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Radiation induced graft polymerization of fluorinated monomers onto flax fabrics for the control of hydrophobic and oleophobic properties

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ABSTRACT

Functional textiles have been one of the most studied topics in recent decades. Due to toxicity concerns, the treatment of fabrics for non-wettable properties with fluorinated molecules is nowadays limited to short fluoro-alkyl chains. In this work, several fluorinated (meth)acrylic monomers such as 1,1,1,3,3,3-hexafluoroisopropyl methacrylate, 2-(perfluorobutyl)ethyl methacrylate, 1H,1H,2H,2H-perfluorooctyl methacrylate, 1H,1H,2H,2H-perfluorooctyl acrylate and 1H,1H,2H,2H-perfluorodecyl methacrylate (denoted as M2, M4, M6, AC6 and M8, respectively) were grafted onto flax fabrics to improve their hydrophobic and oleophobic properties by radio-grafting using a pre-irradiation procedure. The effects of the length of the fluoroalkyl group of the monomer, the irradiation dose and the reaction time on the grafting rate were studied. The functionalization of flax fabrics by these five monomers was confirmed by FTIR spectroscopy analysis. The morphology of the fibers before and after treatment was studied by scanning electron microscopy (SEM). The location of fluorine element in the flax elementary fibers was assessed by SEM-EDX. The hydro- and oleophobic properties were determined by contact angle measurement using water and diiodomethane as solvents, respectively. The sliding angle was also measured to assess the water repellency of hydrophobic fabrics. Significant fluorine contents were obtained for flax fibers irradiated and treated with 10 wt% solutions of monomer. Hydro- and oleophobic fabrics were obtained for flax irradiated even at a low dose of 5 kGy and treated with M4, with water and diiodomethane contact angles (CAs) of about 139° and 120°, respectively. Superhydrophobic fabrics (CA = 150°) were also achieved for samples irradiated at 20, 50 and 100 kGy and treated with 10 wt% of M8. For this monomer, SEM analysis showed the formation of spherical microparticles of fluoropolymer covering the surface of elementary fibers. The formation of these particles is assumed to result from a dispersion polymerization mechanism. This is due to the lower affinity of M8 with methanol and to the incompatibility of the formed polymer chains with this solvent used for the grafting reaction.

Keywords:

Flax fabrics
Fluorinated monomers
Radiografting

1. Introduction

In recent years, superhydrophobic surfaces with a water contact angle (WCA) larger than 150° have attracted a lot of interest both in academia and textile industry, due to their water-repellent and self-cleaning properties. In nature, one part of the surface of some plants or insects have a contact angle with water greater than 150°, such as sacred lotus leaves, water strider's legs and ornithoptera wings [1]. The superhydrophobic nature of a lotus leaf consists of a combination of roughness and the presence of epicuticular wax (CA = 110°) secreted by the leaf itself. This combination results in the superhydrophobicity of the

lotus surface called "lotus effect" which allows water droplets to roll off and collect contaminants from the leaf [1–3].

Textiles produced from natural fibers such as cotton, wool or flax are unsuitable for some applications due to their hydrophilicity. Therefore, many works have been performed to improve the hydrophobicity of natural fibers by introducing substances with low surface energy such as fluorine-containing molecules.

Fluorinated polymers are widely used due to their exceptional properties, which are due to the presence of C–F bonds. The low wettability, low adhesion, and low coefficient of friction associated with fluorinated surfaces play essential roles in microelectronic, antifouling,

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oil/water separation and medical applications [4–8]. Fluoropolymers are well known as low surface energy materials [5,9–11]. Their oil- and water-repellent properties make them good candidates for applications as coatings of substrates such as textiles [12–18]. Per- and poly-fluoroalkyl substances (PFAS) with a fluorinated group containing six or more carbons present a strong hydrophobic and oleophobic character [19–26]. Despite these properties of great interest, these fluorinated compounds are persistent, bioaccumulative and toxic for humans, animals and for the environment [24,25,27–29]. Due to the adverse effects of long-chain PFASs, some of these products are already banned or restricted. A process of substitution with short-chain PFASs (C_nF_{2n+1} with $n \leq 5$) or with non-fluorinated molecules is recommended [30,31].

Different methods can be used for the surface grafting of natural fibers with fluorinated molecules: plasma treatment [32–34], sol-gel [19,35,36] or more recently radiation induced graft polymerization [22,37,38]. Therefore, this radiografting technique for modification of plant fibers becomes the subject of current research works [15,37–42]. Several studies have been carried out to modify the surface of natural fibers using the irradiation method with a simultaneous procedure, for which the irradiation step takes place in presence of the grafting agent. Deng et al. [37] grafted a fluorinated acrylate monomer, 1H,1H,2H,2H-nonafluorohexyl-1-acrylate (F4) onto cotton fibers by simultaneous graft polymerization. They proved that the hydrophobicity of cotton-F4 depends on the degree of grafting (DG), with water contact angles above 150° for DG values higher than 10 wt%. On the other hand, for cotton grafted F4 with DG values lower than 10 wt%, the water droplet rapidly spreads out within 1 min.

Other studies concerned the grafting of 2,2,2-trifluoroethyl methacrylate (TFEM) onto a polypropylene nonwoven fabric using simultaneous process by gamma irradiation to improve its hydrophobicity [13]. The resulting grafted fabric showed a highly hydrophobic character with an increase of the water contact angle, which reached a maximum of about 125° for treatment under N_2 atmosphere with a dose of 25 kGy and a TFEM concentration of 25% (v/v) in THF.

To the best of our knowledge, no article on the grafting of fluorinated monomers onto natural fibers by pre-irradiation method has been reported yet. For such a method, the step of fabric irradiation takes place before the contact with the grafting agent. The present work deals with the radiografting of fluorinated (meth)acrylate monomers bearing per-fluorinated groups of different lengths (from 2 to 8) using e-beam irradiation. The hydro- and oleophobic properties were evaluated as a function of the fluorine content after grafting and the length of the perfluorinated group of the monomer used. The effects of the different parameters such as the absorbed dose, the reaction time and the structure of the monomer on the grafted fluorine content were evaluated. Moreover, the hydrophobicity, oleophobicity and water-repellent capacity of the modified flax fabrics were also studied.

2. Experimental part

2.1. Materials

Flax fabrics were provided by Hexcel (France) with a chemical composition of 81 wt% of cellulose, 13 wt% of hemicellulose and 2.7 wt% of lignin. Fabric weight is 200 g/m².

1,1,1,3,3,3-hexafluoroisopropyl methacrylate (97%, M2), 2-(per-fluorobutyl)ethyl methacrylate (95%, M4), 1H,1H,2H,2H-perfluorooctyl methacrylate (95%, M6), 1H,1H,2H,2H-perfluorooctyl acrylate (95%, AC6) and 1H,1H,2H,2H-perfluorodecyl methacrylate (97%, M8) (Fig. 1) were purchased from ABCR – GmbH (Karlsruhe, Germany) and distilled under vacuum before use. Values of molar mass and fluorine content of the different monomers used are presented in Table 1. Tetrahydrofuran (THF), methanol (CH₃OH) and ethyl methyl ketone (MEK) were purchased from Fisher Scientific (Waltham MA, USA). 1,1,2-trichloro-1,2,2-trifluoroethane (F113) was kindly provided from DuPont Wilmington, USA. These solvents were used without further

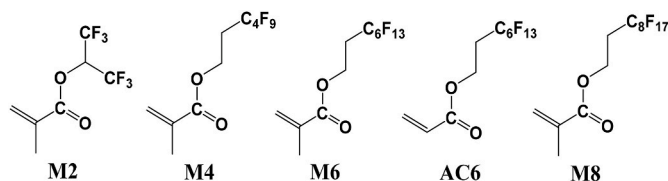


Fig. 1. Chemical structures of the fluorinated monomers used.

Table 1

Molar masses and fluorine contents of the monomers studied.

Monomer	Monomer molar mass (g/mol)	Monomer fluorine content (wt%)
M2	236.1	48.3
M4	332.2	51.5
M6	432.9	57.0
AC6	418.0	59.1
M8	532.2	60.7

purification.

2.2. Irradiation of flax fabrics

Flax fabrics were irradiated in air and at room temperature with doses of 5, 10, 20, 50 and 100 kGy under e-beam radiation (energy 9.8 MeV, power 34 kW). The treatment was achieved by Ionisos SA (Chaumesnil, France). After irradiation, samples were immediately cold stored (−18 °C) to preserve the generated free radicals and/or peroxides.

2.3. Grafting of fluorinated monomers onto irradiated flax fabrics

An impregnation solution was prepared containing 10 wt% of fluorinated monomer (M2, M4, M6, AC6 or M8) and 90 wt% of methanol. The mixture was purged with nitrogen bubbling for 15 min in order to remove oxygen from the reaction medium. Then, irradiated flax fabrics (5 × 5 cm²) at doses of 5, 10, 20, 50 or 100 kGy were immersed in the impregnation solution (fabric/solution weight ratio = 0.01) at solvent reflux for 24 h. Finally, the grafted flax fabrics were washed three times with methyl ethyl ketone (MEK) at room temperature or at 60 °C to solubilize the different monomers and the corresponding ungrafted fluoropolymers (30 mL per wash).

A grafting kinetics of M8 onto irradiated flax fabrics at 100 kGy was also performed in this article. The grafting protocol is identical to that described above, the only change is that during the impregnation step seven pieces of the irradiated fabric were simultaneously immersed in a solution containing a M8/methanol mixture keeping the same fabric/solution weight ratio of 0.01. Then, the treated pieces of fabric were removed at different times (corresponding to times of 30 min, 1 h, 2 h, 4 h, 6 h, 18 h and 24 h). After 24 h-reaction, the treated samples were washed with MEK at 60 °C and dried under a fume hood.

The solubilities of the different fluorinated monomers and polymers used in this study, in methanol, THF and MEK are listed in Table 2. The purpose of washing the treated fabrics was to remove unreacted monomer and free polymer chains which were not covalently linked to the flax structure. After washing, fabrics were dried under a fume hood until the absorbed solvent has been completely eliminated.

In this article, the different samples are named according to the following code: F-100kGy-M8 (10 wt%, 65 °C, 24 h) for flax fabrics irradiated at 100 kGy and treated with a solution of 10 wt% of M8 at 65 °C for 24 h.

Table 2

Solubility of the different fluorinated monomers and polymers in Methanol, THF, MEK and F113.

Fluorinated monomers and polymers	CH ₃ OH (RT)	CH ₃ OH (60 °C)	THF (RT)	THF (60 °C)	MEK (RT)	MEK (60 °C)	F113 (RT)
M2	✓	✓	✓	–	✓	–	–
M4	✓	✓	✓	–	✓	–	–
M6	✓	✓	✓	–	✓	–	–
AC6	✓	✓	✓	–	✓	–	–
M8	✓	✓	✓	–	✓	–	–
P(M2)	x	x	✓	✓	✓	✓	✓
P(M4)	x	x	✓	✓	✓	✓	✓
P(M6)	x	x	x	x	x	✓	✓
P(AC6)	x	x	x	x	x	✓	✓
P(M8)	x	x	x	x	x	✓	✓

2.4. Instrumentation and characterization

2.4.1. Fourier transform infrared spectroscopy (FTIR)

Fourier transform infrared spectra were obtained using a Bruker VERTEX 70 spectrometer with attenuated total reflectance mode, by performing 32 scans between 400 and 4000 cm⁻¹ with a resolution of 4 cm⁻¹.

2.4.2. Fluorine content measurement

Samples treated with M8 for reaction times of 30 min, 2 h, 6 h, 18 h and 24 h were delivered to SGS France for analysis using a calcination method followed by ion chromatography. The analysis process was not communicated by the company due to confidentiality reasons.

2.4.3. Scanning electron microscopy (SEM)

The fiber section of flax fabrics was analyzed using a scanning electron microscope (FEI Quanta 200). After being cut with a single edge blade, the samples were placed on a vertical sample holder under high vacuum at a voltage of 12.5 kV and a working distance of 10 mm. To locate the presence of the fluorine element in the fiber section, SEM analysis was coupled with an energy dispersive X-ray spectroscopy, EDX, (Oxford INCA Energy system).

2.4.4. Contact angle measurements

A KRÜSS type goniometer was used to measure the contact angle of liquid drops formed on the surface of the flax fabric samples. For the hydrophobicity assessment, water was used as the contact angle measuring liquid (WCA). For the oleophobicity, diiodomethane was used (DCA). After adjustment of the deposition level, a drop of 9 µL of water or 1.5 µL of diiodomethane was placed on the surface of the treated fabrics. The baseline used to measure the contact angle was determined for each analysis by the KRÜSS ADVANCE software. For each sample, five measurements were made in order to ensure reproducibility.

2.4.5. Sliding angle measurements

Measurements of sliding angles of hydrophobic fabrics were carried out using a set up realized in our laboratory. The sample was placed on a plane substrate and then a drop of deionized water of 30 µL was put on the grafted fabrics treated with the four fluorinated monomers: M4, M6, AC6 and M8. The substrate was progressively inclined at angles from 0 to 90°; and the sliding angle corresponds to the angle for which the water drop slides directly off the fabric surface. For each sample, four measurements were performed.

2.5. Synthesis of fluorinated polymers via radical polymerization

To compare the hydro-oleophobic properties of flax fibers treated with the different fluorinated monomers and the corresponding pure P (M2), P(M4), P(M6), P(AC6) and P(M8) homopolymers were synthesized via radical polymerization. A 150 mL two-necked round bottom flask was filled with 50 mL of THF and placed under N₂ atmosphere

(bubbling for 15 min). Then, 4.00 g of monomer (M2, M4, M6, AC6 or M8) and 0.04 g of AIBN were subsequently added under magnetic stirring. The reaction was kept under stirring at solvent reflux for 24 h and then cooled to room temperature (Scheme 1). The resulting fluorinated polymer was precipitated from methanol. A white solid was obtained in the case of P(M2), P(M4), P(M6) and P(M8) while a transparent wax was produced for P(AC6).

2.6. Preparation of fluorinated homopolymer films

1.50 g of fluoropolymer (P(M2), P(M4), P(M6), P(AC6) or P(M8)) were solubilized in 10 mL of 1,1,2-trichloro-1,2,2-trifluoroethane (F113). The mixture was stirred until a homogeneous solution was obtained and was then poured into a flat substrate and dried at room temperature. Finally, contact angle measurements were performed on the obtained films according to the same procedure used for fabrics.

3. Results and discussion

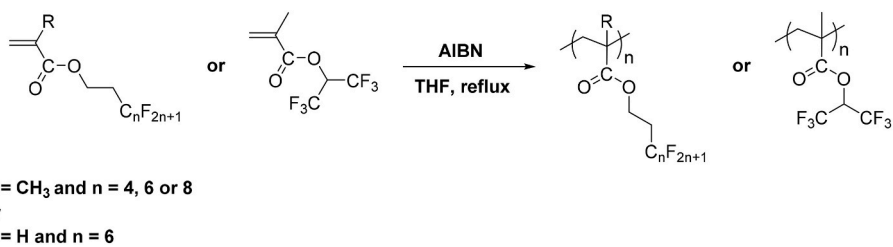
3.1. Radiografting of fluorinated monomers

The pre-irradiation treatment of the flax fabrics was first performed by electron beam irradiation at different doses ranging from 5 to 100 kGy. The second was to bring the generated radicals into contact with the fluorinated monomer to initiate the polymerization (Fig. 2). Then, the grafted flax fabrics were characterized by complementary techniques to ensure the presence of fluoropolymers onto the flax.

3.1.1. FTIR analysis

The chemical composition of flax fabrics, irradiated at 100 kGy and treated with solution of 10 wt% of M8 in methanol at solvent reflux for 24 h, was monitored by infrared spectroscopy and compared with three samples: P(M8) homopolymer, pristine flax fibers and unirradiated fibers treated with M8 in the same grafting conditions (Fig. 3). After the grafting procedure onto irradiated flax fabrics, the FTIR spectrum exhibits the presence of new signals at 1735, 1200 and 1146 cm⁻¹, characteristic of C=O, C-F and C-O-C groups of M8 units of the grafted polymer chains, respectively [14,43,44]. Two bands appear also at 655 and 703 cm⁻¹ resulting from a combination of rocking and wagging vibrations of the CF₂ groups, respectively [4,45]. These bands are also present in the P(M8) spectrum but do not appear for the pristine fabric and the non-irradiated sample treated with M8. First, the absence of signal at 1650 cm⁻¹ characteristic of the (meth)acrylate function can be evidence that the monomer has reacted. Second, the results prove the efficiency of the grafting procedure with M8 and that irradiation is necessary to initiate the monomer polymerization. The absence of characteristic bands of M8 after the grafting procedure for the non-irradiated flax evidences that the washing with MEK after the functionalization reaction is sufficient to remove the unreacted monomer.

The FTIR analysis also confirms the grafting of the other fluorinated monomers on the irradiated fabrics achieved in different reaction



Scheme 1. Schematic representation of the syntheses of P(M2), P(M4), P(M6), P(AC6) and P(M8) homopolymers.

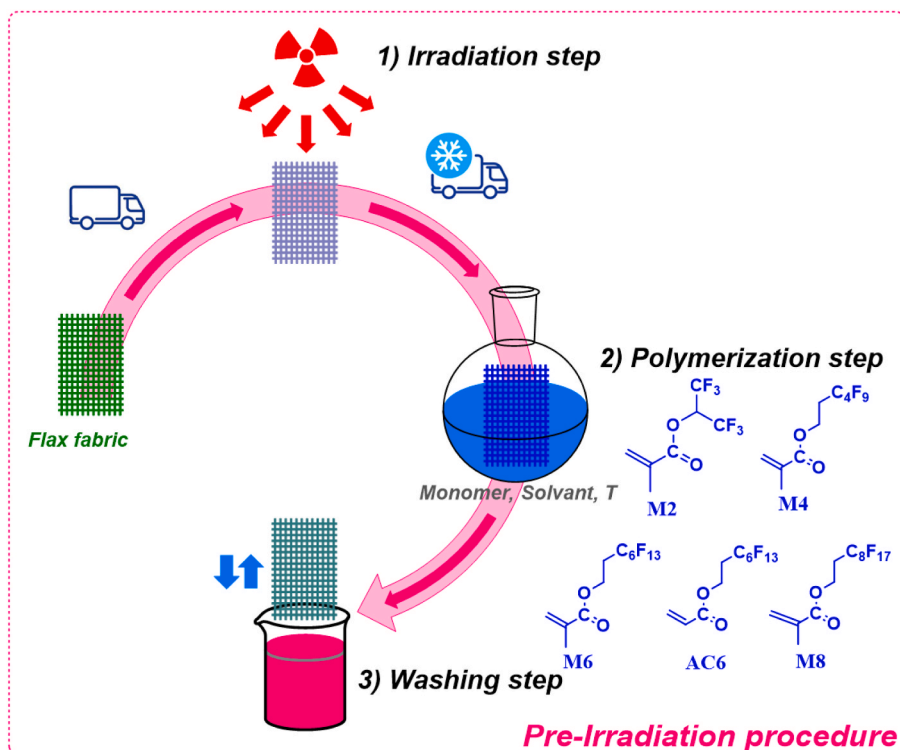


Fig. 2. General process used for the modification of flax fabrics through a pre-irradiation step followed by the polymerization of fluorinated (meth)acrylate monomers.

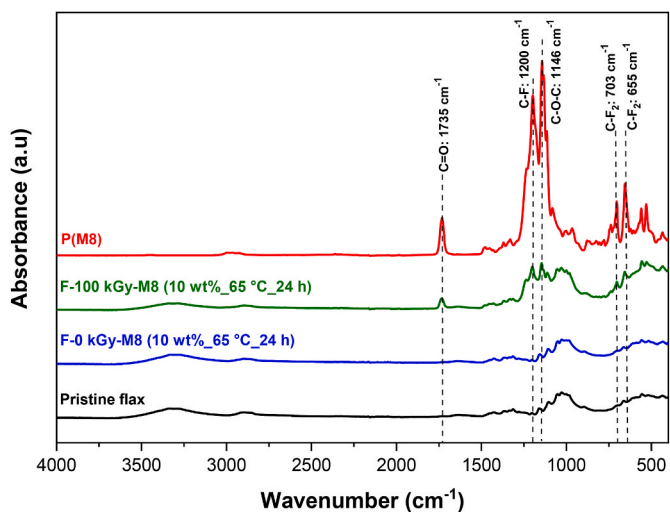


Fig. 3. FTIR spectra of pristine flax fabric, non-irradiated, and irradiated flax fabrics at 100 kGy and treated with M8/MeOH solution (10 wt%_65 °C_24 h) and P(M8) homopolymer.

conditions (Fig. S1, supporting information). Indeed, the grafting is successful with M2, M4, M6, AC6 and M8 monomers at various irradiation doses and for different reaction times.

3.1.2. Fluorine content measurements

In order to determine the fluorine rate of the grafted fabrics, a series of pre-irradiated flax fabrics at 100 kGy treated with M8 for different times ($t = 30$ min, 2 h, 6 h, 18 h and 24 h), was analyzed by calcination followed by ion chromatography. The same samples were also characterized by infrared spectroscopy for comparison (Fig. S2). A correlation between the fluorine rate assessed by ion chromatography and the FTIR results was suggested. Indeed, for the different fluorine concentrations, the measurement of the intensity ratio between the band of the carbonyl group (1735 cm^{-1} - characteristic of fluorinated polymer) and the OH band (3340 cm^{-1} - as a reference) noted $I_{\text{C=O}}/I_{\text{OH}}$, enabled to obtain a calibration curve considering that the samples were dried at $60\text{ }^{\circ}\text{C}$ for 24 h to avoid any moisture. The use of this calibration allows to quantify the total fluorine content of treated fabrics using directly FTIR analysis. These values allowed to establish a calibration curve with a high correlation coefficient ($R^2 = 0.97$) as shown in Fig. S3a. In order to verify that moisture did not influence the intensity of the OH band used as reference, the pristine flax, unirradiated and irradiated fabrics treated with fluorinated monomers were oven dried at $60\text{ }^{\circ}\text{C}$ for 24 h and then

put in a desiccator for 4 days. The $I_{C=O}/I_{OH}$ ratio was checked before and after drying the samples. Fig. S3b shows that functionalized fabrics do not absorb moisture due to the presence of the grafted fluorinated polymer chains and that the intensity ratio remains constant. On the other hand, for unmodified fibers which do not contain any fluorine (pristine flax and F-0 kGy-M8 samples), the intensity ratio $I_{C=O}/I_{OH}$ decreases after drying the fabrics due to the removal of water molecules. Indeed, the intensity of the OH band used as reference also depends on the quantity of absorbed water which can evolve with the grafting of fluorinated polymer chains. In conclusion, the OH band can be used as a reference for normalization of FTIR spectra but it is necessary to dry the samples to eliminate adsorbed water before proceeding to the determination of the fluorine content.

The fluorine content (FC) of modified flax was calculated according to the calibration curve presented in Fig. S3a which links the fluorine content to the $I_{C=O}/I_{OH}$ ratio as follows:

$$FC \text{ (wt\%)} = \left(4.1453 \times \frac{I_{C=O}}{I_{OH}} \right) \quad (1)$$

Then, the fluorine content was converted into grafted monomer concentration by calculation according to equation (2), as illustrated in Table 3.

$$\text{Grafted monomer concentration (mol / g)} = \frac{FC \text{ (wt\%)}}{\text{Monomer fluorine content (wt\%)} \times \text{Monomer molar mass(g/mol)}} \quad (2)$$

Table 3

Fluorine and monomer contents, water and diiodomethane contact angles and sliding angles for different modified flax fabrics obtained according to the nature of the fluorinated monomer, the irradiation dose and reaction time.

Monomer	Reaction time (min)	Dose (kGy)	Washing solvent	Fluorine content (wt %) ^a	Monomer concentration (10 ⁻⁴ mol/g) ^b	Water CA (°)	CH ₂ I ₂ CA (°)	Sliding angle (°)
Pristine flax	–	0	–	0	0	47	0	–
M2	1440	5	MEK (RT)	0.07	0.06	80 ± 4	-	-
				0.12	0.11	83 ± 5	-	-
				0.10	0.09	86 ± 5	-	-
				0.10	0.09	79 ± 6	-	-
				0.14	0.12	77 ± 5	-	-
M4	1440	5	MEK (RT)	0.10	0.06	139 ± 2	120 ± 4	46.5 ± 2.9
				0.11	0.07	139 ± 3	128 ± 3	44.5 ± 4.4
				0.15	0.09	138 ± 1	132 ± 2	43.5 ± 4.7
				0.12	0.07	134 ± 3	130 ± 1	51.3 ± 5.4
				0.22	0.13	130 ± 2	125 ± 5	90.0 ± 0.0
M6	1440	5	MEK (60 °C)	0.21	0.09	125 ± 3	117 ± 1	86.8 ± 4.7
				0.42	0.17	132 ± 2	125 ± 5	65.3 ± 6.3
				0.18	0.07	135 ± 2	130 ± 5	68.3 ± 7.4
				0.19	0.08	136 ± 3	127 ± 3	49.0 ± 7.9
				0.14	0.06	137 ± 3	130 ± 3	50.5 ± 3.1
AC6	1440	5	MEK (60 °C)	0.39	0.16	145 ± 1	130 ± 4	37.0 ± 3.5
				0.33	0.13	149 ± 2	128 ± 3	34.0 ± 7.4
				0.31	0.13	145 ± 4	128 ± 2	38.0 ± 1.6
				0.58	0.23	143 ± 2	132 ± 2	25.5 ± 3.9
				1.09	0.44	147 ± 3	134 ± 3	28.0 ± 3.7
M8	1440	5	MEK (60 °C)	1.35	0.42	145 ± 3	135 ± 2	10.0 ± 0.8
				2.26	0.70	148 ± 1	135 ± 2	9.3 ± 0.5
				1.97	0.61	150 ± 2	133 ± 3	9.5 ± 1.3
				2.33	0.72	150 ± 2	138 ± 1	10.8 ± 1.0
				8.05	2.49	150 ± 1	136 ± 2	9.8 ± 1.3
M8	30	100	MEK (60 °C)	0.50	0.15	–	–	–
				0.37	0.11	143 ± 3	128 ± 2	40.8 ± 1.9
				0.43	0.13	–	–	–
				0.77	0.24	150 ± 3	133 ± 1	14.3 ± 3.2
				3.37	1.04	–	–	–
				9.85	3.05	–	–	–
				13.78	4.27	–	–	–

^a FC calculated according to equation (1).

^b Monomer concentration in modified flax calculated according to equation (2).

3.2. Effect of reaction parameters on grafting efficiency

Different parameters impacting the grafting efficiency of fluorinated monomers such as the irradiation dose and the polymerization time have been studied.

3.2.1. Total absorbed dose

Table 3 summarizes the monomer and the fluorine contents (FC) calculated using FTIR analyses, for the different samples prepared with various grafting conditions (monomer concentration, reaction time, absorbed doses and washing solvent).

The first observation was that generally the FC of treated flax fibers increases with the fluoroalkyl chain length of the used monomer. However, as illustrated in Fig. 4, the treatment with M2 and M4 results in identical values of grafted monomer concentrations of about 0.06×10^{-4} mol/g for a low irradiation dose of 5 kGy. At the same dose, 0.09×10^{-4} , 0.16×10^{-4} and 0.42×10^{-4} mol/g were obtained for M6, AC6 and M8, respectively. An increase of the irradiation dose allows to increase the grafting efficiency for the different fluorinated monomers.

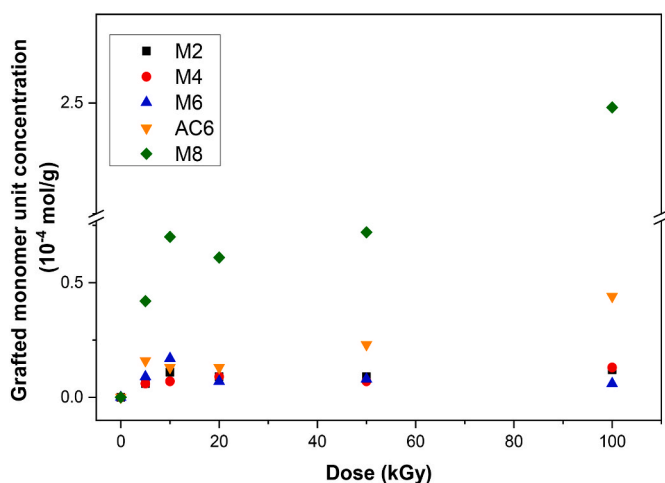


Fig. 4. Evolution of the different monomer contents grafted onto irradiated flax fabrics at different doses.

Indeed, for an irradiation dose of 100 kGy, the molar concentration increased up to 0.12×10^{-5} mol/g for M2 and 0.13×10^{-4} mol/g for M4. When AC6 and M8 were used, 0.44×10^{-4} and 2.49×10^{-4} mol/g were achieved, respectively.

It was also observed that the fluorinated acrylate, AC6, is better grafted than its methacrylic homologue M6 for all irradiation doses tested, except for 10 kGy. This difference of efficiency is greater for high doses of irradiation. The monomer concentrations are about 0.06×10^{-4} and 0.44×10^{-4} mol/g for M6 and AC6, respectively when fabrics were irradiated at 100 kGy. This difference is due to the well-known higher reactivity of acrylates compared to that of methacrylic monomers [46, 47].

Table 3 shows the effect of the absorbed dose on the FC for the treated flax fabrics with the different fluorinated monomers. It was found that the variation of the FC with the applied irradiation dose is not the same for the five fluorinated monomers. For the fabrics treated with M8, the FC increases from 1.35 wt% for a dose of 5 kGy to a maximum of 8.05 wt% for a dose of 100 kGy. The increase of grafting rate with dose can be explained by the fact that more radicals are formed when irradiation dose is increased. These radicals preserved until contact with monomers or transformed as peroxide groups during the storage can then initiate the polymerization of the fluorinated monomers. When other monomers than M8 were used for grafting, the FC increased with the irradiation dose to reach maximum levels of 0.14, 0.22 and 1.09 wt% for fabrics irradiated at 100 kGy and treated with M2, M4 and AC6, respectively. These results are in good agreement with those obtained by Sharif et al. [48] who observed that the degree of grafting by pre-irradiation of glycidyl methacrylate (GMA) onto delignified kenaf fibers increased with the absorbed dose. Madrid et al. [49] also reported that the degree of grafting of GMA onto water hyacinth increased with the irradiation dose. A similar trend was also noted by Moawia et al. [50] who grafted GMA onto flax fibers using a pre-irradiation emulsion method.

For M6, the evolution of the grafting is not uniform with the increasing dose (Fig. 4). The FC first increases to reach a maximum value at 10 kGy (0.42 wt%) and then decreases to reach a minimum at 100 kGy (0.14 wt%) (Table 3). This variation is probably due to measurement uncertainty caused by the low FCs obtained in the case of M6 compared to AC6.

As indicated in Table 3, two different fluorine contents of 8.05 and 13.78 wt% were obtained under identical grafting conditions for flax fabric irradiated at 100 kGy and treated with 10 wt% of M8 for 24 h. This difference is due to the protocol of the grafting kinetics of M8. Indeed, the higher quantity grafted for the sample at 24 h-reaction for studying the grafting kinetics of M8 may be due to the increase over time

of the monomer/fabric ratio. The amount of monomer relative to that of the fabric increases with time due to the collection of samples over time. Thus, for 24 h-treatment, the grafted FC obtained for the kinetics is higher compared to that of the sample for which the monomer/fabric ratio remained constant during all the treatment (FC of 13.78 and 8.05 wt%, respectively).

3.2.2. Kinetics of pre-irradiation grafting

The effect of reaction time ($t = 30$ min, 1 h, 2 h, 4 h, 6 h, 18 h and 24 h) on the FC grafted onto irradiated flax fabrics at 100 kGy and treated with M8 was studied. Fig. 5 shows that the fluorine content increased slightly from 0.50 to 0.77 wt% in a first step from 30 min to 4 h of reaction. Then, in a second step, a fast increase was observed to reach a fluorine rate of 13.78 wt% after 24 h. The slow evolution of the fluorine content at the beginning of the reaction (from 30 min to 4 h) is probably due to the polymerization mechanism with M8 in methanol which is supposed to be dispersion polymerization (as discussed below). This kind of polymerization generally shows a lower monomer conversion rate in the first stages of the process before a more pronounced acceleration of the reaction (Fig. S5).

Huo et al. [51] reported the same evolution for the dispersion polymerization of 2-(perfluorobutyl)ethyl methacrylate (FBEMA) in ethanol at 70 °C. The results indicated two distinct regimes: the polymerization rate was relatively slow during the first 3 h (pre-nucleation), while a rapid increase in the polymerization rate was observed in the following 8 h (post-nucleation). A monomer conversion of 90% was reached after 11 h-reaction.

3.3. Study of the localization of grafted fluoropolymers in treated fabrics by scanning electron microscope coupled with energy dispersive X-ray spectrometer (SEM-EDX)

SEM-EDX analyses (Fig. 6) enabled to evaluate the chemical composition of the modified fabrics and to assess the distribution of chemical elements in the cross-section of the elementary fibers of flax.

Fluorine mapping of transversal sections of flax fibers modified under the same operating conditions with the different fluorinated monomers shows that the fluorine element is located differently depending on the monomer used. For fibers irradiated at 100 kGy and treated with monomers M2 or M4 (fluorine contents of 0.14 and 0.22 wt %, respectively), the fluorine element is homogeneously located on the surface and in the bulk of the elementary fibers (Fig. 6d and f). For identical treatment with M6, AC6 or M8 (fluorine content of 0.14, 1.09 and 13.78 wt%, respectively), fluorine is more present on the surface than in the bulk of the elementary fibers with a marked difference for M8

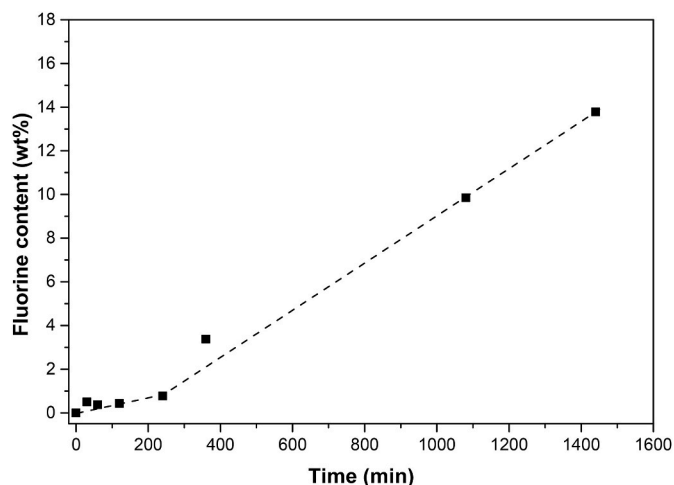


Fig. 5. Kinetics of grafting of M8 onto flax fabrics irradiated at 100 kGy.

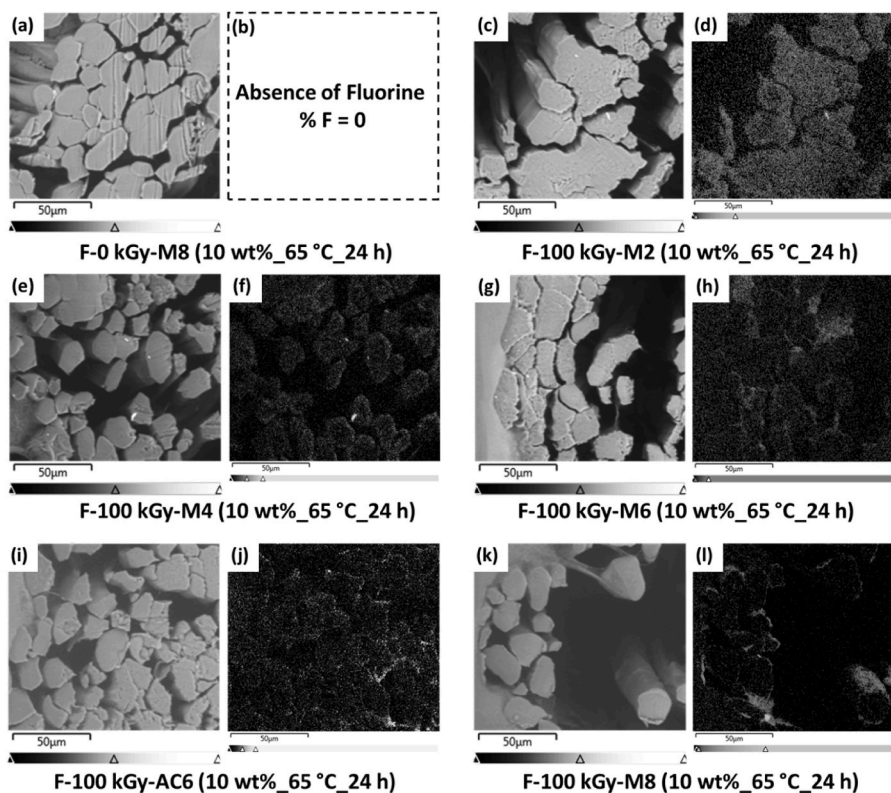


Fig. 6. SEM images of (a) unirradiated flax fibers treated with M8 and (c), (e), (g), (i), (k) irradiated flax fibers at 100 kGy and treated with M2, M4, M6, AC6 and M8, respectively. (b), (d), (f), (h), (j) and (l) are the corresponding EDX fluorine mappings.

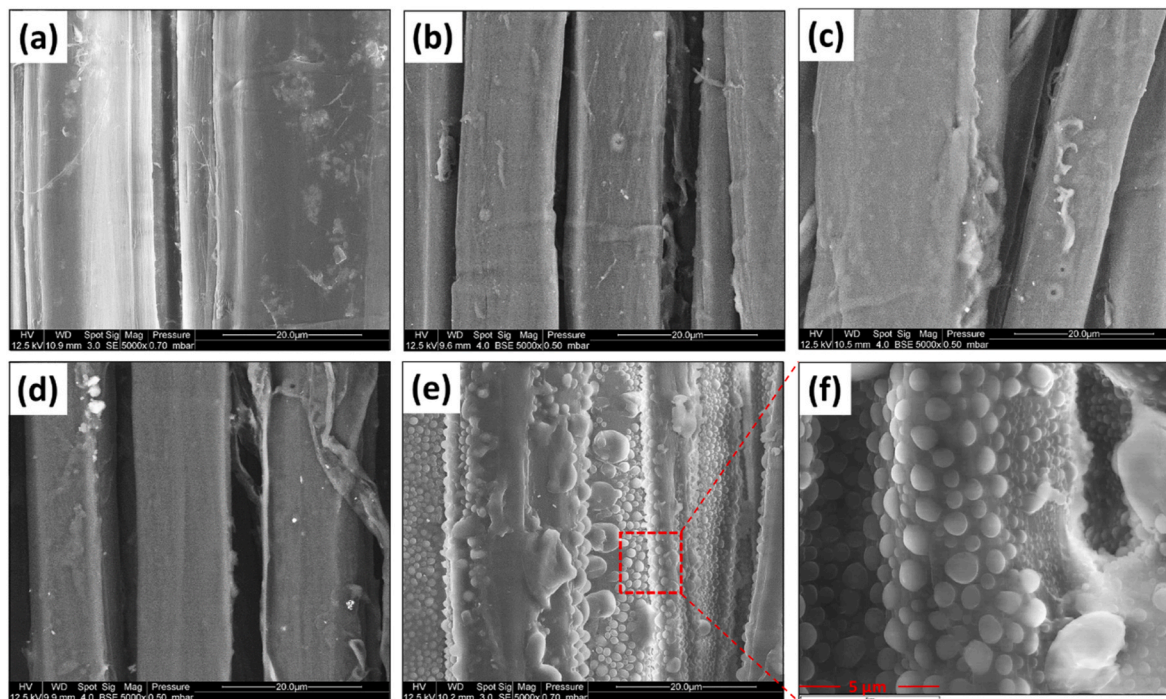


Fig. 7. Representative SEM images of (a) unirradiated and treated flax with M8 and irradiated flax fabrics at 100 kGy and treated with (b) M4, (c) M6, (d) AC6 and (e)(f) M8 for 24 h in MeOH ($\times 5000$).

(Fig. 6h, j and l). This difference of distribution for these various monomers seems to depend on the length of the perfluorinated group. The bigger the fluorinated group, the more difficult the monomer penetrates into the bulk of the elementary fibers.

In order to explain the maximum fluorine content obtained in the case of M8 grafting ($F = 13.78$ wt%), longitudinal observations of unirradiated and M8 treated flax fibers and those irradiated at 100 kGy and treated with the different fluorinated monomers (M4, M6, AC6 and M8)

were also performed by SEM (Fig. 7).

The pictures indicate a smooth surface for unirradiated and M8 treated fibers (Fig. 7a). Moreover, a homogeneous fluorinated coating on the surface of the elementary fibers in the case of treatment with M4, M6 and AC6 (Fig. 7b, c and d) was noted. However, a different microstructure was observed after the radio-grafting using M8. Grafted flax fibers show the presence of spherical particles on the surface of the elementary fibers with diameters ranging from 0.6 to 6.0 μm (Fig. 7e). These spheres are attributed to the polymerization of the fluorinated methacrylate. The lower solubility of M8 monomer in methanol compared to other monomers, and the insolubility of P(M8) in this solvent could explain the formation of these spherical particles during the polymerization step. Indeed, the generation of this kind of particles is generally obtained with a procedure of dispersion polymerization [51, 52]. The formation of similar spherical particles was reported by Yoshida [52] after dispersion polymerization in methanol of two perfluoroalkyl methacrylate monomers: 2,2,2-trifluoroethyl methacrylate (TFMA) and 2-(perfluorooctyl)ethyl methacrylate (POMA). Spherical particles with average diameter of 4.12 μm and 679 nm were produced in the case of PTFMA and PPOMA, respectively.

SEM-EDX mapping confirms that the spheres formed at the surface of the elementary fibers contain fluorine and are therefore made of P(M8) (Fig. S4). It has been observed that the concentration and the size of these spheres depend on the polymerization time (Fig. S5). Indeed, for 1 h and 4 h of reaction, the size and the number of the spheres are less important than after 24 h at 100 kGy. SEM images indicate that after 1 h-polymerization, 300–600 nm spheres were formed, and their size increased with polymerization time to 0.6–6.0 μm after 24 h of reaction. The same results were noted by Huo et al. [51] for the dispersion polymerization of 2-(perfluorobutyl)ethyl methacrylate (FBEMA). These authors reported that the size of the aggregates increased with the polymerization time and that after 3 h-reaction, particles of 15 nm were produced. Then, after 11 h, the size increased to around 217 nm.

The other fluorinated polymers [P(M2), P(M4), P(M6) and P(AC6)] are also not soluble in methanol, but spherical particles as noted in the above case were not observed, probably due to the shorter length of the perfluorinated group for these monomers or their lower polymerization rate.

3.4. Hydro-oleophobic properties of modified flax fabrics

Surface wettability of the treated flax fabrics was examined by measurement of water (WCA) and diiodomethane (DCA) contact angles, as reported in Table 3. The non-grafted flax fabric (WCA = 47° and DCA = 0°) was tested for comparison.

As reported, the hydrophobic and oleophobic properties of the different treated fabrics depend on the FC and the fluorinated chain length. The fabrics treated with M2 are oleophilic as the diiodomethane droplets deposited on the surface are rapidly absorbed (after less than 1 min) even for the highest FC obtained with such a monomer (0.14 wt%). Compared to untreated fabrics, the water contact angle of flax treated with M2 increases from 47° to 80° (Fig. S6). In contrast, all samples modified with M4, M6, AC6 and M8 exhibit high WCA and DCA values and therefore satisfactory hydrophobicity and oleophobicity (Table 3). The M4 treated fabrics are hydro- and oleophobic even for a FC as low as 0.10 wt% (Fig. S7). The WCA and DCA are almost constant with increasing FC (keep in mind that these FCs are very low and probably lower than the measurement uncertainties). For a FC of 0.10 wt% obtained for the grafting of M4 on flax fibers irradiated at 5 kGy, WCA and DCA were 139° and 120°, respectively. For the highest FC of 0.22 wt% obtained from fibers irradiated at 100 kGy, similar WCA and DCA of 130° and 125° were noted, respectively.

For fabrics modified with M6 (Fig. S8) and AC6 (Fig. S9), higher CA values were obtained with the acrylic monomer in comparison with the methacrylate one because of its higher reactivity and hence grafting efficiency [47]. For similar FCs of 0.42 and 0.39 wt% for fabrics treated

with M6 and AC6, respectively, WCA of 132° and 145° and DCA of 125° and 130° were achieved. These results suggest that for a similar fluorine concentration, the acrylic monomer is somewhat more efficient. Moreover, its higher reactivity allows a higher grafting rate to be achieved, such as a maximum FC of 1.09 wt% with WCA and DCA values of 147° and 134°, respectively.

Interestingly, super-hydrophobic and oleophobic properties were noted with M8 grafting at irradiation doses of 20 kGy (FC = 1.97 wt%), 50 kGy (FC = 2.33 wt%) and at 100 kGy (FC = 8.05 wt%) for 24 h-reaction (Fig. S10) and at 100 kGy (F = 0.77 wt%) after 4 h-polymerization (Table 3).

The evolutions of WCA (Fig. 8a) and DCA (Fig. 8b) versus the FC of flax fabrics treated with M8 were studied. It can be observed that for a low FC of 0.37 wt% obtained for 1 h-reaction (at 100 kGy), WCA and DCA of 143° and 128° were achieved, respectively. After 4 h-reaction and at a FC of 0.77 wt%, the grafted flax exhibited WCA and DCA of 150° and 133°, respectively. These values remain stable despite the increase of FCs, for which the spheres were observed at the surface of elementary fibers. In other words, the hydro(oleo)phobic character, as measured by static contact angle, does not seem to change significantly due to the change of the structure of the fluorinated coating and so to the formation of this particular morphology.

The same evolutions of WCA and DCA values for the different monomers studied as a function of the FC are observed in Fig. 8c and d, respectively. It is noted that the WCA and DCA values increased with the FC whatever the irradiation dose and the reaction time. As expected, the WCA seems to also increase with the length of the fluorinated group of the monomer according to the following order: M2 < M4 ~ M6 < AC6 < M8 (Fig. S11) but the difference is less significant for DCA, and M4, M6 and AC6 seem to be equivalent. In the present study, hydro- and oleophobic flax fabrics were produced with M4, M6, AC6 and M8 regardless of the irradiation dose applied and the grafting reaction time with a FC starting from 0.10 wt% to a maximum of about 13.78 wt%.

3.5. Water repellency property of modified flax fabrics

To study the water repellency of the different modified samples, sliding angles were determined and listed in Table 3.

Fig. 9a indicates for functionalized fabrics that the sliding angle decreases rapidly from 90° to 30° with the increase of the grafted FC ranging from 0.1 to 0.4 wt% followed by a slower decrease from 30° to 9° for FC from 0.5 to 8.0 wt%. Furthermore, the evolution of the sliding angle (SA) versus the water contact angle is displayed in Fig. 9b. These results suggest that the SA and the WCA are roughly correlated, with a linear decrease of the sliding angle when the water contact angle increases and thus when the FC increases. For M8 treated fabrics with WCA values ranging from 145 to 150°, a low SA less than 14° was observed and water repellency properties were attained [23,53]. Also, SA values smaller than 10°, with a possible self-cleaning property for the treated surfaces are obtained for the fabrics treated with M8 [53,54]. In the case of AC6, the SA ranges from 40 to 20° while for its equivalent methacrylic M6 and M4 monomers, the angles are higher than 40°. This is mainly due to the greater reactivity of the acrylate monomer, resulting in higher FC.

Furthermore, for low FC of 0.37 wt% and no visible fluorinated polymer spheres on the surface of the fibers irradiated at 100 kGy and treated with M8 for 1 h, a SA of 41° was achieved (Fig. S5). Then, for a FC of 0.77 wt% and for a reaction time of 4 h, the spheres are still not visible but the SA that reaches 14° is much smaller than that from FC of 0.37 wt%. The grafted FC is the main factor controlling the wettability and water repellency of the fibers. When the spheres are well-visible at the elementary fibers surface with FC value equal or higher than 1.3 wt%, a slight improvement of water repellency is achieved and SAs lower than 10° are obtained. This has been assigned to the particular microstructure of these M8-treated fibers (i.e. to the presence of microspheres), but the gain is relatively limited (only few degrees less in

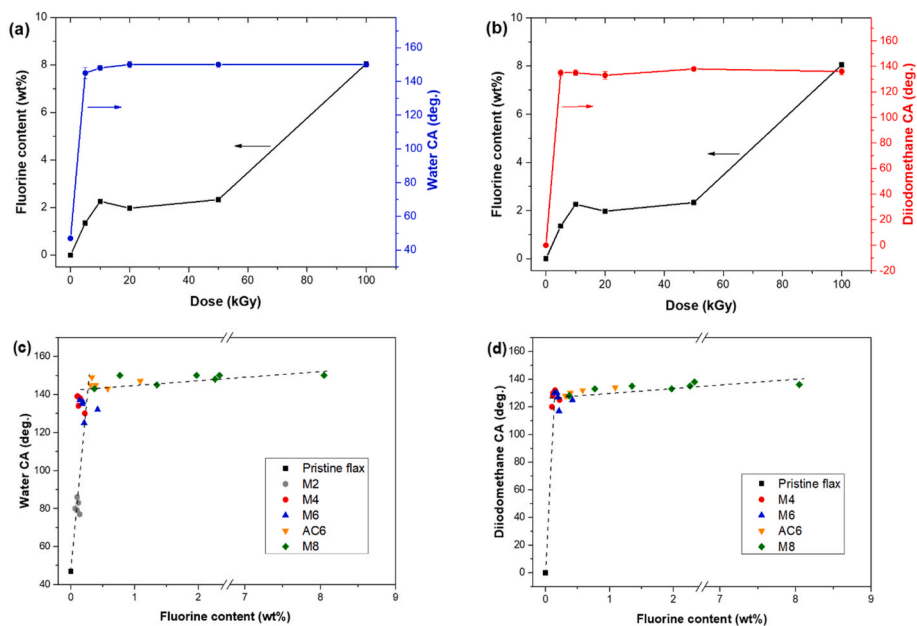


Fig. 8. Evolutions of (a) water and (b) diiodomethane contact angles, and fluorine content of M8 treated fabrics (reaction time = 24 h) versus the absorbed dose. Evolutions of (c) water and (d) diiodomethane contact angles versus the grafted fluorine content (dotted lines are guidelines for eyes).

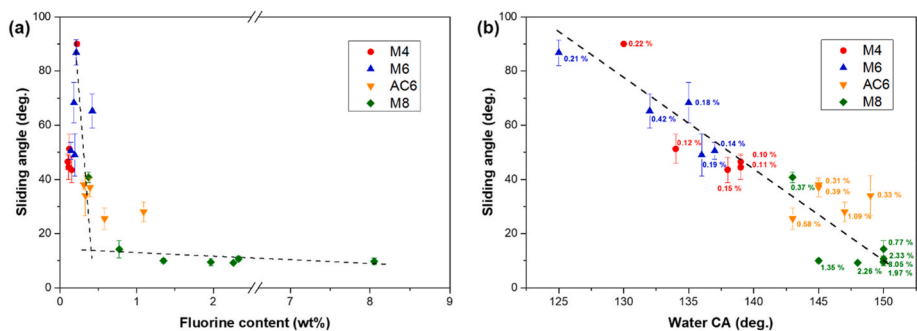


Fig. 9. (a) Effect of the grafted fluorine content on the sliding angle and (b) correlation between sliding and water contact angles (dotted lines are guidelines for eyes and the data correspond to the fluorine content).

presence of these microspheres). By comparing fibers treated with AC6 and M8 it can be observed that the length of the fluorinated group affects the sliding angle as for samples F-100 kGy-AC6 (10 wt%_65 °C_24 h) and F-100 kGy-M8 (10 wt%_65 °C_4 h). Indeed, a larger SA for AC6 than for M8 was achieved (28° and 14.3°, respectively) despite a higher fluorine content for AC6 treatment (1.09 and 0.77 wt%, respectively). This demonstrates that the length of the perfluoroalkyl chain also enhances water repellency of the treated fabrics.

Therefore, a high FC coupled to longer perfluoroalkyl chain are the two main parameters to achieve the best hydro-oleophobic performances. These results explain that M8 compared to other methacrylic and acrylic monomers allows to reach excellent water-repellent properties.

The water repellency mechanism was reported by Honda et al. [5, 11]. These authors proved that poly(perfluoroacrylate)s (PFA-C_y) (with C_yF_{2y+1} group) with $y \geq 8$ induced a high dynamic water repellency due to the low mobility of molecular chains and to the crystallization of the fluorinated groups forming ordered structures on the surface. For PFA-C_y with $y = 1, 2, 4$ and 6, lower contact angles were observed. The mechanism of water repellency of PFA-C_y was attributed to the presence of highly ordered perfluorinated chains with low surface mobility and exposure of the carbonyl groups.

Table 4
Water and diiodomethane contact angle values for fluorinated polymer films.

Fluorinated polymers	WCA (°)	DCA (°)
P(M2)	108 ± 4	96 ± 1
P(M4)	118 ± 3	103 ± 2
P(M6)	120 ± 1	100 ± 4
P(AC6)	121 ± 3	99 ± 5
P(M8)	120 ± 2	108 ± 1

3.6. Hydro-oleophobicity of pure fluorinated polymers

It was worth comparing the surface properties of such above flax grafted with fluoro(meth)acrylates monomers with those of the corresponding pure polymers.

The surface properties of the pure fluoropolymer films, synthesized by radical polymerization of M2, M4, M6, AC6 and M8 monomers were examined by water and diiodomethane contact angles measurements as shown in Table 4. The obtained values in this work are close to those reported by Honda et al. [11]. A comparison of the drop morphologies obtained with water and diiodomethane for P(M4) as film or as grafting agent for flax fabric is presented in Fig. 10. Water and diiodomethane contact angles for P(M4) film of 118° (Figs. 10a) and 103° (Fig. 10b)

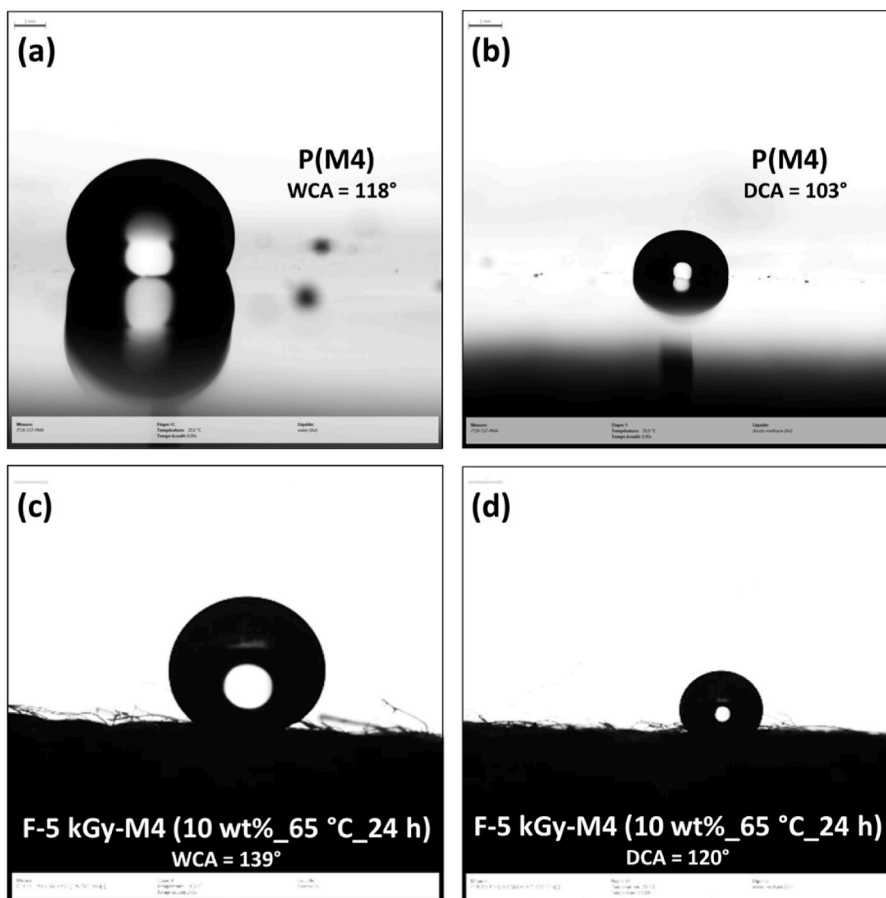


Fig. 10. Water and diiodomethane drop deposits on the surface of (a) (b) P(M4) film and on (c) (d) P(M4) grafted flax fabric irradiated at 5 kGy, respectively.

were obtained, respectively, while higher contact angles were measured for P(M4) grafted fabric even for low FC. As for example, WCA of 139° (Fig. 10c) and DCA of 120° (Fig. 10d) were observed for a sample containing 0.10 wt% of fluorine (flax irradiated at 5 kGy). Similarly, the WCA and DCA values of PM8 film are lower by 25° and 27°, respectively in comparison with PM8 grafted flax fabrics. For all monomers (except for M2 whose the grafting rate is too low) [47], the same tendency is observed: the contact angles are systematically higher for treated fabrics than for fluoropolymer films. These observations may be related to the roughness of the fabrics. Indeed, it seems that the roughness of flax fabric grafted with fluorinated chains allows to achieve higher CAs compared to flat films. Wenzel and Cassie-Baxter's models suggest that the CA increases regularly with the roughness factor and that a rough material has a higher surface area than a smooth one, which changes the contact angle [53,55,56]. The presence of many small fibrils on the surface of fabrics may create a rough surface preventing from the wettability when they are coated with low surface energy molecules, even if these fibrils have diameters of several microns.

4. Conclusion

1,1,1,3,3,3-hexafluoroisopropyl methacrylate (M2), 2-(per-fluorobutyl)ethyl methacrylate (M4), 1H,1H,2H,2H-perfluorooctyl methacrylate (M6), 1H,1H,2H,2H-perfluorooctyl acrylate (AC6) and 1H,1H,2H,2H-perfluorodecyl methacrylate (M8) were successfully grafted onto flax fabric by pre-irradiation induced graft polymerization. The irradiation dose, the reaction time and the nature of the grafted monomer, more precisely the length of the perfluorinated group, and the

acrylate or methacrylate functions, are the parameters that directly influence the efficiency and the localization of the grafting. The functionalization of the flax was confirmed by SEM images which highlight the presence of fluorine in different localizations into the elementary fibers depending on the monomer used. Grafting of P(M4), P(M6), P(AC6) and P(M8) onto flax fabrics induced a strong improvement of the hydro- and oleophobic properties even for low fluorine content of 0.10 wt%. The best results were obtained with M8, with the highest grafting rates and the formation of spherical particles of fluorinated polymer on the surface of the fibers. These high grafting rates allowed to obtain hydrophobic and sometimes superhydrophobic fabrics (150°) endowed with water repellent characteristics with sliding angles lower than 10°, hence revealing self-cleaning abilities. Moreover, it was noted that the grafted fluorine content is the factor directly impacting the surface properties of the treated flax fabrics. The length of the perfluoroalkyl group (and maybe the presence of spherical particles on the surface of the fibers) improves also these properties specifically affecting the sliding angles and makes it possible to obtain water repellent fabrics.

CRediT authorship contribution statement

Jamila Taibi: Investigation, Writing – original draft. **Sophie Rouif:** Resources, Review. **Bruno Ameduri:** Supervision, Writing – review & editing. **Rodolphe Sonnier:** Funding acquisition, Project administration, Conceptualization, Supervision, Writing – review & editing. **Belkacem Otazaghine:** Funding acquisition, Project administration, Conceptualization, Supervision, Writing – review & editing.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Jamila TAIBI reports financial support was provided by Occitanie Region.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.polymer.2023.126132>.

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