Preparation routes to aqueous graphene dispersions and their influence on electrical conductivity of polymer composites

Marcos Ghislandi[1, 3*], Evgeniy Tkalya[2, 3], Alexander Alekseev[1], Cor Koning[2], and Gijsbertus de With[1].

[1] Laboratory of Materials and Interface Chemistry, Eindhoven University of Technology, 5600 MB Eindhoven, The Netherlands
[2] Laboratory of Polymer Chemistry, Eindhoven University of Technology, 5600 MB Eindhoven, The Netherlands
[3] Dutch Polymer Institute DPI, PO Box 902, 5600 AX Eindhoven, The Netherlands
[*] E-mail:m.g.ghislandi@tue.nl

The chemical synthesis of graphene using graphite, graphite oxide (GO) or other graphite derivatives as starting materials have been extensively studied. The conversion of graphite into GO via Hummers or similar methods is an initial stage for different approaches. The water soluble GO can be reduced with the use of chemicals[1,] or quickly thermally expanded[2] to form graphene. Recently, the long-term (e.g. more than 200 h) simple mechanical exfoliation (sonication) of graphite dispersed in polar solvents, as well as in water/surfactant systems, were reported as methods that yield single and multilayer graphene platelets at relatively high concentrations[3]. The chosen conversion techniques not only can be up-scaled but also can provide graphene with improved processability and potentially new functionality. The exfoliated dispersions are most suitable for the preparation of polymer composites with enhanced mechanical and electrical properties. In this work, starting from graphite, we produced graphene dispersed in water following the two main chemical conversion approaches (*Oxi/Red Chemically* and *Oxi/Red Thermally)* and a physical conversion via ultrasonic exfoliation (*Sonic Solution).* Subsequently, graphene /polystyrene (PS) composites were prepared using the well-known latex technology. The latex concept enables the incorporation and proper dispersion of nanofillers into any kind of highly viscous polymer such as PS, e.g. synthesized by emulsion polymerization or similar processes[4]. A comparison of the three chosen techniques with respect to filler morphology and conductive properties of the respective nanocomposites is presented.

Water/surfactant solutions were prepared with the nanofillers prepared via the three methods described above and latex technology was applied for the preparation of conductive graphene/polystyrene composites, with well-dispersed graphene platelets. Each dispersion was mixed with PS latex, frozen in liquid nitrogen for several minutes, and subsequently freeze dried. The resulting composite powders were heated up and then compression molded into films. The samples were characterized (Raman, UV-Vis, AFM, SEM) with respect to filler properties and morphology, and their influences on electrical conductive properties of the composites were compared.

AFM showed that the GO reduction techniques yield thin graphene platelets, and as a consequence also induce wrinkling/agglomeration and possible size reduction of the platelets, especially for the *Oxi/red Thermally* samples. Nevertheless, the thickness of the majority of the sheets measured is between 1 and 3 nm, corresponding to a single or only a few layers of graphene. For the *Sonic Solution* graphene samples analyzed, the thickness measured was higher (5 to 25 nm) and the average size was smaller, indicating multi-layer graphene. As the samples are much thicker, no wrinkling was observed.

The conductivities of the graphene/PS nanocomposites, obtained by both four point and local current measurement techniques, reveal high values up to 15 S/m and a low percolation threshold (0.9 wt.%) for the *Oxi/red Chemically* composites (Fig. 1). SEM and Conductive-AFM (see Fig. 2) show the different graphene shapes, even inside the polymer, depending on the filler production method used. Interesting differences in electronic transport behavior were also noticed, indicating at first glance direct contact transport for *Oxi/red Chemically* graphene in contrast with tunneling for *Oxi/red Thermally* and *Sonic Solution* graphene. The conductive properties of the composites studied mainly depend on the initial morphological characteristics of the produced graphene and its posterior organization inside the polymer matrix. These characteristics may have an important influence also on the electronic transport behavior through the composite.

References

1. S. Stankovich, D. A. Dikin, R. D. Piner, K. A. Kohlhaas, A. Kleinhammes, Y. Jia, Y. Wu, S. T. Nguyen, R. S. Ruoff, *Carbon* **2007,** 45, (7), 1558-1565.
2. M. J. McAllister, J. L. Li, D. H. Adamson, H. C. Schniepp, A. A. Abdala, J. Liu, M. Herrera-Alonso, D. L. Milius, R. Car, R. K. Prud'homme, I. A. Aksay, *Chemistry of Materials* **2007,** 19, (18), 4396-4404.
3. M. Lotya, P. J. King, U. Khan, S. De, J. N. Coleman, *Acs Nano* **2010,** 4, (6), 3155-3162.
4. E. Tkalya, M. Ghislandi, A. Alekseev, C. Koning, J. Loos, *Journal of Materials Chemistry* **2010,** 20, (15), 3035-3039.
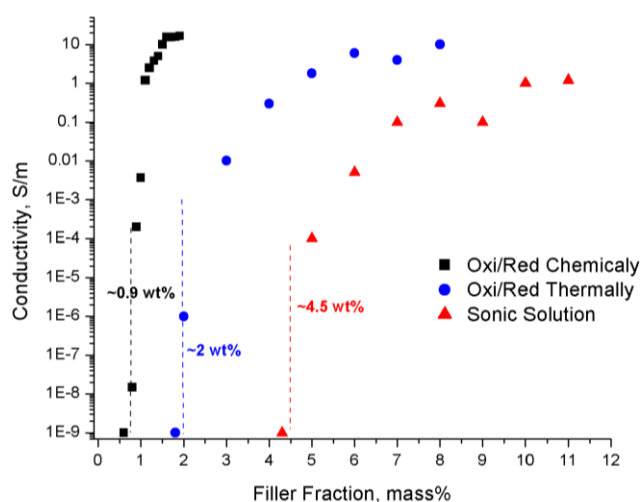
Figures

Fig. 1 – Volume electrical conductivity of graphene/PS composites as a function of graphene weight fraction. Values represent an average of 10 measurements for each sample; standard deviations are below 10%.
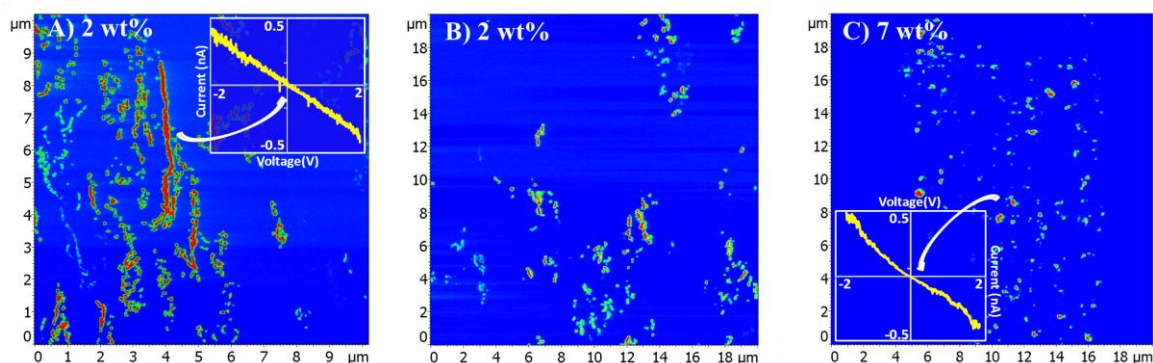

Fig. 2 – C-AFM of the composites cross secrtion areas for the three graphene used. A) Oxi/red Chemically (inset linear I-V curve), B) Oxi/red Thermally and C) Sonic Solution (inset exponential-like I-V curve) composites. Green/red spots correspond to graphene paths wich contributes to conductivity through the sample.