

# Morphology and thermal properties of biodegradable poly(hydroxybutyrate-co-hydroxyvalerate)/tungsten disulphide inorganic nanotube nanocomposites

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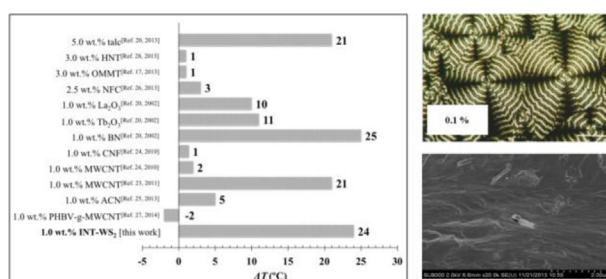
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## HIGHLIGHTS

- Environmentally-friendly INT-WS<sub>2</sub> is used to produce advanced PHBV NCPs.
- Novel INT-WS<sub>2</sub> improve the thermal stability of PHBV.
- INT-WS<sub>2</sub> is effective to accelerate the crystallization of PHBV.
- Ring-banded spherulites of PHBV are observed at low INT-WS<sub>2</sub> contents.
- The benefits of using INTs compared to other nanoscale fillers are highlighted.

## GRAPHICAL ABSTRACT



## ARTICLE INFO

### Article history:

Received 16 June 2015

Received in revised form

5 October 2015

Accepted 19 December 2015

Available online 28 December 2015

### Keywords:

Composite materials

Thermal properties

Differential scanning calorimetry (DSC)

Optical microscopy

X-ray scattering

## ABSTRACT

Promising biodegradable and renewable poly(hydroxybutyrate-co-hydroxyvalerate) (PHBV) nanocomposites based on tungsten disulphide inorganic nanotubes (INT-WS<sub>2</sub>) were efficiently prepared by a simple solution blending method. The structure, morphology, thermal stability and crystallization behavior of the nanocomposites were investigated by ultra-high field-emission scanning electron microscope (FESEM), thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), wide-angle X-ray scattering (WAXS) and polarized optical microscopy (POM) techniques. As previously observed in poly(3-hydroxybutyrate) (PHB) hybrid systems, the dispersion, morphology and thermal properties of PHBV/INT-WS<sub>2</sub> nanocomposites could be tuned by the introduction of small amounts of INT-WS<sub>2</sub>. The results revealed that a good dispersion of INT-WS<sub>2</sub> in the PHBV matrix influenced the morphology and non-isothermal crystallization behavior of PHBV that depends on both the INT-WS<sub>2</sub> concentration and the cooling rate. A significant enhancement in thermal stability of PHBV and a highly efficient nucleating effect of the INT-WS<sub>2</sub> comparable to specific nucleating agents or other nano-sized fillers was observed. These observations are of importance for extending the practical applications of these biopolymer nanocomposites towards eco-friendly (e.g. sustainable packaging) and biomedical (e.g. bone tissue engineering) applications.

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## 1. Introduction

In 2015 it is estimated that around 300 million tons of plastic materials will be produced globally, mainly from petroleum

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feedstocks, and as a result there is growing concern about their future environmental and fiscal impact [1]. In the meantime the uncontrollable economic fluctuations in crude oil clearly indicate that supplies are finite, and “white pollution” originating from mainstream plastics creates an acute problem around the world. Thus, the challenge for scientists and engineers, both in academic and industrial frameworks, to develop alternative bio-based and biodegradable plastic materials is becoming a critical issue with important objectives that must have projected impact within a decade.

In order to address the aforementioned problems, considerable attention has been given in the last two decades to poly-hydroxyalkanoate (PHA) biopolyesters, a family of renewable and biodegradable thermoplastics. The production of PHA biopolymers originates in genetically controlled, energy-storage procedures of a number of microorganisms under certain environmental situations [2,3]. Poly(hydroxybutyrate-co-hydroxyvalerate) (PHBV), the most common PHA copolyester, can be transformed using conventional thermoplastics processing equipment, and has properties comparable to a range of petroleum-based plastics, making it appealing as a biodegradable engineering material. It is highly anticipated as a potential substitute for applications with ephemeral functionality (packaging, pharmacology, farming, etc.) as well as a possible contender for advanced, non-toxic biomedical applications (time-released drug delivery vehicles, biodegradable tissue restoration scaffolds, etc.) [2–6]. However, PHBV typically has a high inherent degree of crystallinity ( $\geq 50\%$ ), and despite being biodegradable and of biological origin, it has not achieved major commercial prosperity. Like other bio-based materials, there are economic, energetic, and mechanical drawbacks for their industrial success, and in particular for PHBV, it has slow crystallization kinetics and a thermal stability limit that is close to the melting point ( $\sim 170$ – $180$  °C) of the polymer [7–9]. During the extrusion process, for example, the copolyester would experience local temperatures higher than that of the bulk due to high shear friction from the rotating screws, leading inevitably to the pre-mature onset of degradation of the material. In molding applications, long mold-injection cycles are required due to slow crystallization, which would cause low productivity and expend large amounts of energy. Likewise, a spun film of PHBV would be more prone to self-adhesion because it remains sticky due to slow conversion from the amorphous phase to the crystalline phase even after cooling.

Thus, in order to compete with commodity plastics, new strategies to improve mechanical, thermal, rheological, and economic limitations of PHBV as an eco-friendly biomaterial are of current interest. One approach has involved blending PHBV with other polymers such as poly(L-lactic acid), poly(dicyclohexylitaconate), poly(ethylene oxide), poly(ethylene succinate), poly(hydroxybutyrate), poly(butylene adipate-co-terephthalate), or poly(propylene carbonate) [10–16]. Other improvement strategies include incorporation of plasticizers such as acetyl tributyl citrate (ATBC) [17] or modified processing techniques such as post-annealing [9]. Also, the incorporation to PHBV of certain additives to create composite, binary or higher, materials that act as heterogeneous nucleating agents (NA) to enhance the crystallization kinetics has been extensively studied, and include kenaf fibers, talc, boron nitride (BN), lanthanum oxide ( $\text{La}_2\text{O}_3$ ), terbium oxide ( $\text{Tb}_2\text{O}_3$ ), wood fiber, cyanuric acid (CA), and raw coir [18–22]. More recently new approaches have appeared using low concentrations of nanoscale particles (i.e. nanoparticles) to create nanocomposite systems in order to improve physical and thermal properties of plastics. The known nanocomposite systems for crystallization studies of PHBV-based materials include small weight fractions of organo-modified montmorillonite (OMMT), carbon nanotubes (CNT), carbon nanofibers (CNF), acetylated chitin nanocrystals

(ACN), nanofibrillated cellulose (NFC), multi-walled CNT grafted with PHBV (PHBV-g-MWCNT), and halloysite nanotubes (HNT) [17,23–28]. Nanoparticles have huge surface area to volume ratios and are incorporated with a view to creating extensive polymer–nanofiller interactions with the potential to yield interesting mechanical and thermal properties. However, most nanoparticles have high surface energies and, as a result, they typically form agglomerates unless chemically modified. Poorly dispersed nanostructures impedes nanocomposite formation and consequently diminishes any potential property improvements. Sanchez-Garcia et al. reported that carbon nanotubes had a limited effect on increasing overall crystallization rates in PHBV [24], attributed to poor nanoparticle distribution, whilst Shan et al. used surface-modified CNT and reported excellent increases in crystallization rates of PHBV [23].

Inorganic nanotubes of tungsten disulfide (INT- $\text{WS}_2$ ) were first reported in the early 1990s by Tenne et al. [29]. In the following years, the development of many other inorganic nanotubes (INT) followed and, due to their unique electronic configurations, processing techniques, and other chemomechanical properties, these are expected to create superb nanocomposite materials [29–38]. Unmodified INT- $\text{WS}_2$  are low-cost, environmentally friendly and biocompatible nanofillers since they possess much lower cytotoxicity than other nanoparticles, such as, silica or carbon black [39]. In particular, these novel nanomaterials have demonstrated interesting properties such as high impact resistance, flexibility under tensile stress, superior tribological behavior, and fracture resistance from shockwaves [38]. With such excellent properties, and relatively simple and inexpensive fabrication, the incorporation of INT- $\text{WS}_2$  in polymer systems has become a field of recent interest as it opens opportunities for many new applications [40–46]. The present research continues work in this field and focuses for the first time on the use of INT- $\text{WS}_2$  as a novel nanoreinforcement for enhancing the processability and performance of PHBV. The influence of the INT concentration on morphology and thermal properties is analyzed in detail. In particular, calorimetric studies were undertaken in order to determine the kinetic parameters during non-isothermal (dynamic) crystallization from the melt, since these conditions are closest to industrial processing conditions.

## 2. Experimental section

### 2.1. Materials and processing

PHBV biopolymer with 2.0 wt.% hydroxyvalerate (HV) content was purchased from GoodFellow Cambridge, Ltd in powder form ( $M_w = 410 \text{ kg mol}^{-1}$ ) and used as received. The tungsten disulfide inorganic nanotubes (INT- $\text{WS}_2$ ) were obtained from NanoMaterials, Ltd (Israel) and used without chemical modification. Various formulations of PHBV/INT- $\text{WS}_2$  nanocomposites were prepared by dispersing INT- $\text{WS}_2$  (0.1, 0.5 and 1 wt.%) in a solution of PHBV in chloroform, then precipitated in methanol and subsequently filtered and dried in a vacuum oven at 50 °C for 24 h. Then, the samples were pressed into films of 0.5 mm thickness in a hot press system at 180 °C using two heating/cooling plates.

### 2.2. Characterization techniques

Surface images using an ultra-high field-emission scanning electron microscope (FESEM) SU8000 (Hitachi Co., Japan) were obtained from samples fractured in liquid nitrogen and coated with a  $\sim 5 \text{ nm}$  chromium.

The thermal stability of the control and binary systems were recorded from room temperature to 600 °C at a heating rate of  $10 \text{ }^\circ\text{C min}^{-1}$  by thermogravimetric analysis (TGA) using a TA

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