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Exploiting hydrohydroxymethylated sunflower oil grafted on polycaprolactone as biodegradable coating material of water-soluble fertilizers

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Abstract:

Biodegradable materials based on branched-architecture vegetable oil have attracted much interest in recent years. In the present study, hyperbranched $poly(\epsilon$ -caprolactones) were prepared and used as coating materials to prepare slow release diammonium phosphate (DAP) fertilizer. Firstly, the sunflower oil was hydrohydroxymethylated by one-pot two-step process using Rh(acac)(CO)₂ as catalyst, and triethylamine as ligand. Next, the bio-based hyperbranched poly(ɛ-caprolactone) (SFO-O-PCLs) were prepared in open air by *in-situ* ring-opening polymerization of ε -caprolactone using hydroxymethylated sunflower oil as macro-initiator and tetra(phenylethynyl)tin (Sn(C=CPh)₄) as catalyst. The structures of the prepared polymers (SFP-O-PCL) were confirmed by nuclear magnetic resonance (¹H NMR) and the infrared spectroscopy (FTIR). Furthermore, the molecular weights of SFP-O-PCL were determined by size exclusion chromatography (SEC), the thermal stability and morphology of the coated film were evaluated respectively by thermogravimetric analysis (TGA) and the scanning electron microscopy (SEM). As the hydrophobic / hydrophilic balance is a key parameter in the coating of fertilizer domain, the hydrophobic character of the prepared SFP-O-PCL was also assessed by measuring the water contact angle (WCA). The final part of this contribution was devoted to the study of phosphorus (P₂O₅) kinetic released in water from coated and uncoated DAP granules. Thus, it was found that the prepared coating materials exhibited good performance in delaying the release of phosphorus and open a wide perspective for combining the advantages of hydrophobic polyesters and biobased oil.

Keywords:

In-situ polymerization, Polycaprolactone, grafting form, biobased oil, slow-release fertilizer.

1.Introduction

Fertilizers have an important role in agriculture. They provide nutrients to crops and also improve the physical, biological and chemical properties of the soil [1]. However, as the main nutrients in conventionally used fertilizers are nitrogen, phosphorus and potassium (N, P, K), their excessive use leads to the depletion of the world's reserves of these valuable and non-renewable elements [2]. In addition, recent studies on the long-term availability of these agrochemicals have confirmed a rapid release of these nutrients from fertilizers into the soil during the direct application process. This application method results in the loss of a large amount of these nutrients (about 40-70% of nitrogen, 80-90% of phosphorus, and 50-70% of potassium) that cannot be absorbed by the crops. In fact, the low efficiency of conventional fertilizers leads to variable mobility of nutrients and losses such as runoff, fixation, eutrophication, and volatilization, which have been shown to have a negative impact on the ecosystem by contaminating aquatic resources and the atmosphere [3,4].

Therefore, to enhance the fertilizers efficiency, improve stability and reduce their environmental impact, coating approach has been investigated during the last decades to obtain a slow and controlled nutrients release from the water-soluble fertilizer granules (SCRF) [5,6]. Indeed, many previous studies have investigated synthetic polymers as hydrophobic coating material such as polyethylene, poly (acrylic acid-co-acrylamide), poly (butyl methacrylate), polystyrene and others [7-10]. However, these coating materials are non-biodegradable and have raised doubts about the sustainability of such alternative. Moreover, it has been estimated that around 50 kg/ha of plastic residue could be cumulated each year in soils and consequently could affects its quality [11]. Thus, research investigations were later oriented on the potential uses of polysaccharides as biodegradable coating materials of granular fertilizers. Indeed, cellulose, chitosan and other polysaccharides were used as sustainable coating materials to overcome such biodegradability issue [12–15]. However, the use of these polysaccharides as coating materials has not led to the expected results, due to their highly hydrophilic character, poor mechanical properties, and their insolubility in organic solvents. Actually, organic solvent affords a uniform coating thickness during the coating processes which could not be unfortunately ensured when water is used as solvent as the granular fertilizers to be coated are water-soluble. Taking into consideration the above conclusions, researchers have recently focused their investigations on hydrophobic biopolymers-based coating such as aliphatic polyesters [16]. In spite the fact that the new approach adopted lead to the elaboration of original coating materials characterized by their biodegradability and hydrophobic character [17–20], it should be noted that the marketability of the coating materials based on aliphatic polyesters remain so far constrained.

Meanwhile, vegetable oil, as a biobased material, has attracted attention in recent years due to its availability, renewable nature, high hydrophobicity, biodegradability, and low cost. However, most vegetable oils have limited technological application in their original forms because of their specific

chemical and physical properties. To work around this, vegetable oils are often modified by hydrogenation, interesterification, fractionation or blending with other moieties [21]. Recently, in the coating fertilizers field, we reported for the first time the possibility of using only vegetable oil as a coating material for fertilizers [22]. In this study, Priamine 1071®, a commercial amino oil, was chosen because of its high hydrophobicity character to prevent rapid water penetration into the fertilizer granules, and also for its low viscosity to avoid the use of solvent in the coating process. With this oil, the rate of nutrient (phosphate) released into the water after coating was significantly delayed, but it was very difficult to dry the encapsulated granules after the coating process which led to granules stick. To circumvent this problem, it has been reported that it is necessary to cross-link the vegetable oil by combining it with other materials. In this respect, recent studies cross-linked hydroxylated vegetable oils using polyisocyanates have shown high efficiency for fertilizer coating. In this case, the drying problem encountered when using neat oils has been surmounted [23]. Nevertheless, the use of isocyanates as cross-linking agents is generally very harmful to human health [24]. Therefore, the idea of this work is not to cross-link vegetable oils to effectively coat phosphate fertilizers, but to use them as a carrier for the grafting of aliphatic polyesters to develop biodegradable coating materials without employing a harmful cross-linking agent.

Among the most widely studied aliphatic polyesters is $poly(\epsilon$ -caprolactone) (PCL) due to its high biodegradability, mechanical properties, and hydrophobic character and miscibility with a wide variety of other polymers. The poly(ε -caprolactone) is widely synthetized by the ring opening polymerization (ROP) of ε -caprolactone using stannous octoate as a catalyst. Indeed, the ring opening polymerization of ε -caprolactone affords polymer with high molecular weight and lower dispersity [25]. The most used catalyst for the ring opening polymerization are tin(II) and tin (IV) complexes [26–28], but tin-octoate is by far the catalyst that has usually used thanks to its effectiveness in the *in-situ* ROP of ε -caprolactone even in presence of organic and inorganic fillers [29,30]. However, as all those tin catalysts required inert gas condition to control polymerization process and to avoid drop down of molecular mass of the polymer [31]. Therefore, this synthetic approach is complicated by the presence of physically or chemically adsorbed water and the high number of hydroxyl groups in polyols oils, which leads to the grafting of only low molecular weight polymers. For instance, Gokhan Acik recently reported the ringopening polymerization of ε -CL using stannous octoate as a catalyst and soybean oil hydroxyl groups (SBO-OH) as macro-initiators (polyol), the grafting of PCL onto oil was achieved but under strict experimental requirements, such as drying of solvent and reagents and working under anhydrous conditions, must be applied to ensure control of the polymerization [32]. With the aim of circumventing the disadvantage of using tin octoate as the standard catalyst for the ROP of cyclic esters, we have investigated a new catalyst based on tetra(alkynyl)tin to prepare a high molar mass grafted biodegradables polymers on hydroxylated organic and inorganic fillers [30,33,34]. Indeed, tetra(phenylethynyl)tin was found as efficient catalyst for the ring opening polymerization of lactide

and ε -caprolactone even in open air at high (monomer)/(catalyst) ratio in the presence of silica nanoparticles [35]. In fact, the stability of tin-alkynyl bond (Sn-C=C-R) in air allows a short time synthesis without inert atmosphere requirement. In addition, the hydrolysis of tetra(phenylethynyl)tin catalyst like stannous octoate affords tin oxide, nontoxic compound approved by the FDA for internal use in human [36].

In this contribution, we report the synthesis in open air of a series of biodegradable polymeric materials via *in-situ* ring-opening polymerization (grafting from) of ε -caprolactone in the presence of hydrohydroxymethylated sunflower oil as a macro-initiator using tetra(phenylethynyl)tin (Sn(C=CPh)₄) as a catalyst. Sunflower oil has been hydrohydroxymethylated (SFO-OH) before the grafting from according to the one-pot two-step process adapted in previous works where the first step is the hydroformylation of the carbon- carbon double bonds (C=C), followed by a subsequent reduction of the formyl group [37]. It should be noted that the one-pot tandem reaction is atom-economical, proceeds very cleanly, and lead to highly reactive primary alcohol than the secondary generally obtained by opening the epoxide ring of epoxidized oils. Once the synthesis was completed, the prepared material was fully characterized to approve the covalent linkage between poly(ε -caprolactone) (PCL) polymerized and hydrohydroxymethylated sunflower (SFO-OH), and to investigate its thermal stability and surface propriety. Afterward, granular fertilizer of diammonium phosphate (DAP) were coated by the prepared material (SFO-O-g-PCL) using a laboratory rotary drum. Finally, the kinetic release of nutrients (phosphorus) in water was studied to evaluate the slow-release proprieties of the coated fertilizer proposed (SRF).

2.Experimental section

2.1 Materials

DAP, a granular diammonium phosphate fertilizer was received from OCP Group (Morocco), Very High Oleic Sunflower Oil (VHOSO) was provided by Oleon (France) (composition in Table 1SI), poly(ε -caprolactone) (PCL) 90000 gmol⁻¹, ε -caprolactone (CL), methanol, toluene, and tetrahydrofuran (THF) were purchased from sigma Aldrich, toluene and ε -caprolactone (CL) were distilled before their uses, hydroxylated sunflower oil, and tetra(phenylethynyl)tin were synthesized.

2.2 Synthesis procedures

One-pot synthesis of hydrohydroxymethylated sunflower oil (SFO-OH)

The hydrohydroxymethylation of sunflower oil was carried out following a previously published procedure [37]. In a typical catalytic experiment, $Rh(acac)(CO)_2$ (7.8 mg, 0.030 mmol), triethylamine (418 µL, 3 mmol, typically), VHOSO (2 mL, 2 mmol), and toluene (10 mL) were added in a 25 mL stainless-steel autoclave (Parr instrument company) equipped with a mechanical stirrer. Then, the reactor was sealed, the reaction mixture was stirred and heated at the desired temperature (typically 80 °C). Later, the reactor was pressurized with a mixture of CO and H₂ (1:1 ratio) at desired pressure

(typically 80 bar). When the reaction is completed, the apparatus is allowed to cool down to room temperature and depressurized. The catalyst was removed by filtration on Celite. The solvent was separated from products under vacuum and the hydrohydroxymethylated sunflower oil was ready to be used in the polymerization.

Catalyst synthesis $(Sn(C \equiv CPh)_4)$

The synthesis pathway of tetra(phenylethynyl)tin catalyst was inspired from previous published work [38]. In fact, a three-necked flask was charged with 9 g of phenylacetylene. Furthermore, toluene was added to butyllithium in hexane. Then 5 g of Sn(IV)chloride in dry toluene was added to the solution under stirring at 70 °C. Finally, the obtained solution was filtrated, and the solvent was evaporated under vacuum. A yellow solid residue was obtained and recrystallized from toluene.

In-situ ring opening polymerization (ROP) of ε -CL from hydrohydroxymethylated sunflower oil

The synthesis approach of $poly(\varepsilon$ -caprolactone) grafted from hydrohydroxymethylated sunflower oil (SFO-O-g-PCL) was carried out in solvent-free conditions by using 5 different ratios of monomer/catalyst/oil (ε -CL/ Sn(CCPh)₄/ SFO-OH) of 50/1/1 (P1), 50/1/3 (P2), 50/1/5 (P3), 100/1/3 (P4) and 1000/1/3 (P5) in open air. It should be noted that the hydroxyl groups in the sunflower oil act as a co-initiator to initiate the ring-opening polymerization (ROP) of ε -CL. The tin catalyst was used in stock solution in dry toluene. The hydrohydroxymethylated sunflower oil (SFO-OH) was solubilized in ε -caprolactone (ε -CL), afterwards, the catalyst in stock solution in dry toluene was added to the mixture and stirred at room temperature for 2 h. Then, the polymerization was conducted at 140 °C for a period of 1 h. At the end of the reaction, the resulting product was dissolved in a minimum of THF, then precipitated in cold methanol and the resulting product was filtered and dried in a vacuum oven at 50 °C for 24 h.

2.3 Coating of granular fertilizers (DAP)

Firstly, the prepared materials SFO-O-g-PCL were solubilized in THF (5%w.t.), then spherical granules (3-4 mm of diameter) of fertilizer were selected and loaded onto a laboratory rotary drum (see **figure 2SI**). The coating was applied by maintaining rotation speed at 100 rpm and alternation of injection/heating inside the pan. In fact, the injection was assured using an appropriate syringe and the heating by using heat flow tube of about 50 °C. After the coating process, the granules were weighed, and the percentage coating was calculated using equation (1):

% Coating =
$$\frac{(M_f - M_i)}{M_i} \times 100$$

Equation (1)

 M_i and M_f are the fertilizer weights before and after coating respectively.

2.4 Phosphorus release test in water

The experiments were performed at room temperature. Uncoated and coated DAP granules (100 mg) were immersed in 250 mL beakers of distilled water, the system was homogenized with slight and continuous stirring. Samples of 100 μ L were taken at different time intervals, diluted, and analyzed by spectrophotometer. The release kinetics of phosphorus in distilled water was determined by colorimetric methods (AFNOR-T90-023) using Ammonium-molybdate/ascorbic acid reagent. The colored complex was analyzed at a wavelength of 880 nm using an ultraviolet-visible spectrophotometer (UV-2600, Shimadzu).

2.5 Characterization methods

Nuclear magnetic resonance (¹H-NMR)

To confirm the grafting of poly(ε -caprolactone) (PCL) into hydrohydroxylated sunflower oil (SFO-OH), the prepared materials were analyzed by ¹H NMR. NMR spectra were recorded at 298K on a Bruker Avance III HD 300 NanoBay spectrometer equipped with a 5 mm broadband probe BBFO with Z-gradients, operating at 7.05 T field strength (300 MHz for ¹H nuclei and 75 MHz for ¹³C nuclei).

Fourier transform-infrared spectroscopy (FT-IR)

Structural interactions were investigated using Fourier transform infrared spectrophotometer (FTIR) (Prestige-21) using a bright ceramic light source, a high sensitivity DLATGS detector and high-throughput optical elements. The analysis was performed at room temperature in a range of wave numbers between 450 and 4000 cm⁻¹.

Size exclusion chromatography (SEC)

Steric exclusion chromatography (SEC) was used to determine the molecular weight of the prepared polymers. Measurements were performed on high resolution GPC/SEC Agilent chromatography equipped with two RI and UV sensors connected to PL-gel (MIXED-C column). Tetrahydrofuran was used as eluent in the chromatographic system, with rate flow of 1 cm³ min⁻¹. The molecular weight distribution was calculated based on the specific calibration curve of poly(styrene) certified (PS calibration Kit S-M2-10).

Thermogravimetric analysis (TGA)

The TGA was performed to investigate the thermal stability of prepared materials (SFO-O-g-PCL). TGA measurement was performed using the TA Instruments Q500 analyzer at a heating rate of 10 °C min⁻¹ under nitrogen atmosphere (40 cm³ min⁻¹). The experiments were performed with a temperature ramp of 10 °C/min in the range of 20-600 °C.

Scanning electronic microscopy (SEM)

The surface morphology and thickness of the coated granules were determined by scanning electron microscopy (SEM), observations were recorded on Vega 3 TESCAN with a conventional tungsten heated cathode, intended for high vacuum and low vacuum operations. All samples were previously sputter-coated with Au-Pd in argon plasma to assure their conductivity.

Contact angle measurement

Contact angle measurements of water droplets on the prepared material surface were performed on EASY DROP machine. Measurements were carried out at room temperature with 2 μ L water droplets.

3. Results and discussion

SFO-OH synthesis

The hydrohydroxymethylated sunflower oil was obtained by one-pot two-step process using $Rh(acac)(CO)_2$ as catalyst, and triethylamine as ligand. The reaction was carried out at 80 °C under 80 bar CO/H₂ (1:1). The first step is hydroformylation of the C=C double bonds, followed by reduction of the formyl group. In this process, the carbon-carbon double bonds can remain unchanged or be isomerized, allowing the hydroxymethyl groups to be randomly located [37].



Scheme 1. One pot tandem rhodium-catalyzed hydrohydroxymethylation (HHM) of sunflower oil (SFO-OH)

SFO-O-g-PCL synthesis

As mentioned above, the SFO-O-g-PCL polymeric materials were prepared by *in-situ* ring-opening polymerization (ROP) of ε -CL using SFO-OH as a macro-initiator and Sn(C=CPh)₄ as a catalyst in solvent free conditions. The polymerization was performed in open air. The mechanism suggested for this synthesis is similar to that already reported in previous studies [30,33,34]. In fact, PCL is grafted form hydroxyl groups of sunflower oil (SFO-OH) through the ring opening polymerization reaction of ε -CL. The catalyst Sn(C=CPh)₄ and hydrohydroxymethylated oil reacted first at room temperature to

form the active center, tin-alkoxy group (SFO-O-Sn-) that acts as an initiator for the ROP of ε -CL. Once the intermediate reactive is formed, the polymerization starts via the reaction of the monomers with the active centers (SFO-O-Sn-) at 140 °C through the coordination of the ε -CL monomers onto the formed alkoxide groups (SFO-O-Sn-) via their carbonyl functions followed by a rearrangement leading to the cleavage of the O-acyl bond and the insertion of the monomer into the RO-Sn-linkage (**Scheme 2**).



Scheme 2. Proposal mechanism of the in-situ ROP reaction of ε-caprolactone in the presence of hydroxylated sunflower oil

Characterization of the prepared materials (SFO-O-g-PCL)

After the ring opening polymerization of ε -CL, the obtained SFO-O-g-PCL materials represented in figure 1 were characterized by ¹H NMR. Figure 2 shows the superposition of ¹H NMR spectra of (1) Neat PCL, (2) hydrohydroxymethylated sunflower (SFO-OH) and (3) the prepared polymer SFO-O-g-PCL. First, neat PCL spectrum shows two triplets corresponding to CH₂-O at 4.10 ppm (e) and CH₂-C=O at 2.34 ppm (a), and two multiplets that correspond to the remaining CH₂ (b, c, d) of each PCL unit. Regarding SFO-OH spectrum, the two multiplets corresponding to the CH group at 5.29 ppm (a) and CH₂ group around 4.10-440 ppm (b) of the VHOSO skeleton were observed, as well as the massive CH₂-OH at 3.55 ppm (f). The remaining signals belong to dangling chains such as CH₂-C=O at 2.34 ppm (a), CH₂ of the carbon chain (c), and a triplet of the methyl protons of aliphatic group (d) around 0.87 ppm. In the spectrum of the prepared polymer SFO-O-g-PCL, it is interesting to mention that we find the different signals of SFO-OH namely the small triplet (c) and the alkyl chain (d). Zooming in on the part of the spectrum between 3.5 ppm and 5.5 ppm, we also find the signals (a) and (b) corresponding to the VHOSO skeleton. Most interesting is the shift of the signal (f) showing the

modification of the CH_2 -O and thus confirming the grafting. Thus, these ¹H NMR results could be considered as evidence of successful grafting of PCL onto hydrohydroxymethylated sunflower.



Figure 1 : Proposed structure of SFO-O-g-PCL



Figure 2. Superposition of ¹H NMR spectra of (1) Neat PCL, (2) SFO-OH, and (3) SFO-O-g-PCL in CDCl₃ at 25°C

The Infrared spectroscopy was performed to identify functional groups of hydrohydroxymethylated sunflower (SFO-OH), the neat PCL and the prepared materials SFO-O-g-PCL. (Figure 3 and Figure 1SI). In fact, characteristic broad bands of sunflower hydroxyl groups (OH) at around 3416 cm⁻¹ and an intense carbonyl band at 1743 cm⁻¹ of C=O are clearly evidenced. Meanwhile, Neat PCL spectra shows similar vibration of carbonyl function (C=O) at 1743 cm⁻¹, but narow one was detected at 3443 cm⁻¹ that is asigned to PCL OH groups. It souhld be noted that C-H vibration characterized by two bands around 2857-2949 cm⁻¹ were revealed for both sunflower and neat PCL spectras. For structural investigation of the prepared material (SFO-O-g-PCL), PCL fingerprints were clearly revealed from FTIR spectra of SFO-O-g-PCL. Furthemore, a significant increase was observed on hydroxyl (OH) vibration of SFO-O-g-PCL compared to neat PCL which could be due to the contribution of

hydrohydroxymethylated sunflower in the prepared material as the grafting of PCL onto SFO-OH leads to polymers with three terminal hydroxyl groups (**scheme 2**) whereas neat PCL possesses only one.



Figure 3. FTIR spectroscopy of Neat PCL, SFO-OH, and SFO-O-g-PCL (P5)

The molecular weight of all prepared polymers was determined using steric exclusion chromatography (SEC). Table 1 summarized the molecular weights Mn and the dispersity \mathcal{P} of prepared polymers. In fact, the high molecular weight (28000 g.mol⁻¹) was obtained with the highest monomer/catalyst/ SFO-OH ratio (P5: 1000/1/1). Furthermore, the effect of hydrohydroxymethylated sunflower ratio on the polymerization reaction was also studied 50/1/1 (P1), 50/1/3 (P2), 50/1/5 (P3).

The molecular weight of polymer decreases by increasing the SFO-OH/monomer ratio. For the PCL obtained with 50/1/5 molar ratio, the molar mass presented the lowest value; it is probably due to the increase of the polymerization sites (hydroxyl co-initiator), which leads to more polymer chains but with shorter chain lengths. The explanation of this results is in good agreement with the assumption that a higher content of hydroxyl group of SFO-OH leads to a higher catalyst-co-initiator, which could generate a higher number of short chains of PCL (**Scheme 2**) [25,30,35]. Analogically, the decrease of SFO-OH ratio leads to a low catalyst-co-initiator, which implies long polymeric chains, thus a high molecular weight (**Table 1**).

The dispersity (D) of the synthesized polymers, remained lower than 1.6 (1.22–1.55) indicating that the polymerization proceeds at least partially by a controlled mechanism with little transesterification side reactions favored by the higher temperature.

Table 1. Results of SEC characterization of PCL

SFO-O-g-PCL	$M_n\left(g/mol\right)$	M _w (g/mol)	Đ
P1 :50/1/1	23641	31286	1.32
P2:50/1/3	21832	28231	1.29
P3 :50/1/5	13210	16197	1.22
P4 :100/1/3	18330	23922	1.30
P5 :1000/1/3	28666	44466	1.55

 M_{n} , M_{w} , and \tilde{D} determined by steric exclusion chromatography (SEC)

The thermal properties of all prepared polymers were investigated by TGA analysis to evaluate the effect of the incorporation of SFO-OH in PCL on the thermal stability of the prepared materials (SFO-O-g-PCL). Indeed, as presented in figure 4 and Figure 3SI, the thermal degradation of the prepared materials (P1, P2, P3, P4 and P5) occurred in a single step while thermal degradation of the neat PCL starts at 340 °C with a weight loss of 5% followed by total degradation at around 480 °C. It should be noted that the molecular mass of synthetized polymers (SFO-O-g-PCL) was significantly lower compared to neat PCL (90000 g.mol⁻¹) used as reference sample. As consequence, the drop down in term of thermal stability could be clearly noticed from **figure 4**. Generally, this degradation behavior is attributed to a transesterification, as secondary reaction that occurs at high temperatures [39].



Figure 4. TGA curve of the SFO-O-g-PCL polymers and Neat PCL.

The hydrophobic/hydrophilic balance was evaluated by determining the contact angle value of droplet water deposed on the prepared materials surfaces. Actually, the hydrophobic character of fertilizer coating materials is a key paramter towards inhibiting water penetration on the fertilizer core. **Figure 5** shows the values of the angles measured with the EASY DROP. In that regards, the results provide more information about the hydrophobicity/hydrophilicity balance by varying the oil and monomer ratios in the prepared materials SFO-O-g-PCL. Although the hydrophobic character was relatively preserved for all prepared SFO-O-g-PCL materials in comparison to neat PCL, the slight decrease in hydrophbic character could be due to the additional OH groupe localized in PCL end chain grafted from the hydrohydroxymethylated sunflower.



Figure 5. Contact angle values of PCL and PCL composites.

To better evaluate the effect of introducing SFO-OH into PCL towards the coating of water-soluble fertilizers, the granular diammonium phosphate fertilizer and SFO-O-g-PCL (P5) were selected. Indeed, this choice was motivated by the fact that P5 has the highest molecular weight which is required to form stable coating films as well as its lower contact angle which would control the penetration of water into the granule through the coating film. **Table. 2** summarized the coating content of selected material, its M_n and its contact angle value. It should be noted that the prepared material was able to be dried at the end of the coating process.

DAP Coating	Coating content (wt%) ^a	Mn (g/mol) ^b	WCA (°) ^c
P5 :1000/1/3	17	28666	66,7

^a Determined by scanning electron microscopy (SEM); ^b Determined by Steric exclusion chromatography (SEC); ^c Determined by EASY DROP machine

The morphology and thickness of the SFO-O-g-PCL coating achieved by a rotary drum was investigated by SEM. Firstly, SEM image (**Figure 6 B and C**) of the cross-section allows the determination the coating thickness that is around 50 μ m. Furthermore, it has been approuved that the coating process developped in this study affords a unifome thickness as reported in previous published work [17,40]. Secondly, from **the figures 6A**, it was observed that the uncoated granule has a rough surface while the coating makes the surface smoother as observed from figure 6C. On the other hand, EDX analysis on the uncoated granule reveals phosphorus and nitrogen signals, whereas in the case of the coated granule, only carbon and oxygen signals were detected which are the only elements constituting the coating material and indicating also the absence of failures and cracks on the surface of the coating.



Figure 6. SEM images of granule surfaces (A) uncoated DAP, cross-section of coated DAP (B and C) and their EDX analyses

Phosphorus release study

In this last part, the kinetic study of the cumulative phosphorus (P₂O₅) released in water from coated and uncoated DAP granules was studied. According to previous investigation [18,41], the release rate depends on the hydrophobicity, molecular weight, and the thickness of the coating materials. **Figure 7** presents the release rate of phosphorus from uncoated and coated DAP granules in distilled water. In fact, the coated fertilizers present a significant slow-release properties. The delay of phosphorus release from coated fertilizers was clearly observed compared to the uncoated one in which less than 2 hours were enough to reach the total release. Meanwhile, the release of phosphorus from coated fertilizer by neat PCL presents the slowed release kinetic compared to prepared material (P5). The later statement was due to the high hydrophobic character of neat PCL that protects well the coated granules and avoids water penetration into fertilizer core. The prepared material (P5) exhibits slow phosphorus release behavior in distilled water, and only 32% was released in the first 10 hours. Indeed, we suggest that the difference in term of slow-release performances noticed between the prepared and neat PCL coating was due to the differences in molecular weight and hydrophobic character. It has been reported before that high molecular weight inhibits the hydrolysis of the polymeric chain and consequently the delaying performance will be enhanced [18]. To conclude, the prepared material P5 proposed in this study as a granular fertilizer coating agent showed a promising result and opens a great opportunity to combine hydrophobic polyesters with biobased oils towards new applications.



Figure 7. The release curves of P in water from uncoated and coated DAP by Neat PCL, the prepared coating agent SFO-O-g-PCL (P5)

4. Conclusions :

In this research work, $poly(\varepsilon$ -caprolacotone) (PCL) was grafted from hydrohydroxymethylated sunflower oil (SFO-OH) following *in-situ* ring openning polymerization (ROP) approach by using efficient tin based catalyst in open air. The prepared polymers (SFO-O-g-PCL) were fully characterized and the covalent bonding of PCL with hydrohydroxymethylated sunflower was approved by ¹H NMR and infrared spectroscopy. As revealed from SEC measurment, the PCL molecular weight grafted on the biobased oil could reach 28000 gmol⁻¹ with high monomer to catalyst ratio. Moreover, the films formed from the prepared polymers showed a slight decrease in term of hydrphobic property which was probably due to the presence of hydroxyl fuctions as a polar groups. Furthermore, the thermal stability of the prepared material was compared to the neat PCL and a significant decrease was noticed, which

could be related to the lower molecular weight of grafted PCL on SFO-OH oil. Furthemore, the prepared SFO-g-PCL (P5) and neat PCL were used for coating diammonium phosphate (DAP) granular fertilizer. From SEM observation, an uniform coating thickness was achieved without cracks or failures. The invistigation of phosphorus release in distilled water from diammonium phosphate (DAP) coated granules and uncoated ones was carried out and it was found that granules coated with SFO-O-g-PCL and neat PCL show slow release of nutrients compared to uncoated granules.

In fact, the use of prepared material (P5: SFO-O-g-PCL) as coating agent of granular fertilizer displays promising result that open the opportunity of combining hydrophobic polyesters and biobased oil toward original coatings materials for fertilizers.

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