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PAPER
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Insights into hydrophobic (meth)acrylate polymers as coating for slow-release fertilizers reduce nutrients leaching

Asma Sofyane, [a] Salima Atlas, [a,b] Mohammed Lahcini, [a,c] Elvira Vidović,[d] Bruno Ameduri, [e]* Mustapha Raihane [a,f]*

[a] IMED-Lab. Faculty of Sciences and Techniques, Cadi-Ayyad University, Av. A. Khattabi. BP 549, 40000 Marrakech, Morocco

[b] ERSIC, FPBM, Sultan Moulay Slimane University, PO. Box. 592, Mghila, 23000, Beni Mellal, Morocco

[c] Mohammed VI Polytechnic University, 43150 Ben Guérir, Morocco

[d] Faculty of Chemical Engineering and Technology, University of Zagreb, Marulićevtrg 19, 10000 Zagreb, Croatia

[e] ICGM, University of Montpellier, CNRS, ENSCM, 34095 Montpellier, France

[f] Applied Chemistry and Engineering Research Centre of Excellence (ACER CoE), Mohammed VI Polytechnic University, Lot 660, Hay Moulay Rachid Ben Guérir, 43150, Morocco

* Corresponding authors: M. Raihane (Email: m.raihane@uca.ma) and B. Ameduri (Email: bruno.ameduri@enscm.fr)

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Abstract

To solve the problem of low utilization rate of conventional fast water-soluble release fertilizers and to minimize their negative impact on the environment, slow-release fertilizers (SRF) have emerged as sustainable solution to limit their losses, reduce fertilizers dosage and improving crop production. In this study, new hydrophobic (meth)acrylates polymers (poly(2,2,2-trifluoroethyle methacrylate)(PTFEMA) and poly(2-(perfluorohexyl)ethyl acrylate) (PPFEHEMA)) with different fluorinated side chains were synthesized by free radical polymerization and used as coatings for SFR. These polymers were characterized by ^{1}H and ^{19}F NMR, FTIR, WCA, TGA and DSC. Compared to PTFEMA, PPFEHEMA with a higher content of F atoms content displayed improved thermal stability and an elastomer property (T_g= -10 °C) leading a satisfactory film formation. Indeed, contact angle measurements (WCA) were carried out on films of both materials, PPFEHEMA with WCA= 109° indicated a highly hydrophobic character with an excellent water-repellent surface, resulting in a coating layer. The use of these polymers as SFR coatings was explored using dip-coating. SEM and EDX mapping were performed to study the morphology of the coated fertilizer granules and showed the formation of a cohesive film with good adhesion between the DAP fertilizer and the coating films, limiting water diffusion. The N, P nutrients release profile was studied, the corresponding release time increased with the coating thickness (single layer: 1L or second layer: 2L). Compared to uncoated DAP granules which is totally solubilized after less than 2 h, DAP coated with 2 L of PPFEHEMA has the slowest N and P nutrients releases, the time to reach the

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maximum N and P releases were 30 and 38 times higher than that of uncoated DAP. The significant delay in the release of nutrients from the DAP coated with PTFEMA and PPFEHEMA is consistent with the nutrient demand during crop growth and increases the efficiency of fertilizer use and therefore enhancing agricultural productivity.

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1. Introduction

From the data of the population projections published by the United Nations, the world population will reach 9.5 billion people by 2050, [1] with a planned increase in food supply of 70 %. [2] The forecast of the Food and Agriculture Organization of the United Nations (FAO) estimates that a quarter of this growing population could suffer from food insecurity. Around 30% of arable land will be lost due to soil degradation. [3] In order to meet the growing global demand for food and to address food security challenges by promoting sustainable agriculture, the use of inorganic nitrogen (N), phosphorus (P) and potassium (K) fertilizers will expectedly increase because they can improve the crop productivity to about 60%.[4] However, current conventional fertilizers are highly water-soluble, meaning that only 30-60% of N, 10-20% of P and 30-50% of K could be absorbed by plants. A large amount of these micronutrients is released into the environment through leaching, runoff, volatilization etc, which has a negative impact on ecosystems and biodiversity such as soil disturbances and groundwater contamination. These losses result not only in low absorption efficiency of the nutrients by plant roots, [5] but also in financial losses due to the waste of energy associated with their productions. [6,7] Therefore, in order to maximize the crop productions one of the major challenges is to rationalize the use of fertilizers. Slow-release fertilizers (SRFs) are proposed as a promising technology to improve nutrient uptake by plants and to minimize environmental pollution. [8] SRFs designed to release nutrients slowly to meet their needs during crop growth[9]. Fertilizer coated with polymers are the most important candidates for SRFs which act as a diffusion barrier membrane. Polyolefin, alkyd-resin and polyurethane-coated fertilizers are important commercially available synthetic polymers coatings for SRF, manufactured by JCAM AGRI Co, ICL Specialty Fertilizers and Koch agronomic Services, Inc. as Nutricote®, Osmocote® and Polyon® trademarks[10], (more details in Supporting information). The synthetic polymers coatings can be divided into two classes: (i) hydrophobic polyolefins which are soluble in organic solvent (*e.g.,* polyethylene [11] and polyacrylonitrile [12]), and (ii) superabsorbent hydrogels as three-dimensional or crosslinked matrices composed of linear or branched polymers with abundant hydrophilic groups[13] which in agriculture lead to increased water storage capacity, limited irrigation amount, and increased crop production in semi-arid and arid areas. [14]

Poly(acrylate)s (PAs) have been widely used to produce SRF to increase agricultural yields of corn and wheat [15] and as superabsorbents. [16] PAs waterborne coatings using aqueous solution in their preparation are known for their appropriate viscosity, good film-forming ability, and strong adhesion to substrates through polar groups. [17] Polysaccharides such as starch, cellulose,

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etc. are used as biopolymers for the synthesis of bio-superabsorbent in which vinyl monomers such methacrylic acid, acrylamide, acrylic acid etc. were grafted on their backbones to increase the hydrophilicity and swelling capacity of these superabsorbent. [18] To elaborate these networks with enhanced water-retention capacity and regulated slow-release of nutrients, the grafting reactions were performed in an aqueous solution by free radical (co)polymerization of these monomers using ammonium persulfate and N,N'-methylenebisacrylate (MBA) as initiator and crosslinking agent, respectively. [16] Recently, Zhu et al.[19] prepared superabsorbent hydrogels composites based on Okara, a byproduct derived from soybean oil milk, grafted on poly(acrylic acid), by *in-situ* radical polymerization to improve vegetable cultivation through increasing water holding capacity in soils. Jumpapaeng et al.[20] prepared bionanocomposite hydrogels (BHM) as a promising material by combining cassava starch, polyacrylamide, natural rubber, and various montmorillonite clay loadings. These low-cost biohydrogels exhibit high-strength properties and serve as coating membranes for slow-release urea fertilizers. However, these hydrogels present some defect pores when used as coating on the surface of urea increasing the solubility of the N nutrient and thus reduce the slow-release effect. To address this issue, the wax hydrophobic polymer solution was used to encapsulate the BHM hydrogel surfaces as an outer layer by filling in all cracks and defects detected on the surface. These hydrophobic and continuous wax layers improve the structural stability of the coating materials and enhance slow-release performance by preventing water penetration into the fertilizer core.

According to above problem about the use of superabsorbent hydrogels based on hydrophilic acrylic polymers, hydrophobic polymer coating films presents a challenge by acting as good barrier membranes to limit the diffusion of water, and thus delay the nutrients release from coated fertilizers. Among of these polymers, fluorinated acrylates polymers are the most proposed materials thanks to their remarkable properties such as UV photo-chemical stability, remarkable weatherability, semi-permeable membranes, self-cleaning surfaces and so on. [21–23] Homo-and copolymers of fluorinated (meth)acrylates with perfluoroalkyl side chains (C_nF_{2n+1}) are an important class of such materials that exhibit unexpected hydrophobicity in comparison to the corresponding *n*-alkyl chains (PAs). In fact, the rigid fluorocarbons side chains pack less densely on surfaces leading to poorer van der Waals interactions with water and thus to good water repellent properties. [21,24–26] Their low surface energies attributed to the properties of fluorine atom enable them to be widely used in high-performance coatings. [25–29]

To our knowledge, there are only two papers reported the use of hydrophobic fluorinated polymers as SRFs coatings. To enhance the performance of polymer encapsulated urea fertilizers, Chen et al. [30] developed a novel waterborne hydrophobic polymer coating using

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nano-SiO_2 and 1H,1H,2H,2H-perfluorooctyltriethoxysilane to modify water-based polyvinyl alcohol. More recently waterborne copolymers prepared by pickering emulsion copolymerization of butyl methacrylate (BMA) with 2-(perfluorohexyl)ethyl acrylate (PFEHEMA) were recently reported by our team. The resulting waterborne latexes were tested as coating materials for granular water-soluble fast-release fertilizers. [31] The P(BMA-*co*-PFEHEMA) copolymer containing 8 wt. % starch nanocrystals and a low PFEHEMA percentage (6.5 mol. %) showed better slow-release properties compared to those of non-fluorinated P(BMA) attributed to the presence of fluorinated units conferring improved hydrophobic properties for P(BMA-*co*-PFEHEMA) copolymer coating.

The aim of this work deals with the preparation of hydrophobic poly(meth)acrylates with different fluorinated side chains such as poly(2,2,2-trifluoroethyl methacrylate) (PTFEMA) and poly(2-(perfluorohexyl)ethyl acrylate) (PPFEHEMA) by free radical polymerization. These polymers were characterized by NMR ^1H, ^{19}F and IR spectroscopy, WCA, DSC and TGA, and applied as coating materials for Diammonium Phosphate (DAP) fertilizers. The morphology and chemical composition of coated fertilizer surfaces and cross sections were investigated using SEM-EDX mapping, while the UV-visible spectrophotometer was utilized to monitor the phosphorus (P) and nitrogen (N) release rates in water. Finally, the le structure of fluorinated polymers- N and P nutrients release profiles relationship was studied to evaluate the performance in terms of slowing the release rate of nutrients through these fluorinated hydrophobic polymers coatings.

2. Experimental section

2.1. Materials

Diammonium phosphate (DAP) ($(NH_4)_2HPO_4$) was chosen as granular phosphate fertilizer to prepare SRFs. This commercial granular fertilizer, containing 46 % of Phosphorus (P_2O_5) and 18 % of Nitrogen (N) was generously provided by the OCP Group in Morocco. 2(perfluorohexyl)ethyl acrylate (PFEHEMA) (CAS: 17527-29-6) was kindly provided by Atofina (Pierre Bénite, France), while 2,2,2-trifluoroethyl methacrylate (TFEMA) was kindly supplied by Tosoh Finechemi Corp, Yamaguchi (Japan). Azobisisobutyronitrile (AIBN) and all the solvents (hexafluorobenzene, acetonitrile, pentane, tetrahydrofuran, and methanol) were purchased from Sigma-Aldrich (France). Before usage, TFEMA and PFEHEMA were purified by distillation under reduced pressure.

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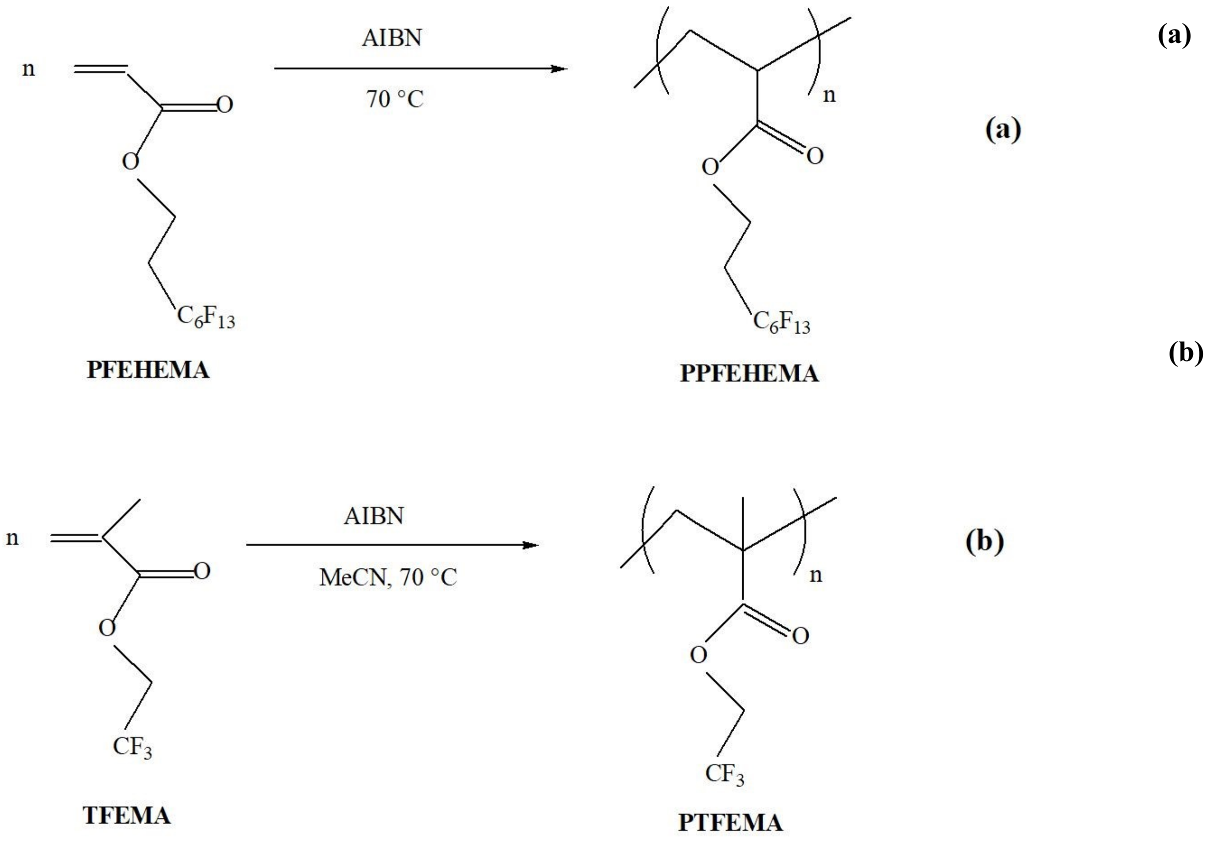
2.2. Synthesis of fluorinated homopolymers

2.2.1. Synthesis of poly(2-(perfluorohexyl)ethyl acrylate) (PPFEHEMA)

The bulk radical polymerization of 2-(perfluorohexyl)ethyl acrylate, PFEHEMA, was performed according to the procedure described by Stone et al. [32] Briefly, 12 mmol (5.03g) of PFEHEMA monomer were placed in a glass flask equipped with a reflux condenser, thermometer, and a magnetic stirrer. AIBN as initiator (0.3 mmol, 2.5 mol. % related to the monomer) was then added, the solution was purged with nitrogen gas for 15 min and heated in an oil bath at 70 °C for 24 h to complete the polymerization. After cooling the reactor, the final mixture was dissolved in hexafluorobenzene and precipitated from methanol. The obtained PPFEHEMA polymer was collected by filtration, washed by methanol, and dried under vacuum at 60 °C. The yield of the PPFEHEMA (white powder) was closed to 60%. The synthesis route of PPFEHEMA is displayed Scheme 1a.



Scheme 1 Radical polymerization of: (a) PFEHEMA and (b) TFEMA monomers.

2.2.2. Synthesis of poly(2,2,2-trifluoroethyl methacrylate) (PTFEMA)

2,2,2-trifluoroethyl methacrylate (TFEMA) in acetonitrile (MeCN) was polymerized according to the same protocol described above (Scheme 1b). Briefly, 8 mL of MeCN, 36 mmol of

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TFEMA (6.02 g; 5.1 mL; 2.7 mol/L) and 0.18 mmol of AIBN (0.06 g, 1% wt. of monomer) were charged in a glass Schlenk flask reactor with a magnetic stirrer. After the polymerization reaction was completed, the resulting solid was solubilized in a minimal amount of tetrahydrofuran and then the resulting polymer was purified by precipitation in pentane and subsequently dried in the oven under vacuum at 50 °C. The yield of the obtained PTFEMA (white powder) is 75%.

2.3. Coating technique

To favor a suitable viscosity for coating process, we have prepared PTFEMA and PPFEHEMA polymer solutions in THF and hexafluorobenzene, respectively (in 40% w/v ratio). The commercially available granular DAP fertilizers were coated by dip-coating process as described in previous studies.[9,31]. Dip-coating was achieved by immersing DAP granules (with diameters of 2-4 mm and weight of ca. 35 mg) in the corresponding solutions for 10 min. The DAP pellets were then removed from solution and placed on a Teflon ® film surface. Subsequently, the coated DAP granules were dried at room temperature, hence leading to a coated fertilizer with single layer (1L). To create a coated DAP with a second layer (2L), this operation was repeated a second time on the coated DAP (1L) using the same coating solution. The percentage of coating (CC) was calculated according to the following equation (1):

$$\mathrm{CC}\ \% = \frac{m_f - m_i}{m_i} \times 100 \qquad (1)$$

where m_f and m_i are the weights of the granular fertilizer after and before the coating, respectively.

2.4. Characterizations

2.4.1. Fourier-Transform Infrared spectroscopy (FTIR)

The powder samples were taken into KBr pellet. FTIR analyses were carried out using a Perkin Elmer 1725X spectrometer in transmittance mode. The spectra were recorded at room temperature with a scanning in the range 400-4000 cm^{-1} range with 16 acquisitions.

2.4.2. Nuclear Magnetic Resonance (NMR) spectroscopy

The ^1H and ^{19}F NMR spectra were recorded at room temperature using Bruker AC 400 spectrometer at ambient temperature. Deuterated chloroform ($CDCl_3$) and the 1:1 mixture of $CDCl_3/CF_3CO_2H$ were used as NMR solvent for PTFEMA and PPFEHEMA, respectively. Chemical shifts are given in ppm. ^1H and ^{19}F NMR spectra were performed in the following

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experimental conditions: a flip angle of 90° for ^{1}H (30° for ^{19}F), acquisition time of 4.5 s (0.7 s), pulse delay of 2 s (5 s), 16 scans (64 for ^{19}F), and a pulse width of 5 µs for ^{19}F NMR.

2.4.3. Size Exclusion Chromatography

Size Exclusion Chromatography (SEC) analysis was carried out on a Polymer Laboratories PL-GPC 50 Plus instrument using 2 PL gel Mixed-C 5 µm columns (molar masses ranging from 200 to 2×10^6 g/mol) thermostated at 35 °C equipped with a refractive index detector. Tetrahydrofuran (THF) with 1 % LiBr was used as an eluent (1.0 mL min^{-1}). The calibration was performed using Varian Polymethylmethacrylate (PMMA) standards.

2.4.4. Water contact angle (WCA) measurements

Water contact angles measurements (WCA) were performed to investigate the degree of hydrophobic character of synthetized fluorinated polymers. The KRUSS GmbH Easy Drop goniometer (Germany) equipped with a charge-coupled device camera was used to measure the contact angle of a water droplet in contact with a solid surface. An image capture program using SCAT software was utilized for recording the measurements. To measure the contact angles, a circle was defined around the drop, and the tangent angle formed at the substrate surface was recorded. To ensure the reproducibility of measurements, three experiments were conducted for each formulation.

2.4.5. Thermogravimetric analysis (TGA)

To determine the thermal stability of the obtained polymers, TGA was performed on a TA-55 discovery equipment. Few milligrams of each sample were heated at rate of 10 °C/min from room temperature to 800 °C under a nitrogen gas (60 mL min^{-1}).

2.4.6. Differential scanning calorimetry (DSC)

DSC analyses were performed on 10-15 mg samples and under nitrogen flow on a Netzsch DSC 200 F3 instrument to observe thermal transitions using the following cycles: first heating from -60 °C to 120 °C at 10 °C min^{-1}, cooling from 120 to -60 °C at 20 °C min^{-1}, and finally second heating from -60 °C to 120 °C at 10 °C min^{-1}. From the DSC thermograms (second heating), the inflection point of the step-change in heat capacity corresponds to T_g. Indium sample (T_m = 156.6 °C) was used to calibrate the instrument.

2.4.7. Scanning Electron Microscopy (SEM)

SEM analysis was recorded to characterize the morphology of uncoated and coated fertilizers, using the VEGA-3 instrument (TESCAN-France) with an accelerating voltage of 10 kV. The Energy-Dispersive X-ray (EDX) analysis was also used to identify the chemical composition

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of the coatings. Indeed, SEM was utilized to examine the maps of the spatial distribution of elements within the samples.

For this analysis, an axial rupture containing the fertilizer and the coating material was created using a razor blade. The coated granule and its cross-section were spread out on a carbon band and fixed to the surface of a metal disc using double-sided adhesive tape. Additionally, by examining the cross-section surface of coated DAP granular fertilizer, the coating thicknesses were determined.

2.4.7. Release assays of Nitrogen and phosphorus in water

The P and N release profiles for the coated and uncoated TSP fertilizers were determined according to protocol described in our previous works.[9,31] Briefly, uncoated and coated DAP granules (50 mg) were placed in a 125 ml beaker filled with distilled water and slightly stirred at room temperature. The sample (100 µL) was collected at different time intervals, diluted 100 times, and analyzed in the spectrophotometer. Nitrogen (NH_4^+) and phosphorus (P_2O_5) release profiles were then conducted by colorimetric process, using AFNOR-T90-015 and AFNOR-T90-023 norms, respectively. Ultraviolet–Visible (UV–Vis) spectrophotometer (UV-2600, Shimadzu) was used to characterize the resulting complex-colored solutions at 630 nm and 880 nm for NH_4^+ and P_2O_5, respectively. The absorbance of all solutions was measured, and the standard curve was drawn. Linear fitting was made and yielded a correction equation of $Y = 0.741X$ ($R^2 = 0.997$) and $Y = 0.615X$ ($R^2 = 0.997$) for N and P nutrients, respectively.

3. Results and discussion

3.1. Preparation and characterization of PTFEMA and PPFEHEMA (coating materials)

Excellent weatherability, semi-permeable membrane based on fluorinated acrylic polymers should be covered by as many fluorine-containing groups as possible [25,27,29,32]. In contrast to some low molar-mass per- and polyfluoroalkyl substances (PFASs), well-established to be water soluble, toxic, persistent, bioaccumulative and mobile, fluoropolymers are insoluble in water and thus not mobile, are bio-inert, safe and with unique properties that are essential for our daily life (coatings, electronics, internet of things, energy, transportation, etc.). Indeed, these materials are possibly irreplaceable since the suggested alternative products as hydrocarbon polymers used in similar conditions failed. Interestingly, these high-performance polymers satisfy the 13 polymer of low concern (PLC) criteria in their recommended conditions of use.[33] Therefore, these specialty polymers must be separated from the PFAS family. Shirai

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et al.[34] has recently reported that poly(fluoroalkyl (meth)acrylate)s containing extended perfluoroalkyl groups (C_nF_{2n+1}) can degrade, leading to the formation of perfluorooctanoic acid ($C_7F_{15}CO_2H$, PFOA). These authors showed also that the polymers featuring short fluorinated side chains (n≤6 fluorocarbons) present less bioaccumulative PFAS compared to those with n ≥ 7. Therefore, taking in account the hydrophobic coating performances with fluorine-containing groups and to address environmental concerns with less bioaccumulation of PFOA, we have chosen using TFEMA (-CF_3) and PFEHEMA (C_6F_{13}) as fluorinated monomers to prepare PTFEMA and PPFEHEMA polymers with high molar masses compared to those of PFASs which can be applied as coating fertilizers to achieve slow-release nutrients. These polymers have been successfully synthesized by free radical polymerization (Scheme 1). The resulting polymers were then analyzed, and finally used as coating materials to cover the Diammonium Phosphate (DAP) fertilizers.

3.1.1. Infrared spectroscopic analysis (FTIR)

Fig. S1 (Supplementary Information) shows the FTIR spectra of the TFEMA and PFEHEMA monomers and the corresponding PTFEMA and PPFEHEMA homopolymers. Fig. S1 displays the characteristic FTIR absorption peaks assigned to different chemical bonds as summarized in Table 1. These assignments confirm those of fluorinated (meth)acrylate polymers described in the literature. [35–39] Meanwhile, the characteristic stretching of the TFEMA and PFEHEMA double bond observed at 1649 and 1638 cm^{-1}, respectively disappeared indicating that the polymerization reaction and purification of the resulting polymers were successful achieved.

Table 1 Principal FTIR characteristic bands of PTFEMA and PPFEHEMA polymers.

Bands	**PTFEMA (cm^{-1})**	**PPFEHEMA (cm^{-1})**
C-F symmetric stretching	1225	1202
C-F asymmetric stretching	1176	1145
C=O ester stretching	1753	1737
C-H: symmetric and asymmetric stretching	2850 and 2960	2875 and 2972
C-H (out of plane)	973	844
C-O stretching	1176	1116

3.1.2 ^{1}H and ^{19}F NMR spectroscopies

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The white powders (purified copolymers) were characterized by NMR spectroscopy. Fig. 1 provides the ^1H and ^{19}F NMR spectra of the PTFEMA polymer recorded in deuterated chloroform, while the NMR spectra of PPFEHEMA were recorded in a 1:1 mixture of $CDCl_3/CF_3CO_2H$, since PPFEHEMA is not soluble in organic solvents.

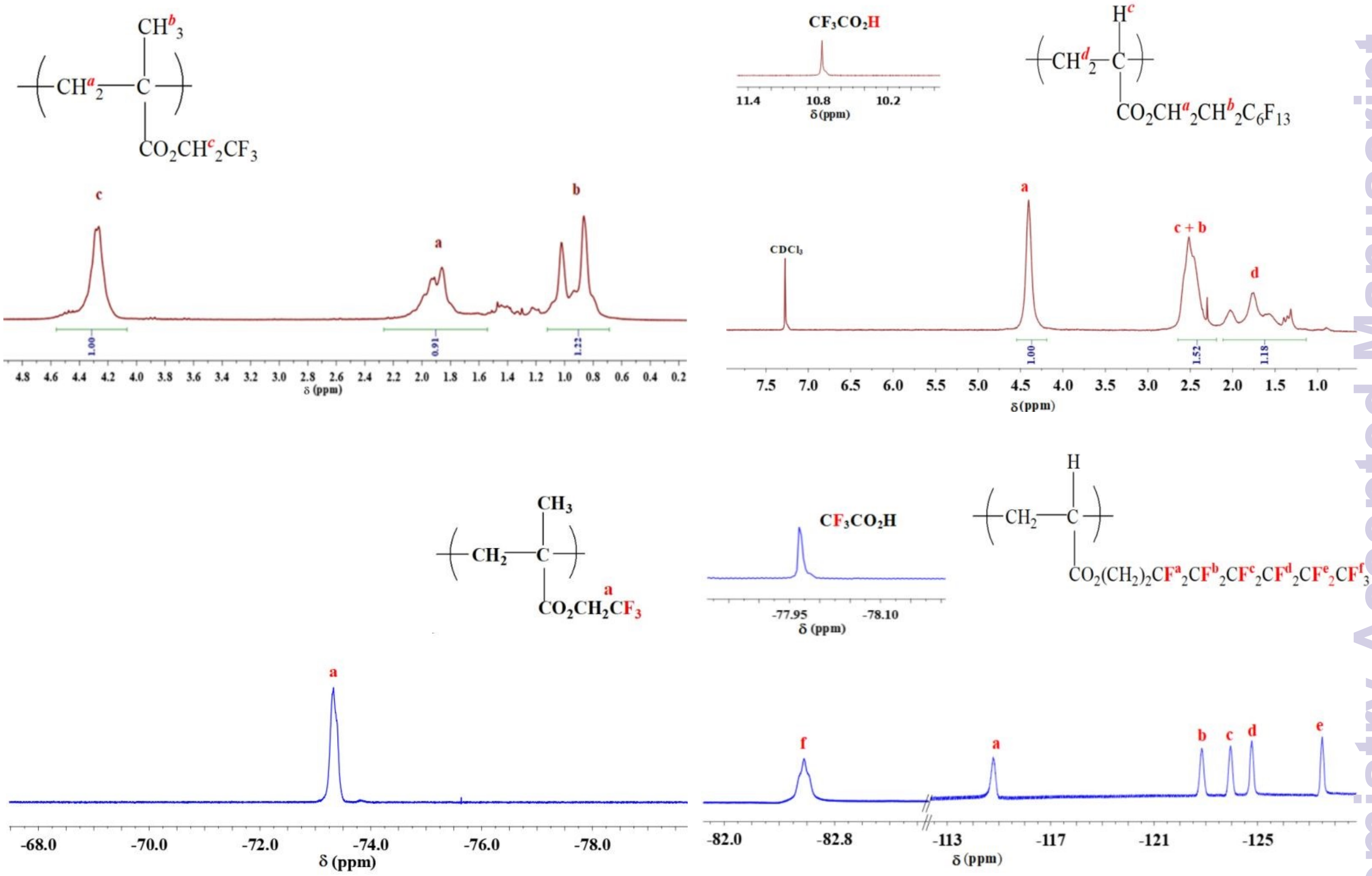

Fig. 1 ^1H and ^{19}F NMR spectra of PTFEMA (left) ($CDCl_3$ as the solvent) and PPFEHEMA (right) (the mixture of $CDCl_3$ and CF_3COOH as NMR solvent in mode ^1H-$\{^{19}F\}$ decoupling NMR. (Chemical shifts in the inserts correspond to $C\underline{F}_3$ and $CO_2\underline{H}$ groups).

The assignments of the chemical shifts were derived by comparison with the values reported in the literature for TFEMA based polymers [38] and poly(perfluoro (meth)acrylate)s [29] and are summarized in Table 2. For example, the ^1H NMR spectrum of PTFEMA shows a signal of the methylene of ester group ($-O-C\underline{H}_2-CF_3$) centered at 4.3 ppm. The methyl group of PTFEMA ($-C\underline{H}_3$) was observed in the range of 0.8-1.1 ppm, while the methylene protons of the backbone ($C\underline{H}_2$) appear between 1.8 and 2.1 ppm. The ^{19}F NMR spectrum of PTFEMA exhibits the $C\underline{F}_3$ peak at -73 ppm. The vinylic proton signal centred at 6.1 ppm for TFEMA and peaks at 6.5; 5.9 and 5.0 for PFEHEMA were not present in these spectra.

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Table 2 Assignments of chemical shifts/ ppm for PTFEMA and PPFEHEMA polymers.

^{1}H NMR		
Type of proton	PTFEMA	PPFEHEMA
C**H**$_3$	0.8-1.1	-
C**H**$_2$ (main chain)	1.8-2.1	1.2-2.2
C**H** (main chain)	-	2.2-2.7
OC**H**$_2$CF$_3$	4.3	-
OC**H**$_2$CH$_2$C$_6$F$_{13}$	-	4.2-4.5
OCH$_2$C**H**$_2$C$_6$F$_{13}$	-	2.2-2.7
^{19}F NMR		
Type of fluorine	PTFEMA	PPFEHEMA
OCH$_2$C**F**$_3$	-73.0	-
O(CH$_2$)$_2$C**F**$_2$CF$_2$CF$_2$CF$_2$CF$_2$CF$_3$	-	-114.8
O(CH$_2$)$_2$CF$_2$C**F**$_2$CF$_2$CF$_2$CF$_2$CF$_3$	-	-124.8
O(CH$_2$)$_2$CF$_2$CF$_2$C**F**$_2$CF$_2$CF$_2$CF$_3$	-	-122.8
O(CH$_2$)$_2$CF$_2$CF$_2$CF$_2$C**F**$_2$CF$_2$CF$_3$	-	-123.9
O(CH$_2$)$_2$CF$_2$CF$_2$CF$_2$CF$_2$C**F**$_2$CF$_3$	-	-127.5
O(CH$_2$)$_2$CF$_2$CF$_2$CF$_2$CF$_2$CF$_2$C**F**$_3$	-	-82.6

3.1.3. Size Exclusion Chromatography

The molar masses of poly(2,2,2-trifluoroethyl methacrylate), PTFEMA, have been determined using size exclusion chromatography (SEC) in tetrahydrofuran (THF), calibrated with polymethylmethacrylate (PMMA) standards. The obtained $\overline{M}_{\boldsymbol{n}}$ and $\overline{M}_{\boldsymbol{w}}$ and dispersity (Đ= $\overline{M}_w/\overline{M}_n$) values are equal to 26,000 g/mol, 52,000 g/mol and 2.0, respectively. Of course, these are relative values. However, it is not possible to determine the molar masses of poly(2-(perfluorohexyl)ethyl acrylate) (PPFEHEMA) as it is not soluble in organic solvents, but only in fluorinated solvents such as hexafluorobenzene or 1, 1, 1, 3, 3, 3-hexafluoro-2-propanol. Actually, our SEC apparatus are not equipped with columns related to fluorinated solvents.

3.1.4. Water contact angle (WCA)

WCA is one of the most important parameters affecting the release kinetics since the hydrophilic character of polymer films reduces the diffusion of water through these films and gives them water-repellent properties. [40] WCA value for the PTFEMA film was about 97°, while that of PPFEHEMA reached a value of 119°, as shown in Fig. S2 (Supporting Information). The WCA difference between both homopolymers (22°) indicates a more pronounced hydrophobic character of PPFEHEMA film compared to those of PTFEMA film.This can be attributed to the difference in the surface energy value in the chemical structure

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at the surface of the both fluorinated polymers. [39] Barbu et al. [41] reported that the constituent groups affect the surface energy in the following order: CH_2 (36 mN.m^{-1}) > CF_2 (23 mN.m^{-1}) > CF_3 (15 mN.m^{-1}). Tsibouklis et al. [42] studied also the surface organization phenomena and the surface energy of poly(perfluoroalkyl methacrylate)s films. They observed the influence of the length of the pendent fluorocarbon moiety on the surface energy, and concluded that increasing the chain length induces a lower surface energy. Indeed, as the pendent chain length increases, the average surface roughness (R_a) of the corresponding film structures, determined by AFM, follows the same trend, and therefore serves to inhibit the absorption of liquids by the bulk sample. [42] In fact, R_a value of PPFEHEMA is close to 3.1 nm[42] while that of PTFEMA worths 0.41 nm.[43] The surface properties of comb-shaped polymers with perfluoroethyl side-chains (R_f) are also strongly related to the ordered structure of the side-chains at the surface. Our team reported the thermal behavior, liquid-crystalline structure, and functional group orientation of comb-shaped polymers poly(2-(perfluorooctyl)ethyl acrylate) containing perfluorooctyl side-chains.[24] A tilted hexatic smectic-B phase was obtained, the R_f side chains playing the role of mesogens to form a bilayer lamellar structure with lateral hexagonal translational order producing a well-ordered structure and it exhibits better liquid repellency compared to those of the analogues with short fluorinated chain. According to different parameters involved above, the hydrophobic characteristic of the fluorinated polymer, PPFEHEMA, was improved compared to that of PTFEMA based on the fluorinated chain length with a lower surface energy, a high average surface roughness (R_a) and well-ordered structure of PPFEHEMA. This result is in good agreement with previous works. [31,44] Comparing two fluoroalkyl methacrylate polymers, Phillips and Dettre [44] found that a polymer bearing a longer fluoroalkyl side chain displays the highest WCA value.

3.1.5. Thermal properties (TGA and DSC)

DSC and TGA analyses were used to study the thermal properties of the PTFEMA and PPFEHEMA. copolymers were studied by (Fig. 2).

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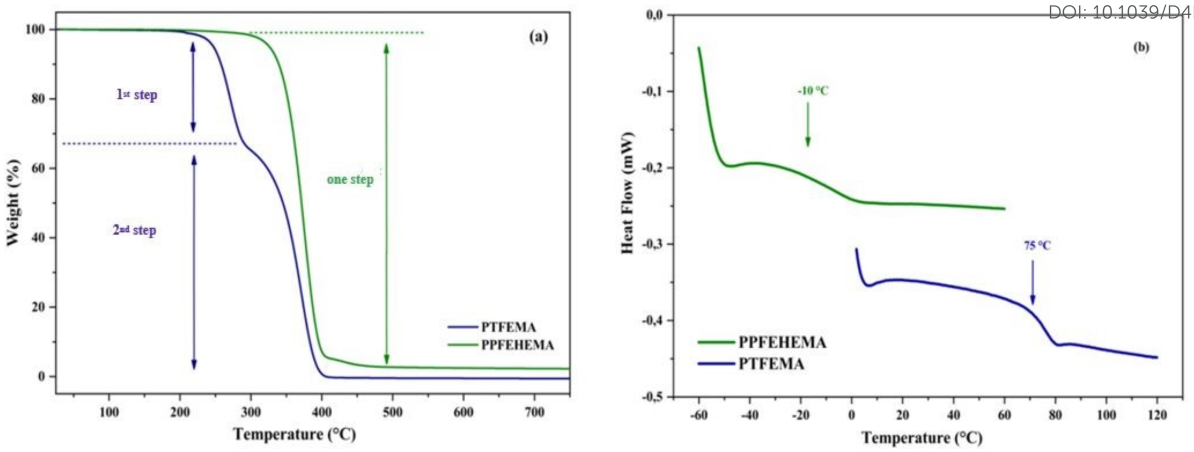

Fig. 2 TGA (a) and DSC (b) thermograms of PTFEMA and PPFEHEMA (N_2 gas).

The degradation of PTFEMA takes place in two steps (Fig. 2a). The first one, in the range of 200-300 °C, corresponds to the volatilization of side-chain fragments including CO_2, vinylidene fluoride and 2,2,2-trifluoroethanol which are determined as pyrolytic decomposition products (weight loss 26%), and the second decomposition step, in the range of 305-420 °C (weight loss 74%), is attributed to a depolymerization reaction. [45,46] PPFEHEMA decomposes in a single step, in the range of 280-420 °C, which is attributed to a random cleavage leading to the depolymerization mechanism (Fig. 2a). PPFEHEMA exhibits higher thermal stability compared to PTFEMA (Fig. 2a), which can be attributed to the better thermal stability of C_6F_{13} pendant group in PPFEHEMA due to the strong C-F bond ($E_{\text{C-F}}$ = 450 kJ/mol) that makes it possible to increase the heat resistance performance of the polymeric materials by adding more fluorinated components. [31] Table 3 lists the thermal characteristics of PTFEMA and PPFEHEMA.

The DSC second heating thermograms of both fluorinated polymers showed no melting temperature when the samples were heated from -60 °C to 120 °C (Fig. 2b). Only a sharp transition from the glassy state to the viscoelastic one was observed, as evidenced by the presence of a neat T_g indicating that these fluorinated polymers exhibited an amorphous behavior (Table 3), the T_g were close to -10 and 75 °C for PPFEHEMA and PTFEMA, respectively.

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Table 3 Thermal data of PTFEMA and PPFEHEMA by TGA and DSC.

Polymers	TGA*			DSC
	$T_{d\ 10\ \%}$ (°C)	$T_{d\ 50\ \%}$ (°C)	Residue at 600 °C (%)	T_g (°C)
PTFEMA	256	345	0.0	75
PPFEHEMA	339	371	2.0	-10

* $T_{d\ x\%}$: Temperature of x % of decomposition (N_2 gas, 10°C/min)

The decrease in T_g for PPFEHEMA compared to PTFEMA is related to the structure of the FPA units. In fact, the long alkyl dangling chains of the acrylate moiety ($-CO_2CH_2CH_2C_6F_{13}$) serve as internal plasticizers, resulting in low T_g and giving PPFEHEMA a more elastomeric behavior at room temperature as shown in Fig. S3.[47] The T_g decrease leads to excellent film-forming properties at room temperature for fertilizer coating. The PPFEHEMA coating films also help to improve the physical quality of granular fertilizer and are expected to have a positive effect on the compressive strength so that they do not break easily, thus preventing the generation of excessive dust during the handling and storage process.

3.2. Morphological characterization of coated DAP Fertilizers

The film forming from polymer solutions coatings for DAP fertilizers was performed using the dip-coating method. [9,30] The percentages of the different coating materials (calculated according to Eq. 1) are given in Table 4.

Table 4 Percentages of coating materials, PTFEMA and PPFEHEMA, with different layers (L).

DAP Coatings	Weight Coating percentage (%)	Average thickness (µm)
PTFEMA 1L	4.5	51.0
PTFEMA 2L	10.7	90.0
PPFEHEMA 1L	7.7	27.0
PPFEHEMA 2L	16.0	73.0

To investigate the coating quality between the fertilizer and the coating, the morphology of the surface and cross-section of uncoated and PTFEMA and PPFEHEMA coated DAP with as a single layer (1L) and as a second layer (2L) was performed by SEM (Fig. 3).

A first overview of the SEM results exhibited that the surface of the uncoated DAP granule has an irregular and rough structure (Fig. 3a. bare scale: 1 mm).

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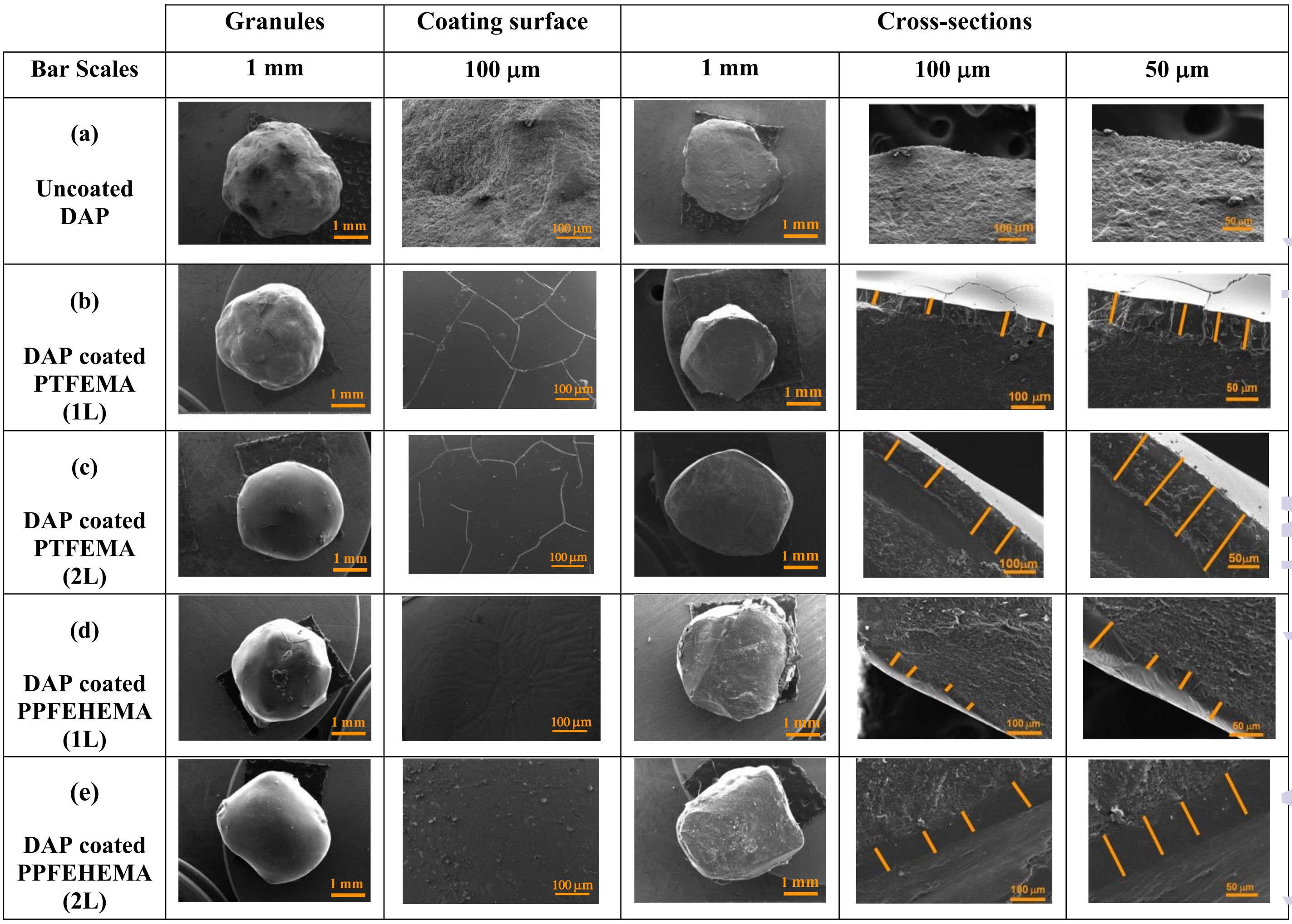

Fig. 3 SEM analysis of fertilizer granule and its cross-section containing the interface between DAP and tested PTFEMA and PPFEHEMA (single layer (1L) and second layer (2L)).

The highly magnified surface (bar scale: 100 µm. Fig. 3a) showed some pinholes and an irregular morphology, due to the granulation process during the production of DAP fertilizers. [40,48] When the DAP fertilizer was coated with the two PTFEMA and PPFEHEMA polymers, the coating surfaces exhibited a smoother and denser structure compared to uncoated DAP, especially when the fertilizers were covered with the second layer, as the content of the coating membrane on the surface of the fertilizers increased (Fig. 3b-d). This is in good agreement with our previous works. [9,31,40,48,49]

When analyzing the outer surface of the DAP granules coated with PTFEMA (Fig. 3b-c), we find that there are some microcracks in the surface compared to the granules coated with PPFEHEMA, which may be related to the structure of these polymers. PPFEHEMA has a T_g that is lower than the ambient temperature (-10 °C), so the PPFEHEMA coating has a high

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flexibility and good film-formation, resulting in improved impact and crack resistance (Fig. S3). In contrast, PTFEMA with a T_g around 70 °C (Table 3) exhibits a glassy state at room temperature, which leads to some cracking when the solvent evaporates. These cracks could be reduced when the second layer was applied to the surface of the coated fertilizer. To eliminate these cracks or prevent their formation, Devassine et al.[50] reported that controlling the rate of solvent evaporation or performing annealing could prevent the formation of cracks and pores. Yadavalli et al. [51] observed some cracks in the SEM of the composite thin films and reported another additional explanation, which is the electron-beam-induced rapid volatilization of the organic species, such as residual solvent from the surface of these films during SEM analysis, leading to the buildup of tensile stress that causes cracks in the grain boundaries.

The cross-section images of coating materials observed by SEM with different magnitudes are shown in Fig. 3b-e. The contact surface between PTFEMA or PPFEHEMA (1L and 2L) coatings and the DAP core fertilizers is continuous with no gaps or voids present in it. In fact, the interaction between the hydrophilic inorganic DAP granules ($(NH_4)_2HPO_4$) and the hydrophilic side (ester groups $-CO_2-$) in the PTFEMA and PPFEHEMA coatings could be responsible for the good adhesion between both compounds. [47] Indeed, the border line between fertilizer and the film coatings are irregular due to the non-spherical irregular shape of the initial DAP granules (Fig. 3b and Fig. 3d, bar scale :100 μm). Poly(fluorinated (meth)acrylate)s are viable option for use in agriculture as coatings for SRFs, as confirmed by the formation of cohesive films. [31]

From the cross-section of core (fertilizer)-shell (coating) (Fig. 3b-e), the thicknesses of polymer coating were assessed by SEM at different points due to irregular shape of DAP fertilizers and the average thicknesses were calculated (Table 4). These values are a function of the type of the coatings (PTFEMA, PPFEHEMA) and their content (1L or 2L) as displayed in Fig. S4.

The thicknesses of the different PTFEMA and PPFEHEMA coatings are also shown in Fig. S4. The average thickness of the DAP coated with PTFEMA (1L) and (2L) are close to 51 and 90 μm, respectively, while those achieved when PPFEHEMA is used as the coating are around 27 and 73 μm for 1L and 2L, respectively. The measured thicknesses of the two-layer (2L) coating are 1.5 and 2.7 times higher than those of the single-layer (1L) PTFEMA and PPFEHEMA coatings, respectively.

Energy dispersive X-ray analysis (EDX) is used to reveal the chemical compositions on the surface of the coated and uncoated DAP fertilizers to evaluate the quality of the coatings. The results are shown in Fig. 4 and Table 5.

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The N and P signals as the essential macronutrients of the DAP fertilizer were only detectable on the uncoated DAP surface. Their percentages are 21.55 % and 10.10 %, respectively. (Table 5). Other microelements with a low content (0.67 %) including Mg, Al and Ca were also observed. The signal related to carbon (19.54%) was related to the DAP granules metallization because the samples needed to be conductive to perform the SEM analysis.

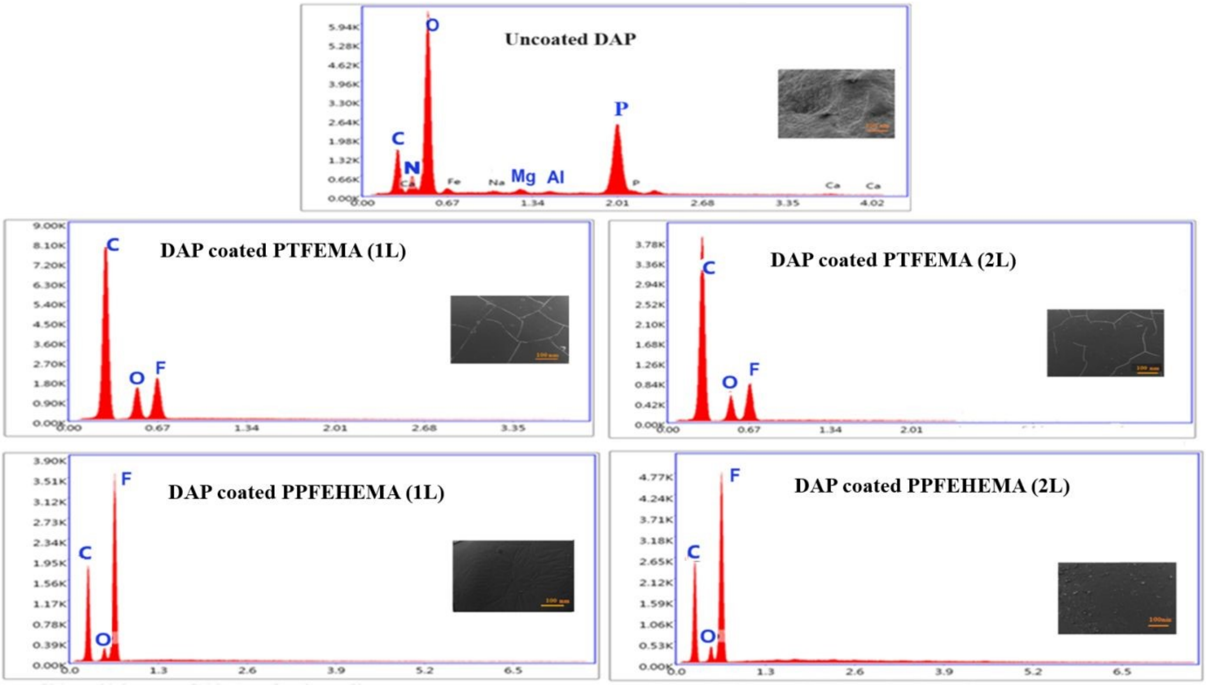

Fig. 4 EDX analysis on the surface of uncoated DAP and coated DAP using PTFEMA and PPFEHEMA 1L and 2L.

Table 5 EDX elemental weight percentages of uncoated and coated DAP by different tested polymers (1L and 2L).

		Detected nutrients (wt.%)					
		C	**F**	**O**	**N**	**P**	**Other elements**
Uncoated DAP		19.54	0	46.98	10.10	21.55	0.67
DAP coated	**1 L**	67.03	15.42	17.55	0	0	0
with PTFEMA	**2 L**	73.41	14.37	12.21	0	0	0
DAP coated	**1 L**	44.28	50.12	05.59	0	0	0
with PPFEHEMA	**2 L**	44.79	49.57	05.64	0	0	0

The absence of N and P macronutrients on the outer surface of the coated DAP granules confirms that the PTFEMA and PPFEHEMA coatings covered the granular fertilizers successively with a good adhesion and without any diffusion of the macronutrients N and P of

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DAP fertilizer. These results are also corroborated with the SEM analyzes. In the DAP coated with PTFEMA and PPFEHEMA membranes, the carbon content increases compared to that of the non-coated DAP fertilizer, which is attributed to the carbon atoms in the fluorinated (meth)acrylate units of the polymer coatings. As expected, the DAP coated with PPFEHEMA has a higher percentage of F-atoms than those coated with PTFEMA (Table 5, Fig. 4).

The spatial distribution of the elements was investigated using the EDX technique. For example, Fig. 5 shows the element mapping (C, N, P, O and F) in the cross-section of DAP encapsulated with PPFEHEMA 2L. The C, N, P, O and F are the constituent elements of the core-shell that displays a more homogeneous distribution on the cross-section of DAP coated with the PPFEHEMA.

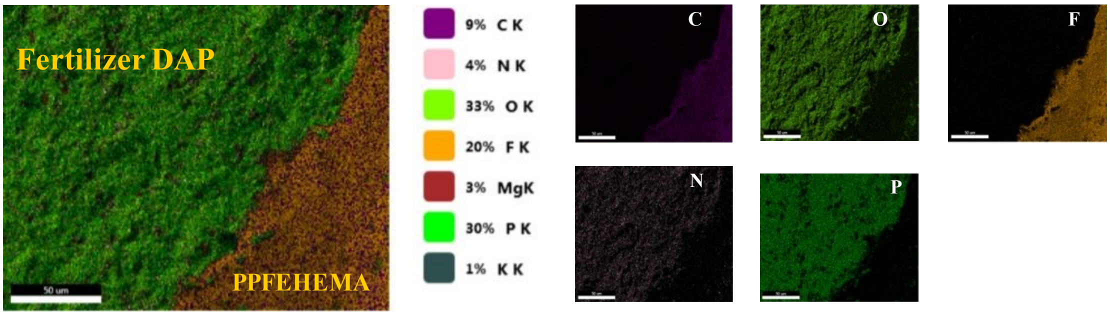

Fig. 5 Chemical mapping obtained from the cross-sections of DAP coated with PPFEHEMA (2L) (Bar scale:10 µm).

3.3. Phosphorous and nitrogen release behavior of coated and non-coated DAP fertilizers

To predict the slow macronutrient releases for practical application, the nitrogen (N) and phosphorus (P) release patterns of uncoated and coated DAP fertilizer granules in water were studied according to the procedures described by Li et al. [52]and Pereira et al. [53] This allows to evaluate the effects of coating on the slow release and retarding performance of coatings. The total percentage releases of P and N in water *versus* time for the uncoated and coated DAP with PTFEMA and PPFEHEMA polymers (1L and 2L) at pH 7 and ambient temperature are shown in Fig. 6.

Fig. 6 shows that the uncoated DAP is completely dissolved in water in less than 2 h, whereas the rate of dissolution of nutrients in water is much slower with encapsulated fertilizers than with uncoated DAP. For example, the time to reach the maximum percentage release of P is 3.3 and 14.5 times higher than uncoated DAP when the fertilizer is covered with PTFEMA single-layer (1L) and double-layer (2L), respectively.

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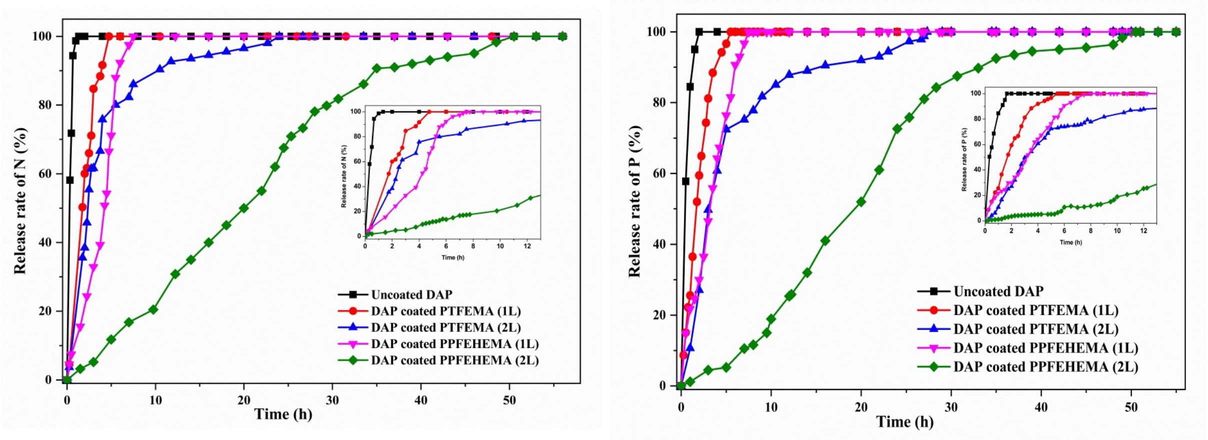

Fig. 6 Release rate of P and N for uncoated DAP and coated DAP using PTFEMA and PPFEHEMA 1L and 2L in water at pH=7 and ambient temperature.

When the DAP was coated with PPFEHEMA 1L and 2L, respectively, the P release profiles of the coated granules reached the equilibrium stage approximately at 7.5 h and 50.5 h, indicating significantly slower P release or delaying performance properties of DAP fertilizers, and thus their potential applications as coating films in crop agriculture. [31,40,47,48] DAP coated with 2 L of PPFEHEMA presents the slowest macronutrient releases, the time to reach the maximum of N and P release is 30 and 38 times higher than those of uncoated DAP, respectively. Indeed, compared to PTFEMA, the PPFEHEMA coating significant slower release of nutrients (Fig. 6 and Fig. S5). In fact, the chemical structure of the coating is one of the key parameters determining the release rate of P nutrient from the coating. The presence of a larger number of F-atoms and C-F bonds in the PFEHEMA monomer with hydrophobic properties attributed to the -C_6F_{13} side groups gives the PPFEHEMA coating a very hydrophobic character, that acts as a physical barrier and reduces the water diffusion, contributing to a slow release of P and N nutrients compared to the PTFEMA coated DAP. [21,22,26] This hydrophobic character was confirmed by water contact measurement (WCA) (Fig. S2), where the value of PPFEHEMA (WCA=109°) is higher than that of PTFEMA (WCA=79°). The soft structure of PPFEHEMA, which was confirmed by DSC (Fig. 2b, Table 3) gives the polymer good film-forming ability and good adhesion properties. [31]

An important parameter that can contribute significantly to nutrient release is also the thickness of the coating. The higher thickness of these coatings resulted in lower nutrients release, as the coating film creates a diffusion resistance to water and hinders nutrients diffusion. According to Cruz et al, [54] the DAP coated with 3.0 and 4.5 w% of polyurethane prepared from castor oil

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polyol showed a notable phosphorus release delay. 80 % of P was released in 50 h and 75 h when the coating percentage was close to 3.0 wt% and 4.5 wt%, respectively. In our case, the results indicated that thicker PPFEHEMA coatings may shift the maximum nutrient availability towards longer periods. The maximum release rate of P was reached after 7.5 h for the DAP coated with single layer (1L) (thickness = 27 µm), whereas those covered with a double layer (2L) coating (thickness = 73 µm) resulted in a maximum release after 50.5 h (Fig. S5).

To enhance the efficiency of fertilizer, use and to minimize adverse environmental effects, the performance in terms of slow-release nutrients of fertilizer coatings is governed by expanding Nitrogen (N) and Phosphorus (P) release properties by delaying the time to reach the equilibrium, and therefore matching with the nutrient demand during crop growth. A comparison of P release times at equilibrium of PTFEMA and PPFEHEMA coatings with various previous studies using acrylate coating polymers is given in Table 6.

Using immersion method, the P release profiles of the coated fertilizers with PPFEHEMA reached the equilibrium stage after 50 h higher than those encapsulated with poly(butyl methacrylate (BMA)-*co*-PFEHEMA) (ca. 32 h). This copolymer was synthesized by emulsion copolymerization from an initial ratio $[BMA]_0/[PFEHEMA]_0$ = 90/10. [31] Indeed, the molar PFEHEMA incorporation in the copolymer, assessed by elemental analysis, was close to 6.5% [31] which is much lower than that of PFEHEMA units in PPFEHEMA homopolymer (100%). The structure and hydrophobic properties of PFEHEMA homopolymer and P(BMA-*co*-PFEHEMA) copolymer coatings could explain the difference of their slow-release performance. In fact, PPFEHEMA (i.e., with high PFEHEMA molar percentage) compared to that incorporated in poly(BMA-*co*-PFEHEMA) (only 6.5%) exhibits a higher hydrophobic character confirmed by WCA measurements, close to 110° and 80°, respectively[31]. Table 6 also reveals that the DAP coated with PPFEHEMA exhibits a slower P release than those covered with PBMA. The time to reach the maximum P release of the granule encapsulated with PPFEHEMA was 2.0 times lower than that of DAP coated with PBMA coating. The increasing hydrophobicity of the fluorinated homopolymer (WCA = 110°, Fig. S2) compared to that of non-fluorinated PBMA (WCA = 74°)[31] suggests a reduction of the water diffusion and contributes to a slow release of P nutrient due to the presence of the fluorinated comonomer bringing better water repellency attributed to the -C_6F_{13} side groups.

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Table 6 Comparative of the results of previous published poly(acrylates) coating materials

Coating Fertilizer*	**Coating Process**	**Total release of (P_2O_5) in water (hours)**	**Ref**
Uncoated DAP		2.0	-
DAP coated starch nanocrystal/PBMA	Immersion	25.2	[31]
DAP coated starch nanocrystal/P(BMA-*co*-PFEHEMA)	Immersion	32.5	[31]
DAP coated by Polymethyl methacrylate-*g*-carboxymethyl cellulose	Rotary pan	30.0	[49]
PMMA	Rotary pan	23.0	[49]
DAP coated with PTFEMA (Double layer)	Immersion	24.0	This work
DAP coated with PPFEHEMA (Double layer)	Immersion	50.5	This work

* BMA: Butyl methacrylate, PFEHEMA: 2-(perfluorohexyl)ethyl acrylate and TFEMA: 2,2,2-trifluoroethyl methacrylate and PMMA : poly(methyl methacrylate)

This comparison shows that the release properties of PPFEHEMA 2L lead to better results thanks to its fluorinated structure, which improves the slow release of nutrients and avoids the loss of nutrients and their negative impact on the environment when uncoated fertilizer is used. Therefore, the better bioavailability of N and P nutrients is better for the plants.

3.4. Mathematical Modeling of release kinetics

To confirm the above interpretations on the behavior of nutrient release in water and to describe the release kinetics and the nutrient transport mechanism through the polymer coatings, the data curves (Fig. 6) were fitted following the semi-empirical Ritger-Peppas model [55] (Eq.S1 in Supporting Information, ESI). More details about this model and the corresponding mechanisms based on the diffusional exponent (n) characterizing the release mechanism are supplied in ESI.

The diffusion exponent (n), correlation coefficient (R^2) and release factor (k) of each coating system were calculated by plotting Ln (M_t/M_∞) *versus* Ln (t). Fig. S5 exhibits some curves (according to Eq. S2 in ESI) whereas Table 7 supplies the resulting data of N and P nutrient releases from both polymers corresponding to the first and second layers for the first release step before reaching the equilibrium.

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Table 7. Kinetic parameters of N and P releases in water calculated according to the Ritger-Peppas model from DAP coated with PTFEMA and PPFEHEMA 1L and 2L.

			Release exponent n [a]	Release factor k x 10^2 (h^{-1}) [a]	Correlation coefficient (R^2)	Release mechanism
DAP coated	PTFEMA (1L)	P	0.96	57	0.98	Non-Fickian
		N	0.65	65	0.99	Non-Fickian
	PPFEHEMA (1L)	P	0.78	51	0.97	Non-Fickien
		N	1.30	34	0.97	-
DAP coated	PTFEMA (2 L)	P	0.52	51	0.97	Fickian
		N	1.28	46	0.97	-
	PPFEHEMA (2L)	P	0.48	46	0.98	Fickian
		N	1.29	32	0.98	-

[a] Assessed from Eq. S2 (ESI).

PTFEMA and PPFEHEMA with double layer 2L present a Fickian release mechanism for P nutrient as their n values (0.52 and 0.48) are close to 0.5. However, those corresponding to N nutrient are greater than 1 indicating that the diffusion occurred from the pores in the coatings, which gradually becomes modified by the diffusion process itself. Furthermore, both PTFEMA and PPFEHEMA with 2L display a non-Fickian release mechanism for P nutrient as their n values are ranging between 0.5 and 1.0 while for those corresponding to N release, the n values are greater than 1.

It is also noted that the k release factor values of P and N nutrients decreased for both PTFEMA and PPFEHEMA polymers when the percentage of coating or the layer coating number increased and vice versa. For example, when the DAP was coated with PTFEMA, k value of slow release of decreases from 57×10^{-2} to 51×10^{-2} h^{-1} while the percentage of coating increases from 4.5 % to 10.7 % for PTFEMA 1L to PTFEMA 2L, respectively. Compared to PTFEMA coating, PPFEHEMA exhibits slower N and P release profiles when using the same number of layers, k value of P release decreases from 51 10^{-2} to 46 10^{-2} h^{-1}, while those of N release decreases from 46 10^{-2} to 32 10^{-2} h^{-1} for PTFEMA 2L to PTFEMA 2L, respectively (Table 7). This attests that the nutrient releases are slower when DAP was coated by PPFEHEMA. This comparison is in good agreement with the release rates of N and P coated with both fluorinated polymers versus time (Fig. 6). Indeed, according to WCA measurements, fluorinated PPFEHEMA is more hydrophobic than PTFEMA and therefore the swelling content is lower than that of PTFEMA leading to low release factor k value.

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4. Conclusion

Poorly bioaccumulative of fluorinated (meth)acrylic polymers were used as hydrophobic coating materials for granular water-soluble fast acting fertilizers. PTFEMA and PPFEHEMA were successfully synthesized, characterized, and applied to DAP fertilizers. PPFEHEMA, with highly hydrophobic character due to the presence of a large number of fluorine on side chain (-C_6F_{13}), indicates a high water repellent surface with good film-forming properties. The characterization of the surface and cross-section of the DAP coating as well as the release rates of N, and P nutrients were investigated. The following conclusions were drawn: *(i)* a good adhesion between the granules and the coating films, *(ii)* the total N and P nutrients release time of the coated DAP could be controlled by adjusting the thickness of the PTFEMA and PPFEHEMA coatings (1L and 2L), *(iii)* compared to uncoated DAP granules which is totally solubilized after less than 2h, coated DAP with 2 L of PPFEHEMA has the slowest N and P nutrients releases, the P release profile of the granules coated with PPFEHEMA 2L reached the equilibrium stage approximately after 50.5 h, respectively. The applied strategy is a promising technology allowed a very slow release and long-term availability of nutrient sources with highly hydrophobic coatings. Therefore, the SFRs proposed coatings exhibited promising applications for the development of modern agriculture by improving nutrient uptake by plants, minimizing nutrient losses, and reducing environmental pollution.

The kinetic release of N and P nutrients in the soil and the agronomic studies are under investigation.

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ORCID

Mustapha Raihane https://orcid.org/0000-0001-9284-8428
Mohammed Lahcini https://orcid.org/0000-0003-1049-7906
Elvira Vidović https://orcid.org/0000-0001-6779-6312
Bruno Ameduri https://orcid.org/0000-0003-4217-6664
Salima Atlas https://orcid.org/0000-0001-6742-0710

Authorship contribution

Asma Sofyane: Methodology, Investigation, Writing-original draft. **Salima Atlas:** Visualization, formal analysis, Writing-review, and editing. **Mohammed Lahcini:** Formal analysis, Review, and editing. **Elvira Vidović:** validation, Review, and editing. **Bruno Ameduri:** Visualization, formal analysis, validation. **Mustapha Raihane**: Conceptualization, Methodology, Supervision, Project administration, Funding acquisition, Validation, Writing-review, and editing. All authors have read and agreed to the published version of the manuscript.

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Conflicts of interest

There are no conflicts to declare.

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Supporting Information

The Supporting Information is available free of charge.

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Caption Scheme

Scheme 1 Radical polymerization of: (a) PFEHEMA, and (b) TFEMA monomers.

Figure Caption

Fig. 1 ^{1}H and ^{19}F NMR spectra of PTFEMA (left) ($CDCl_3$ as the solvent) and PPFEHEMA (right) (the mixture of $CDCl_3$ and CF_3COOH as NMR solvent in mode ^{1}H-{^{19}F} decoupling NMR. (Chemical shifts in the inserts correspond to $C\underline{F_3}$ and $CO_2\underline{H}$ groups).

Fig.2 TGA (a) and DSC (b) thermograms of PTFEMA and PPFEHEMA (N_2 gas).

Fig. 3 SEM analysis of fertilizer granule and its cross-section containing the interface between DAP and tested PTFEMA and PPFEHEMA (single layer (1L) and second layer (2L)).

Fig. 4 EDX analysis on the surface of uncoated DAP and coated DAP using PTFEMA and PPFEHEMA 1L and 2L.

Fig. 5 Chemical mapping obtained from the cross-sections of DAP coated with PPFEHEMA (2L) (Bar scale:10 µm).

Fig. 6 Release rate of P and N for uncoated DAP and coated DAP using PTFEMA and PPFEHEMA 1L and 2L in water at pH=7 and ambient temperature.

Table Captions

Table 1 Principal FTIR characteristic bands of PTFEMA and PPFEHEMA polymers.

Table 2 Assignments of chemical shifts/ ppm for PTFEMA and PPFEHEMA polymers.

Table 3 Thermal data of PTFEMA and PPFEHEMA by TGA and DSC.

Table 4 Percentage of coating materials, PTFEMA and PPFEHEMA, with different layers (L).

Table 5 EDX elemental weight percentages of uncoated and coated DAP by different tested polymers (1L and 2L).

Table 6 Comparative of the results of previous published poly(acrylate)s coating materials

Table 7. Kinetic parameters of N and P releases in water calculated according to the Ritger-Peppas model from DAP coated with PTFEMA and PPFEHEMA 1L and 2L.

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Data Availability Statement (DAS)

Industries of commercially available coated fertilizers by polymers, Mathematical Modelling of Release Kinetics, FTIR spectra of TFEMA , PTFEMA , PFEHEMA and PPFEHEMA; Water Contact Angle (WCA) of: (a) PTFEMA and (b) PPFEHEMA; Elastic behavior of PPFEHEMA after stretching; Thickness of DAP coated with PTFEMA and PPFEHEMA 1L and 2L and the corresponding percentage coating weight % (red color); Nutrients saturation time of uncoated DAP and coated DAP using PTFEMA and PPFEHEMA 1L and 2L; Example of release kinetic plots Ln (M_t/M_∞) *versus* Ln(t) of coated DAP with PTFEMA and PPFEHEMA. All the data have been supplied in the Electronic Supporting Information.

Data provided in that manuscript are directly associated with the article.

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