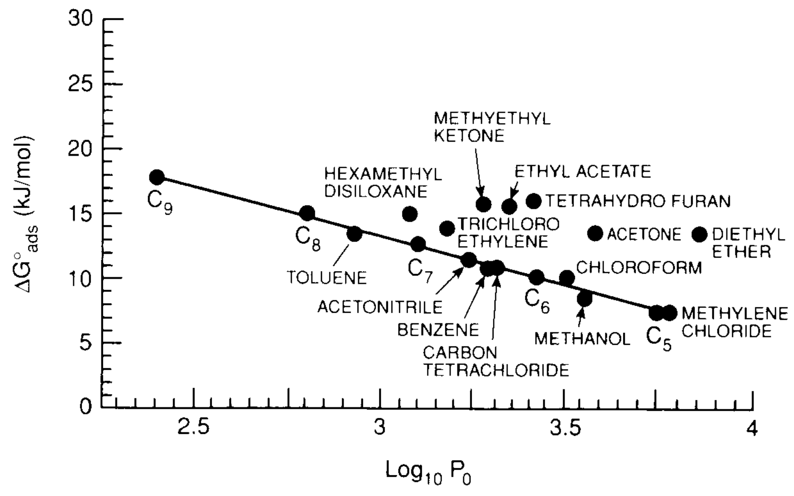

FIGURE 2 Retention diagram for hydrophobic, dimethyldichlorosilane-treated fumed silica (Degussa R972) at 110°C.

strong interactions with both basic and amphoteric probes such as tetrahydrofuran (THF), diethyl ether (DEE), methyl ethyl ketone (MEK), acetone (AC), ethyl acetate (ETAC), and hexamethyldisiloxane (HMDS), thus confirming the acidic nature of fumed silica, assuming the applicability of the acid/base theory that identifies probes as acids and bases. The magnitude of interactions for the untreated fumed silica with the basic probes was much greater relative to the interactions for the silane-treated filler. In particular, I_{sp} for the basic probes ranged from 10.3 to 4.2 kJ/mol for the untreated fumed silica and from 4.5 to 1.3 kJ/mol for the silane-treated silica, as summarized in Figure 3. The decreased activity of silane treated fillers is consistent with the observation that the more acidic bound water and silanols were replaced or shielded by the more neutral dimethylsiloxane groups. The FTIR spectra shown in Figure 4 are for the (a) untreated and (b) treated fillers. The silane-treated filler had a lower concentration of surface hydroxyl groups (particularly isolated silanols) and bound water (3000–3750 cm^{-1}) and exhibited a new absorbance corresponding to methyl groups (2880–3000 cm^{-1}) as a result of the silane treatment. The dispersive component of the free energy also was affected by silane treatment. γ_S^D decreased from 50.6 mJ/m^2 for the untreated silica to 36.2 mJ/m^2 for the treated silica as a result of replacing or shielding the electron-dense hydroxyl groups with methyl groups.

3.3 Surface Energetics of Heat-Treated Fumed Silicas

The hydroxyl content of fumed silica is affected not only by surface treatment but, as discussed in this section, is also a function of many factors including processing conditions (flame temperature and feedstock), handling conditions, and thermal history. Physisorbed water is easily removed from the surface of fumed silica; how-

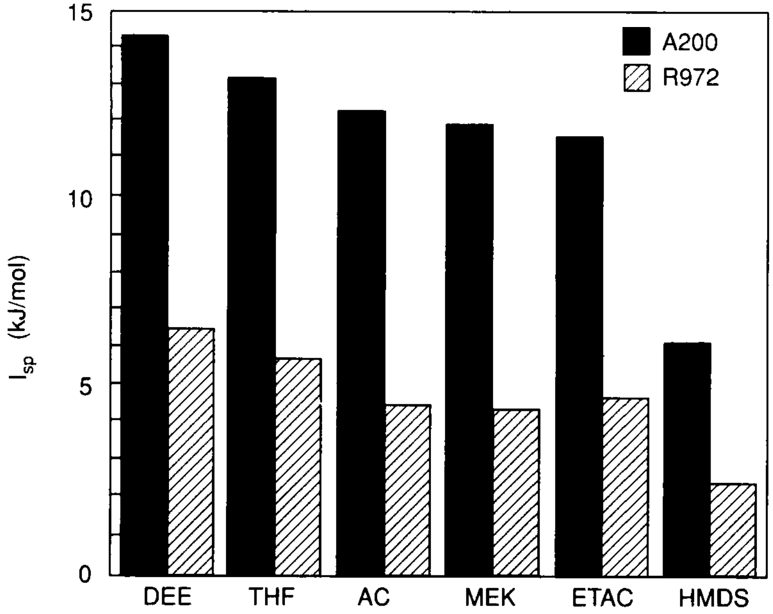

FIGURE 3 Specific free energy of interaction for various basic probes with untreated (Degussa A200) and treated (Degussa R972) fumed silicas at 110°C.

ever, chemisorbed water is removed completely only by heat treatment to approximately 800°C. A thermogravimetric analysis (TGA) of HS-5 at 25°C revealed a decrease of 1.5 wt% physisorbed water within the first 30 min after being loaded into a nitrogen purged chamber (see plot inset in Figure 5). Upon heating at a rate of 10°C/min, bound water was removed from the sample with an initial decrease in mass between 200 and 400°C followed by a continuous but more gradual decrease up to 800°C. The change in concentration of various hydroxyl species upon heating can be seen from the FTIR spectra in Figure 6. The concentration of bound water and adjacent silanol decreased markedly upon heat treatment. Adjacent silanols have been reported to condense, assuming the bonds are given sufficient thermal energy and are in close proximity to one another, thus forming strained Si—O—Si bonds.[58-60] IGC was used to study the effects of heat treatment of untreated fumed silica (Cabot HS-5) at 150, 250, 350, 450, 550, 650, and 750°C. In general, the magnitude of the specific interactions decreased with increasing temperature (Figure 7); however, some probes, such as diethyl ether and ethyl acetate, exhibited little change beyond 450°C. This is in agreement with the TGA data (Figure 5) indicating only minor changes in bound water concentration beyond 450°C. The dispersive interactions increased upon heat treatment from 67.6 mJ/m^2 at 150°C until reaching a maximum at 87.8 mJ/m^2 at 600°C, as shown in Figure 8. These results are consistent with earlier observations supporting the formation of higher energy strained Si—O—Si bonds at elevated temperature as a result of the condensation of adjacent silanol groups.[58-60]

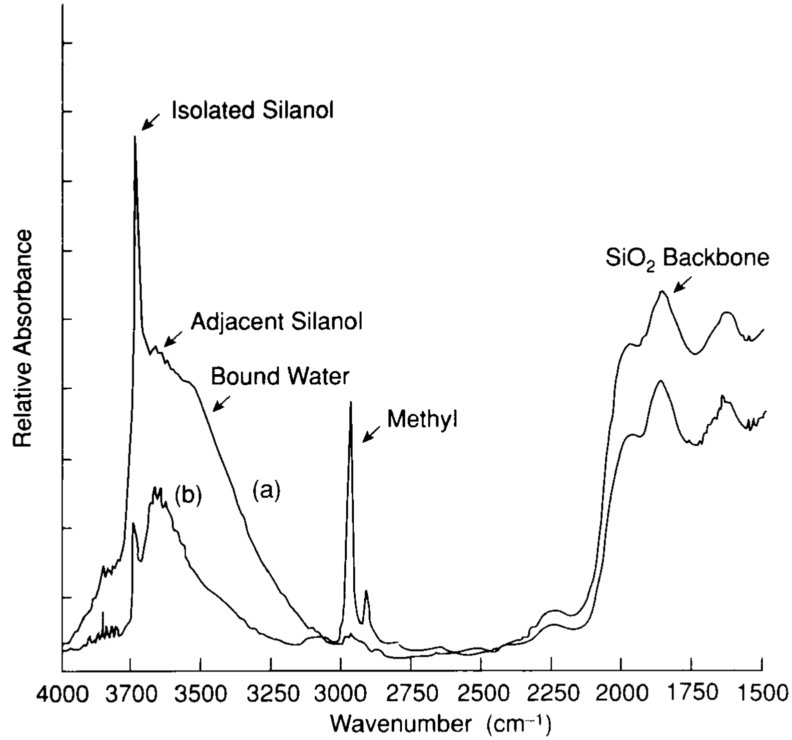

FIGURE 4 Infrared spectra of (a) untreated fumed silica (Degussa A200) and (b) treated fumed silica (Degussa R972).

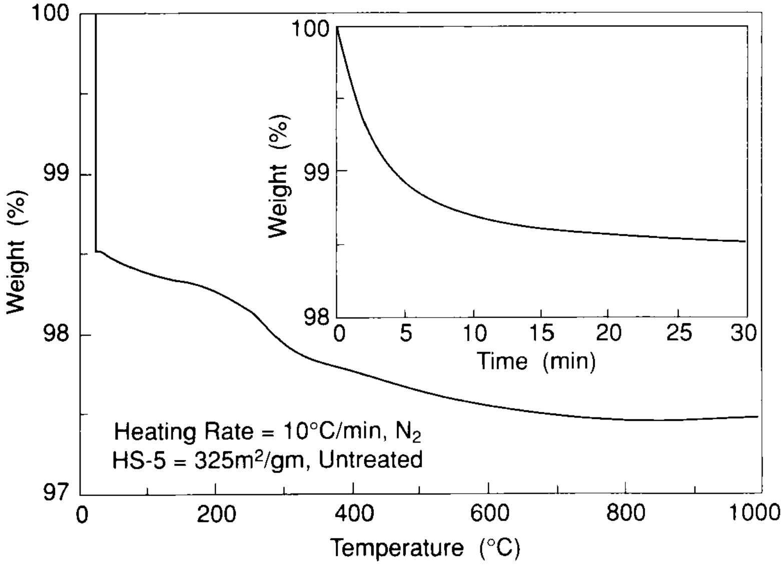

FIGURE 5 Thermogravimetric analysis of untreated fumed silica (Cabot HS-5).

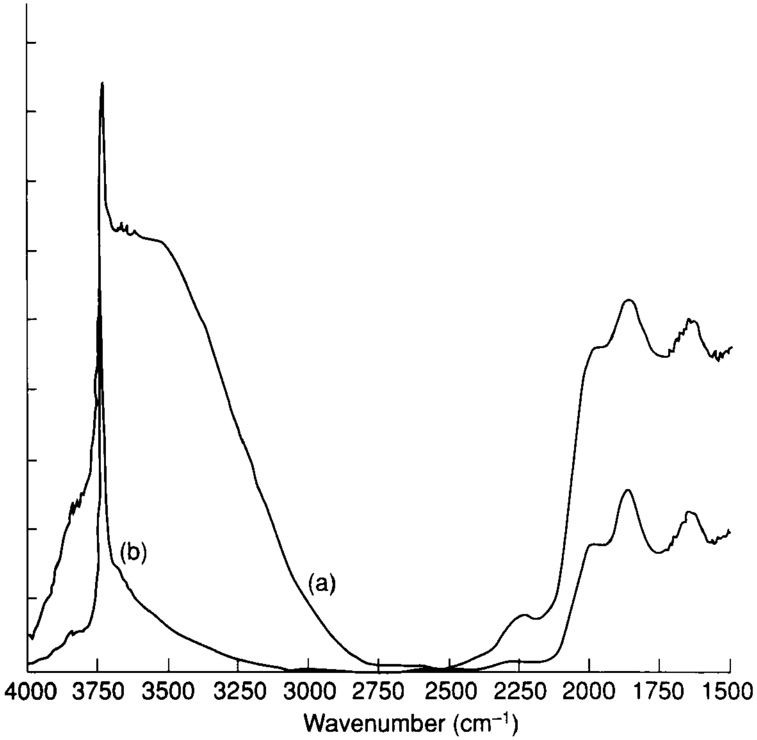

FIGURE 6 Infrared spectra of untreated fumed silica (Cabot HS-5) (a) before and (b) after heat treatment.

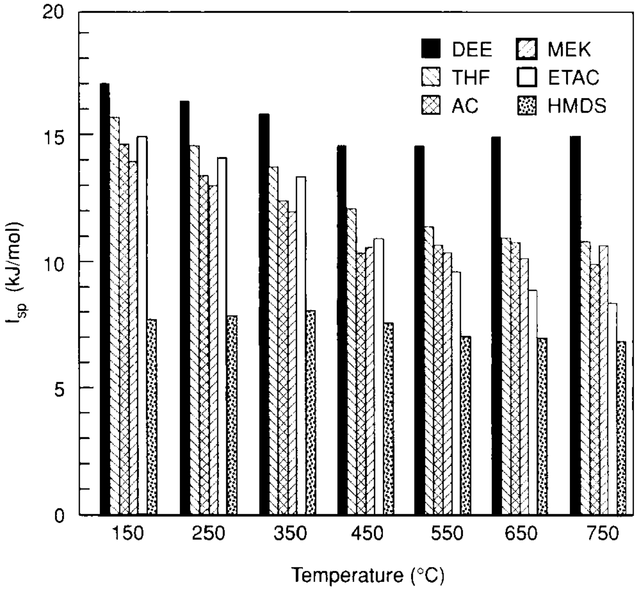

FIGURE 7 Effects of heat treatment on the specific interactions of Cabot HS-5 at 110°C.

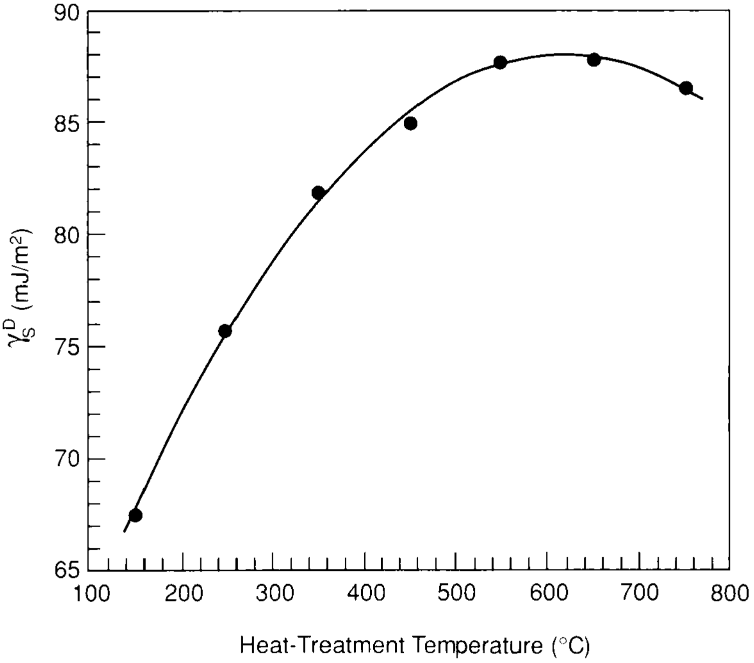

FIGURE 8 Dispersive free energy of interaction for Cabot HS-5 heat treated at various temperatures.

In addition to the work on untreated fumed silicas, the effects of heat treatment on the free energy of adsorption for silazane-treated fumed silicas were investigated. Two samples of HS-5 were treated with hexamethyldisilazane, as described in Section 2.1. One sample was dehydrated and subsequently treated (HS-5DT). The second sample was treated as received (HS-5T). The FTIR spectra of the two treated fillers are shown in Figure 9. The reaction of surface hydroxyls with hexamethyldisilazane results in a surface covalently functionalized with trimethylsilyl groups, as evidenced by the absorption at 2950 cm^{-1}. After silazane treatment, no isolated silanols remained on the surface of either sample and the relative integrated absorbance for the CH stretch was equal for the two samples. The most significant difference between the two samples was the concentration of bound water; HS-5DT contained very little bound water relative to HS-5T. These hydrophobic fillers were evaluated by IGC. Figures 10 and 11 depict the retention diagrams for the hydrated and the heat treated samples, respectively. The specific interaction parameter for HS-5T was found to be a factor of 2–30 times greater than the interaction for HS-5DT, depending upon the probe (see Figure 12). In particular, I_{sp} for THF was 1.4 mJ/m^2 for HS-5DT and 9.0 mJ/m^2 for HS-5T. These results suggest that specific interactions in fumed silica are directly related to the concentration of hydroxyl groups, especially bound water. The dispersive free energy of interaction was 27.2 mJ/m^2 for HS-5T and 57.8 mJ/m^2 for HS-5DT. This observation indicates that the strained Si—O—Si bonds formed upon heat treatment result in a surface capable of more extensive London interactions even with the surface relatively free of bound

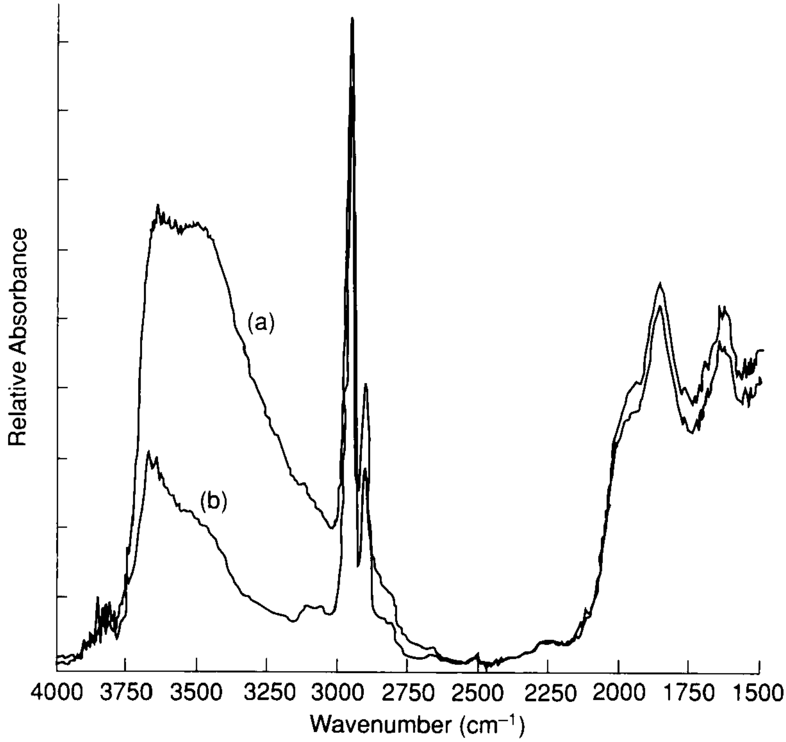

FIGURE 9 Infrared spectra of (a) HS-5T and (b) HS-5DT.

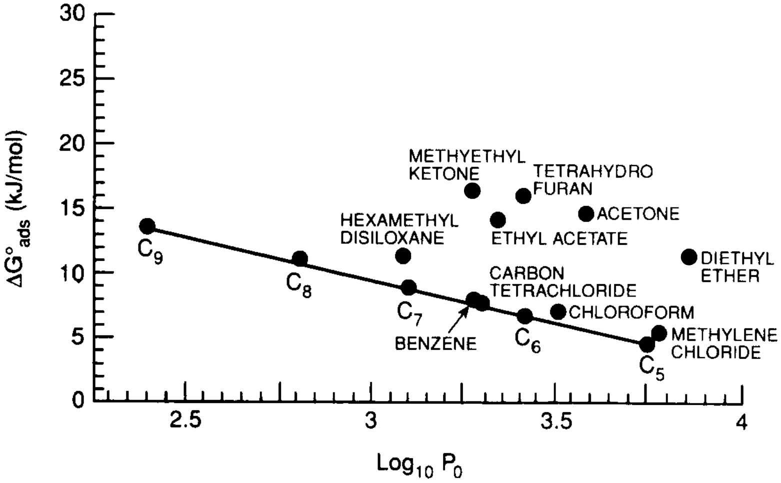

FIGURE 10 Retention diagram for HS-5T.

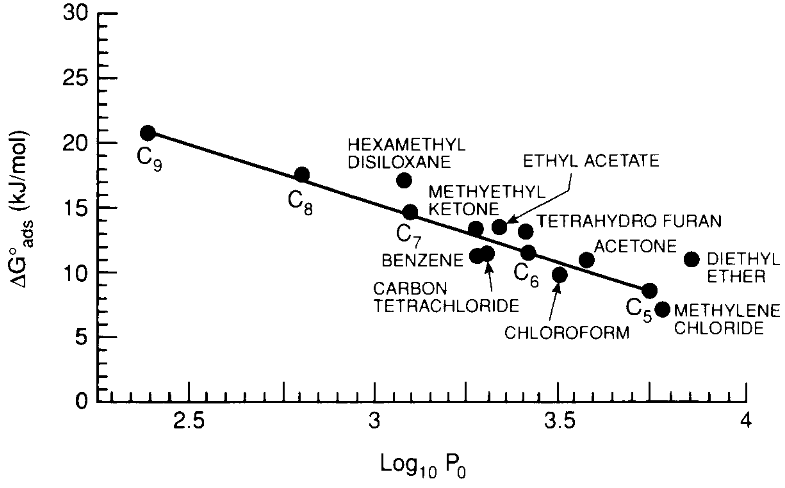

FIGURE 11 Retention diagram for HS-5DT.

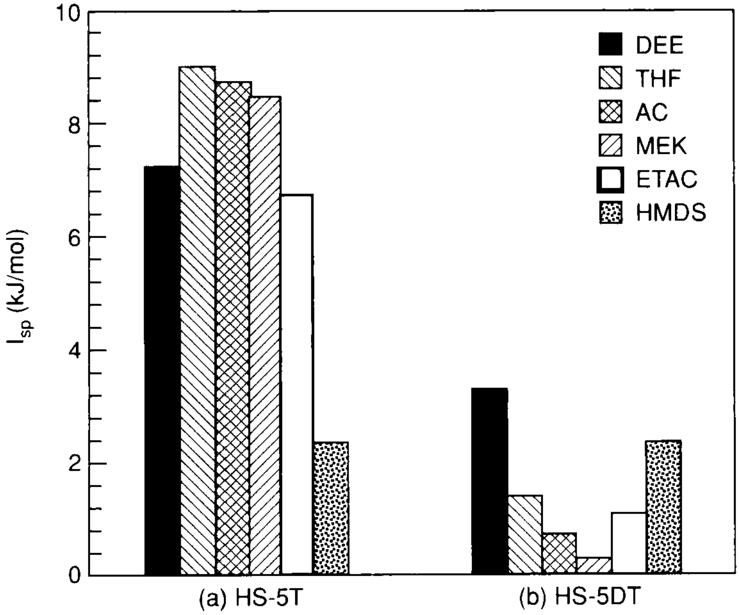

FIGURE 12 Effects of thermal history on the specific interactions of basic probes with (a) HS-5T and (b) HS-5DT.

water and covered with trimethyl silyl groups. In addition, the γ_S^D for HS-5T of 27.2 mJ/m^2 was similar to the γ_S^D for polyethylene of 31.1 mJ/m^2, indicating that the silazane-treated filler has a significant hydrocarbon character.

4 CONCLUSIONS

IGC provided an opportunity to characterize the surface chemistry attributes of fumed silica fillers of controlled thermal history and surface treatment. Heat treatment of raw fumed silica (Cabot HS-5) resulted in decreased specific interactions. In particular, I_{sp} for THF decreased from 15.3 kJ/mol at 150°C to 10.5 kJ/mol at 750°C. This is consistent with the loss of polar species such as bound water and adjacent silanols. The dispersive interactions increased with heat treatment from 67.6 mJ/m^2 at 150°C to 87.8 mJ/m^2 at 650°C. This increase in γ_S^D was attributed to the formation of strained Si—O—Si bonds arising from the condensation of adjacent silanols. The effects of heat treatment on the specific free energy of adsorption for the two hexamethyldisilazane-treated fillers was also considered. I_{sp} for the heat treated sample (HS-5DT) was 2–30 times lower, depending upon the probe, as compared with the hydrated sample (HS-5T), emphasizing the importance of bound water concentration. The dispersive interactions increased from 27.2 mJ/m^2 to 57.8 mJ/m^2 upon heat treatment at 750°C, indicating that many of the strained Si—O—Si bonds were not destroyed during the silazane treatment. In general, this work has shown that I_{sp} depended upon both the concentration of hydroxyl groups (bound water and adjacent silanols) and the coverage with trimethyl silyl groups in the case of silazane-treated fillers. Furthermore, γ_S^D depended upon the ability of the trimethyl silyl groups to shield the electron-rich silica, including strained Si—O—Si bonds formed during the heat treatment process.

Acknowledgements

The author gratefully acknowledges E. Thaler for many helpful discussions concerning fumed silica properties and production and for carefully reviewing this paper. J. Burness and J. Dillard are acknowledged for their assistance in initiating this work. S. Buddle conducted the BET surface area measurements. The Perkin-Elmer Corp. is acknowledged for supplying the Autosampler GC to evaluate its capabilities as an IGC.

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