Analysis and Characterisation of Non-aqueous Dispersions of Commercial Carbon Blacks Using NMR Solvent Relaxation

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Carbon blacks are used extensively in a wide variety of applications, often at high solids concentrations and in both aqueous and non-aqueous media. An important use is as a conductive additive in Li-ion batteries to improve the fast-charging ability of anodes. Indeed, improvements in energy and power densities, charge and discharge times, cost, lifetime, and safety are all critical to the success of next generation batteries.

It is well-recognised that the particle size/surface area of a carbon black directly affects its performance properties but the surface chemical properties are of equal import. These are determined, to a large extent, by the presence of functional groups - hydrogen, oxygen, nitrogen and sulphur, etc. - that arise because of different sources of the raw feed material and subsequent processing conditions.

Thus, accurate and repeatable evaluation of the morphology and surface characteristics of carbon black particles is important for the formulation of any products that depend on it as a raw material. Further, the ability to predict the most appropriate liquid(s) to use for wetting/dispersing a given carbon black is of considerable interest to the formulator. However, in addition to being opaque, many real-world suspensions of carbon blacks can also be pasty/thick and/or viscous. This makes analysis of these suspensions by traditional particle characterisation instrumentation difficult, if not impossible.

Thus, in any application - and especially those involving carbon blacks - accurate, quantitative, and reliable characterisation and analysis methods are needed from the initial stage of checking incoming raw materials, to development of new formulations, and through to quality control within high volume manufacturing. To be truly versatile, such a method would allow any sample to be measured quickly, easily, and without special preparation.

NMR solvent relaxation time provides this versatility, and it can be measured directly using the *Mageleka MagnoMeter* XRS *RelaxoMeter.*

About NMR Solvent Relaxation

NMR spectroscopy is one of the most powerful analytical tools used to probe details of molecular structure and dynamics. Traditional devices require high magnetic fields and, hence, large magnets and related instrumentation. However, the advent of small powerful magnets has allowed a small footprint, benchtop device - the Mageleka MagnoMeter XRS™ RelaxoMeter (www.mageleka.com) - to be designed that is well-suited to normal, routine laboratory analysis.

The basic technique used in the RelaxoMeter is NMR solvent relaxation. The relaxation time is a fundamental intrinsic property of solids and liquids and its measurement provides direct information about two important features of any particle-liquid interface (i.e., a suspension). The first, and most obvious, is the extent of wetted surface in a suspension. Here we can include particle size, shape, morphology and, indeed, porosity. A second, and less appreciated feature, is that NMR relaxation is also sensitive to the chemical nature of a particle surface. This would include the fundamental surface charge and, thereby, the type and number of functional groups. Thus, NMR is unique in this respect because, typically, traditional characterisation instruments are only sensitive to one of the features (e.g., particle size or zeta potential, but not both simultaneously).

The MagnoMeter RelaxoMeter

The RelaxoMeter can be employed flexibly in virtually any environment, requires limited input data, and provides measurements in just a few minutes. Moreover, it has easy-to-use software, so it has the additional benefit of being able to be operated by a non-NMR specialist.

A major practical advantage of the RelaxoMeter is that the measurement is noninvasive and nondestructive. This means that samples can be stored in an NMR tube and re-analysed at any later date. This allows for investigation of stability, sedimentation, accelerated aging and shelf-storage issues. Furthermore, and of practical utility, the RelaxoMeter can work with any industrially relevant solids concentration and with virtually any liquid - which is especially important for slurries, which can be highly concentrated - thereby eliminating dilution issues inherent in making measurements using, for example, traditional light scattering techniques. Since dilution is never an innocuous process, wherever possible suspensions or slurries should be analysed as they are prepared, and the RelaxoMeter makes this possible.

In this article, we will demonstrate how NMR solvent relaxation time measurements using the RelaxoMeter can be used for quick, routine interrogation of carbon blacks dispersed in non-aqueous media. Both studies investigate the effect of solvents and reveal how useful NMR relaxation time measurements can be in characterising carbon blacks to compare materials from different manufacturers and revealing, for example, variations in batches of the same material. Further, each example highlights the potential utility of the RelaxoMeter's measurements in QC and R&D contexts.

STUDY 1.

Here, seven commercial carbon blacks, from five different manufacturers, were dispersed (at approximately 9% w/w) in two solvents - isopropanol (IPA) and hexane - as typical examples of polar and non-polar media.

Surface area data (measured independently by gas adsorption) for the carbon blacks agree with values provided in the manufacturer's literature and are presented in *Table 1*. Note that the two samples of the CABOT Regal 300 were different batches obtained from two suppliers.

Table 1. N_2/BET gas adsorption surface area values for commercial carbon blacks.

Carbon Black	Surface area (m^2g^{-1})
DEUTSCHE GRW	130.4
CABOT VULCAN 1391	122.1
CABOT REGAL 300 (1)	57.5
CABOT REGAL 300 (2)	57.5
SID RICHARDSON N326	60.6
ORION	58.3
BIRLA CD2125X7	88.4

The effect of solvent (which could include dispersants, additives, etc.) can be normalised out to assess the strength of solvent-surface interaction. To do this, the relaxation time can be presented as a relaxation number, which is a useful, dimensionless parameter, R_{no}, defined as:

$$R_{no} = [R_{suspension}/R_{solvent}] - 1$$
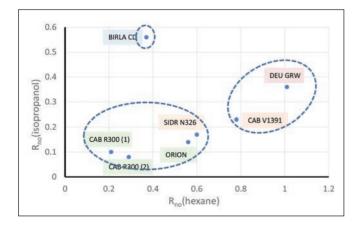$$\text{Where, } R = 1/T$$

Figure 1. Plot of relaxation numbers for isopropanol vs. hexane for various carbon blacks using data from Table 2.

Table 2 compares the calculated Relaxation Numbers and rankings according to solvent efficiencies for the seven carbon black dispersions. *Table 2. Relaxation numbers, R_{no}, for carbon black suspensions.*

Carbon Black	RELAXATION NUMBER, R_{no}	Solvent Efficiency Ranking
HEXANE		
DEUTSCHE GRW	1.01	1 (Best dispersed)
CABOT VULCAN 1391	0.78	2
SIDRICHARDSON N326	0.60	3
ORION	0.56	4
BIRLA CD2125X7	0.37	5
CABOT REGAL 300 (2)	0.29	6
CABOT REGAL 300 (1)	0.21	7 (Least dispersed)
ISOPROPANOL		
BIRLA CD2125X7	0.56	1 (Best dispersed)
DEUTSCHE GRW	0.36	2
CABOT VULCAN 1391	0.23	3
SID RICHARDSON N326	0.17	4
ORION	0.14	5
CABOT REGAL 300 (1)	0.10	6
CABOT REGAL 300 (2)	0.08	7 (Least dispersed)

The relaxation numbers (R_{no}) for hexane are consistently larger than those for IPA, which indicates a stronger solvent-surface interaction (and, hence, better wetting by hexane). Further, they clearly differentiate the interaction of each of the solvents with the individual carbon blacks. This is a consequence of not only true variations in geometric surface area (because of both the size and surface roughness of the carbon black particles) but also the wettability (determined in large part by surface chemistry) between the carbon black particles and the solvents.

Even though their surface areas are identical, the basic relaxation times for the two CABOT REGAL 300 samples differ in both hexane and isopropanol. This should not be surprising since N_2/BET gas adsorption is measured on samples of the dry material. It illustrates why such measurements can have limited use when dealing with wetted suspensions, and why the NMR relaxation technique used by the RelaxoMeter can be more accurate and reliable in such instances.

The interaction of a liquid with a surface is dictated, in large part, by its cohesive energy. This has three components - dispersive energy, polar-dipolar energy, and hydrogen bonding energy - that are memorialised as the Hansen Solubility Parameters (HSP). It is known that HSP can help in the selection of the most suitable solvent for initial wetting and dispersing of powders.

NMR solvent relaxation measurements are sensitive to the same intermolecular forces (as well as the dynamics) between solvent and surfaces with which HSP are concerned and so is a very useful technique for determining HSP of materials [1]. However, determination of the HSP requires using a minimum of 12 solvents for each individual carbon black, which is beyond the remit of this study.

Nevertheless, we can plot the correlation of the Relaxation Numbers for the two solvents used in this first study *(Figure 1)*.

The plot shows that the NMR results cluster into three 'areas of 2-D HSP space' - defined by IPA and hexane data - in which reside different groupings of the seven carbon black materials:

Group 1: CABOT REGAL 300 (1), CABOT REGAL 300 (2), ORION, SID RICHARDSON N326

Group 2: CABOT VULCAN 1391, DEUTSCHE GRW

Group 3: BIRLA CD2125X7

It is possible that the carbon blacks in Group 1 could be substituted for each other without too much variation in dispersion performance - and, potentially for the two carbon blacks in Group 2. However, the materials in Group 1 are simply not interchangeable with those in Group 2.

The BIRLA CD2125X7 material is clearly atypical compared with all the other carbon blacks.

STUDY 2.

Suspensions of the carbon blacks in acetone were prepared in the same manner and conditions as in the study above. The surface tensions of IPA and acetone are similar, but IPA has a greater potential for hydrogen bonding compared with acetone: IPA can H-bond as both a donor and acceptor, while acetone is capable of H-bonding only as an acceptor [2].

A comparison of the relaxation times of acetone and IPA carbon black suspensions is useful because it further sheds light on the differences that can exist in carbon black surface chemistry, in particular for the two CABOT Regal 300 samples. This, in turn, will impact any subsequent choice of, for example, dispersing agents. The results - for Relaxation Number and Solvent Efficiency Ranking - are summarised in *Table 4*.

Table 3. Summary of NMR relaxation data for suspensions of carbon blacks dispersed in acetone.

Sample	Relaxation Number, R_{no}	Solvent Efficiency Ranking
ORION	1.39	5
CABOT REGAL 300 (1)	0.49	7 (least)
CABOT REGAL 300 (2)	1.34	6
SID RICHARDSON N326	1.83	3
CABOT VULCAN 1391	1.47	4
DEUTSCHE GRW	2.55	2
BIRLA CD2125X7	2.85	1 (best)

The relaxation numbers (R_{no}) for acetone are significantly larger than those for both IPA and hexane *(Table 2)*. This is likely a consequence of a stronger interaction of the more polarised acetone molecule with a carbon surface, which can contain a heteroatom such as oxygen that can produce a δ^+ charge on neighbouring 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 are capable of interacting with a polarised molecule such as acetone and IPA, but the interaction will be stronger for acetone owing to its higher polarisability - the dipole moment of acetone is significantly larger (2.69D) than that for IPA (1.66D).

The difference in ranking of any carbon black-solvent interaction is always attributable to the difference in one, or more, of the three Hansen Solubility Parameters (dispersive energy, δd; polar-dipolar energy, δp; and hydrogen bonding energy, δd) between solvents, and this can be readily probed using NMR solvent relaxation.

In acetone, the relative order of interaction for the Regal 300 (1) and Regal 300 (2) is reversed, potentially indicating a reduced H-bonding surface for Regal 300 (2) compared with Regal 300 (1). This finding is important since it will impact not just the choice of wetting liquid but also any subsequent dispersing or stabilising agent(s) that will be used in preparing formulations of this carbon black.

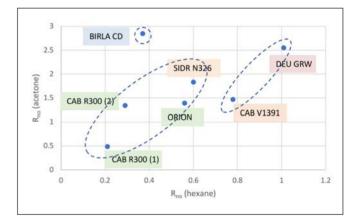Finally, *Figure 2* compares the effects of hexane and acetone solvent efficiencies.

Figure 2. Plot of relaxation numbers for acetone vs. hexane for various carbon blacks using data from Tables 2 and 3.

Three clusters (Groups 1, 2 and 3) again result - and remain with the same sets of carbon blacks - and with the BIRLA carbon black still atypical. However, the envelopes for Groups 1 and 2 are more stretched reflecting the relative differences between hexane/acetone in comparison to IPA/acetone. Interestingly, in Group 1, the relative positions of the two Cabot Regal 300 samples are reversed, again highlighting the difference in the surface chemistry between two samples of, ostensibly, the same carbon black.

Figures 1 and 2 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 understanding the role of the solvent cohesive energy in formulating dispersions of them.

In Conclusion

NMR solvent relaxation measurements can quantitatively determine the effect of solvent affinity in relation to the surface chemistry of the various carbon blacks and provide critical information regarding the role of the solvent cohesive energy in formulating dispersions of them.

The methodology and analysis employed using the RelaxoMeter can be applied to any applications involving non-aqueous dispersions of carbon blacks of any type/grade.

For example, improvement in storage capacity, charge rate, and lifetime are common goals in battery development. A main challenge in advancing battery technology is to optimise the complex composition of the different types of slurry mixtures used.

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Small particles provide a large surface area (and, more specifically the wetted surface area) for better power production; large particles provide better electrolyte mobility for energy storage. In both cases, thorough characterisation of all the materials/components is essential. Using the MagnoMeter RelaxoMeter, NMR solvent relaxation measurements can provide characterisation of materials in the wetted state that is more appropriate for such applications. Moreover, the characterisation is low-cost and economical in time.

References

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2. V. Gutman, "The Donor-Acceptor Approach to Molecular Interactions." Plenum Press, New York (1978).

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