Indirect characterization of the surface properties involved by the adsorption of polymers on carbon black filler particles

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✍ Abstract

This paper is an attempt to illustrate the interest of using IGC at infinite dilution for the characterization of the surface interactions involved by polymer adsorption on filler particles. The method is based on the assessment of the surface properties displayed by the areas of carbon black particles left uncovered by the polymer deposits (these later being previously deposited from a polymer solution).

Three types of surface properties are considered:
- the dispersive component of surface energy (as determined by using n-alkanes probes);
- the nanoroughness as determined by the difference in adsorption behaviour between linear and branched alcanes;
- the specific interactions as detected by probes able to interact by acido-basic interactions, as for example benzene.

From the progressive disparition of the highest energetic sites associated with the increase in the amounts of adsorbed polymers, it is possible to identify those involved by the polymer adsorbtion. By changing the nature of the polymer (poybutadiene and polyethylene glycol), it is also possible to show how the nature of the chemical groups on the polymer influence the adsorption site on the carbon particles.

Keywords

Inverse Gas Chromatography, Infinite Dilution, IGC-ID, carbon black, poly(ethylene oxide), poly(butadiene), impregnation, γ_s^d, nanoroughness, acid-base interactions, surface modification.

Introduction

It is now generally accepted that the performances of polymer compounds reinforced by solid filler particles are strongly influenced by strength of the interactions established at the surface between the filler and the polymer. Like most solid fillers, the surface of carbon black particles is not homogeneous[1] but consist of a mosaic of areas differing by a large number of characteristics, which also behave differently toward the adsorption of polymers.

While IGC at infinite dilution was revealed to be an interesting tool for the assessment of the surface interactions of solid fillers toward gaseous molecules, it is not suitable to study the interactions toward non volatile macromolecules.

However, since macromolecules once adsorbed may be considered as definitely pinned on the surface, and since the surface interactions displayed by the polymer are generally much weaker than those displayed by the carbon surface, it is possible to assume that IGC remains a suitable technique to assess the surface characteristics of the areas left uncovered by the polymer. By difference with the surface characteristics of clean carbon particles, it becomes possible to ascribe the missing components to those involved by the polymer adsorption.

The various informations suitable to be obtained by IGC were already previously described [2, 3]

In order to illustrate its interest for the identification of the surface components involved by polymer adsorption, this paper considers only three parameters :

- γ_s^d the dispersive component of surface energy ;
- IM the nanoroughness ;
- ISP the specific interactions parameter.

Experimental

Fillers

For the present study the chosen filler sample is a carbon black having a specific surface area of 120 m²/g.

Polymers

Two polymers have been chosen to carry out these experiments: poly(butadiene) and poly(ethylene oxide). The poly(ethylene oxide) was provided by Aldrich (Ref. 372773-250G batch n° 17505MU) and possesses an average MW of about 400 000. The poly(butadiene) was also provided by Aldrich (Ref. 181382). It is formed of cis and trans poly(butadiene) having a Mw of about 420 000 and with respective ratios of 0.36 cis, 0.55 trans and 0.09 of 1,2 addition.

Polymer impregnation procedure

Those polymers were used to impregnate the filler. For each of the polymer-filler couples, twelve samples differentiated only by the amount of deposited polymer were prepared.

The impregnation procedure occurs as follows.

- Several solutions of the selected polymers, of chosen concentrations, were prepared. The solvent used for the poly(butadiene) solution preparation was cyclohexane of chromatographic grade, whereas the solvent for poly(ethylene oxide) was distilled water.
- A precise quantity, between 100 and 400 mg, of carbon black is placed in a beaker.
- To obtain the wished impregnation ratio, a precise volume of the best-adapted solution is added in the beaker.
- The solvent is then slowly evaporated.

The impregnation ratios are given on table 1. Those ratios are expressed in milligram of deposited polymer per square meter of filler. The reference filler surface area taken to compute the impregnation ratio is that given previously.

Table 1 : *Carbon black polymer impregnation ration [mg/m²].*

Samples	Carbon Black-POE	Carbon Black-PBut
0	0.000	0.000
1	0.003	0.003
2	0.015	0.015
3	0.030	0.030
4	0.061	0.060
5	0.089	0.089
6	0.120	0.117
7	0.180	0.178
8	0.237	0.238
9	0.298	0.286
10	0.387	0.387
11	0.497	0.503
12	0.723	0.721

Assuming a surface area covered per monomer unit of 24.4 and 28 square angstrom, respectively for the PEO and the PBut, the theoretical monolayer corresponds approximately to 0.3 mg/m² for both polymers.

The dried impregnated samples were used to fill the chromatographic columns.

Columns

All samples have been studied using 1/8" external diameter columns. The column length was adapted in function of the estimated sample interactivity. Usually, the samples corresponding to low polymer impregnation amounts were investigated using 10 cm long columns. The highest impregnation ratio samples were investigated with longer columns (20 cm).

Carbon black amounts between 200 and 50 mg were introduced in the columns.

Column conditioning

The aim of the sample conditioning is to clean the solid surface by eliminating all volatile pollutants (water, organics…). Obviously, these pollutants molecules are modifying the surface properties of the solid. This is very important in the present case where the samples have been impregnated into water or cyclohexane.

The chosen conditioning condition are the following:
- Conditioning temperature: 110°C.
- Duration: 15 hours.
- Carrier gas flow: 12-15 ml/min.

IGC-ID measurements

The IGC measurements, at infinite dilution conditions, were performed only at one temperature (110°C), using a helium flow rate of 20 ml/min (precisely measured).

Under these conditions, the following measurements were made:
- Dispersive component of the surface energy (γ_s^d) using n-alkane probes.
- Nanoroughness of the surface using branched and cyclic alkane probes.
- Specific interactions level of the surface by injecting different polar probes.

Results

Effect of polymer impregnation onto γ_s^d

From the results depicted in figure 1, it appears that both polymers behave differently when they are deposited on the carbon black surface.

The impregnation with minor amounts of poly(butadiene) (first impregnation ratio) induces a strong decrease of γ_s^d from 240 to 160 mJ/m². Increased impregnations ratios induce further and progressive decrease of γ_s^d values. The final γ_s^d value is of about 65 mJ/m².
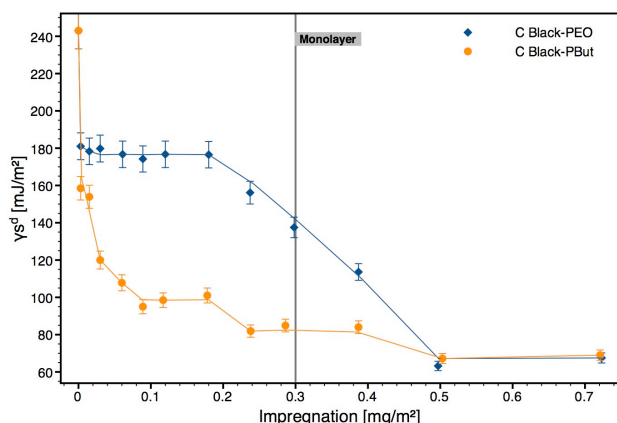

Figure 1 : *Evolution of γ_s^d with the polymer impregnation ratio.*

The variation induced by the PEO impregnation on the carbon black's γ_s^d values are different. Indeed, the first impregnation induces a strong decrease from 240 to 180 mJ/m². Thereafter, a plateau is observed followed by a progressive decrease and a plateau value corresponding to 65 mJ/m².

Both polymers are first interested by the high-energy adsorption sites that become occupied. However, the ways to reach the final γ_s^d value diverge thereafter.

The fact that 65 mJ/m² is very high compared to the awaited γ_s^d value for polymers suggests that all the carbon black surface is not covered in spite of the rather high quantities deposited, sufficient to form a double layer and even more.

It is assumed that the extremely high γ_s^d observed, by IGC, 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 be inserted. This will of course favour additional interaction energy and lead to apparently excessive γ_s^d values that, in no way, are representative of the average surface energy of carbon black.

The contact of carbon black with PBut, although it does not have the flexibility of alkane chains, will possibly screen those high adsorption sites. Furthermore, acidic oxygenated surface groups are also located at the border of the "molecular cradles" and may attract PBut through acid base interactions with the double bonds of PBut.

Such a strategy does not hold for the interaction with PEO. Indeed we may, as before, attribute the initial decrease of γ_s^d 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 (prismatic structure). We may postulate that the fixed PEO molecules will act as attractive centres for the incoming PEO molecules. PEO islands are formed and are growing until the entire periphery of the layered polyaromatic structures is covered. This of course is a progressive process as indicated by the IGC results.

Effect onto nanoroughness

Again the observed behaviours are depending on the used polymer. In the case of the impregnation with PBut, we observe an increase of the IM index from 0.25 to 0.43 when the impregnation ratio is varying from 0 to 0.1 mg/m². A long plateau follows this augmentation up to 0.8 mg/m².
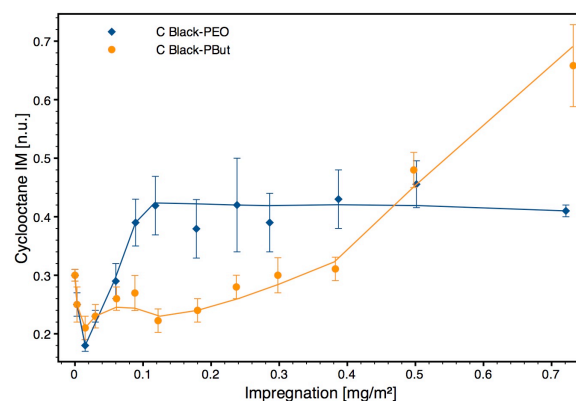

Figure 2 : *Evolution of Cyclooctane IM values with the polymer impregnation ratio.*

In the case of the PEO impregnation, a significant IM value increase is observed after a coverage ratio of about 0.4 mg/m². Thereafter, an increase is observed and an IM value of about 0.7 is reached for a coverage ratio of 0.7 mg/m².

It seems that the PBut, at the first stages, is, as we have suggested it earlier, more capable to smooth the carbon surface than does PEO. The fact that the IM values remain lower than 1, even at the high impregnation ratio suggests also that the polymer

do 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 it before when looking at the γ_s^d results.

Effect onto specific interactions

The previous part of our report described only the dispersive, i.e. the non-polar (or non specific) interaction ability of the surface. In this part, polar probes will be used in order to estimate the specific interaction ability of the filler samples. The specific interaction parameter (ISP) determination method is also described in the "IGC-ID sheet".
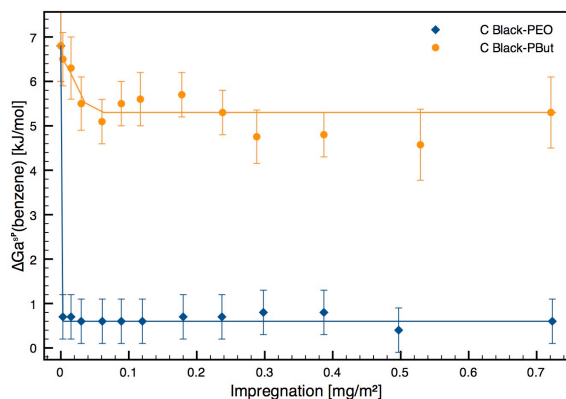

Figure 3 : *Evolution of Benzene's ISP values with the polymer impregnation ratio.*

Concerning the ISP variations as observed in function of the polymer impregnation ratio, two different behaviours are observed on figure 3.

In the case of PBut, only few variations of the benzene ISP values are observed. PBut is not interested by the same adsorption sites than is benzene.

In contrast when the carbon black is impregnated with PEO, an important ISP modification is observed at the first impregnation ratio. Indeed, the benzene ISP value decrease from 6.8 to about 0.7 kJ/mole. It seems that PEO blocks the high interactive adsorption sites (possibly acidic groups) is favourable to strong benzene adsorption.

Conclusion

This short study show 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 recovered by the polymer or not. Thus, one can make use of it in order to determine the quantity of polymer necessary to entirely cover surface.

Moreover, this method is also able to give information about the nature of the sites the most favourable to the adsorption of polymers, including chemical and topological aspects.

The surface energetic heterogeneity is an important parameter governing the strength of the interactions between fillers and polymers. The IGC-ID technique provide an interesting tool to understand and control this heterogeneity.

References

1. E. Papirer, E. Brendlé, H. Balard, F. Ozil; IGC determination of surface properties of fullerenes: comparison with other carbon materials.; <u>Carbon</u> (1999) **37**, 1265-1274.
2. IGC-ID sheet, Adscientis
3. IGC-FC sheet, Adscientis

EXTRAS

1. GLOSSARY

★ **ΔGa:**
Free enthalpy variation of adsorption of a probe.

★ γ_s^d:
Dispersive component of the surface energy.

★ Nanoroughness:
Surface roughness at the molecular scale corresponding to all the surface asperities or pores generating exclusion effects of probes.

★ ISP:
Specific interaction parameter that corresponds to ΔGa^{sp}, the contribution of the polar forces to the free enthalpy variation of adsorption of a polar probe onto the surface.

★ Probe(s):
Molecule(s) injected in order to explore the solid surface.

★ Infinite Dilution:
Dilution level that corresponds to an absence of interaction between the injected probes.

2. HINTS

Another way to accede to the surface energetic heterogeneity is to carry out IGC at finite concentration (IGC-FC) measurements.

This method allows the determination of desorption isotherms having several hundred of expertimental points. We are taking advantage of it for the computation of adsorption energy distribution functions.