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Preparation and characterization of polymeric nanocomposites containing exfoliated tungstenite at high concentrations

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ABSTRACT

For the first time, ultrasonication was exploited for obtaining tungstenite nanoparticles directly into a monomer (tetraethyleneglycol diacrylate) to be eventually polymerized without any further manipulation. The resulting liquid dispersions were characterized by Raman, transmission electron and scanning electron microscopies. Eventually, they were directly used for preparing nanocomposites containing a relatively large amount of exfoliated tungstenite. Differential scanning calorimetry and thermogravimetric analyses were performed in order to assess the effect of the presence of the exfoliated nanofiller on the thermal features of the polymer matrix: a clear improvement of the thermal and thermo-oxidative stability was observed. At variance, the effect of the exfoliated tungstenite on the glass transition temperature of the polymer matrix was negligible. Furthermore, the mechanical behavior of the obtained nanocomposites was evaluated by means of flexural and shore A hardness tests: the exfoliated nanofiller turned out to exert a strong reinforcing effect on the polymer matrix even at very low concentration.

1. Introduction

In the latest years, enormous scientific efforts have been done in order to seek for new methods to isolate, synthesize and apply new nanoparticles to advanced technologies. Among all, graphene has been largely studied; as known, it is a two-dimensional network of sp^2-hybridized carbon atoms exhibiting unique properties, partially related to its 2D nature, and a phenomenological behavior that can be exploited for a wide range of applications [1]. However, only more recently also other bidimensional nanomaterials have attracted the interest of the scientific community: among them, one of the most important classes is represented by transition metal dichalcogenides (TMDs). TMDs consist of hexagonal layers of metal atoms (M) sandwiched between two layers of chalcogen atoms (X) with MX_2 stoichiometry [2]. Analogously to graphite, the atoms in the layer are bound by strong covalent forces, while van der Waals interactions hold the layers together. In this context, monolayers of MoS_2 and WS_2 have received great attention because they are 2D semiconductor with tunable band gaps depending on size [3–5]. In particular, exfoliated WS_2 (EWS_2) was found to exhibit novel and superior properties with respect to the bulk structure, and hence such a nanomaterial has been used for the fabrication of catalysts [6], lubricants [7], lithium batteries [8], photoconductors [9], probes for scanning probe microscopy [10], shock absorbers [11], solar cell films [12]. The synthetic routes to prepare WS_2 nanomaterials include magnetron sputtering [13], thermal decomposition [14], laser ablation [12], chemical vapor deposition [15], sonochemical synthesis [16], hydrothermal/solvothermal routes [17,18] and mechanical activation [19]. However, the isolation of single atomic WS_2 layers is not easy because of their natural tendency to form fullerene-like, nanotube, or stacked multilayered geometries [20,21]. One of the most promising methods to produce 2D materials is the non-chemical liquid exfoliation by ultrasonication. This technique, initially developed for the obtainment of graphene [22], is based on the assumption that the energy required to exfoliate the layered material is balanced by the solvent-layer interaction when the solvent surface energy matches that of the nanomaterial to exfoliate. This route is very simple and allows avoiding the use of special apparatuses and any chemical manipulation that might introduce defects in the exfoliated structures. Liquid exfoliation was successfully used to obtain high concentration of graphene in liquid solvents [23–27] and reactive compounds [28–32]; some of these were employed to synthesize polymer nanocomposites [25,27,28,30–32]. Similarly, tungsten disulfide can be exfoliated to give single and few

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layered nanoparticles as reported by Coleman et al. [33] and Notley [34], who were able to disperse WS_2 in NMP and a surfactant, respectively.

This work aims to assess the use of EWS_2 as a new nanofiller in nanocomposite acrylic polymers and study its effect on the thermal and mechanical properties of the obtained materials. In addition, for the first time, an acrylic monomer (tetraethyleneglycol diacrylate, TEGDA) was used to exfoliate and disperse WS_2, instead of employing an inert solvent. Thus, the resulting dispersions were directly used for the preparation of the nanocomposite polymers without recovering the solid WS_2 nanoparticles, hence avoiding any possible restacking phenomenon. TEGDA was chosen because it has demonstrated an excellent ability to disperse and exfoliate tungsten disulfide; this monomer has been already used by our research group to obtain highly concentrated graphene dispersions and prepare the corresponding polymer nanocomposites [30,32].

2. Materials and methods

2.1. Materials

TEGDA (MW = 302.32, d = 1.11 g/ml) and WS_2 powder (particle size: 2 μm) were purchased from Sigma Aldrich and used as received without further purification. Trihexyltetradecylphosphonium persulfate (TETDPPS) was used as the radical initiator and was synthesized according to the procedure described in the literature [35].

2.2. Preparation of EWS_2 dispersions in TEGDA

Mixtures containing various amounts of tungstenite (0.1, 0.5, 1.0, 2.5 and 5.0 wt.%) in TEGDA (10 g) were put in a tubular plastic reactor (i.d. 15 mm) and placed in an ultrasonic bath (0.55 kW, water temperature 40 °C) for a selected time (0.5, 1.5, 2.5, 6.0, 12.5, 19.0 and 24.0 h). Finally, they were centrifuged for 30 min at 4000 rpm; the dark green liquid phase containing exfoliated WS_2 was recovered.

2.3. Characterization of EWS_2 dispersions

The concentration of EWS_2 was determined by filtration through polyvinylidene fluoride (PVDF) filters (pore size, 0.22 μm), in order to directly weigh the amount of EWS_2 dispersed.

UV–Vis spectroscopy measurements (Hitachi U-2010 spectrometer, 1 cm cuvette, λ = 630 nm [33]) were performed to find the actual tungstenite content in any diluted dispersion used for the nanocomposite preparation. To determine the absorption coefficient α from a known volume of initial dispersion, several dilutions were done and the absorbance was measured. The α value, which was found equal to 360 ml mg^{-1} m^{-1}, was calculated from absorbance vs. concentration plots.

Raman analyses were performed on EWS_2 flakes deposited on PVDF filters (see above) with a Bruker Senterra Raman microscope using an excitation wavelength of 532 nm at 0.5 mW. The spectra were acquired by averaging six acquisitions of 5 s with a 20× objective. For WS_2 powder, a laser power of 5 mW was used.

TEM analyses were performed with a ZEISS EM 109, operating at 80 kV. EWS_2 dispersion was washed three times with acetone, and the resulting TEGDA-free EWS_2 was deposited onto copper grids covered with a film of formware/carbon (300 mesh) and the solvent was evaporated.

SEM micrographies were obtained by using a SEM ZEISS DSM 962. Analyses were performed both on WS_2 powder and exfoliated tungstenite deposited on a silicon substrate.

2.4. Synthesis of TEGDA/EWS_2 nanocomposites

The masterbatch dispersion of EWS_2 in TEGDA was diluted with suitable amounts of this latter to achieve the desired concentration of exfoliated WS_2; then 0.5 mol% of TETDPPS were added and the mixture was homogenized. The polymerization reaction was performed in an oil bath at 80 °C for 1 h; DSC analysis performed on these samples showed residual polymerization peaks. Accordingly, the monomer conversion was completed by treating the samples in an oven at 100 °C for 48 h. DSC analyses on the post-cured samples showed a complete conversion.

2.5. Characterization of EWS_2 nanocomposites

Raman analysis on polymers were performed with a Bruker Senterra Raman microscope using an excitation wavelength of 532 nm at 5 mW. The spectra were acquired by averaging six acquisitions of 5 s with a 20× objective.

The surface hardness was measured on cylindrical samples (diameter = 22 mm, height = 5 mm) according to ASTM D2240 (Shore A) at 23 ± 2 °C. For each sample, five measurements were performed along different points, and the mean value was considered.

Differential Scanning Calorimetry (DSC) measurements were performed by means of a Q100 Waters TA Instruments calorimeter, equipped with TA Universal Analysis 2000 software, from −30 to 250 °C at a heating rate of 10 °C/min in inert atmosphere (nitrogen flow: 40 ml/min).

The thermal and thermo-oxidative stability of the materials was evaluated by thermogravimetric (TG) analyses using a Q500 TA analyzer. The measurements were performed placing the samples in open alumina pans (ca. 10 mg) in nitrogen or air atmosphere (gas flow: 60 ml/min) from 50 to 800 °C with a heating rate of 10 °C/min. In the followings, T_{10} and T_{max} are defined as the temperatures corresponding to 10% weight loss or to the maximum weight loss rate, respectively. The accuracy of the used thermogravimetric balance is ±1 °C on the temperature and ±1 wt.% on the weight, on the basis of the temperature and weight calibration. The measurements of each sample were repeated twice in order to ensure reproducible data.

The surface morphology of the samples was investigated using a Scanning Electron Microscope (SEM, LEO 1450VP). The specimens were fractured in liquid nitrogen, fixed to conductive adhesive tapes and gold-metallized.

Three point bending flexural tests, according to ASTM D790, were performed, using a Zwick–Roll Z010 apparatus, equipped with a 5 kN load cell, 30 mm support span, at 23 ± 2 °C and 50 ± 5% relative humidity. At least five tests were repeated for each material in order to have reproducible and significant data.

3. Results and discussion

First of all, the best conditions to obtain high concentrations of EWS_2 dispersed in TEGDA were investigated.

As described in the Experimental, the adopted procedure to obtain dispersions is extremely simple and envisages the direct sonication of tungsten disulfide powder in TEGDA without any chemical manipulation.

A preliminary test usually confirming the nanometric dimensions of the dispersed particles was the occurrence of the Tyndall effect [36] (not shown).

In a first series of experiments, keeping constant the sonication time, a study on the effect of initial WS_2 concentration on the resulting concentration of exfoliated tungstenite EWS_2 was carried out. In particular, five dispersions containing from 0.1 to 5.0 wt.%