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Electrical conductive behavior of polymer composites prepared with aqueous graphene dispersions

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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 concept was applied for the preparation of conductive graphene/polystyrene composites with well-dispersed graphene platelets. The samples were characterized with respect to filler properties and morphology, and their influences on electrical conductive properties of the composites were compared. Microscopic studies showed that both reduction processes lead to agglomeration/wrinkling of the platelets, 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. Differences in electronic transport behavior were observed, which suggest direct contact transport competing with tunneling.

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1. Introduction

The new rising star of nanofillers, graphene, with its combination of extraordinary physical and electrical properties plus the ability to be dispersed in various polymer matrices, has enabled the manufacturing of a new class of polymer composites [1,2]. Various methods to obtain graphene have been reported, since it was first mechanically isolated from graphite by Novoselov et al. [3], facilitating its production on large scales. The growing of graphene sheets from substrates [4,5] and, in particular, the controlled deposition from carbon vapor [6,7] have been recently described in literature as techniques that enable the production of single graphene layers in large 2D dimensions [8]. These materials find potential applications mainly in nanoelectronic devices [9,10].

The chemical synthesis of graphene using graphite, graphite oxide (GO) or other graphite derivatives as starting materials have also been studied. The conversion of graphite into GO via Hummers [11] or similar methods is an initial stage for graphene preparation.

The water soluble GO can be reduced with the use of chemicals [12,13] (*ORchem*) or by quick thermal expansion [14] (*ORtherm*) 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 [15–17]. The chosen conversion techniques [18] cannot only be up-scaled but also provide graphene with improved processability and, potentially, new functionality. The preparation of highly conductive paper-like graphene has been reported, yielding conductivities ranging from 10^3 to 10^4 S/m for the above chemical exfoliation approaches [17,19,20]. The exfoliated dispersions are most suitable for the preparation of polymer composites with enhanced mechanical and electrical properties [1,21–25].

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

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or similar processes. There are proven significant reduction in the conductivity percolation threshold and an overall increase in the final conductivity of polymer composites when using this approach as compared to others [22,26–28]. In the following, a detailed comparison of the three chosen techniques with respect to filler morphology and conductive properties of the respective composites is presented.

2. Experimental

2.1. Chemicals and polymer latex

Sodium dodecyl sulfate (SDS) (90%, Merck), sodium carbonate (99%, Aldrich), sodium peroxodisulfate (SPS) (90%, Merck), poly(sodium 4-styrene sulfonate) (PSS) (Aldrich, M_w 70 kg/mol) and sodium cholate (SC) (99%, Aldrich) were used as received. Styrene (99%, Merck) was passed over an inhibitor remover column prior to use. SP-2 graphite (Bay Carbon) powder was used as obtained.

PS latex was synthesized via conventional free radical emulsion polymerization. The reactor was charged with: styrene (252 g, 0.09 mol), SDS (26 g, 0.09 mol), sodium carbonate (0.7 g, 6.6 mmol), and H_2O (712.2 g). The reaction mixture was degassed by purging with argon for 30 min. A solution of SPS (0.45 g, 1.9 mmol) in H_2O (10 g) was also degassed. The reaction was started upon the introduction of the initiator solution and was performed at 70 °C with an impeller speed of 400 rpm for 1 h. The average latex particle size, as determined by dynamic light scattering, was 90 nm. Size exclusion chromatography analysis showed M_n , M_w and PDI values of 495 kg/mol, 944 kg/mol, and 1.9, respectively.

2.2. 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 [11] 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. [12]. 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 (1 mg/ml) by a 40 min 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 to lower the solution temperature.

2.3. 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 [29] 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. [14]. 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).

2.4. Preparation of graphene sonicated in solution

In the third approach, graphene (designated *Sonic*) was prepared following the method described by Coleman's group [15,17].

Graphite exfoliation was 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).

2.5. 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 mbar and -50 °C for 24 h). The resulting composite powders were heated quickly to 150 °C and then slowly heated, using small temperature steps, for 20 min until reach precisely 180 °C, between Teflon sheets, using a Collin Press 300 G. Subsequently the heated material was compression molded into films of 0.5 to 1 mm thickness at 100 bar for 2 min.

2.6. Characterization

UV–vis absorption spectra were recorded with a Hewlett–Packard 8453 spectrometer operating between 200 and 1100 nm. Small sample volumes of the surfactant/graphene dispersions were taken after the sonication processes and diluted with water by shaking, resulting in a graphene concentration of 0.0125 mg/ml for all samples. As control experiment the original SC/PSS solutions were diluted and analyzed as above.

A LABRAM confocal Raman spectroscope equipped with an optical microscope was utilized. Samples were irradiated with a red laser (632.8 nm) supplied by Melles Griot.

Atomic force microscopy (AFM) characterization of graphene was performed with a NT-MDT NTEGRA operated in tapping mode using silicon tips NSG11 (NT-MDT). We deposited our graphene/graphite dispersions onto freshly cleaved mica substrates by spraying a pipette-held droplet (~10 μ L) with a burst of compressed air. The samples were rinsed with water/alcohol solution for removal of surfactant. The conductive AFM (C-AFM) measurements on composite cross-sections were performed by an NTEGRA Tomo (NT-MDT Co.). The device is a combination of a microtome EM UC6-NT (Leica) and an SPM measuring head. This design allows for alternate microtome cutting and SPM measurements of the sample block-face. The local current measurements were performed in C-AFM mode with a gold-coated silicon cantilever NSC36/Cr–Au (Micromash). The sample was electrically connected to a grounded holder; and a bias of 2 V was applied [30].

The electrical conductivity was measured using the standard four-point method. The dc electrical resistance of all the samples was measured and compared for the in-plane (longitudinal) direction. Measurements on the transversal direction (through the sample) were not conducted; the anisotropy caused by the compression molding is studied in details somewhere else [31]. Parallel contact lines, with 1 cm in length and with a 1 cm interval, were drawn on the composite film with conductive-silver paint (Fluka). All conductivity measurements were performed at room temperature with a Keithley 6512 programmable electrometer. For each sample, conductivity data represent the average over 10 consecutive measurements in a voltage range from 0 to 10 V and at frequencies between 50 and 60 Hz.

3. Results and discussion

3.1. Graphene platelets: dispersion and morphological analyses

Raman spectra (Fig. 1a) were first investigated in order to determine the “quality” of the exfoliated graphene. It is well known that Raman spectroscopy is suitable not only for determination of the number of layers, but also for detecting the presence of structural

Fig. 1. (a) Average Raman spectra of the graphenes prepared plus raw graphite powder and mechanically cleaved graphene used as references, and (b) UV–vis spectra of the three dispersions used for composite manufacturing. No dispersion was prepared using Graphite powder and Reference mechanically cleaved graphene.

defects [32–34]. Thin films were produced from all three graphene dispersions by drop casting [35]. For each film we measured Raman spectra at multiple locations. The spectra for the untreated graphite powder and the micro-mechanically cleaved graphene reference are shown for comparison.

For *ORchem* and *ORtherm* graphene, the prominent D peak (absent in mechanically cleaved graphene and small in graphite powder references) is attributed to the presence of sp^3 carbon vibrations in the basal carbon plane. Several forms of defects, which could include residual carboxylic acids, epoxides, or ketones, may well cause lattice distortions, accounting for the increased D band intensity. The intensity of the 2D peak of the *ORchem* and *ORtherm* samples with respect to the D and G peaks is very small, most likely due to the discussed structural disorder. On account of the low intensity and broadness, we only report here a small shift for the 2D peaks to lower wavenumbers as compared to the untreated graphite sample. The absence of any prominent shoulder on the 2D peak indicates that only graphene having a few layers are present in solution [32,36].

The introduction of edge defects in graphene dispersions submitted only to long-term sonication (*Sonic*) is unavoidable, as large crystallites are cut into smaller platelets during processing. However, the D band observed for *Sonic* platelets (see Fig. 1a) is both narrower and less intense as in *ORchem* and *ORtherm* samples, strongly suggesting that the former graphene contains less defects [15]. Overall for sonic platelets, the 2D band displays a non-graphite-like character. The spectra were consistent with platelets having a few graphene layers. As mentioned before for *ORchem* and *ORtherm* samples, the also non-homogeneous and low 2D band intensity of sonic platelets prevents a more detailed conclusion.

By UV–vis analysis the highest absorbance, i.e. the best dispersion, was measured for the *Sonic* samples, followed by the *ORchem* samples (Fig. 1b). The selection of surfactants for each dispersion method was based on the best performing combinations (surfactant + method) as learned from previous reports [17,21]. We would like to stress that a good dispersion with high absorbance measured by UV–vis does not necessarily mean that it has a large number of single layer graphene platelets. It should be more seen as an indication that a large amount of small particles are present, which remain suspended and absorb radiation [37,38]. Although all sample dispersions were visually stable, black colored and without any signs of settling in the short term (1 week), the only dispersion without any trace of settling in the long-term (6 months) was the *Sonic* sample.

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 [12,22]. The oxidation process yielded almost 100% of GO with a thickness of around 1 nm and surface areas between 1 and 3 μm^2 . Images are not shown.

AFM analyses of the chemically treated graphene after reduction are shown in Fig. 2. A wrinkling of the platelets is visible (see Fig. 2a and d, and black arrows in Fig. 2c 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 were between 1 and 3 nm for more than 90% of the *ORchem* sheets and for more than 75% of the *ORtherm* sheets (see Fig. 2b and e). The roughness of exfoliated graphene is higher than the mechanically cleaved graphene reference prepared via the scotch tape method [3], probably due to defects, un-removed functional groups, or surfactants on treated surfaces.

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 [15,17], a great majority (>90%) of small multi-layer graphene particles are present, exhibiting a thickness between 5 and 25 nm (see Fig. 2h). Some traces of more than 100 nm thick graphite platelets were also found, but discarded from further analysis. Obviously, for more than 5 nm thick platelets, no wrinkling was observed. The average surface areas were below 1 μm^2 . 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.

Table 1 summarizes the main results obtained from the Raman spectroscopy, UV–vis absorbance analysis, and AFM morphological characterization of the graphene samples.

3.2. PS/graphene composite analyses

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 to 1.0 mm. The composite processing was identical for all dispersions. Finally, the electrical conductivity of the composites was measured as a function of the

Fig. 2. AFM topography tapping mode of graphene: (a and c) oxidized/reduced chemically (*ORchem*), (d and f) oxidized/reduced thermally (*ORtherm*), and (g and i) sonicated in solution (*Sonic*). Images b, e, and h show the thicknesses profile of chosen sheets which in average represent *ORchem*, *ORtherm*, and *Sonic* samples, respectively. Arrows indicate wrinkling/folding of the sheets.

Table 1
Summary of dispersion and morphological analyses of the fillers.

Graphene sample	Dispersion (UV-vis)	Amount of defects (Raman)	Lateral dimension (μm^2)	Platelet thickness (nm)	Wrinkling/folding
<i>ORchem</i>	Good	High	1–3	1–3 (>90%)	Average
<i>ORtherm</i>	Average	High	1–3	1–3 (>75%)	High
<i>Sonic</i>	Excellent	Low	<1	5–25 (>90%)	Low

Fig. 3. 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%.

nanofiller content (Fig. 3). 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 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 composites 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 conductivities measured were 10 S/m for *ORtherm* and 1 S/m for *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 show 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.

Based on Raman and UV–vis alone, one would expect the lowest percolation threshold for the *Sonic* composites, as they presented the least structural damage during exfoliation and the most stable suspensions (highest UV–vis absorption and long-term stability). This was not observed in the actual conductivity measurements; therefore, conductivity is not only determined by defect density in the exfoliated graphite or the stability of the dispersion. Besides

the fact that aqueous graphene dispersions with relatively low stability and relatively low degrees of exfoliation might exhibit lower percolation thresholds when compared to PS composites based on more stable dispersions with higher degrees of graphene exfoliation [31], we speculate that the percolation threshold is, in our case, mainly related to the different dimensions of the nanofillers. Long term sonication of graphite leads to a reduced lateral size of the platelets as compared to the other techniques, and mainly leads to thicker samples. These features might have a crucial influence on the higher percolation threshold obtained for these samples as compared to the ones obtained for *ORchem* and *ORtherm* samples.

A nano-scale view of the conductive network is provided by conductive atomic force microscopy. The C-AFM tip measures the current throughout the volume of the composites 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 a different resistivity [30]. 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. 4, 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 a high number of conductive paths at 2 wt.% filler contents.

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, we observed for the first time that I – V curves obtained from *ORchem* composites show a linear I – V relation (inset in Fig. 4a) for most graphene clusters, indicating predominantly Ohmic contacts between graphene sheets [39]. For the other two samples we observe the conventional exponential-like I – V curve relation. This latter behavior is associated to tunneling electron transport [40,41], 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. 5 shows charge contrast SEM images of composite cross-sections as presented in Fig. 4. 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

Fig. 4. 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.

Fig. 5. 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.

Table 2

Summary of the electrical conductive behavior and morphological analyses of the graphene/PS composites.

Composite sample	Max. electrical conductivity (S/m)	Percolation threshold (filler wt.%)	Electronic transport (C-AFM)	Filler dispersion (SEM)	Filler morphology (SEM)
ORchem	15 ^a	0.9 ^a	Ohmic	Good	Elongated
ORtherm	10 ^a	2 ^a	Tunneling	Good	Elongated
Sonic	1 ^a	4.5 ^a	Tunneling	Good	Bulk pieces

^a Standard deviations are below 10%.

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) [42]. Therefore, by 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. 5b) 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. The bright white dot that can be seen in Fig. 5c most probably is a piece of graphite inside the composite. Overall, in all samples the graphene filler was homogeneously distributed within the matrix.

Table 2 summarizes the main results obtained from the composite characterization, which includes the four-point conductivity measurements, C-AFM and high-charge contrast SEM morphological analyses.

4. Conclusions

Graphene, produced via difference water-based methods, was successfully used for the manufacturing of conductive graphene/PS composites, using latex technology. With respect to graphene production, Raman analyses confirmed that oxidation/reduction methods introduce structural distortions/defects to the basal plane of graphene. Less damage was noticed for graphite which was submitted only to long-term sonication. Dispersions produced with graphene using this latter approach showed also higher long-term stability. 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 (5–25 nm) and the average size was smaller. As these samples are much thicker, no wrinkling was observed.

The conductivities of the *ORchem* composites (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 the final stage, on these properties. However, surfactants have an important role during initial dispersion in water. Utilizing our dispersions, optimized with ionic surfactants and ultra-sonication, and same composite processing conditions, we confirm 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 [43,44]. Notably, we verified that these characteristics have an important influence on the type of electronic transport behavior through the composite.

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