

Electrical conductivities of carbon powder nanofillers and their latex-based polymer composites

M. Ghislandi^{ad}, E. Tkalya^{bd}, B. Marinho^{ac}, C.E. Koning^b and G. de With^a

^a Laboratory of Materials and Interface Chemistry, Technische Universiteit Eindhoven, 5600 MB Eindhoven, The Netherlands, ghislandi@gmail.com

^b Laboratory of Polymer Chemistry, Technische Universiteit Eindhoven, 5600 MB Eindhoven, The Netherlands, c.e.koning@tue.nl

^c Department of Chemical Engineering, Federal University of Minas Gerais, Av. Antônio Carlos 6627, 31270-901, Belo Horizonte, Brazil

^d Dutch Polymer Institute DPI, PO Box 902, 5600 AX Eindhoven, The Netherlands

ABSTRACT

The electrical conductivity of graphene, multi-wall carbon nanotubes, carbon black nanopowders and graphite powder is characterized using paper-like films and by means of powder compression. For the graphene and nanotube nanopowders, maximum macroscopic conductivity can be obtained by filtering well dispersed water/filler solutions into a dense and well-oriented paper-like structure. The results are compared with the percolation threshold and final conductivity of polypropylene (PP) composites, using latex technology for the incorporation of the carbon fillers in the polymer. PP composites produced in this work showed well-dispersed fillers inside the polymer, with percolation thresholds as low as 0.3 wt.%. The final conductivity for all the composites is below 1.5 S/m, not reaching the high value of $\sim 10^3$ S/m, which are obtained for graphene- and nanotube-based paper films or graphite compacts.

Keywords: carbon nanotubes, graphene, powder pressing, nanocomposites, electrical conductivity.

1 INTRODUCTION

Since the conductive performance of a composite is directly related to the formation of a conducting network through the polymer matrix [1,2], its understanding depends critically, on the knowledge of the electrical behavior of the agglomerated nanoparticles, e.g. in the form of a bulk powder or a paper film. Paper-like structures, known as “buckypapers”, in which the nanoparticles are joined together by van der Waals interactions, present promising materials for macroscopic investigations of their conductive properties, not only for the nanotubes [3] but also for graphene [4]. Similar structures can be made from other carbon fillers and we refer to these from now on as “buckypapers” or simply “papers”.

For manufacturing of composites, latex technology has already been applied, e.g. for the incorporation of carbon nanotubes into a polymer matrix [1], or graphene in

polystyrene [2]. The latex approach facilitates the incorporation of nanofillers, via liquid phase mixing, into any kind of highly viscous polymer which can be synthesized by emulsion polymerization or similar processes. This yields highly dispersed filler composites, that often have a low (~ 1 wt.% of filler content) electrical percolation threshold [5].

In this work, three different carbon nanofillers have been studied: multi-walled carbon nanotubes (MWCNTs), graphene, and carbon black (CB). Graphite was also used as reference filler for comparison. In order to study the electrical conductivity of the raw powders, two different characterization methods were used. The first one consists of monitoring the electrical conductivity during the compression of powders, whereas the second involves the preparation of paper films and subsequent electrical characterization. The relevance for the field of nanocomposites processing technology is discussed by comparing the powder and papers conductivities with the final conductivity and percolation threshold of the composite produced with these carbon fillers.

2 EXPERIMENTAL

2.1 Powder pressing

The compression assays were performed in specially designed equipment sketched in fig. 1. The device consists of a thick isolating ceramic die vertically fixed to a heavy circular copper support containing a stationary piston that closes the bottom of the cylinder. A close-fitting copper plunger, which can move up and down in the cylinder, closes the compression chamber. A more detailed description of the equipment and powder pressing procedure is reported, in work done by our group, elsewhere [6].

The dc electrical resistance of the compressed powders was measured via the four-point method. The electrical current was provided by a source-measure unit (Keithley 237), while the voltage was measured by an electrometer (Keithley 6517A). For each pressure, five currents were

applied and their corresponding voltages were registered, and the resistance calculated.

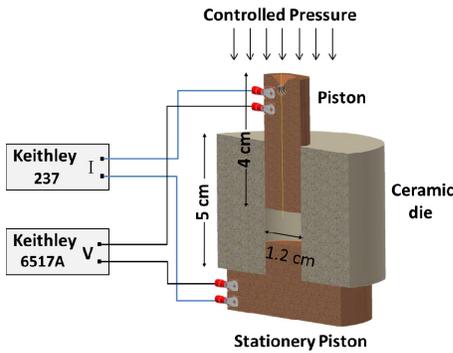


Fig. 1. Schematic representation of the experimental set-up involved in the measurement of the powder conductivity under pressure.

2.2 Paper film and composite processing

CB and MWCNTs dispersions were prepared by mixing 0.06 g of each filler with 60 ml of an aqueous SDBS solution in a round flask (SDBS/filler ratio of 2/1) and subsequently sonicating the suspension for 50 min [1]. Graphite and graphene filler dispersions were prepared identically, except for an increase sonication time to 2 h for further exfoliation of these fillers. All sonication processes were carried out with a horn sonicator (Sonic Vibracell VC750) with a cylindrical tip (13 mm end cap diameter). The output power was fixed at 25 W, thus delivering energy of 1300–1400 J/min. The flask was placed in an ice bath in order to prevent a temperature rise during sonication.

For paper film preparation, 10 ml of each filler dispersion was transferred into a filtration set up containing a polyamide membrane (pore size of 0.45 μm). The dispersion was then connected to a vacuum pump for pressurization. As a result of the filler's sedimentation, a smooth and black film was formed on the filter surface. In order to remove residual moisture, the films were dried at 90 $^{\circ}\text{C}$ and 200–400 mbar in a vacuum oven for 3 h.

For composite preparation, each dispersion was mixed with PP latex by stirring, to a final filler content between 0.1 wt.% and 10 wt.%. Each mixture was then frozen in liquid nitrogen for several minutes and the aqueous solvent was removed with a Christ Alpha 2–4 freeze dryer operated at 0.2 mbar and -50 $^{\circ}\text{C}$ for 48 h. The resulting composite powders were heated quickly to 140 $^{\circ}\text{C}$ and then for 20 min until 163 $^{\circ}\text{C}$ between Teflon sheets, using a Collin Press 300G. Subsequently the heated material was compression molded into films of 0.5 to 1 mm thickness at 100 bar for 3 minutes, and then cooled at room temperature in air. Prior to final compression, the composite was degassed via 3 consecutive fast compressions for 20 seconds at 50 bar.

The electrical conductivity of paper and composites were measured using a standard four-point method. Parallel contact lines (on which the electrodes are placed) with 1 cm

in length and with a 1 cm interval were drawn with conductive-silver paint (Fluka) on the samples, and all conductivity measurements were performed at room temperature with a Keithley 6512 programmable electrometer. For each sample, conductivity data represent the average value of 10 consecutive measurements.

3 RESULTS AND DISCUSSION

The conductivities of both, powder and buckypaper, were plotted (fig. 2) as a function of the bulk density ρ , $\rho = m/V$, where m is the mass of material, and V is the volume of the chamber at a certain pressure. As can be seen, the different fillers find themselves in different stages of compression, hampering direct conductivity comparison. For graphite and carbon black, the buckypaper conductivity value practically fits in the powder curve. CB as employed in this work can be considered as an agglomerate of primary spheres, and hence identical contacts in both, powder and buckypaper, are expected. At the same density, the slightly lower conductivity value obtained for CB buckypaper, in comparison with CB powder compression curve, is most likely caused by SDBS retained from film preparation. Nevertheless, the influence of SDBS is insignificant, considering conductivity standard variations. In the case of MWCNTs and graphene, the buckypaper density was not achieved by the powder pressing even at maximum pressing load. Henceforth, large discrepancies are observed between the powder curves and the buckypaper values, which suggests that filler particles are preferentially orientated in papers on account of the paper preparation method combined with shape anisotropy of particles.

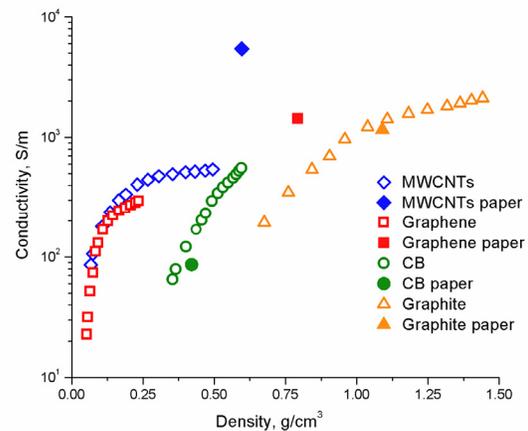


Fig. 2. Electrical conductivity behavior of the different carbon powders as a function of density and conductivity value of paper-like structures. For each material the data points represent an average of at least 3 identical assays differing not more than 3%.

A comparison of powder and paper conductivities is given in table 1, together with data on specific surface area

and intrinsic conductivity. Clearly the constriction of the current flow due to contact spots plays a major role when comparing the bulk conductivity of different powders. As expected, for none of the carbon materials the single particle conductivity was reached by powder compacts, due to the impossibility of annulling the contact resistance effect. Interestingly, the conductivity of a single particle of carbon black differs by only a factor of 2 with the conductivity obtained by powder pressing. For nanotubes and graphene this difference reaches up to 5 and 6 orders of magnitude, respectively. Due to the much higher surface area of the nanoparticles (MWCNTs, graphene), as confirmed by BET, the number of contacts is much higher and so the contact resistance influence is far more pronounced as compared to the micro-particles (graphite, CB agglomerates).

| Filler | BET Surface Area (m ² /g) | Conductivity (S/m) | | |
|----------|--------------------------------------|-------------------------|-----------------------|---|
| | | Powder Compact at 5 MPa | Paper | Isolated Single Particle Conductivity |
| MWCNT | 272 | 5.43 x 10 ² | 5 x 10 ³ | 10 ⁶ -10 ⁷ ^a |
| Graphene | 180 | 2.62 x 10 ² | 1.4 x 10 ³ | 10 ⁷ -10 ⁸ [7] |
| CB | 56.9 | 5.58 x 10 ² | 9 x 10 ¹ | 10 ³ [8] |
| Graphite | 3.08 | 2.12 x 10 ³ | 1.2 x 10 ³ | 10 ⁵ [9] |

Table 1. Material and compact characteristics.

SEM measurements obtained by charge contrast imaging confirm a homogeneously dispersed organization of the nanofillers inside the polymer matrix (fig. 3). Because of the differences in charge transport between the conductive fillers and the polymer matrix, the secondary electron emission is higher at the filler location. This results in the contrast between the filler network (bright) and the polymer matrix (dark). The poor charge contrast achieved for the CB composites images is a result of nano-dimensional and well-dispersed agglomerates. Graphene and nanotubes have at least one dimension in the micrometer range, allowing more efficient charge emission and consequently charge contrast.

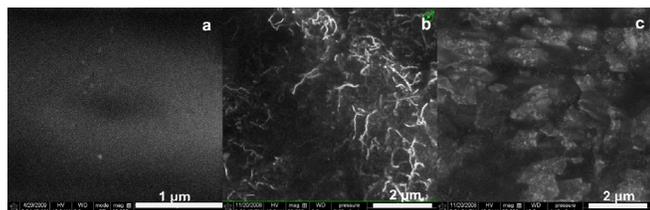


Fig. 3. SEM images of PP composite with barely visible CB at 5 wt.% (a), the organization of the tubes inside the PP polymer composites (b) and the structure of wrapped graphene platelets inside the PP polymer matrix (c).

^a Nanocyl Company: <http://www.nanocyl.com/en/CNT-Expertise-Centre/Carbon-Nanotubes>.

Figure 4 shows a comparison of the conductive percolation threshold and final conductivity obtained for the different composites. All the filler dispersions were mixed with PP latex and processed following the same procedure. The maximum conductivity values are below 1.5 S/m, for all the samples. These values are much lower than the ones obtained for paper-like structures or powder compacts. As verified for powder compacts and paper samples, the conductivity is limited by filler-filler inter-particle contact resistance, with the addition, in the case of composites, of possible polymer/SDBS-filler contact resistance.

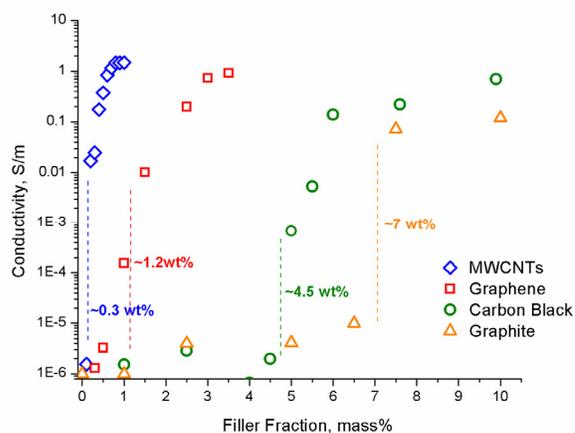


Fig. 4. Percolation threshold of carbon composites prepared via latex technology. Electrical conductivity as a function of filler mass concentration. Values represent an average of 10 measurements; standard deviations are below 10%.

The amount of effective charge carriers (fillers) contributing to the overall conductivity (σ) is much lower for the composites (due to the much lower filler content in the same corresponding volume) than for powder compacts or paper films. If we consider, e.g., nanotubes composites with 1 wt.% of filler content, assuming that all the fillers are connected and contribute to the overall conductivity, we still have a total density of material, which effectively contributes to conductivity, 100 times lower than the intrinsic density attributed to the MWCNTs composite ($\sim 1 \text{ g/cm}^3$) at this filler content. This means that an effective density of $\sim 0.01 \text{ g/cm}^3$ for these composite is still much lower than the ones measured for powder compacts or paper films, hindering any direct comparison.

Overall, a much lower percolation threshold is observed for the nanocomposites of graphene and MWCNTs when compared to graphene and CB percolations. The higher surface areas and aspect ratios allow these composites to form a conductive network at much lower filler contents. It is important to mention that the state of dispersion during the preparation phase plays an important role. The successful exfoliation of the MWCNTs and homogeneous dispersion in the PP polymer using latex technology was confirmed, with composites exhibiting a percolation as low as 0.3 wt.%, a value that is lower than previous results

reported using polystyrene (PS) latex [1]. For graphene, the purity and dimensions (size and thickness) of the starting filler may influence this property. A percolation threshold as low as 0.9%, with a final conductivity of 15 S/m, was already reported [2], using similar preparation methods but different graphene and latex (PS) sources. The advantage of graphene over nanotubes may be the possible reduction of the percolation threshold by optimizations of filler properties (dimensions, purity, dispersibility) and processing conditions, added to potential lower production costs and superior gas barrier properties.

For the studied CB and graphite, the percolation threshold is much higher as compared to MWCNTs and graphene. The low surface area associated to low dispersibility in water may have shifted the percolation threshold to 4.5% for CB and at least 7% for graphite. Still these percolations are considerably lower than in other processing technologies [5]. New techniques of long term exfoliation of graphite, in water and organic solvents, using different surfactants have shown improved dispersibility [10, 11], with the drawback of low maximum concentration and reduced filler dimensions.

4 CONCLUSIONS

MWCNTs, graphene, CB and graphite bulk powders exhibit different packing densities during compression and henceforth different macroscopic conductivities, even at high pressing loads up to 5 MPa. Moreover, powder compact conductivities never reach the intrinsic single particle conductivity value. For the nanoparticles graphene and MWCNTs, due to the much higher surface area and number of contacts in compacts, this difference reaches up to 5 and 6 orders of magnitude, respectively.

Well-exfoliated water/SDBS/filler dispersions were produced with graphene, and MWCNTs; CB dispersion presented a slightly lower exfoliation than the former two, whereas the dispersions obtained with graphite were poor and less stable than all the others. Smooth paper-like films, produced with graphene and MWCNTs dispersions, yielded macroscopic conductivity values ($\sim 10^3$ S/m) approximately one order of magnitude higher than those of powder compacts ($\sim 10^2$ S/m at 5 MPa), indicating that, for the former, even with the presence of surfactant, filler orientation, due to controlled dispersion and settling under pressure, helps to increase the apparent density and final conductivity of the bulk material.

Carbonaceous nanofiller/polypropylene composites exhibiting really low conductivity percolation thresholds were successfully produced using a latex technology process. A homogeneous distribution of the nanofillers inside the polymer matrix was confirmed by SEM. The conductivity measured for the composites show maximum values around 1.5 S/m, a value which is three orders of magnitude lower than the conductivity obtained for paper films (graphene and MWCNTs) or powder compacts (graphite). This maximum conductivity may be greatly

limited by the amount and nature of conducting contact spots; most probably the contact resistance is increased by the presence of isolating polymer/SBDS covering the fillers. The amount of conductive paths per unit volume that effectively contribute to the overall conductivity is also much lower for the composites (due to the much lower filler content in the same corresponding volume) as compared to the amount of conductive paths in the powder compacts and paper samples. Nevertheless, the conductivity values for composites above the percolation threshold are in agreement with results obtained for powder compacts. This leads to a clear sign that for composites at low filler contents (1-5 wt.%) it is impossible to reach the high conductivities obtained for powder compacts, due to huge mismatch of effective conductive filler densities.

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