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In-situ graphene oxide reduction during UV-photopolymerization of graphene oxide/acrylic resins mixtures

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ABSTRACT

The preparation of electrically conductive acrylic resins containing reduced graphene oxide (rGO) by photopolymerization is presented. The synthesis consists of a single-step procedure starting from a homogeneous water dispersion of GO, which undergoes reduction induced by the UV radiation during the photopolymerization of an acrylic resin. The role played by the amount of radical photoinitiator added to the resin has been evaluated in relation to the in-situ reduction of GO, that was monitored by X-ray photoelectron spectroscopy. Results show that the UV-induced photopolymerization of acrylic resins with added GO gives rise to conductive acrylic composites thanks to the simultaneous reduction of GO to rGO and crosslinking of the resin. On this basis UV-induced photopolymerization is proposed as a sustainable strategy for the production of conductive graphene/polymer composites.

1. Introduction

In the last few years the range of carbon-based polymer composites has been mainly dominated by carbon nanotubes (CNTs) due to the development of various functionalization techniques and polymer-grafting procedures that allowed the efficient dispersion of CNTs bundles in polymer matrices [1–3]. In order to find convenient solutions to the high costs and technical difficulties associated to the use of CNTs, the scientific interest recently moved towards different forms of graphitic carbon as fillers to prepare polymer composites, and graphene has rapidly become the most intensively investigated allotropic form of carbon due to its extraordinary electronic transport properties [4] associated with exceptional thermo-mechanical features, which can be successfully provided to polymer composites [5,6]. Numerous strategies for the preparation of homogeneously dispersed graphene-polymer composites have already been presented for a variety of advanced polymer matrices [7,8], but the literature unanimously agrees that a significant amount of research efforts still has to be dedicated to the development of easy and cost-effective methodologies towards the large-scale application of graphene in functional polymer-composite materials for technological uses, as biosensors, energy storage, electronic devices. Unfortunately graphene sheets, similar to CNTs, present strong $\pi-\pi$ stacking between sp^2 carbon layers and poor surface interactions with the polymer matrices, resulting in extended filler–filler aggregation in composites.

This major drawback to the use of graphene as functional filler for high performance composites has been addressed by developing strategies involving the oxidation of graphene to GO and its exfoliation by chemical process which generates epoxy, alcohol and carboxylic acid groups on its surface [9], followed by partial reduction to achieve rGO which is easily processable in both aqueous and organic media as single layer sheets [10,11].

The presence of hydrophilic organic functional groups facilitate exfoliation and dispersion of GO in aqueous solution, but the material shows insulating properties because of the numerous defects which disrupt the sp^2 structure. To improve electrical performance subsequent reduction processes are necessary to restore the planar sp^2 structure. Several types of reduction agents have been reported in literature such as hydrazine [12] or strong alkaline media [13]. Besides the reduction with chemical agents, electrochemical [14], photochemical [15] and thermal [16]

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reduction methods have been developed as well, and were demonstrated to be more sustainable reduction strategies with respect to the chemical approach.

In this context photoreduction induced by interactions with radiation recently attracted the greater attention due to the observation that irradiation of GO in solid state or in solution by sunlight, UV or excimer laser radiation reduces it to graphene with a strongly reduced amount of oxygen functionalities onto the surface [17,18]; detailed investigation into the GO photoreduction process has just begun [19] and can be considered at an early state. It has been demonstrated that irradiation by excimer laser or by UV light with high energy per unit pulse can break the bonds between the graphene sheet and the oxygen functionalities in GO thus inducing a reduction of the oxygen related functionalities; the threshold of excitation light resulting in photolysis products corresponds to an energy of 3.2 eV and the conductivity of the GO layers is enhanced by exposure to UV light [20]. rGO produced by interactions with radiation has advantages over other techniques, mainly related to the lower level of impurities retained.

We recently demonstrated that the mentioned strategy of in-situ reduction of GO to rGO by UV exposure can be efficiently exploited during the UV-induced photopolymerization of acrylic resins [21]. The observed electrical conductivity of the hybrid films obtained by photopolymerization of GO-acrylic resins mixtures is not consistent with the insulating behaviour of both GO flakes and acrylic resin.

In this paper the reduction of GO oxygen functionalities to the graphene basal plane operated by the radicals generated during the photopolymerization of an acrylic resin has been demonstrated and quantitatively evaluated by spectral investigations performed by XPS spectroscopy. Finally, the properties of the cured rGO/acrylic resin mixtures have been extensively investigated by electrical characterization (I–V curves), morphological analysis (AFM) and thermal studies (DSC).

2. Experimental

2.1. Materials

Single-layered GO made by modified Hummers method (Cheaptubes USA, average thickness 0.7–1.2 nm). The acrylic resin polyethyleneglycol diacrylate (PEGDA, Ebecryl11®, Mw ≈ 740 g/mol, density = 1.12 g/cm3, CYTEC). The radical photoinitiator 4-(2-hydroxyethoxy)phenyl-(2-hydroxy-2-propyl)ketone (PI, Irgacure® 2959, BASF).

2.2. Experiments of UV-induced photoreduction of GO

GO was dispersed in water (1 mg/ml) by Ultraturrax mixing until a homogeneous dispersion was obtained (30,000 rpm for 5 min). PI was added in amounts ranging from 0 to 3% wt/vol and the solutions were UV-irradiated with a medium pressure mercury lamp under nitrogen with a light intensity on the surface of the sample of 30 mW/cm^2 for different time up to 5 min. The irradiated GO was separated from the solutions by evaporation of water to be ready for further characterization.

2.3. Preparation of graphene-acrylic composites

GO was dispersed in water (1 mg/ml) by Ultraturrax mixing (30,000 rpm for 5 min) and the water dispersion was mixed with PEGDA in order to add an actual content of GO in the range from 1 to 4% by weight with respect to the resin. The formulations were added to 4 %wt of PI, coated on glass slides or silicon wafers and UV-cured, under nitrogen, with a light intensity on the surface of the sample of 30 mW/cm^2 for different time up to 10 min. The cured GO/PEGDA composites were ready for further characterization without need of further actions.

2.4. Characterization

Acrylic double bond conversion, as a function of irradiation time, was evaluated by means of FT-IR spectroscopy, employing a Thermo-Nicolet 5700 instrument. For this purpose, the GO/PEGDA formulations were coated on silicon wafers (Olivetti, Italy) by using a wire wound applicator with a controlled thickness of 25 microns for the deposited wet film, and simultaneously exposed to the UV beam, which induces polymerization, and to the IR beam, which makes an in-situ evaluation of the extent of reaction. Acrylic double bonds conversion was monitored through the decrease in the absorbance peak centred at 1630 cm^{-1}, normalized with respect to the carbonyl peak centred at 1700 cm^{-1}. A medium pressure mercury lamp (Hamamatsu) equipped with an optical guide was used to induce photopolymerization. The irradiation was performed under nitrogen atmosphere.

The gel content was determined on the cured composites by measuring the weight loss of a one-piece specimen (200 mg) after 24 h extraction in chloroform (10 ml) at room temperature (25 °C).

Differential scanning calorimetry (DSC) was performed under nitrogen flux, in the range between −20 °C and 100 °C, with a DSCQ 1000 of TA Instruments equipped with a low temperature probe.

The electrical characterization was performed using a 2-probe method by computer-controlled Keithley 4200 Source Measure Unit. GO dispersions were drop cast on Al-electrodes (1 mm × 10 mm) spaced 1 mm having an average thickness of ~70 nm thermally evaporated on glass substrate. The current/voltage characteristic was recorded through Al-electrodes thermally evaporated on the GO/PEGDA coated quartz substrates. A voltage sweep was sourced between the electrodes and the output current flowing across the sample was measured in the direction parallel to the surface of the sample; therefore the measured value of current flow takes into account both surface and volume resistivity contributions [22].

The morphology of the prepared samples was investigated by atomic force microscopy (AFM) and field emission scanning electron microscopy (FESEM, Zeiss Supra 25). AFM images were obtained operating in phase contrast tapping mode with a scanning probe microscope (Nanosurf easyScan DFM). Height and phase images were obtained under ambient conditions with a typical scan speed of 0.5–1 line/s, using a scan head with a maximum range of 40 μm × 40 μm. The films surface was observed by FESEM operating at 5.0 kV accelerating voltage without deposition of any conductive coating; images were constructed from the detector of secondary electrons.

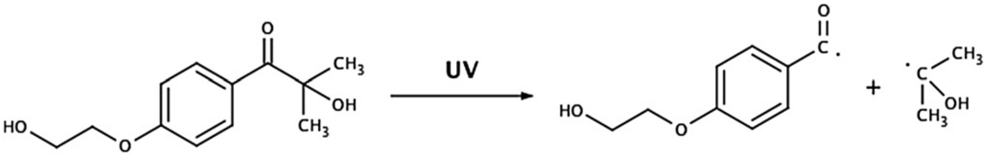

Fig. 1. α-Cleavage process of the photoinitiator aryl-alkyl ketone.