Investigating the preparation routes to aqueous graphene dispersions and their influence on electrical conductivity of polymer composites

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ABSTRACT

Graphene was produced from graphite powder using the three best known water-based conversion approaches. The first two are based on chemical oxidation methods, only differing in the reduction process, either by the use of hydrazine or by thermal expansion, respectively. The third one is based on long-term ultrasonic exfoliation. Water/surfactant solutions were prepared with these three nanofillers and latex technology was applied for the preparation of conductive graphene/polystyrene composites, with well-dispersed graphene platelets. Microscopic studies showed that both reduction processes lead to agglomeration/wrinkling of the nanoplatelets, even though they yield composites with high conductivity and low percolation threshold. Although mechanical ultrasound exfoliation of graphite produces less defective multi-layer graphene, these platelets have a smaller lateral size and their composites exhibit a higher percolation threshold.

Keywords: graphene, aqueous dispersion, polymer composites, electrical conductivity

1 INTRODUCTION

The conversion of graphite into graphite oxide (GO) via Hummers [1] or similar methods is an initial stage for graphene preparation. The water soluble GO can be reduced with the use of chemicals [2,3] (ORchem) or by quick thermal expansion [4] (ORtherm) to form graphene. Recently, the long-term (e.g. more than 200 h) simple mechanical exfoliation (sonication) of graphene 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 [5,6]. The chosen conversion techniques can not only be upscaled but also 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 [7,8].

In this work, we produce graphene dispersed in water starting from graphite following the two main chemical conversion approaches (ORchem and ORtherm) and one physical conversion, using long term ultrasonic exfoliation (Sonic). Subsequently, graphene/polystyrene (PS) composites are prepared by the well-known latex technology. The latex concept enables the homogeneous incorporation of nanofillers into any kind of highly viscous polymer matrix, e.g. PS synthesized by emulsion polymerization or similar processes [8-9]. In the following, a detailed comparison of the three chosen techniques with respect to filler morphology and conductive properties of the respective nanocomposites is presented.

2 EXPERIMENTAL

2.1 Preparation of graphene via chemical oxidation/reduction treatment

In the first approach, graphene, designated ORchem, was synthesized via oxidation of SP-2 graphite using the Hummers method [10] and subsequent sonication of graphene oxide (GO), followed by reduction with hydrazine in the presence of a ten-fold excess of PSS (wt./wt. GO). The entire procedure is described in detail by Stankovich et al. [2]. After the synthesis, the graphene was filtered off with a polyamide membrane filter, which also removes excess of PSS, and dried under vacuum. The product was then re-dispersed in water (1mg/ml) by a 40 minutes sonication treatment (Sonics Vibracell VC750 horn sonicator with a 10 mm diameter tip) at 20 W during cooling in an ice-bath to maintain or even lower the solution temperature.

2.2 Preparation of graphene via chemical oxidation and thermal reduction treatment

Graphene (designated ORtherm) was obtained via initial preparation of GO from graphite using the Staudenmaier method [10] followed by a thermo-expansion process. The thermal expansion process consists of a quick exposure of dry GO to a pre-heated tubular furnace at 1025 °C. A detailed description of this process is given by McAllister et al. [4]. Aqueous exfoliated graphene dispersions (1 mg/ml) were then prepared with the use of SC or PSS surfactants.
Both polymers resulted in well exfoliated and stable dispersions using a 1:1 graphene/surfactant wt.% ratio. Energy for exfoliation was supplied by sonication following procedure described above (20 W for 40 min).

2.3 Preparation of graphene Sonicated in Solution

In the third approach, graphene (designated Sonic) was prepared following the method described by Coleman’s group [5,6]. Graphite exfoliation is carried out in SC/water solution using low power ultra-sonication (Bransonic® 1510E, ~16 W) for long times (up to 400 h) followed by centrifugation (2000 rpm for 1 h).

2.4 Composites processing

The compounding procedures for the three different graphene dispersions were identical. Each dispersion was mixed with PS latex, frozen in liquid nitrogen for several minutes, and subsequently freeze dried (Christ Alpha 2–4 freeze dryer operated at 0.2 mbars and -50 °C for 24 h). The resulting composite powders were heated quickly to 150 °C and then for 20 min until 180 °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 2 minutes.

3 RESULTS AND DISCUSSION

Atomic force microscopy (AFM) was extensively applied to determine the sheet thickness, morphological features and lateral dimensions of the graphene samples. Right after chemical oxidation, the first step for preparation of ORchem and ORtherm graphene, the formation of a great majority of 1 nm thick GO platelets was confirmed [2, 8]. The Oxidation/Reduction route followed by sonication yielded almost 100% of GO with a thickness of around 1 nm and surface areas between 1 and 3 μm². AFM analyses of the chemically treated graphene shows that a wrinkling of the platelets is visible (see black arrows in Fig. 1 - c and f). This wrinkling is clearly more severe for the ORtherm graphene, probably because of the fast “explosion” that the GO is submitted to, during reduction. It was also observed that sheet agglomeration and a decreasing sheet surface area may be a result of the chemical reduction process. The decreasing sheet size is just indicative as the folding/agglomeration of graphene prevents to obtain reliable statistical data. Measurements of the sheet thickness on flat areas indicated mostly monolayers or a few layers of graphene stacked together. Thicknesses was between 1-3 nm for more than 90% of the ORchem sheets and for more than 75% of the ORtherm sheets (see Fig.1 - b and e).

AFM analysis of non-oxidized (Sonic) graphene submitted only to long-term mechanical sonication shows on average, thicker and smaller platelets. In contrast to previous studies [5,6] a great majority (> 90%) of small multi-layer graphene particles are present, exhibiting a thickness between 5 and 25 nm (see Fig. 1 h). Some traces of more than 100 nm thick graphite flakes were also found, but discarded from further analysis. Obviously, for more than 5 nm thick flakes, no wrinkling was observed. The average surface areas were below 1 μm². In summary, the Sonic approach provides smaller multi-layer graphene platelets as compared to the two oxidation/reduction methods. Nevertheless, Sonic dispersions show a much better long term-stability after centrifugation, without visible settling of particles.

Fig. 1 - AFM topography tapping mode of graphene: a and b - oxidized/reduced chemically (ORchem), d and e - oxidized/reduced thermally (ORtherm), and g and f - sonicated in solution (Sonic). Images b,e, and f show the thicknesses profile of chosen sheets which in average represent ORchem, ORtherm, and Sonic samples, respectively.

The three different graphene dispersions were mixed with polystyrene (PS) latex and manually stirred, followed by freeze-drying and compression molding, resulting in composite tablets with thicknesses ranging from 0.5 mm to 1 mm. The composite processing was identical for all dispersions. Finally, the electrical conductivity of the nanocomposites was measured as a function of the nanofiller content (Fig. 2). The composites exhibit a conductivity percolation threshold when the filler content is increased to form a continuous conductive path. The percolation threshold depends critically on the dispersion


323
state, the nature of the contacts which defines the electron transport mechanism, and filler content, type, and dimensions.

For the ORchem samples, at a concentration of ~0.9 wt.% the conductivity increases dramatically and reaches 15 S/m at 1.5 to 2 wt.%. This value is to the best of our knowledge, the highest value measured for graphene/PS nanocomposites with graphene loadings below 10 wt.%.

For the remaining two approaches, percolation occurs at loadings of ~2 wt.% for the ORtherm and ~4.5 wt.% for the Sonic composites, respectively. Here, the maximum conductivity was measured to 10 S/m (ORtherm) and 1 S/m (Sonic). ORtherm graphene/PS composites, prepared from the same optimized dispersions and stabilized with PSS or SC surfactants, show similar degrees of exfoliation, exhibit almost identical percolation threshold curves (~2 wt.%), and the same final conductivity values (~10 S/m). Therefore, the choice of SC or PSS does not significantly influence the final conductivity and percolation in the final composites. However, we cannot deny the importance of the choice of the surfactant for a proper initial exfoliation in water.

**Fig. 2** - 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%.

A nano-scale view of the conductive network is provided by conductive atomic force microscopy (C-AFM). The C-AFM tip measures the current throughout the volume of the nanocomposites specimen at a given voltage, which is transported via the graphene network to the ground contact. That means that only platelets that are grounded are monitored. Observed differences in current are determined by the path length and the intra-network graphene junctions, which may have different resistivity [11]. Graphene sheets forming sub-networks without ground connection show no current. In this way, C-AFM provides a current distribution image from which the conductive network can be distinguished from the insulating polymer/filler matrix. In Fig. 3, the red/green brighter colored areas (which correspond to graphene in a cross-section topographic image) show non-zero current levels, indicating the presence of conductive pathways. The ORchem composites show the presence of a high number of conductive paths at 2% filler contents.

**Fig. 3** - C-AFM of the composites cross section areas for the three graphene used. a) ORchem (inset linear I-V curve), b) ORtherm and c) Sonic (inset exponential-like I-V curve) composites. Green/red spots correspond to graphene paths which contribute to conductivity through the sample.

In addition, a current vs. voltage (I-V) curve was measured at different points from at least 5 graphene clusters. When analyzing the various I-V curves, corresponding to each of the different composites, we observed differences in the curve shapes. Most notably, I-V curves obtained from ORchem composites show a linear I-V relation (inset in Fig. 3a) for most graphene clusters, indicating predominantly ohmic contacts between graphene sheets. For the other two samples we observe the conventional exponential-like I-V curve relation. This latter behavior is associated to tunneling electron transport [12,13], due to non-perfect contacts and the presence of surfactant or polymers in between the graphene sheets. AFM and SEM analyses show that ORchem graphene platelets are larger, thinner and less wrinkled than the other two graphene types. This would allow a larger direct contact area between the platelets, considering that the same filler weight concentration is present. A more detailed investigation on this topic is ongoing in our group.

**Fig. 4** - SEM analysis of composites: (a) ORchem, 2 wt.% of filler loading, (b) ORtherm, 2 wt.% of filler loading, (c) Sonic, 2 wt. % of filler loading. Bright charging features correspond to the conductive graphene fillers inside the isolating PS polymer.

Fig. 4 shows charge contrast SEM images of composite cross-sections as in Fig. 3. Besides a more or less dark background, referring to the non-conductive matrix, bright areas are visible, which represent the graphene sheets. Because of the differences in charge transport between graphene and the polymer matrix, the secondary electron emission is higher at the graphene location. This results in
the contrast between the graphene network (bright) and the polymer matrix (dark) [14]. Therefore, using charge contrast imaging at high acceleration voltage, we are able to gain representative information on the organization of a conductive network of graphene sheets in a polymer matrix. We could again notice the presence of more elongated filler arrangements for the ORchem material. It is also possible to identify the wrinkled and agglomerated graphene structures (the not so bright features in the background of Fig. 4b) for the ORtherm composites. For the Sonic composites we can only observe non-defined bulk pieces of filler material along the cross-section area, instead of platelets. Overall, in all samples the graphene filler was homogeneously distributed within the matrix.

4 CONCLUSIONS

Graphene, produced via difference water-based methods, was successfully used for the manufacturing of conductive graphene/PS nanocomposites, using latex technology. AFM showed that the GO reduction techniques used in this work yield thin graphene platelets, and as a consequence also induce wrinkling/agglomeration and possible size reduction of the platelets, especially for the ORtherm samples. Nevertheless, the thickness of the majority of the sheets was between 1 and 3 nm, corresponding to a single or only a few layers of graphene. The Sonic graphene was thicker, indicating multi-layer graphene (5 to 25 nm) and the average size was smaller. As these samples are much thicker, no wrinkling was observed.

The conductivities of the ORchem nanocomposites, (by both four point and local current measurements), reveal high values up to 15 S/m and a low percolation threshold (0.9 wt.%). By the use of latex technology, well-dispersed graphene sheets in PS matrix were obtained and visualized using charge contrast SEM. SEM and C-AFM illustrate the different graphene shapes, even inside the polymer, depending on the filler production method. Interestingly, differences in electronic transport behavior were observed, which suggest mostly direct contact transport for ORchem graphene in contrast to tunneling for mostly of the ORtherm and Sonic graphene conductive paths. ORtherm composites produced with both PSS and SC surfactant exhibited almost identical percolation thresholds and final conductivities, indicating negligible influence of the surfactant, at final stage, on these properties. However, surfactants have an important role during initial dispersion in water. Utilizing our dispersions, optimized with ionic surfactants and ultrasonication, and same composite processing conditions, we conclude that the conductive properties of the final composites mainly depend on the initial morphological characteristics of the produced graphene and its self-organization inside the polymer matrix. The characteristics may have an important influence also on the type of electronic transport behavior through the composite.

REFERENCES