



Biodegradable poly(ethylene succinate) nanocomposites. Effect of filler type on thermal behaviour and crystallization kinetics



George Z. Papageorgiou^{a,b,*}, Zoe Terzopoulou^a, Dimitris S. Achilias^a, Dimitrios N. Bikiaris^a, Maria Kapnisti^b, Dimitrios Gournis^c

^aLaboratory of Organic Chemical Technology, Department of Chemistry, Aristotle University of Thessaloniki, Thessaloniki GR-541 24, Greece

^bTechnological Educational Institute of Thessaloniki, Sindos GR -574 00, Thessaloniki, Greece

^cDepartment of Materials Science and Engineering, University of Ioannina, Ioannina GR-45110, Greece

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ABSTRACT

Nanocomposites based on poly(ethylene succinate) (PES) containing different types of inorganic nanofillers, including graphene oxide, modified graphene oxide, multi-walled carbon nanotubes and silver nanoparticles at a concentration of 2.5 wt% were prepared by solution casting. Good dispersion of the nanomaterial in the polymer matrix was verified with SEM microphotographs. WAXD patterns showed no change in crystal type of PESu in the nanocomposites. Crystallization was studied with DSC and involved non-isothermal melt and cold crystallization, as well as isothermal crystallization from the melt. All nanocomposites presented faster crystallization compared to pristine polymer with MWCNT resulting in the faster crystallization rate. Avrami's method was applied to simulate crystallization kinetic data and a good fitting was observed for the whole relative degree of crystallinity range in pristine PESu and all nanocomposites, except those with MWCNT, where it failed at high conversions. The activation energy of non-isothermal crystallization was calculated using the isoconversional model of Friedman and the nanocomposites with MWCNT exhibited higher values compared to other materials, though corresponding to higher (melt crystallization) or lower (cold crystallization) temperatures. Moreover, MWCNT was found also to have the higher nucleation activity. The Lauritzen–Hoffman analysis was also applied to analyse isothermal crystallization data and the generated morphology on isothermal crystallization from the melt was studied by Polarized Light Microscopy. The size of spherulites decreased as the polymer crystallization was nucleated by the nanoparticles and also the texture was affected.

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1. Introduction

Recently, an increasing interest in biodegradable polymers, such as aliphatic polyesters has appeared. Biodegradable polyesters can be either naturally occurring or chemically synthesized. Poly(ethylene succinate), 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 [1–7].

The formation of hybrid nanocomposite materials based on a polymeric matrix with some inorganic nanofiller results in a synergistic effect of the two respective components in the nanometer scale leading to considerable improvements of various characteristics of the pristine polymer, such as mechanical, thermal, and gas-barrier properties [8]. 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 [9]. Typical filler amounts of less than 5 wt% result in effective enhancement of the nanocomposite properties [10]. There is a large variety of inorganic nanofillers, including nanotubes, layered silicates (e.g., montmorillonite, saponite), nanoparticles of metals (e.g., Au, Ag), metal oxides (e.g., TiO₂, Al₂O₃), semiconductors (e.g., PbS, CdS), and so forth [11].

Carbon nanotubes (CNTs) which were first reported by Iijima [12]. Carbon nanotubes in addition to the exceptional mechanical properties, also possess superior thermal and electric properties:

* Corresponding author. Laboratory of Organic Chemical Technology, Department of Chemistry, Aristotle University of Thessaloniki, Thessaloniki GR-541 24, Greece. Tel.: +30 2310 997812.

E-mail address: gzpap@chem.auth.gr (G.Z. Papageorgiou).

thermally stable up to 2800 °C in vacuum, thermal conductivity about twice as high as diamond, electric-current-carrying capacity 1000 times higher than copper wires [13]. Because of their unique properties, CNTs find applications in nanoelectronics [14], superconductors, nanowires, composite materials [15], nanomedicines [16], etc.

Graphene has emerged to be an exciting material with potential applications [17]. Theoretical and experimental results show that single-layered two-dimensional (2D) graphene sheets are the strongest materials developed thus far. Due to their extraordinary electronic and thermal properties, nanoscale materials based on individual graphene sheets have recently attracted tremendous attention [18]. The discovery of graphene with its combination of extraordinary physical properties and ability to be dispersed in various polymer matrices has created a new class of polymer nanocomposites [19–21]. Graphite oxide is a layered material produced by the oxidation of graphite. The graphene derived sheets in graphite oxide (graphene oxide sheets) are heavily oxygenated, bearing hydroxyl and epoxide functional groups on their basal planes, in addition to carbonyl and carboxyl groups located at the sheet edges [22]. Since exfoliation of graphite oxide is the only way to produce stable suspensions of quasi-two-dimensional carbon sheets, graphite oxide has attracted attention as filler for polymer nanocomposites [23].

Silver nanoparticles have been used in nanocomposite preparation in recent works aiming to antibacterial properties and electric conductivity. Thus, silver nanocomposites based on UHMWPE, poly(vinyl alcohol) (PVA), methacrylates, poly(*p*-phenylene vinylene), poly(lactic acid), epoxy resins and other have been studied [24–30].

Crystallization of polymers and composites during processing determines the final solid state characteristics of the materials [31]. So, crystallization kinetics is a crucial issue for polymer and composites processing. It is well-known that addition of nanoparticles affects crystallization of the polymer matrix in nanocomposites [32,33].

In this work, a series of nanocomposites of poly(ethylene succinate) were prepared by adding graphene oxide, graphene oxide modified with amines, multi-walled carbon nanotubes and silver nanoparticles. The thermal properties of the nanocomposites and the crystallization under dynamic conditions from the melt and the glass as well as the isothermal crystallization kinetics were studied. To our knowledge, comparative studies on similar nanocomposites of PESu have never been reported before.

2. Experimental

2.1. Materials

Succinic acid (purity >99%), 1,2-ethylene glycol (Purity: >99.8%) and titanium (IV) butoxide ($\geq 97\%$) (TBT) catalyst of analytical grade were purchased from Aldrich Chemical Co. Neat multi-walled carbon nanotubes (MWCNTs) were synthesized by the chemical vapour deposition (CVD) process and were supplied by Timesnano Chengdu Organic Chemicals Co. Ltd (China). Their length was about 10 μm and their diameter 10–20 nm. Silver nanopowder (Ag) used in this research was of 40–90 nm of average nanoparticle size, supplied by Inframat Advanced Materials™.

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 [34].

2.3. Synthesis of graphene oxide

The GO was produced through a modified Staudenmaier's method [35–38]. In a typical synthesis, 10 g of powdered graphite were 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 days. 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 1 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

Biodegradable nanocomposite materials based on PESu and graphene oxide (GO), or org-GO, or silver nanoparticles (SN), or Multi-Walled Carbon Nanotubes (MWCNT) were prepared. The nanofiller content in the nanocomposites was 2.5 wt%. The materials were prepared by applying the solvent evaporation method from solution/suspension of PESu and the nanoparticles in NN-dimethyl-formamide (DMF) under sonication for 1 h. The mixture was cast on a petri dish at room temperature. The solvent was allowed to evaporate in air for 3 days and then at 50 °C for 1 day in vacuum. Thus, after complete solvent removal thin films of the nanocomposites were obtained. The prepared films were placed in a desiccator to prevent any moisture absorption. Nanocomposites containing 2.5 wt% GO, 2.5 wt% org-GO, 2.5 wt% silver nanoparticles or 2.5 wt% oxidized MWCNTs were prepared with code names PESu/GO, PESu/org-GO, PESu/Silver and PESu/MWCNT.

2.6. Morphological examination

Scanning electron microscopy (SEM) study was carried out using a JEOL JMS-840A scanning microscope equipped with an energy-dispersive X-ray (EDX) Oxford ISIS 300 microanalytical system. For this purpose fractured surfaces as well as thin films were used.

2.7. Wide-angle X-ray Diffraction (WAXD) 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).

2.8. Differential scanning calorimetry (DSC)

A Perkin–Elmer Pyris Diamond DSC differential scanning calorimeter, equipped with a Perkin–Elmer Intracooler II and calibrated

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