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Effect of Silica Particle Size on Polymer Adsorption. Morphological, Energetic and Conformational Relationships

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Summary: A series of six chemically treated and untreated fumed silicas with increasing particle size (ranging from the nano- to the micrometer size) was prepared. Surface areas (and morphologies) and surface energies were determined by nitrogen adsorption and inverse gas chromatography, respectively. The adsorption of a series of PDMS with different and well-defined molecular weights was studied at different polymer concentrations. Amounts of adsorbed polymer were determined by gravimetry and the energies of adsorption were assessed by flow-microcalorimetry. Results are discussed in terms of particle surface energy and morphology effects on the conformation and the inter-connectivity of adsorbed polymer molecules.

Keywords: adsorption; conformation; morphology; poly(dimethylsiloxane); silica; surface energy

Introduction

Polymer adsorption on solid particles is a key factor of material behavior in both colloidal and composite applications. Two measurable characteristics can theoretically define the resulting hybrids: i) the conformation of polymer chains on the solid surface, consequently the amount of adsorbed chains; ii) the strength of the polymer-solid connection. Both characteristics, for a given polymer/solid couple, are essentially governed by the particle morphology and surface energy, on the one hand, and by the affinity of the polymer towards the solid surface and consequently its adsorption energy, on the other hand. Few studies in the literature cover simultaneously these two aspects. The particular shape of the solid (finely divided particles) imposes additional specific limits on the polymer/filler organization, i.e., particle aggregation, polymer chain adsorption on multi-particles, polymer confinement, etc. The aim of the present work is to address the above-mentioned questions, the investigation part being based on several type of adsorption (physical, chemical, by condensation or by dispersive/specific interactions…). Under these conditions varying at least the two major constituents (the probe

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and the solid surface) becomes an essential requirement. Probes should differ in their nature and size and silica of different particle diameters ought to be investigated.

Materials

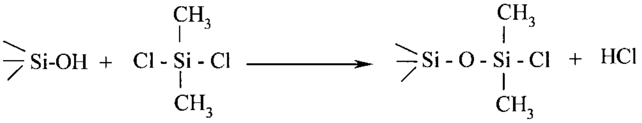
Table 1. Silicas samples.

Silicas	S_0 (m^2/g)
S05	50
S13	120
S15	150
S20	190
S30	310
S40	400

Six different fumed silicas, Table 1, were provided by WACKER-CHEMIE GmbH. Their surface areas and structures were defined by controlling flame temperature and combustion time reaction.

Modification, chemical adsorption

Thanks to a rigorous control of the combustion silica synthesis, the different untreated particles turned out to present the same density of OH groups per surface unit (1.83 OH/nm^2) disregarding the actual surface area. These different silicas were progressively modified by chemical reaction with dimethyldichlorosilane (DMCS).



$$\equiv Si\text{-}OH + Cl - \overset{CH_3}{\underset{CH_3}{Si}} - Cl \longrightarrow \equiv Si - O - \overset{CH_3}{\underset{CH_3}{Si}} - Cl + HCl$$

Elemental analysis points at a complete absence of chlorine in the treated samples. In order to explain this behavior, carbon content, %C, associated with the number of grafted group per unit surface area, n_g, was monitored by elemental analysis while OH residual groups were determined by acid-base titration. Figure 1 shows the evolution of the number of residual OH groups per unit surface area, n_{OH}, vs. n_g (the number of grafts per unit surface area, based on C% and the original surface area S_0). The number of grafts attached to the surface is higher than the number of disappeared OH groups, which indicates the occurrence of a substantial condensation reaction of DMCS. Thus, the complete disappearance of chlorine atoms after grafting suggests a surface reaction of the condensed chlorosilane molecule with an accessible surface hydroxyl group. In addition, we notice a similar behavior at both the molecular and surface unit levels for all studied silicas. Grafting efficiency decreases proportionally with decreasing the remaining n_{OH} irrespectively to the total OH number that is surface dependent.

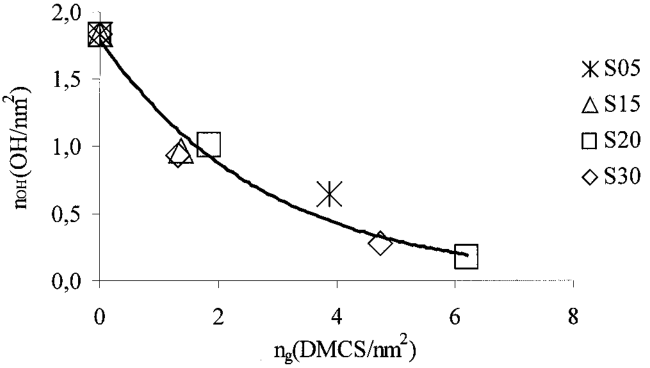


Figure 1. Grafted groups as a function of residual OH groups.

N_2 adsorption at low temperature, molecular condensation

The specific surface areas of silicas were measured before and after modification with DMCS from N_2/77K adsorption isotherms, using the BET mathematical treatment[1].

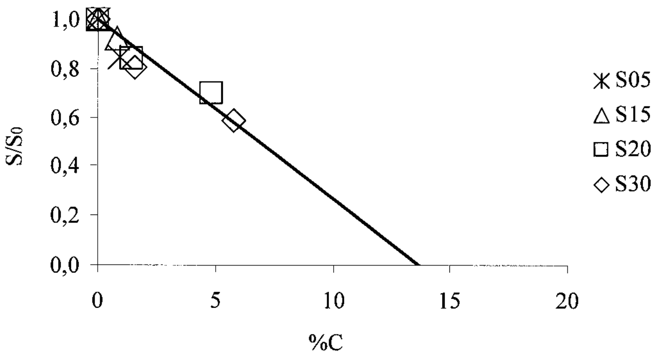


Figure 2. Evolution of reduced surface area, S/S_0, with the extent of surface modification of silicas.

Figure 2 shows that the reduced surface area (S/S_0, where S_0 refers to the untreated surface) decreases monotonically with increasing surface treatment [%C directly proportional to the total number of grafted groups; notice that C% is expressed with reference to mass unit (g) and not to the surface area unit (nm^2)]. This decrease seems to be quite similar for all silicas, i.e. one grafted group reduces the measured BET surface area by an identical percentage independently of the actual surface area. As one graft hinders or modifies the nitrogen adsorption by an extent proportional to the surface area of the silica, the higher the surface area, the lower the number of N_2 molecules which can be adsorbed on this surface after treatment. In addition, a quite good linear proportionality exists between both parameters.

Surface energy, adsorption at high temperature

Inverse Gas Chromatography (IGC) is a direct tool for the determination of the surface free energy of powders[2]. It was used in this study under infinite-dilution conditions within the 150-210°C temperature range. Results can be expressed in term of increment of free energy of adsorption, ΔG_a (related to the retention volume, V, of series of solutes, alkanes or siloxanes, of an increasing size) or in term of γ_S^D, dispersive component of the surface free energy. The latter is in the case of alkanes equal to[3,4]:

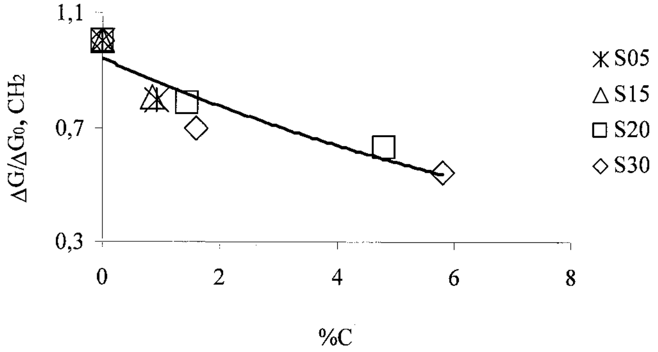


Figure 3. Evolution of the reduced free energy of adsorption of silicas with the surface modification degree (alkanes, T=160°C).

$$\Delta G_a(CH_2) = -RT.\ln\left(\frac{V_{n+1}}{V_n}\right)$$

$$\gamma_S{}^D = \left(\frac{\Delta G_a(CH_2)}{2N.aCH_2}\right)^2 \frac{1}{\gamma_{CH2}}$$

where γ_{CH2} and a_{CH2} are respectively the surface energy of a surface containing CH_2 groups only and the surface area corresponding to a methylene group.

The free (surface) energy obtained using alkane probes is shown (as reduced values or $\Delta G / \Delta G_0$, where ΔG_0 refers to the untreated silica surface) in Figure 3 as a function of the surface modification, %C, for the different silicas. ΔG_a decreases substantially with surface treatment, this reduction is similar for all silicas, whatever their surface area.

It seems that the effect of the chemical modification on the alkane free energy of adsorption goes beyond the molecular level of a graft, similarly to its effect on N_2 adsorption. Grafted molecules decrease the surface energy by an extent, which is proportional to the original surface area. This behavior is similar for all temperatures by using n-alkane probes. For siloxane probes, although we obtain qualitatively the same kind of ΔG_a reduction upon surface treatment (Figure 4), such reduction, conversely to the alkane behavior, remains dependent on the surface area (results not shown), and therefore the effect of the graft on silicas in ΔG_a is only associated with its molecular level.

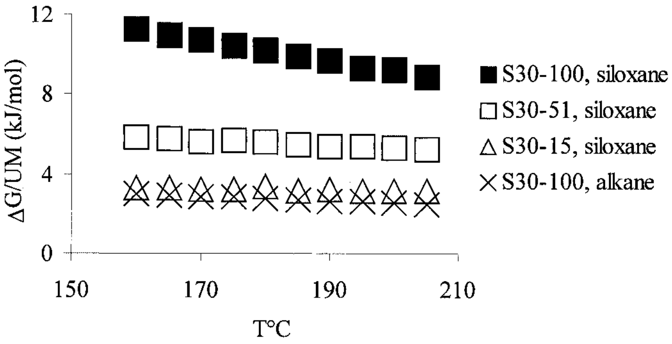


Figure 4. Siloxane free energy of adsorption-temperature dependence of untreated silica S30-100 and treated ones with 51 and 15% residual OH groups; alkanes free energy of adsorption is reported for the same untreated silica.

It is worth noticing that siloxane-silica interactions are far stronger than alkane-silica ones. Figure 4 reports ΔG_a as a function of IGC measurement temperature for untreated S30-100 and treated S30-51 and S30-15 silicas, with respectively 51 and 15% residual OH groups. ΔG_a decreases with temperature, but most of all that siloxane free energy of adsorption (thus surface energy), as well as its temperature-dependence, decreases upon treatment. Figure 4 includes for comparison $\Delta G_{a\,\mathrm{alkanes}}$ for the untreated S30 silica.

We should notice here that even though upon surface grafting, ΔG_a siloxanes decreases with respect to ΔG_a alkane in a different way that the behavior of both probes facing modified surfaces. Furthermore, the IGC technique is highly sensitive to the surface sites of high energy and therefore could not give a "complete" picture of the actual activity for a given surface. The adsorption of polymer probes has thus to be investigated.

Flow micro calorimetry, polymer adsorption from solution

Polymer adsorption measurements, conversely to those of small molecules, need necessarily to be performed either in the melt or from solution. They can be monitored by the determination of the amount of adsorbed polymer or by the measurement of its heat (enthalpy) of adsorption. The flow microcalorimeter, FMC[5], is built to measure the small heat exchange, which occurs when molecular bonds on a surface are made or broken. It is also able of measuring the quantity of material involved in such phenomenon, thanks to an appropriate detector (UV, refractive index...).

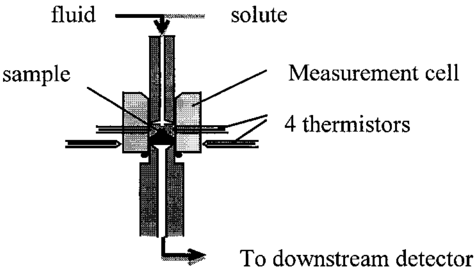


Figure 5. FMC apparatus, schematic representation.

Its fundamental principle is the following: the sample under investigation is placed in a test cell (Figure 5); a fluid (polymer solvent) is then allowed to percolate through the sample bed. All thermal events are detected thanks to four thermistors connected to a Wheatstone bridge and controlling units. Calibration is effected using a small heating coil located in the cell through which a small and controlled electric current is passed for a known time. After equilibrium is established, any modification of the fluid stream composition alters the equilibrium and the heat exchange outcome is recorded. Un-adsorbed and/or desorbed probes are detected by an appropriate downstream (refractometer or UV) detector. In this study adsorption enthalpies were determined in "pulsed mode" using a Microscal FMC with a

Perkin Elmer Totalchrom Workstation integrator. The constant flow rate was insured thanks to a Gilson 307 pump. The adsorbent was placed in the flow cell and brought in contact with n-heptane, maintained constantly under an inert atmosphere (argon). 10g/l poly(dimethylsiloxane) (PDMS) solutions were prepared using the same solvent and were introduced into the FMC, in a typical "pulsed mode" experiment, through a 20 µl loop. The actual amount of injected polymer is quite small (0.2 mg) as compared to the available large silica surface area in the cell (sample of about 100 mg). Three different PDMS (P4, P29, P420) the molecular weights (MW) of which are respectively 4000, 29000 and 420000 g/mol as well as oligomers of the same polymer such as hexamethyldisiloxane $(CH_3)_3Si\text{-}O\text{-}Si(CH_3)_3$ (HMDS), were purchased from GELEST-ABCR.

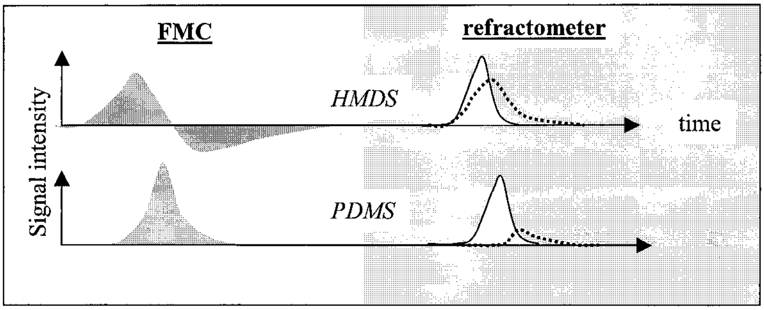


Figure 6. HMDS temporary adsorption and PDMS permanent adsorption on silica. Gray areas represent FCM thermogrammes while refractometer results are presented by continuous and dashed lines for reference injected directly in the detector and desorbed solute, respectively.

Generally in the pulsed FMC mode, low molecular weight probes (HMDS in Figure 6) show an exothermal adsorption peak upon adsorption of the solute followed by an endothermal one as the solute is desorbed from the solid surface. Almost the total amount of solute injected in the FCM through the loop gets out the cell and is detected by the downstream detector (as seen by the comparable surface of the two peaks). When a polymer such as PDMS is used as a solute it shows a peculiar behavior. Although it exchanges as much enthalpy, exothermal peak, with the silica surface as oligomers, it exhibits almost no endothermal peak (no desorption) and the fraction of retained polymer is very close to total (as supported by the small downstream detector recorded peak compared to the reference one). In this case, the adsorption is said to be permanent.

The present work offers for the first time, to our knowledge, a relatively complete and comprehensive FMC study of polymer adsorption on filler. An illustration of the usefulness of this technique is illustrated by the study of the effect of surface area on the enthalpy of adsorption. Indeed, Figure 7 shows the molar enthalpy of adsorption, E_{mol}, (the experimental heat of adsorption normalized with reference to one gram of both silica and effectively adsorbed polymer) as a function of the silica surface area for the three PDMS with different MW. It is obvious that the enthalpy involved with polymer adsorption is quite large even for the shortest chain (energy close to that of covalent bond). It gives a reasonable explanation to the permanent adsorption in the case of macromolecules in general.

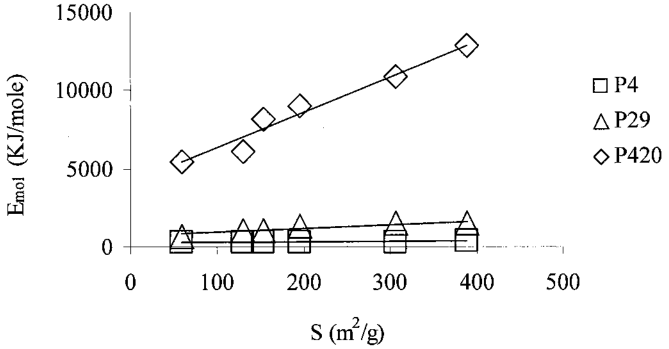


Figure 7. Molar enthalpy of adsorption, E_{mol}, as a function of surface area of silica for PDMS with different MW.

For a given molecular weight, the enthalpy of adsorption increases with the surface area of the solid. In view of the facts that (i) E_{mol} can be reasonably considered as directly proportional to the number of polymer-surface junctions; (ii) for a given molecular weight the conformation of a chain is realistically supposed to be independent of the surface area on which it may adsorb, since the only driving forces affecting the degree of spreading of a macromolecule are its molecular weight and concentration; (iii) for each molecular weight, experiments are performed under surface excess and constant concentration criteria, E_{mol} should be independent of the surface area. However, two factors may, at this point, explain the E_{mol} surface dependency. The first one is *conformational*, and is related to surface activities as expressed by surface energy, γ_s^D, which were observed to increase with increasing surface area (results not shown here but identical ones are reported by Thielmann[5]); consequently, this would rise the strength and/or the number of attractive forces which in turn would force a given chain to adopt progressively a flatter conformation.

The second is purely *geometrical* and scale-related; in fact, when dealing with closely packed powders, increasing surface area means a reduction of particle size and thus of the size of the inter-particle cavities. Consequently, for a polymer of a given molecular weight having the same conformation (random coil as a first approximation) on all surfaces, increasing surface area would lead to an increase of the number of possible contact points with the silica by multiple or inter-particle connections.

Figure 7 shows also, as expected, that the higher the molecular weight, the higher the enthalpy of adsorption. However, and in view of the above results, it is obvious that in order to compare different molecular weights and the extent of spreading of each macromolecule one should normalize the results by a conformational factor such as the gyration radius in a first approach.

In Figure 8 two kind of normalizations are made. The first one with respect to the polymer molecular weight, i.e. E_{Rg} where

$$E_{Rg} = E_{mol} / MW^{1/2}$$

$MW^{1/2}$ reflecting the gyration radius of the adsorbed molecule. The second one with respect to a state of reference, E_{Rg} / E_{Rg0}, that was taken arbitrarily as being the smallest surface, S05, of the studied silica series.

It is observed that the enthalpy of adsorption of P4 can be distinguished by a surface area-independence, conversely to what is observed for P29 and P420 which show proportionally an identical increase of the enthalpy of adsorption with increasing surface area. P4 behaviour could be explained by its eventual high and equal accessibility to all cavities without being caught up by other particles (intra-particle adsorption), given its relatively small radius of gyration. In opposition, high molecular weight adsorption seems to proceed by, essentially, an inter-particle process. It is worth noticing that the two high MW's show the same degree of inter-particles adsorption despite the significant difference in their sizes. This may be an indication that the arbitrary chosen factor of normalization is quite reasonable and not too far from reality.

Conclusion

In order to reveal surface complexity, structural, geometrical, chemical and energetic, of solids in a powder form, for instance filler particles, one should use appropriate experimental approaches specifically designed for such solids. Gas condensation at low temperature (BET) and adsorption at high temperatures (IGC) are commonly used for this purpose. FMC technique turned out to be a very valuable approach too, with the significant advantage of testing high molecular weight probes (polymers) through a fairly direct way. Furthermore, adsorption ability at variable scales (of both solid and probe) and conditions is a highly productive source of information.

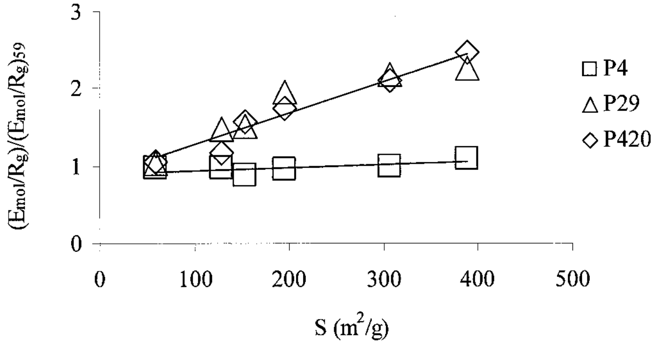


Figure 8. Reduced molar enthalpy in reference to S05 as a function of the surface area for different molecular weights.

Thanks to this approach we may underline the following conclusions:

- The effect of surface modification of silica may be both limited to the only graft size and position or overwhelming those limits to larger scale depending on the chemical nature of the probe approaching such a modified surface. Such control of chemical and energetic specificity helps out a better design of surface engineering.
- Inter-particle adsorption leads to an unusual MW-energy dependency (compared to adsorption on a flat surface or separated particles[7]; it may reveal the internal structure of filler aggregates.
- Particle packing and arrangement has a decisive role in controlling polymer-filler adsorption energy. Together with the size of the polymer (MW) it settles the adsorption nature to be of inter- or intra-particle form.

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