

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

MERAL AKKOYUN, CHRISTIAN CARROT*, BENOÎT BLOTTIÈRE

Université de Lyon & CNRS & Université de Saint-Etienne – Jean Monnet, UMR 5223,
Ingénierie des Matériaux Polymères, 23 rue du Dr. Paul Michelon, 42023 Saint-Etienne, France

* Corresponding author: carrot@univ-st-etienne.fr
Fax: x33.4.77485126

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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 carbonaceous 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, triethyl amine, ethyl acetate, tributyl amine) have been used as probing liquids for the adsorption properties of CB [10].

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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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