#### **ORIGINAL CONTRIBUTION**



## Using NMR solvent relaxation to determine the Hansen solubility parameters of a carbon black and as a quick method to compare the surface quality of carbon blacks

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#### Abstract

The selection of appropriate solvents into which carbon blacks can be dispersed optimally is important for product manufacture and performance. Molecular-level interactions determine solvent suitability but are difficult to measure; existing experimental approaches require slow/expensive tests of dispersion stability. NMR solvent relaxation measurements are shown to be a fast indicator of solvent suitability, with sensitivity to the solvent-particle intermolecular forces making it a reliable proxy for determining optimum dispersibility. A structured approach to relaxation measurements with a selection of both good and poor solvents yields the Hansen solubility parameters (HSP) for the particle surface. Once obtained, suitable solvents (or solvent mixtures) can be selected from a database of HSP values to match the particle interface. The application of the NMR solvent relaxation approach for determining the HSP values is illustrated for a commercially available carbon black. Furthermore, individual solvent relaxation data for two solvents (e.g., hexane and IPA) with a variety of carbon blacks may be plotted against each other to highlight differences in surface chemistry. Using this approach, results are compared, for the first time, with data from inverse gas chromatography (IGC) with a relatively similar outcome. NMR solvent relaxation analysis provides a quick, facile, and cost-effective methodology to identify the replacement of both powder and solvent raw materials.

Keywords Hansen solubility parameter · NMR solvent relaxation · Carbon blacks

### Introduction

A recent paper [1] describes how nuclear magnetic resonance (NMR) solvent relaxation measurements can be used as a fast indicator of solvent suitability for powder wetting and can be sensitive to solvent-particle intermolecular forces making it a reliable proxy for stability measurements. Furthermore, relaxation can be used to determine the HSP values of a powder material. In that paper, the materials

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investigated were uncoated and silane-coated samples of two *inorganic* oxides—alumina and zinc oxide.

In this paper, our attention is focused on characterizing solvent interactions for a variety of carbon black powders. The selection of appropriate solvents into which these can be dispersed is critical for product manufacturability and the performance of products containing carbon black, such as batteries, inks, and conductive plastics.

The production and properties of carbon black powders have been discussed in several publications [2-5], as well as in a comprehensive reference book [6]. Briefly, carbon black is the result of incomplete combustion, or thermal cracking, of hydrocarbon feedstock. During combustion, primary particles of carbon (roughly 30 nm in size and composed of graphitic zones and amorphous carbon) are formed, and these particles fuse together to form chain-like fractal aggregates of around 50–500 nm. An aggregate is practically indivisible and represents the base unit of a carbon black particle with characteristic shape, structure, and size. These aggregates adhere together forming larger agglomerates (often > 1 mm). During the dispersion process, the agglomerates are usually broken down by mechanical forces to the aggregate state. Together with the physical properties, surface chemical properties of the aggregate control the incorporation and stability of carbon black in solvents, liquid dispersions, and other formulated products.

Although elemental carbon is considered *inorganic*, the manufacturing process leaves various forms of functional groups on the carbon black surface, such as phenolic, quinolic, carboxyl, carbonyl, pyrone, lactol, and ether groups. Therefore, even though carbon black is > 95% elemental carbon, and hence mostly inorganic, in the context of this study, the surface of a carbon black particle can be considered to have an *organic* character. We are interested in exploiting the relative strength interactions between solvent and groups present at the surface of carbon black to promote dispersion. The organic components of the surface provide an opportunity for solvents to interact with carbon black by polar and hydrogen bonding interactions in addition to the ever-present van der Waals forces. The application of HSP methodology which inherently calls out these types of interaction is, therefore, well suited to characterizing the compatibility of carbon black with solvents.

Carbon blacks are used extensively in a wide range of applications [7, 8]. Major uses are in the production of tires (as well as synthetic rubber products, seals, etc.) and formulation of paint/inks, but they are also used extensively as a conductive additive in lithium-ion batteries to improve the fast-charging ability of anodes [9]-improvements in energy and power densities, charge and discharge times, cost, lifetime, and safety are all critical to the success of next-generation batteries. Carbon black is also used as a surrogate for soot in the development and testing of engine oil additives because of the technical difficulty and the time-consuming effort in obtaining a well-characterized soot [10, 11]. Harmful debris generated during the operation of an engine comprises soot particles (amongst other materials) that can thicken the oil, cause wear, and plug oil filters. Engine oil additives (suspending and dispersing agents) are critical as they disperse particulate debris by helping to reduce the formation of deposits on metal surfaces and inhibit soot agglomeration via stable micelle formation [12, 13].

The particle morphology and physical surface properties of a carbon black directly affect its performance behavior [14–16], and so an accurate and repeatable evaluation of those characteristics is important. The surface chemical properties of carbon blacks are equally important, and they can vary considerably [17]. The surface chemical properties are determined, to a large extent, by the presence of functional groups containing oxygen, nitrogen, and sulfur that arise because of different sources of the raw feed material. Different processing methods (such as the thermal dehydrogenation of hydrocarbons) will also have an impact. Interparticle bonding strength is also important since different surfaces may be exposed depending on the mechanical stresses and the chemical environment during manufacture, processing, or formulation (for example, using sonication to prepare dispersions [5]).

In any application, accurate, quantitative, and reliable characterization and analysis methods are needed to support consistent formulation and manufacturing process control. Current characterization methods can be expensive and are often time-consuming. Furthermore, commonly used surface characterization methods such as BET [18] and Inverse Gas Chromatography (IGC) [19] utilize gas and vapor, respectively, to probe the carbon black surface. However, many applications require carbon black to be incorporated into a liquid or a polymer melt. It is therefore a question as to how relevant the results are of for example IGC characterization for such application: a method that characterizes the interaction directly with liquids may be more informative. Furthermore, in addition to being opaque, many real-world suspensions of carbon blacks can also be pasty/thick and/or viscous; direct analysis of them by traditional particle characterization instrumentation based on light scattering is difficult, if not impossible.

The use of NMR solvent relaxation time overcomes these concerns and provides a versatile means of interrogating virtually any solid-liquid or liquid-liquid dispersion, including carbon blacks. The NMR relaxation time is a fundamental intrinsic property of solids and liquids, and it is sensitive to both the extent of wetted surface area in a suspension as well as the chemical nature of a particle surface, and so measurements in dispersions will reflect the contribution of both features. The relaxation time can be measured directly using a small benchtop low-field NMR spectrometer [20-22], and we note that the technique is becoming an active area of research [23–27]. Also, NMR relaxation is quantifiable and fast, without the need for dilution or other sample preparation, and so offers practical advantages as a technique to directly characterize, and quantitatively discriminate, the interaction of solvents with carbon blacks. This study also compares, for the first time, NMR relaxation measurements of carbon blacks dispersed in solvents with corresponding IGC data.

# Using NMR relaxation data to derive the HSP for a carbon black

Hansen suggested [28] that particle-solvent interactions can be characterized by splitting the total cohesion energy (E) of a liquid into three separate energies: dispersion energy ( $\delta D$ ), polar-dipolar energy ( $\delta P$ ), and hydrogen bonding energy ( $\delta H$ ). These Hansen solubility parameters (HSP) can be used to select the most appropriate solvents for wetting and dispersing a given particulate powder. NMR solvent relaxation measurements are sensitive to the same intermolecular forces (as well as the dynamics) between solvent and materials with which HSP are concerned [21]. Hence, a logical step is to combine quantitative relaxation data (relaxation number,  $R_{no}$ , values) with computational analysis using commercially available HSPiP software [29]—created by, and available from, Prof. Steven Abbott (see Acknowledgements section)—to determine accurate, and precise, HSP values for the carbon black material used in this study.

The relaxation number,  $R_{no}$ , is defined as as follows:

$$R_{no} = \left[ R_{supension} / R_{solvent} \right] - 1$$

where R = 1/T and T is the relaxation time.

In this study, we used the  $T_2$  spin-spin relaxation measurement, hence  $R_2 = I/T_2$ .

 $R_{no}$  is, thus, a useful, *dimensionless parameter* in which the effect of solvent (which could include dispersants, additives, etc.,) is normalized out and it allows us to rank the strength of solvent-surface interaction (as shown later in Table 2). Solvents with strong interaction with a powder result in a larger  $R_{no}$  value for the suspension of that powder. Since the relaxation time is a function of the affinity of the adsorbing solvent molecules for a surface, such values are a measure of particle wettability. However, impurities, oxygen content, and any dissolved moieties will certainly affect the relaxation values. The latter case has been used to great advantage to measure the adsorption of polymers and surfactants [30] since solvent at the surface is displaced or restricted which changes the relaxation time. Thus, in each system that is measured, it is important to take care that the solvent system is prepared carefully such that each sample is exposed to the same solvent composition.

A solvent with known energy characteristics can be characterized as being either a good solvent or a poor solvent depending on its ability to interact with a surface. In the calculation of HSP, the user is required to input this solvent quality information. Solvents can be rank ordered as "good/ poor" (i.e., strong/weak interaction) based on visual observations or using a more quantitative technique, analytical centrifugation (AC) [31]. However, the AC method is timeconsuming and requires dilute suspensions to avoid hindered settling [1].

In contrast, the determination of  $R_{no}$  is straightforward and fast, and  $R_{no}$  values provide a direct, reliable, and quantitative means to categorize solvents as good or poor. The procedure for ranking the strength of solvent-surface interaction is iterative and is described in detail elsewhere [1].

For a specific material, although the choice of solvents is somewhat arbitrary, the solvents must encompass a range of behavior characteristics from highly polar to highly nonpolar. Hansen recommends that a minimum of twelve probe solvents be used to ensure maximum interrogation of a material (and, hence, the most precise construction of the 3D sphere). In this study, we used seventeen solvents.

Many factors play a role in determining the values of the relaxation time such as particle concentration and surface area; also, a specific solvent may expose more inner surface than another. As we are in the situation of fast exchange, the number of surface adsorbed solvent molecules determines the overall bulk average solvent relaxation times. The fast exchange limit is the condition when each solvent molecule visits the particle surface over the relaxation time period [32]. Since the surface relaxation is determined by all possible solvent proton-surface interactions, then the molecular structure of the solvent is important as is its rotational and translational correlation times. In effect, the surface relaxation is a combination of many parameters and is a *fingerprint* for a particulate solvent particle system. For any suspension, a fingerprint may be tracked to detect changes in particle size due to agglomeration (a reduction in surface area)-provided surface chemistry has not changed with time. If both vary, evaluation is more complicated and often requires other approaches to separate the factors that are causing the change.

The lower bound of sensitivity depends on the available surface area in the system and is system specific. Also, the requirement of fast exchange imposes a lower limit to the particle concentration because every solvent molecule in the dispersion must visit a surface site during the relaxation decay. Because of this, an absolute lower limit is hard to define, but typical measurements are made in dispersions between 5 and 50 wt%.

#### Materials and instrumentation

#### **Carbon blacks**

One carbon black sample (CCML) is of a type and grade used as a surrogate for soot and was obtained from Cabot. The other seven samples were provided by one of the authors (R. Dümpelmann, Inolytix). They are of the type and grade of interest to tire manufacturers and were obtained from a variety of manufacturers. However, all the carbon blacks may be used in other applications such as printing inks. The manufacturers of the carbon blacks and their surface area data are presented in Table 1. In this paper, their measurement and analysis are an independent assessment.

#### Solvents

The following solvents were used for the NMR relaxation studies: acetone (>99.9%), butanol (>99%), cyclohexanone (99.5%), 1,4 dioxane (>99%), dimethylformamide (DMF)

Table 1  $\,\mathrm{N_2/BET}$  gas adsorption surface area values for commercial carbon blacks

Carbon black	Manufacturer	Surface area (m <sup>2</sup> g <sup>-1</sup> )	
CCML	Cabot	137.3	
DGRW	Deutsche Gasrusswerke	130.4	
CCV13	Cabot	122.1	
BCD2	Birla	88.4	
SRN3	Sid Richardson	60.6	
ORN	Orion	58.3	
CCR3(1)	Cabot	57.5	
CCR3 (2)	Cabot	57.5	

(99.8%), dimethyl sulfoxide (DMSO) (>99%), dodecane (>99%), ethanol>99.5%), ethylene glycol (>99%), hexane (>98%), isopropanol (IPA) (>99.7%), N-methyl pyrrolidone (NMP) (>99.7%), methylethylketone (MEK) (>99%), monoethanolamine (>99%), n-pentane (99.7%), trichloroethylene (>99.9%), xylene (98%). They were obtained from a variety of sources and used as received: Sigma-Aldrich, LabAlley, and Wako Pure Chemical Corporation.

It is cautioned that the NMR relaxation time of any liquid is sensitive to both the water content and the presence of any dissolved oxygen (which is paramagnetic) [33, 34]. Thus, the purity and source of a solvent are critical when making comparisons. Indeed, it has long been recognized that traces

Table 2Solvent quality ratingsfor the Cabot CCML carbon

black

of polar impurities and, especially, water play a key role in any non-aqueous application [35–38]. Hence, this sensitivity of NMR relaxation suggests that the measurement can also be used as a fast quality control (QC) tool to fingerprint solvents for industrial applications. The water content could also have an effect on the interaction of solvents with a particle surface.

#### Instrumentation

The carbon black dispersions were analyzed using a *M*agno*M*eter XRS<sup>TM</sup> NMR spectrometer, operating at 12.5 MHz, (Mageleka Inc., Naples, FL, USA) using Mageleka *M*agno-Soft<sup>TM</sup> software version 2\_7. The device utilizes proton (<sup>1</sup>H) NMR—in principle, any NMR active nucleus would work—and so any solvent that contains a hydrogen atom can be measured. Hence, it would be suitable for methylene chloride (CH<sub>3</sub>Cl), but it would not be appropriate for a solvent such as carbon tetrachloride (CCl<sub>4</sub>). A CPMG pulse sequence [39, 40] was used to measure the (*T*<sub>2</sub>) spin–spin relaxation time; a 180° pulse spacing of 1000 µs and up to 20,000 echoes were recorded with a 90° pulse length of 4.5 µs.

Surface area data, presented in Table 1, were measured independently (Particle Sciences Inc., Bethlehem, PA) by  $N_2$ /BET gas adsorption using a HORIBA Model SA-9600 Surface Area Analyzer (Horiba Scientific, Irvine, CA) in accordance with NIST recommended practice guides [41] and using the single point method [18]. Prior to

Solvent	Relaxation data					
	Suspension		Solvent		Relaxation	Solvent affinity
	$\overline{T_2 (\mathrm{ms})}$	$R_2 (\times 10)  \mathrm{s}^{-1}$	$T_2$ (ms)	$R_2 (\times 10) \text{ s}^{-1}$	number, <i>R</i> <sub>no</sub>	ranking
Acetone	1335	7.49	3216	3.11	1.41	4
Butanol	677	14.77	960	10.42	0.42	11
Cyclohexanone	785	12.74	1542	6.49	0.96	6
1,4 Dioxane	895	11.17	2239	4.47	1.5	3
DMF	220	45.45	1078	9.28	3.90	1 (best)
DMSO	1162	8.61	2026	4.94	0.74	8
Dodecane	812	12.32	974	10.27	0.20	14
Ethanol	904	11.06	1707	5.86	0.89	=7
Ethylene Glycol	310	32.26	369	27.10	0.19	15
Hexane	1536	6.51	2044	4.89	0.33	13
IPA	776	12.89	1134	8.82	0.46	9
MEK	1182	8.46	2420	4.13	1.05	5
Monoethanolamine	210	47.62	288	34.72	0.37	12
NMP	523	19.12	1894	5.28	2.62	2
n-Pentane	2144	4.66	2227	4.49	0.04	16 (worst)
Trichloroethylene	1089	9.18	1557	6.42	0.43	10
1,4 Dioxane	1089	9.18	2060	4.85	0.89	=7

The best affinity was shown by DMF and the least by n-pentane

measurement, the samples were degassed at 75 °C for 12 h. The data are in general agreement with values provided in the manufacturer's literature [42]. Note that the two samples of the CCR3 were two different batches. Also, the SRN3 and ORN carbon blacks are thought to have similar qualities in applications to the CCR3 material [42].

Inverse Gas Chromatography measurements were made using the automated IGC NeuronIC device of Adscientis, Wittelsheim, France, and the software module SoliD. The seven carbon black samples are of interest to tire manufacturers and were independently analyzed (by Adscientis) at the behest of one of the authors (R. Dümpelmann, Inolytix). The methodology is well-described and established [19]. For the current analysis, first, a series of n-alkanes (n-butane to n-octane) and then a variety of polar solvents (acetonitrile, chloroform, acetone, iso-propanol, methyl acetate, diethyl ether, tetrahydrofuran, and benzene) were injected into an inert gas (He) carrier stream under infinite dilution conditions. The resulting retention times correlate to the free energies of adsorption (see later).

#### Sample preparation

Each carbon black was dispersed at approximately 9 wt % in the various solvents using a mixture of initial vortexing (Grant Instruments Model PV-1) for 30 s followed by bath sonication (Onezili Ultrasonic Cleaner Model OZL-800) to ensure good homogeneity—as determined later by the repeatability of NMR relaxation time measurements—typically a coefficient of variance (COV) of 1% or better. The suspensions were sonicated for 3 min at maximum bath power (35W). Measurements were made directly on the resulting carbon black suspensions.

#### Analysis results and discussion

#### **HSP** values for CCML carbon black

This specific carbon black is of a type and grade used as a surrogate for soot. Suspension and solvent quality information are summarized in Table 2 and shown graphically in Fig. 1.

The HSP value for the CCML carbon black was determined using a modification of the Hansen method. In brief, the approach seeks to find a cluster of good solvents within the 3D HSP space; good solvents will have HSP values close to those of the particle surface while the rest of the HSP space will contain poor solvents. The boundary between good and poor solvents is taken to be at the surface of a sphere centered on the HSP values for the particle surface. The HSPiP software [29] automates the calculations for finding the region of good solvents (and identifying further suitable solvents) as follows:

- 1. Order the  $R_{no}$  values from largest to smallest for the range of solvents used.
- 2. Assign the three highest  $R_{no}$  values a score of 1 (for strong affinity), with the rest being scored 0 (for weak affinity).
- 3. Use the HSPiP software to construct an initial Hansen sphere for the boundary between the strong and weak affinity solvents.
- 4. Sequentially expand the number of solvents scored as a "1" until it is no longer possible to fit a spherical boundary between the strong and weak affinity solvents without "wrong in" and "wrong out" solvents. In the pre-



**Fig. 1** Relaxation numbers,  $R_{no}$ , for CCML carbon black in various solvents

sent study, a good fit was attained when the first twelve solvents were assigned a "1." These solvents had  $R_{no}$  values > 0.40. The remaining five solvents were assigned a "0." By implication, solvents with an  $R_{no}$  value < 0.40 had a weak interaction with the CCML carbon black.

5. The center of this "best-fit sphere" is the effective HSP for the particulate material under investigation. The HSP locations of the final solvents with a score of "1" define the maximum value for the radius of the Hansen sphere. Further analysis may be undertaken within HSPiP by looking for solvents with suitable HSP values using the database of solvents provided.

In essence, the protocol (i) accelerates the whole process of HSP determination and (ii) provides a well-defined evaluation procedure for the reliable ranking of good and poor solvents for dispersing the particles. Thus, for the creation of the Hansen sphere for the CCML carbon black, the solvents n-pentane, hexane, dodecane, monoethanolamine, and ethylene glycol were assigned a score = 0 and the rest a score = 1. The result is shown (as a screenshot from the HSPiP software) in Fig. 2. Note that the axes are labeled simply as *D*, *P*, and *H* and not  $\delta D$ ,  $\delta P$ , and  $\delta H$ .

The average HSP values for this batch of CCML were determined to be as follows:

$$\delta D = 17.2, \ \delta P = 7.1, \ \delta H = 10.4$$

These HSP values lie within the wide range of values (found from a literature search and shown in Table 3) for available diverse commercial carbon blacks [28].



**Fig. 2** Hansen sphere (interaction radius, R=9.6) for the carbon black CCML and solvent scores. Good=1; twelve solvents shown in blue within the sphere, and poor=0; five solvents shown in red outside the sphere (note that three red data points are obscured) using relaxation data from Table 1

R in Table 3, termed the interaction radius, defines the radius of the Hansen sphere. Good solvents are located within the sphere, and poor solvents are located outside the sphere. The coordinates of the sphere and the calculated radius are subjective in that R depends on the criterion used to define good and poor solvents for the study.

The HSP component values for the CCML are similar to those found by Süß et al. [43] for a PRINTEX L carbon black (obtained from EVONIK), using an analytical centrifugation (AC) method viz,  $\delta D=17.2$ ,  $\delta P=8.5$ ,  $\delta H=11.6$ . However, determination by NMR relaxation is considerably simpler and faster [1].

The study here characterizes the surface quality of a carbon black so that it is a known quantity for subsequent determination of dispersants in a solvent of choice. Furthermore, based on the hypothesis that "like dissolves like," solvent blends *even mixtures of individually poor solvents*—having volume average HSP values like that for a carbon black will be effective. This can provide the formulator with greater flexibility to improve any carbon black dispersion. With blending, it should be noted that synergistic/anti-synergistic effects—such as preferential adsorption of one solvent—can have an impact [4].

Dodecane is often used as a "model" solvent for carbon black studies [11]. The HSP values for dodecane are  $\delta D = 16.00$ ,  $\delta P = 0$ , and  $\delta H = 0$ . The latter two values are both zero and so all interaction is via Van der Waal's attraction (and soot is even more polar than most carbon blacks). Hence, dodecane would not be a good wetting solvent for the carbon black (CCML) used in this study. This conclusion is also apparent from the relaxation number for dodecane/CCML which was found to be one of the lowest (0.2, Table 2) amongst the 17 solvents tested in this study.

The determination of the HSP of an engine oil would allow the most suitable solvent to be selected for experimental evaluation of suspending and dispersing aids. It may very well be that dodecane, for example, is an appropriate liquid for such studies, since the goal might not be to completely wet the carbon black but to provide a realistic fluid substitute that mimics the wetting behavior of an engine oil. However, until representative oils are evaluated, this remains unknown. The HSP of an oil (including diesel) may be obtained by assessing its miscibility with a range of good and poor solvents with known HSP values. Solvent relaxation NMR can be used to quickly determine the interaction of the candidate oil with solvents. Then, as described above, the relaxation number  $R_{no}$  is rankordered and inputted into the HSPiP software to compute the HSP of the oil.

Table 3 Range of HSP values for commercial carbon blacks

Carbon black	$\delta D$	$\delta P$	$\delta H$	R
Lowest value	16.5	8.1	6.8	6.9
Highest value	20.4	10.9	13.0	11.5

# Comparison of Cabot carbon blacks via relaxation number (using a limited selection of solvents)

As mentioned, the HSP of carbon blacks are sensitive to manufacturing variables such as the feedstock used and so can be an important surface property metric, in addition to surface energy (by IGC) in R&D and marketing. However, although it quantifies the surface quality of a carbon black, the requirement for at least twelve solvents makes it less suitable for use in QC. It should be possible to obtain useful information relatively quickly about the surface quality of any carbon black by challenging it with just two or three selected (i.e., polar, and non-polar) solvents rather than attempting to run a complete HSP panel.

This is illustrated in the following example where we compare the CCML sample with three other carbon blacks, viz CCV13 and different batches of two samples of CCR3. As mentioned previously, the former is used as a surrogate for soot and the latter carbon blacks are of interest to tire manufacturers. In this study, only three solvents were used: acetone, hexane, and isopropanol (IPA). These latter two solvents are typical examples of, respectively, non-polar and polar solvents that are often used to probe such interactions with surfaces. The surface tension values of IPA and acetone are quite similar-they differ only by 2.2 mNm<sup>-1</sup> at 20 °C [44]—but IPA has a greater potential for hydrogen bonding because it can bond as both a donor and acceptor, while acetone is capable of H-bonding only as an acceptor [45]. Differences in the interaction of IPA and acetone are related to the relative concentration of H-bond donor and acceptor moieties on surfaces. There are substantial differences in the polarizability of the two solvents (see later) which can impact solvent affinity. Furthermore, they have different viscosities that can likely change penetration into agglomerates, whereby different inner surfaces are accessed. However, the fast exchange limit is determined by the diffusion of the solvent. For the solvents used here, the fast exchange condition is expected. However, a very viscous solvent may control the lowest particle concentration where this limit holds.

Figure 3 shows a plot of the correlation of the relaxation numbers for carbon blacks (color coded for clarity) in hexane and IPA. The data are provided in Table 2 (CCML) and Table 4.

The plot shows that the NMR results reside in different "areas of 2-D space"—defined by the IPA and hexane data. With the tire grade carbon blacks, the relaxation numbers  $(R_{no})$  for the non-polar solvent (hexane) are—possibly not surprisingly—larger than those for the polar solvent (IPA) which indicates a stronger solvent-surface interaction (and, hence, better wetting with hexane for those carbon blacks). It is important to emphasize that while plotting data using two solvents can be instructive, it cannot provide a full picture of solvent interaction profile. For example, interestingly,



Fig. 3 Plot of relaxation numbers for IPA vs. hexane for various carbon blacks

with the soot surrogate carbon black, the  $R_{no}$  values for the two solvents are similar, suggesting that both hexane and IPA interact with CCML to approximately the same degree. However, a more comprehensive 17-solvent HSP analysis concludes otherwise—IPA resides within the HSP sphere and hexane does not. The CCV13 and the CCML materials have somewhat similar surface areas of 122 m<sup>2</sup> g<sup>-1</sup> and 137 m<sup>2</sup> g<sup>-1</sup>, respectively (Table 1), but the  $R_{no}$  values differ considerably indicating a large contrast in the surface affinity of the solvents. In both instances, the data speaks to the critical nature of the carbon black surface chemistry and solvent cohesive energy.

Of potentially practical significance is that the relaxation data demonstrates that the surface chemistry of these two different batches of the CCR3 material, though similar, are clearly not the same even though the surface areas (and particle sizes) are equivalent according to the manufacturer's Technical Data Sheet [42]. However, it is possible that the differences we have found could well be within the overall average of many batches. This warrants further investigation. However, it may be due to aging—particularly in the case of surface-treated carbon blacks. For example, highly oxidized carbon black surfaces are known to have limited shelf life [46].

**Table 4** Summary of inverse gas chromatography data and NMR solvent relaxation numbers ( $R_{no}$ ) for hexane and isopropanol for a series of carbon black samples from different manufacturers

Carbon black	$\frac{\Sigma I_{SP}}{(kJmol^{-1})}$	$\gamma_{sd}  (mJm^{-2})$	$R_{no}$ hexane	<i>R<sub>no</sub></i> isopropanol
CCR3 (1)	55.0	257	0.21	0.10
CCR3 (2)	64.6	171	0.29	0.08
CCV13	35.2	484	0.78	0.23
BCD2	78.5	391	0.37	0.56
DGRW	28.1	485	1.01	0.36
ORN	57.5	231	0.56	0.14
SRN3	35.5	197	0.60	0.17

Finally, Fig. 4 compares the effects of hexane and acetone solvent efficiencies for the same carbon blacks. The data are provided in Table 2 (CCML) and Table 4.

The NMR results once more site into different areas of 2-D space—but defined now by the acetone and hexane data. Interestingly, the relative positions of the two CCR3 samples are reversed and are very different, again emphasizing the potential disparity in the surface chemical characteristics between two samples of, ostensibly, the same physical grade of carbon black.

The relaxation numbers  $(R_{no})$  for acetone are considerably larger than those for both IPA and hexane which indicates a much stronger solvent-surface interaction with acetone. This is likely a consequence of a stronger interaction of the more polarized acetone molecule with a carbon surface, which can contain a heteroatom such as oxygen that can produce a  $\delta^+$  charge on neighboring carbon atoms. The surface of carbon black is known to contain a variety of oxygenated species (e.g., carboxylic acid, ethers, lactones, phenols, ketones), all of which can interact with a polarized molecule such as acetone and IPA, but the interaction will be stronger for acetone owing to its higher polarizability—the dipole moment of acetone is a lot larger (2.69D) than that for IPA (1.66D).

Thus, Figs. 3 and 4 demonstrate the utility of NMR solvent relaxation measurements in quantitatively determining the effect of solvent affinity in relation to the surface chemistry of the various carbon blacks. It also underscores the importance of better understanding the role of the solvent cohesive energy components in formulating dispersions of them.

We suggest that it may be useful to generate HSP numbers routinely to economically track the surface quality of carbon blacks from manufacturers to determine interfacial "equivalency" and even from the same manufacturer to determine if significant batch-to-batch variations exist.



Fig. 4 Plot of relaxation numbers for acetone vs. hexane for the various carbon blacks

# Comparison of inverse gas chromatography with NMR solvent relaxation

Inverse gas chromatography (IGC) is used to identify differences between treated and non-treated surfaces, or even significant variations between materials from different providers or different batches; aging of a material can result in a change in surface energy. IGC has been used to characterize carbon blacks [47, 48] as well as to determine the HSP of solid materials [49, 50] and oils [51–53], but it requires the time-consuming step of packing the solid material into a column or, in the latter application, depositing the oil on a solid support and running the chromatograph. Furthermore, such instrumentation is expensive, has significant experimental complexities, and requires a long measurement time (many hours)-characteristics that make it acceptable for basic research and product development but unsuited for quick, routine, laboratory analysis. In addition, IGC relies on *vapor*-solid interaction analysis. Hence, when dealing with issues of wettability in the formulation of suspensions, it cannot provide as complete an assessment of how a liquid will wet a rough, porous, and heterogeneous surface which, of course, is a critical metric in understanding the dispersibility of powders (such as carbon blacks in solvents).

The results of the IGC analysis for seven carbon blacks are summarized in Table 4. The values for  $\gamma_{sd}$  the dispersive component of the surface energy [54] were calculated using six n-alkane probes.  $\sum I_{sp}$  is the sum of the individual polar interaction parameters (ISP) of the polar probes used [19]. It encompasses the additional polar interactions as compared to the n-alkanes, which are assumed to have only dispersive interactions. The values were calculated based on eight polar solvent probes. Also, the ISP is related to known acceptor  $(A_N)$  and donor  $(D_N)$  numbers of solvents, which, in turn, arise from the semi-empirical acid/base scale of Gutmann [45] and, hence, is a measure of the relationship between the acid/base properties of both solvent and surface.

A plot (Fig. 5), as defined by specific polar and dispersive interaction, shows that the seven carbon blacks (again color coded for clarity) cluster into three different groups: Group 1, CCR3 (1), CCR3 (2), SRN3, and ORN; Group 2, CCV13, DGRW; and Group 3, BCD2.

The BCD2 material is clearly atypical compared with all the other carbon blacks. The IGC data for the two CCR3 materials is different which confirms that the surface chemistry clearly cannot be the same even though the surface areas (and particle sizes) are the same. The ORN carbon black has a similar surface energy to the CCR3(1), which suggests they could be comparable as alluded to earlier (see page 6).

For comparison, we can also plot the correlation of the relaxation numbers for the two solvents (Fig. 6) which shows that the NMR results also cluster into three circled areas—defined by IPA and hexane data. The seven carbon black



**Fig. 5** Plot of inverse gas chromatography results (polar vs dispersive contributions) for various carbon blacks using data from Table 4

materials remain grouped in similar clusters to those defined using IGC viz: Group 1, CCR3 (1), CCR3 (2), SRN3 and ORN; Group 2, CCV13, DGRW; and Group 3, BCD2.

Again, the BCD2 material is clearly atypical compared with all the other carbon blacks. The results also confirm the IGC conclusion that the two batches of the CCR3 have differing surface chemical features. The SRN3 and ORN carbon blacks have similar solvent interaction to the CCR3 blacks, but they are not entirely equivalent with the ORN being the closest of the two.

A significant advantage is that NMR relaxation data can be obtained in a very short time. For example, the longest measurement time—for CCR3 in hexane—took approximately 35 s per run, and the shortest time—for BCD2 in IPA—was only 14 s per run. Thus, reliable data from multiple runs can be obtained in a few minutes, which is important in QC where many samples may need to be analyzed. These results demonstrate that NMR solvent relaxation provides a technique that can directly—and quickly—characterize the interaction of solvents with carbon blacks in order to prioritize the need, if required, for quantitative testing and analysis using IGC.



**Fig. 6** Plot of relaxation numbers,  $R_{no}$ , for IPA vs. hexane for various carbon blacks using data from Table 4

IGC involves injecting a series of *vapor* phase probe molecules through a sample-packed column. The *retention time* is then measured and used in the evaluation of the surface properties of the sample material under investigation. The advantage of IGC is that the measured data are based on adsorption effects which are well defined and so it can provide excellent insight into the probe molecule-material surface interaction with good, mechanistic interpretations. As such IGC is well suited for complex questions in product development or root causes of quality issues.

NMR relaxation is determined by two major factors, viz the chemical structure and mobility (translation and rotation) of the solvent molecule in question, and its interaction with its physical environment—hydrogen bonding and solvation can affect the inter-nuclear relaxation behavior. Pragmatically, the *liquid* probe molecule affinity is reflected by its average *relaxation time*. As we have shown, a panel of different solvents with varying polar, dispersive, and H-bonding properties provides a measure of surface properties (for example, in 3D space HSP in Fig. 2, or as a coordinate in 2-D space in Figs. 3 and 4).

Since both NMR solvent relaxation and IGC results depend on the affinity of the probe molecules for the surface being investigated, it should not be surprising that the principal findings (Figs. 5 and 6) are similar—when, of course, the same molecular probes (as a vapor phase for IGC and liquid phase for NMR) are used. Thus, NMR relaxation and IGC should be considered ideal complementary techniques. However, it is important to note that when preparing and formulating dispersions, it is advantageous to be able to track dispersion quality in virtual real time as it informs on wetted surface area and stability of suspensions. In particular, when tracking suspensions over time, a reduction in  $R_{no}$  indicates a decrease in wetted surface area suggesting an increase in particle size because of agglomeration. Although not a subject of this paper, this can be accomplished quickly and easily via NMR relaxation studies [20, 22, 25, 27].

In an analogous manner in which surface area measurement of dry solid materials by N<sub>2</sub> gas adsorption was extended to measure porosity and pore size distribution [18, 55], the nature (morphological and chemical) of porous materials in liquids can be studied using NMR relaxation measurements [56, 57]. With dispersions containing aggregates, there can be intraparticle penetration of solvent. In such cases, where overall fast exchange is not possible, there will be two signals and the composite relaxation decay can be resolved by a double exponential fit to the raw data. However, there are complications when dealing with conventional porous media such as activated charcoal. Here, there may be multiple signals and the NMR solvent relaxation behavior will differ depending upon factors such as the pore volume, the pore throat diameter, and the interfacial chemistry. Further discussion is beyond the scope of this paper;

however, future publications dealing with solvent relaxation in porous media are planned. No matter the system, it is essential in order to distinguish samples to utilize all the information one already has and to vary only one parameter systematically, e.g., solid/liquid ratio, or to use displacers to detect differences in surface chemistry.

Finally, also from a formulation perspective, a major concern is the ability to find replacement raw materials more quickly and cost-effectively. Though the NMR data here are limited, we can see from Fig. 6 that it might be possible that the carbon blacks in Group 1 could be substituted for each other without a major variation in dispersion performance. This also potentially holds for the two carbon blacks in Group 2. What is clear, however, is that the materials in Group 1 are not interchangeable with those in Group 2.

### Conclusion

The current work suggests that NMR solvent relaxation is a useful, rapid complimentary technique to traditional characterization methods and measurements can be used to (i) accelerate the whole process of HSP determination of a carbon black to provide a well-defined evaluation procedure for the reliable ranking of good and poor solvent affinity for dispersing carbon blacks, and (ii) potentially quantitatively discriminates between different surface chemical characteristics of carbon blacks by comparing their interaction with solvents (as in the example of IPA *vs* acetone). The HSP methodology and analysis, as exploited using NMR solvent relaxation to rank-order solvent-particle interaction, can be applied to any applications involving non-aqueous dispersions of carbon blacks of any type/grade.

NMR relaxation measurements of carbon blacks have been compared with corresponding IGC data. The results show that, when the same molecular probes (as a vapor phase for IGC and liquid phase for NMR) are used, the results are similar. The techniques are complementary and NMR solvent relaxation can be used to directly—and quickly—characterize the interaction of solvents with carbon blacks in order to prioritize the need, if required, for quantitative testing and analysis using IGC. From a formulation perspective, NMR solvent relaxation measurements can also provide a fast and cost-effective methodology to identify the replacement of both powder and solvent raw materials.

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#### Declarations

**Competing interests** The authors declare that they have no known competing financial interests or personal relationships that could have

appeared to influence the work reported in this paper. The authors declare the following financial interests/personal relationships which may be considered potential competing interests: Mageleka Inc., manufacturers benchtop NMRs; Lubrizol Ltd., markets surfactants and dispersants; Adscientis SARL manufactures, and is a service provider of, IGC instrumentation.

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