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

Tyler Silverman , Mohammed Naffakh , Carlos Marco, Gary Ellis

g r a p h i c a l a b s t r a c t

- Environmentally friendly INT WS₂ is used to produce advanced PHBV NCPs
- Novel INT WS₂ improve the thermal stability of PHBV
- INT WS₂ is effective to accelerate the crystallization of PHBV
- Ring banded spherulites of PHBV are observed at low INT WS₂ contents.
- The benefits of using INTs compared to other nanoscale fillers are highlighted.

a b s t r a c t

Promising biodegradable and renewable poly(hydroxybutyrate co hydroxyvalerate) (PHBV) nanocomposites based on tungsten disulphide inorganic nanotubes (INT WS₂) 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 WS₂ nanocomposites could be tuned by the introduction of small amounts of INT WS₂. The results revealed that a good dispersion of INT WS₂ in the PHBV matrix influenced the morphology and non-isothermal crystallization behavior of PHBV that depends on both the INT WS₂ concentration and the cooling rate. A significant enhancement in thermal stability of PHBV and a highly efficient nucleating effect of the INT WS₂ 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.

1. Introduction

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

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 (~ 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 premature 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 (La_2O_3), terbium oxide (Tb_2O_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 nano structures 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 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 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 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 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 WS_2) were obtained from NanoMaterials, Ltd (Israel) and used without chemical modification. Various formulations of PHBV/INT WS_2 nanocomposites were prepared by dispersing INT 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 ~ 5 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 °C min^{-1} by thermogravimetric analysis (TGA) using a TA

Instruments Q50 thermobalance in an oxidative (air) atmosphere.

Non isothermal (dynamic) crystallization of the neat PHBV and PHBV/INT WS₂ nanocomposites was measured using a Perkin Elmer DSC7/Pyris differential scanning calorimeter (DSC) (Perkin Elmer Espana SL, Madrid, Spain), calibrated with indium (T_m 156.6 °C, ΔH_m 28.45 kJ kg⁻¹) and zinc (T_m 419.47 °C, ΔH_m 108.37 kJ kg⁻¹). All samples of between 6 and 11 mg weight were placed in sealed 40 μ L aluminum pans in a nitrogen flowing atmosphere. The thermal cycle employed consisted in holding the samples at 180 °C for 5 min to erase any thermal histories [20–22] and subsequently cooling to 40 °C at six different cooling rates (ϕ): 2, 5, 10, 15, 20 and 25 °C min⁻¹. After the dynamic crystallization process, the samples were heated at a rate of 5 °C min⁻¹ to the aforementioned holding temperature. The crystallization temperature (T_p) were determined from the minimum of the crystallization exotherm observed during the cooling scan, respectively. The estimation of crystallinity ($1 - \lambda_c$) of the neat polymer and its nanocomposites was calculated by:

$$(1 - \lambda_c) = \frac{\Delta H_c}{\Delta H_m^0} \quad (1)$$

where ΔH_c is the apparent crystallization enthalpy and ΔH_m^0 is the enthalpy of melting for perfect crystals: 146 J g⁻¹, which is appropriate for this copolymer of low HV content [2,17].

Wide angle X ray scattering (WAXS) experiments of pure PHBV and PHBV/INT WS₂ nanocomposites (0.1 wt.% sample excluded from WAXS) were performed using a Bruker D8 Advance diffractometer (Bruker AXS GmbH, Karlsruhe, Germany) with Ni filtered Cu K α radiation (λ 1.5418 Å) over a double Bragg angle (2θ) regime between 12° and 40° with a resolution of 42 points per degree. The equipment includes a temperature controlled chamber to analyze the dynamic crystallization and melting behavior over a broad range of temperatures. Each sample was held at 180 °C for 5 min, then cooled to 30 °C and subsequently heated to 180 °C, both at $\phi \approx 7$ °C min⁻¹.

The crystalline morphology of the samples was examined with a Reichert Zetopan Pol polarized light microscope (POM). Samples were melted and compressed between two glass slides at 180 °C for 5 min in a Mettler FP82HT hot stage. All samples were cooled to room temperature ϕ 2 and 10 °C min⁻¹ and single images were obtained at room temperature.

3. Results and discussion

3.1. Dispersion of INT WS₂ in the PHBV matrix

The dispersion of the nanoparticles in the polymer matrix as well as interfacial interaction between the polymer matrix and nanoparticles play important roles in the crystallization behavior of polymers. Fig. 1a and b show an overview of the fracture surfaces of the PHBV/INT WS₂ nanocomposites with 0.5 and 1.0 wt.% of INT WS₂, respectively. It can be clearly seen that INT WS₂ are well dispersed within the PHBV matrix without any apparent aggregation. It is important to point out that the INT WS₂ do not require exfoliation or chemical modification, making it possible to obtain new biopolymer nanocomposite formulations without the complexity and processing costs associated with such treatments. In particular, the efficient dispersion of INT WS₂ at the nanoscale is likely related to the lubricant character of these inorganic nanotubes and the consequent improvement in tribological properties [45,46]. Thus, the INT WS₂ acted as lubricant nanoadditives during the processing of the PHBV biopolymer nanocomposites. An analogous behavior has been reported for PHB and PEEK based composites reinforced with INT WS₂ [45,46].

Fig. 1. FESEM image of PHBV/INT-WS₂ nanocomposites. (a) PHBV/INT-WS₂ (0.5 wt.%) and (b) PHBV/INT-WS₂ (1.0 wt.%).

3.2. Thermal stability of PHBV nanocomposites with INT WS₂

Thermogravimetric analysis (TGA) of the PHBV/INT WS₂ nanocomposites in air was studied to determine the effect of the inorganic nanotube concentration in the PHBV matrix. TGA studies help establish limiting processing conditions for thermoplastic materials, which is very important for PHBV with its narrow processing window. An initial degradation temperature (T_i) was marked when the original sample weight decreased by 2% ($T_{2\%}$) during the heating process. For neat PHBV and the 0.1 wt.% INT WS₂ nanocomposite there was no noticeable difference, whereas for the 0.5 wt.% and 1.0 wt.% nanocomposites T_i increased by almost 10 °C and 20 °C, respectively, as shown in Fig. 2, which is very important for PHBV with its narrow processing window. The temperature at which thermal degradation achieves its maximum rate (T') also occurred at higher temperatures for the 0.5 and 1.0 wt.% nanocomposites. However, this trend was not observed for the reported poly(3-hydroxybutyrate) (PHB)/INT WS₂ nanocomposites by varying the INT WS₂ concentration [44]. The addition of INT WS₂ had no influence on the thermal stability of PHB matrix. Therefore, the noticeable degradation temperature increment observed in the PHBV copolyester could be attributed to a remarkable stabilization effect induced by the strong adhesion and homogenous dispersion of the INTs within the matrix, combined with the steric effect of HV units in the PHBV/INT WS₂ systems. Consequently, the presence of

Fig. 2. TGA curves of PHBV and PHBV/INT-WS₂ nanocomposite systems in air.

INT WS₂ and HV effectively hinders the diffusion of degradation products from the bulk of the polymer to the gas phase, hence slowing down the decomposition process.

3.3. Non isothermal crystallization behavior

In semicrystalline polymers, the crystallization behavior governs not only the crystalline structure and morphology, but also the final mechanical properties of the material. PHBV is a semi crystalline polymer that can crystallize from either molten or glassy states, corresponding to melt crystallization and cold crystallization, respectively. The widespread industrial use of PHBV as a biodegradable material is mostly limited by its slow crystalline transformation. Therefore, if poly(hydroxybutyrate co hydroxyvalerate) based plastics are to be exploited in the market place as eco friendly and biologically apt materials, a comprehensive understanding of the kinetics of non isothermal (dynamic) crystallization, i.e. crystallization rate, crystal structure, nucleation activity, effective energy barrier, etc., is of significant importance.

As underlined in the experimental section, an unfilled PHBV control sample and INT filled nanocomposites with three different compositions were tested under six nonisothermal conditions from 180 °C to 40 °C at ϕ ranging from 2 to 25 °C min⁻¹, corresponding to temperature variations commonly found in thermoplastic fabrication setups. For all samples, the slower cooling rates showed higher crystallization peak temperatures (T_p) and inversely, faster cooling rates showed lower T_p . For example, cooling from the melt at ϕ 25 °C min⁻¹, $T_{p, \text{PHBV}}$ 76.5 °C and, at ϕ 2 °C min⁻¹, $T_{p, \text{PHBV}}$ 102.4 °C. The DSC cooling curves corresponding to these and other ϕ for unfilled PHBV are shown in Fig. 3a. As expected, at slower ϕ more time was available for polymer chain reorganization, the initiation of homogeneous nucleation, and subsequent chain growth into crystalline domains. On the contrary, at faster ϕ from the molten state macromolecular chain mobility was rapidly impeded with insufficient time for the polymer chains to organize into crystalline domains, thereby shifting the entire crystallization process to lower temperatures, as observed in the DSC cooling curves. Fig. 3b–d show the DSC cooling curves obtained from PHBV/INT WS₂ nanocomposite systems at the same ϕ tested in the neat PHBV. It can be observed that the addition of as little as 0.1 wt.% INT WS₂ generates a significant shift to higher temperatures of T_p for all cooling rates, Fig. 3b. At higher INT WS₂ concentrations the values of T_p continued to increase, tending to plateau at the highest concentration of 1.0 wt.%. For example, at ϕ 10 °C min⁻¹, $T_{p, \text{PHBV}}$ 88.0 °C, $T_{p, 0.1 \text{ wt. \%}}$ 100.4 °C, $T_{p, 0.5 \text{ wt. \%}}$ 108.0 °C, and $T_{p, 1.0 \text{ wt. \%}}$ 110.0 °C.

Fig. 3. DSC thermograms for non-isothermal crystallization of (a) PHBV and with PHBV/INT-WS₂ nanocomposites of (b) 0.1, (c) 0.5, and (d) 1.0 wt.% of INT-WS₂ at indicated cooling rates.

0.5 wt.% 107.4 °C, and T_p , 1.0 wt.% 112.4 °C. Thus, the addition of INT WS₂ had a remarkable heterogeneous nucleation capacity for accelerating the crystallization process of PHBV by providing stable nucleation platforms not observed in the control sample at higher temperatures. The data supports that both independent variables (cooling rates and INT WS₂ concentrations) were responsible for the observed variations in T_p . This observation is quite reproducible for nanocomposites crystallized at different cooling rates (Table 1). Fig. 4 compares the T_p values observed for the PHBV/INT WS₂ nanocomposites with those of PHB containing similar amounts of inorganic nanotubes. The data clearly shows that the addition of INT WS₂ plays a remarkable role in accelerating the crystallization rate of PHBV. Nevertheless, for the same nanofiller loading, the improvements in T_p for the PHBV based samples are lower than those observed for the corresponding binary PHB INTs composites [44]. This may attributed to the steric effect of ethyl side chain of HV units for the PHBV polymer crystallization.

The dependence of crystallinity $(1 - \lambda)_c$ of PHBV and its INT nanocomposites, shown in Table 1 both as a function of ϕ and INT concentration, almost mirrors the T_p trends previously mentioned, and is expected because at slower ϕ the polymer chains have more time to organize into crystalline domains with fewer defects, and thus higher $(1 - \lambda)_c$. The addition of INT WS₂ showed a similar trend as a function of ϕ but a much higher $(1 - \lambda)_c$ was observed as a result of earlier nucleation at higher temperatures where higher mobility facilitates chain entry into crystalline domains. Thus, very large increments in crystallinity were observed between the neat polymer and the nanocomposites, shown in Table 1 along with other dynamic crystallization data and results. In the same way, Fig. 5 compares the $(1 - \lambda)_c$ values observed for the PHBV/INT WS₂ nanocomposites with those of PHB containing similar amounts of inorganic nanotubes. In contrast to the results shown in Fig. 4, for the same nanofiller loading, the improvements in $(1 - \lambda)_c$ for the PHBV based samples are higher than those observed for the corresponding binary PHB INT composites [44].

Fig. 4. Comparison of the crystallization temperature (T_p) of PHBV and PHB [44] nanocomposites with INT-WS₂ content at indicated cooling rates.

Fig. 5. Comparison of the crystallinity $(1 - \lambda)_c$ of PHBV and PHB [44] nanocomposites with INT-WS₂ content at indicated cooling rates.

Table 1
Non-isothermal crystallization parameters for PHBV/INT-WS₂ nanocomposites.

INT-WS ₂ (wt.%)	ϕ (°C min ⁻¹)	T_p (°C)	$(1 - \lambda)_c$ (%)	ϕ^a ($0 \leq \phi \leq 1$)	ΔE^b (kJ mol ⁻¹)
0.0	2	102.4	43.8	1.00	-114.3
	5	94.1	42.5		
	10	88.0	41.4		
	15	84.1	38.7		
	20	79.9	36.4		
0.1	25	76.5	34.5	0.64	-235.4
	2	108.1	52.1		
	5	104.4	52.5		
	10	100.4	50.3		
	15	98.8	48.2		
0.5	20	97.0	46.9	0.49	-271.4
	25	95.2	45.3		
	2	113.1	54.8		
	5	110.7	54.3		
	10	107.4	52.4		
1.0	15	105.7	50.9	0.44	-163.2
	20	103.9	48.8		
	25	101.7	46.4		
	2	122.4	62.6		
	5	117.3	57.2		
	10	112.4	55.1		
	15	109.2	52.4		
	20	106.1	50.1		
	25	102.3	47.8		

^a Nucleation activity (ϕ) calculated with Dobrev-Gutzow equation.

^b Effective energy barrier (ΔE) calculated with Kissinger equation.

3.4. Nucleation activity

Dobrev and Gutzow [47,48] suggested a simple method for calculating the nucleation activity of foreign substrates in polymer melts. Nucleation activity (ϕ) is a factor by which the work of three dimensional nucleation decreases with the addition of a foreign substrate. If the foreign substrate is extremely active, ϕ approaches 0, while for inert particles, ϕ approaches 1. The nucleation activity (ϕ) of the INT WS₂ at various nanofiller concentrations was determined by the ratio:

$$\phi = \frac{B^*}{B} \quad (2)$$

where B is a parameter for the pristine polymer, and B^* is for the polymer/nucleator system. B and B^* can both be experimentally determined from the slope of the following equation:

$$\ln \phi = A - \frac{B(\text{or } B^*)}{\Delta T_p^2} \quad (3)$$

where ϕ is the cooling rate, A is a constant, ΔT_p is the supercooling ($T_m - T_p$), T_m is the melting temperature (data not shown) and T_p is the crystallization peak temperature. A linear relationship was obtained for each sample, Fig. 6. The values of B and B^* are obtained from the slope of the fitted lines, and the ϕ calculated from this ratio. Values of $\phi = 0.64, 0.48$, and 0.44 were obtained for the 0.1, 0.5, and 1.0 wt.% nanocomposites, respectively (Table 1). The nanocomposite with the lowest concentration (0.1 wt.%) presented a much lower value of ϕ than that of pure PHBV ($\phi = 1$), showing that INT WS₂ effectively contribute to the nucleation of PHBV, and higher concentrations showed even lower values of ϕ although tended to asymptote. These results demonstrate the excellent nucleating effect of INT WS₂ on the crystallization of PHBV. In order to put this into perspective the nucleating capacity of INT WS₂ was compared with that of other PHBV based composite materials reported in the literature incorporating nucleating agents (NA) for PHBV, such as carbon nanotubes, halloysite nanotubes, etc. where the nanosized fillers were shown to have the added advantage of acting as reinforcements for the polymer. Since the intrinsic properties of the different PHBV copolyesters employed in the reported studies (such as molecular weight and HV content) varied, the increment of crystallization peak temperature, ΔT between that of the neat polymer and the composite materials, defined as

Fig. 6. Dobrev-Gutzow plots for PHBV/INT-WS₂ nanocomposites.

Fig. 7. Increment of T_p for various fillers studied to improve the crystallization of PHBV.

$\Delta T = T_{p, \text{PHBV+NA}} - T_{p, \text{PHBV}}$, was calculated, allowing a direct comparison. In all cases, ΔT was at a common rate of $\phi = 10^\circ \text{C min}^{-1}$. From the results in Fig. 7, incorporating 1.0 wt.% INT WS₂ effectively increased the peak crystallization temperature to a value comparable to that of BN, and greater than all other NAs. BN is currently estimated to be more expensive than INT WS₂ and, like talc, is not a nanoparticle filler, also possibly leading to deficient mechanical reinforcement qualities that are observed with other nano sized filler materials [20]. Also noteworthy, MWCNT filled PHBV [23] showed an appreciable ΔT but the nanotubes were chemically modified to incorporate carboxyl group tails on the nanotube surface to reduce surface tension for better dispersion within the PHBV matrix. Non modified MWCNT [24] showed a low ΔT attributed due to poorer dispersion, as mentioned before. Whilst the available literature on NA for PHBV is relatively limited, the data presented here shows that INT WS₂ is one of the best alternatives currently available.

3.5. Effective energy barrier

Another common correlation used in the characterization of the non isothermal crystallization behavior is the effective (or activation) energy barrier (ΔE). This describes macromolecular chain mobility and crystal growth ability of a polymer during the crystallization process from the Kissinger equation [49] using crystallization peak temperatures T_p for given cooling rates, ϕ :

Fig. 8. Kissinger plots for PHBV/INT-WS₂ nanocomposites.

$$\ln\left(\frac{\phi}{T_p^2}\right) = \text{Constant} - \frac{\Delta E}{RT_p} \quad (4)$$

where ΔE is the effective energy barrier and R is the universal gas constant. The activation energies for the four samples were calculated by plotting $\ln(\phi/T_p^2)$ against $1/T_p$ to generate the linear slopes of $\Delta E/R$ shown in Fig. 8 (data in Table 1). The resulting slopes indicated that all nanocomposites presented lower energies than that of the neat sample. Thus, ΔE of the neat polymer is about $114.3 \text{ kJ mol}^{-1}$ and decreases by 106%, 137%, and 43% upon addition of 0.1, 0.5 and 1.0 wt.% INT WS₂, respectively (i.e.

$\Delta E_{0.1 \text{ wt.\%}} = 235.4 \text{ kJ mol}^{-1}$, $\Delta E_{0.5 \text{ wt.\%}} = 271.4 \text{ kJ mol}^{-1}$ and $\Delta E_{1.0 \text{ wt.\%}} = 163.2 \text{ kJ mol}^{-1}$), suggesting that INT WS₂ facilitated molecular chain transport on the growing crystal surfaces. The increase in the apparent ΔE in the 1.0 wt.% nanocomposite with respect to the lower concentration samples indicates that any restriction of molecular mobility of PHBV chains through volume does not appear to be a limiting factor on the crystallization rate, and since the T_p for this composition appears at higher temperatures, it further demonstrates that the nucleation activity of these inorganic nanotubes plays a dominant role in accelerating the crystallization process of PHBV. The reduction of the ΔE obtained in this work are lower than those observed for the corresponding binary PHB INT composites ($\Delta E_{\text{PHB}} = 76 \text{ kJ mol}^{-1}$,

Fig. 9. WAXS diffractograms of neat PHBV and PHBV/INT-WS₂ (1.0 wt.%) obtained during cooling from the melt to room temperature and subsequent heating.

$\Delta E_{0.1 \text{ wt.}\%}$ 232 kJ mol⁻¹, $\Delta E_{0.5 \text{ wt.}\%}$ 225 kJ mol⁻¹ and $\Delta E_{1.0 \text{ wt.}\%}$ 200 kJ mol⁻¹) [44].

3.6. Crystal structure and morphology

Wide angle X ray diffraction (WAXS) measurements were made to determine whether the addition of INT WS₂ affects the crystal form of the PHBV, and the evolution of the crystal structure during crystallization and melting was investigated in a temperature controlled chamber, with cooling and heating rates of approximately 7 °C min⁻¹, close to the values of ϕ in the DSC experiments. Fig. 9 presents representative WAXS diffractograms obtained during crystallization and subsequent melting for neat PHBV and a nanocomposite with 1.0 wt.% INT WS₂. For both the neat PHBV and the PHBV/INT WS₂ (1.0 wt.%) samples it can be seen that the

crystalline structure developed was identical, with diffraction peaks at 2θ 13.4°, 16.8°, 20.1°, 21.5°, 22.5°, 25.5°, 27.2°, the first two being the most intense corresponding to planes (020) and (110), in respective order, characteristic of orthorhombic PHBV crystalline α type structure [8,50]. The nanocomposite sample presented an additional diffraction peak at 14.2°, which corresponds to the (002) plane of the inorganic nanotubes [30]. On the other hand, the pure PHBV crystallized at around 90–100 °C, in close agreement with the DSC results (i.e. at ϕ 5 °C min⁻¹, $T_{p, \text{PHBV}}$ 94.1 °C). Similarly, the WAXS data also confirms crystallization onset at higher temperatures for the 1.0 wt.% sample compared to neat PHBV.

In addition to the above WAXS observation, polarized optical microscopy (POM) was used to visually examine the crystalline morphology of PHBV and the nanocomposites, in particular their

Fig. 10. POM images of PHBV under dynamic crystallization rates of (a) 10 °C min⁻¹ and (b) 2 °C min⁻¹. PHBV/INT-WS₂ (0.1 wt.%) under dynamic crystallization rates of (c) 10 °C min⁻¹ and (d) 2 °C min⁻¹. Images (e) and (f) are the 0.5 wt.% and 1.0 wt.% nanocomposites, respectively, under crystallization conditions of 10 °C min⁻¹. Scale bars 100 μm.

spherulitic structure. Under dynamic crystallization conditions, neat PHBV and (particularly) the 0.1 wt.% samples showed ring banded spherulites with concentric bands and Maltese crosses after cooling to room temperature at 10 and 2 °C min⁻¹ as shown in Fig. 10. The observed ring bands are thought to originate from either stress induced twisting [51–53] or other non lamellar twisting phenomena [54]. However, the increase of concentration of INT WS₂ (0.5 and 1.0 wt.%) clearly disturbed spherulite formation, possibly due to the dramatic increase of the nucleation density and faster crystal formation of PHBV, which were consistent with the DSC results in the previous section.

4. Conclusions

In the present work, a series of biopolymer PHBV/INT WS₂ nanocomposites have been successfully prepared at various INT WS₂ loadings ranging from 0.1 to 1.0 wt.%, without the use of surface modifiers. The non isothermal crystallization behavior and kinetics were studied, and the results demonstrated that the INT WS₂ content are very efficient factors for controlling overall crystallization rate and crystallinity of PHBV. Compared to those of neat PHBV, the crystallization rate and the nucleation density of PHBV matrix of the composites were improved remarkably due to a strong heterogeneous nucleating effect of INT WS₂ in the matrix. Nevertheless, for the same nanofiller loading, the improvements in T_p for the PHBV based samples are lower than those observed for the corresponding binary PHB INT nanocomposites. This may be attributed to the steric effect of ethyl side chain of HV units for the PHBV polymer crystallization. The well dispersed INT WS₂ nanoparticles in the nanocomposites enhanced the nucleation capacity and crystallinity of PHBV matrix without altering its crystal structure. The nucleation activity of INT WS₂ plays a crucial role in accelerating the crystallization rate of PHBV, reducing the effective barrier energy compared to neat PHBV. In particular, it was shown that INT WS₂ exhibits a much more prominent nucleation activity on the crystallization of PHBV than other possible nucleating agents or nano sized fillers. More importantly, these nanocomposites also show strong improvement in the thermal stability in comparison to those of PHB containing similar amounts of inorganic nanotubes. These features may be advantageous for the enhancement of the mechanical properties and processability of PHBV based materials. The good thermal properties and desired morphology obtained by incorporating INT WS₂ in PHBV can enhance its use as a low cost renewable and environmentally friendly biopolymer material for many applications.

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