



Characterization of glycerol-plasticized starch and graphene oxide extruded hybrids



Willian Hermogenes Ferreira, Cristina T. Andrade*

Instituto de Macromoléculas Professora Eloisa Mano, Universidade Federal do Rio de Janeiro, Centro de Tecnologia, Bloco J, P.O. Box 68525, 21941-598 Rio de Janeiro, RJ, Brazil

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ABSTRACT

Melt extrusion was chosen to exfoliate graphite oxide (GO) incorporated to glycerol-plasticized corn-starch, aiming to produce hybrids with improved mechanical and barrier properties. The effect of increasing GO content, from 0.5 to 2.0 mass%, on the extruded and compression-molded samples was evaluated by X-ray diffraction (XRD), capillary rheometry, and dynamic mechanical analysis (DMA). The results suggested that the polymer-intercalated filler was well-dispersed within the thermoplastic starch (TPS) matrix, and corroborated the expected interaction between the functional groups of both components. Submitted to aging tests at 80% relative humidity conditions for ninety days, XRD data revealed that GO, independently of its content, could not prevent retrogradation of the starch matrix. Tensile tests, carried out for the hybrid samples before and after the aging tests, indicated improved stiffness as the GO content was increased. Before aging, the E values increased continuously, from 16.3 ± 2.9 MPa to 60.0 ± 3.9 MPa, with the increase of GO content from 0 to 2.0 mass%. Conversely, the variation of GO content led to a complex behavior in the E values for the aged TPS/GO hybrids. Images obtained by transmission electron microscopy revealed the presence of exfoliated and aggregated GO sheets.

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1. Introduction

Results from the literature have proved that the physical and functional properties of polymers are improved by the incorporation of nanoparticles. Among those nanoparticles, graphene – the two-dimensional sheet consisting of sp^2 -hybridized carbon atoms, arranged in a honeycomb structure – and some derivatives have been incorporated to numerous polymeric systems for applications as sensors (Chang et al., 2014), energy storage systems (Sun and Shi, 2014), in water remediation (Chowdhury and Balasubramanian, 2014), and in drug delivery (Shim et al., 2014).

Graphene may be prepared from graphite, in two steps. The first step, leading to graphite oxide, is carried out in the presence of strong oxidizing systems, based on sulfuric acid, sodium nitrate and potassium permanganate (Hummers and Offeman, 1958). The second step consists of a reduction reaction, usually conducted with sodium borohydride or hydrazine.

In relation to the oxidized product, which is denoted graphene oxide (GO) after exfoliation, some models were proposed to represent its structure (Dreyer et al., 2010). The most accepted model,

known as the Lerf–Klinowski model, was based on ^{13}C CP/MAS NMR and FTIR results. This model represents GO as composed of isolated aromatic rings, separated from each other by aliphatic structures containing hydroxyl and epoxide groups, and $\text{C}=\text{C}$ double bonds. Carboxylic acid groups may be linked to the periphery of the platelets basal phase (Lerf et al., 2010). The presence of these groups makes GO attractive to be used as reinforcing filler in polymer composites, particularly when the polymer matrix also has polar groups, capable of forming hydrogen bondings with the groups introduced to the GO structure. In this context, melt-compounded polyamide 1212/GO (Cai et al., 2015) materials and epoxy resin/GO nanocomposites (Li et al., 2013) were obtained.

Recently, an improved method to synthesize graphene oxide (the product of graphite oxidation, before exfoliation) was reported, which consists of adding a 9:1 mixture of sulfuric acid and phosphoric acid to the graphite and potassium permanganate mixture, followed by cooling in ice and oxygen peroxide (Marcano et al., 2010). In this method, no toxic gas is evolved, which is certainly an improvement, and constitutes an incentive to the preparation of starch nanocomposites.

Starch-based materials have emerged as an alternative to synthetic polymers, associated with the accumulation of plastics waste in the environment. Because starch is a low-cost raw material, obtained from renewable resources on a large scale, sus-

* Corresponding author. Fax: + 55 21 2270 1317.

E-mail address: ctandrade@ima.ufrj.br (C.T. Andrade).

tainable products may be developed from this natural material. Starch can be transformed into a thermoplastic material (TPS) by thermomechanical treatment in the presence of plasticizers. However, this material has limited applications because of its high hydrophilic character and inappropriate mechanical properties. To overcome this disadvantage, blending with hydrophobic or less hydrophilic polymers, and the incorporation of inorganic nanoparticles were recommended to improve physical properties (Reddy *et al.*, 2013). In the first case, polyethylene/TPS blends presented high elongational properties at break even without addition of an interfacial modifier (St-Pierre *et al.*, 1997; Rodriguez-Gonzalez *et al.*, 2003). At a glycerol content of 36%, the blends showed low levels of sensitivity to moisture (Rodriguez-Gonzalez *et al.*, 2003). Maleic anhydride-modified poly(lactic acid)/TPS blends were shown to present greatly improved ductility (Huneault and Li, 2007). For TPS/polycaprolactone blends, even at 10 wt% polycaprolactone composition, the sensitivity to moisture was reduced (Avérous *et al.*, 2000). Recently, hydrophobic bioelastomers were produced by incorporating granular cornstarch in acetoxypolyorganosiloxane (Ceseracciu *et al.*, 2015). Also, the incorporation of inorganic nanoparticles, such as organoclays (Magalhães and Andrade, 2009), silica (Milionis *et al.*, 2014) and carbon nanotubes (Taghizadeh and Favis, 2013; Swain *et al.*, 2013), to the starch matrix led to materials with improved resistance to humidity.

Recently, some researchers reported the preparation and characterization of starch/GO films. In these works, glycerol was used as plasticizer for pea starch (Li *et al.*, 2011) and potato starch (Ma *et al.*, 2013), and films were prepared by casting. The starch/GO films were shown to have improved tensile strength and stiffness, thermal stability and moisture barrier properties in relation to neat plasticized starch films. However, the preparation of TPS/GO hybrids by melt processing, a much more convenient method for industrial production, and the characterization of such materials, particularly aging have not been addressed.

The aim of this work was to obtain and characterize thermoplastic starch/GO hybrid materials with improved barrier and mechanical properties. GO was chosen instead of graphene because of the expected favorable interactions of its polar groups with hydroxyl groups of starch molecules. For this, graphite oxide was prepared from graphite by the Marcano's method, and characterized. Glycerol-plasticized cornstarch was mixed to water-dispersed GO, at different contents. The mixtures were extruded at the same conditions, and the resulting materials were characterized by X-ray diffraction, capillary rheometry, dynamic mechanical analysis, tensile tests, and transmission electron microscopy. The effect of aging at high-humidity atmosphere on the crystallinity and mechanical properties was evaluated for the TPS/GO hybrids.

2. Experimental

2.1. Materials

Regular cornstarch (CS) was supplied by Ingredion Brasil—Ingredientes Industriais Ltda. (São Paulo, SP, Brazil). According to the producer, this material is composed of 26–30 mass% amylose and 74–70 mass% amylopectin, with less than 0.5 mass% gluten. The gravimetric method was used to determine the humidity content (12 mass%). Analytical grade glycerol was purchased from Vetec Química Fina (Rio de Janeiro, RJ, Brazil) and was used as received. Natural graphite flakes was purchased from Sigma–Aldrich (São Paulo, SP, Brazil). Purified water from a Millipore water purification system, model Direct Q-3 (São Paulo, SP, Brazil) was used in the experiments. All other analytical grade

reagents were purchased from Vetec Química Fina (Rio de Janeiro, RJ, Brazil) and were used as received.

2.2. Preparation of graphite oxide

Graphite oxide was prepared from graphite flakes, using a modified Hummer's method (Marcano *et al.*, 2010). Briefly, a 9:1 mixture of concentrated $\text{H}_2\text{SO}_4/\text{H}_3\text{PO}_4$ (400 mL) was added to a 1 L flask. The flask was adjusted to an ice-bath, and 3 g of graphite (1 mass eq.), and then 18 g of KMnO_4 (6 mass eq.) were added slowly to the acid mixture under stirring. The reaction conditions were maintained for 1 h. Then, the reaction mixture was heated to 50 °C and stirred for 12 h. The product was poured into a 1 L becher filled with ice cubes/water, and homogenized with 3 mL of 30% H_2O_2 . The oxidized product was filtered, and washed three times with water (~200 mL), 30% HCl aqueous solution (~200 mL), and ethyl alcohol (200 mL). Finally, the resulting yellow-brownish material was filtered under vacuum, and dried in an oven at 60 °C for 48 h.

2.3. Preparation of CS/graphite oxide mixtures

The mixture of CS and glycerol, added at 30 mass% based on starch dry mass, was homogenized in a conventional mixer (Ika Works, Wilmington, NC, USA) for 30 min, and maintained in sealed polyethylene bags for 2 days at 4 °C. Graphite oxide at 0.5, 1.0, 1.5 and 2.0 mass%, weighed over the total mass of CS and glycerol, were dispersed separately in 50 mL of water each, under magnetic stirring for 30 min. Then, the water dispersion was added slowly, under mechanical stirring, to the glycerol-plasticized CS. The resulting mixtures were dried in an oven at 60 °C for 48 h, and were maintained in a desiccator until processing.

2.4. Processing

Extrusion processing was carried out in a Coperion ZSK 18 (Werner & Pfleiderer, Stuttgart, Germany) co-rotating twin-screw extruder, with L/D ratio of 40 and seven heating zones. For glycerol-plasticized CS and the GO hybrids, the seven heating zones were maintained at 110, 110, 120, 120, 120, 110, 110 °C, from feed zone to die end, and the screw speed was set at 200 rpm. The extruded materials were pelletized and compression-molded by heating at 120 °C under 68.9 MPa for 10 min, and cooling for 5 min in a cold press. To prepare the composite specimens for analyses, the resulting sheets, with 12 cm × 10 cm × 2 mm dimensions, were cut appropriately in a digital engraving machine, model EGX-300 (Roland DG Brazil, São Paulo, SP, Brazil). The TPS specimens were cut with a cutting die.

2.5. Aging

Seven replications of tensile specimens type V, according to ASTM D638-72 (thickness 2.0 ± 0.1 mm), and square samples (25 mm × 25 mm, thickness 2.0 ± 0.1 mm) were conditioned at 25 °C and 80% relative humidity (RH) in a climate-controlled chamber M.S. Mistura, model MS 012 (Rio de Janeiro, RJ, Brazil), for 90 days. The aged materials were analyzed by X-ray diffraction and tensile tests.

2.6. Characterization of materials

2.6.1. Raman spectroscopy

The Raman spectra for graphite and graphite oxide were recorded from 5000 to 3000 cm^{-1} with a Horiba Jobyn Ivon spectrometer, model LabRAM 800HR (Kyoto, Japan), with the laser frequency of 514 nm. The laser spot size was 1 μm , and the power

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