

Follow the evolution of grafted materials by their surface properties: Influence of grafting on the dispersive surface energy (γ_s^d)

Application note | May 2020

Field of applications

Powders and fibres materials | Surface properties tailoring | Grafting and coating

Executive summary

Modifications and optimizations of material's surface properties are important issues for Research and Development in industry and academic departments. Several questions often arises:

How can we identify the modifications of the surface - beyond simple application test ? What are the real impacts of such modifications on the surface properties and the interaction potential of solid material?

Inverse Gas Chromatography has proved its capability to provide detailed information on a material's surface. This technique probes the surface of a material by dynamic gas adsorption of different molecular compounds interacting with the surface of the solid material. These molecular probes help to access many different properties of a surface. Among the properties provided by the IGC technique, the notion of dispersive

component of the surface energy (γ_s^d) is introduced through an example. Silica materials grafted at different ratios are compared on basis of the surface energy. Thereby, the methods and its basics are explained in details.

IGC can easily be applied to any kind of solid materials, especially powders and fibers, but also flat, coated surfaces. It provides insights into surface modifications and subsequent optimizations.



Objectives

This application note describes the influence of grafting onto the dispersive surface energy of a material in detail and explain thereby the basics of IGC. This technique provides sensitive and quantitative information on the material’s surface interaction property. This is demonstrated herein by studying silica samples with increasing grades of organic grafting. The basics and calculations of the disperse surface energy are outlined in detail to provide a solid understanding of the unique capabilities of IGC. The silica samples serve thereby only as an example of the many hundred different materials and thousands of samples which have been analyzed during the last twenty years.

Principle

The dispersive component of the surface energy (γ_s^d) can be determined by Inverse Gas Chromatography at Infinite Dilution (IGC-ID) [1-2]. Note that, the term “dispersive” is based herein on the definition of the dispersive London forces, meaning non-polar, van der Waals forces. It is used like this in the literature, but it has nothing to do with two-phase dispersions (suspensions or emulsions), which is sometimes misleading.

The method to determine the dispersive component of the surface energy has been pioneered by Dorris and Gray in 1979 [3]. They discovered, that the residence times of a homologous series of n-alkanes (hexane, heptane, octane...) respond in a very linear way if the logarithm is used. But first some basics. The powder samples (e.g. silica) is filled in a small tube (e.g. Ø 2 or 4 mm) and inert gas passed over it. At time zero a very small concentration of a probe molecule plus a trace amount of CH_4 is injected. CH_4 acts as inert tracer and marks t_0 . The effective residence time t_N is calculated by the subtraction of the residence time of the probe (t_R) by t_0 (Figure 1).

In fact, t_N represents the surface residence of the probe molecules adsorbed on the surface sites and thus correlates with the strength of the interaction. The used n-alkanes have two special properties. First, they are highly “flexibles” and therefore are able to access easily all sites (porosity, defect, adsorption site, dislocation, adsorbed impurities, specific structure...). Second, in a homologous series, their adsorption behavior is determined just by an additional “-CH₂-”. This allows a relatively simple approach, but very consistent and with highly linear results.

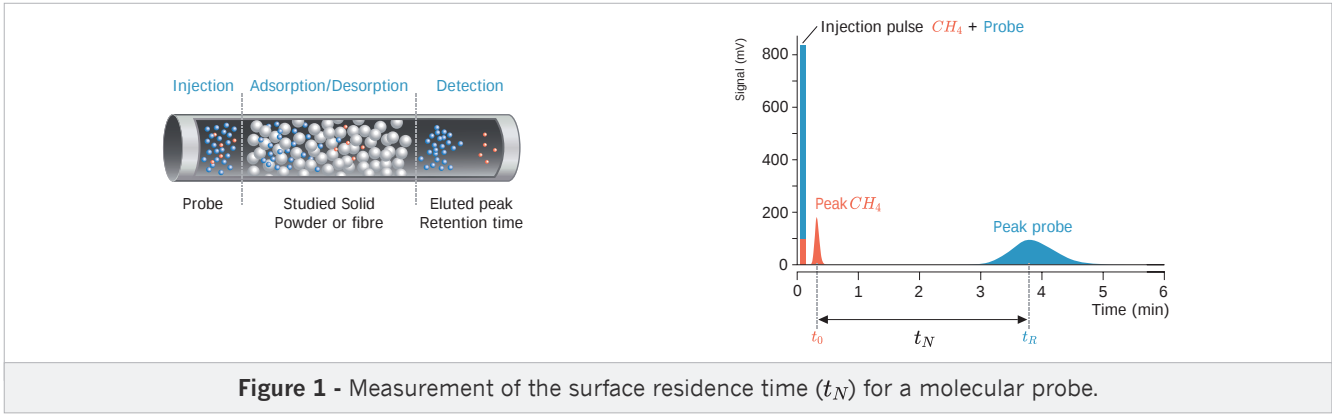


Figure 1 - Measurement of the surface residence time (t_N) for a molecular probe.

Under the assumption of very low, ideal concentrations, so-called “infinite dilution” conditions, the measured t_N are directly related to their free energy change of adsorption (ΔG_a) (Equation 1 & 2).

Equation 1
$$V_g = \frac{273.15}{T} \cdot \frac{D_c}{m_s} \cdot t_N$$

with V_g the specific retention volume, T the measurement temperature, R the gas constant, D_c the carrier gas flow in the column and m_s the weight of the sample.

Equation 2
$$\Delta G_a = RT \ln(V_g)$$

Dorris and Gray proposed an approach based on the following statement: for n-alkanes, ΔG_a varies in a linear way with the number of their carbon atoms. Surprisingly, a highly linear, straight line can be obtained by plotting the variation of free energy change of adsorption (ΔG_a) of n-alkanes probes as a function of their corresponding carbon atom number or Wiener topology index (χ_t) [4-6] (Figure 2). The slope of the n-alkanes line corresponds thereby to a free energy increment of a methylene group “-CH₂-” ($\Delta G_a^{CH_2}$). From this value, the dispersive surface energy γ_s^d can be determined by the Dorris and Gray equation (Equation 3). Note that, the slope, and consequently the value of γ_s^d , is independent of the specific surface area of the measured samples, since surface area specific terms are cancelling out.

This means, samples of different specific surface areas can easily be compared without any ambiguity due to their different surface area.

Equation 3
$$\gamma_s^d = \frac{1}{\gamma_{CH_2}} \cdot \left(\frac{\Delta G_a^{CH_2}}{2N \cdot a_{CH_2}} \right)^2$$

with N the Avogadro’s number, a_{CH_2} the area of an adsorbed “-CH₂-” group (6 Å) and γ_{CH_2} the surface energy of a solid entirely constituted by “-CH₂-” groups ($\gamma_{CH_2} = 35.6 - 0.058 \cdot (T - 20)$, with T in °C).

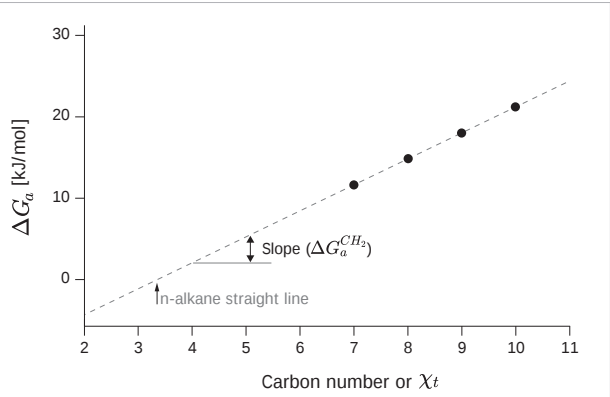


Figure 2 - Variation of free energy change of adsorption (ΔG_a) of n-alkanes probes as a function of their corresponding carbon atom number or Wiener topology index (χ_t).

Examples

General scope:

The present study aims to follow by IGC-ID the surface properties of modified silica at various grafting ratios (coverages) with a silanisation agent (octyltriethoxysilane) focusing changes of the surface energy (γ_s^d). The examined silica samples include the non-grafted starting material PS U22 (Ultrasil 7000) and several PS U22 grafted samples (with grafting ratios ranking from 3 to 12.5 %m). Here, several questions can be raised: **How does this silanisation agent modify the surface properties? What is the impact on the surface energy γ_s^d ?**

Results:

The values of γ_s^d , for each impregnation ratio, are calculated from the slopes of the straight lines representing ΔG_a versus the number of carbons of the alkane probes, according to the Dorris and Gray approach (Figure 3, left). It can be noticed that the straight lines become significantly less steep when increasing the grafting ratio from 0 to 12.5 %m. This indicates a weaker interaction of the surface with “-CH₂-” groups and therefore a lower disperse (non-polar) surface energy. In other words, the surface energy value γ_s^d is much lower for the highly grafted silica than for the non-grafted silica.

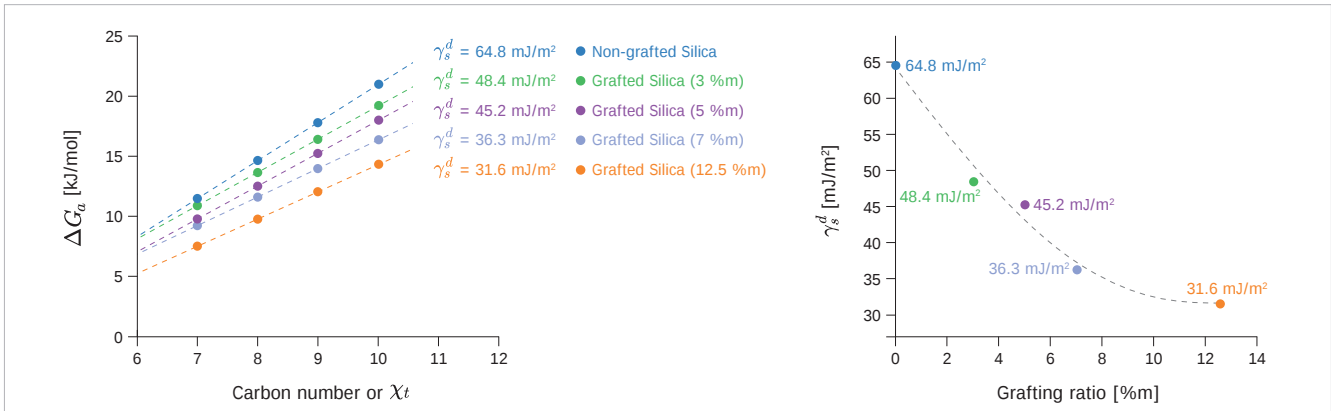


Figure 3 - (Left) n-alkanes straight lines obtained from IGC-ID measurements at 110°C for the grafted silica and (Right) evolution of the surface energy (γ_s^d) values as a function of the grafting ratio.

Figure 3 (right) shows the decrease of γ_s^d values for the modified samples upon increasing the grafting ratio. It can be noticed that the surface energy (γ_s^d) decreases readily from 64.8 to 31.6 mJ/m² with the increase of the grafted ratio until it reaches a value of 12.5 %m. The highest γ_s^d value is measured for the starting material, i.e. the non-grafted silica whereas the lowest value was determined for the most grafted silica (31.6 mJ/m²). Due to the grafting, the accessibility to the silica surface is lesser, therefore even though the alkane probe interacts with the organic, the surface energy is decreasing.

Conclusions

This application note explains in detail the basics of inverse gas chromatography at infinite dilution (IGC-ID) and the calculation of the disperse surface energy (γ_s^d). The example of silica-based materials with different grafting ratios, shows nicely, how the changes in surface properties can be measured step-by-step. In this case, increasing grafting ratios decrease progressively the dispersive component of the surface energy. In this study, as well as in many other published studies, IGC-ID has demonstrated

its ability to determine surface properties quantitatively and highly sensitive.

To go further on the investigation of the surface properties, other questions can be raised: what would be the influence of grafting onto the surface morphology or nanoroughness? What is the impact on the surface polarity (specific interactions)? Look forward to our next application notes to find out the answer to these questions.

References

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Customers



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