Follow the evolution of grafted materials by their surface properties:
Influence of grafting on the surface nanomorphology (IM, RIM)

Application note | June 2020

Field of applications

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

Executive summary

Adscientis has developed a unique concept of molecular “nanoroughness” describing the surface morphology of a material by very subtle differences towards linear, branched and cyclic probe molecules and thereby adding a very powerful concept to characterize and understand solid material surfaces.

How can we define “nanoroughness”? What experiences have been made? Which story can inverse gas chromatography tell about your material surface?

Inverse gas chromatography has proven its potential ability to deliver accurate information on surface properties such as the adsorption free enthalpy variation (ΔG_a), the dispersive surface energy (γ_s^d), the surface polarity character and the nanomorphology of the surface. In practice, the concept of nanomorphology or nanoroughness has been proven to very be useful, but its definition is not straightforward. Furthermore, alternative IGC suppliers are not capable of exploring it due to limited number of probe molecules.

The concept is described using the example of differently grafted silica samples. The evolution of the nanoroughness, upon increasing the grafting ratio of the silica material, provides valuable information on the surface interactivity and property. The method has been applied to hundreds of other solid materials as carbon blacks, calcium carbonates, excipients, active pharmaceutical ingredients, carbon fibers and even treated hair. It is very sensitive and reproducible and can thereby provide excellent guidance towards an ideally tailored surface treatment.

Objectives

This application note is to describe the influence of grafting onto the nanomorphology or "nanoroughness" of a material's surface and explain thereby this concept in detail. Inverse Gas Chromatography (IGC) is a unique surface analytical technique [1, 2] to measure nanoroughness on a subtle molecular level and to provide a better understanding of a solid surface morphology, its properties and/or behaviour. Here, several organically grafted silicas are used as an example to demonstrate the influence of grafting onto a material's surface nanoroughness.

Principle

To measure surface "nanoroughness", Adscientis has developed an IGC method that compares the behaviour of **linear n-alkane** probes with less "flexible" molecules, i.e. **branched and cyclic alkanes** (e.g. cyclooctane and isooctane). Due to their structure and shape, these branched and cyclic probes are less able to access the surface "nanoroughness" (i.e. porosity, microporosity, surface defects, specific structure, size exclusion phenomenon). For an easier indication of the surface "nanoroughness", a morphology index has been defined. **The morphology index (IM)** is given by the ratio of the retention time of the branched/cyclic alkane molecule (t_N) and the theoretical retention time of this probe (t_N^{ref}) assuming its behavior is similar to a linear alkane, i.e. using the calculated carbon number of this probe molecule (Equation 1).
Below, three different situations are described to explain how the morphological index can be interpreted in term of surface properties. See our publications or application note for further details [1, 2, 3].

Situation 1: ΔG_a **values of the branched and cyclic alkanes are located on** the n-alkanes straight line:

- Linear, branched and cyclic alkanes have the same accessibility ($IM_{branched/cyclic} \approx 1$).
- The surface is considered flat or smooth at the molecular level (**no nanoroughness**).

Situation 2: ΔG_a values of the branched **and cyclic alkane are located below** the n-alkanes straight line:

- The accessibility to the solid's surface of these probes is lower to those of the linear n-alkanes molecules (**size exclusion effects**) ($IM_{branched/cyclic} < 1$).
- The surface is considered "clean and nanorough" (**hard surface**).

Situation 3: ΔG_a **values of cyclic alkane is located above** the n-alkanes straight line while the ones of branched alkanes are located below the n-alkanes straight line:

- Generally observed in the case of organically coated or soft materials (**soft surface**) ($IM_{branched/cyclic} > 1$).
- Cyclic molecular probes are able to penetrate the organic coating or soft domains of the materials which can be related to "dissolution effect" and/or "3D interactions". Other causes of such behavior are polluted surfaces, amorphous phases, polymer coating or molten solids.

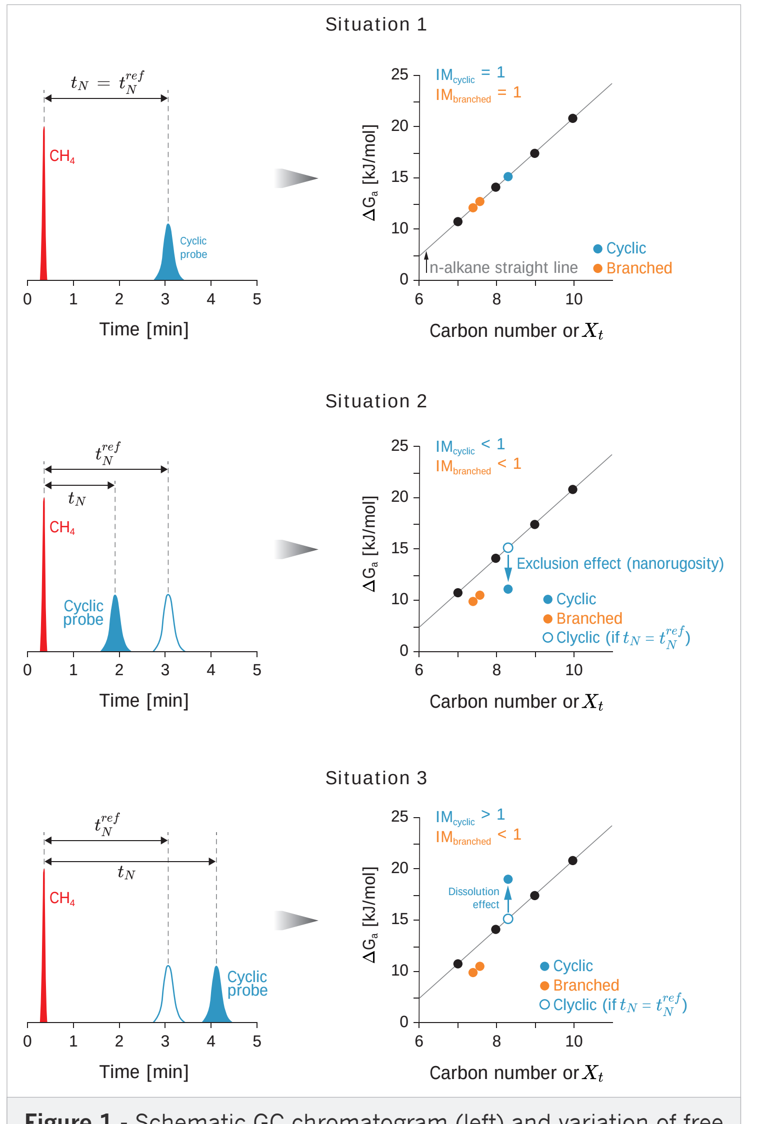

Figure 1 - Schematic GC chromatogram (left) and variation of free energy change of adsorption (ΔG_a) of n-alkanes, branched and cyclic probes as a function of their corresponding carbon atom number or Wiener topology index (X_t) (right).

Note that the situations described previously, i.e. "clean and nanorough" surfaces and "coated or soft" material are extreme. Intermediate situations, where hard and soft domains coexist are also possible. To describe such situations, Adscientis has developed the RIM index (Equation 2) based on numerous observed behaviours for coated, grafted and polluted surfaces.

Four different situations are commonly encountered:

- $IM_{cyc} \sim IM_{iso} \sim 1$, ($RIM = 1$): flat surface at the molecular scale
- $IM_{cyc} < IM_{iso} < 1$, ($RIM < 1$): clean and nanorough surfaces (hard surface)
- $IM_{iso} < 1 < IM_{cyc}$, ($RIM > 1$): organically coated or molten solids (soft surface, dissolution effect, 3D interactions)
- $IM_{iso} < 1 < IM_{cyc} < 1$, ($RIM > 1$): co-existing hard and soft domains

The term "nanoroughness" in the IGC field is a general term to describe the morphological state of the material. It uses two parameters (IM, RIM) to differentiate in great detail several aspects of the material surface.

Equation 1 $$IM = \frac{t_N}{t_N^{ref}} = \frac{V_N}{V_N^{ref}}$$

Equation 2 $$RIM = \frac{IM_{cyc}}{IM_{iso}}$$

Examples

General scope:

The present example demonstrates the changes in surface properties of silica modified at various grafting ratio (coverage) with a silanisation agent (octyltriethoxysilane). Measurements were done by IGC at infinite dilution (IGC-ID) using the concepts of nanoroughness. The examined silica samples include the starting material PS U22 (Ultrasil 7000) and several PS U22 grafted samples. The obtained grafting ratios are ranking from 3 to 12.5 %m. Numerous questions can be raised: **How does this silanisation agent modified the surface properties? How is this represented in terms of morphology index (IM)?**

Results:

Two probes are injected to assess the "nanoroughness" of the surface: cyclooctane and isooctane (cyclic and branched probe, respectively). Figure 2 shows the different behavior of isooctane (IM_{iso}) and cyclooctane (IM_{cyc}). The retention times of isooctane are practically unchanged by grafting, but increasing grafting increases significantly the retention time of isooctane. At the highest coverage ratio (12.5 %m) IM_{cyc} even exceeds 1.0. Such behaviour discrepancies between branched and cyclic probes can be attributed to the difference in solubility with respect to their structure. According to the Hildebrand solubility parameters approach [4, 5], the alkane solubility is classified in the following order: Branched alkanes < linear n-alkanes < cyclic alkanes.

When a solid is partially covered with organic material, not only surface interactions, but also probe-grafted molecules interactions can occur. The latter interactions are higher for cyclic than for branched alkanes. Increasing the grafting ratio enhances the probe solubility effects (dissolution of the probe) and consequently the IM value of the cyclic probe exceeds 1.0. On the other hand, the branched alkane solubility is not so favorable, therefore the silica-branched probe interaction remains the most important contribution for these probes. Accordingly, the results demonstrate nicely, how the surface of the silica changes from a clean and nanorough surface (starting material) to a fully organic coated and soft surface upon increasing grafting (Figure 3).

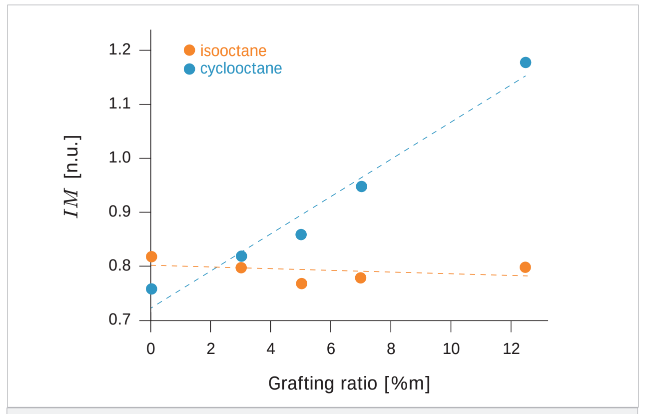

Figure 2 - The IM values as a function of the grafting ratio.

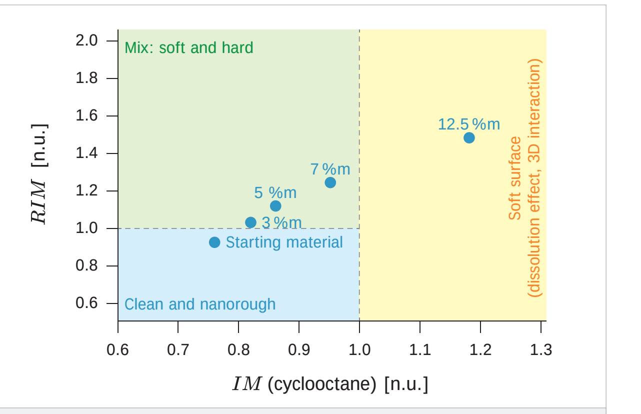

Figure 3 - Evolution of the surface behaviours with the grafting ratio.

Conclusions

This application note gives a concrete approach to better understand the IGC concept of "nano-roughness" based on different behavior of linear n-alkanes, branched and cyclic alkanes. The resulting parameters morphology index (IM) and relative morphology index (RIM) are highly sensitive to describe on a quantitative basis surface property as nanoroughness, cleanness, softness, amorphous phases or coatings with an organic material.

Inverse gas chromatography proves once again its potential ability to perfectly detect the presence of a surface morphology by playing on the probe molecules affinity/interactions with the solid surface. Moreover, by developing quantitative parameters as the IM and RIM, IGC opens the door to a well-understood product development and optimization as well as a better understanding of the morphology and the interactivity of any kind of powder, fiber or even flat surface.

References

ref 1. Adscientis, Technical sheet on IGC-ID, **2017**

ref 2. E. Brendlé et al., "Surface Properties Characterization by Inverse Gas Chromatography (IGC) Applications", *Powders and Fibers*, **2006**, 47-122

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ref 4. J. H. Hildebrand, "The Solubility of Non-Electrolytes", 2nd edition, New York: Reinhold, **1936**

ref 5. J. Burke, Part 2. «Hildebrand Solubility Parameter», The American Institute for Conservation, Washington, **1984**, 121

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