Study of graphene oxide-based 3D printable composites: Effect of the in situ reduction

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ABSTRACT

This study demonstrates that, PEO-acrylates composite containing graphene oxide (GO) can be easily 3D printed from water based formulations. Exploiting the good water affinity of graphene oxide, the filler can be easily dispersed in oligomers formulations and printed by using a low cost DLP equipment. Then the UV post curing process, which is always mandatory after a DLP process, is exploited to in situ reduce the graphene oxide embedded in the matrix; similarly a thermal treatment is also investigated as post process. Different 3D structures are submitted to the reduction post-treatments and the influence of the UV and thermal reduction on the mechanical and electrical properties of the printed objects is investigated. The present work shows the possibility to easily produce 3D shaped GO-based composites whose final properties can be tailored trough a UV or thermal post process performed on the printed parts that induces the in situ reduction of GO embedded in the polymer matrix.

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1. Introduction

Graphene holds nowadays great promise for potential applications in high tech fields [1]. In fact it is one of the stiffest and strongest materials, with a Young's modulus of almost 1 TPa and strength of 130 GPa [2], and it shows extremely appealing electrical and thermal characteristics [3].

Thanks to its properties, graphene is also a perfect candidate to act as a functional nanofiller for polymer composites [4]. Graphene and graphene-related materials (graphene oxide (GO) and reduced graphene oxide (rGO)) have been added to many different polymer matrices for enhancing their properties such as mechanical [5,6], electrical [7,8], thermal [9,10] properties and so on [11–13].

In composite materials, properties' improvements are already observed with low amounts of filler [6]. However a good distribution of graphene sheets within the polymer matrix is necessary in order to achieve an effective change. This results to be often problematic being graphene hardly dispersible into polymers/monomers without the use of unhealthy solvents [14]. In contrast, graphene oxide is dispersible and stable in most of the polar solvent, including water, since it presents hydrophilic moieties on its sheet [15].

However, because of the loss of the full aromatic structure, GO does not present all the intriguing features typical of graphene, in particular electrical and thermal conductivity [16]. Thus in the recent years different techniques were developed to induce in situ reduction of GO to rGO, gathering good dispersability and the superior properties of graphene [17–20]. In particular some techniques involve the reduction of GO once it has been already embedded into a polymer matrix, completely avoiding dispersion problems [21]. Among them, the most used are chemical [22], thermal [23–25] or UV –light induced [26–28] techniques.

UV induced reduction involves the formation of light-generated radicals, which spontaneously lead to reduction of GO to formation of rGO, recovering some of the pristine properties of graphene sheets [29].

A field particularly indicated for the development of suitable polymeric functional materials is three-dimensional (3D) printing [30–32]. This term is often used synonymously with additive manufacturing associated to machines that are low end in price and/or overall capability, meaning production methods in which an object is fabricated through the deposition of a material layer-by-layer using a printing head, nozzle or another printer technology [ASTM F2792] [33]. Among the different 3D printing approaches,

those based on light induced polymerization e.g. Stereolithography (SLA) and Digital Light Processing (DLP) are becoming particularly interesting. These systems, which allow to produce 3D objects by the spatially controlled solidification of a liquid resin exploiting the fast photopolymerization process [34,35], have seen a huge development in the last years.

Polymeric 3D printing in its early stages was mainly used to create models or prototypes using common structural materials [36]. However, the simultaneous recent advances in the printing technologies and in the study of printable materials have now enabled the use of 3D printing for the production of objects for many advanced applications, from medicine to electronics or aerospace, giving the possibility to realize geometries that conventional production techniques cannot achieve [37]. Nevertheless, to further enlarge the range of applications of this technique, the assortment of existing printable functional materials has to be enriched.

In this paper the development of new graphene-based 3D printable photocurable formulations is proposed. Graphene Oxide is added to a PEO-diacrylate monomer that is commonly used in printable formulations. GO is easily dispersible in water thanks to its polarity, allowing to simply obtain water-based formulations that, with the addition of suitable initiators, can be printed by DLP or SLA techniques. Few works could be found in literature reporting the production of GO composite 3D objects by light-based printing systems [38,39] and, to the best of our knowledge, the UV-in situ reduction to rGO and its effects on the properties of 3D printed objects was never investigated.

In the present paper the influence of GO on the mechanical and electrical properties of the printed objects is firstly investigated, then GO is in situ reduced exploiting the UV post curing process that is always mandatory after the SLA and DLP printing processes. The influence of the UV induced reduction on the final properties of the three-dimensional structures has also been compared with that of a more common thermal process.

2. Experimental

Materials: Poly (ethylenglycol)diacrylate, PEGDA, Mw 600 g mol^{-1} was kindly provided by Allnex, GO (thickness 0.7–1.2 nm) was purchased from Cheap Tubes Inc. (USA). Bis-(2,4,6-trimethylbenzoyl) phenylphosphineoxide (Irgacure 819) was provided by BASF and added in the amount of 2 phr (per hundred resin) with respect to the monomer, while 2-hydroxy-2-methyl-1-phenyl-propan-1-one (UV-In) was purchased by Sigma-Aldrich; also in this case 2 phr were used. The dye selected, Methyl red, was purchased from Sigma-Aldrich and used as received (0,2 phr); the addition of the dye was necessary to obtain a better resolution limiting the light diffusion in neat PEGDA that is colorless.

Formulation preparation and printing: GO was dispersed in bidistilled water and sonicated in an ultrasonic bath for 1 h. The dispersion was then mixed to the monomers and further sonicated for 5 min to obtain homogeneous brownish formulations. In the case of the reference sample, MR was added to a mixture of PEGDA and water and sonicated for 1 h to obtain homogeneous red formulations. At last the initiators were also added. The compositions

of the final formulations are listed in Table 1.

The prepared formulations were then printed using a DLP printer HD 2.0 (Robot Factory), equipped with a projector with a resolution of 50 μm corresponding to 1920 × 1080 pixels (intensity 10 mW/cm^2 measured with a Hamamatsu Power meter). The build area is 100 × 56.25 × 150 mm with a layer thickness adjustable from 10 to 100 ìm. The printing time ranged from 1.5 to 2 s/layer for different amounts of GO. The obtained samples underwent a post curing process (8 min) performed with a medium−pressure mercury lamp also provided by Robotfactory equipped with a rotating platform (intensity 10 mW cm^{-2}).

The in situ reduction process was performed with an irradiation in a Helios Italquartz medium−pressure mercury lamp (intensity 30 mW cm^{-2} measured with EIT instrument) for 1 h. Sample for thermal reduction were stored in oven at 70 °C for 24 h.

A scheme summarizing all the printing and post-treatment procedure id reported in the SI (Scheme S1).

Characterization: An Anton Paar rheometer (Physica MCR 302) in parallel plate mode was used for photorheology tests. The instrument was equipped with a Hamamatsu LC8 lamp with visible bulb and a cut-off filter below 400 nm with light guide (intensity 10 mW/cm^2). The gap between the two plates was set to 0.1 mm and the sample was kept at a constant temperature (25 °C) and under constant shear frequency of 1 rad/s, light was turned on after 1 min in order to stabilize the system. The measurement was performed in the linear viscoelastic region (strain amplitude 1%), changes in viscoelastic material moduli during polymerization were measured as a function of exposure time.

Differential scanning calorimetry (DSC) experiments were performed using a Netzsch DSC 204 F1 Phoenix instrument, equipped with a low temperature probe. The experiments were carried out between −70 and 80 °C with a scan rate of 10 °C min^{-1} in nitrogen atmosphere (20 ml min^{-1}).

For the determination of the insoluble fraction (gel content) printed flat samples (1 cm^2) were held in a metal net, accurately weighed, and subsequently extracted with CHCl$_3$ to dissolve the not cross-linked polymer chains. Extraction included 24 h of residence time for the solvent to appeal the samples at room temperature. The cross-linked fraction was then calculated by dividing the mass of the dry sample left after the extraction by the calculated mass of the original sample.

ATR spectra were collected using a Tensor 27 FTIR Spectrometer (Bruker) equipped with ATR tool. The averaged signal over 32 spectra was collected with a resolution of 4 cm^{-1} from 4000 to 600 cm^{-1}. Flat samples (0.2 mm) were printed and exposed to the UV post treatment only on one side; ATR spectra were then collected on the opposite side in order to simulate the conversion in the core of the printed structures. The conversion of acrylate double bonds was calculated by following the decrease of the peak area of C=C group at 1640 cm^{-1} and normalized with the peak area of C=O group at 1730 cm^{-1}.

The UV-visible spectra were recorded by means of a double beam Lambda 40 instrument (Perkin-Elmer). The range between 280 and 800 nm was monitored with a scan step of 1 nm. All the experiments were performed on 100 μm films coated on a glass slide.

Table 1
Composition of the different formulations, the values are given in phr with respect to the weight of the PEGDA monomer.

	GO (phr)	Water (phr)	MR (phr)	Irgacure (819) (phr)	UV-In (phr)
PEGDA MR	—	30	0.2	2	2
PEGDA 0.3	0.3	30	—	2	2
PEGDA 0.5	0.5	30	—	2	2