Thermochimica Acta 614 (2015) 116–128

Contents lists available at ScienceDirect

Thermochimica Acta

journal homepage: www.elsevier.com/locate/tca

Effect of graphene oxide and its modification on the microstructure, thermal properties and enzymatic hydrolysis of poly(ethylene succinate) nanocomposites

George Z. Papageorgiou[a], Zoe Terzopoulou[b], Vasilios Tsanaktsis[b], Dimitris S. Achilias[b], Kostas Triantafyllidis[b], Evmorfia K. Diamanti[c], Dimitrios Gournis[c], Dimitrios N. Bikiaris[b,*]

[a] Chemistry Department, University of Ioannina, P.O. Box 1186, 45110 Ioannina, Greece
[b] Department of Chemistry, Aristotle University of Thessaloniki, GR-541 24 Thessaloniki, Greece
[c] Department of Materials Science and Engineering, GR-45110 Ioannina, Greece

ARTICLE INFO

Article history:
Received 9 April 2015
Received in revised form 9 June 2015
Accepted 10 June 2015
Available online 17 June 2015

Keywords:
Graphene
Biodegradable polymers
Poly(ethylene succinate)
Nanocomposites
Crystallization

ABSTRACT

In this work, two series of biodegradable nanocomposites of poly(ethylene succinate) (PESu) containing either graphene oxide (GO) or organomodified GO (org-GO) with 1-dodecylamine have been prepared and studied. GO was synthesized using a modified Staudenmaier method from of powdered graphite and PESu/GO and PESu/org-GO nanocomposites with GO or org-GO concentrations 0.5, 1 or 2.5 wt% were prepared with the solvent evaporation method. The nanocomposites were characterized with several techniques. Microscopic and XRD study showed intercalated dispersion of GO into PESu matrix while in the case of org-GO fully exfoliated nanocomposites were obtained. Isothermal and nonisothermal crystallization was studied from the melt or from the glass state by using DSC and it was found that nanocomposites crystallized faster than the neat PESu under both conditions. Crystallization rates increased with increasing filler content and it seems that GO have higher crystallisation effect than org-GO. This is due to the stronger interactions that are taking place between PESu and GO, as was confirmed by FTIR and DSC. In the case of the nanocomposites interesting crystalline morphologies and different to those for neat PESu were observed with PLM. Enzymatic hydrolysis studies revealed that nanocomposites have higher hydrolysis rates than neat PESu, while GO accelerates in higher extent the hydrolysis of PESu than org-GO.

1. Introduction

Biodegradable polyesters can be either naturally occurring or chemically synthesized. PESu is a biodegradable aliphatic semi-crystalline polyester synthesized by the polycondensation of an aliphatic diacid (i.e. succinic acid) and an aliphatic diol (i.e. 1,2-ethanediol). PESu shows besides biodegradability also very attractive properties including, melt processability, chemical resistance and mechanical properties similar to that of high density polyethylene and polypropylene. These properties give to PESu wide potential applications [1–4]. The addition of nanofillers was found to enhance a lot of polymer properties including mechanical, thermal and electrical conductivity, gas barrier properties and thermal stability [5]. This is because the formation of hybrid nanocomposite materials based on a polymeric matrix with some nanoadditives results in a synergistic effect of the two respective components in the nanometer scale. The small size of the fillers leads to a dramatic increase in interfacial area and this creates a significant volume fraction of interfacial polymer with properties different from the bulk polymer even at low loadings. Typical filler amounts of less than 5 wt% result in effective enhancement of the nanocomposite properties [6].

Graphene is an exciting material with a wide variety of potential applications [7]. Theoretical and experimental results show that single-layered two-dimensional (2D) graphene sheets are the strongest materials developed so far [8]. Due to their extraordinary electronic and thermal properties, nanoscale materials based on individual graphene sheets dispersed in various polymer matrices, have created a new class of polymer nanocomposites [9,10]. However, it is very difficult to separate the graphene layers from graphite due to the existed strong interactions. Graphite oxide is a hydrophilic layered material produced by the oxidation of graphite and is the simplest way to disperse graphene sheets from graphite [11]. The graphene derived sheets in GO are heavily oxygenated,

---

* Corresponding author. Fax: +30 2310 997769.
E-mail address: dbic@chem.auth.gr (D.N. Bikiaris).

http://dx.doi.org/10.1016/j.tca.2015.06.016

bearing hydroxyl and epoxide functional groups on their basal planes, in addition to carbonyl and carboxyl groups located at the sheet edges [12]. Since exfoliation of graphite oxide is the only way to produce stable suspensions of quasi-two-dimensional carbon sheets, graphene oxide has attracted attention as filler for polymer nanocomposites [13]. Moreover, chemical functionalization of GO is a well establish technique in order to obtain nanomaterials with desired properties since this can affect their dispersability and interactions with polymeric matrices [14]. Hydrophilic GO, for example, can be easily converted in an organophilic material via the surface modification of GO with primary aliphatic amines (nucleophilic substitution reactions on epoxy groups of GO) [14].

Polymer/graphene based nanomaterials have attracted significant scientific interest in the recent years due to marked enhancement in the polymer properties at low filler fractions [15]. The property enhancements are attributed commonly to high aspect ratio of graphene platelets, filler–polymer interactions at the interface, as well as uniform dispersion of the platelets in the polymer matrices. In literature several aliphatic polyesters/graphene nanocomposites have been reported with emphasis to be given in reinforcement and thermal properties effect of graphene in polymer matrices [9,16–22]. However, till now, only a few works have appeared on the synthesis and characterization of graphene reinforced PESu [23–25]. Almost all of them are dealing with the effect of graphene on crystallization behavior of PESu and on its mechanical properties. It was confirmed that graphene could act as nucleating agents and thus crystallization rates were increased in the dynamic mode [23]. However, the overall crystallinity remained almost unchanged. The same effect was observed when thermally reduced graphene (TRG) was added into PESu matrix [25] or when graphene oxide was grafted by *in-situ* polymerisation with PESu [24].

The aim of the present study was to prepare nanocomposites based on PESu and either GO or organomodified GO (org-GO) in order to investigate the effect of the type and the amount of the nanoadditive on the microstructure and thermal properties of PESu. Emphasis was also given to study the effect of these GO types on the enzymatic hydrolysis of PESu, since in literature there are not such studies available.

2. Experimental

2.1. Materials

Succinic acid (purum 99+%), 1,2-ethylene glycol (Purity:>99.8%) and titanium (IV) butoxide (≥97%) (TBT) catalyst of analytical grade, graphite flakes with particle size +100 mesh (≥75%) were purchased from Aldrich Chemical Co. All other reagents were of analytical grade.

2.2. Synthesis of poly(ethylene succinate)

Poly(ethylene succinate) was prepared by the two-stage melt polycondensation method (esterification and polycondensation) using succinic acid and ethylene glycol in a molar ratio 1/1.1 and TBT as catalyst (10^{-3} mol TBT/mol SA) in a glass batch reactor. Polycondensation was performed at 230 °C for 60 min. After the polycondensation reaction was completed, the polyester was removed, milled and washed with methanol. Detailed presentation of the synthesis of the PESu samples can be found in a previous paper [26–28].

2.3. Synthesis of graphene oxide

The GO was produced through a modified Staudenmaier's method [14]. In a typical synthesis, 10 g of powdered graphite was added to a mixture of concentrated sulphuric acid and nitric acid while cooling in an ice-water bath. Potassium chlorate powder was added to the mixture in small portions while stirring and cooling. The reactions were quenched after 18 h by pouring the mixture into distilled water and the oxidation product washed until a pH 6. The sample was then dried at room temperature.

2.4. Organic modification graphite oxide

In a typical experiment 200 mg of GO was dispersed in 100 mL of water and the mixture was stirred for 1 day. A solution of 1-dodecylamine (600 mg) in ethanol (100 mL) was then added dropwise to the GO suspension and the mixture was stirred for another day at room temperature. The GO derivative was isolated by centrifugation and washed three times with 1:1 (v/v) ethanol/water and dried in air. The sample was denoted as org-GO.

2.5. Preparation of PESu nanocomposites

PESu nanocomposites with GO or org-GO were prepared by applying the solvent evaporation method from solution/suspension using *N,N*,-dimethyl-formamide (DMF) as a mutual solvent. The desired amounts of the nanofillers were first added into DMF at a concentration of 1 mg/mL, and the mixture was subjected to sonication for 1 h to obtain a uniform dispersion. At the same time, PESu was completely dissolved in DMF at a concentration of 20 mg/mL. The PESu solution was then mixed with the nanofiller suspension followed by stirring and sonication for 30 min. The solvent was allowed to evaporate in air for 3 days with slightly stirring for the first day and then at 50 °C for 1 day in vacuum. after complete solvent removal thin films of the nanocomposites were obtained. The prepared films were placed in a desiccator to prevent any moisture absorption. According to this procedure PESu/GO and PESu/org-GO nanocomposites containing 0.5, 1 and 2.5 wt% GO or org-GO nanofillers have been prepared.

2.6. Gel permeation chromatography (GPC)

GPC analysis was performed using a Waters 150C GPC equipped with a differential refractometer as detector and three ultra-styragel (10^3, 10^4, 10^5) columns in series. $CHCl_3$ was used as the eluent (1 mL/min) and the measurements were performed at 35 °C. Calibration was performed using polystyrene standards with a narrow molecular weight distribution. Results showed that the number average molecular weight (M_n) of PESu was equal to 23,200 Da with polydispersity $M_w/M_n = 2.21$.

2.7. Transmission election microscopy (TEM)

Transmission electron microscopy (TEM) observations were made on ultra thin film samples of the various nanocomposites prepared by an ultra-microtome. These thin films were deposited on copper grids. TEM micrographs were obtained using a JEOL 120CX microscope operating at 120 kV. The thin films were subjected to coating with carbon black prior to the measurement, to avoid the destruction of the films after exposure to the electron irradiation.

2.8. X-ray diffraction (XRD) study

XRD study of PESu nanocomposites, in the form of thin films were performed over the range 2θ from 5 to 50°, at steps of 0.05° and counting time of 5 s, using a MiniFlex II XRD system from Rigaku Co. with Cu K_α radiation ($\lambda = 0.154$ nm).