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

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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 (PMATRIF and PPFA) with different fluorinated side chains were synthesized by free radical polymerization and used as coatings for SFR. These polymers were characterized by ¹H and ¹⁹F NMR, FTIR, WCA, TGA and DSC. Compared to PMATRIF, PPFA with a higher content of F atoms content displayed improved thermal stability and an elastomer structure ($T_g = -10$ °C) leading a satisfactory film formation. Indeed, contact angle measurements (WCA) were carried out on films of both materials, PPFA 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 PPFA has the slowest N and P nutrients releases, the time to reach the 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 PMATRIF and PPFA is consistent with the nutrient demand during crop growth and increases the efficiency of fertilizer use and therefore enhancing agricultural productivity.

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 projected 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 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 by 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 minimize environmental pollution.⁸ SRFs designed to release nutrients slowly to meet their needs during crop growth⁹. Fertilizer coated with polymers are the most important candidates for SRFs which act as a diffusion barrier membrane. They can be divided into two classes: (i) hydrophobic polyolefins that are soluble in organic solvent (*e.g.*, polyethylene¹⁰ and polyacrylonitrile¹¹), and (ii) superabsorbent hydrogels as three-dimensional or crosslinked matrices composed of linear or branched polymers with abundant hydrophilic groups¹² which in agriculture lead to increased water storage capacity, limited irrigation amount, and increased crop production in semi-arid and arid areas.¹³

Poly(acrylates) (PAs) have been widely used to produce SRF to increase agricultural yields of corn and wheat¹⁴ and as superabsorbents.¹⁵ 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.¹⁶ Polysaccharides such as starch, cellulose, 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.¹⁷ 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.¹⁵ Recently, Zhu et al.¹⁸ 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.¹⁹ 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.²⁰⁻²² 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.^{20,23-25} Their low surface energies attributed to the properties of fluorine atom enable them to be widely used in high-performance coatings.²⁴⁻²⁸ 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.²⁹ developed a novel waterborne hydrophobic polymer coating using nano-SiO₂ and 1H,1H,2H,2H-perfluorooctyltriethoxysilane to modify water-based polyvinyl alcohol. Waterborne copolymers prepared by pickering emulsion copolymerization of butyl methacrylate (BMA) with a fluorinated monomer such as 2-(perfluorohexyl)ethyl acrylate

(PFA) were recently published by our team. These waterborne latexes were tested as coating materials for granular water-soluble fast-release fertilizers.³⁰ The P(BMA-co-PFA) copolymer containing 8 wt. % starch nanocrystals and a low PFA 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-PFA) copolymer coating.

The aim of this work is the preparation of hydrophobic poly(meth)acrylates with different fluorinated side chains such as poly(2,2,2-trifluoroethyl methacrylate) (PMATRIF) and poly(2-(perfluorohexyl)ethyl acrylate) (PPFA) by free radical polymerization. These polymers were characterized by NMR ¹H, ¹⁹F, 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 study 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

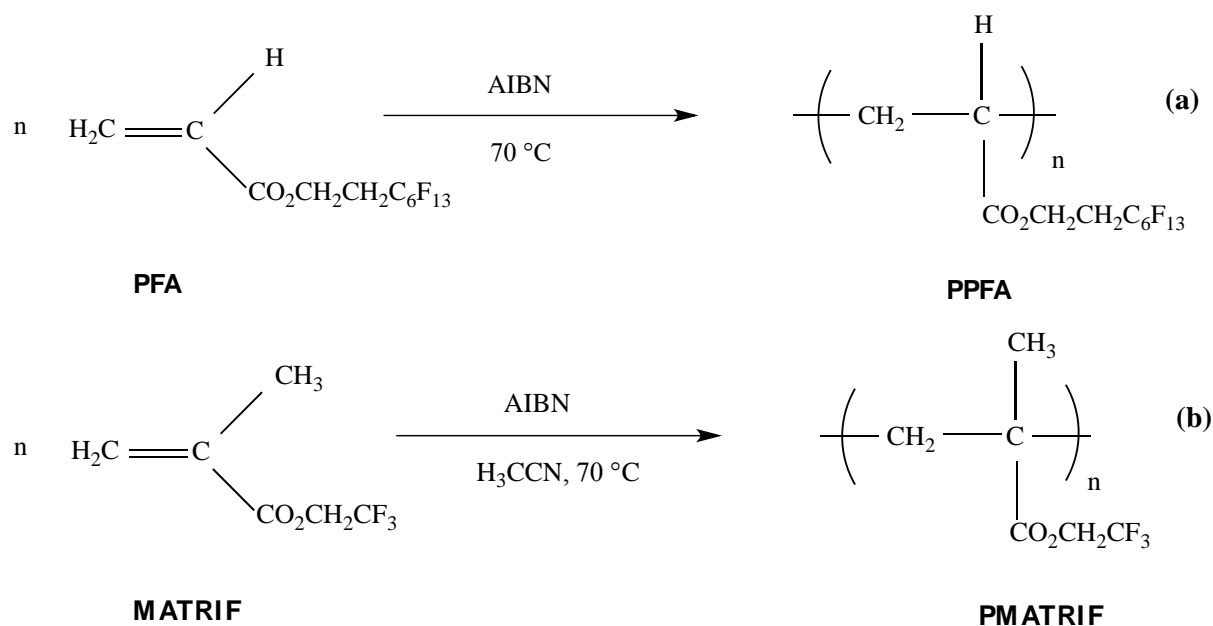
2.1. Materials

Diammonium phosphate (DAP) ((NH₄)₂HPO₄) was chosen as granular phosphate fertilizer to prepare SRFs. This commercial granular fertilizer, containing 46 % of Phosphorus (P₂O₅) and 18 % of Nitrogen (N) was generously provided by the OCP Group in Morocco. 2(perfluorohexyl)ethyl acrylate (PFA) (CAS: 17527-29-6) was kindly provided by Atofina (Pierre Bénite, France), while 2,2,2-trifluoroethyl methacrylate (MATRIF) 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, MATRIF and PFA were purified by distillation at reduced pressure.

2.2. Synthesis of fluorinated homopolymers

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

The bulk radical polymerization of 2-(perfluorohexyl)ethyl acrylate, PFA, was performed according to the procedure described by Stone et al.³¹ Briefly, 5g of PFA monomer was placed in a glass flask equipped with a reflux condenser, thermometer, and magnetic stirrer. AIBN as initiator (0.05 g, 1wt. % 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 PPFA polymer was collected by filtration, washed by methanol, and dried under vacuum at 60 °C. The synthesis route of PMATRIF is displayed [Scheme 1a](#).



Scheme 1 Radical polymerization of: (a) PFA, and (b) MATRIF monomers.

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

A solution of 2,2,2-trifluoroethyl Methacrylate (MATRIF) in acetonitrile was polymerized according to the same protocol described above ([Scheme 1b](#)). 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.

2.3. Coating technique

The commercial granular DAP fertilizers were coated following a methodology similar to that reported in our previous publications.³⁰ Brief, the coating process involved the dip-coating, wherein specific DAP granules (with diameters of 2-4 mm and weight ranging from 34-35 mg) were immersed in the corresponding solvent-solubilized fluorinated homopolymers

(Tetrahydrofuran for PMATRIF and hexafluorobenzene for PPFA). Subsequently, the coated DAP granules were then dried at room temperature obtaining coated fertilizer with single layer (1L). To create a coated DAP with a second layer (2L), this operation was carried out twice on the coated DAP (1L) using the same coating solution.

The percentage of coating (CC) was calculated according to following equation (1):

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

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 analysis 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} with 16 acquisitions.

2.4.2. Nuclear Magnetic Resonance (NMR) spectroscopy

The ^1H and ^{19}F NMR spectra were obtained at room temperature using Bruker AC 400 spectrometer at ambient temperature. Deuterated chloroform (CDCl_3) and the 1:1 mixture of $\text{CDCl}_3/\text{CF}_3\text{CO}_2\text{H}$ were used as NMR solvent for PMATRIF and PPFA, respectively. Chemical shifts are presented in ppm. ^1H and ^{19}F NMR spectra were performed in the following experimental conditions: a flip angle of 90° for ^1H (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. Water contact angle (WCA) measurements

Water contact angles measurements (WCA) were performed to investigate the degree of hydrophobic character of synthesized 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.

2.4.4. 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).

2.4.5. 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.

2.4.6. 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 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 Nitrogen and phosphorus in water

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 (NH₄⁺) and phosphorus (P₂O₅) 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 NH₄⁺ and P₂O₅, 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 PMATRIF and PPFA (coating materials)

Excellent weatherability, semi-permeable membrane based on fluorinated acrylic polymers should be covered by as many fluorine-containing groups as possible^{24,26,28,31}. 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.³² Therefore, these specialty polymers must be separated from the PFAS family. Shirai et al.³³ 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 ($n \leq 6$ fluorocarbons) present less bioaccumulative PFAS compared to those with $n \geq 7$. 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 MATRIF ($-CF_3$) and PFA (C_6F_{13}) as fluorinated monomers to prepare PMATRIF and PPFA 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). After purification, the yields of the obtained polymers were closed to 60 and 75% for PPFA and PMATRIF, respectively. The obtained 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 MATRIF and PFA monomers and the corresponding PMATRIF and PPFA homopolymers. Fig. S1 shows 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.^{34–38} Meanwhile, the characteristic stretching of the MATRIF and PFA 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 PMATRI and PPFA polymers.

Bands	PMATRIF (cm^{-1})	PPFA (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 ^1H and ^{19}F NMR spectroscopies

The white powders of the purified copolymers were analyzed by NMR spectroscopy. [Fig. 1](#) provides the ^1H and ^{19}F NMR spectra of the PMATRIF polymer recorded in deuterated chloroform, while the NMR spectra of PPFA were recorded in a 1:1 mixture of $\text{CDCl}_3/\text{CF}_3\text{CO}_2\text{H}$, since PPFA is not soluble in organic solvents.

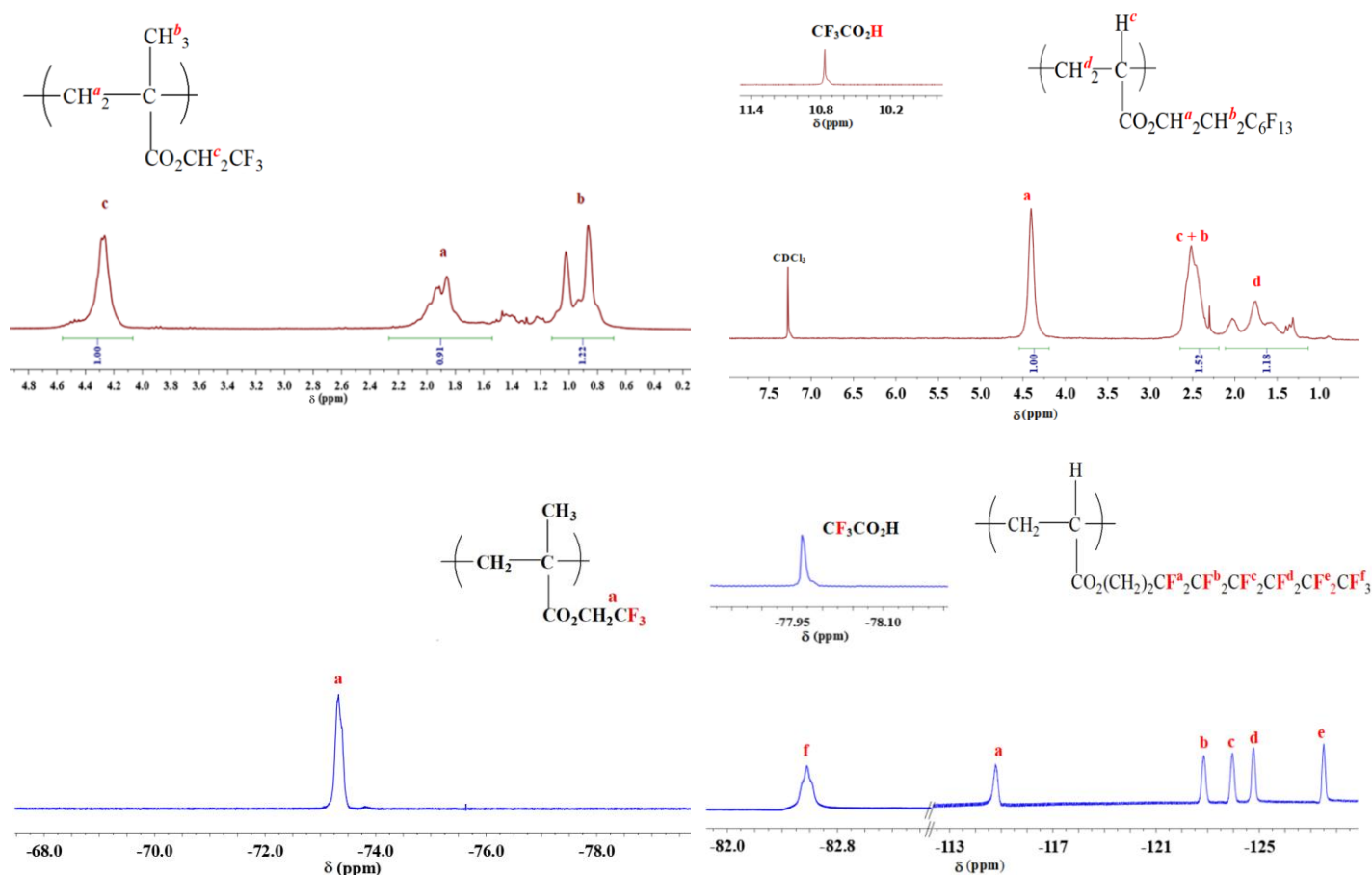


Fig. 1 ^1H and ^{19}F NMR spectra of PMATRIF (left) (CDCl_3 as solvent) and PPFA (right) (the mixture of CDCl_3 and CF_3COOH as NMR solvent in mode $^1\text{H}\{-^{19}\text{F}\}$ decoupling NMR. (Chemical shifts in the windows correspond to CF_3 and CO_2H). The assignments of the chemical shifts were derived by comparison with the values reported in the literature for MATRIF based polymers³⁷ and poly(perfluoro (meth)acrylate)s²⁸ and are summarized in Table 2. For example, the ^1H NMR spectrum of PMATRIF shows a signal of the methylene of ester group ($-\text{O}-\text{CH}_2-\text{CF}_3$) centered at 4.3 ppm. The methyl group of PMATRIF ($-\text{CH}_3$) was observed in the range of 0.8-1.1 ppm, while the methylene protons of the backbone (CH_2) appear between 1.8 and 2.1 ppm. The ^{19}F NMR spectrum of PMATRIF shows the CF_3 peak at -73 ppm. The vinylic proton peak centred at 6.1 ppm for MATRIF and peaks at 6.5; 5.9 and 5.0 for PFA were not present in these spectra.

Table 2 Assignments of chemical shifts/ ppm for PMATRIF and PPFA polymers.

Type of proton	^1H NMR	
	PMATRIF	PPFA
CH_3	0.8-1.1	-
CH_2 (main chain)	1.8-2.1	1.2-2.2
CH (main chain)	-	2.2-2.7
OCH_2CF_3	4.3	-
$\text{OCH}_2\text{CH}_2\text{C}_6\text{F}_{13}$	-	4.2-4.5
$\text{OCH}_2\text{CH}_2\text{C}_6\text{F}_{13}$	-	2.2-2.7
Type of fluorine	^{19}F NMR	
	PMATRIF	PPFA
OCH_2CF_3	-73.0	-
$\text{O}(\text{CH}_2)_2\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_3$	-	-114.8
$\text{O}(\text{CH}_2)_2\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_3$	-	-124.8
$\text{O}(\text{CH}_2)_2\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_3$	-	-122.8
$\text{O}(\text{CH}_2)_2\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_3$	-	-123.9
$\text{O}(\text{CH}_2)_2\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_3$	-	-127.5
$\text{O}(\text{CH}_2)_2\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_3$	-	-82.6

3.1.3. 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.³⁹ WCA value for the PMATRIF film was about 97° , while that of PPFA reached a value of 119° , as shown in Figure S2 (Supporting Information). The WCA difference between PMATRIF and PPFA (22°) indicates a more pronounced hydrophobic character of PPFA film compared to those of PMATRIF film, this can be

attributed to the difference in the surface energy value in the chemical structure at the surface of the two fluorinated polymers.³⁸ Barbu et al.⁴⁰ reported that the constituent groups affect the surface energy in the following order: CH_2 ($36 \text{ mN}\cdot\text{m}^{-1}$) > CF_2 ($23 \text{ mN}\cdot\text{m}^{-1}$) > CF_3 ($15 \text{ mN}\cdot\text{m}^{-1}$). Therefore, the hydrophobic characteristic of the fluorinated polymer PPFA was improved compared to that of PMATRIF since PPFA has a more zig-zag linear conformation of the side chain ($-(\text{CF}_2)_5\text{CF}_3$) and a lower surface energy value than PMATRIF ($-\text{CF}_3$). This result is in good agreement with previous work.^{30,41} In comparison of two fluoroalkyl methacrylate polymers, Phillips and Dettre⁴¹ found that a polymer with a longer fluoroalkyl side chain had the highest WCA value.

3.1.4. Thermal properties (TGA and DSC)

DSC and TGA were used to study the thermal properties of the PMATRIF and PPFA.

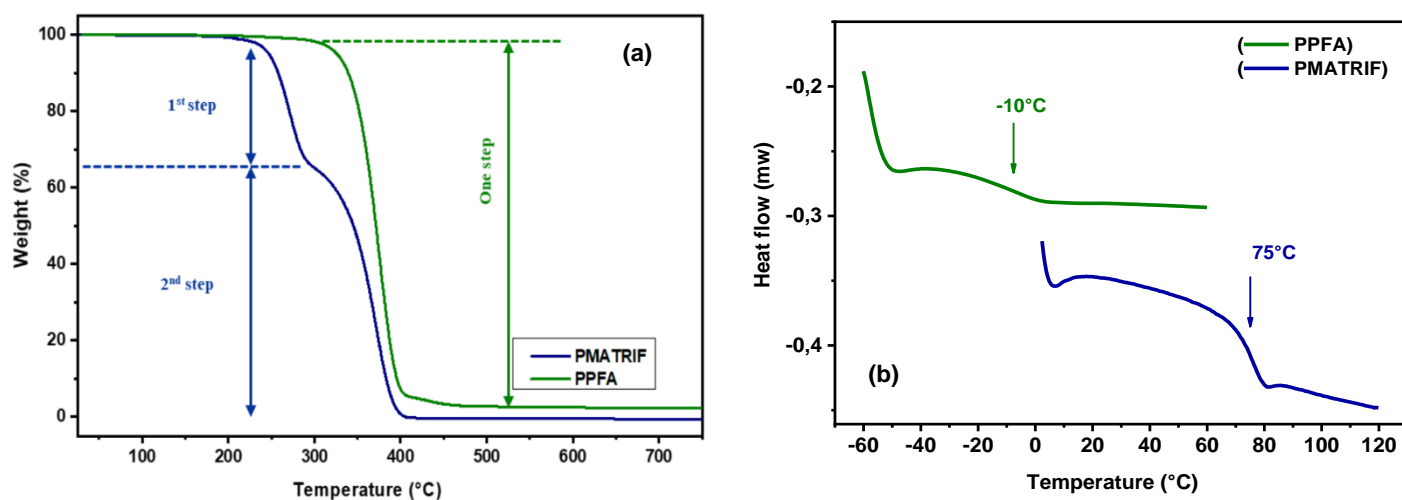


Fig. 2 TGA (a) and DSC (b) thermograms of PMATRIF and PPFA (N_2 gas).

The degradation of PMATRIF 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.^{42,43} PPFA 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). PPFA exhibits higher thermal stability compared to PMATRIF (Fig. 2a), which can be attributed to the better thermal stability of C_6F_{13} pendant group in PPFA due to the strong C-F bond ($E_{\text{C-F}} = 450 \text{ kJ/mol}$) that makes it possible to increase the heat resistance performance of the polymeric

materials by adding more fluorinated components.³⁰ Table 3 lists the thermal data of PMATRIF and PPFA.

The DSC second heating thermograms 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 PPFA and PMATRIF, respectively.

Table 3 Thermal data of PMATRIF and PPFA by TGA and DSC.

Polymers	TGA*			DSC
	T_d 10 % (°C)	T_d 50 % (°C)	Residue at 600 °C (%)	T_g (°C)
PMATRIF	256	345	0.0	75
PPFA	339	371	2.0	-10

* T_d x%: Temperature of x % of decomposition (N₂ gas, 10°C/min)

The decrease in T_g for PPFA compared to PMATRIF is related to the structure of the FPA units. In fact, the long alkyl dangling chains of the acrylate moiety (-CO₂CH₂CH₂C₆F₁₃) serve as internal plasticizers, resulting in low T_g and giving PPFA a more elastomeric behavior at room temperature as shown in Fig. S3.⁴⁴ The T_g decrease leads to excellent film-forming properties at room temperature for fertilizer coating. The PPFA 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. To investigate the coating quality between the fertilizer and the coating, the morphology of the surface and cross-section of uncoated and PMATRIF and PPFA coated DAP with as a single layer (1L) and as a second layer (2L) was performed by SEM (Fig. 3).

Table 4 Percentage of coating materials, PMATRIF and PPFA, with different layers (L).

DAP Coatings	Weight Coating percentage (%)	Average thickness (μm)
PMATRIF 1L	4.5	51.0

PMATRIF 2L	10.7	90.0
PPFA 1L	7.7	27.0
PPFA 2L	16.0	73.0

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).

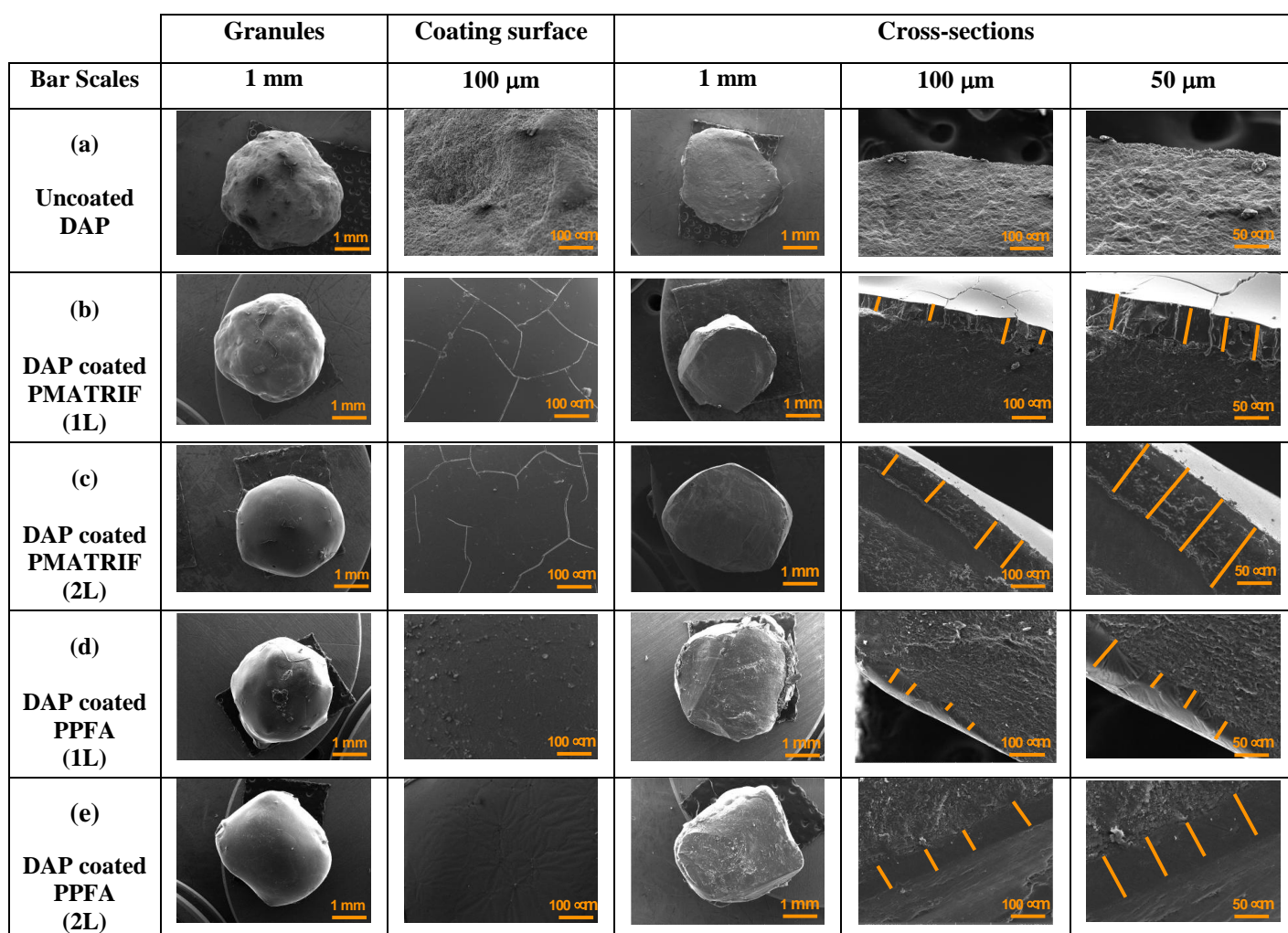


Fig. 3 SEM analysis of fertilizer granule and its cross-section containing the interface between DAP and tested PMATRIF and PPFA (single layer (1L) and second layer (2L)).

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.^{39,45} When the DAP fertilizer was coated with the two PMATRIF and PPFA 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.^{9,30,39,45,46}

When analyzing the outer surface of the DAP granules coated with PMARIF (Fig. 3b-c), we find that there are some microcracks in the surface compared to the granules coated with PPFA, which may be related to the structure of these polymers. PPFA has a T_g that is lower than the ambient temperature (-10 °C), so the PPFA coating has a high flexibility and good film-formation, resulting in improved impact and crack resistance (Fig. S3). In contrast, PMATRIF 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.⁴⁷ reported that controlling the rate of solvent evaporation or performing annealing could prevent the formation of cracks and pores. Yadavalli et al.⁴⁸ 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 PMATRIF or PPFA (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 ((NH₄)₂HPO₄) and the hydrophilic side (ester groups -CO₂-) in the PMATRIF and PPFA coatings could be responsible for the good adhesion between both compounds.⁴⁴ 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.³⁰

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 (PMATRIF, PPFA) and their content (1L or 2L) as displayed in Fig. S4.

The thicknesses of the different PMATRIF and PPFA coatings are also shown in Fig. S4. The average thickness of the DAP coated with PMATRIF (1L) and (2L) are close to 51 and 90 μm, respectively, while those achieved when PPFA 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) PMATRIF and PPFA 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.

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.

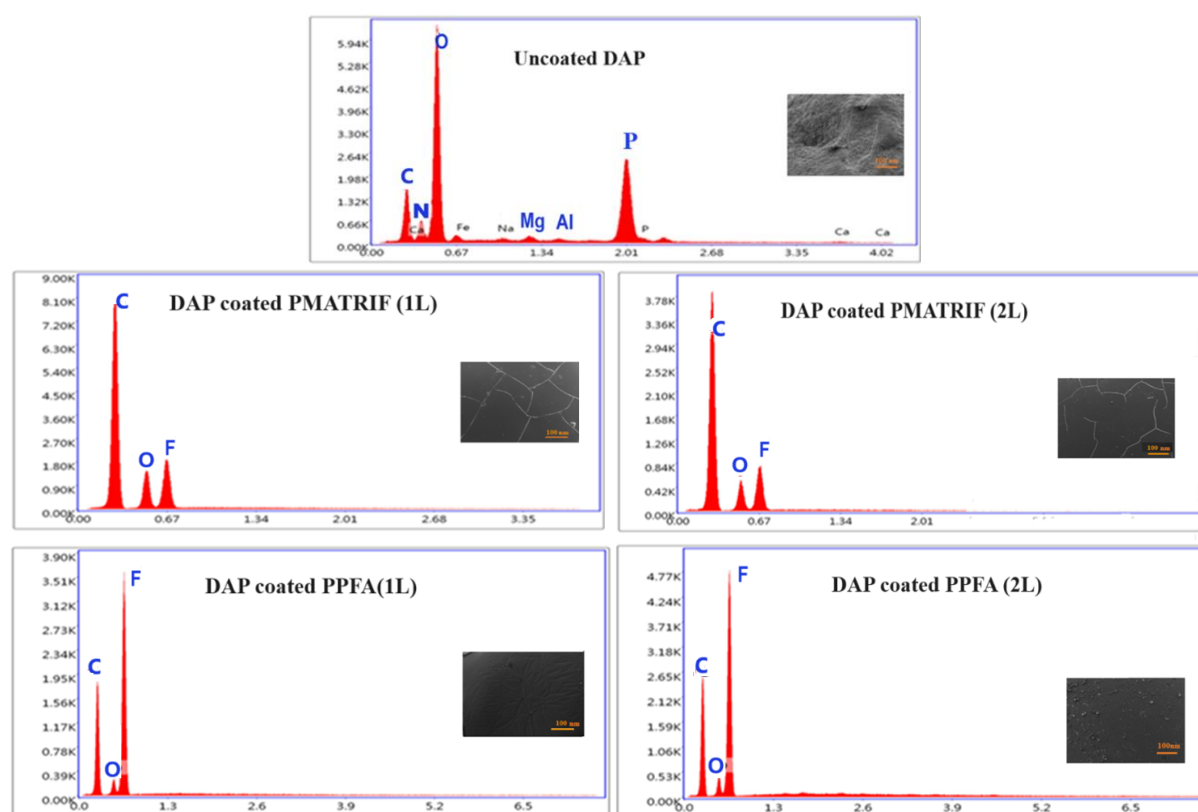


Fig. 4 EDX analysis on the surface of uncoated DAP and coated DAP using PMATRIF and PPFA 1L and 2L.

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 PMATRIF	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 PPFA	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 PMATRIF and PPFA coatings covered the granular fertilizers successively with a good adhesion and without any diffusion of the macronutrients N and P of DAP fertilizer. These results are also corroborated with the SEM analyzes. In the DAP coated with PMATRIF and PPFA 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 PPFA has a higher percentage of F-atoms than those coated with PMATRIF (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 PPFA 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 PPFA.

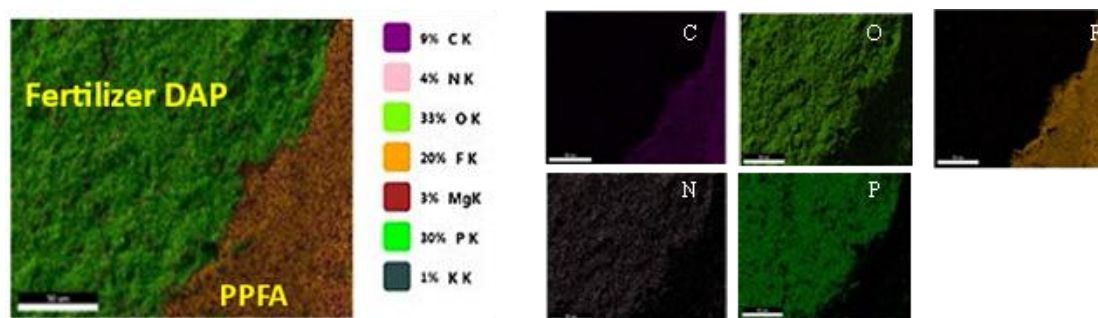


Fig. 5 Chemical mapping obtained from the cross-sections of DAP coated with PPFA (2L) (Bar scale:10 μ m).

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.⁴⁹ and Pereira et al.⁵⁰ 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 PMATRIF and PPFA 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 PMATRIF single-layer (1L) and double-layer (2L), respectively.

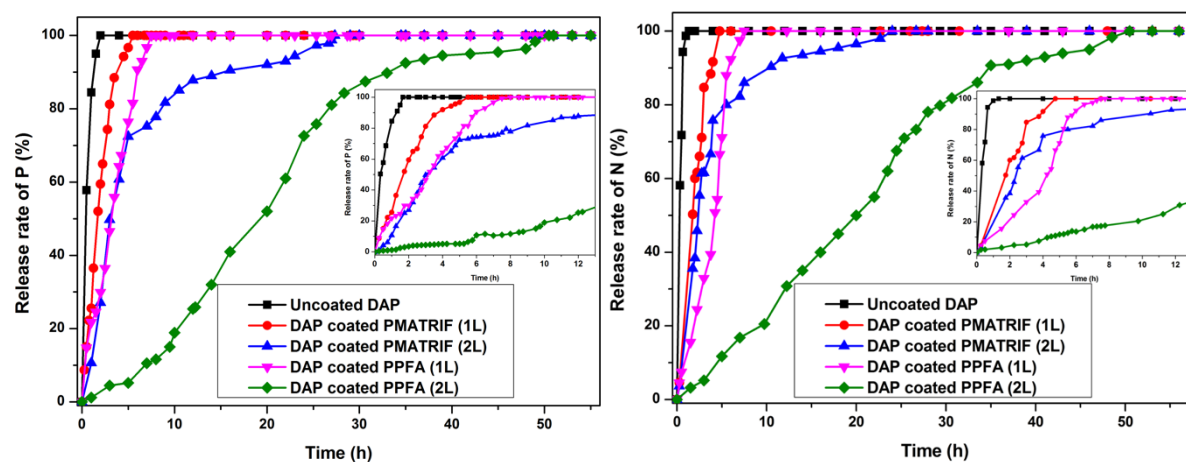


Fig. 6 Release rate of P and N for uncoated DAP and coated DAP using PMATRIF and PPFA 1L and 2L in water at pH=7 and ambient temperature.

When the DAP was coated with PPFA 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.^{30,39,44,45} DAP coated with 2 L of PPFA 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 PMATRIF, the PPFA 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 PFA monomer with hydrophobic properties attributed to the -C₆F₁₃ side groups gives the PPFA 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 PMATRIF coated DAP.^{20,21,25} This hydrophobic character was confirmed by water contact measurement (WCA) (Fig. S2), where the value of PPFA (WCA=109°) is higher than that of PMATRIF (WCA=79°). The soft structure of PPFA,

which was confirmed by DSC (Fig. 2b, Table 3) gives the polymer good film-forming ability and good adhesion properties.³⁰

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,⁵¹ the DAP coated with 3.0 and 4.5 w% of polyurethane prepared from castor oil 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 PPFA 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 maximum release after 50.5 h (Fig. S5).

A comparison of P release times at equilibrium of PMATRIF and PPFA coatings with various previous studies using acrylate coating polymers is given in Table 6.

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	30
DAP coated starch nanocrystal/P(BMA-co-PFA)	Immersion	32.5	30
DAP coated by Polymethyl methacrylate-g-carboxymethyl cellulose	Rotary pan	30.0	46
PMMA	Rotary pan	23.0	46
DAP coated with PMATRIF (Double layer)	Immersion	24.0	This work
DAP coated with PPFA (Double layer)	Immersion	50.5	This work

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

This comparison shows that the release properties of PPFA 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 nutrients N and P is better for the plants.


4. Conclusion

Poorly bioaccumulative of fluorinated (meth)acrylic polymers were used as hydrophobic coating materials for granular water-soluble fast acting fertilizers. PMATRIF and PPFA were successfully synthesized, characterized, and applied to DAP fertilizers. With their highly hydrophobic character due to the presence of a large number of fluorinated atoms leading to a high water repellent surface with good film-forming properties attributed to the flexible zig-zag side chain ($-C_6F_{13}$). 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 PMATRIF and PPFA coatings (1L and 2L), (iii) compared to uncoated DAP granules which is totally solubilized after less than 2h, coated DAP with 2 L of PPFA has the slowest N and P nutrients releases, the P release profile of the granules coated with PPFA 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 application 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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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) PFA, and (b) MATRIF monomers.

Caption figures

Fig. 1 ^1H and ^{19}F NMR spectra of PMATRIF (left) (CDCl_3 as solvent) and PPFA (right) (the mixture of CDCl_3 and CF_3COOH as NMR solvent in mode $^1\text{H}\{-^{19}\text{F}\}$ decoupling NMR. (Chemical shifts in the windows correspond to CF_3 and CO_2H).

Fig.2 TGA (a) and DSC (b) thermograms of PMATRIF and PPFA (N_2 gas).

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

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

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

Fig. 6 Release rate of P and N for uncoated DAP and coated DAP using PMATRIF and PPFA 1L and 2L in water at $\text{pH}=7$ and ambient temperature.

Caption tables

Table 1 Principal FTIR characteristic bands of PMATRI and PPFA polymers.

Table 2 Assignments of chemical shifts/ ppm for PMATRIF and PPFA polymers.

Table 3 Thermal data of PMATRIF and PPFA by TGA and DSC.

Table 4 Percentage of coating materials, PMATRIF and PPFA, 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(acrylates) coating materials