



# Effect of nanofiller's size and shape on the solid state microstructure and thermal properties of poly(butylene succinate) nanocomposites



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## ABSTRACT

We report a study of the solid state microstructure and crystallization kinetics of poly(butylene succinate) (PBSu) reinforced with nanofillers of different shapes, sizes and geometries such as silver, silica (SiO<sub>2</sub>), multi-walled carbon nanotubes (MWCNTs) and graphene oxide (GO). The solid state structure of neat polymer and nanocomposites were investigated by X-ray diffraction (XRD), polarized optical microscopy (POM) and transmission electron microscopy (TEM). The results indicated that the nanocomposite samples exhibited enhanced crystallinity and nucleation density, along with smaller spherulite size. Additionally, the spherical nanofillers were dispersed more uniformly in the polymeric matrix, than the other two filler types. The crystallization kinetics under both isothermal and dynamic conditions were also studied and as was expected, the nanocomposite samples, crystallize at higher rates due to the increased number of nucleation sites, as was calculated with Avrami, Dobreva and Friedman's methods. From the crystallization study it was found that the nanocomposite filled with Ag nanoparticles exhibited the highest rates from all other fillers followed from SiO<sub>2</sub> and MWCNTs while GO showed the lowest rates.

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## 1. Introduction

The interest and demand in aliphatic polyesters that can be energy recovered or recycled has been constantly growing over the last years, due to the environmental problems caused by the massive use of conventional polymers. Poly(butylene succinate) (PBSu) belongs to a family of biodegradable polyesters synthesized from succinic acid and it is considered one of the most promising polymers from this family of materials [1]. PBSu possesses very important and interesting properties since it is biodegradable, it is easily processed from the melt and demonstrates good chemical resistance [2,3]. Many efforts from industry and academia are currently being made for massive PBSu production, since the PBSu market is expected to grow as demand for biodegradable plastics constantly increases.

Polymer-matrix based nanocomposites belong to an emerging area of research and development. Various additives in the nanoscale are being tested for their compatibility and the improvements that they can bring to the physicochemical

properties of polymers. PBSu did not stay unaffected from the current progress and many attempts have been made for its reinforcement with different nanofillers such as silica or multi-walled carbon nanotubes [4–7]. So far PBSu has been used in various applications in agriculture, fishery, forestry, civil engineering, biomedicine, automotive and other fields. For example, PBSu is actually used for packaging materials, fishing and vegetation nets, mulching films, delivery systems for fertilizers and pesticides, compost bags, disposable bags and cutlery, bottles, diapers, cups and many other applications [1]. However, more advanced applications demand enhancement of the properties of the pristine material and especially to increase mechanical performance, thermal stability and gas and humidity barrier properties. The insertion of nanofillers into the polymeric matrix is expected to cover many of these demands and attribute the desired performance [8–10].

The reactive groups of the filler and its hydrophobicity, its dispersion into polymer matrix as well as its particle size or shape plays the most important role to the final properties of nanocomposites. For this reason, nanofillers of different shapes, geometries and sizes which will attribute different properties to the PBSu matrix, will be used in the current manuscript. The fillers that will be used are silver nanoparticles (Ag), silica nanoparticles

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(SiO<sub>2</sub>) with reactive silanol surface groups, multi-walled carbon nanotubes (MWCNTs) and graphene oxide (GO). Silica and silver nanoparticles are spherical nanofillers with sizes 10–12 nm, MWCNTs exhibits the well-known, multi-layer nanotube geometry, while graphene exhibits a layered structure and will be oxidized in order to enhance the polymer–filler interactions and thereafter to facilitate the exfoliation of the nanosheets in the matrix and improve its dispersion [11].

The current research paper focuses mainly on the differences of the thermal properties and solid state structure of PBSu-based nanocomposites. X-ray diffraction and polarized optical microscopy were utilized in order to export viable conclusions regarding the crystalline structure and the nucleation density of each sample. TEM was also employed for the observation of dispersion quality, since it is well known that dispersion is one of the most significant factors, affecting the final physicochemical properties of the nanocomposites. Emphasis was given to the crystallization behavior of the prepared samples, as they were tested under isothermal and dynamic conditions with various crystallization temperatures and rates. Finally, a detailed kinetic analysis of the obtained data was performed in order to export comparative conclusions regarding the effect of each nanofiller on the PBSu-based samples.

## 2. Experimental

### 2.1. Materials

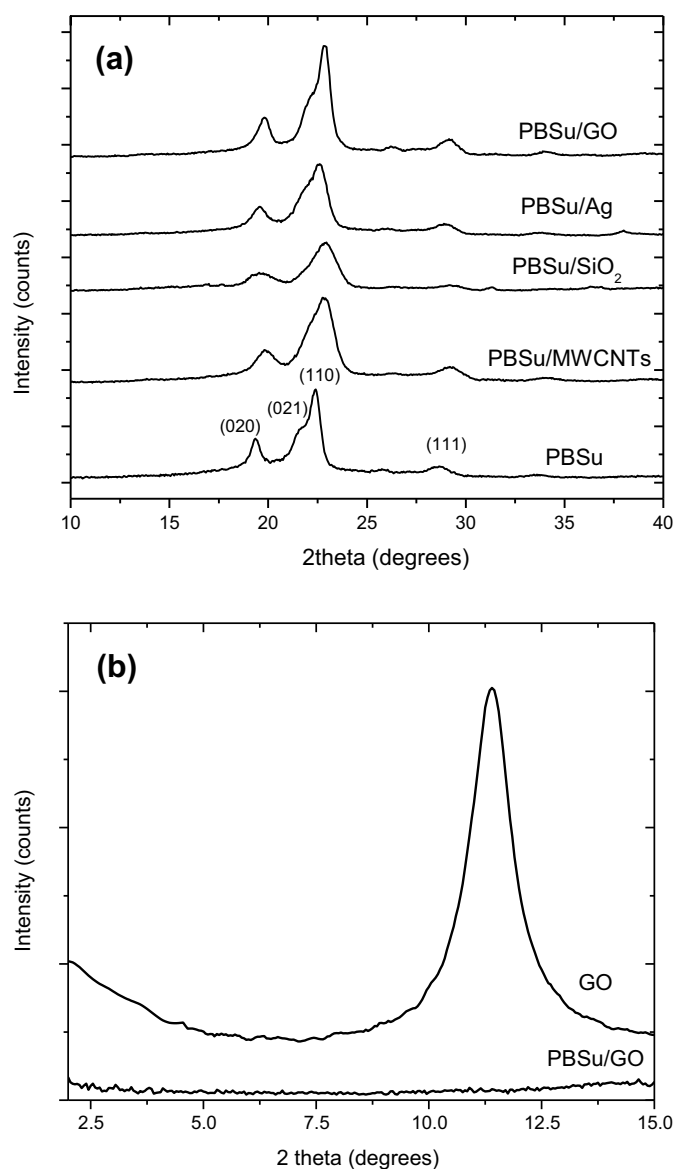
PBSu under the trade name Bionolle 1020 and  $M_w = 1.4 \times 10^5$  was purchased by Showa Chemicals (Japan). Silver nanoparticles (Ag) were supplied by Inframat Advanced Materials (Manchester, USA). Their size was about 10 nm and their purity 99.95% of metal. Fumed silica (SiO<sub>2</sub>) nanoparticles were supplied by Degussa AG (Hanau, Germany) under the trade name AEROSIL<sup>®</sup> 200, having a specific surface area of 200 m<sup>2</sup>/g, SiO<sub>2</sub> content >99.8%, and average primary particle size 12 nm. Neat multi-walled carbon nanotubes (MWCNTs) were synthesized by chemical vapor deposition (CVD) process and were supplied by Timesnano Chengdu Organic Chemicals Co. (China). Their length was about 10 μm and their diameter 10–20 nm. Chloroform and dimethylformamide of analytical grade were purchased from Aldrich Chemical Co.

### 2.2. Synthesis of graphene oxide and organic modification

GO was synthesized according to the modified Hummers method [12]. Commercial graphite powder (10 g) was stirred in concentrated solution of sulfuric acid (230 mL, 0 °C). Then, 30 g of potassium permanganate was slowly added to the suspension. The rate of addition was controlled in order to prevent the rapid rise of suspension's temperature, which should be less than 20 °C. The reaction mixture was then cooled to 2 °C. After the removal of ice-bath, the mixture was then stirred at room temperature for 30 min. 230 mL of distilled water were slowly added to the reaction vessel, keeping the temperature less than 98 °C. The diluted suspension was stirred for additional 15 min. Further dilution with 1.4 L of distilled water was realized and then 100 mL of solution of hydrogen peroxide (30 wt%) was added. The mixture was left overnight. The GO particles settled at the bottom were separated from the excess liquid by decantation. The remaining suspension was transferred to dialysis tubes. Dialysis was carried out until no precipitate of barium sulphate was detected by addition of aqueous solution of barium chloride. Then, the wet form of graphite oxide was separated by centrifugation. The gel like material was freeze-dried and the fine dark brown powders of the initial GO were obtained.

### 2.3. Preparation of PBSu nanocomposites

PBSu nanocomposites with GO and SiO<sub>2</sub> were prepared by solvent evaporation using *N,N*-dimethylformamide (DMF) as a mutual solvent with sonication and stirring. The desired amount of the nanofillers was first added into DMF at a concentration of 1 mg/mL, and the dispersion was subjected to sonication for 1 h to obtain a uniform dispersion. At the same time, PBSu was completely dissolved in DMF at a concentration of 20 mg/mL. The PBSu solution was then mixed with the nanofiller suspension followed by stirring and sonication for 30 min. The solvent was evaporated at room temperature for two days with slightly stirring at first day and the nanocomposite films were obtained. The same procedure was followed for the preparation of PBSu nanocomposites with MWCNTs and Ag but using CHCl<sub>3</sub> as solvent, since a better dispersion of nanofillers was achieved. According to the described procedures nanocomposites containing 2.5 wt% of each nanofiller were prepared with code names PBSu/SiO<sub>2</sub>, PBSu/Ag, PBSu/GO and PBSu/MWCNT. For comparison purposes a film of neat PBSu was also prepared after evaporation by dissolving PBSu in CHCl<sub>3</sub>.



**Fig. 1.** X-ray diffraction patterns for PBSu and nanocomposite samples, (b) evidence of the exfoliation of graphene oxide into the PBSu matrix.

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