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Tailoring the physical properties of nanocomposite films by the insertion of graphene and other nanoparticles

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ABSTRACT

New polymeric nanocomposite films containing graphene and Ag, Au or ZnO nanoparticles were synthesized, and their morphological, thermal, surface and dielectric properties were studied. Graphene was obtained by the sonication method, which allows to obtain "real" graphene, without any chemical manipulation of graphite. This method preserves graphene lattice symmetry, which is responsible for its exceptional properties. The interaction between graphene and the other nanoparticles (NPs) confers to these polymeric films interesting characteristics, thus making them suitable for different applications. For example, the wetting property can be tuned by the insertion of nanofillers. Furthermore, the presence of these latter increases the dielectric strength of the polymer films.

1. Introduction

In recent years, graphene, a monolayer of carbon atoms packed into a honeycomb network, has attracted great attention from scientific community for its outstanding properties that can be successfully exploited in many advanced applications [1–6]. Graphene-based polymer composites can also be used in packaging for food, medicine, electronics and beverages due to low permeability of gas molecules [1], in energy storage [2], and electrically conductive polymers [3], in making transparent conductive electrode for dye-sensitized solar cells with conducting polymer [4], and electrode for electrochromic devices [5]. Recently, poly(tetraethyleneglycoldiacrylate) (PTEGDA) has shown to be an interesting candidate to obtain few-layer graphene in a reactive medium [6–12].

The so obtained few-layer graphene is easily exploitable to obtain polymeric nanocomposites. In fact, graphene is formed directly into the monomer, thus allowing for the direct, *in situ* polymerization of the graphene/monomer dispersion. It should be underlined that the nanomaterial obtained by this method is "real graphene". This means that, unlike the traditional methods for obtaining it, the direct sonication method does not involve the synthesis of graphite oxide and, more generally, any chemical manipulation of graphite; actually, it has been demonstrated that graphite oxidation results in considerable damaging of graphene electronic structure, which is only partially restored by reduction processes [13]. In addition, the chemical agents which are commonly used for reducing graphene oxide can leave contaminations in the "so-called graphene" (often named reduced graphene oxide) that may induce restacking of the sheets [14]. Furthermore, several studies demonstrated that graphene oxide is potentially cytotoxic [15], while graphene obtained by direct exfoliation in liquid media does not seem to be so [16]. These latter findings should be taken into proper account when some of more or less reduced forms of graphene oxide are used in biomedical applications instead of "real graphene". Various metals, metal oxides and semiconducting nanoparticles have been used together with graphene to achieve exceptional properties and impart new functionalities aiming at catalytic, energy storage, photocatalytic, sensor, and optoelectronics applications [17,18].

Herein, we report on the synthesis of a new type of polymeric nanocomposite films by combining "real graphene" and Ag, Au or ZnO nanoparticles embedded into a PTEGDA matrix. Their morphological, thermal, electrical and surface properties were investigated.

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2. Experimental

2.1. Materials and methods

Tetraethyleneglycol diacrylate (TEGDA), graphite flakes, silver nitrate ($AgNO_3$), tetrachloroauric acid (III) trihydrate zinc choride, and sodium carbonate anhydrous were purchased from Sigma–Aldrich and used as received. Trihexyltetradecylphosphonium persulfate (TETDPPS) was synthesized according to the method described in the literature [19].

2.2. Graphene dispersion

To prepare a graphene dispersion, 5 wt.% of graphite flakes were added to TEGDA, placed into a tubular plastic reactor (i.d. 15 mm) and ultrasonicated (Ultrasound bath EMMEGI, 0.55 kW, water temperature ≈ 40 °C) for 24 h. Then, the dispersion was centrifuged for 30 min at 4000 rpm; finally, the gray-to-black liquid phase containing graphene was recovered. The concentration of the dispersion, determined by gravimetry after filtration through polyvinylidene fluoride filters (pore size 0.22 μm), was found to be 9.45 mg/mL and the calculated absorption coefficient was 436 mL/(m mg) [12].

The graphene dispersion was diluted (0.05 mg/mL) and analyzed by UV–VIS spectroscopy, using a Hitachi U-2010 spectrometer (1 mm cuvette) to determine the concentrations of the diluted dispersions.

Raman spectroscopy was carried out with a Bruker Senterra Raman microscope, using an excitation wavelength of 532 nm at 5 mW. The spectra were acquired by averaging 20 acquisitions of 5 s with a 50× objective.

High resolution TEM images were obtained with a TEM FEI Tecnai G12, with an acceleration voltage of 120 kV. TEM analyses were performed, under vacuum at room temperature for 2 h, on the samples after solvent evaporation.

2.3. Ag, Au and ZnO nanoparticles

Ag and Au nanoparticles were synthesized by the chemical reduction method with sodium citrate of metal precursor, as described in literature [20]. In a typical experiment, 100 mL of 1 mM $AgNO_3$ or 1 mM $HAuCl_4$ aqueous solution was heated to boiling and 10 mL of trisodium citrate aqueous solution (1 wt.%) was added. The reduction of the metal ions to yield silver and gold nanoparticles was confirmed by the immediate appearance of a pale yellow and red color colloidal solutions, respectively. The obtained nanoparticles were lyophilized and stored at ambient temperature.

ZnO nanoparticles were synthesized by modification of the direct precipitation method from aqueous solutions of $ZnCl_2$ (10.0 mL, 0.5 M) e Na_2CO_3 (10.0 mL, 0.25 M) [21]. After precipitation, the nanoparticles were aged several hours and washed for three times with distilled water and ethanol. Finally, the nanoparticles were dried in oven at 60 °C overnight, and then calcined at 450 °C for 3 h.

The optical absorption spectra of all the nanoparticles were obtained using an UV–Vis spectrophotometer (Hitachi U-2010).

The morphology and particle size were analyzed by Transmission Electron Microscopy FEI Tecnai G12. The samples were analyzed on a copper grid (400 mesh), coated with Formvar film, operating with an acceleration voltage of 120 kV.

X-ray diffraction (XRD) analysis of ZnO nanoparticles was carried out by Bruker D8 Advance diffractometer using Cu Kα radiation ($\lambda = 0.15418$ nm) the operating conditions were 40 kV and 30 mA in a 2θ scanning range from 20° to 80°.

2.4. Polymeric nanocomposite films

Ag, Au, or ZnO nanoparticles were homogeneously dispersed in the TEGDA/graphene dispersion obtained previously. The nanoparticle/graphene dispersion in TEGDA was diluted to obtain different ratios of graphene and nanoparticles; then, the so-obtained dispersions were used to synthesize the polymeric nanocomposite films. For each dispersion, TETDPPS radical initiator was added (1 wt.% respect to the monomer); the polymerization of a few drops of mixture was performed on silicon wafers (3 cm × 3 cm) located on a heating plate at ca. 100 °C for some minutes. The composition of the polymeric nanocomposite films is reported in Table 1. The polymeric nanocomposite films were characterized by DSC, using a DSC Q100 Waters TA Instruments and a TA Universal Analysis 2000 software, by performing on each sample a cycle heat/cool/heat from −80 to 300 °C, with a heating and cooling rate of 10 °C/min, under argon atmosphere. The first heating was carried out to calculate the eventual residual polymerization enthalpy, the second one allowed obtaining the T_g values.

The morphological characterization was investigated by using a Zeiss EVO LS 10 ESEM, in high vacuum modality with secondary electron detector. Before the examination, the samples were mounted on a carbon stub, coated with a carbon film using an auto-carbon coater evaporator (Agar Instruments) and observed with back scattered electron detector in high vacuum modality. The microanalysis was carried out using a Zeiss EVO LS 10 ESEM with an energy dispersive system (EDS), Inca X-Act (Oxford Instruments).

The absorbance was studied in the 200–3200 nm range with a Cary 5 UV-VIS-NIR spectrophotometer by Varian.

The surface wettability was investigated by measuring water contact angles (CAM 200 optical Contact Angle Meter, KSW LTD Instruments, Helsinki).

The dielectric measurements have been carried out using an EG&G 273A galvanostat-potentiostat/impedentiometer controlled by the impedance software M398 in order to acquire the real (ReZ) and imaginary (ImZ) parts of impedance in the frequency range of 1 mHz–100 kHz with a maximum applied voltage of 1.4 V (RMS). No bias voltage was applied.

3. Results and discussion

3.1. Graphene/TEGDA dispersion characterization

The masterbatch dispersion of graphene in monomer was obtained as described in an our previous work [12]. For this study, a dilution of the masterbatch dispersion was used and deeply analyzed. In particular, Raman characterization was performed to determine the number of graphene layers (Fig. 1).

Through a comparison of the relative intensity of the characteristics G peak (at ≈1580 cm^{-1}) and the 2D peak (at ≈2680 cm^{-1}), and by the symmetry of the 2D peak in the Raman spectra, it is possible to make an unambiguous distinction among single, bi- and multi-layer graphene [22,23]. As it is well known in literature, the 2D peak of graphite is made of two components; by contrast, the peak of graphene is symmetric. The inspection of the shape and position of the peaks of the Raman spectra of graphite and graphene obtained by us after filtration of TEGDA/graphene dispersion suggests that the sample under examination is constituted of few-layer graphene [22]. The disorder-related D peak at ca. 1350 cm^{-1} is higher for graphene; this can be attributed to the new edges produced during the sonication process; the ultrasonic treatment causes the decrease in size of the flakes compared to the original graphite, with a consequent increase of the total edge length [24]. The noise registered in the