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Poly(ε-caprolactone)-g-Guar Gum and Poly(ε-caprolactone)-g-Halloysite Nanotubes as Coatings for Slow-Release DAP Fertilizer

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Abstract

Biodegradable coating materials based on PCL grafted on guar gum and halloysite nanotubes have been synthetized and used to delay the nutrients release from Diammonium Phosphate (DAP) as water-soluble fertilizer granules. The combination of hydrophobic character of PCL as biodegradable polymer and the swelling behavior of guar gum (GG) and halloysite nanotubes (HNT) as natural fillers were evaluated in this study with a view of the slow release of fertilizers. Indeed, the hydroxyl groups on the guar gum (GG) and halloysite (HNTs) surfaces act as initiators for caprolactone in situ ring opening polymerization and the developing polymers are covalently grafted to the GG and HNTs. Moreover, the hydrophilic character of fillers (GG & HNT) improves the adhesion between the coating agent and the surface of the (DAP) granules and consequently DAP granules were successfully coated by the dip-coating process with fixed thickness of ~ 25 μm as revealed by the scanning electron microscopy. The evaluation of the release behavior of DAP coated by the composites (PCL-g-GG and PCL-g-HNT) demonstrates that the liberation rate could be controlled by adjusting the fillers (GG or HNT) contents in the coating materials (PCL-g-GG and PCL-g-HNT). This encapsulation expands the nitrogen and phosphorus release to more than 50 h instead of only 2 h for uncoated DAP granules.

Keywords Slow release · Water retention capacity · Poly(ε-caprolactone) · DAP fertilizers · Guar gum · Halloysite nanotubes · In situ polymerization

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Introduction

Fertilizers are considered as important elements to maintain the soil fertility and to supply the human demands of food. From now on, more than 70% of the seed yield will have to depend on fertilizers [1]. Besides, the fertilization process is referred to as the main way to work around the decrease of the arable land over the past few decades due to urbanization and climate change. As consequence of the fertilization process, a rapid release of nitrogen, phosphorus and potassium as major nutriments (NPK) from fertilizers rises up many doubts on their sustainability and efficiency against the plant's needs [2]. In this context, researchers have realized the environmental and economic problems associated to the excessive and unbalanced use of fertilizers [3]. To overcome this problem, controlled and slow release fertilizers (CSRF) seem to be the best solution for better use of water-soluble fertilizers and to protect the environment from the drawbacks linked to nutrient's excess [4–6]. Indeed, the challenge consists

on delaying nutrients release, and preserving soil quality from the accumulation of non-biodegradable residues by using natural and ecofriendly polymer as coating material of granular fertilizer [7–11]. In fact, the combination of fertilizers and biodegradable coating polymer is not only beneficial for crops but also for soil aeration, friability and erosion prevention [12]. Concisely, generating a slow release of nutrients in order to meet the plant's requirement and therefore limiting the application of fertilizers frequency, followed by an easy biodegradation of the coating material are the main approaches solicited.

During the last two decades, several investigations have been performed to develop composites materials by combining biopolymers and natural fillers to prepare sustainable coating agent with the principal sought after properties in this field [13–16]; The hydrophobic character is the first parameter to be taken in consideration to prevent fast water penetration inside the core of fertilizer granules. Furthermore, the holding water capacity of the coating agent is highly useful, where the coating membrane acts a water reservoir in the semi-arid and arid regions. Therefore, the combination of swelling behavior and the hydrophobic character in one coating material remains a delicate task to achieve. In this way, Rui Liang and Mingzhuliu have proposed a double coating of urea fertilizer by polystyrene as inner coating and poly(acrylic acid) as outer coating, this system shows that the product not only had a good slow release behavior but also a high water retention property [17]. The strategy of double coating was reproduced in numerous reported studies to ensure the same combination. Lan Wu et al. investigated a double coating of water-soluble NPK fertilizer based on chitosan and poly(acrylic acid) as inner and outer coating respectively, around 8% of water absorbency was reached as well as slow release property [8, 18]. The poly(acrylic acid-co-acrylamide) and ethyl cellulose was also tested as partially biodegradable double coating system for slow release and water retention of urea pellets [19]. Even if the double coating approach presents a good coating performance, it requires a high quantity of polymers, which definitely rises the price of the coated granular fertilizer in one hand, and affects the soil quality when the non-biodegradable materials were used on the other hand. To insure the slow release and water retention by only simple coating, our strategy consists on combining the hydrophobic character (slow release) and water retention capacity in one coating material. For that, the composite materials prepared by grafting hydrophobic polymer on hydrophilic filler could be considered as an interesting way for the replacement of the double coating system already reported. Recently, our team has successfully carried out the grafting from of PCL on different hydrophilic substrates namely cellulose, halloysite nanotubes and guar gum by in situ ring opening polymerization of the ε-caprolactone using tin and titanium complexes as catalysts [15, 20, 21].

The Poly(ε-caprolactone) (PCL) is a semi-crystalline and biodegradable polymer that is widely used for replacing the non-biodegradable petrochemical polymers [22–25], it can be synthesized even by the polycondensation reaction of a hydroxycarboxylic acid (6-hydroxyhexanoic acid) or by the ring opening polymerization (ROP) of ε-caprolactone [26]. To the best of our knowledge, only one article concerning the use of commercial PCL as hydrophobic biodegradable polymer as a coating material for water-soluble fertilizers has been reported [27]. The low capacity of holding water and the poor compatibility with the fertilizer granules could be the main reason of the unattractiveness of PCL for such application. However, it has been also reported that PCL composites prepared by blend melting were successfully used as cell encapsulation agent of phosphate-solubilizing-bacteria (PSB) [28]. Since the highly hydrophilic fillers and hydrophobic PCL characters have low compatibility, their blinding causes poor dispersion of filler in the resulting composites and consequently the optimal properties of the bio-composite are not achieved [29]. For that, the use of compatibilizers was commonly needed to overcome this immiscibility problem [30, 31]. To get through this limitation, our strategy is based on the covalent grafting of PCL in hydrophilic fillers (guar gum and halloysites nanotubes) to prepare bio-composite materials. The latter as it combines the hydrophobic character of PCL and hydrophilic one of fillers could be a suitable coating agent candidate. The guar gum (GG) is obtained from the endosperm of guar bean (*cyamopsis tetragonoloba*) and was used in a wide range of food applications, it has been also reported that the guar gum is capable of absorbing and retaining large amount of water due to its swelling behavior [32–35]. It should be noted that previous studies established the helpful effect of such polysaccharide amendments on improving the soil's physical properties [32, 36, 37]. While the choice of halloysite nanotubes as filler was motivated by the fact that it presented inner and outer hydroxyl groups, which leads to the easy graft of PCL by in situ ROP of ε-CL on one hand and of its nontoxicity on the other hand [38–41].

In this study, the bio-composites prepared by grafting from of PCL in two hydrophilic substrates nominated PCL-g-GG and PCL-g-HNT were tested as coating agents for the diammonium phosphate (DAP) granules. The association of slow release property and water retention for the coating agent based on PCL and GG (PCL-g-GG) were deeply investigated, and the effect on the mechanical performance of the HNT based coating agent was studied. The delaying release rate of nitrogen and phosphorus in water from the coated and uncoated DAP granules has been also compared and studied using Ritger-Peppas model [42].

Experimental

Materials

Diammonium phosphate (DAP) fertilizer granules were obtained from OCP group (Diameter 4 mm), poly(ε-caprolactone) (*Mn*=98100 g/mol, *Đ1.9*), powder of guar gum (GG) (*molecular weight* 1300 kg/mol) with ratio of mannose/galactose of about 1.8, ε-caprolactone (CL) (liquid), ethanol, chloroform, dichloromethane, and tetrahydrofuran were purchased from sigma Aldrich and were used as received. Halloysite nanotubes (HNT) was given from Applied Mineral Incorporation.

Table 1 Composites material used as coating agent

Material code	Wt% of GG/εCL	Wt% of HNTs/εCL	Mn (g/mol)
PCL	–	–	98,100
PCL-g-GG 1%	1	–	86,104
PCL-g-GG 3%	3	–	47,559
PCL-g-GG 5%	5	–	30,108
PCL-g-HNT 1%	–	1	97,217
PCL-g-HNT 3%	–	3	85,023
PCL-g-HNT 5%	–	5	52,260

Methodology

Bio-composites Materials Preparation

According to a published procedure [20, 21], all the coating materials were synthetized by in situ ring opening polymerization of the ε-CL from the guar gum polysaccharide (GG) and hallylosite nanotubes (HNT) as organic and inorganic substrates respectively by using tetra(phenylethyl)tin as catalyst. Indeed, the hydroxyls groups on the surface of guar gum and the halloysite clay nanotubes act as co-initiator for the in situ ring opening polymerization of ε-caprolactone, which was performed in open air. The polymerization was conducted in a Erlenmeyer flask and the procedure started with the dispersion of (1,3 and 5%wt) of the organic or inorganic (GG & HNT) in the liquid monomer using an ultrasonic equipment. Afterwards, the catalyst (tetra(phenylethynyl)tin) with [ε-CL]/[Sn(C≡CPh)$_4$] ratio of 1000/1 was added in the form of stock solution in toluene, stirred at room temperature and heated at 120 °C for 15 min in which total conversion was accomplished (proposal of in situ polymerization reaction mechanism in Fig. 1SI). The molar masses (Mn) of different prepared composites materials, which were used as coating agents, are presented in the Table 1. All the composites were solubilized in THF (5%wt) for the coating process.

Free Polymer Extraction

In order to determine the molecular weight of the grafted PCL on the fillers (GG or HNT) the free PCL chains was separated from the crud bio-composites (PCL-g-GG/PCL-g-HNT) following extraction process described by Boujemaoui et al. [15]. Indeed, the obtained bio-composites were ultra-sonicated in THF then centrifuged and the free PCL (homopolymer) was trapped on the supernatant phases. Moreover, the precipitation of the homopolymer (PCL) was achieved in cold methanol,

filtrated and drayed in vacuum oven at 50 °C before the SEC analysis. The recovered free PCL represents about 10% of the total mass of the obtained materials.

Preparation of Coated DAP Granules

The commercial granular DAP (diammonium phosphate 18-46-00) produced by OCP group with 4 mm of diameter and spherical form was selected and used in the laboratory test to prepare coated granules. The preparation of the coating solutions was realized by solubilization of composites (PCL-g-HNT, PCL-g-GG) in THF (5 wt%). The coating was performed following the dip-coating process [11, 43–45], where the DAP fertilizer was successively immersed in the coating solution and discharged afterwards placed in an oven at 30 °C for complete removal of the solvent. The DAP granules were covered by a thin layer. After the coating process, the granules were weighted and the percentage of coating was calculated using Eq. (1):

$$\% \text{ Coating } = \frac{(Mf - Mi)}{Mi} \times 100 \tag{1}$$

Where M_f is the mass of the coated granules and $M_{i\ is}$ the mass of the granule before the coating. Generally, the use of low percentage of coating is cost-effectively desirable. All the percentages of coating by PCL-g-GG and PCL-g-HNT are reported in (Table 2).

The comparative study of the different coating percentage gives a general idea of the coating amount on the granules; in fact, it is approximately ~5% of the coating percentage for the PCL-g-GG material. The PCL-g-HNT coating material presents a random coating percentage in the range of 5 to 7.7%.

Table 2 The weight of DAP granules before and after the coating with PCL-g-GG

Coating composite	Medium value of coating weight %	Error
PCL-g-GG 1%	5.18	1.61
PCL-g-GG 3%	5.49	1.68
PCL-g-GG 5%	5.03	1.37
PCL-g-HNT 1%	6.22	1.21
PCL-g-HNT 3%	4.86	1.52
PCL-g-HNT 5%	7.66	1.63

Characterization of the Coating Material

Size Exclusion Chromatography (SEC)

The distribution of the polymer molecular weight (Free PCL chains) was achieved by the SEC analysis, where the measurement were carried out on PL-GPC Polymer laboratory chromatography equipped with RI sensor *($\lambda = 264$* nm) and two serially connected columns PLgel Mixed-B (*styrene-co-divinylbenzene copolymer gel with* 3–100 µm *of particle size*). THF was used as solvent and eluent wherein the flow rate was 1 ml/min. The calibration of molecular weight was done by poly(styrene) (certified reference material EasiCal-PS1B).

Contact Angle Measurement (AC)

Contact angle measurements with droplets of water on the surface of bio-composite samples were measured on EASY DROP contact angle system. Measurements were carried out at room temperature with 2 µl water droplets.

Suspension Stability

To confirm the grafting efficiency, the recovered *PCL-g-GG and PCL-g-HNT bio-composites* by centrifugation were suspended in dichloromethane, stirred, and the stability of the resulting suspension was compared to that of neat filler (GG and HNT) and the physical mixture of the filler (GG and HNTs) with homo-PCL.

Mechanical Properties Measurements

The tensile mechanical behavior of the films was analyzed using an Instron Universal Testing Machine (*Model 3369, Instron*). The experiments were performed at room temperature, with a crosshead speed of 5 mm/min. The rectangular samples dimensions were ($50 \times 18 \times 0.08$ mm); the results were averaged on three measurements. The tensile strength at break, and young modulus of the prepared film were determined and compared.

Mass Variation Measurement of the Coated Granules in Water

A DAP coated granule of fertilizer was immersed into distilled water at 25 °C. The granule was removed and filtrated using filter paper to remove non-absorbed water and weighted after 5, 10, 15, 20, 25, 30, 35, 40, 45, 50, 55, 60 min of distilled water immersion. The procedure was averaged on three measurements, and the mass variation was determined following Eq. (2) and plotted versus immersion time:

$$\text{Mass variation} = \frac{M - M_0}{M_0} \times 100 \qquad (2)$$

where M and M_0 denote the weight of coated granule of fertilizer after the immersion and the weight of the coated granule before the immersion respectively, the Mass variation denotes the water absorbency of the coated granules.

Scanning Electron Microscopy (SEM-EDX)

The structure, morphology and thickness of the coating layers were visualized and analyzed by scanning electron microscopy (SEM), it was recorded on Vega 3 TESCAN with conventional tungsten, heated cathode intended both for high vacuum and for low vacuum operations. All the samples were previously sputter coated with Au–Pd in argon plasma to enhance their conductivity. The quality of fertilizer coverage and the coating thickness were also inspected using the SEM-EDX.

Release Essay of Nitrogen (NH_4^+) and Phosphorus (P_2O_5) in Water

Uncoated and coated DAP granules (100 mg) were immersed in 250 ml beakers of distilled water by continuous and slight stirring at 25 °C. Three samples of 1 µl were collected at different time intervals, diluted 100 times and analyzed in the spectrophotometer. The release profiles of nitrogen (NH_4^+) and phosphorus (P_2O_5) in distilled water were determined by colorimetric methods, using Indophenol reagent and Ammonium-molybdate/ascorbic acid methods (AFNOR-T90-015) and (AFNOR-T90-023) respectively. Colored complexes were analyzed at a wavelength of 630 nm (for NH_4^+) and 880 nm (for P_2O_5) using ultraviolet–visible spectrophotometer (UV-2600, Shimadzu).
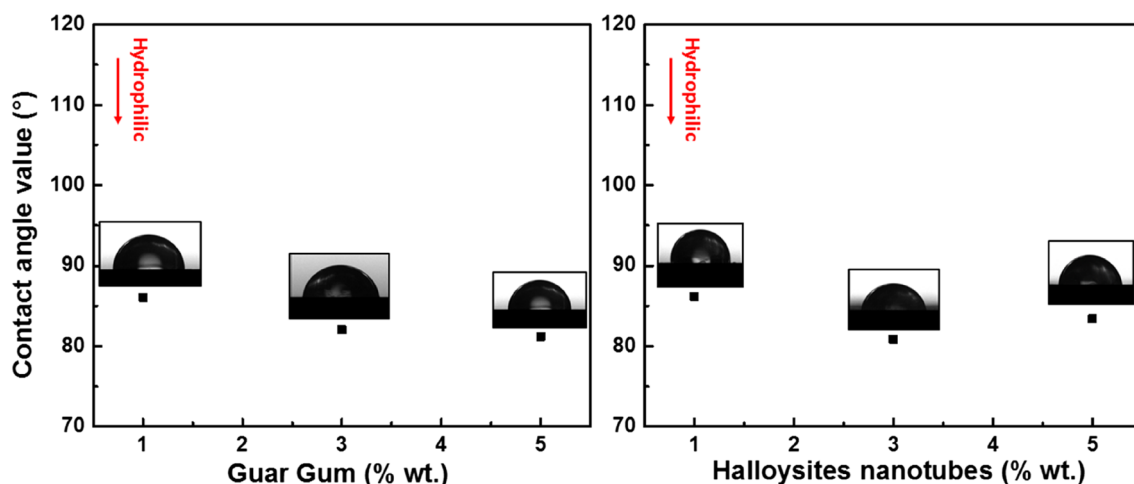
Fig. 1 Contact angle value of water drop on the PCL-g-GG and PCL-g-HNT bio-composites films

Modeling of Release Kinetic

According to Ritger-Peppas equations, the results of the release kinetic were analyzed using Eqs. (3) and (4) to describe the nitrogen and phosphorus release behavior from the composites coating of the DAP granules. The diffusional exponent (n) estimation characterizes the release mechanism, the k as a constant was also determined [46, 47].

$$\frac{M_t}{M_\infty} = Kt^n \tag{3}$$

and

$$Log\left(\frac{M_t}{M_\infty}\right) = Log(K) + nLog(t) \tag{4}$$

where M_t/M_∞ is the released fraction at time t, n is the release exponent, and K the release factor. By the slop and intercept of the plot $Log(Mt/M) versus Log(t)$, the n and K value were determined (see the plot of Eq. (3) in Fig. 3SI). The n value predicts the release mechanism, for the spherical form pure Fickien release mechanism occurred when n = 0.5. The diffusion is considered as quasi-Fickien when n < 0.5, and non-Fickian when 0.5 < n < 1. The case II transport if n = 1. The initial diffusion coefficient (Di) was also calculated using the Eq. (5) below:

$$\frac{M_t}{M_\infty} = 4\sqrt{\frac{Di \times t}{\pi l^2}} \tag{5}$$

where $l = 25\ \mu m$ the thickness of the coating.

Results and Discussion

The grafting of PCL on GG and HNT was carried out by surface-initiated ring opening polymerization of ε-caprolactone in solvent free condition at different percentages of fillers (GG and HNT) (1%, 3% and 5%) and fixed amount of catalyst tetra(phenylethynyl)tin [εCL/SnAK = 1000/1]. The molecular weight (Mn) of the free PCL separated from the bio-composites (PCL-g-GG and PCL-g-HNT) was determined using size exclusion chromatography (Table 1). By considering the approximate equality of molecular weight between free PCL and grafted one into the filler [15]. It was observed that, the molar masses decrease by increasing the filler contents; it should probably be due to the increase of polymerization sites (OH groups on the surface of GG and HNT) that are considered as initiator of this reaction. Indeed, higher hydroxyl content leads to new and short grafted polymer chain. This result is in good agreement with previous reported studies on grafting PCL [26, 48].

As mentioned earlier, the hydrophobic-hydrophilic balance is a crucial parameter to be investigated to control water penetration inside the core of fertilizer granules. For that, the hydrophobic nature of the prepared *PCL-g-GG, PCL-g-HNT* and neat *PCL* has been evaluated and compared by measuring a droplet contact angle value of distilled water on their surfaces. Indeed, contact angle measurements provide more information on the variation of the hydrophilic-hydrophobic balance of the *PCL-g-fillers* films comparing to the neat PCL (neat PCL contact angle value 88°). As expected, all composites based PCL samples afforded a low contact angle

values (enhanced hydrophilicity of grafted PCL) compared to the neat PCL. This could be tentatively attributed to the polar nature of the covalently linked fillers (GG and HNT). The hydroxyl groups of the filler decreases the hydrophobic character of PCL composites. It should be noted that the hydrophobic character of the coating material is generally desired, it is considered as the first barrier against precocious water penetration (Fig. 1).

To confirm the success of PCL grafting on the filler (GG and HNT), the comparison of the suspension stability in dichloromethane of the bio-composites prepared by the in situ procedure, neat filler (GG and HNT) and physical mixture of homo-PCL with fillers (prepared in the same proportion as in the bio-composites) has been carried out. As shown in Fig. 2, the suspension of the physical mixture of homo-PCL with fillers and those of neat fillers (GG and HNT) precipitate much rapidly than the bio-composites (PCL-g-GG and PCL-g-HNT). Indeed the grafted PCL chains are able to keep the filler particles in suspension in the solvent even after 24 h (turbidity in pictures c′). While,

Fig. 2 Suspension stability of the bio-composites prepared in dichloromethane
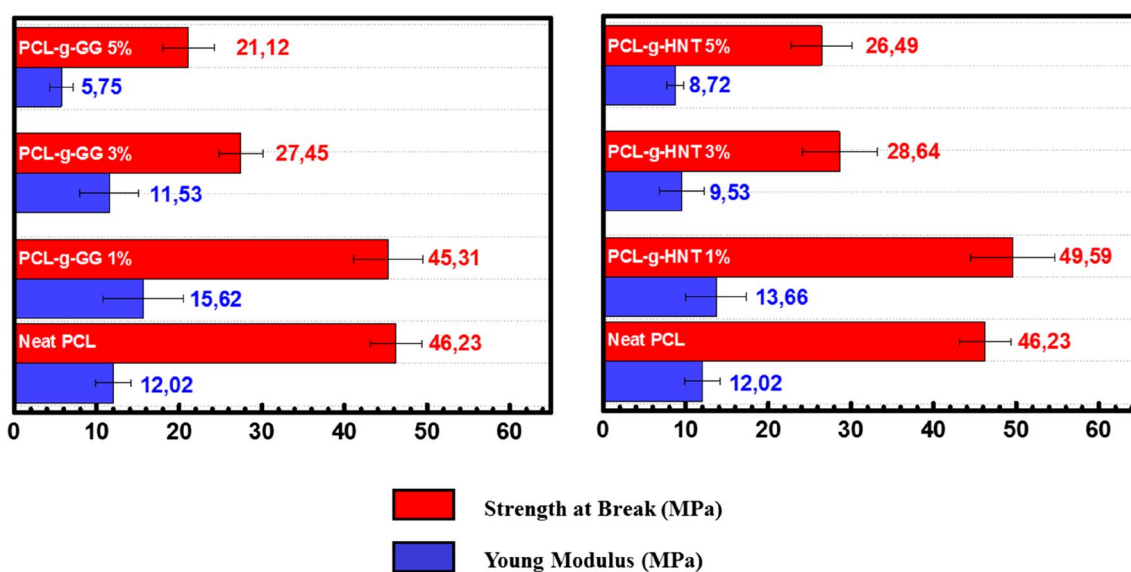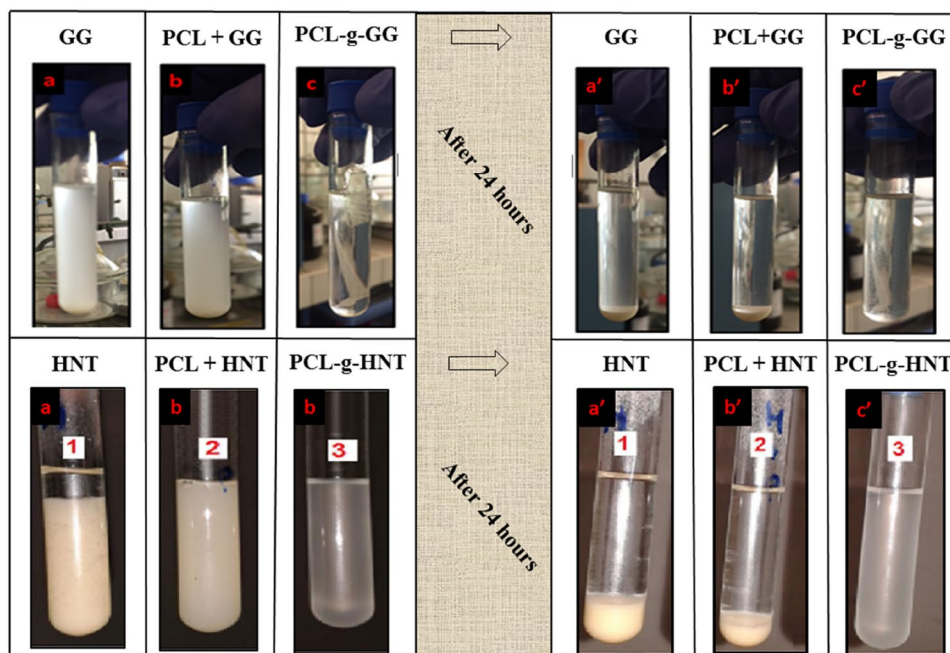
Fig. 3 Strength at break and young modulus of the composites materials

the composites prepared by solution blending are completely precipitated with clear supernatants (phase separation in pictures b′) after 24 h.

The mechanical properties are sought after parameters of the fertilizers coating materials. Hence, the improving mechanical proprieties of the coating material generate resistant granules under stress constraint, which could be interesting during the storage and transportation operations. The mechanical properties of prepared materials were presented in Fig. 3 and compared with those of neat PCL, both the young modulus (E) and the strength at break (SB) of neat PCL and all the bio-composites used as coating agent were described. The bio-composites containing 1% of the filler (GG or HNT) showed the highest value of young modulus and strength at break compared to other ones; this could be explained by the molecular weight of the grafted PCL chains on filler at 1% content, which is closer to that of neat one. The decrease of the mechanical proprieties for the composites with higher content of added filler (> 1%) could be explained by the decrease of molecular weight of grafted PCL compared to the neat one. Indeed, the decrease of polymers molar mass by increasing the monomer/filler ratio is due to the raise of the hydroxyl groups which are the co-initiators of the polymerization, leading to short polymer chains [21]. On the other hand, the HNT reinforcement effect was confirmed by comparing the neat PCL to PCL-g-HNT 1% which have 98,100 g/mol and 97,217 g/mol of molecular weight respectively. Even if the molecular weight of neat PCL and PCL-g-HNT 1% were closer, the strength at break and young modulus of the bio-composite (PCL-g-HNT 1%) were significantly higher by HNT incorporation. The hydroxyl groups on the edge and surface of the tubulars

clay could interact with the Poly(ε-caprolactone) chains by the formation of hydrogen bridge, similar effect was reported in previous work [49]. To conclude, the mechanical proprieties (SB, E) of all the prepared bio-composites were classified as follow; PCL-g-HNT 1% > PCL commercial > PCL-g-GG 1% > PCL-g-HNT 3% > PCL-g-GG 3% > PCL-g-HNT 5% > PCL-g-GG 5% for the Strength at break (SB) and PCL-g-GG 1% > PCL-g-HNT 1% > PCL commercial > PCL-g-GG 3% > PCL-g-HNT 3% > PCL-g-HNT 5% > PCL-g-GG5% concerning the Young modulus (E).

As mentioned before, in the semi-arid and arid regions the encapsulation membrane could play a water reservoir role. Hence, the swelling behavior of the coating agent is highly required for such application. For that, the weight variation percentage of the uncoated and coated DAP granules of fertilizer at different immersion time in water has been studied and significant changes have been observed (Fig. 4). Indeed, it has been shown that the uncoated granules loss 100% of weight after only 20 min of water immersion (Fig. 2SI), while the coated granules by neat PCL present slight variation of weight during the first 60 min of the immersion, due to the hydrophobic character of neat PCL. Regarding the bio-composites coating, a positive variation has been observed of the weight during the first 15 min, which is probably due to interaction between water molecules and hydroxyl groups on the surface of the coating materials. It was observed that only the PCL-g-GG bio-composites show an important positive weight variation during all the experimentation. This behavior could probably be due to the high water holding capacity of guar gum, similar effect has been reported in previous studies when other polysaccharide was a part of coating material [50, 51].
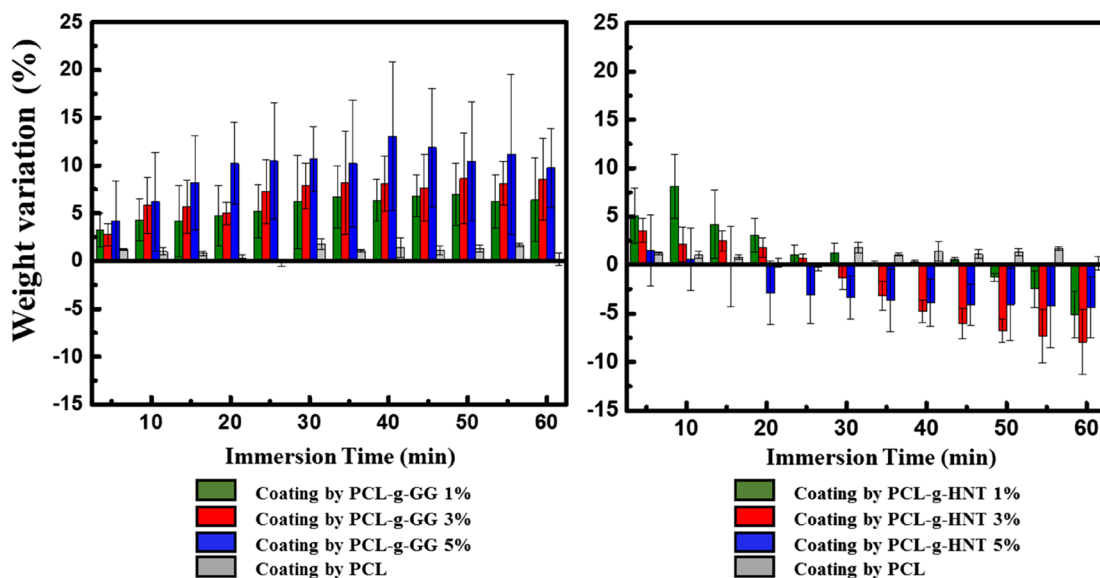

Fig. 4 Weight variation percentage of the uncoated and coated DAP granules of fertilizers

The scanning electron microscopy was used to compare the surface morphology of the granules before and after the coating by different formulations. The SEM image of the uncoated DAP granule presents a rough surface structure (Fig. 5a). The SEM image of the cross-section of the DAP granule coated by neat PCL shows weak adhesion between the granules and the coating film (Fig. 5b). The surfaces and cross-sections of the applied coating by PCL-g-GG and PCL-g-HNT were reported in Fig. 6, all the surfaces were smoother and the overall thickness were around 25 μm. The PCL-g-GG composites coating has several voids resulting from non-uniform surface that traps air bubbles underneath the coating layer. A good adhesion between all the composites materials films and the DAP granules has been observed which could be due the integration of hydrophilic filler in PCL matric allowing the formation of hydrogen bonds between DAP granules and bio-composites coating material. It should be noted that in the PCL-g-HNT SEM images (the bellow part in Fig. 6), an uniform micro-pores were exposed (diameter about 4 μm).
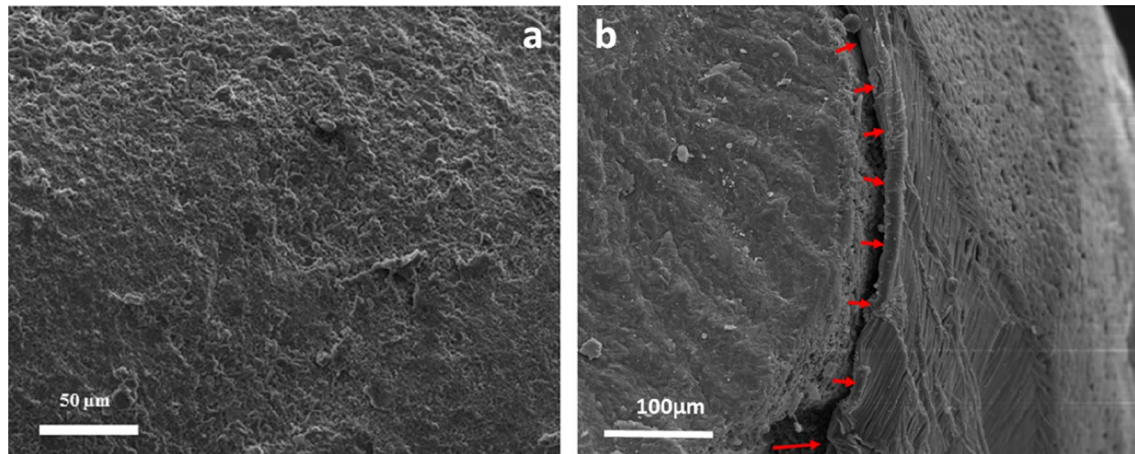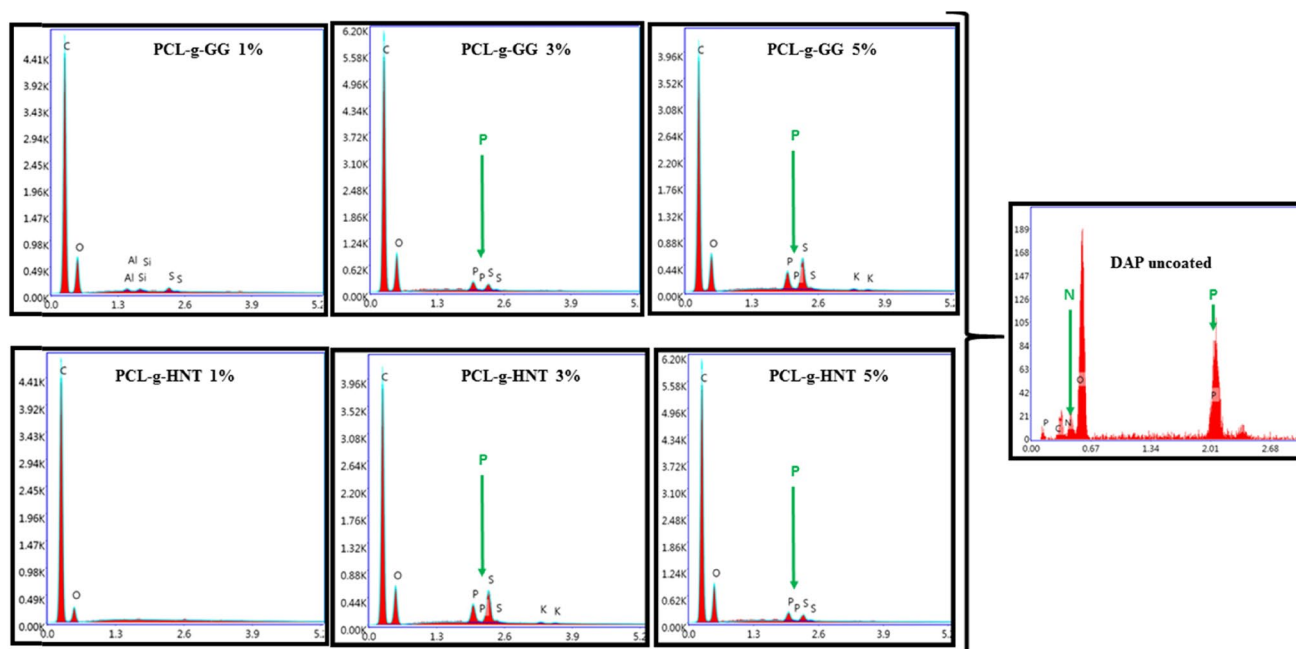

Fig. 5 **a** surface of uncoated DAP granules, **b** cross-section of the coated DAP granules by neat PCL
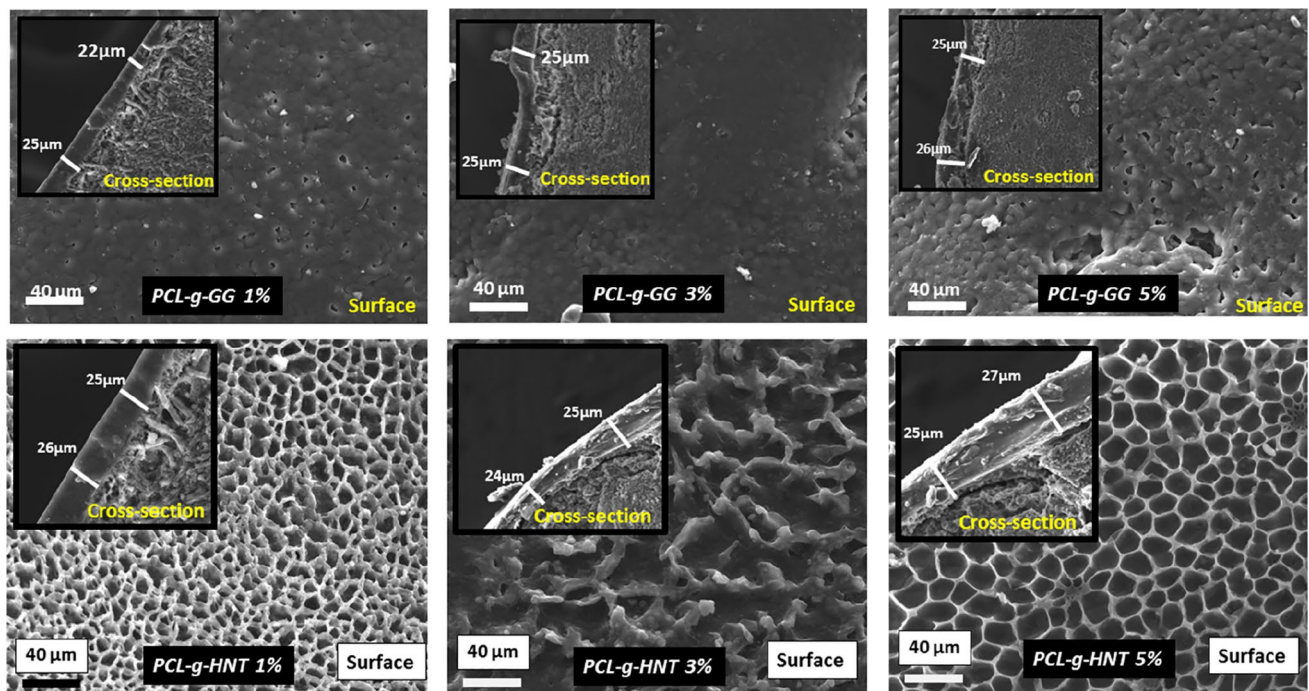
Fig. 6 the surface and the cross section of the DAP granule PLC-g-GG/HNT coated

Fig. 7 EDX surface analysis of the uncoated and coated granules

From Fig. 7, phosphorus and nitrogen signal were observable in the EDX analysis from the surface of the uncoated DAP granules. Based on the visibility of these signals (P, N), the quality of the coating films could be evaluated. EDX signal of the six coating bio-composites proposed was also presented in Fig. 6. Phosphorus and nitrogen signals disappear completely from the DAP surface coated by the composites with 1% of the added charges (PCL-g-GG 1% and PCL-g-HNT 1%), which implies that the encapsulation of DAP granules by those composites provides the best coating coverage. In fact, only the carbon and oxygen signals which are generated from the coating polymer have been observed. While, the composites materials prepared with 3–5% of filler contents (GG and HNT), the EDX spectrums show not only carbon and oxygen signals related to the polymers but also traces of phosphorus signals. This result could be explained by the lowest molecular weight of the grafted polymer onto GG and HNT in one hand and to the size of the pores in the coating surface on the other hand.

The kinetic study of the cumulative nitrogen (NH_4^+) and phosphorus (P_2O_5) released in water from coated and uncoated DAP granules has been carried out to evaluate the effect of the coating on the delaying performance. As revealed in Fig. 8, the release rates of nitrogen and phosphorus from the uncoated granules are very fast; all the nutrients have been liberated at only 1.5 h. While, the coated granules present a slow release property of phosphorus and nitrogen into the distilled water. As mentioned before, the encapsulation of the DAP granules by hydrophobic polymer films enhances significantly the resistance of granules to water

solubility. Indeed, for the granules coated by PCL-g-GG 1% and PCL-g-HNT 1%, respectively around 35 and 50 h were needed to reach complete release of phosphorus and 45 and 50 h to achieved a total release of nitrogen. While, a coating with more hydrophilic composites (3% and 5% wt of GG and HNT) presents lower delaying performance and similar behaviour. Here in, with the bio-composites prepared by 3 and 5% wt. of filler the time needed to reach the total release of phosphorus and nitrogen are 16 and 30 h respectively. All the release rates obtained from the coated granules by PCL-g-GG and PCL-g-HNT were in good agreement with the EDX analysis of the granular coated surface and the contact angle value of the coating films. These results approved the statement presented earlier in which the PCL grafted on hydrophilic filler at 1% wt. present the best coating coverage. Regarding the granules coated by the neat PCL, very slow release performance was achieved. Actually, 65 h are required to attain total release of phosphorus and nitrogen. This result was predictable due to the high hydrophobic character of the neat PCL polymer. In conclusion, the grafting from of PCL on polysaccharide and clay (GG and HNT) as hydrophilic fillers decreases the hydrophobicity and consequently influences the delaying performance of nutriments from coated granules in water medium. Furthermore, the molecular weights of grafted PCL on the fillers (GG and HNT) were different (Table 1) which could be another factor affecting the delaying performance of the coated DAP granules.

Using a semi-empirical model named the Ritger-Peppas, the nitrogen (NH_4^+) and phosphorus (P_2O_5) mechanism
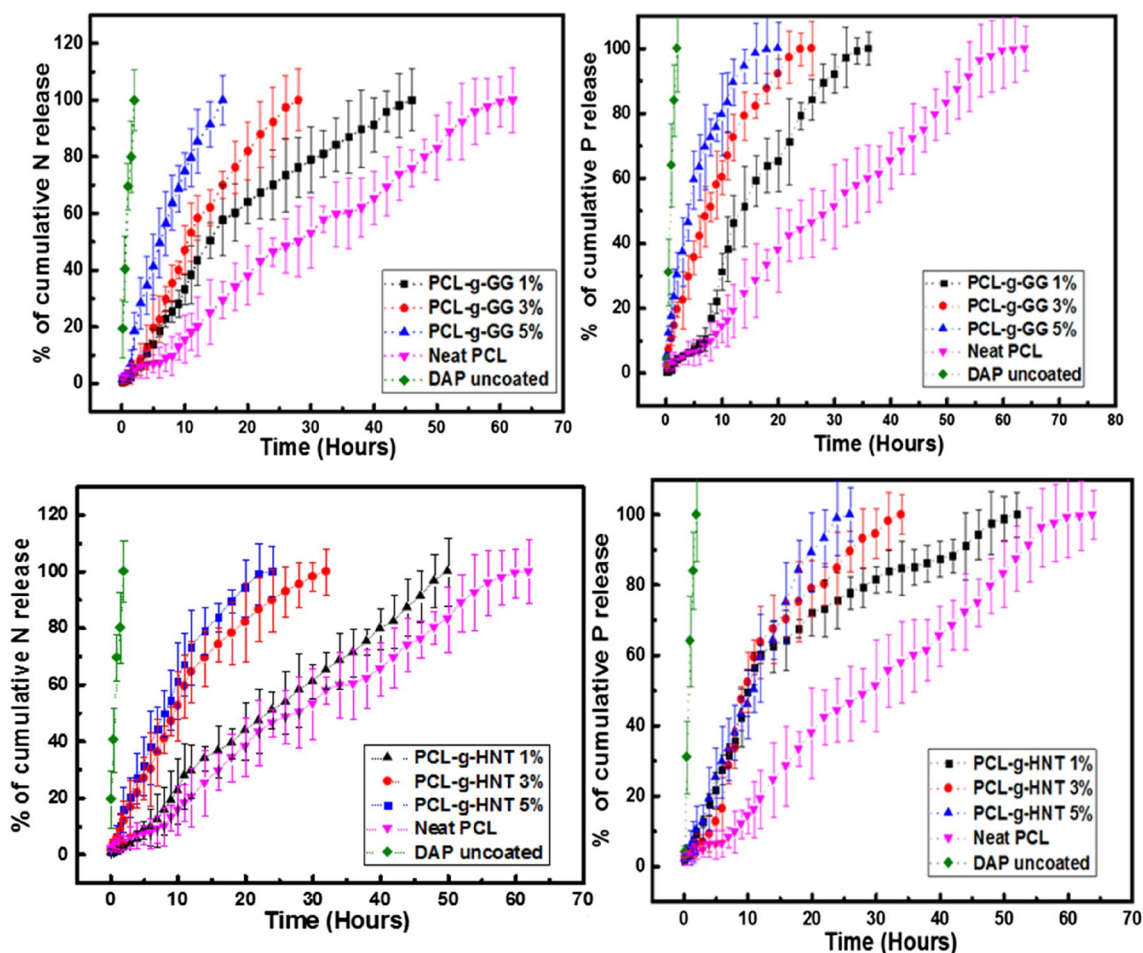
Fig. 8 Release curves in distilled water of N and P from uncoated and coated DAP by PCL-g-GG/HNT composites

Table 3 (n, k, r²) modelling parametrs obtained from fitting the empirical Eq. (3), (Dᵢ) the initital diffusion coefficient calculated from Eq. (5), molecular weight of free PCL fom composies obtaiend by SEC mesurement (Mn) and the time needed to reach half and total release (t $_{(½)}$, t $_{(∞)}$)

	n	k	r²	Di (cm²/s)	Mn (g/mol)	t $_{(½)}$ (hours)	t $_{(∞)}$ (hours)
Nitrogen release (NH$_4^+$)							
PCL	0.8	0.22	0.93	8.28×10^{-17}	98,100	25	60
PCL-g-GG 1%	1.09	0.19	0.97	37.7×10^{-17}	86,104	14	46
PCL-g-GG 3%	1.09	0.22	0.97	127×10^{-17}	47,559	10	28
PCL-g-GG 5%	1.05	0.31	0.94	191×10^{-17}	30,108	7	16
PCL-g-HNT 1%	1.05	0.16	0.98	16.4×10^{-17}	97,217	22	50
PCL-g-HNT 3%	0.83	0.31	0.99	93.5×10^{-17}	85,023	10	32
PCL-g-HNT 5%	0.94	0.30	0.98	75.6×10^{-17}	52,260	8	24
Phosphorus release (P$_2$O$_5$)							
PCL	0.82	0.21	0.93	6.96×10^{-17}	98,100	30	64
PCL-g-GG 1%	1.18	0.17	0.96	33.1×10^{-17}	86,104	13	35
PCL-g-GG 3%	0.73	0.37	0.99	123×10^{-17}	47,559	7	26
PCL-g-GG 5%	0.62	0.48	0.98	215×10^{-17}	30,108	4	18
PCL-g-HNT 1%	0.79	0.28	0.96	82.7×10^{-17}	97,217	10	51
PCL-g-HNT 3%	0.89	0.26	0.93	92.8×10^{-17}	85,023	10	36
PCL-g-HNT 5%	0.84	0.31	0.98	71.7×10^{-17}	52,260	10	26

of release from the coated DAP granules by all the PCL bio–composites was investigated and compared to the release mechanism from the granules coated by the neat PCL. The diffusion exponent (n), correlation coefficient (r^2) and release factor, (k) of each coating system were calculated by plotting of log (M_t/M_∞) versus log time [46, 47]. The initial diffusion coefficient Di (first 10 h) was determined by employing Eq. (5). The results of diffusion exponent, release factor and initial diffusion coefficient of all the coating material tested were summarized in Table 3. Neat PCL as coating, presents a non-Fickian release mechanism (anomalous transport) for both nutrients (NH_4^+, P_2O_5), with diffusional exponent value of 0.8 (0.5 > n > 1). Concerning the nutrients release mechanism from the PCL bio-composites coated granules; the phosphorus diffusion was similar to those of neat PCL (not-Fickian). Regarding, the nitrogen release, the diffusion mechanism approaches to case II transport (zero order), the values of diffusional exponent were close to 1 (n = 0.8). The diffusion from granules coated by PCL-g-GG 5% could be closer to Fickian (n = 0.65 ~ 0.5). The neat PCL as coating material presents the lowest value of the initial diffusion coefficient (Di) of the nutrients across the coating. As illustrated in Fig. 9, the D_i value of N and P increases significantly by increasing the fillers (GG & HNT) contents in the bio-composites (PCL-g-GG and PCL-g-HNT). This behavior could be due to the hydrolytic degradation of ester groups of PCL chains. In that regard, it was reported in previous studies that the rate of hydrolysis degradation could be affected by the introduction of hydrophilic moieties that favored the water penetration inside the polyester chains [52–54] and consequently enhances the hydrolysis of the ester-groups of PCL. Therefore, the initial diffusion coefficient (D$_i$) of the nutrients (N, P) thought the coating system was nicely correlated to the amount of hydrophilic fillers (especially guar gum). Moreover, it should be pointed out that an unexpected decrease of

the D_i of N and P diffusion from the granules coated by the PCL-g-HNT 5% was observed. In fact, in this context, the adsorption capacity of the ammonium and phosphate ions of HNT at 5% as amount could be the main cause of such diffusion decrease [55–57].

As reported earlier, GG and HNT act as initiator of the in situ ring opening polymerization via their –OH groups. Additionally, by adjusting the amount of those fillers (GG or HNT) a controlled release perspective could be conceivable. Through those results, it can be concluded that only the bio-composites PCL-g-GG as coating material could substitute the double coating approach used for combining the slow release behaviour and the water absorbency capacity.

Conclusion

This study presented a new approach for preparing new types of slow-release membrane-encapsulation of granular DAP fertilizer by using PCL-g-GG and PCL-g-HNT as biodegradable carriers materials. Simple dip-coating process and drying at 30 °C of the DAP granules leads to a covered granular by a thin layer within the PCL matrix grafted on guar gum or halloysite nanotubes. The release rate of nutrients from covered DAP was evaluated, and the subsequent conclusions were achieved: (i) the DAP release rate could be controlled by adjusting fillers (GG or HNT) contents on the coating composites. The total nutrients release time can be varied from 1.5 h for uncoated DAP granules to 50 h with coated DAP granules by materials prepared with 1% wt. of GG and HNT. (ii) The SEM cross-section images revealed a coating thickness around 25 μm and show a good adhesion between the granules and the coating films while weak adhesion has been observed when the DAP has been coated by the neat PCL. (iii) Composite materials prepared with 1% wt of HNT present the best performance in term of mechanical
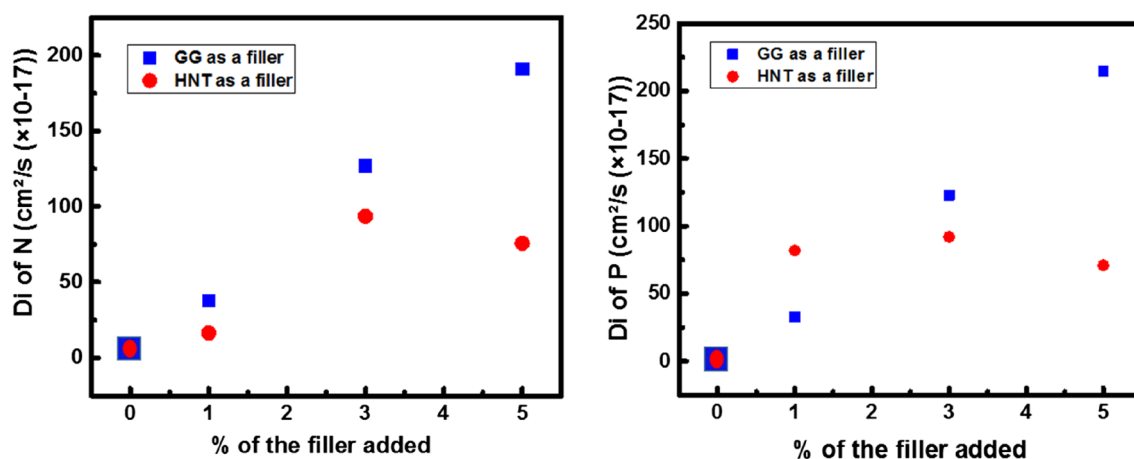

Fig. 9 Coefficient Diffusion (Di) versus the amount of filler added in the bio-composites coating

properties. (iv) The introduction of guar gum not only raises the water holding capacity of PCL matrix but also opens a controlled release of nutrients perspective by adjusting in amount during the polymerization. Therefore, the modified PCL products as coating material could substitute the double coating approach used for combining the slow release behaviour and the water absorbency property.

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