A way to better understand surface properties of carbon black fillers upon different polymers and coverages' evolution

Application note | April 2020

Field of applications

Carbon black | Polymers | Impregnation | Surface modification

Executive summary

When modifying the surface of a solid material by impregnation, e.g. to obtain a polymeric layer on carbon black filler particles for improved compatibility, several questions usually arise:

Is the surface totally or only partially covered by the polymer? How much polymer is needed to cover the surface entirely? How does the choice of the polymer influence the surface properties?

Inverse Gas Chromatography at infinite dilution (IGC-ID) is a useful technique to evaluate the quality of the impregnation and to explore the surface interactions between the polymer and the carbon black filler. The method used here is based on the assessment of the surface properties displayed by the areas of carbon black particles left uncovered by the polymer deposits. Three types of surface properties are determined: the dispersive component of surface energy (γ_s^d), the nanoroughness defined by the morphological index (*IM*) and the specific interaction parameter (ISP). By the combination of these properties, it is possible to determine:

— the quality (i.e. the covering ratio) of the polymer deposition on the filler particles

— the quantity of polymer necessary to cover the whole surface area of

— the carbon black filler particles

— the energetic sites involved by the polymer adsorption

— the difference of adsorption behavior between two polymers

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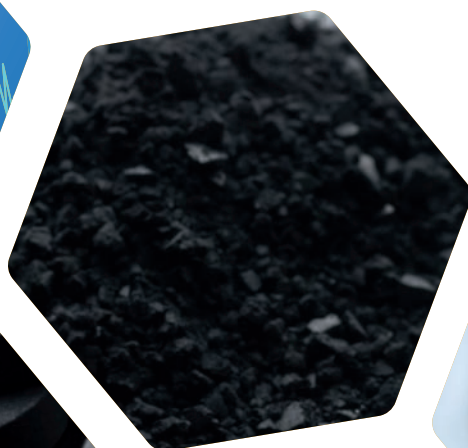
Objectives

This application note presents an example of Inverse Gas Chromatography at infinite dilution (IGC-ID) study for the characterization of surface interaction [1, 2]. Here, carbon black fillers impregnated by polymers are examined. The performances of polymer compounds reinforced by solid filler particles are strongly influenced by the strength of interactions at the interface between the filler and the polymer. However, most solid fillers, such as carbon black particles, do not have a homogeneous surface [3]. As a result, the surfaces can behave differently toward the adsorption of polymers. **The objective herein is to characterize the surface properties as function of different polymers and coverages and to determine thereby its suitability for industrial applications.**

Principle

IGC-ID measurements (110°C, helium flow rate of 20 mL/min) are performed on samples of carbon black fillers (specific surface area of 120 m²/g). These are impregnated at different ratios by two polymers: poly(butadiene (Pbut) and poly(ethylene oxide) (PEO). Samples have been preliminary conditioned to remove potential volatile pollutants (water, organics...) resulting from the sample production process. A set of 20 molecular probes (solvents) are injected at very low concentrations (infinite dilutions) in a stainless-steel column filled with the materials to characterize [2]. Under these conditions, the dispersive component of the surface energy (γ_s^d) using n-alkanes, the nanoroughness of the surface using branched and cyclic alkanes (cyclooctane), and the specific interactions level of the surface by injecting different polar probes (e.g. benzene...) are determined. From the obtained chromatogram, a retention time for each probe is obtained. The samples surface properties presented in the Results section are calculated from the retention times by different methods explained in detail in our technical sheet or article [1, 2].

Results

Effect of the polymer impregnation ratio onto the γ_s^d

From the results shown in Figure 1, it appears that both polymers behave differently when they are deposited on the carbon black surface. Their behavior is similar at low and high impregnation ratios but differs significantly in between.

The strong decrease at low impregnation ratios (< 0.1) indicates that the polymers are preferably adsorbed on the high-energy adsorption sites. At high impregnation ratios, the plateau reaches a value of 65 mJ/m², which is very high compared to the expected γ_s^d value for polymers (generally < 60 mJ/m²) [4]. Moreover, the plateau is not achieved at the value of 0.3 mg/m², corresponding to the theoretical monolayer for both polymers, assuming a surface area covered per monomer unit (24.4 and 28.0 Å², respectively for the PEO and the Pbut). Both observations suggest that the carbon black surface is not totally covered at a theoretical monolayer deposition, but with Pbut a coverage effect seems to be effective at much lower impregnation ratios compared to PEO on carbon black.

How can we interpret the polymer adsorption behaviour in between low and high ratio: It is assumed that the extremely high γ_s^d value observed on carbon blacks are related to the presence of so called "molecular cradles" at the edges of the layered polyaromatic structures in which the linear and flexible alkane chains may be temporally inserted. This favours additional interaction energy and leads to apparently excessive γ_s^d values which are not representative of average surface energies of a flat and homogeneous carbon black.
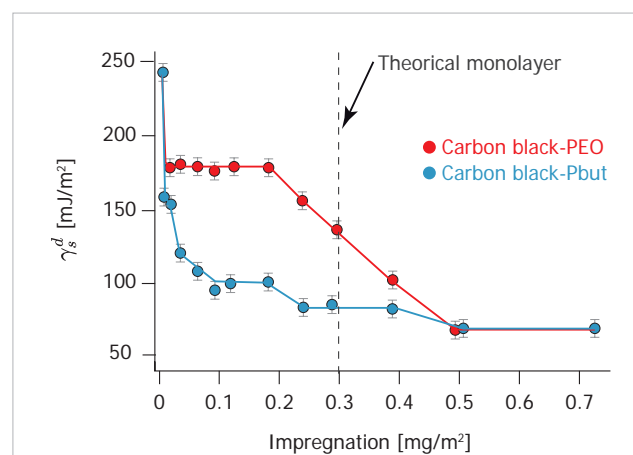

Figure 1 - Evolution of γ_s^d with the polymer impregnation ratio (milligram of deposited polymer per square meter of filler).

The following scenario seems a likely explanation of the observed results. The contact of carbon black with Pbut seems to screen the high adsorption sites very efficiently. In carbon black, acidic oxygenated surface groups are also located at the border of the "molecular cradles" which seem to attract Pbut through acid base interactions with the double bonds of Pbut.

Such an interaction is not possible with PEO. The initial decrease of γ_s^d can be attributed to a blocking of the polar acidic groups on the carbon black surface. But thereafter, there is no driving force to oblige the adsorbed PEO chains to conform the morphology of the high-energy part of the carbon black surface. It seems likely that the fixed PEO molecules act as attractive centers for the incoming PEO molecules. Thus, PEO islands are formed and growing until the entire periphery of the layered polyaromatic structures is covered. This is a progressive process as indicated by the IGC results.

Effect onto the surface nanoroughness

The morphological index (*IM*) for each impregnation ratio is shown in Figure 2. This value defines the surface morphology (or nanoroughness). Like with the surface energies, the *IM* values differ between the polymers. With low impregnation ratios, it appears that PEO is more capable to smoothen the carbon surface than does Pbut. The fact that the *IM* values remain < 1, even at high impregnation ratios suggests also that the polymer does not cover the entire surface in spite of quantities deposited sufficient to form a double layer and more. Pbut and PEO moreover do not have the same affinities for the carbon black surface. Consequently, the configuration they will adopt on the carbon black surface will not be comparable, as we already indicated before when looking at the γ_s^d results.
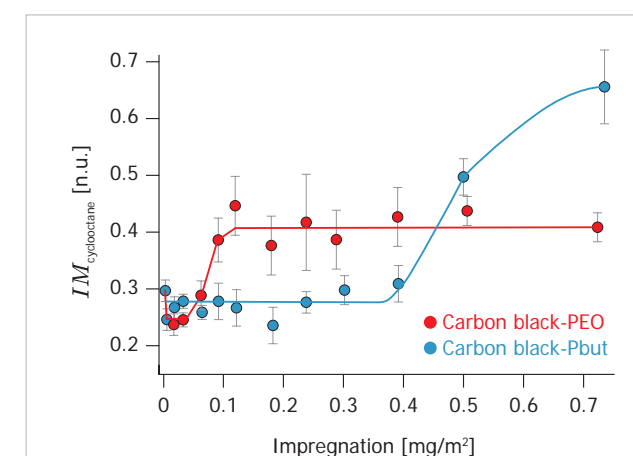

Figure 2 - Evolution of cyclooctane *IM* values with the polymer impregnation ratio.

Effect onto specific interactions

The specific interaction ability of the carbon filler samples is determined by several different polar molecules and expressed as specific interaction parameter (ISP). In this special case, only benzene is shown as a "polar" probe, see Figure 3. Once again, a different behavior is observed among the polymers. For Pbut, only a small decrease of benzene's ISP values is observed, indicating that Pbut is covering different adsorption sites than benzene. In contrast when the carbon black is impregnated with PEO, an important ISP modification is observed even at very low impregnation ratios resulting in a sharp decrease of the benzene ISP value to really low energy values. It seems that PEO blocks the high interactive adsorption sites (possibly acidic groups) which are favorable to strong benzene adsorption.
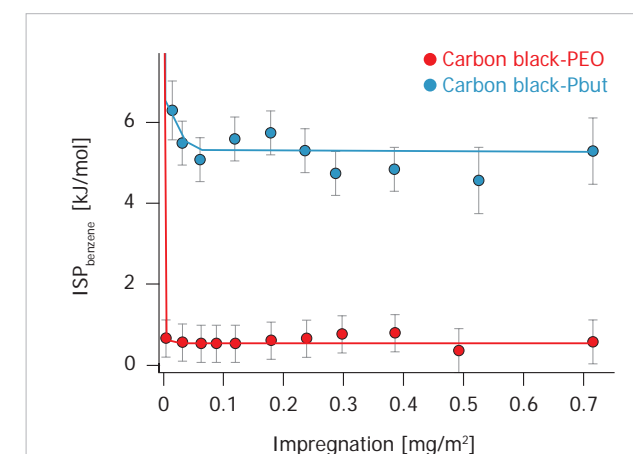

Figure 3 - Evolution of benzene ISP values with the polymer impregnation ratio.

Conclusions

This application note shows the ability of IGC-ID to follow the evolution of the surface properties of fillers or surfaces modified by polymer deposition. This technique is able to inform the experimenter if the surface is totally covered by the polymer or not as a function of the polymer addition. This way, real knowledge - and not guessing - is being acquired about the necessary quantity of polymer to cover the surface. Moreover, this method gives additional information about the sites of the carbon black surface which are most preferably being covered by the different polymers, including chemical and topological aspects. Finally, the surface energetic heterogeneity is an important parameter governing the strength of the interactions between fillers and polymers. The IGC-ID technique provides an interesting tool to understand and control this heterogeneity.

References

ref 1.   E. Brendlé et al., "Surface Properties Characterization by Inverse Gas Chromatography (IGC) Applications", *Powders and Fibers*, **2006**, 47-122

ref 2.   Adscientis, Technical sheet on IGC-ID **2017**

ref 3.   E. Papirer et al., "IGC determination of surface properties of fullerenes: comparison with other carbon materials", *Carbon*, **1999**, 37, 1264-1265

ref 4.   Z.Y. Al-Saigh, "Inverse gas chromatographic characterization of poly(ethylene oxide)", Polymer, **1999**, 40, 3479–3485

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