

Influence of Processing Conditions on Morphological, Thermal and Degradative Behavior of Nanocomposites Based on Plasticized Poly(3-hydroxybutyrate) and Organo-Modified Clay

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Abstract The effect of processing conditions (casting and extrusion) and plasticization on the disintegrability in compost of organically modified clay poly(3-hydroxybutyrate) nanocomposites was studied. Tributylhexadecylphosphonium bromide (TBHP) was used as organic modifier. As revealed by WAXS and TEM observations, intercalated nanobiocomposites with clay stacks and some individually dispersed platelets were obtained. The melting temperature of the neat PHB diminished with the addition of plasticizer, thus broadening the processing window. Biodegradation test revealed that while the clay slows down the degradation rate, the plasticizer increases the degradation of the samples, reaching a similar final percentage of disintegrability when both plasticizer and clay were added in the formulation.

Keywords Poly(3-hydroxybutyrate) · Nanoclay · Plasticizer · Nanocomposites · Disintegrability compost

Introduction

Poly(3-hydroxybutyrate) (PHB), which is biosynthesized by a wide variety of bacteria, is a biodegradable thermoplastic with biocompatibility and ecological safety [1, 2]. Therefore, it has great potential in applications such as surgical sutures, long-term carriers for drugs [3], and degradable plastics. PHB is completely biodegradable in the environment and can be extruded, molded and spun using conventional plastic processing equipment [4, 5]. These features make this polymer an ideal candidate for the production of biodegradable packaging materials and other disposable articles. However, the industrial scale production of PHB is hindered by roadblocks. At first, thermal processing is challenging because of its relative low decomposition temperature near its melting point, pronounced brittleness, very low deformability and susceptibility to a rapid thermal degradation. Furthermore, the current production cost of PHB is high when compared to other high-volume synthetic plastics. PHB slow crystallization rates also lead to tacky products (e.g. fibers, films, etc.) [6]. In addition, this material shows poor thermal stability at temperature just above the melting point (thermo-mechanical degradation of polyhydroxyalkanoates (PHAs) occurs rapidly at temperatures close to the melting point). Consequently the melt flow index changes rapidly with time and its volatile decomposition products need to be handled safely. During the mechanical processing in the molten state, such as those carried out in internal mixers and twin-screw extruders, the polymers are subjected to relatively high temperatures, shear stresses, and pressures, which could cause thermal degradation reactions. Various approaches, such as the use of nucleating agents, plasticizers and agents that promote crystallization of the polymer, modification of the polymer structure, blending [7], have been carried out to overcome

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the processing and product difficulties [5, 8, 9]. These drawbacks in PHB can be overcome by internal or external plasticization to improve impact strength, elongation at break and ductility. Plasticizers for PHB should preferably also be biodegradable, because in case of packaging formed by different components, the packaging as a whole should result compostable. For food packaging and hygiene applications, only non-toxic substances can be considered as plasticizers. Citrate plasticizers are derived from naturally occurring citric acid. Acetyl tributyl citrate (ATBC) has been found to be one of the best indicated plasticizers for polymers for biomedical and biodegradable applications, and is known to bring good performances when added to the PHAs [10–13] and PHAs blends [14, 15]. The literature reports also the use of plasticizers that are cheap and readily available materials on the market, such as dodecanol, lauric acid, tributyrin, and trilaurin [16]. Besides, the combined use of a plasticizer and a nanofiller in biodegradable polymers like PHAs seem to be a good answer, since hybrid systems based on nanoclays (e.g., montmorillonite) have raised great interest in recent years especially due to the resulting enhancement of material properties [17]. However, the conventional and most efficient surfactants (quaternary ammonium salts), used to organomodify the nanoclays, could dramatically enhance in certain cases the PHB degradation in the molten state at high temperature or its degradation in composting conditions [18]. In addition, it has to be considered that the introduction of low molecular weight additives has also a visible effect on the biodegradation of poly(3-hydroxybutyrate) materials [19] since biodegradation is influenced by several factors including the crystallinity and hydrophobicity of the material, dispersion, antimicrobial and acid properties of the fillers. Recently, some authors reported a very promising study about the addition of plasticizer (ATBC) to poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV) nano-biocomposites with organo-modified montmorillonite (OMMT) clay (PHBV/OMMT) [20]. In this study, the authors observed that the addition of plasticizer causes a decrease of the PHBV biodegradation process, while on the other hand, the nanofiller was responsible for a significant enhancement in the biodegradation one, by acting as a prong and trap for the water molecules, promoting biotic and abiotic degradation of the polymer. On the basis of these previous results, it is clear that the modification in the polyhydroxyalkanoate biodegradation rate strongly depends on the predominance attributed to each phenomenon.

To the best of our knowledge, no examples of research papers are present in the literature about the effect of both processing conditions and plasticization on the disintegrability in compost of organically modified clay poly(3-hydroxybutyrate) nanocomposites. According to this, in the present work, we aimed to clarify the synergic effect of

plasticizer and modified nanoparticles in the case of extruded and/or solvent cast formulations, on morphology and thermal properties of the obtained materials. Moreover, the effect of tributylhexadecylphosphonium bromide clay modification, combined with the presence of tributyrin, on the disintegration pattern of PHB (obtained by extrusion or casting in chloroform) was investigated.

Experimental Part

Materials

Poly(3-hydroxybutyrate) (PHB) (kindly supplied by PHB Industrial S. A., Brazil) with a molecular weight of $M_n = 240.000$ g/mol was used as polymeric host. Tributyrin (TBL) was employed as plasticizer of polymeric matrix. Montmorillonite (Cloisite® Na⁺) with a cation exchange capacity (CEC) of 92.6 meq/100 g clay was supplied by Southern Clay Products (Texas, USA). Tributylhexadecylphosphonium bromide (TBHP) organic modifier was purchased from Aldrich and used as received. Other solvents were purified by conventional drying and distillation procedures.

Clay Preparation: Acid Activation and Ion Exchange

The montmorillonite was first activated by treatment with mineral acid, and then it was further modified by cationic exchange reaction with TBHP. Activation treatment: 5 g of montmorillonite was dispersed in 200 mL of water. Then 10 mL of H₂SO₄ were added and stirred at room temperature during 6 h, yielding a stable colloid due to increased hydrophilicity. The dispersion was centrifuged and the activated clay (supernatant) was separated. The clay was washed by 30 mL of distilled water, then stirred and centrifuged at 10.500 rpm during 10 min (in triplicate). Finally, the clay was lyophilized for 72 h.

Cation exchange: A 2.5 g sample of activated clay was dispersed in 100 mL of distilled water and 1.1 g of tributylhexadecylphosphonium bromide (TBHP) was added. The dispersion was kept under stirring at the temperature of 70 °C for 4 h. The clay was then filtered and washed several times with distilled water until no more trace of TBHP was found by FTIR analysis of the filtrate. Finally, the exchanged clay was dispersed in ethanol and dried in an oven at 80 °C for 24 h. This clay was denoted as MAI which has a basal interlayer distance of 2.05 Å and an organic content of 22.9 % (calculated by means of TGA experiment) [21].

Sample Preparation

Melt Processing

Samples containing 22 wt% of plasticizer (PHB/TBL Ext) and 22 wt% of plasticizer + 4 wt% MAI (PHB/TBL/4MAI Ext), were extruded by using a DSM Research micro 15 twin screw extruder, having a volume of 15 mL with three heating zones (the % of plasticizer was selected as the optimum, on the basis of previous investigation). All formulations were recirculated in the extruder channel for 2 min. The billets of material were cut into small pellets. A twin screw rate of 50 rpm and a temperature profile of 170–175–180 °C were used during the process. All the samples were prepared under inert atmosphere under a nitrogen gas flow. The pellets obtained by microextrusion were then pressed at 190 °C under a pressure of 50 bars during 3 min in a Dragon Press, and films of 150 µm in thickness were molded using, as template, an aluminium square of 10 cm × 10 cm.

Casting Processing

Films with the same formulations were obtained by casting process. A homogeneous solution of PHB/plasticizer in chloroform was prepared by stirring at 450 rpm while heating at 60 °C for 15 min. Then the solution was placed on a glass Petri dish and it was allowed to evaporate at room temperature (PHB–TBL cast). Nanocomposites were prepared by the addition of clay containing chloroform solution, previously sonicated, to the PHB (PHB/4MAI cast) or PHB/plasticizer solution (PHB/TBL/4MAI cast). Thereafter, the same procedure to obtain the neat PHB films was applied. All films were stored in a desiccator at room temperature for 30 days to allow complete crystallization of PHB. The final thickness of PHB and PHB based nanocomposite films were 0.05 mm. The compositions of the produced films are reported in Table 1.

Table 1 Materials formulation

Materials	PHB (wt%)	TBL (wt%)	MAI (wt%)
PHB	100	0	0
PHB/4MAI cast	96	0	4
PHB/TBL cast	78	22	0
PHB/TBL/4MAI cast	74	22	4
PHB/TBL ext	78	22	0
PHB/TBL/4MAI ext	74	22	4

Characterization Methods

X-Ray Diffraction (XRD)

The analyses at low angles of the composites were done using a X-Pert diffractometer (40 kV and 40 mA) at 2°/min with a radiation of CuK_α ($\lambda = 1.54 \text{ \AA}$), in the 1.5°–35° range. The Wide Angle X-ray Scattering analyses were carried out at room temperature in transmission mode. The CuK_α radiation ($\lambda = 1.54 \text{ \AA}$) was generated by a Genix microsource (Xenocs, France) and collimated and monochromatized by a FOX2D-12Inf optic (Xenocs, France). WAXS patterns were recorded on a CCD detector (Photonic Sciences). Standard corrections were applied to the WAXS patterns before their treatments. The intensity profiles were obtained by 360° azimuthally integration of the 2D WAXS patterns using the fit 2D software®.

Transmission Electron Microscopy (TEM)

Transmission electron microscopy (TEM) observations have been carried out on a FEI Tecnai G2-20 apparatus equipped with a LaB6 filament. About 90 nm thin slices have been prepared from the bulk samples using a Leica ultramicrotome at −30 °C. The TEM bright field micrographs were recorded under an acceleration voltage of 200 kV.

Differential Scanning Calorimetry (DSC)

DSC was performed on a Pyris Diamond apparatus from Perkin Elmer. The first heating run was made from ambient temperature to 195 °C, at a rate of 10 °C/min. Then, the samples were cooled up to −50 °C at a rate of 80 °C/min, and a second heating run was carried out at a rate of 10 °C/min from −50 to 195 °C. The temperature and heat flow were calibrated using a high purity indium and zinc samples according to standard procedures. The overall crystallinity was calculated according to the following Eq. 1:

$$X_c(\%) = \frac{\Delta H_m \cdot (m_c/m_p)}{\Delta H_0} \cdot 100 \quad (1)$$

where ΔH_m is the melting enthalpy measured from heating experiments, ΔH_0 is the theoretical enthalpy of 100 % crystalline PHB ($\Delta H_0 = 146 \text{ J/g}$) [22], m_c is the nanocomposite weight and m_p is the weight of PHB in the plasticized sample or in the nanocomposite.

Thermogravimetric Analysis (TGA)

Thermal degradation measurements were carried out using a Seiko Exstar 6300 TGA/DTA system under nitrogen atmosphere (flow rate 250 ml/min). Temperature programs

were run from 20 to 600 °C at 10 °C/min heating rate. The sample weight in each run was approximately 10 mg.

Disintegrability in Composting Conditions

Disintegrability of neat PHB and PHB composite films was observed by means of a disintegration test in composting conditions according to the ISO 20200 standard. A specific quantity of compost inoculum, supplied by Gesenu S.p.a., was mixed with the synthetic biowaste and certain amount of sawdust, rabbit food, starch, sugar, oil, and urea. The water content of the substrate was around 50 wt% and the aerobic conditions were guaranteed by mixing it softly. The samples cut to have approximately $15 \times 15 \times 0.05 \text{ mm}^3$ (casting) and $15 \times 15 \times 0.15 \text{ mm}^3$ (extrusion) specimens were then buried in perforated boxes, containing the prepared mix, and incubated at 58 °C. The samples were recovered at different disintegration steps, washed with distilled water, dried in oven at 37 °C for 24 h, and weighed. The disintegrability value was obtained normalizing the sample weight, at different stages of incubation, to the initial one.

Results and Discussion

Chemical and Structural Characterization

In order to analyze the dispersion degree of MAI in PHB matrix, X-ray measurements were performed (Fig. 1). A displacement of d_{001} peak to lower angles was observed in all the nanocomposites indicating a higher basal spacing of

clay in the polymer. The nanocomposite obtained by casting without plasticizer showed a d_{001} peak at $2\theta = 3.81^\circ$ corresponding to a basal spacing of 23.2 Å. Whereas, it was observed that the plasticized nanocomposite obtained by melt processing presents the d_{001} peak at 2.33° (37.9 Å), similar to that found for the nanocomposite with TBL obtained by casting. But, in the last, there is a greater spacing distribution because the peak was broader than that of the extruded film. Further, the second diffraction peak d_{002} is observed at $2\theta = 4.77^\circ$, which realizes the periodic system of the clay. So, an intercalated structure remains in the nanocomposites despite of the used processing method [23]. Crystal morphology of plasticized PHB was also studied in the samples obtained by both processing methods. Diffractograms appear almost superimposed so, no changes in the crystal morphology or in the degree of crystallinity of PHB with the addition of 4 wt% of MAI and TBL were observed. Figure 2 shows, as an example, the diffractograms of the extruded samples [24]. The X-ray diffraction (WAXD) patterns of PHB and its composites in the range 5° – 35° show 5 main peaks (centered at $2\theta = 13.6^\circ$, 16.7° , 22° , 25.4° and 27° , attributed to the 020, 110, 111, 121, and 040 planes respectively) and the presence of one peak (at 19.3° , attributed to the 021 plane). It can be seen that the diffraction peaks of pure PHB and PHB in presence of the clay were similar. Moreover, WAXS measurements revealed no change in the diffraction patterns of plasticized samples, as already observed in previous works [20, 25].

In order to further investigate the morphology of the composite and, in particular, the clay dispersion in the PHB

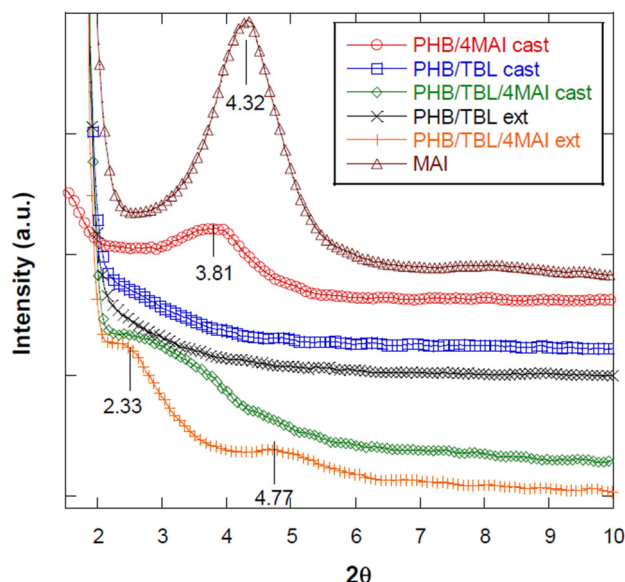


Fig. 1 XRD patterns of the clay, PHB and PHB nanocomposites

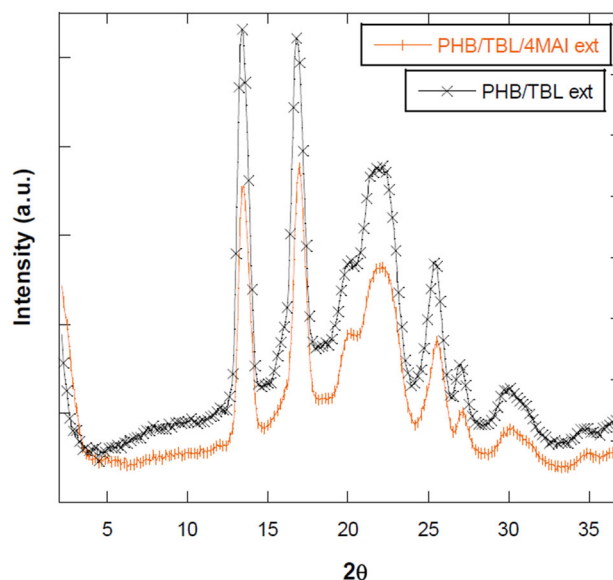


Fig. 2 WAXS curves of extruded plasticized PHB and PHB nanocomposite with MAI

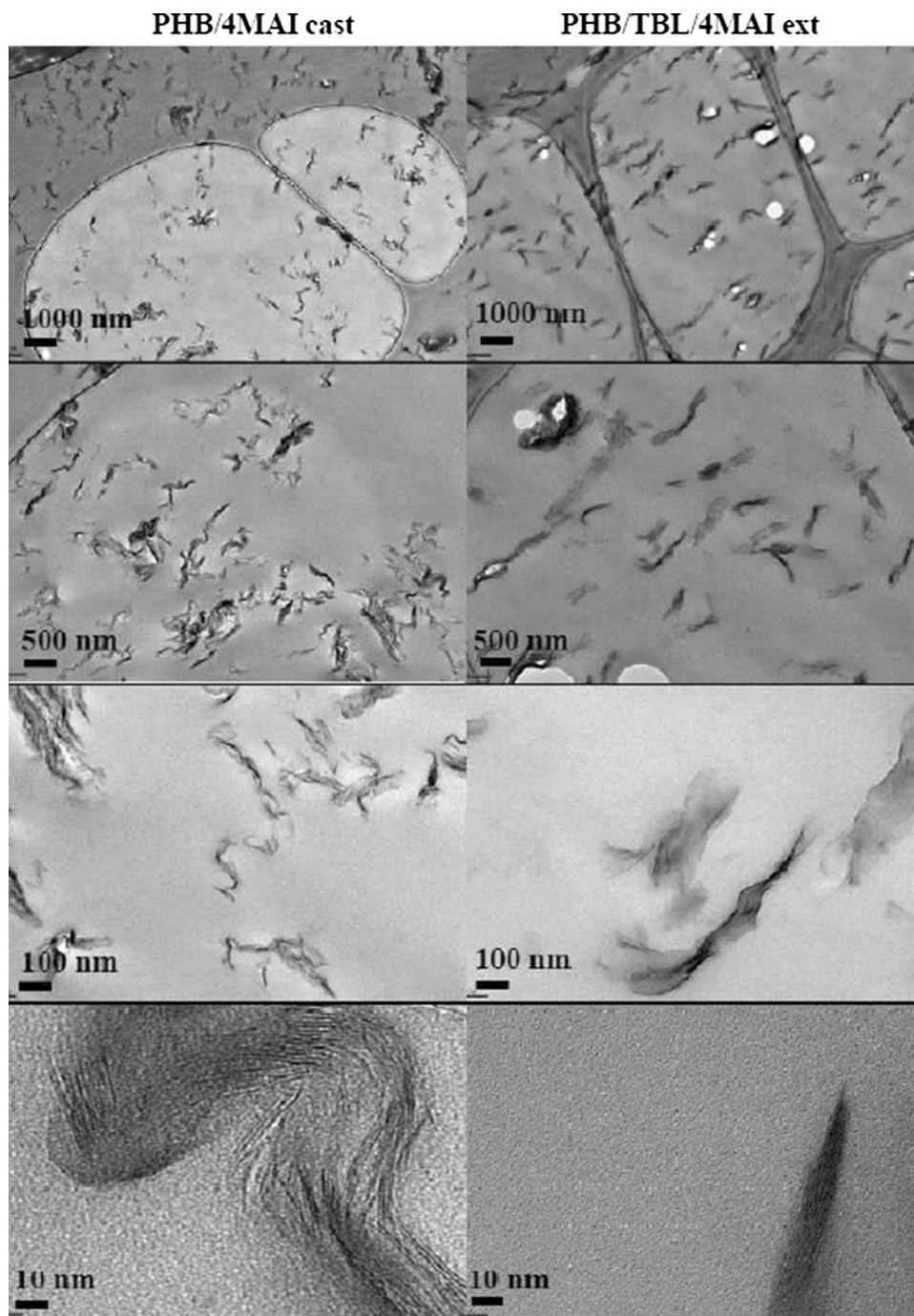
films, TEM analyses were also performed. Figure 3 shows that there was a good distribution of clay layers into the matrix. Further, a preferred orientation of the clay in the extruded samples, related to the processing phase, was observed. These images confirmed the results obtained by X-ray experiments, where an intercalated structure of the clay was found; the darker regions correspond to the inorganic fillers, with the formation of intercalated nanobiocomposites with clay stacks and some individually

dispersed platelets, attesting for partial clay exfoliation [20, 24].

Thermal Properties

DSC analyses of the samples were performed in order to determine the combined effect of the processing, plasticizer and clay presence on the thermal properties of PHB matrix. The results obtained for melting temperature, glass

Fig. 3 TEM micrographs of the MAI nanocomposite, produced by casting and melt processing



transition temperature and crystallinity of the materials are shown in Table 2. From the thermograms, it has been ascertained that the solvent was completely evaporated during the casting (Fig. 4a). For the determination of the glass transition temperature, a fast cooling of the molten sample was performed (to avoid recrystallization); after that, a second heating at 10 °C/min until melting, was performed. The addition of plasticizer decreased the T_g (Table 2), as expected, for the materials obtained by both processing methods. The TBL is a plasticizer with similar chemical structure and completely compatible with the polymer, and then lowers the glass transition temperature and the melting points in both processing conditions (Fig. 4a, b). As a consequence, the incorporation of TBL allows processing at lower temperature, avoiding thermal degradation. The observed glass transition temperatures are in line with the ones already observed in [19], in which PHB samples containing 23 wt% of TBL, obtained by casting in chloroform, showed a shift to lower temperature of T_g values, with respect of neat PHB, compatible with the decrease observed in our system. Furthermore, the T_g for the extruded systems was higher than that for systems obtained by casting, probably due to the loss of TBL during the melt process. This condition was confirmed by our TGA experiment (insert Fig. 5b), in which we revealed a reduced weight loss rate for extruded PHB/TBL with respect of cast PHB/TBL, due to a reduced amount of plasticizer present in the final product, still not critical for preparation of extruded plasticized PHB films. In addition, the plasticizer also caused a decrease in melting temperature. This decrease was also evidenced for the material containing both plasticizer and nanofiller. It has been observed that the melting temperature of the neat PHB (175.9 °C) diminished with the addition of plasticizer when the films were obtained by casting or melting processing. This behavior is due to the fact that the plasticizer favors the displacement of the chains with the temperature during the melting process. However, the clay addition did not significantly affects the melting temperature, nor the crystallinity, consistent with that found by WAXS. This is

probably due to the preferential location of the clay in the amorphous region [10].

In order to study the effect of the addition of the plasticizer and the clay MAI as well as the processing conditions on the thermal resistance of PHB, thermogravimetric analyses were carried out. The residual mass versus temperature curves of the materials (and their derivatives curves) are shown in Fig. 5a, b, respectively. A single drop in the residual mass was observed for the materials without TBL, indicating that the degradation process occurs in a single step [26]. In the materials with presence of TBL, two drops in the weight loss curve can be clearly seen, being the first loss due to the evaporation of TBL and the second related to PHB degradation [27].

The derivative curves of the residual mass versus temperature are reported in Fig. 5b. A shift to higher temperatures of the maximum degradation rate peak of PHB was clearly observed with the addition of MAI. Usually, it has been reported that the incorporation of clays in polymer matrix improves its thermal stability by acting as a heat barrier. The good dispersion of the clay platelets promotes the restriction in the mobility of the polymer chains and the formation of char during thermal decomposition [28, 29]. In the plasticized materials, the peak of maximum degradation rate of PHB slightly shifted to higher temperatures. The presence of TBL in the nanocomposites, completely miscible with PHB [19], would produce a dilution effect on the matrix, slowing the diffusion of the degradation products. The same behavior has been found on the crystallization of polypropylene from the melt, wherein the plasticizer retards the diffusion of the polymer chains, avoiding the nuclei formation [30]. On the other hand, it seems that the processing does not change significantly the thermal resistance. The decrease in molecular weight occurring during the melt processing would not affect the thermal degradation of the obtained materials [31, 32].

Disintegrability in Composting Conditions

Disintegrability in composting conditions was firstly evaluated by visual observation of the PHB and PHB

Table 2 Thermal properties from DSC analysis of the materials

Materials		1st scan				2nd scan	
		T_g (°C)	T_m (°C)	ΔH_m (kJ/mol)	Xc (%)	T_g (°C)	T_m (°C)
Melt extrusion	PHB/TBL ext	–	166.4	73.2	58.7	–24.7	165.7
	PHB/TBL/4MAI ext	–	167.1	69.2	59.9	–19.6	166.6
Solvent casting	PHB cast	–5.8	175.9	97.1	66.5	–2.5	174.5
	PHB/TBL cast	–	163.4	70.7	62.1	–30.2	163.5
	PHB/4MAI cast	–3.9	175.1	88.7	63.3	–	–
	PHB/TBL/4MAI cast	–	165.5	74.3	68.7	–28.4	164.9

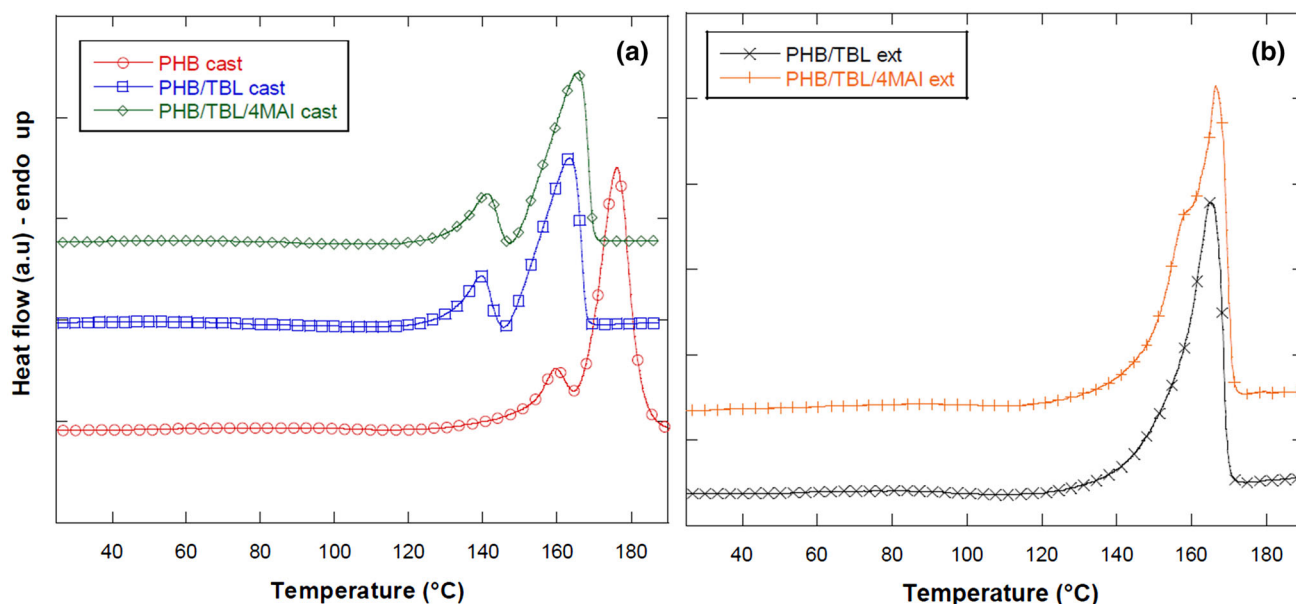


Fig. 4 DSC thermograms of PHB nanocomposite samples produced by casting (a) and melt processing (b)

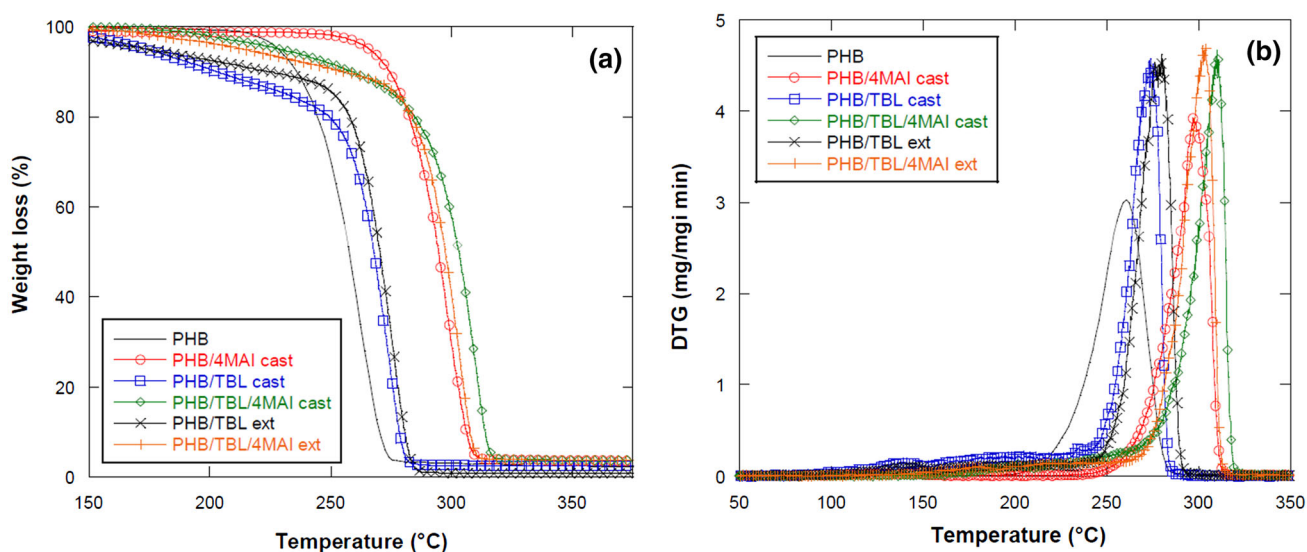


Fig. 5 Residual mass curves (a) and derivative curves vs temperature (b) of the PHB and PHB based nanocomposites produced by casting and melt processing

nanocomposites at different times of incubation. Figure 6 shows that all samples changed their color and became opaque after 7 days of incubation, while some of them exhibited a considerable surface deformation and fractures starting from 14 days in composting. This effect was more evident in the case of neat PHB after 14 days of incubation and in solvent cast materials in presence of plasticizer (PHB/TBL cast) and MAI (PHB/TBL/4MAI cast). The changes in sample color is a consequence of water absorption and/or presence of products formed by the hydrolytic process that induced a change in the refraction

index of the specimens [33]. Some authors reported that disintegrability under composting conditions starts in the amorphous phase, mostly attacked by microorganisms at the initial stage of this process and this effect is apparent by the loss of transparency in films after treatment [34, 35]. The visual observation highlighted also that cast samples were visibly disintegrated after 28 days, with exception of the clay containing sample (PHB/4MAI cast), while in the case of extruded materials only the sample containing the plasticizer (PHB/TBL ext) was still present at 35 days in compost, while the formulation containing both plasticizer

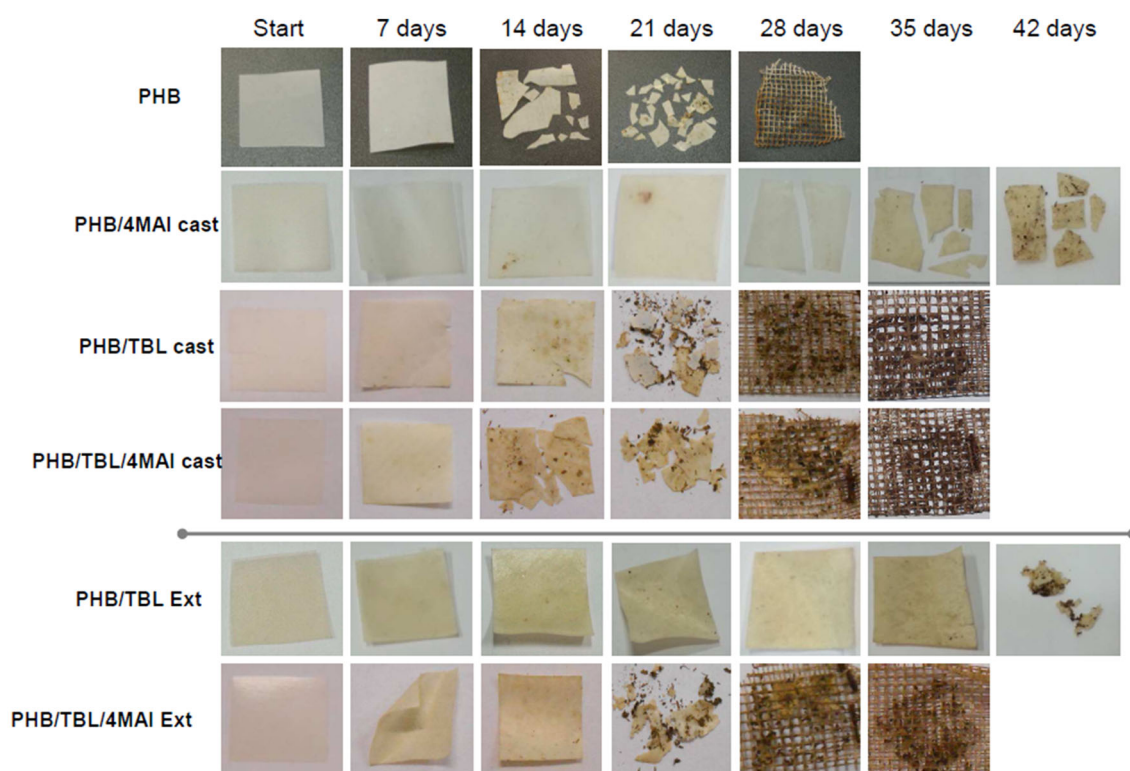


Fig. 6 PHB and PHB nanocomposites before (0 day) and after different stages of disintegration in compost at 58 °C

and clay (PHB/TBL/4MAI ext) showed a clear disintegration pattern even at 21 days. The results of visual observation seem to confirm, in general, that the introduction of the clay has a different effect in terms of disintegration of polymeric phase in the extruded or cast materials. During the initial phases of the disintegration,

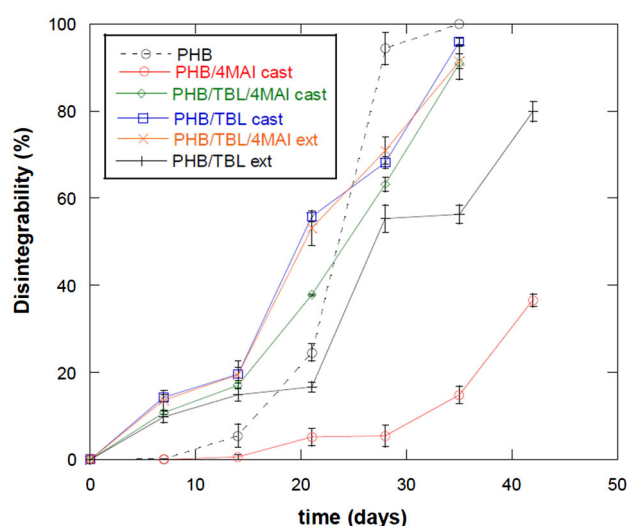


Fig. 7 Disintegrability values of PHB and PHB nanocomposites at different stages of incubation in compost

the high-molecular weight PHB chains are hydrolyzed to form lower molecular weight chains and this reaction can be delayed by the presence of organo-modified clays. They hinder the segmental motion of the PHB chains and the diffusion into the bulk of the film through a more tortuous path [36]. Moreover, the acid activated clay could attach to the cellular surface of bacteria, with resulting bacteria death [37, 38]. Since the crystallinity extents of the different formulated systems are similar, variations in the disintegration behavior should only result from the formulation and the resulting nanostructure differences, between the samples. It has been observed [39] that, in the case of plasticized PLA, the hydrophobic ATBC decreased the degradation rate compared with pure polyester, because of the increased hydrophobicity of the material. This is confirmed by the lower weight loss values observed when adding 20 wt% of plasticizer. On the other hand, in that case, the nano-filler was responsible for a significant enhancement in the biodegradation process. In our case, even if no substantial differences were detected in terms of crystallinity, as already observed by XRD, for extruded or solvent cast samples, the disintegration experiment confirmed that a different interaction of the plasticizer with the PHB matrix (and the resulting final morphology) could have induced a different bacterial attack on the surface of the materials. If the comparison is done between

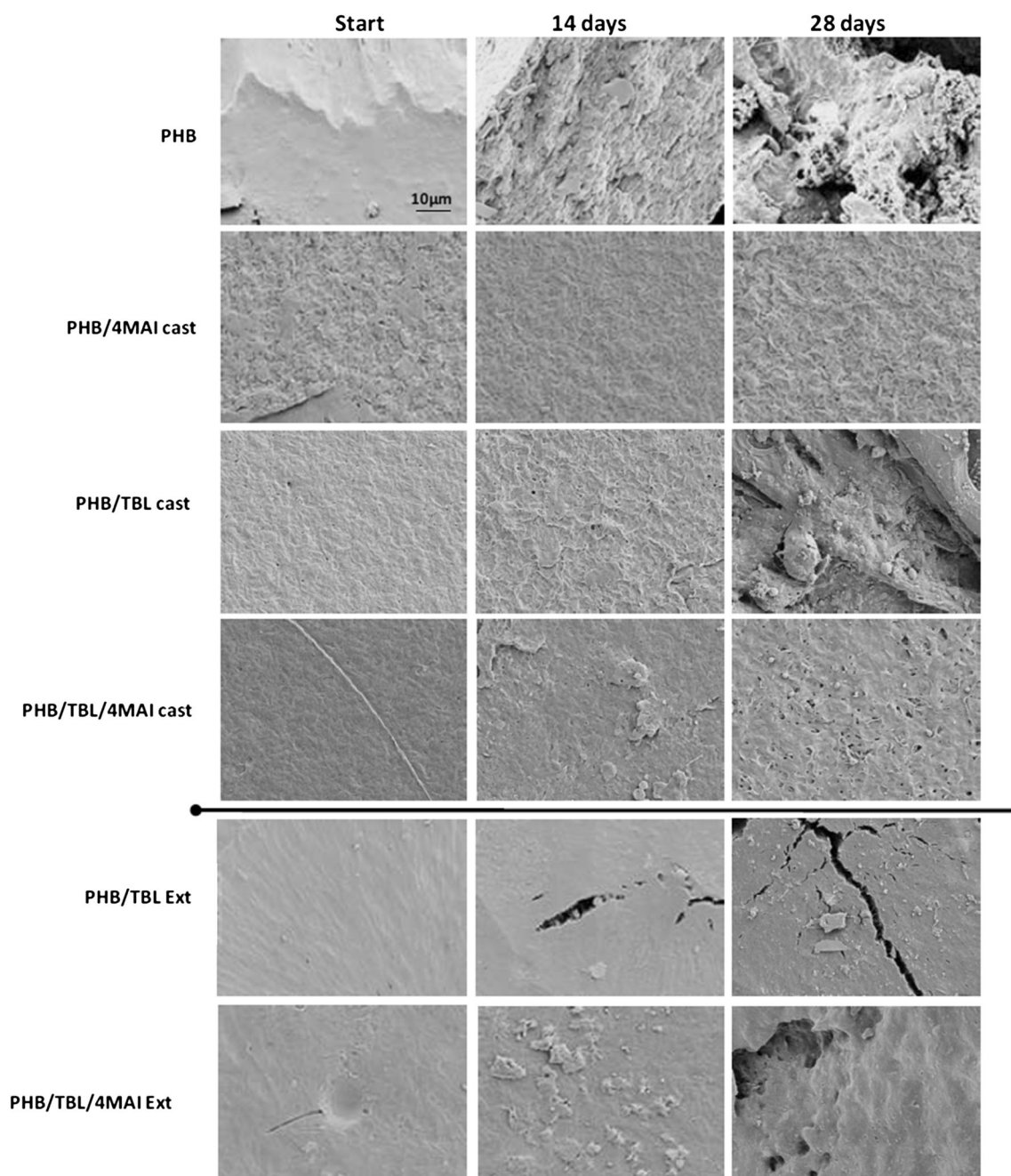


Fig. 8 FESEM images of PHB and PHB nanocomposites at different stages of incubation in compost

plasticized solvent cast PHB/TBL/4MAI cast and extruded PHB/TBL/4MAI ext at 14 days, it seems that the biodegradation have been delayed in the last one, but the whole disintegrability behavior of both samples was similar (Fig. 6).

The discussed results are confirmed by disintegrability values (Fig. 7) that remain nearly constant for all systems until 14 days of incubation, while a 25 % at 21 days and a 95 % at 28 days of disintegrability was detected for neat

PHB film. A different behavior is detected for all plasticized materials PHB nanocomposites, indifferently for extruded or cast materials, for which a similar mass loss, nearly 20 %, is detected only after 7 days (stable up to 14 days) principally due to the loss of plasticizer (being the mass loss, 22 %, almost coincident with the initial content of plasticizer). After that, while only the extruded sample PHB/TBL ext retains the weight loss, with all the other systems an increase in weight loss was detected with

similar final values, limited only in the case of PHB containing MAI that, as already observed, delayed the disintegration of the produced materials. The clay, in fact, is able to increase the barrier properties of PHB reducing the diffusion mechanism and delaying the disintegrability process [40].

The morphology of PHB films, retrieved regularly from the soil, was characterized by field emission scanning electron microscopy. It can be seen from the FESEM images (Fig. 8) that the surfaces of PHB films were smooth before degradation, while a higher surface roughness characterized the PHB nanocomposite films due to the presence of the plasticizer. After 14 days of composting, the surfaces of neat PHB film were eroded with an evident surface irregularity, while morphologies of PHB/TBL samples (that showed lower disintegration rate with respect of neat PHB after 28 days of composting) did not show significant surface erosion at the equivalent composting time. Only after 28 days, FESEM micrographs of the PHB/TBL system in composting conditions showed evident signs of surface erosion with deep fractures. The surface of the polymeric samples is progressively degraded by extracellular enzymes produced by fungi or other microorganisms in the incubation soil. The morphologies of the PHB samples exposed to biodegradation are not as homogeneous as the morphology of the pristine surface. Grooves, cracks and pores are observed for the biodegraded samples: in the case of extruded samples, the micrographs suggest that the biodegradation occurred in a layer-by-layer mode [41]. Moreover, the disintegration characteristics of the plasticized nano-biocomposites indicated that, while the addition of the plasticizer leads initially to an increase of the disintegration (evident variation at 28 days in the morphology of PHB/TBL cast), the presence of the nanofiller seems to stop the action of microorganisms (PHB/4MAI cast) [40]. Accordingly, the combined incorporation of the plasticizer and nanofiller into PHB caused, as an additive property, little change in the final morphology of degraded sample (PHB/TBL/4MAI cast). The order of disintegration rate determined from the FESEM analysis was in accord with the visual observation (Fig. 6) and disintegrability percentage (Fig. 7).

Conclusions

Intercalated nanocomposites were obtained by means of two types of processing (casting and extrusion) with the addition of plasticizer (tributyrin) and a modified clay with tributylhexadecylphosphonium bromide. The effect of plasticizer and modified nanoparticles in the case of extruded and/or casting samples on the disintegrability of the PHB was analysed. Plasticized samples begin to

biodegrade immediately on compost; however PHB and the nanocomposite with MAI start to degrade after 14 days. The sample containing only clay degraded slowly throughout the time period studied. Thus, it can be concluded that the clay slows degradation rate and the plasticizer accelerates the degradation of the samples. Then, the combined incorporation of the plasticizer and clay into PHB (in the percentage used in this work) caused a little change in the final percentage of disintegrability of PHB, and the retarding effect of the clay in the disintegration would be offset by the addition of plasticizer. While the clay increases the barrier properties of PHB, the plasticizer favors the diffusion mechanism into the bulk of the film, enhancing the degradation in compost.

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