Preparation of electrical conductive polymer/graphite oxide composites through the functionalization of graphite oxide sheets


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ABSTRACT

Synthesis of pentadecane-, polyethylene (PE)- and polydimethylsiloxane (PDMS)-decorated thermally reduced graphite oxide (GO) sheets has been studied as a tool for the preparation of PE/GO composites exhibiting rheological and electrical percolation thresholds. It was accomplished through pentadecane and PE based radical addition onto unsaturated bonds located on the GO sheets' surface using dicumyl peroxide as hydrogen abstractor. Moreover, PDMS was grafted onto graphite oxide sheets through two routes. In the latter case, the grafting reactions were performed in toluene as solvent via a hydrosilylation reaction and a hydrolysis condensation reaction in presence of SiH-terminated PDMS and ethoxysilane-terminated PDMS, respectively. Rheological and electrical percolation thresholds were found between 10 and 15 wt% for polyethylene/pentadecane functionalized graphene oxide composites while the composite graphite/PE at the same loading percentage did not reach any percolation threshold.

Keywords: graphite oxide sheets, PE, PDMS, composites, percolation threshold

1 INTRODUCTION

Graphite flakes are composed of sp2-hybridized carbons covalently bonded in a hexagonal manner forming individual graphene sheets bounded together by Van der Waals forces and separated with a distance of 3.35 Å. Graphene is an atomically thin, 2-dimensional network of sp2-hybridized carbons that can be derived from naturally abundant, low cost graphite [1,2]. Since the successful isolation of graphene layers by simple mechanical exfoliation, the fundamental properties of the single flat monolayer of graphite have been intensively investigated [3-6]. One of the potential applications of graphene is as reinforcing fillers for polymers, significantly improving electrical, mechanical and gas barrier properties of graphene/polymer nanocomposites [7-9]. However, preparation of graphene-based composite materials is not a trivial task because graphene sheets are held together by electrostatic forces into stacky agglomerates. Herein, the preparation of polyethylene/graphite oxide composites exhibiting rheological and electrical percolation thresholds was accomplished by radical addition reactions onto the unsaturated system of graphite oxide sheets through the use of pentadecane and polyethylene in presence of peroxides as well as azide-terminated polyethylenes [10, 11]. In addition, the grafting of PDMS onto graphite oxide sheets through two routes : a)through the grafting of trimethoxy(7-octen-1-yl)silane (TMOS) onto graphene oxide sheets followed by an hydrosilylation reaction with Si-H terminated PDMS b)by he hydrolysis-condensation reaction of triethoxysilane-terminated PDMS onto GO [12, 13]. All the grafting procedures were studied with the help of FTIR spectroscopy, XPS, TGA, X-ray diffraction, AFM, SEM and TEM observations and dispersions in solvent.

2 RESULTS AND DISCUSSION

2.1 Radical grafting of PE onto graphite oxide sheets

Functionalization and dispersion of graphene sheets are of crucial importance in their applications. Graphite oxide (GO) has been used widely as a starting material for the synthesis of processable graphene. Herein, as shown in Scheme 1, the covalent functionalization of GO sheets with pentadecane and low molar mass PE chains was first conducted in presence of a suspension of GO in 1,4-dioxane, DCB and benzoyl peroxide as hydrogen abstractor followed by a subsequent solvothermal reduction at 150°C in order to restore the conductivity (scheme 1).

Scheme 1. Grafting of pentadecane onto GO sheets in presence of dicumyl peroxide including its solvothermal reduction

First of all, the grafting of pentadecane and PE onto GO was qualitatively evidenced by FTIR and analysis and X-ray diffraction [10, 11]. A quantitative approach by thermogravimetric analysis allowed us to accurately determine the grafting of the PE chains onto the GO surface.
and the calculation gave a polymer graft density of $7.6 \times 10^{-3}$ mmol/g (lowered by a factor 10 in comparison with the pentadecane one). In order to detect the presence of PE onto GO sheets, the stability of the dispersion of PE-g-rGO was also checked by the use of a DMF/heptane immiscible mixture (Figure 1).

**Figure 1.** Digital images of graphite oxide derivative based-dispersions in DMF/heptane 50/50 with a concentration of 0.35 mg/mL a) GO, b) GO solvothermal reduced in 1,4-dioxane and DCB mixture at 150 °C and c) PE-g-rGO

As expected, the stability of GO in heptane is very poor and GO sheets moved immediately to the DMF phase and a rather stable dispersion was obtained (Fig. 1a) while the dispersion of the PE coated graphite oxide is exclusively in the heptane phase (Fig. 1b).

Electrical conductivity is an important intrinsic property of graphene and the functionalization may break the conjugation network through the conversion of $sp^2$ into $sp^3$ bonds. So, it is important to measure the electrical conductivity after the grafting step. During the grafting reaction, the GO is simultaneously solvothermally reduced to graphene, causing the color of the reaction mixture to turn from light brown to dark brown and then to black, which is a sign that GO has been reduced [14]. The measured electrical conductivity of our pristine graphite of 1.9 S.m$^{-1}$ is consistent with the literature [15] while the GO displays a very low conductivity of $9.8 \times 10^{-7}$ S.m$^{-1}$, as expected. It should be noted that the electrical conductivity of grain packings ($c \approx 2$ S.m$^{-1}$) is lower than the electrical conductivity of highly compact grains ($c = 10^4$-10$^5$ S.m$^{-1}$) because of a lower contact between the grains [16, 17]. The improved conductivities of GO (after the thermal treatment at 200°C in dioxane/pentadecane mixture with no peroxide and pentadecane grafted GO indicate the reduction of GO sheets in the synthesis process. A second route for grafting PE onto GO sheets was based on the functionalization of GO and GO-grafted-TMOS (GO-g-TMOS) by azide terminated PE at a temperature of 190°C in order to ensure the thermal cleavage of azide groups (Scheme 2).

The effective solvothermal reduction of PE-N-g-rGO and PE-N-g-rGO-TMOS has been also demonstrated by the powder electrical conductivity measurements: after the grafting reaction at 190°C, electrical conductivities of $4.9 \times 10^{-3}$ S m$^{-1}$ and $4.2 \times 10^{-3}$ S m$^{-1}$ were measured for PE-N-g-rGO and PE-N-g-rGO-TMOS, respectively. An improvement of more than 4 decades is observed for the conductivities of PE-N-rGO and PE-N-rGO-TMOS in comparison with that of GO. Thermogravimetric analyses performed in He, confirmed the presence of PE chains after the grafting procedure. The TGA curves of pristine GO, GO-g-TMOS, PE-N-g-rGO, PE-N-g-rGO-TMOS and both solvothermo reduced GO and GO-g-TMOS (rGO and rGO-TMOS respectively) are shown in Figure 2.

**Figure 2.** Thermogravimetric data obtained for a) GO, b) PE-N-g-rGO-TMOS, c) rGO-TMOS (in TCB, 190°C 64h), d) PE-N-g-rGO and e) rGO (in TCB, 190°C 64h) under He

No significant difference in weight loss is noticeable between the PE-N-rGO and the solvothermal reduced GO (rGO) suggesting a very low grafting content of PE onto the GO surface (Fig. 2d and 2e). Despite, this low grafting content, the amount of grafted PE is high enough to dramatically improve its affinity with the heptane media. Using GO-g-TMOS, the grafting of PE-N$_3$ is more efficient giving a higher weight loss by TGA (Figure 2d). A grafting ratio of $5.7 \times 10^{-3}$ mmol g$^{-1}$ is calculated.

Then, compounding of the composites pentadecane grafted GO/PE was performed at a processing temperature of 140°C with 25, 20, 15, 10, 8 and 5 wt% loadings. The onset of network formation can be determined by rheology and
Figure 3 shows the viscolastic behavior of the PE nanocomposites for a series of concentrations of pentadecane grafted GO in PE.

![Figure 3](image)

Figure 3. Viscolastic behavior (frequency dependence) of PE filled pentadecane grafted GO with loadings varying from 4.8 to 25 wt%: a) Variation of the storage modulus \(G'(\omega)\); b) Variation of the absolute complex viscosity \(|\eta^*(\omega)|\).

Actually the percolation threshold is in the range 10-15%. The conductivity was determined from the slope of the linear dependence between the measured current and the applied voltage (Figure 4).

![Figure 4](image)

Figure 4. Resistivity of rGO-penta filled PE at different loadings.

Up to loadings of 10%w, the intensities of the electrical currents were below the resolution limit of the instrument, which corresponds to a resistivity value of \(10^{14}\) Ωcm (Figure 4).

2.2 Radical grafting of PDMS onto graphite oxide sheets

In addition, among the ways to graft silicones onto organic and inorganic substrates, hydrosilylation [18, 19] and sol-gel reactions [20] are widely used. Herein, two routes, involving a hydrosilylation reaction and a sol-gel reaction respectively, were used and compared to graft PDMS onto GO. The first route is a two step procedure based on the treatment of GO with trimethoxy(7-octen-1-yl)silane (TMOS) which provides a vinyl group decorated GO surface (scheme 3a). Then, the dangling surface vinyl groups were used for Pt-catalysed hydrosilylation reaction with SiH-terminated polydimethylsiloxane to obtain PDMS-grafted GO (Scheme 3b).

![Scheme 3](image)

Scheme 3. Grafting of a) TMOS and b) SiH-terminated PDMS onto GO sheets.

The second route is a one step procedure based on the use of reactive alkoxyisilane-terminated PDMS that can be grafted onto both hydroxyl and carboxylic acid groups of GO through hydrolysis-condensation reactions according to the sol-gel process (scheme 4).

![Scheme 4](image)

Scheme 4. Grafting of ethoxysilane-terminated PDMS onto GO sheets.

X-ray photoelectron spectroscopy allowed us to confirm grafting content (Figure 5).

![Figure 5](image)

Figure 5. X-ray photoelectron spectroscopy spectra of Si 2p for GO-PDMS.
The chemical state of the Si in GO-PDMS is similar to that of Si in GO-TMOS at 102.1 eV being associated with polysiloxane and Si-O-graphite oxide, respectively and a Si/C ratio two times lower (0.13) has been obtained compared to GO-TMOS-PDMS 6000 (Figure 5). The fitted results of C 1s spectrum for pristine GO and GO-PDMS are shown is Figure 6.

As for the GO-PDMS, the increase of the peak at 284.6 eV is noticed while the ratio C-O/C=O is constant before and after grafting of PDMS which is consistent with the presence of PDMS. The calculated relative atomic concentration of silicium from XPS (5.4 mmol Si.g⁻¹) is also higher than the calculated value (1.5 mmol Si.g⁻¹) from the corresponding elemental analysis results suggesting the difficulty to quantify the PDMS grafting by XPS. Depending of the PMDS molar mass, PDMS graft densities varying from 0.7 10⁻³ mmol.g⁻¹ to 12.7 10⁻³ mmol.g⁻¹ were determined by TGA for the PDMS grafted GO resulting from the hydrosilylation reaction. The route based on hydrolysis-condensation of the reactive triethoxysilane-terminated groups of PDMS onto GO did not permit to increase the PDMS grafting density.

To obtain more understanding of the morphology developed as a result of the grafting of PDMS onto GO sheets, electron microscopy (SEM and TEM) was conducted (Figure 7).

The general structure of GO-PDMS consists of randomly aggregated, thin crumpled sheets closely associated with each other and exhibiting polymer protuberances (Figure 8a). The TEM measurement shows the presence of attached tufts of polymer (Figure 8b) confirming that reactive alkoxysilane-terminated PDMS was successfully grafted onto GO through hydrolysis-condensation reactions according to the sol-gel process.

2.3 References