



PHB and Montmorillonite Clay Composites as KNO_3 and NPK Support for a Controlled Release

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Abstract

In order to improve nutrient uptake by plants and at the same time decrease losses by leaching, polymeric compounds based on biodegradable poly(3-hydroxybutyrate) (PHB) and montmorillonite clay (MMt) were melt processed with KNO_3 and NPK fertilizers (Fert). We present a comprehensive analysis of releasing profile of the potassium (K^+), nitrogen (NH_4^+ and NO_3^-) and phosphorous (PO_4^{3-}) from PHB/MMt/fertilizer at 90/0/10, 50/0/50, 80/10/10, 40/10/50, 25/25/50 formulation. The amount and type of the fertilizer and the presence of clay delineated the release of the cations and anions from the matrix. Cations released faster than anions through MMt composites due to cations–MMt interactions and its diffusion through MMt phase. The nutrients delivery from composites was lower than pure fertilizer. Composites formulations with smaller amount of PHB and MMt (25 wt%) were enough to encapsulate the fertilizer and delay the ions releasing. Further, the simple method of preparation also attains the sustainability of the whole process.

Keywords Biodegradable polymer · Clay · Fertilizers · Controlled release · Thermal stability · Crystallinity · Composites

Introduction

Slow/controlled release fertilizer system is a way to delivery essential nutrient, such as potassium, nitrogen and phosphorus for plants, according to absorption curve of the culture [1, 2]. Polymer-based fertilizer releasing system is an area of increased interest seeking to protect the fertilizers availability from adverse environmental conditions by increasing their shelf-life and assure their health-promoting properties [3, 4]. Clays, silica, lignin and polymeric particles are used as the holder to fertilizer and other agrochemical products [5]. Clay minerals are hydrated layer silicates able to exchange cations and intercalate species between the interlayer regions. Pereira et al. [6]. prepared slow release fertilizer nanocomposite based on urea intercalation into montmorillonite clay by an extrusion process and observed a

slow urea release even for composites with 20 wt% of MMt. Biodegradable materials are specially suitable as carrier for fertilizers and other agrochemical products due to their low toxicity, high degradability in soil and controlled releasing capacity of active ingredient [7, 8]. Poly(hydroxybutyrate) (PHB) is a polymer produced by different types of microorganisms from sugarcane and molasses as intracellular storage materials [9]. PHB is fully biodegradable polyester with hydrophobic properties, low O_2 , CO_2 and H_2O permeability and high melting temperature and crystallinity [10–12]. The development of composites by incorporating low percentages of clay into a PHB matrix is known to improve properties such as ion exchange capacity, water absorption speed and mechanical resistance [1]. The higher surface area created for polymer/clay interaction compared with conventional composites enhances the thermal and oxidative barrier [13]. In a previous work Souza et al. [14] prepared composites based on PHB, starch, glycerol and montmorillonite clay (MMt) as carrier for KNO_3 and NPK. They observed PHB/starch compatibility and homogeneity increased in presence of MMt, KNO_3 and NPK. MMt–NPK particles were dispersed in the homogeneous and compatible polymeric phase while MMt– KNO_3 was set preferentially on the PHB phase.

In this way, the present study investigates the polymeric composite based on biodegradable polymers (PHB) and

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natural clay (montmorillonite) to control the NPK and KNO_3 release. The hydrophobicity and high crystallinity of PHB make it insoluble in water. Although, this polymer may be suitable and employed in nutrients delivery when it is processed with MMT, which may facilitate the water permeability and the host nutrient release. The effect of clay amount on nutrients release time will be discussed in the present work. In addition, the nutrient amount was also evaluated to understand the relationship between the structure and the nutrient ions release.

Experimental

Chemicals

Poly(3-hydroxybutyrate) powder ($T_m = 160\text{--}175\text{ }^\circ\text{C}$; $T_{\text{decomp.}} = 230\text{ }^\circ\text{C}$; Biocycle, Brazil), sodium montmorillonite clay (MMtNa^+ , Brasgel Aço A, Bentonit União, Brazil), KNO_3 (Salpêtre Krista, K) and commercial granular NPK 4-14-8 (NH_4^+ , P_2O_5 , K_2O) from Yara Brazil Fertilizantes S.A. were used without purification. Table 1 shows the percentage of each nutrient in fertilizers.

Preparation of MMT– KNO_3 and MMT–NPK

Firstly, a mixture of montmorillonite and fertilizers was prepared by the mechanochemical method [14], which is a manual grinding in the agate mortar of the MMT (7 g) with distilled water (couple of droplets) and 7 g of fertilizer (NPK or KNO_3) until a homogeneous material were achieved. The compound was dried in the oven at $60\text{ }^\circ\text{C}$ and crushed to obtain a homogeneous powder.

Preparation of Composites

The composites based on PHB, MMT and fertilizers (KNO_3 and NPK (4-14-8), Fert) were processed in an internal mixer chamber of a Haake torque rheometer with cam roller motors at $160\text{ }^\circ\text{C}$, 50 rpm for 6 min. The composites PHB/Fert 90/10 and 50/50 (wt%) and PHB/MMT/Fert 80/10/10, 25/25/50 and 40/10/50 (wt%) were hot pressed at $150\text{ }^\circ\text{C}$, 14 MPa for 3 min and the composites ($0.5 \times 0.5 \times 0.1\text{ cm}^3$) were used to accomplish the ion release analysis and characterizations.

Table 1 Amount of nutrient in fertilizers

Fertilizer	Nutrient (%)		
	K_2O	NH_4^+	P_2O
KNO_3	47.43	5.7	–
NPK	13	1.8	10

Characterization of Composites

X-ray diffraction (XRD) were recorded using a Shimadzu LAB 600 diffractometer in a diffraction range $2^\circ\text{--}90^\circ$ with a $\text{CuK}\alpha$ incident beam ($\lambda = 0.1546\text{ nm}$). The scanning speed was 2° min^{-1} and the voltage and current of the X-ray tubes were 30 kV and 30 mA, respectively.

Spectroscopic analyses in the infrared region of the polymers and composites were analyzed using reflectance measurement in the range of $4000\text{--}500\text{ cm}^{-1}$. The FTIR spectra data was obtained using Perkin Elmer Spectrum One instrument.

The morphology of the samples was analyzed by scanning electron microscopy (SEM) (FEI Magellan microscope 400L) equipped with an energy dispersive analysis system of X-ray spectrometer-EDX. The samples were fractured for cryo-SEM by immersing in liquid nitrogen. Cross-sections of fractured samples were mounted with the cross-section positioned upward on the stubs and dispersed over carbon tape pasted on the surface of a metallic disk (stub). The disk was then coated with gold and palladium in an ionization chamber and analyzed.

Thermogravimetric analysis (TGA) was performed on SDT 2960-TA Instruments, from $40\text{ to }900\text{ }^\circ\text{C}$ under synthetic air flow of $100\text{ cm}^3\text{ min}^{-1}$ and heating rate of $10\text{ }^\circ\text{C min}^{-1}$, using 10 mg of the sample. DSC was carried on DSC-60 Shimadzu under 5 mg of the sample, nitrogen air flow of 50 mL min^{-1} and heating rate of $10\text{ }^\circ\text{C min}^{-1}$ on sealed aluminum pans, from $40\text{ to }350\text{ }^\circ\text{C}$.

Release Rate of Nutrients in Water

Potassium, nitrogen and phosphorous releasing in ultrapure water (Milli-q) was quantified by flame photometer (Digimed DM-62, Brazil), total organic carbon analysis (TOC-L with TNM, Shimadzu) and colorimetry by UV-Visible DR5000 (Hach), respectively. The cumulative concentrations were determined as a function of time using a calibration curve of the fertilizers (KNO_3 and NPK) ($80\text{--}800\text{ mg L}^{-1}$). The composite [$0.50\text{ g} \pm 0.01\text{ g}$ (w/w) with $0.5 \times 0.5 \times 0.1\text{ cm}^3$ size] was immersed in 50 mL of ultrapure water at $25\text{ }^\circ\text{C}$ and the ions released were determined after 1 h and until 25 h (three replicates). The final amount of nutrient released from the composites was expressed as a percentage based on the initial amount of nutrients in the materials.

Results and Discussions

Structural, Morphological and Thermal Properties

The diffraction patterns at $2\theta = 13^\circ, 17^\circ, 19^\circ, 21^\circ, 22^\circ, 25^\circ$ and 27° (Fig. 1a) are according to the orthorhombic structure

of PHB [15, 16]. Montmorillonite clay (Fig. 1b) shows d_{001} basal spacing at $2\theta = 5.46^\circ$ corresponding to a 1.63 nm [17]. The PHB–KNO₃ 90/10 (Fig. 1e) and PHB–NPK 90/10 (Fig. 2e) composites retain the main reflection peak of PHB. The clay interlamellar distance after fertilizers or PHB mixture can be monitored by the displacement of the diffraction angle d_{001} (Figs. 1 and 2 detailed). MMt peak at 5.46° displaced to 6.11° after PHB incorporation and to 6.75° for KNO₃-containing PHB–MMt–KNO₃ 25/25/50 composite (Fig. 1C, I—detailed). Similar behavior was observed for NPK-based composite (Fig. 2). The MMt diffraction peak displaced from 5.46° to 6.58° for PHB–MMt–NPK 80/10/10 and 6.71° for PHB–MMt–NPK 25/25/50 (Fig. 2F–I). These displacements are related to the decrease of the interlayer space (1.63 nm for MMt to ~ 1.30 nm for PHB–MMt–fert) and an indicative of ions exchange (Fig. 2). NPK and KNO₃ fertilizers comprise cations such as ammonium and potassium and anions from phosphate and nitrate. Then, both

positive ions will be able to exchange for sodium ions in the interlamellar region. However, NH₄⁺ and K⁺ have smaller hydration sphere than Na⁺, which explains the decrease of the basal space for MMt–fert materials [18].

From infrared spectroscopy analyses results (Supplementary Fig. S1), the incorporation of MMt and/or fertilizers into PHB did not change the PHB spectrum since there were no significant interactions among the components. Characteristic absorption bands of PHB are attributed to CH₃ (2978, 1454, 1379 cm⁻¹), CH₂ (2930 cm⁻¹), C=O stretching (1727 cm⁻¹), and C–O–C stretching (1182 cm⁻¹) [19–21]. The MMt main band is related to Si–O vibrations at 900 cm⁻¹. The FTIR spectrum of KNO₃ shows a band at 1385 cm⁻¹ assigned to the NO₃⁻ symmetric stretching, at 821 cm⁻¹ due to NO group bending and at 690–763 cm⁻¹ assigned to NO₂ deformation [22]. However, the NO₃⁻ band is suppressed by CH₃ band observed in the PHB samples. FTIR spectrum of NPK shows bands at 1631 cm⁻¹ assigned

Fig. 1 **a** XRD patterns from 2θ 1.5° to 60° and **b** XRD patterns from 2θ 4° to 10° of PHB (A), MMt (B), PHB–MMt 90/10 (C), KNO₃ (D), PHB–KNO₃ 90/10 (E), PHB–MMt–KNO₃ 80/10/10 (F), PHB–KNO₃ 50/50 (G), PHB–MMt–KNO₃ 40/10/50 (H) and PHB–MMt–KNO₃ 25/25/50 (I)

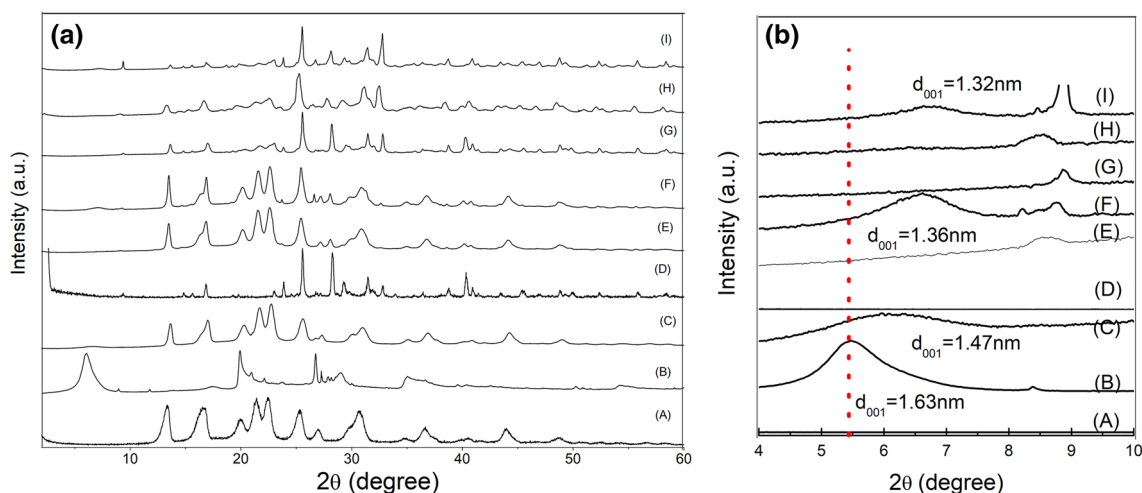
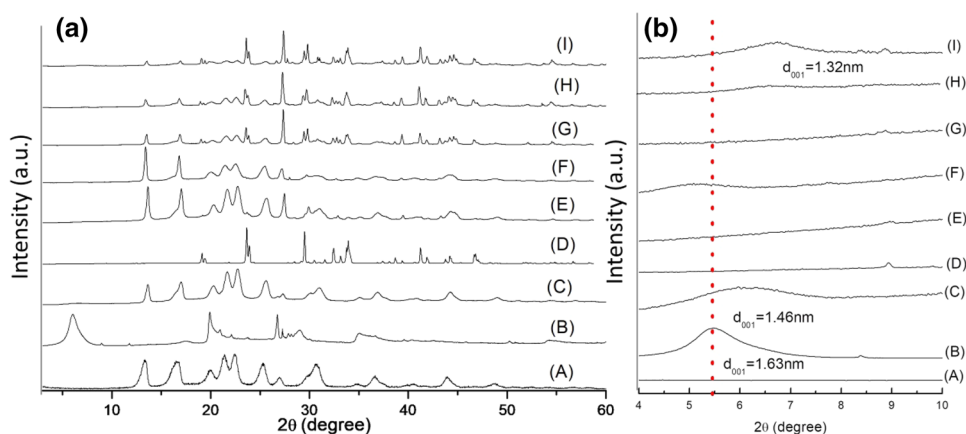


Fig. 2 **a** XRD patterns from 2θ 1.5° to 60° and **b** XRD patterns from 2θ 4° to 10° of PHB (A), MMt (B), PHB–MMt 90/10 (C), NPK (D), PHB–NPK 90/10 (E), PHB–MMt–NPK 80/10/10 (F), PHB–NPK 50/50 (G), PHB–MMt–NPK 40/10/50 (H) and PHB–MMt–NPK 25/25/50 (I)

to the N–H angular deformation and 3421 and 3211 cm^{-1} of the asymmetric and symmetric axial deformation of N–H, respectively. Bands at 1154 cm^{-1} of P–O axial deformation (P_2O_5) and between 597 and 675 cm^{-1} are characteristic of PO_4^{3-} . The overlaying around 1018 cm^{-1} is due to the axial deformation of P–O (NPK) and the Si–O group of MMT [23].

Figure 3 shows the morphological aspects of the PHB and its MMT and KNO_3 containing composites. MMT or KNO_3 were dispersed on PHB, for binary composites, PHB–MMT (Fig. 3a) generated a heterogeneous interface due to MMT weak interactions with PHB matrix. For PHB– KNO_3 (Fig. 3b, d), the interactions between the nutrient and matrix depends on the amount of nutrient. The KNO_3 dispersion on PHB-matrix was higher for PHB– KNO_3 50/50 than 90/10 since nitrate acts as plasticizer [14, 24] (as it can be corroborated by DSC analysis) that promotes the percolation of nutrient into PHB matrix. For ternary composites (PHB–MMT– KNO_3) the fertilizer was associated with both polymeric matrix and MMT, as evidenced by EDS analysis (Fig. 3c, e, f). Also, PHB–MMT– KNO_3 , 40/10/50 (Fig. 3e) and 25/25/50 (Fig. 3f) showed great dispersion for higher fertilizer amount assigned to the plasticizing effect as well. Panayotidou et al. [25] observed high clay dispersion due to the chain diffusion through the clay galleries for PHB/MMT with low amount of clay (1–5 wt%). In our work, besides the high amount of clay, the presence of fertilizer precludes the intercalation of the polymer into clay galleries.

NPK-contained composites (Fig. 4a, c), showed heterogeneous surface independently of NPK amount. The nutrient (NH_4^+ , PO_4^{3-} , K^+) are associated with clay (Fig. 4b) for composites with small amount of NPK (10%) and dispersed on the polymer/clay matrix for higher NPK content (50%) (Fig. 4d, e). EDS analyses (Fig. 4) realized on selected points presented clay and fertilizers trace dispersed in the polymeric matrix. Differently from KNO_3 -containing composites, NPK did not act as plasticizer as can also be observed on DSC analysis.

TG/DTG curves of PHB/Fert and PHB/MMt/Fert composites are given in Fig. 5 and Table S1 (Supplementary Material) shows the onset temperature. Two main stages of mass loss for KNO_3 -containing composites were observed (Fig. 5 and Table S1, Supplementary Material). The first, 250 – $300\text{ }^\circ\text{C}$, attributed to PHB and the second one, 600 – $850\text{ }^\circ\text{C}$, assigned to inorganic components degradation. The addition of KNO_3 decreased the PHB–MMt thermal stability from 261 to under $234\text{ }^\circ\text{C}$, Table S1. This behavior was associated with the polymer chains intercalation in clay, which promotes polymer thermal stability. However, the thermal stability of PHB/MMt/ KNO_3 decreased because the K^+ into the clay lamellas preventing the entry of the polymer which leaves the polymer more susceptible to thermal degradation.

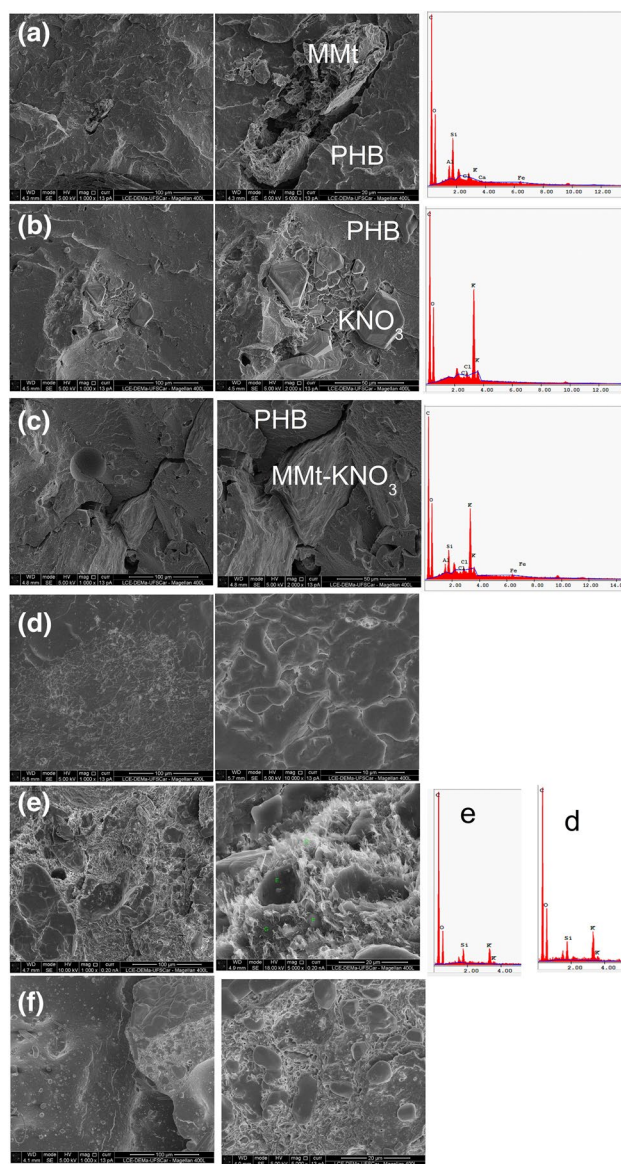


Fig. 3 SEM micrographs of **a** PHB–MMt (90/10), **b** PHB– KNO_3 (90/10), **c** PHB–MMt– KNO_3 (80/10/10), **d** PHB– KNO_3 (50/50), **e** PHB–MMt– KNO_3 (40/10/50), **f** PHB–MMt– KNO_3 (25/25/50)

In a recent study Harmaen et al. [26] showed that residues from NPK reaction accelerated the thermal degradation of PLA. However, the presence of NPK on PHB composites changed the T_{onset} of PHB to higher values, which corroborate with DSC thermal degradation results (Table S2, Supplementary Material).

Additionally, K_2O is the residue from composites containing KNO_3 , which is taken to calculate the total KNO_3 in the material, resulting in residue of 45% [17]. NPK residues of thermal degradation are related to N_2O , N_2 , NO_2 , H_2O , Cl , NH_4Cl , etc. [26]. NPK residue is referenced in 70% [14]. The residue value of the MMT and fertilizers calculated are

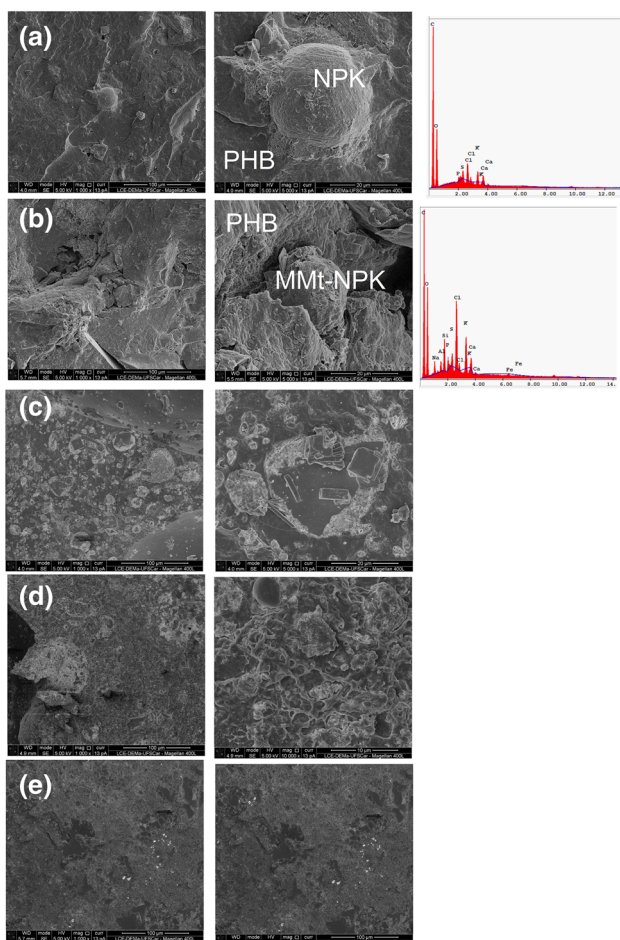


Fig. 4 SEM micrographs of **a** PHB–NPK (90/10), **b** PHB–MMt–NPK (80/10/10), **c** PHB–NPK (50/50), **d** PHB–MMt–NPK (40/10/50), **e** PHB–MMt–NPK (25/25/50)

similar from theoretical value, Table S1. The small difference was related to the losses during the sample thermal processing.

DSC curves and data are shown in Fig. 6 and Table S2, respectively. MMt affected the PHB nucleation and decreased its crystallinity (reported around 70% for neat PHB) [27]. According to Teixeira [2], MMt reduces the crystallinity of PHB, since MMt prevents the organization of PHB molecules (breaking the chains). Consequently, lower crystallinity of PHB was observed when MMt clay is present.

The addition of 10 wt% of KNO_3 (PHB–MMt– KNO_3 80/10/10) reduced the T_m from 174 to 170 °C and degradation temperature (T_{degrad}) from 286 to 210 °C comparing to the PHB–MMt 90/10. Although, the crystallinity kept higher than other samples due to the high PHB percentage. On the other hand, higher amount of KNO_3 (PHB–MMt– KNO_3 25/25/50 and 40/10/50) reduced even more the crystallinity degree and the degradation temperature. These effects are caused by the plasticizing effect of nitrate in PHB [14]. It agreed with the lower values of T_{onset} on TG curves and the greater dispersion of the clay/nutrient in the polymer matrix observed on SEM analysis (Fig. 3) and XRD results.

NPK-containing composites behaved differently than KNO_3 ones. PHB/MMt/NPK presented two melting peaks. The first T_m peak is characteristic of less ordered crystal fractions, and the second one to more ordered crystals, which melt at a higher temperature (Table S2). In this case, NPK did not act as a plasticizer for PHB and degradation temperature arose between 290 and 300 °C for all NPK-containing composites. However, higher values of NPK fertilizer, also, decreased significantly the PHB crystallinity.

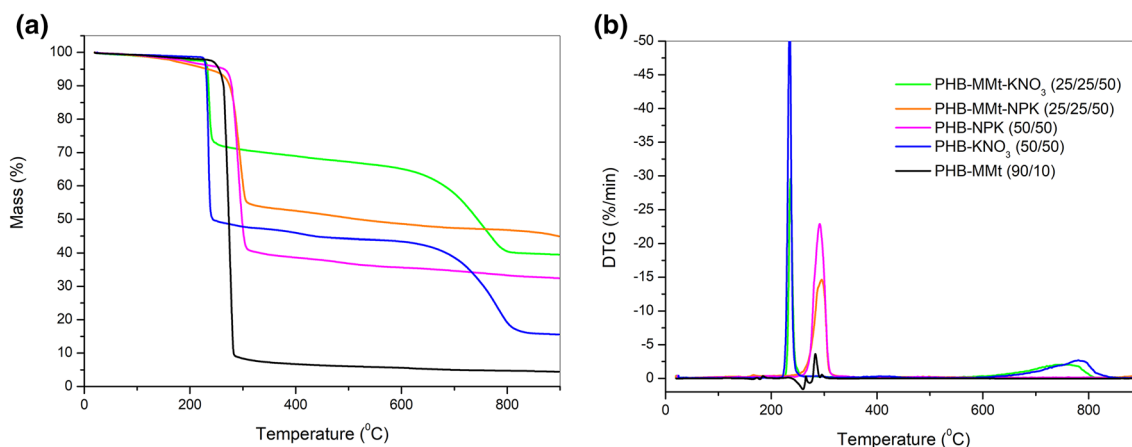
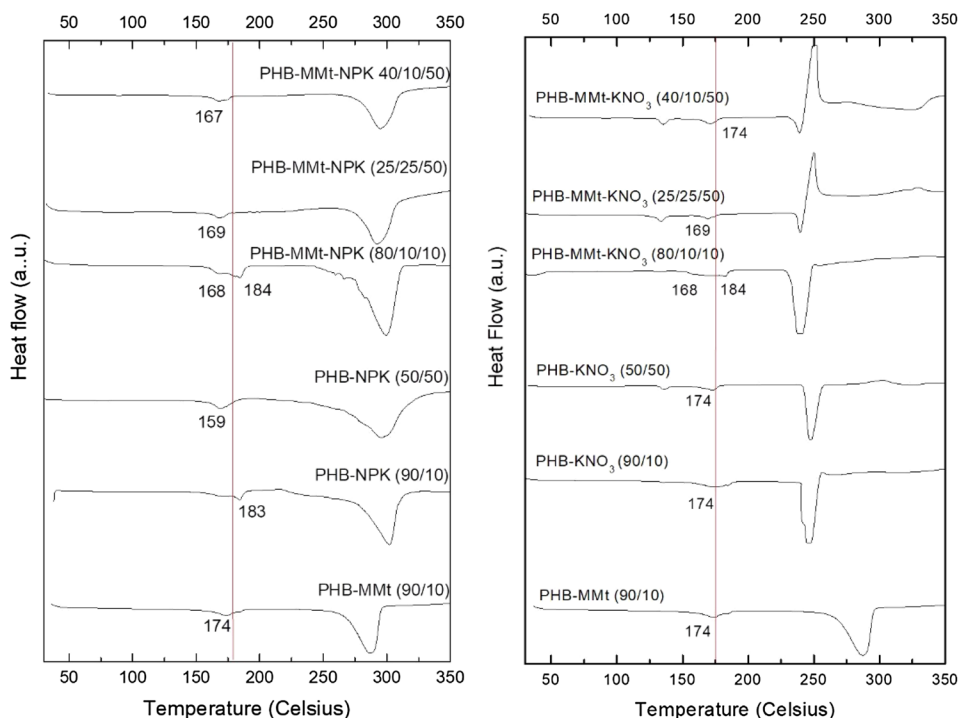


Fig. 5 TG and DTG of PHB–MMt (90/10), PHB– KNO_3 (50/50), PHB–NPK (50/50), PHB–MMt– KNO_3 (25/25/50) and PHB–MMt–NPK (25/25/50)

Fig. 6 DSC curves of PHB composites with KNO_3



Effect of Clay on Nutrient Release in Water

Nitrogen, Phosphorus and Potassium Delivery from NPK Fertilizer

Nutrients release from PHB–NPK and PHB–MMt–NPK are shown in Fig. 7. The amount of the nutrients affected the release profile, since nutrients delivery for nitrogen and potassium are dependent of the concentration but not for P. For example, for both PHB/NPK 90/10 and 50/50 the phosphorous delivery did not reach 50% of the total amount. The presence of clay slows down the phosphorous released for PHB–MMt–NPK 25/25/50 and 40/10/50. Phosphorus interacts with MMt and its release is inhibited once it is adsorbed by colloidal complex (clay) which characterize a

promising composition for phosphorus fertilizer in NPK-containing material.

In general, the nutrient releases were directly associated to MMt in the matrix. The higher the amount of clay, the greater the nutrient release due to the hydrophilicity of the MMt-composite, which increases the solubility of the nutrients, following the sequence: potassium, nitrogen and phosphorus. Once MMt has high affinity with nutrients and water, and also, the nutrients are less protected by PHB.

This observation leads us to conclude that as K^+ interacts physically with MMt it is not easily leached and may be replaced by other cations. Whereas anions such as nitrate and sulfate tend to be repelled by the negative charge of the clay and remain dissolved in the solution. For this reason, they tend to interact with the polymer matrix while the cations are dispersed in the composite clay. Thus, the presence

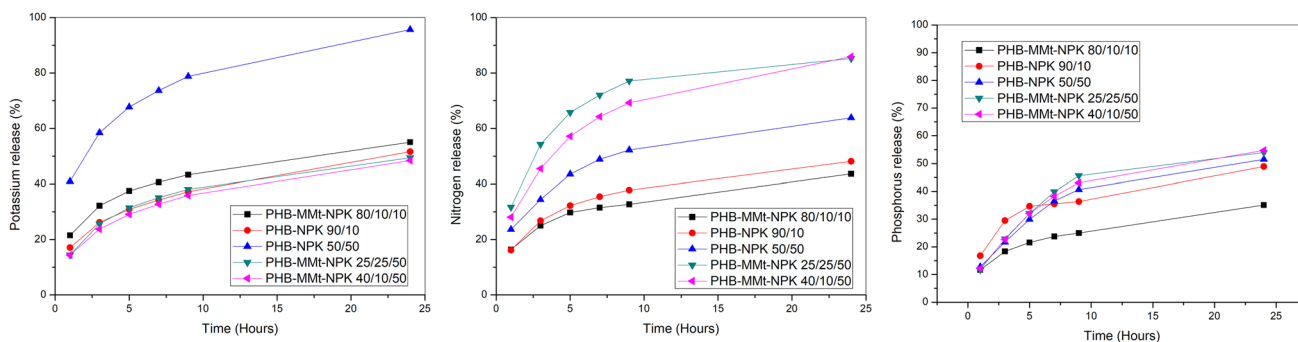


Fig. 7 Release profile of NPK in water of PHB–MMt–NPK composites

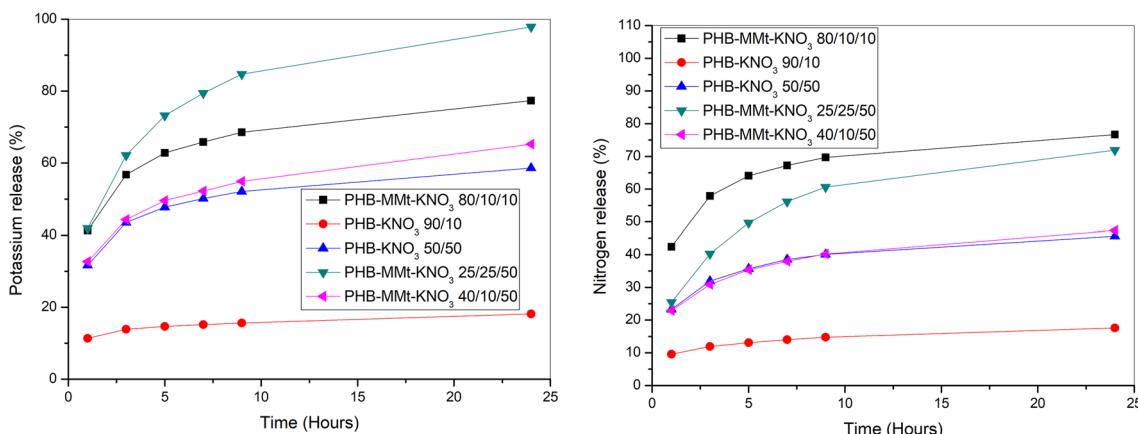


Fig. 8 Release profile of KNO₃ in water of PHB–MMt–KNO₃ composites

of clay in the composite is important to control the release of cationic nutrients while accelerating the release of anionic ones.

Nitrogen and Potassium Delivery from KNO₃ Fertilizer

The delivery of KNO₃ in PHB matrix is presented in Fig. 8. The release of potassium and nitrogen was increased when the amount of KNO₃ was up to 50% (PHB–KNO₃ 90:10 to PHB–KNO₃ 50:50). However, the presence of MMt on composites performed a distinct effect on potassium and nitrogen delivery. Comparing the composites PHB–MMt–KNO₃ 80:10:10 and PHB–MMt–KNO₃ 40:10:50, the same rate of nitrogen release (40%) was observed when clay amount was increased by only 10% and the amount of PHB was decreased.

Once nitrate acts a plasticizing for PHB, the nitrogen interacts with the polymer and protected it while the potassium mixes with MMt. This behavior increased the potassium delivery due to its high hydrophilicity. (Figure 8) For PHB–KNO₃ and PHB–MMt–KNO₃ the ions release order was potassium > nitrogen. Thus, the presence of clay in the composite is important to control the release of anionic nutrients while accelerating the release of cationic ones.

Release Kinetic

In the present study the release kinetic was evaluated using a semi-empirical model, known as the power law or the Korsmeyer–Peppas model [28, 29]. The kinetic parameters for studies of drugs or nutrients release were obtained using the Eq. 1:

$$\frac{C_t}{C} = Kt^n \tag{1}$$

Table 2 Release exponent (n), release factor (K) and correlation coefficient (R²) in water for composites

Samples	Release exponent, n	Release factor, K	Correlation coefficient, R ²
PHB–MMT–NPK 80/10/10	K	0.29	22.64
	N	0.30	17.25
	P	0.33	12.13
PHB–NPK 90/10	K	0.35	17.46
	N	0.34	17.50
	P	0.32	18.70
PHB–NPK 50/50	K	0.27	42.64
	N	0.32	24.63
	P	0.46	13.62
PHB–MMT–NPK 25/25/50	K	0.39	15.84
	N	0.32	36.02
	P	0.50	13.22
PHB–MMT–KNPK 40/10/50	K	0.38	15.14
	N	0.36	30.17
	P	0.50	13.44
PHB–MMT–KNO ₃ 80/10/10	K	0.2	43.91
	N	0.19	46.23
	P	0.19	9.32
PHB–KNO ₃ 90/10	K	0.14	11.51
	N	0.19	9.32
	P	0.19	9.32
PHB–KNO ₃ 50/50	K	0.19	33.65
	N	0.21	25.07
	P	0.21	25.07
PHB–MMT–KNO ₃ 25/25/50	K	0.27	44.93
	N	0.34	28.03
	P	0.34	28.03
PHB–MMT–KNO ₃ 40/10/50	K	0.22	33.97
	N	0.23	24.03
	P	0.23	24.03

where Ct/C is the fraction of nutrients release at any time t, K is a constant depending on the kinetic features and experimental conditions, and n is a diffusion exponent related to

the release mechanism. The K and n values are obtained from $\log Ct/C$ versus $\log t$ [30] by the Eq. 2:

$$\log \frac{Ct}{C} = \log K + n \log t \quad (2)$$

The release mechanism was investigated fitting data according to Eq. 1. Plots of $\log (Ct/C)$ versus $\log t$, Eq. 2, provide the release exponent, n , the release factor K , and the correlation coefficient R^2 , listed in the Table 2. Potassium and nitrogen release for KNO_3 -contained composites, and potassium, nitrogen and phosphorus release for PHB–MMT–NPK 80/10/10 and PHB–NPK 90/10 and 50/50 show release exponent $n \leq 0.5$, this indicate a quasi-Fickian diffusion mechanism [31, 32], in which nutrients diffuses partially through a swollen matrix and water filled pores in the composites, similarly observed for potassium release based on chitosan hydrogels [30]. However, the n values were 0.5 for phosphorus from PHB–MMT–NPK 25/25/50 and 40/10/50 suggesting the release was controlled by diffusion based, due the higher size of ion PO_4^{3-} in high concentration.

Conclusions

The fertilizer interacts physically with PHB and PHB/MMt, and the MMt had the influence to increase the rate of the fertilizer release in water. This behavior is according with the morphology, due to the clay and fertilizer agglomerates in a heterogeneous structure. The water was efficiently diffusion due to the more affinity with MMt as demonstrated by the kinetic model. The release of fertilizers in composites was efficient even for MMt-containing composites (release about 30% in 9 h) enable them to be used as controlled release fertilizers. Composites made with higher concentration of fertilizer and clay and lower PHB amount are potential for industrial application with cost reduction. PHB was considered as an expensive material however its cost has been reduced to €1.5/kg in 2010 since new processes and production optimization have been achieved. This scenario is expected to be more rentable for 2020 [33] since its use for fertilizer encapsulation drives interesting attributes such as eco-friendly composites, easily formulation and processing.

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Data Availability The raw/processed data required to reproduce these findings cannot be shared at this time due to technical or time limitations.

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