

ON THE USE OF AN INTERNAL MIXER TO STUDY THE IMPREGNATION OF CARBON FILLERS BY ORGANIC LIQUIDS

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ABSTRACT:

Impregnation of organic liquid electrolytes in conductive powders is of major importance in the field of energy storage devices such as batteries or super-capacitors. Impregnation during mixing and processing operations becomes usual for practical reasons and requires a better understanding of the changes of the rheological behavior of the mix. In this paper, the impregnation of propylene carbonate (PC) and dimethyl sulfoxide (DMSO) in activated carbon (AC) and carbon black (CB) was studied by using an internal mixer. Monitoring of the torque of the filler/liquid blend as a function of the amount of liquid fed in the mixing chamber, enables to detect the transition from the solid friction of the dry powder to the lubricated liquid (or viscous) behaviour of the concentrated paste of wetted powder. The results were compared with data obtained by conventional nitrogen adsorption porosimetry combined with the knowledge of the molecular diameter of the liquids. A characteristic change was observed as soon as the liquid completely fills the porosity of the filler. Both tested liquids (DMSO and PC) impregnate more carbon black and the take-up rate is slightly higher for DMSO in comparison to PC because, as a polar liquid, DMSO has a better interaction with both fillers.

KEY WORDS:

impregnation, propylene carbonate, dimethyl sulfoxide, activated carbon, carbon black, internal mixer

1 INTRODUCTION

The impregnation of filler by liquids is of particular importance for carbaceous materials since they are major components of energy storage devices such as batteries or super-capacitors. These materials combine electronic conductivity together with high porosity, the latter being filled by a protonic charge carrier such as an electrolyte. Impregnation of fillers generally takes place by three steps during the impregnation process: adsorption, filling of pores and coating [1]. The adsorption capacity of a molecule is proportional to the surface area of the adsorbent and it is strongly influenced by the structure of the adsorbate (liquid or gas and of the adsorbent (solid) depending on area, volume, functional groups and solubility [2]. As a first approximation, it is necessary that the pore diameter is greater than the molecule size, so that it can diffuse rapidly and reach the adsorption site. This is especially relevant for liquids [3, 4]. Though, polymer materials with a relatively low surface tension [5] can wet the fillers of high surface energy fulfilling the thermodynamic conditions of wetting, the size of macromolecules is not kinetical-

ly favourable. The situation can be even worse for molten polymers because of the high melt viscosity. Furthermore, in a mixture of compounds, there is also a competition of adsorption between the various components and a decrease in the capacity of adsorption.

Carbon black (CB) is used in electrodes of batteries for its electrically conductive properties. Impregnation of 3 to 10 cm³/g of aqueous solutions of zinc or manganese chloride was reported depending of the structure of CB aggregates [6]. The influence of the polarity of the liquids have been studied by Mazgebe et al. [7] and the adsorption rate on dried CB was found to be smaller for polar liquids (water: 1.78 g/g, formamide: 1.55 g/g) in comparison with non-polar liquids (hexane: 2.73 g/g, diiodomethane: 2.73 g/g). Because of the technological importance of carbon blacks in the formulation of polymers, their interaction with chemical species such as stabilizers or antioxidants have been studied [8–9] and many organic liquids (stearic acid, secbutylamine, benzoic acid, piperidine, phenol, aniline, propan-1-ol, pyridine, octadecan-1-ol, triethylamine, ethyl acetate, tributyl amine) have been used as probing liquids for the adsorption properties of CB [10].

The specific infiltration of polymer liquids into CB agglomerate has been studied by Yamada et al. [11], the CB of the study were reported to absorb 70 to 112 cm³/g of dibutyl phthalate. Kawazoe et al. [12] investigated the selective adsorption of the mixture of elastomers on CB showing that the critical radius of gyration must be slightly less than the pore size.

Activated carbon (AC) is another carboneous filler that is also used as an active material especially for super-capacitors based on double-layer capacity. It is known for its capabilities of adsorption and is widely used in wastewater treatment. AC generally has a very porous structure with a large specific surface area ranging from 600 to 2000 m²/g and various pore size distributions. The AC is a multipurpose absorbent that can trap various types of pollutants in water as shown by recent reviews [13, 14]. This capability extends to organic liquids so that characterization of the pore size of AC can be performed by intrusion of liquids in comparison with the molecular size. Extensive work has been performed with large series of esters and aldehydes [15–17] showing intrusion of quantities between 0.26 to 0.60 g/g of liquid depending on the parameters of AC and of the liquid. Adsorption of polymers on AC has also been studied for polystyrene, polybutadiene and their copolymers and for polymethylmethacrylate starting from solutions showing a preferential initial adsorption of short chains [18] followed by that of long chains. The adsorption of polyethylene glycol (PEG) on AC depends on the pore size limit of AC [19] and adsorption capabilities of 0.44 g/g were reported for PEG and polyoxyethylene [20].

Capillary experiments are widely used as a mean of characterizing macroporous materials (pore size > 50 nm). They have been extensively described and often rely on the intrusion of liquids [4]. Among other physical techniques, conventional rheometry has also been used to study the impregnation of spherical silica powders by polymer solutions in the frictional regime [1]. The aim of this work is to investigate the rheological changes that occur during the impregnation of liquid electrolytes (PC and DMSO) on fillers (AC and CB) by an experimental analysis carried out with an internal mixer. This change is shown to be clearly related to porosity as can be measured by classical nitrogen adsorption porosimetry.

2 MATERIAL AND METHODS

2.1 MATERIALS

Two organic liquids, propylene carbonate (PC, from Sigma Aldrich) and dimethyl sulfoxide (DMSO, from Arkema), representative of liquid electrolytes that are used

Properties	PC	DMSO
Melting point [°C]	-55	18.5
Boiling point [°C]	240	189
Flash point [°C]	132	87
Vapor pressure, 20°C [hPa]	0.17	0.56
Vapor pressure, 50°C [hPa]	1.31	4.00

Table 1: Physico-chemical properties of propylene carbonate (PC) and dimethyl sulfoxide (DMSO).

Properties	PC	DMSO
Density [g/cm ³]	0.62	0.80
Surface area [m ² /g]	1420-1700	70
Particle size, major mode [μm]	5	0.045
Pore volume [cm ³ /g]	0.6	6
Pore size, major mode [nm]	1.3	65

Table 2: Physico-chemical properties of activated carbon (AC) and carbon black (CB).

in energy storage devices were investigated in this study. Table 1 presents some physical and chemical properties of PC and DMSO.

Two carboneous fillers, active carbon and carbon black, commonly used as active conductive materials were chosen as powdery substrates with high porosity. The commercial activated carbon (AC) used in this work is in powder form. It is obtained from coconut shells after steam activation with an ash content less than 1 wt-%. Its bulk density is 0.34 g/cm³. The specific surface area obtained by the BET method is 1420–1700 m²/g. The particle size is between 1.6–20 μm with a major mode at 5 μm. The volume of micropores is 0.55 cm³/g and the volume of pores that have a size less than 15 nm is 0.60 cm³/g. The pore volume is mainly microporous as it is generally the case for activated carbon [21].

The carbon black (CB), in powder form, has a density of 0.80 g/cm³. The surface area of this acetylene black is 70 m²/g. The average size of the elementary particles is 45 nm. The carbon blacks are more mesoporous than the activated carbons. Their mesoporosity originates in the voids being between primary particles within a secondary particle or aggregate and the pore size depends on the shape of the carbon black aggregates [21]. The volume of pore is 6 cm³/g with a major mode of the pore size between 65 and 80 nm [22, 23]. All materials were used as received. Table 2 summarizes the data.

2.2 EXPERIMENTS

The porosimetry of AC was measured by nitrogen adsorption porosimetry and Brunauer-Emmett-Teller (BET) surface area analysis. The pore size distribution was obtained by the method of Non Local Density Functional Theory (NLDFT). The specific surface area was calculated by the BET method for pressures between the transition mono/multilayers [24] and at a temperature

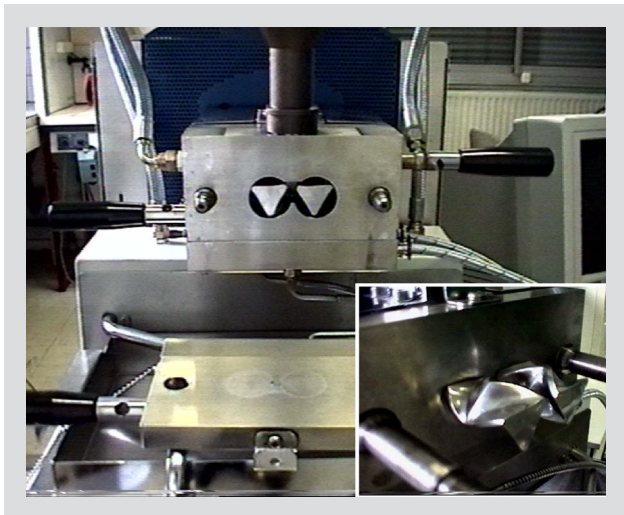


Figure 1: Measuring cell (Rheomix) of the internal mixer.

of 77 K. The linear range used in this work to calculate the surface area is between $1.2 \cdot 10^{-7} < P/Po < 0.968$. The adsorption of organic liquids (DMSO and PC) on fillers (AC and CB) was analysed by monitoring the torque of the filler/liquid blend, as a function of the volume of liquid incorporated in the mixture. This measurement was performed in an internal mixer for a rotation speed of 30 rpm. This mixer (Figure 1) consists of a base device (Polylab) and a measuring cell (Rheomix) commercialized by Thermo Scientific Company. The measuring cell is made of an eight-shaped chamber in which two rotors rotate in contrarotation with a ratio of speed of 2/3 to increase friction. The optimum filling volume of the chamber is 50 cm³ and is limited by a valve driven by a piston. The local shear rate in the mixing chamber varies because of the complex geometry of the rotors. Several authors have proposed empirical relationships relating the shear rate and shear stress with the rotation speed and torque [25–28]. The following Equations 1 and 2 derived from experimental results and analytical calculations assuming a Couette flow in the chamber can be used:

$$\dot{\gamma} = C_1 \Omega \quad (1)$$

$$\sigma = C_2 \Gamma \quad (2)$$

Where $\dot{\gamma}$ is an average shear rate, σ is an average stress, Ω is the rotational speed, Γ is the torque and C_1 , C_2 are geometrical constants, all in SI units. In the conditions of the experiments, the values $C_1 = 0.5$ and $C_2 = 7500$ in SI units were used [28]. The study was carried out at three temperatures (20, 80, and 130°C) and the reproducibility of the results was checked on three measures. The experimental protocol consists of making an initial mixture of 25 g of AC or 15 g of CB with 5 mL of liquid (PC or DMSO) up to the stabilization of the torque then gradually adding the liquid using a syringe

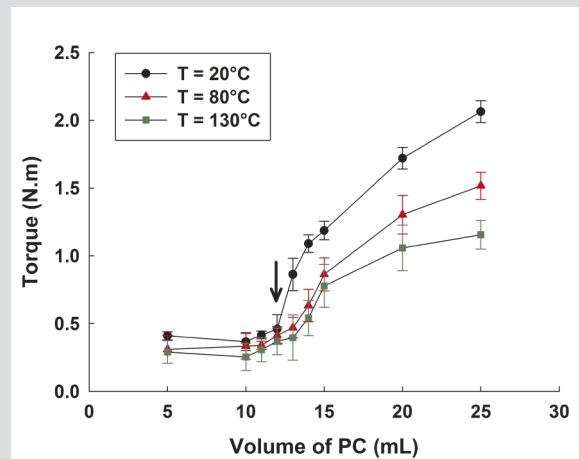


Figure 2: Torque variation as a function of PC volume, in the case of AC at 20, 80, and 130°C.

3 RESULTS AND DISCUSSION

3.1 INTRUSION OF DMSO AND PC IN ACTIVATED CARBON: RESULTS FROM INTERNAL MIXER

Figures 2 and 3 show the torque variation of the mixture AC/PC or DMSO as a function of the liquid (PC or DMSO) volume added in the mixing chamber, for various mixing temperatures (20, 80, and 130°C). The rotation speed was kept constant at 30 rpm and AC was premixed with 5 mL of liquid. The curves show two distinct behaviours. For low amounts of liquid, the torque is low and nearly constant. However, at a critical volume of added liquid, a sharp increase of the torque is observed as the amount of liquid increases. Furthermore, the torque is regularly increasing with the amount of liquid above this critical volume after the sharp increase. The opening of the mixing chamber below this volume shows that the material inside the mixer looks like a dry powder while above the volume, it is wetted by the organic liquid. The critical volume can be obtained graphically on Figures 2 and 3 as indicated by the arrow, at the point where the torque increases sharply. The critical value of the volume of liquid was divided by the mass of powder that was initially incorporated in the mixing chamber. This yields a value of a specific critical volume and at a temperature of 20°C, this volume is 0.48 ± 0.01 cm³/g in the case of PC and 0.56 ± 0.01 cm³/g for DMSO. The comparison of the curves obtained at various temperatures and for a given volume of liquid, also shows that for low amounts of liquid, the torque remains independent of the temperature, while for higher amounts of liquid, above the critical value, the torque decreases when the temperature increases. The overall effect of temperature on the critical volume is minor though in the case of DMSO, a slight increase of the volume can be noticed.

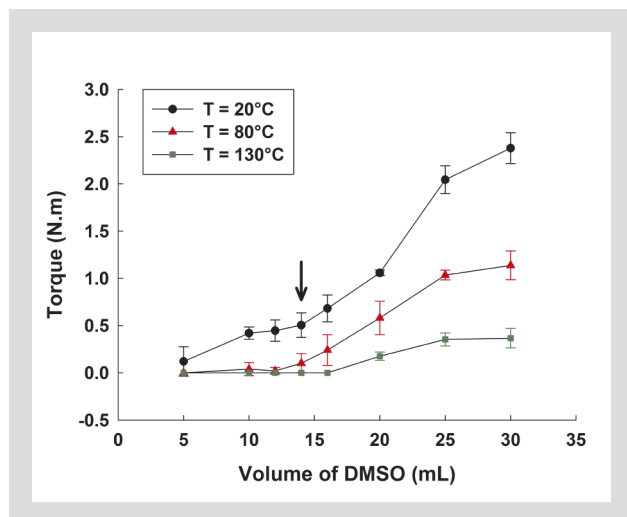


Figure 3: Torque variation as a function of DMSO volume, in the case of AC at 20, 80, and 130°C.

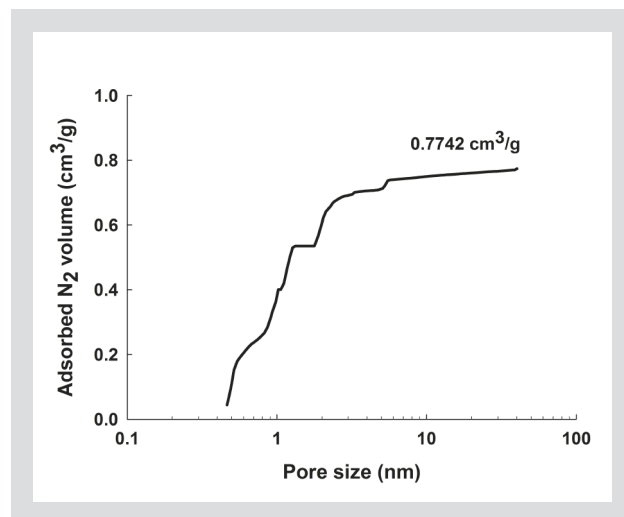


Figure 4: Cumulative pore volume obtained by applying the DFT method to the N_2 adsorption isotherm.

3.2 ADSORPTION OF DMSO AND PC ON ACTIVATED CARBON: RESULTS FROM NITROGEN POROSIMETRY

The observation of either a dry or a wet powder in the chamber in correspondence with two specific behaviours indicates the correlation with the absorption of the liquid into the filler in close relation with the porosity of the carbonaceous filler. A classical analysis of the porosity has been carried out by nitrogen porosimetry measurements. Figure 4 shows the pore size distribution of AC derived from the BET/NLDFT method. The specific surface area obtained by the BET method is $1700 \text{ m}^2/\text{g}$.

The volume accessible to liquid can be determined from the porosimetry curves obtained previously and also from molecular diameters of liquids. This was done by considering that each molecule can only penetrate in the pores whose diameters are larger than the molecular diameter of the liquid. The accessible volume was calculated by subtracting the adsorbed N_2 volume at this limiting pore size from the maximum porous volume. The molecular diameter of the liquid was obtained from their molar volume, assuming that the molecule is spherical. These molecular diameters were compared with the values of the greatest distance between atoms in the molecules. The results for both liquids are summarized in Table 3 in comparison with values of the literature. The diameter of PC is larger in any case.

The excluded volume was calculated from Figure 4 by taking the ordinate of the plot when the pore size is equal to the molecular diameter of the liquid calculated with the molar volume. This allowed getting the accessible volume that was found to be $0.56 \text{ cm}^3/\text{g}$ for PC and $0.57 \text{ cm}^3/\text{g}$ for DMSO. These results correlate well with values obtained from torque measurements with an error of 14 % in the case of PC and 2 % for DMSO. Therefore the critical volume determined from the experiments in the mixer is the porosity that is accessible to the liquid. The change of the behaviour is relat-

Properties	PC	DMSO
Molar volume (cm^3/mol) [29]	85.0	71.3
Molecular diameter (nm) (from molar volume)	0.646	0.610
Molecular diameter (nm) (from distance between atoms)	0.544	0.448
Molecular diameter (nm) [30]	0.550	0.513

Table 3: Molar volume and molecular diameter of propylene carbonate and dimethyl sulfoxide.

ed to the trapping of the liquid into the filler porosity below the critical value and to the occurrence of liquid in excess in comparison to the porosity above the critical volume, this liquid behaving as an intergranular medium for the filler particles. The slight increase of the critical volume that is observed for DMSO may indicate a change of chemical affinity with temperature but also that the accessible volume is increased by a dilatation effect of the porous volume.

3.3 ADSORPTION OF DMSO AND PC ON ACTIVATED CARBON: THE TRANSITION FROM FRICTIONAL TO HYDRODYNAMIC REGIME

The observed variation of the torque is characteristic of a transition between the behaviour of a dry homogeneous powder below the critical (or porosity) volume because the liquid was fully adsorbed into the porosity and a concentrated paste above this volume because the porosity is saturated. Two types of interactions between particles may occur during the flow of a granular paste: frictional or hydrodynamic. In the frictional regime, there exists a continuous network of contacting particles having direct contacts with each other. This network gives rise to typical rheological properties of the frictional regime with a tangential stress that is simply described by the Coulomb Equation 3:

$$\sigma = \mu N \quad (3)$$

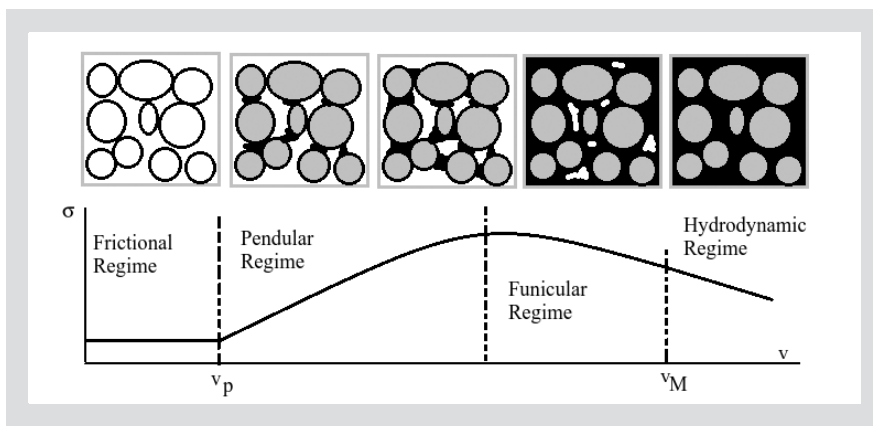


Figure 5: Structure of the solid-liquid mix upon addition of a volume v of liquid, corresponding regime and shear stress.

the stress being related to the product of the number of contacts N by the coefficient of static friction μ . In this regime, the stress is independent of the liquid content as far as the liquid is adsorbed in the pores of the solid. In the hydrodynamic regime, or lubricated, or viscous regime, a thin interstitial film layer separates the particles creating indirect contacts and the hydrodynamic interactions dominate the friction. The direct contacts may exist but their network is not continuous and direct contacts are partially or totally substituted by indirect contacts through interstitial fluid. In the hydrodynamic regime the stress is defined by an equation including a viscosity for example in the form of the Krieger-Dougherty model, Equation 4:

$$\sigma = \eta_s \dot{\gamma} \left(1 - \frac{\Phi}{\Phi_M} \right)^{-[\eta]\Phi_M} = \eta_s \dot{\gamma} \left(\frac{v - v_M}{1 - v_M} \right)^{-[\eta](1 - v_M)} \quad (4)$$

where $\dot{\gamma}$ is the shear rate, η_s is the viscosity of the suspending medium, Φ is the volume fraction of particles, Φ_M is the packing fraction, v is the volume fraction of liquid and $v_M = 1 - \Phi_M$. Between these two regimes, there is a transition when the energy dissipated by friction between particles becomes lower than that dissipated by the viscous dissipation. Clearly, in our experiments, below the critical value of the added volume, the torque in the mixer depends neither on the volume, nor on the temperature and this indicates a pure frictional behaviour. However, above the critical value, the observed behaviour is not that of a concentrated suspension in a hydrodynamical regime for which an increase of the amount of the liquid would result to a decrease of the viscosity, stress and torque at constant shear rate after saturation of the porosity. As a torque increase is observed when the amount of interstitial liquid increases, it is rather the behaviour of a granular paste in the transitional regime, for which the cohesion is ensured by liquid bridges that progressively substitute the frictional contacts. Thus, increasing the amount of liquid first increases the number of bridges until the intergranular spaces are filled. Indeed, in the transitional

regime, the energy dissipated by the movement of particles separated by a fluid bridge is higher than that dissipated by the frictional contacts. Within the unsaturated granulars, the liquid and the air phases coexist in the interstitial space. On the basis of the amount of water trapped in a granular medium, one can distinguish different sub-regimes that are well known for granulars wetted by water [31, 32]. In non-porous granular surface, there is first a hygroscopic regime where the liquid is essentially retained by the asperity. This regime is not observed in the present case because the liquid is first adsorbed in the porosity. With an amount of liquid slightly larger, at the critical volume exceeding the porosity, capillary bridges appear between the grains; this is generally called the pendular regime. At a higher liquid content, air can be trapped and this state is named as the funicular regime. The presence of small amount of liquid on the particle surface modifies the physical properties of the granular medium. For two grains in contact, if the amount of liquid is sufficient to form a liquid bridge at the contact point, the capillary cohesion force between the grains can give rise to a stress given by Equation 5:

$$\sigma = N' 2\pi\gamma \cos\theta R \quad (5)$$

where γ is the surface tension, θ is the angle of partial wetting, R is the spherical grains radius, N' is the number of bridges. As soon as the volume of liquid trapped around the granular contacts is large enough to overflow the asperities or pores, the capillary force becomes independent of the volume of the liquid bridge [33]. However, in a packing of grains, the presence of liquid creates a distribution of capillary bridges. The increasing number of capillary bridges as a function of water content increases the cohesion as shown by many authors [34–37]. However, the force will saturate to a constant value of the number of liquid bridges per grain [38]. Thus, increasing the water content will just increase the volume of the bridge but will not affect the capillary force as seen previously. This situation will last until the whole intergranular space is filled in the funic-

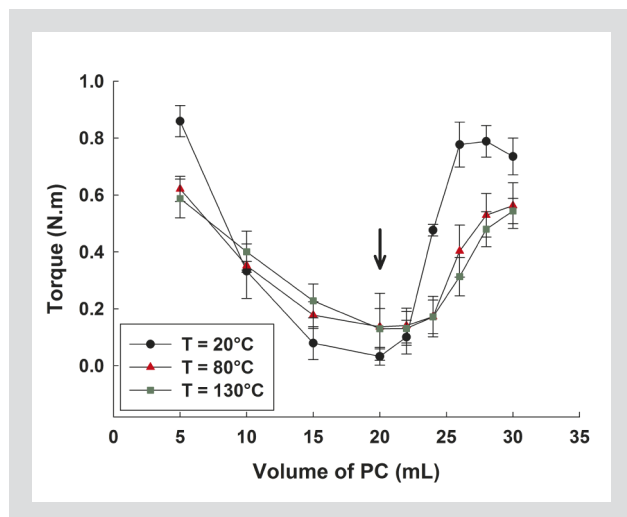


Figure 6: Torque variation as a function of PC volume, in the case of CB at 20, 80, and 130°C.

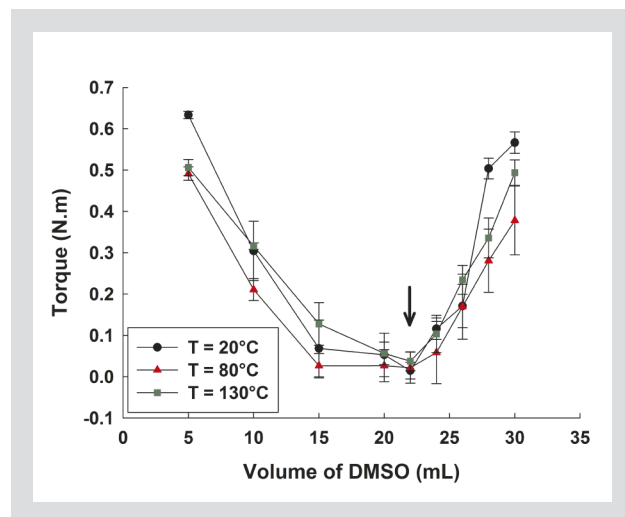


Figure 7: Torque variation as a function of DMSO volume, in the case of CB at 20, 80, and 130°C.

ular regime and then, the cohesive force with start to decrease. Figure 5 aims to sketch the various regimes in terms of the volume fraction of added liquid showing the frictional, pendular, funicular and hydrodynamic regimes in relation to the stress and structures. The characteristic volume fraction is v_p and the packing of solid is lost at v_M .

3.4 INTRUSION OF DMSO AND PC IN CARBON BLACK

The correspondence between the porosity and the characteristic volume gives an additional major interest to the use of the internal mixer for this type of study. Indeed, this provides a method for rapid porosity measurements in the case of very powdery materials that can hardly be analyzed by the classical porosimetry methods. This is especially the case for carbon black. Figures 6 and 7 show the torque variation of the filler-in-liquid blend, in the internal mixer, as a function of the volume of liquids (PC or DMSO) in the case of CB. The overall evolution of the torque with CB is slightly different from that of AC in the frictional regime although a torque increase is observed when the behaviour turns to that of a concentrated paste when entering the pendular regime. The difference of behaviour observed in the frictional could be due to a stronger attrition of CB particles compared to the AC particles. The approximate stress and shear rate were calculated by the use of Equation 1 and 2 from the data of torque. Theoretically, these equations can only be used for the liquid mix in the hydrodynamic regime but the value remains indicative of the state of stress in the mix. Values are summarized in Table 4 at 20°C. The rotational speed was kept constant during the experiments at 30 rpm corresponding to an average shear rate of 15 s^{-1} . For CB, in the frictional regime, the stress with 5 mL of liquid is 2–5 times higher than in the case of AC. This could be mainly due to the agglomerated structure of carbon black that is responsible for roughness which promote enhanced friction as shown on other particulate systems [39]. This higher

Filler Liquid	AC		CB	
	PC	DMSO	PC	DMSO
Stress (kPa) with 5 mL of liquid	1.02	0.30	2.15	1.59
Stress (kPa) at the porosity volume	1.15	1.26	0.08	0.04

Table 4: Approximate shear stress during mixing at 20°C.

stress combined to the looseness of the structure will induce a strong tendency of CB agglomerates towards attrition and reduction of the surface asperities. Indeed, the cohesive stress of fluffy dry carbon black has been measured between 1 and 10 kPa [40] and, according to Table 4, the stress in the mixer is in the same order of magnitude (1 to 2 kPa) in the case of carbon black. This process that leads to a dispersion of the CB powder towards the aggregates is not influenced by temperature as shown by the experiments. At the limit of the pendular regime, the torque increases sharply. The volume accessible to liquids can be determined graphically at the minimum of the torque. For a temperature of 20°C, the volume accessible to PC is found to be $1.33 \pm 0.02 \text{ cm}^3/\text{g}$ while that accessible to DMSO is $1.47 \pm 0.02 \text{ cm}^3/\text{g}$. The plot at 20°C with PC also displays a decrease of the torque that marks the occurrence of either the funicular regime or the hydrodynamic one after the saturation of the maximum number of liquid bridges or of the intergranular space.

3.5 COMPARISON OF THE INTRUSION OF PC AND DMSO IN ACTIVATED CARBON AND CARBON BLACK

The results show a higher intrusion of both liquids (DMSO and PC) on CB, but also a better intrusion of DMSO on both substrates in comparison to PC. This is mainly related to the particular structure of CB that consists of spherical particles (10 to 500 nm) amorphous and aggregated (tens to hundreds of particles, or an

average diameter of 0.1 to 0.8 mm) [41]. Therefore, there exists a macroporosity between the particles though the elementary particle of carbon black has no porosity on its own. On the contrary, in the case of AC, the micropores (diameter < 2 nm) represent the largest part of the inner surface of the AC particles (90 to 95 % of the total surface of the material) and the adsorption takes place essentially in the micropores. The mesopores and macropores only allow access to the micropores acting as free spaces in which molecules move freely to access the micropores.

4 CONCLUSIONS

The intrusion of organic liquids such as propylene carbonate and dimethyl sulfoxide into carbonaceous materials (activated carbon and carbon black) and its influence on the rheological behaviour of the wetted granular mix was studied using an internal mixer. The monitoring of the torque during the mixing of the powder upon progressive addition of the liquid at constant rotation speed shows characteristic events related to various regimes and structures of the granular paste or suspension. During impregnation of the filler by the liquid, the rheological behaviour is first related to solid friction. As soon as the liquid amount exceeds the accessible porous volume, it turns to that of a concentrated paste and this induces a remarkable change in the torque signal. In particular, a sharp increase of the stress, related to the onset of a pendular regime dominated by capillary effect in liquid bridges is noticeable. The critical volume at this point was considered to be the accessible porous volume. This was confirmed by conventional nitrogen adsorption porosimetry. Further addition of liquid first saturates the number of liquid bridges and then drives the system into the hydrodynamic regime where it behaves as a concentrated suspension. In this regime, the decrease of the stress at constant rate reflects the decrease of the viscosity upon volume fraction of solids as usually observed. The direct relation between the porosity and a rheological change makes the method suitable for a quick determination of the liquid take-up limit or porosity. This can be of interest for powdery materials such as carbon black that can hardly be analyzed by conventional porosimetry. The use of the heated chamber of the mixer also enables the measure at various temperatures. From the material point of view, the volume accessible to liquids (DMSO and PC) in filler porosity (AC and CB), as determined using the internal mixer, shows a better adsorption of liquids on the CB and a slightly higher adsorption of DMSO compared to PC. In fact, the DMSO being a polar liquid has a better interaction with fillers independently of temperature.

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