



Thermal and electrical properties of starch–graphene oxide nanocomposites improved by photochemical treatment

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ABSTRACT

Bionanocomposite films have been prepared by casting an aqueous suspension of acetylated starch (ST) and poly(vinyl alcohol) (PVA) loaded with graphene oxide (GO). A photochemical and reagentless method has been successfully performed to convert the GO phase into reduced graphene oxide (RGO). The nanocomposites have displayed improved thermal and electrical properties when the amount of the GO phase is increased and properly converted to RGO. The molecular-level interactions between components are mainly hydrogen-bonding type according to attenuated total reflectance-Fourier transform infrared (ATR-FTIR) and Raman spectroscopies, as well as thermogravimetric analysis (TGA). Scanning electron microscopy (SEM) has confirmed the effective mixing between the GO and the ST–PVA matrix. The thermal diffusivity and electrical resistivity of ST–GO nanocomposites have increased one order and decreased two orders of magnitude, respectively, after the photochemical treatment. These findings have confirmed the effectiveness of the proposed approach to produce starch-based nanocomposites with improved thermal and electrical properties.

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1. Introduction

Bionanocomposites today, represent an environmentally friendly strategy for the production of novel materials while employing raw components from the plenty source provided by biomass. These systems are comprised by a continuous biopolymer matrix loaded with nanofillers, usually inorganic in nature. While the biopolymer matrix ensures the material's biodegradability, nanofillers provide the required thermal, mechanical, and electrical properties, usually very poor in the biopolymer alone (Darder, Aranda, & Ruiz-Hitzky, 2007).

Among several biopolymers for bionanocomposites, starch is very appealing because of its low cost and availability from different natural sources such as vegetables and cereals (Paraginski et al., 2014). Besides the nourishing value, the film forming ability has given to starch a more remarkable role, for example, in food packaging. Starch-based films are biodegradable and edible and therefore, are potential substitutes for many synthetic

packaging materials and pose negligible harm to the environment (Tang, Kumar, Alavi, & Sandeep, 2012).

On the other hand, starch exhibits poor thermal and electrical properties, which restrict its widespread use. This apparent limitation can be, however, circumvented by adding nanofillers such as graphene oxide (GO) sheets. GO can be considered a precursor for the preparation of graphene-based materials (Zhu et al., 2010). Besides that, GO is highly hydrophilic and dispersible in water, features that readily enable mixing and compatibility of GO and starch, as well as with other polymeric matrixes (Jaber-Ansari & Hersam, 2012). In fact, this possibility has been recently verified by different research groups. For example, Li et al. (Li, Liu, & Ma, 2011) and Ma et al. (Ma, Liu, Li, & Wang, 2012) have carried out a pioneer research on nanocomposites made of starch and GO when they found that GO increases the Young modulus and the thermal stability of pure starch. A subsequent investigation has been conducted by He and colleagues (He et al., 2013) when they observed that GO prevents starch from degradation in both acidic and alkaline environments. Rodríguez-González et al. (2012) have observed that the mechanical properties (storage modulus) of a chitosan–starch matrix is substantially improved (about 900%) with only 0.5 wt% of GO. Ashori's group have introduced the

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melting processing of polypropylene composites with either sugar cane bagasse or wood flours, both enriched with graphene nanoplatelets (Sheshmani, Ashori, & Fashapoyeh, 2013; Chaharmahali, Hamzeh, Ebrahimi, Ashori, & Ghasemi, 2014). They have observed that there is an optimum graphene content for the bionanocomposites to reaching the best mechanical properties.

However, another main interest on introducing GO into common polymeric matrices is to provide or enhance their optoelectronic properties. GO is usually obtained after chemical exfoliation of graphite which is a more affordable and readily available carbon source (Jaber-Ansari & Hersam, 2012). GO resembles graphene by its monoatomic dimension, but it also differs significantly from it because of oxygen bearing functionalities such as hydroxyl, carbonyl, carboxyl, and epoxy. These functionalities disrupt part of the sp^2 conjugation and turn GO into an electrical insulating material. However, part of optical, electronic and many other properties of pristine graphene can be restored after proper reduction of GO (Stankovich et al., 2007; Tung, Allen, Yang, & Kaner, 2009). Concerning that, we have produced starch-based nanocomposite films in which GO is introduced and photochemically converted into its reduced form, namely reduced graphene oxide (RGO). The reduced nanocomposite has thermal and electrical properties improved after the photochemical process, which is easy to perform and does not demand for hazardous chemicals such as hydrazine or sodium borohydride.

Herein, we describe the preparation and investigate the properties of bionanocomposite cast films made of starch filled with GO sheets (ST–GO). UV–vis, attenuated total reflectance-Fourier transform infrared (ATR-FTIR) and Raman spectroscopies are employed to determine the structure and infer about the molecular-level interaction between the starch matrix and GO sheets. An additional study performed with thermogravimetric analysis (TGA) provides further evidence for the interaction of bionanocomposites' components. In order to restore part of the outstanding properties of graphene, we have submitted the bionanocomposite films to UV radiation (254 nm). After a proper irradiation time, the thermal diffusivity and electrical properties of ST–GO films are significantly improved, due to partial reduction of GO, as confirmed by Raman and UV–vis spectroscopies.

2. Experimental

2.1. Materials

Graphite powder (Union Carbide, SP-1 grade, 100 μm), acetylated starch (Avebe Guaíra Amidos, Brazil), poly(vinyl alcohol)-PVA (Sigma–Aldrich, 89,000–98,000 g mol^{-1}), H_2SO_4 98%, HNO_3 67%, KClO_3 , KHCO_3 , HCl 37%, NH_4OH 47%, were purchased from Sigma–Aldrich, Merck and Carlo Erba, all analytical grade or better and used as received. Ultrapure water (18.2 $\text{M}\Omega\text{ cm}$) purified by a Milli-Pore Milli-Q system was used throughout all procedures. Graphene oxide (GO) was obtained via a two step procedure. In the first, graphite powder was oxidized in a mixture of 1:2 $\text{H}_2\text{SO}_4/\text{HNO}_3$ (2:1 v/v) and KClO_3 as originally described by Staudenmaier (1898) with some modification as described elsewhere (Silva, Costa, Triboni, Politi, & Isolani, 2010). In the second step, the as-obtained graphitic oxide was suspended in NH_4OH aqueous solution (pH 10) under sonication (150 W, 1 h). The resulting GO suspension was centrifuged at 15,000 rpm for 20 min to remove remaining solids and stored for the nanocomposites' preparation.

2.2. Preparation of starch–GO (ST–GO) nanocomposites.

5 g of acetylated starch (ST) and 0.15 g of PVA were suspended together in 40 mL of deionized water. PVA was used as an additional

plasticizer (besides water) for starch. The milky ST–PVA suspension was kept under magnetic stirring at 90 °C for 1 h in order to gelatinize starch and ensure their complete mixing. In another vessel, additional 0.05 g of PVA were dissolved in deionized water (70 °C) under magnetic stirring until reaching its complete dissolution. A fixed volume of the GO aqueous suspension was then added to this PVA solution under magnetic stirring at 70 °C until a homogenous solution was obtained. This procedure was adopted to enhance compatibility between GO and starch and to avoid GO flocculation. Four different PVA–GO solutions with different GO concentrations were prepared. A fifth PVA solution absent of GO was prepared and used for the preparation of the control film. For the preparation of ST–GO nanocomposite films, the PVA–GO solution was added slowly to the ST–PVA suspension under magnetic stirring at 60 °C. The stirring and temperature were maintained for more than 1 h after addition of the PVA–GO solution. The resulting pale yellow suspension was then cast onto Petri dishes (diameter: 10 cm) and left drying in oven (60 °C) for 24 h. The control film (absent of GO) was prepared under the same procedure. Five nanocomposite samples were prepared, labeled as: ST–C (control), ST–GO-010, ST–GO-025, ST–GO-050, and ST–GO-075. The numbers refer to the weight percentage of GO in the nanocomposite (regarding the starch mass).

2.3. UV treatment of ST–GO samples

In order to induce the photochemical reduction of GO, ST–GO samples (1.0 \times 2.5 cm^2) were exposed to UV light (254 nm) (Boitton Instrumentos, Brazil) for different periods of time up to 2 h. UV–vis spectra of films were obtained after different irradiation time to monitor the photochemical effect. For comparison, the control film (absent of GO) underwent the same treatment and monitoring. The ATR-FTIR and Raman spectra, thermal diffusivity, and current versus potential curves of un- and treated samples were measured in order to evaluate the effectiveness of the photochemical treatment.

2.4. Film characterizations

The chemical structure of nanocomposite films was assessed by UV–vis (Varian Cary 5000), ATR-FTIR (Varian 640IR) and Raman (Jobin Yvon T 6400, 514 nm laser line, 0.3 mW) spectroscopies.

Film's morphology (surface and cross-section areas) was evaluated by scanning electron microscope (JEOL 440A). Film's cross-section was made after submitting films to liquid nitrogen and further cracking. Samples were attached to brass stubs with the aid of conductive carbon tape and gold-coated by sputtering.

Thermogravimetry (TGA) and derivative thermogravimetry (DTG) analysis were conducted in a DTG-60H Shimadzu thermo-analyzer. Powdered samples (\sim 5 mg) were filled in platinum pans and evaluated under nitrogen atmosphere (30 mL min^{-1}), at heating rate of 10 °C min^{-1} .

The thermal diffusivity of film samples was determined by photopyroelectric spectroscopy (PPS) as described by Mandelis and Zver (1985), with the aid of a home-made experimental setup. The PPS working principle bases on the irradiation of a solid sample with a monochromatic source and measurement of that part of optical energy that is converted into heat by non-radiative deexcitation processes within the solid. According to the model described by Mandelis and Zver, a non-uniform variation on temperature leads to a voltage drop in the pyroelectric transducer. The voltage drop is related to the sample's thermal diffusivity, according to Eq. (1) as follows:

$$V(\omega) = A \left[\frac{\eta_s \alpha_s}{k_p (1 + b_{sp}) \omega} \right] \exp \left[- \left(\frac{\omega}{2\alpha_s} \right)^{1/2} L_s \right] \quad (1)$$

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